EFFECT OF DIFFERENT CHEMICAL TREATMENTS FOR DEVELOPMENT OF FIRE RETARDANT JUTE FABRIC

THESIS SUBMITTED BY

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DOCTOR OF PHILOSOPHY (ENGINEERING)

DEPARTMENT OF CHEMICAL ENGINEERING
JADAVPUR UNIVERSITY
KOLKATA, INDIA

2015

INDEX NO: 212/09/E

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ii) Ashis Kumar Samanta, Reetuparna Bhattacharyya (Roy), Ranjana Chowdhury. "Fire-retardant Chemical Finishing of Jute Fabric Using Sulfamate and Urea Mixture." *AASCIT Journal of Materials* (ISSN 2472-9736) . Vol. 1, No. 4, 2015, pp. 98-110.

iii) Ashis Kumar Samanta, Reetuparna Bhattacharyya, Seiko Jose, Gautam Basu & Ranjana Chowdhury. "Fire retardant finish of jute fabric with nano zinc oxide." *Cellulose* (ISSN 0969-0239), 2017, Vol. 24, No. 2:1143-1157

04. List of Patent: NA

05. List of Presentation in National / International Seminar/Conference:

A) National:

i) Ashis Kumar Samanta, Reetuparna Bhattacharyya(Roy) and Ranjana Chowdhury "Eco-friendly Fire retardant finishing of Jute Fabric by Impregnation or coating Phosphorylated PVA and its effect on physical properties and thermal behaviour of treated jute fabric." *Book of paper of _All India Seminar on Innovation and Emerging Trends of Jute, Textile and Garment Products* held at Sir R N Mukherjee Hall, WBSC,IE(I); 8, Gokhale Road, Kolkata – 700 020, on 17th -18th February, 2012.

B) International :

i) A K Samanta, A Bagchi, Reetuparna Bhattachrya(Roy) and Ranjana Chowdhury "Studies on Fire Retardant Protective Chemical Finishing of Jute Based Textiles" *Book of Papers of International conference on Environment and its Impact on Society (ISBN 978-93-5126-892-5), August, 2013, P-164-178* held on 18th -20th August 2013 at J D Birla Institute, Kolkata-20.

ii) A K Samanta, Reetuparna Roy, Seiko Josh and Ranjana Chowdhury "Fire Retardant Finish of Jute Fabric using Zinc Oxide Nano particle" in Indo-Czech International Conference (ICIC 2014) on "Advancements in Specialty Textiles and their Applications in Material Engineering and Medical Sciences" held at Dept. of Fashion Technology, Kumaraguru College of Technology, Chinnavedampatti POST, Coimbatore – 641 049 on 29th & 30th April, 2014.

iii) A K Samanta, Reetuparna Bhattachryya (Roy) and Ranjana Chowdhury "Fire Protective Chemical Finishing of Jute Fabric as Industrial Protective Textiles using Sulfamate and Urea Mixture" in Second International Conference on Industrial Textiles – Products, Applications and Prospects held at PSG College of Technology, Coimbatore, India on 22nd & 23rd August 2014.

iv) A K Samanta, A Bagchi, Reetuparna Bhattachryya(Roy) and Ranjana Chowdhury "Eco-friendly Fire Resistance Chemical Finishing of Jute Fabrics for its use as Protective Technical Textiles" in International Conference on Technical Textiles and Nonwovens (ICTN-2014) at IIT-Delhi, 6th -8th November, 2014.

CERTIFICATE FROM THE SUPERVISORS

This is to certify that the thesis entitled *"*Effect of Different Chemical Treatments for Development of Fire Retardant Jute Fabric.*"* submitted by Smt Reetuparna Bhattacharyya (Index No. 212/09/E) who got her name registered on 16th March, 2009 for the award of Ph.D. (Engg.) degree of Jadavpur University, is absolutely based upon her own work under the joint supervision of Prof (Dr) Ashis Kumar Samanta, HOD & Professor, Department of Jute & Fibre Technology, Institute of Jute Technology, Calcutta University, Kolkata and Prof. (Dr.) Ranjana Chowdhury, Professor (Department of Chemical Engineering), Jadavpur University and that neither her thesis nor any part of the thesis has been submitted for any degree / diploma or any other academic award anywhere before.

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Dedicated
to
My Daughter
Damayitri Roy

ACKNOWLEDGEMENT

The author expresses his deep sense of gratitude to **Prof. (Dr.) Ranjana Chowdhury,** Professor (Department of Chemical Engineering), Jadavpur University and **Prof (Dr) Ashis Kumar Samanta**, HOD & Professor, Department of Jute & Fibre Technology, Institute of Jute Technology, Calcutta University for their valuable guidance, continuous help and motivation during the course of the work.

The author is also grateful to Prof (Dr.) Ashis Kumar Samanta, HOD & Professor, Department of Jute & Fibre Technology, Institute of Jute Technology, Calcutta University for valuable technical discussion with constant guidance and touch, unremitting inspiration and support for the course of the work carried out at Institute of Jute Technology, Kolkata. The author is thankful to Project Authority of Ministry of Textiles, Govt. of India and National Jute Board for sponsoring JTM R&D Project – 10 on development of Fire-retardancy for Jute Fabric to Department of Jute & Fibre Technology, Institute of Jute Technology, Calcutta University.

The author is indebted to Prof Chiranjib Bhattacharyay, Head, Chemical Engg. dept. of Jadavpur University, to Prof (Dr.) Ashis Kumar Samanta, Head of the Department, DJFT, IJT, CU for their keen interest and all administrative support for allowing the undersigned to enjoy all necessary laboratory and library facilities required to carry out the substantial part of the present work at the Institute of Jute Technology, Kolkata.

All the staff members of Chemical Engg. Dept. of Jadavpur Univerisity, and all the staff members of Textile Chemistry and Textile Physics Sections, DJFT, IJT, CU, Kolkata are specially thanked for providing necessary help and cooperation in carrying out some of the experimental work and analysis facilitating timely completion of this study; special mention in this regard is due to Dr. S. K. Biswas, Associate Professor, Dr. Asis Mukhopadhaya, Associate Professor, Mr. Amitava Chakraborty, Jr. Tech Asst. and Mr. Sanat Ray, Lab attendant of the Textile Physics Section and Mr. Debashish Roy, Sr. Tech Asst., Mr. Pratap Chottoraj, Jr. Tech Asst. and Mr. Mohan Jaiswar, Lab attendant of the Textile Chemistry Section of DJFT, IJT, CU.

A special note of thanks is extended to Dr. Ammayappan Lakshmanan, Senior Scientist, C & BP Div and Mr. Seiko Josh, Scientist, National Institute of Research on Jute and Allied Fibre Technology for Scanning Electron Microscopy (SEM), FTIR analysis and X-ray- diffraction study of differently treated and chemically modified jute samples.

The author would like to express deep gratitude to her parents, spouse (Mr. Debraj Roy), daughter (Damayitri Roy), brother (Reetabrato Bhattacharyya), Sister-in-law (Shimantini Bhattacharyya), and relatives for being a constant source of inspiration, moral support, help and encouragement during many arduous hours of work.

The author owes a great deal to many others, who have helped towards the successful completion of this work: special mentions are to Mr. Debjyoti Kundu, Mr. Suvendu Ghosh, Mrs. Kuheli Das & family, Mrs. Sarmistha Mukharjee & Family, Mrs. Kashmita Bhattacharya, Dr. Swapan Kr. Ghosh, Professor, Fabric Manufacture, DJFT,IJT, CU Mr. Kalyan Roy Gupta, Asst. Professor, DJFT, IJT CU and Nanda Gopal Chakraborty, Project Asst.(Technical) ISDS Project and all the ISDS and JTM-R&D project fellows/assistants of DJFT, IJT, CU, Kolkata. The author wishes to express his gratitude to all other persons whose involvement and cooperation enable this work to see the light of the day.

Date: ……………….. **(Reetuparna Bhattacharyya)**

PREFACE

The investigations embodied in this thesis entitled, **“Effect of Different Chemical Treatments for Development of Fire Retardant Jute Fabric.”** was initiated by the author in 2008-2009 (PhD Registration Date 16.03.2009), with the following three objectives-

i) To develop suitable eco-friendly fire resistant chemical finishing for jute fabrics.

ii) To study the efficacy of fire-resistant finishing action of jute with the use of indigenous common chemicals and formulations to broaden the scope of using jute fabrics in the field of fire-protective textiles (like brattice cloth used in mines) and home textiles (as fire-retardant furnishing fabrics, kitchen apron etc.) having required level of Limiting Oxygen Index (LOI >>27) for use as fire-retardant textiles for specific purposes.

iii) To study the low add on application of fire-retardant finish by use of nanotechnology (i.e. application of fire-retardant nano material).

With the above objectives in mind, some newer process of fire-retardant finishes have been attempted to apply selected fire-retardant chemicals in conventional and newer route on jute fabrics to improve fire-retardant performance with minimum loss/detoriration of other textile properties by adopting and standardizing newer chemical formulations and associated processing conditions applicable for jute fabric.

This thesis consists of the following five chapters:

Chapter 1 of this thesis gives a brief **introduction** on jute fibres along with introduction fire-retardant finishing and its current status in the domestic as well as international front.

Chapter 2 provides a detailed **review of literature** dealing with different types of fire-retardant techniques for jute and other cellulosic and ligno-cellulosic fibre for last few decades, mentioning the major findings of each process / study. A brief introduction on the theme of the present work is also mentioned in ‘**Theme of the Thesis**’.

Chapter 3 deals with the different **methodologies** adopted for chemical finishing of jute fabric samples and a thorough evaluation of these treated fabrics through different instrumental techniques with includes general testing of physical property parameters of textiles with particular emphasis on Scanning Electron Microscopy (SEM), FTIR-Analysis, TGA-DSC Study, etc.

Chapter 4 shows and deals with the **results & discussion** of observed experimental data and the analysis of results obtained for all the parts of the studies incorporated in this thesis after evaluation of differently chemically finished samples (jute fabrics) produced under varying conditions of treatment by different processing techniques. Thus, a detailed discussion and interpretation of the results on the experiments carried out during this study are also described in this chapter under following three broad sections (1) Effects of phosphorylated poly vinyl alcohol treatment on the fire-retardant performance of bleached jute and oxy-jute fabrics. (2) Effect of various individual fire retardant chemicals and their mixtures on bleached jute fabrics. (3) Effect of treatment with combination of ZnO nano-particles and silicone emulsion (Formulation Code J-ZnO nano-particle) for improved flame retardancy of bleached jute fabric.

Chapter 5 provides the **summary and conclusions** of all the said three sections of the total R & D work incorporated in this thesis.

References are given chapter-wise at the end of each chapter of the thesis in the following format: Serial Number, Name of the Author, Name of the Journal, Volume of the Journal (Number of the Journal Issue) (Year) and Page Number.

Tables, Figures (including Scanning Electron Micrographs, FTIR-Spectra and DSC-Thermograms), Reaction Mechanisms, Chemical Structures and Graphs showing some important results are inserted at appropriate places in the thesis.

Suggestion for future work and a **copy of the reprints of three publications** are also incorporated at the end of the thesis.

The author is of the opinion that these results obtained from the PhD level research work for investigations on efficacy of fire-retardant finishing chemicals on jute, would be very useful in understanding and building a knowledge base in this field of textile chemical processing technology. The advantages of these new processes developed relate to ease of application, eco-friendliness, lower cost and lower add on (by application of Nano technology). Hence, it is expected that it will promote the uses of chemically processed/ finished jute fabrics in diversified areas of application for home textiles/Protective textiles as fire-retardant sheets for mines and kitchen apron etc.

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Chapter I

INTRODUCTION

1. General Introduction

Stiff competition from synthetic counterpart in the area of conventional use of jute products as packaging materials is being declined day by day. Hence the need of the hour is an all-round diversification of jute products by promoting and developing decorative and functional uses of jute as technical textiles in other areas. This is why, it is essential to make jute fabric more useful by imparting different value added functional finish on it for its wider application as technical textiles, including fire-protective textiles for specific end uses.

With this in mind, different Jute Research Laboratories is pursuing studies to develop value added and functionally diversified products from jute fibres such as carpets, blankets, upholstery fabrics, wall coverings and window curtains and many other household/home textiles including fire protective jute based furnishing fabrics. Since, jute products are vulnerable to fire; it is desirable to make them flame retardant with newer eco-friendly formulations. As such maximum flame retardant formulations so far attempted or applied on jute fabrics are based on available flame-retardant chemicals meant for cellulosic or cotton fibre. But, due to compositional differences between jute and cotton, the flame retardant finish of jute needs to be separately found out to perform well for jute for its balanced flame retardant performances with minimum deterioration of tensile strength.

Studies on application of flame retardant finishes on jute are few [1-4], which warrants for an integrated study on this aspect with particular reference to jute. Unlike cotton, jute being a multi-cellular and multi-constituent fibre composed of cellulose, hemicellulose and lignin, any chemical processing aimed at modifying any one of its constituents would obviously degrade or modify the other constituents as well, and thus, precision process control to prevent such degradation action on other constituents becomes difficult during any of its chemical processing. Moreover, the recipe and conditions suitable for the chemical processing of cotton cellulose is not exactly applicable for similar chemical modification of jute products. Hence unlike cotton, any chemical processing of jute has to be optimised /standardized separately.

Since the last decade, extensive research has been going on by using new ecofriendly chemical formulation for improving flame retardant (FR) property on cellulosic [5-8] and even on synthetics[9-12].

Flame retardancy may be non-durable, semi durable or durable. Several types of Flame retardants such as halogen[13-15] as well as phosphorous[16-17] based FR-agents and their derivatives have been used in past to improve the flame retardancy of textiles. However the application of halogen FR is being greatly limited due to the possible production of dioxin, large amount of smoke and corrosive gases during the combustion of the said halogen based flame retardant materials. Some of the commercially available phosphorous based FR compounds are also susceptible to minor toxicity, heavy colour e.g. Tetrakis hydroxymethyl phosphonium chloride (THPC) based flame retardant formulations have formaldehyde release problem. So, in the present work, use of Ammonium sulfamate with or without Urea or phosphorylated polyvinyl alcohol (P-PVA) (having no methylol groups) and inert inorganic oxide like ZnO that too in nano particle form (to the extent possible).

However, before we proceed further, it may be justifiable to understand the chemistry and structure property criteria for jute fibres.

1.1 Introduction to Jute Fibre

1.1.1 General Information about Jute

Jute is a common name given to a textile fibre that extracts from the stem of plant belongs to the genus Corchorus, family Tiliaceae. There are nearly thirty Corchorus species available in the world for jute fibre production; however Corchorus capsularis (White Jute) and Corchorus olitorius (Tossa Jute) are widely known.[18]

Jute is one of the most affordable natural fibres and is second only to cotton in amount produced and variety of uses of vegetable fibres. Jute fibres are composed primarily of the plant materials cellulose (major component of plant fibre) and lignin (major components of wood fibre). It is thus a ligno-cellulosic fibre which is partially a textile fibre and partially wood. It falls into the bast fibre category (fibre collected from bast or skin of the plant) along with Kenaf, industrial hemp, flax (linen), ramie, etc. The fibres are off-white to brown, and 1–4 meters (3–12 feet) long.

Agricultural production of jute fibres is mainly concentrated in India and some parts in Bangladesh. The major producers of raw jute fibre are India, Bangladesh, China and Nepal, which possess agro-climatic and socio-economic conditions suitable for cultivation of jute. Table 1.1 & Table 1.2 [Source: Food and Agriculture Organization of the United Nations 2015] shows the some common statistics related to production & consumption of jute during the last five years.

Table 1.1: World production of jute during the last five years.

Country	2009-10	2010-11	2011-12	2012-13	2013-14
Bangladesh	1070.1	1404.4	1404.9	1363.0	1354.0
India	1488.88	1660.0	1705.0	1554.0	1490.0
Myanmar	4.3	9.6	8.2	1.0	0.6
Nepal	17.7	14.4	14.4	15.0	15.7

- Unit in Thousand Tonnes

Table 1.2: Monthly production of jute products by type in India in last five years

Calendar Year	Production in Thousand Tonnes			
	Hessian	Sacking	Carpet Backing	Total
2010	225.4	927.7	2.4	1501.4
2011	228.3	1139.7	3.3	1557.5
2012	226.9	1207.6	3.0	1606.4
2013	199.2	1247.6	3.3	1610.5
2014	211.2	859.1	2.7	1230.9

- [Source: Food and Agriculture Organization of the United Nations 2015]

Jute is used mainly to make wrapping cloth (Hessian), and as sacks for agricultural commodity. In diversified jute sector the major end uses of jute are as furnishing and decorative fabrics, curtains, chair cover, jute based carpets, carpet backing, floor covering, jute shopping bags, rugs, hessian cloth, and backing for linoleum etc. where all comes under the category of jute diversified products(JDP). However, some specific end uses of jute goods has been already replaced by synthetic materials in many of the areas such as cement bag, fertilizer bag, onion bag etc. reducing domestic consumption of jute bags. Jute fibres have many advantages such as low cost, eco-friendly and moderate mechanical properties[19-22] which makes them better alternative of synthetic fibre in many applications [23]. However, the common uses of jute are stated in Table 1.3 below.

Table 1.3: Common uses of jute

A. Packaging Textiles (including Wrapping and Backing Fabrics)
(i) Sackings
(ii) Hessian
(iii) Carpet Backings
(iv) Webbings
(v) Carpet Yarns or Sale Yarns
B. Home Textiles
(i) Decorative Fabrics
(ii) Furnishing Fabrics
(iii) Draperies and Upholstery Fabrics
(iv) Decorative Handicraft items
(v) Decorative Utility Items
(vi) Kitchen and Gardener’s Apron
(vii) Fancy Bags and Shopping Bags
(viii) Soft Luggage
(ix) Floor Matting and Carpets
(x) Shoe Upper
(xi) Outer Apparels/Trimmings of Apparels
(xii) Hat/Gloves/Table mats.

C. Geo-textiles	
(i)	Soil Saver Fabrics for Erosion Control
(ii)	Jute Geo-textiles for Road Construction etc.
(iii)	Jute Geo-textiles for Canal Bank Protection
(iv)	Jute Geo-textiles for Vegetation in arid Zones
D. Agro Textiles	
(i)	Wind-Screen. Sun-Screen/Nets for Sericulture plants and cocoons
(ii)	Mulching fabric
(iii)	Sleeve for Plant Saplings, etc.
E. Others	
(i)	Laminated/Coated Flexible Composite of Jute Fabrics.[24]
(ii)	Making of Paper pulp from Jute for high Quality Paper.
(iii)	Jute non-woven Felt Fabric for Back-Liner

To diversify the newer end-use of jute fabrics, particularly as home textiles and furnishing fabrics, meaningful R & D effort is required, either with an objective to eliminate or to partly reduce some of the disadvantages associated with jute.

However, the growing consciousness regarding environment preservation has changed the situation in the recent years. For instance, a comparative study of environmental attribute of jute and polypropylene (PP) products, as studied by IIT-Kharagpur[25] the extract of which is shown below in Table 1.4.

Table 1.4: Environmental Attributes of Jute and PP sacks considering their Life Cycle Analysis

Parameters	**Jute**	**PP**
Water (litre/TMHLT*)	161 litre/TMHLT	0.607 litre/TMHLT
Energy (Kwh/TMHLT*)	4500 litre/TMHLT	10990 litre/TMHLT
$C0_2$ Emission (litre/TMHLT*)	----	1.03 litre/TMHLT

* Ton of Material Handled during life time

The data in Table 1.4 shown above indicate that the energy requirement for production of 1 ton of jute product is much less than that required for PP product. Cultivation of jute plants can also contribute to reduction of greenhouse effect due to absorption of carbon dioxide from the air per ton of jute fibre and hence there is no emission of CO_2 from jute plant while for PP CO_2 emission is 1.03 litre / TMHLT.

1.1.2 Morphology and Fine Structure of Jute Fibre

The structural features of the fibre are of basic importance in understanding its physical properties. Fine structure of a fibre represents the arrangement of the cellulose molecules into crystalline and non-crystalline regions.

Jute fibre extracted by the retting process from the bast of the parent plant, which comes in the form of long mesh of interconnecting fibres commonly known as the jute reed. The jute reed is usually 2–5 meter long. Typical yield of jute fibre based on weight of stem from which it is derived, is about 6%. The top of jute reed is thinner than the root. The reeds are then split-open in carding machine into the component fibres called the spinner's fibre [26]. Jute is a multi-cellular fibre and each single fibre is a bunch of 5-15 ultimate cells cemented together laterally and longitudinally by means of non-cellulosic materials like lignin and pectin. The number of ultimate cells per cross section has varied due to random disintegration of cell bundles by microorganisms during retting. For the ultimate cells of the jute fibre, the length ranges between 0.75 – 6.0 mm and the diameter ranges between 0.0051 – 0.0254 mm[26-28]. Each ultimate cell has thick cell wall and cements to neighbouring cell at middle lamella. In the middle of ultimate cell, it has oval shaped lumen, which covers 10% of its cross section. The ultimate cell is considered as natural composite since it comprises ultrafine fibrils that reinforces the matrix of hemi-cellulose and lignin [29, 30]. The ultrafine fibrils are lying in criss-cross manner in primary wall and parallel as right hand spirals in the secondary wall. Each fibril has the highly ordered crystalline region (about 65-70%) with oriented alpha cellulose, less ordered amorphous region with short chain hemicellulose, and bulky lignin [31]. The schematic diagram of morphology of a raw jute fibre is given in Figure 1.1[32,33].

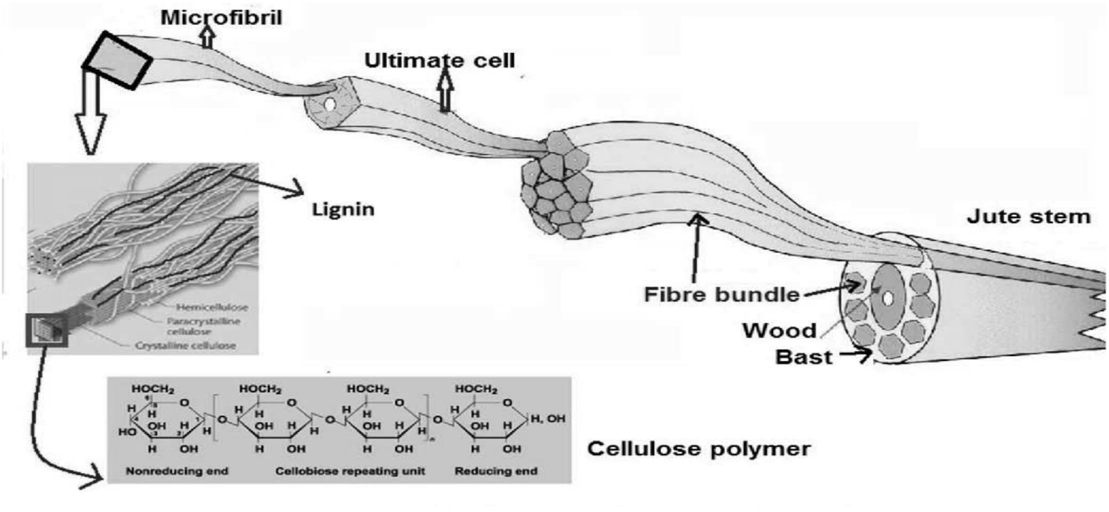


Figure 1.1: Morphology of raw jute fibre.

1.1.3 Physical Structure and Properties of Jute

Depending upon the six fibre quality attributes *viz.* bundle strength, fibre fineness, weight (length of root part over total reed weight / length) & root content, defects, bulk density, colour & lustre, the White (W) and Tossa (TD) jute are graded into eight varieties[34], *viz.* W1 (or TD1), W2 (or TD2), W3 (or TD3) and so on till W8 (or TD8), in the descending order of their quality. Table 1.5 illustrates the range and average of different physical and other textile related properties of the jute fibre[35-37]. Jute fibres or filaments (also termed as spinner's fibre after carding), contain a variable number of cells; so the individual values for filament fineness and strength, within a sample, vary widely. Messy jute fibres are gradually split up during the carding process to obtain spinner's fibre or single jute filament of variable length. The maximum length of filament in a jute yarn is about 30 cm. Specific surface area of jute fibre, as measured by air-flow technique, is about 1000 cm^2/ml. Single jute filament or spinner's fibre has varied fineness, which is usually 2 – 2.5 tex. Thus a jute yarn having 70 – 80 fibres in the cross section is about 140 – 210 tex (4 – 6 lbs/spy)[38].

Moisture regain value of jute fibre is higher than that of cotton, viz. at 70% relative humidity, moisture regain value of jute is about 13.75%, while that of cotton is 8% or so. This has been mainly attributed [39] to the presence of hemicellulose in jute. Transverse swelling of jute fibre in water has been observed to be about 23% in diameter and it increases appreciably on removal of either lignin or hemicellulose [40]. With increase in relative humidity up to 70%, it follows a decreasing trend [39,41]. Moisture absorption is reported to bring about a reduction in the degree of crystallinity of jute [42,43].

In addition to being mildly acidic, jute is also chemically reducing in nature. Copper number of jute[44] varies roughly from 1.5 to 4. Compared to cotton and ramie, jute is somewhat more resistant to the action of acid due to presence of lignin [45]. Mild alkali such as, soda ash, borax, ammonia, etc., in cold aqueous solution, imparts a yellowish red shade to jute with almost no loss of weight. Loss of weight (about 10%), however, occurs when jute is treated at ambient temperature or boiled with aqueous soda ash solution of medium (~10%) strength [45].

Table 1.5: Important Physical Properties of Jute Fibre [38]

Sl. No.	Properties		Range
1	Length of Ultimate Cell (mm) -- -- -- -- -- -- -- -- --		0.75 - 6.0
2	Width of Ultimate Cell ($\times 10^{-3}$) (mm) -- -- -- -- -- -- --		5 -25
3	Fibre Fineness (Linear Density)	(tex) *	1.80 - 3.50
		(den)**	8.00 - 31.0
4	Aspect Ratio		110
5	Fibre Density (g/cm ^{3}) -- -- -- -- -- -- -- -- -- -- --		1.45 - 1.52
6	Single Fibre Tenacity	(g/den)	2.7 – 6
7	Breaking Elongation (%) -- -- -- -- -- -- -- -- -- -- -- -- --		0.8 - 2.0
8	Work of Rupture (g/tex) -- -- -- -- -- -- -- -- -- -- -- -- --		0.18
9	Modulus of Torsional Rigidity (dyne/cm ^{2}) $\times$ 10 ^{10} --		0.25 – 1.25
10	Initial Modulus (g/den) (Modulus at 0.1% Extension) -		130 - 220
11	Young's Modulus (dyne/cm ^{2}) $\times$ 10 ^{11} -- -- -- -- -- -- --		0.86 - 1.94
12	Bundle Tenacity (g/den) -- -- -- -- -- -- -- -- -- -- -- -- --		2.2 – 4.0
13	Refractive Index (*Parallel to fibre axis*)		1.577
	(*Perpendicular to fibre axis*)		1.536
	Birefringence (Double refraction)		+ 0.041

14	(a)	Swelling in Water -- -- -- -- -- -- -- -- -- -- -- -- -- --		
			Diametrical %)	18.0 - 22.0
			Area-wise (%)	40.0 - 50.0
	(b)	Moisture Regain (%) at 65% RH and at 27^{0}C -- --		12.5 – 13.8
15	Stiffness Index (g/den) -- -- -- -- -- -- -- -- -- -- -- -- -- -- --			300 - 400
16	Specific Heat (cal/g/^{O}C) -- -- -- -- -- -- -- -- -- -- -- -- -- --			0.324
17	Dielectric Constant (at 50 HZ) -- -- -- -- -- -- -- -- -- -- --			10^{14} - 10^{17}
18	Insulation Resistance (KV/cm) -- -- -- -- -- -- -- -- -- -- --			450 - 550
19	Heat of Combustion (J/g) -- -- -- -- -- -- -- -- -- -- -- -- -- -			16.0 - 17.0
20	Specific Internal Surface (m^2/g) -- -- -- -- -- -- -- -- -- --			10 - 200
21	Coefficient of Friction (*inclined plane method*) -- -- --			0.3 - 0.54
22	Crystallinity (%) -- -- -- -- -- -- -- -- -- -- -- -- -- -- -- -- --			50 - 60
23	Copper Number -- -- -- -- -- -- -- -- -- -- -- -- -- -- -- -- -- --			1.5 – 4.0
24	Herman’s Angle of Orientation (degree) -- -- -- -- -- -- -- --			7 – 9

1.1.4 Chemical Composition and Structure of Jute Fibre

Chemically, long vegetable fibres are ligno-cellulosic in nature, comprising mainly of polysaccharides and lignin. A number of minor components, such as pectin, inorganic salts, nitrogenous substance, colouring mater, wax, etc. are also found in Jute. Details of the chemical composition [26] of jute fibre is given below in Table 1.6.

Table 1.6: Average Chemical Composition (in Percent of Bone Dry Weight of the Fibre) of Jute[26] [*C. Capsularis* (White), *C. Olitorious* (Tossa)]

Constituents	Capsularis (White) Jute	Olitorius (Tossa) Jute
Cellulose *	60.0 – 63.0	58.0 – 59.0
Lignin	12.0 - 13.0	13.0 – 14.0
Hemicellulose **	21.0 - 24.0	22.0 - 25.0
Fats and waxes	0.4 - 1.0	0.4 - 0.9
Proteins or Nitrogenous Matter etc. (% Nitrogen × 6.25)	0.8 – 1.87	0.8 – 1.56
Pectins	0.2 – 1.5	0.2 - 0.5
Mineral Matter (Ash)	0.7 – 1.2	0.5 – 1.2

* Major constituents of jute-cellulose include glucosan (55.0 – 59.0%), xylan (1.8-3.0%) and polyuronide (% CO_2 % 4) (0.8-1.4%).

** Major constituents of jute-hemicellulose includes xylan or pentosan (15.5-16.5%), hexosan (2.0- 4.0%), polyuronide (3.0- 5.0%) and acetyl content (3.0-3.8%).

1.1.4.1 Jute Cellulose

The total carbohydrate material in jute is usually designated as holo-cellulose, which is further divided into two groups, namely, cellulose or alpha- cellulose and hemicellulose. Hemicellulose is not a homogeneous substance and generally comprises of polysaccharides of a relatively low molecular weight. The nature of association of these constituents is complex in nature and is difficult to be completely understood. Cellulose is a linear condensation polymer consisting of D- anhydroglucopyranose units joined together by 1- 4- β- glycosidic bonds (***Fig.* 1.2**). It has more than 50% degree of crystallinity [46].

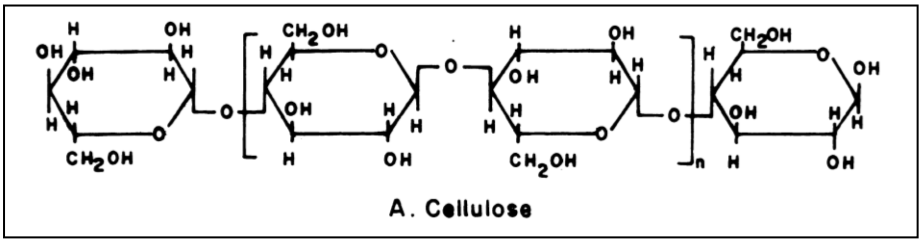


Fig. 1.2: Structure of Cellulose

Cellulose from different sources differ in their degree of polymerization which is possibly the single most important attribute influencing the physio-mechanical properties of this polymer. Degree of polymerization of cellulose in jute is reported to be the lowest among all the vegetable fibres [47] and according to an estimate [48] it is 1150.

Cellulose reacts as a trihydric alcohol with one primary and two secondary hydroxyl groups per glucose unit. The reactions of cellulose may be conversantly divided into the following two kinds: (i) those involving the hydroxyl groups leading to substitution, addition and oxidation and (ii) those involving glycosidic linkage leading to chain degradation by hydrolytic mechanism [46]. The first and former type includes such reactions as acetylation, phosphorylation, nitration, xanthation, alkylation (etherification), etc.

The second and other type include hydrolytic breakdown of cellulose takes place in the presence of acids, while oxidative degradation may occur in an alkaline, acid or neutral medium [46].As measured by deuterium exchange technique, the percentage accessibility of jute cellulose is reported to be lower than that of ramie, mercerized cotton and finely ground cotton [46].

1.1.4.2 Jute Hemicellulose

Hemicellulose is composed of mainly pentosan (xylan) as shown in ***Fig.* 1.3,** polyuronide and a little hexosan. This is a polymeric chain of molecular substance somewhat like cellulose, but is distinguished from the latter in having a pentosan backbone with gluco-uronic acid residue occasionally attached to it and having a relatively short chain length (DP $\leq$ 150) and being soluble in cold 18% aqueous NaOH solution. Jute hemicellulose (*Fig.* 1.4) generally comprises of a number of polysaccharides of comparatively low molecular weight composed mainly of pentoses such as xylose and uronic acid having backbone of

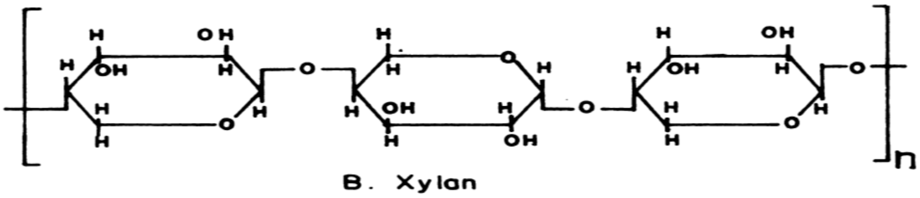


Fig. 1.3: Structure of Xylan

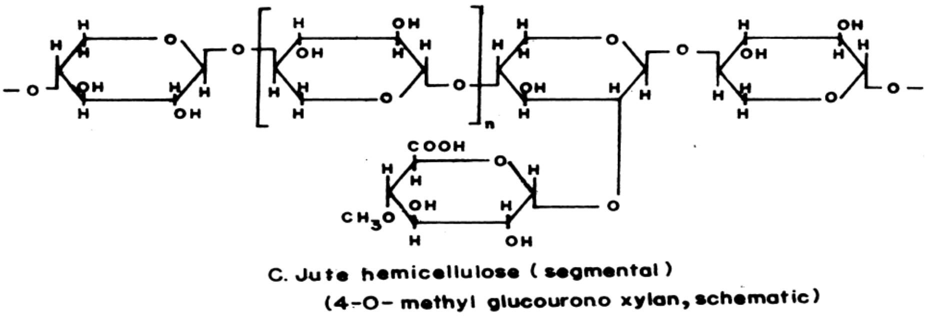


Fig. 1.4: Structure of Jute-Hemicellulose

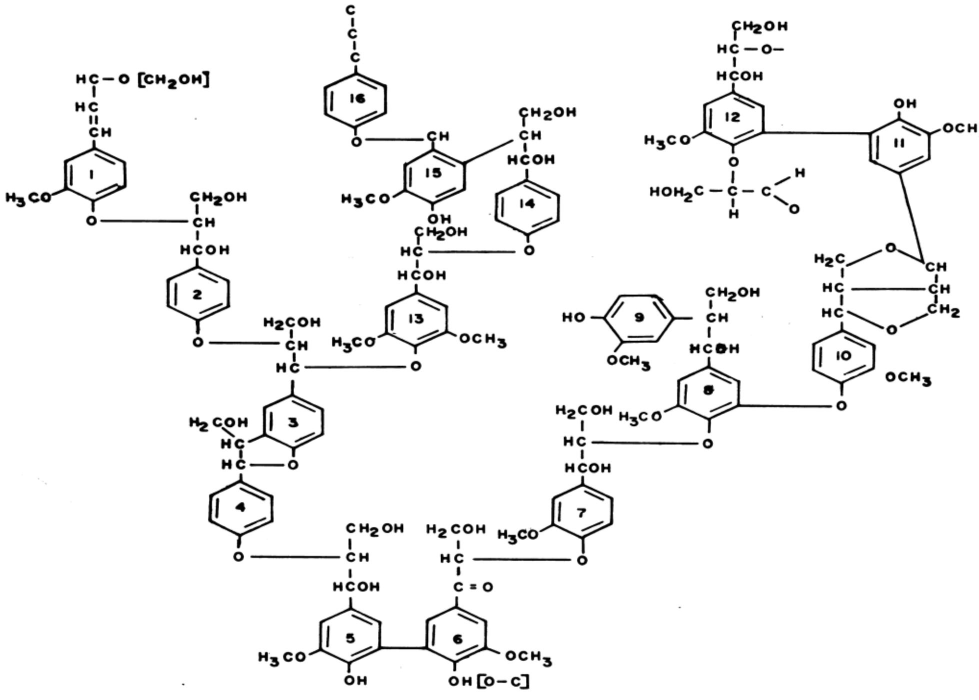
β-D-xylopyranose units with every seventh unit carrying a terminal 4-O-methyl-α-D-glucouronic acid residue (*Fig.* 1.3), linked through position C_2. Some of the xylose units in the main chain are acetylated [49,50]. The degree of polymerisation (DP) of this polysaccharide of jute hemicellulose, as estimated by osmotic pressure method is reported [50] to be low, i.e., an average of nearly 140.

The hemicellulose also posses reducing (–CHO) end groups in a relatively less measurable concentration and is mainly responsible for the relatively strong reducing action exhibited by jute contribute largely to the observed copper number around 2.0 for the raw jute fibre[50].

1.1.4.3 Jute-Lignin

Lignin is a complex amorphous polymer which functions as the structural support material in jute plants. During bio-synthesis of plant cell-walls, polysaccharides such as cellulose and hemicelluloses are laid down first and lignin fills the spaces between them, thereby cementing them together. Lignification causes stiffening of the cell walls and the corresponding cells are thus protected from physical and chemical damage [51]by environment and other effects.

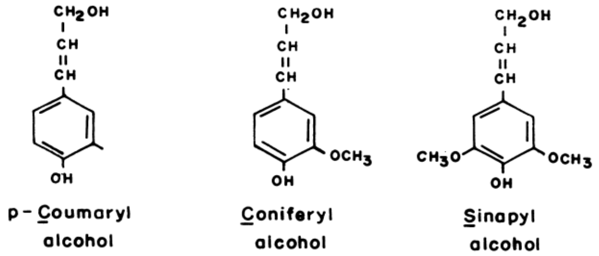
Lignin from all sources has more or less a similar basis of composition in a qualitative sense, although the topology may be different [52-54]. Thus, the same functional groups are always found in all samples of lignin; hydroxyl (alcoholic and phenolic), methoxy, dioxyethelene (–OCH_2O–), iodoform yielding complex, etc.[55]. Among these, carbonyl, ether, methoxy; phenolic hydroxyl and conjugated double bonds in appropriate position to benzene ring in lignin structure, [*Fig.* 1.5] attribute major chemical properties to lignin.



A. lignin structure (Schematic)

Fig. 1.5 : Schematic Structure of Jute-Lignin

The structural units of lignin precursors are aromatic alcohols with a phenyl-propane backbone such as, p-cumaryl alcohol, coniferyl alcohol and sinapyl alcohol [51] [***Fig.* 1.6**].



B. Lignin precursors

Fig. 1.6 : Schematic Structure of Lignin Precursors

Lignin is believed to be formed by oxidative co-polymerisation of the phenyl-propane units which gives large cross-linked molecules containing carbon-carbon and ether linkages [51,56]. It is a short-chain, isotropic and non-crystalline material with a DP of about 60. High rigidity of lignin is partly due to its non-linear cross-linked structure [57]. According to one source [58], the molecular weight of lignin moieties varies from 300 to 1, 40,000 depending on the source and method of estimation.

Two types of lignin associations have been reported in jute [59-61]; the first kind being more easily accessible to bleaching chemicals and reagents than the other. This has been corroborated by studies on wood lignin [57], on the basis of which lignin is known to comprise of about 20% of relatively low molecular weight components (which are relatively readily soluble and lost when treated with dilute acid or alkali), called hemi-lignin and about 80% of relatively high molecular weight components which are bound to the carbohydrate components and are called glycolignin.

1.1.4.4 Fats and Waxes in Jute

Fats and waxes [62] are present as protective coatings on the cuticle or primary wall of cells in the jute fibre. It is soluble in organic solvents e.g. benzene and ethyl alcohol mixture. The extracted wax is greenish brown in colour. It is basically an impurity present in the jute fibre.

1.2.4.5 Pectin in Jute

The word ‘pectin’ is derived from the Greek word ‘*pektions*’, meaning jelly. A small quantity of pectin is present [63] in the jute fibre which holds the fibre bundles together. Pectin is a large molecule built up of repeating units called, hexouronic acid, which is a derivative of hexose sugar and undergoes decomposition during retting of the jute plant to form water soluble products through bacterial action. It has greater hygroscopic than cellulose and swells quickly in the presence of water. However, in raw jute, there is always some residual pectin left; higher is the pectin content, higher is the stiffness of the jute fibre.

1.2.4.6 Inter-unit Linkages in Jute

Jute fibre may be considered to be a composite with the an-isotropic cellulose microfibrils acting as the load-bearing entity in an isotropic lignin matrix with the hemicellulose acting as the coupling agent between the two [46].

The hemicelluloses are strongly bound to the cellulose micro-fibrils by hydrogen bonds[46,50,64] and a portion of hemicellulose is linked to lignin hydroxyls through its uronic acid groups forming ester linkages [64,65]. It has been suggested that the −OH group in the propyl side chain in the phenyl-propane unit of lignin may be involved in this linkage [51]. Some of the –COOH groups of hemicellulose seem to be involved in such ester linkages, while most others appear to be occupied by basic radicals like Ca^{2+}, Mg^{2+}, etc. and the rest appear as free carboxyl groups [64,65].

De-fatted jute has been found to possess an acid value of 3.0 milliequivalents per 100 g which increases to about 12.0 milliequivalents per 100 g on rendering jute mineral-free (removal of Ca^{2+}, Mg^{2+}, etc.) by treatment with 0.1N HCl. There are different opinions about the origin of acidity of jute; an early group of investigators [66] attributed this to –COOH groups of hemicellulose, while a report of relatively recent origin [40] attributes the free acidity of jute to the phenolic −OH groups in the lignin component. However, it is believed that jute possess some acidity due to both the –COOH group content of polyuronic acid residue in jute hemicellulose and phenolic −OH group content in lignin residue.

It has been observed that when jute is treated with any chemical reagent employed in textile pre-treatment (desizing, scouring, woollenisation and bleaching processes) and dyeing and finishing etc. the lignin, hemicellulose and other encrusting substances of jute are attacked, degraded, dissolved and to some extent removed. The greater is the extent of such removal of either lignin or hemicellulose or both, the more the strength of the jute fibre is diminished, particularly when the material is treated in the wet state [30] with acid/ alkali/ oxidising agent/reducing agent or any other finishing chemicals.

1.1.5 Role of Jute fibre components on physico-chemical properties

All the major components of the jute fibre i.e., cellulose, hemicelluloses, and lignin are jointly responsible for its over-all physical, mechanical and chemical properties [16-18]. In jute there are two types of hemicelluloses-first relatively free hemicelluloses (alkali soluble in raw jute) and secondly cross-linked hemicelluloses forming ester linkages with cellulose or lignin residue (soluble in alkali after removal of lignin). These two types of hemicelluloses are mainly responsible for moisture sorption and chemical reactions besides the accessible cellulose in amorphous parts. There are two types of lignin in jute – first easily accessible, lignin, and surface of crystalline cellulose also play major roles in chemical modifications. The microorganisms easily attack the jute fibre since the hemi-cellulose portion could easily hydrolyzed into digestible units by its specific enzyme systems. When ultraviolet light exposed on the jute fibre, it undergo photochemical degradation due to presence of lignin. Jute fibre burns in the fire because hemicellulose and cellulose polymers degraded by heat and undergo pyrolysis reactions to give off volatile, flammable gases. The lignin component contributes to char formation, and the charred layer helps insulate the fibre from further thermal degradation. Since hemicelluloses present in the inter-fibriler regions of ultimate cell, their removal during chemical treatment affects the stress development and relaxation during stretching of jute fibre. Lignin is located in the inter-cellular region of ultimate cells and their removal is mainly responsible in determining the tensile characteristics of the jute fibre [26,33]. Some of the important chemicals treatments used for fibre modifications are phosphates, acid anhydride, acid chlorides, carboxylic acids, isocyanates, formaldehyde, and vinyl monomers etc. [45]. The order of importance of individual components of the jute fibre for improving any specific performance properties has been given in Table 1.7 [35].

Table 1.7: The order of importance of components of the jute fibre which are responsible for the modification:

Property	**Priority**
Biological Degradation	1. Hemicellulose 2. Accessible Cellulose 3. Non-Crystalline Cellulose
Moisture Sorption	1. Hemicellulose 2. Accessible Cellulose 3. Non –Crystalline 4. Lignin 5. Crystalline Cellulose
Ultraviolet Degradation	1. Lignin 2.Hemicellulose 3.Accessible Cellulose 4.Non-Crystalline 5.Crystalline Cellulose

Thermal Degradation	1. Hemicellulose 2. Cellulose 3. Lignin
Strength	1. Crystalline Cellulose 2. Matrix (Non-Crystalline Cellulose + Hemicellulose + Lignin) 3. Lignin

1.1.6 Introduction on Chemical treatments of jute fibre

Chemical treatments have always used to enhance the utilization of the textile fiber and its diversification in the product development. Here are some examples of important/ essential chemical treatments, their condition and their influence on the performance property of the jute products.

Jute material is usually scoured by 5 g/L NaOH, 2 g/L non-ionic detergent, and 0.5 g/L sequestering agent at 95°C for 60 minutes, with 1:10 material: liquor ratio. After scouring, it is washed with 2 g/L non-ionic detergent at 95°C, neutralized with acetic acid, rinsed at 40°C for two times, followed by cold rinsing, and dried [67,68] .The crystallinity of jute fibre increases with increasing in scouring time due to removal of materials like hemicellulose, lignin, and some other non-cellulose materials in the amorphous region of the jute fibre[69,70].Samanta et.al[71] inferred that after the removal of components of amorphous regions, the molecular chains would be reoriented by the plasticizing and swelling action of alkali.

Bleaching is a chemical process to remove natural colouring matter present in the fibre by either a oxidizing or a reducing agent. After scouring, the jute fibres get reddish tone and so bleaching is necessary for light colouration. For jute goods, amongst sodium hypochlorite (NaOCl), calcium hypochlorite ($CaOCl_2$), hydrogen peroxide (H_2O_2), Per-acetic acid (CH_3COOOH), potassium permanganate ($KMnO_4$) and sodium chlorite ($NaOCl_2$) as bleaching agent. Hydrogen peroxide is preferred commercially since it is chlorine free and eco-friendly. Though reducing agents viz., sodium hydrosulphite, sodium bisulphite and sodium borohydride may also be used for bleaching of jute, but, they develop reddish or brown tinge on jute during storage [72,73] due to aerial oxidation. Jute fabric is bleached using

10g/L hydrogen peroxide (35% v/v), 6g/l sodium silicate, 0.5 g/l Lissapol, 1g/l sodium carbonate, pH 10-11 and 80-85°C for 1-2 hour with material to liquor ratio of 1:2069. Samanta et.al[71] inferred that peroxide bleaching in presence of 3% hydrogen peroxide (i.e 6% of 50% H_2O_2) for 2 hours at 85°C in pH 11 or combined bleaching treatment at room temperature with 3% H_2O_2 and 0.75% $K_2S_2O_8$ for 2 hours at 30°C at pH 11. The H_2O_2 bleaching followed by silicone finishing gave soft, smooth and bright jute fibre with noticeable reduction in coefficient of friction without much change in bundle tenacity. Yellowing of jute under sunlight exposure can be significantly prevented by hutex bleaching using calcium hypochloride at pH 6. Followed by anti-chlorine treatment with bi-sulphite wash, but fibre become weakened by partly removal of lignin [74]**.** Also, a bleaching treatment of jute with an aqueous solution of potassium permanganate and sulfuric acid followed by washing with sodium bisulfate [75] can be useful for reduction in yellowing of jute under sunlight. However, $KMnO_4$ based bleaching could not be preferred in the conventional jute processing due to discharge of its bye products like MnO_2 which increase the COD of effluent and these processes are costly. Another alternative is to treat jute with suitable UV-absorbers. Combined scouring and bleaching of cellulosic fibre textiles can done in one-step using alkali as scouring agent and hydrogen peroxide as bleaching agent [76,77].Being one stage process, it saves energy as well as reduces processing time[78]. Bleaching process of jute textiles makes it more susceptible to more yellowing for exposure to sunlight or UV rays due to presence of lignin[79] in jute. An UV absorber has UV protection agent i.e. Cibatex UPF[80] is found to provide high UV protection for jute. Jute/cotton union fabric with titanium dioxide also provides partial protection against fading in UV rays. Farouqui and Hossain et al, [81] inferred that 2, 4 Dihydroxy-benzophenone is also effective in preventing yellowing of jute under exposure to sunlight and consequent loss of fibre tenacity and tensile strength loss in jute fibers after bleaching. Samanta et. al.[71] reported a specific recipe for an energy efficient eco-friendly process using Hydrogen peroxide and potassium per-oxo-disulphate combinedly at room temperature for bleaching of jute.

However old literature reports that Wang et al.,[82] has shown a specific recipe for mild sodium chlorite bleaching of jute (1.5g/l $NaClO_2$, pH 3, 1:10 MLR, 30°C , 30 min) followed by scouring treatment (12g/l NaOH, 3.0g/l Na2SiO3, 2.0g/l scouring aid, 2.0g/l wetting agent at 100°C / 105 min/ 1:20 MLR) which partially removes hemicellulose and lignin partially at the extent of 73% and 35% respectively and weakens jute fibre.

For jute, the liquid ammonia treatment is reported to be preferred as an alternative process to caustic mercerization of cellulose materials for increasing the strength, softness, luster and dye absorption [83,84]. Jute yarn treated with liquid ammonia at -33°C for ten minutes has shown higher extension at break and tenacity than that for normal caustic treated jute yarn, and it is suitable for tufting of carpet due to optimum elasticity [85] . Moreover, liquid ammonia treated jute fabric is reported to be shown relatively better flame retardant property than raw jute fabric[86].

When jute materials is treated with 10-18% NaOH at 2-10°C for 30 minutes, it will show profound changes in its physical structure i.e. lateral swelling occurs with considerable shrinkage in length as well as chemical property. It resulted in soft effect with formation of a high degree of crimp or waviness, which gives a wool-like appearance and so this process has known as woolenisation. It is also known as chemical texturing since it imparts bulkiness to jute yarn [87,88].

Cellulase, hemicellulase, xylanase and pectinase enzyme individually or in combination may be used form for the softening of jute fibre. Cellulase enzyme catalyses the breakdown of a cellulosic substrate at the ß-glucosidic bond [89] and de-polymerizes the cellulose molecule starting from its surface with formation of some additional functional groups –OH and -CHO at the end of cellulose chain molecules which results in surface fuzziness and increasing softness.

Recent literature reviewed that by plasma technique (defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles), the energetic ions of argon or oxygen plasma caused quick heating effect and bombarding etching the surface of jute changing its nature and properties. It results in partial removal of amorphous constituents and rearrangements of crystalline region and so increases in the crystallite size and crystallinity of jute fibre. The oxidation of cellulose polymer also leads to form carboxyl group [89, 90].

There are different functional groups like –OH, -COOH, $-CH_2OH$, >C=O, CHO groups and =NH present in the total macromolecules of the jute fibre [91]. To improve the resistance of the jute fibre against the microorganism partial, selective, or complete chemical modification might be required. Different chemical modifications enhances the value addition and diversification [92,93] of jute product**.** When jute fibre is soaked in known amount of acetic anhydride for 3 minutes at 120^{o}C and then excess acetic anhydride taken out by vacuum; acetylated at 120°C for 2 hour; acetylated slivers are then oven-dried at 105°C for 10 hours[94] . Acetylation with 10% weight gain has showed the degree of rot resistance over a 5-months test period, while untreated samples failed in less than one month [94-96]**.** Acetylation also covers the gaps between the fibrils which made the surface of jute fibre very smooth[97]. Cyanoethylation is the addition of cyanoethyl group ($-CH_2-CH_2-CN$) to the hydroxyl group of cellulose moiety of the jute fibre. It is carried out by prior alkali treatment followed by acrylonitrile treatment [98], which involves addition of an activated >C=C< bond of acrylonitrile to a partially anionised cellulosic hydroxyl of the jute fibre [99]**.** Treatment with diazomethane combined with a reduction process using sodium borohydride, confers methylation but it cannot prevent yellowing of jute under sunlight. This treatment is expensive and not simple to use. Sulphonation can used for partial removal of lignin and hemicelluloses of the jute fibre by converting them into their sulphonates at neutral condition. During the neutral sulphite treatment, jute fibre undergoes sulphonation, condensation and hydrolysis of lignin. Lignin is sulphonated at the solid phase and became soluble due to hydrolysis of ligno-sulphonic acids in water. Pectic substances and hexosan of hemicellulose are dissolved at the early stage of the sulphonation, followed by dissolution of xylan along with ligno-sulphonate [100,101]. The sulphonation makes bright, soft, improved fine and flexible jute fibre and so improves yarn making and the textile performance of jute fibre.

Polymer grafting using vinyl monomers is preferred to improve the dimensional property, softness, tensile strength, and durability of the jute fibre [102-104]. If oxy-jute is treated with any vinyl-based (CH_2=CHX) monomers like ethylene glycol / acrylamide / methyl methacrylic acid / methyl methacrylate, they would form acetal linkages / acetal cross linking by simple addition reaction with –OH group of the jute fibre. Jute fibre is treated with polyethylene glycol (PEG), it is forming acetal crosslink between –CHO group in oxy jute and –OH groups of PEG that shown higher thermal stability than raw jute fibre [105].

Wang et.al, [106] identified a quaternary ammonium compound called Glycidyl trimethyl ammonium chloride (GLYTAC), that could be used to modify the surface of the jute fibre. It is also found that GLYTAC treated jute fibre is dyed with reactive dye in lesser amount of salt and alkali than control jute fibre. It led to better dye build-up and higher K/S values of the fibre substrate than un-modified jute fibre[106] .Tannins are high molecular weight poly-phenolic compounds with sufficient amount of phenolic hydroxyl groups and carboxyl group. The phenolic hydroxyl groups in tannin are mild acidic in nature and have strong affinity towards metal ion to form the chelating complex [107,108].Chitosan, an amino polysaccharide being composed of poly-2-acetamido-2-deoxy-D- glucose, which is obtained by 60-85% deacetylation of chitin. It is polycationic in nature and so it has potential applications in textiles as antimicrobial agent[109].

1.2 Introduction to Flame Retardancy

There is high demand for flame retardant fabrics for protection from catching fire in variety of end-uses. Jute based fabrics used in mines, car upholstery and home textiles particularly for kitchen apron and gloves as well as jute-cotton union fabrics as curtains in public places, it need to be preferably fire resistant. Cellulosic fabrics can be made flame retardant by treatment with different non-durable and durable flame retardant formulations, which are readily available in literature[110].

Several works has been reported on flammability of cellulosic textiles like cotton, rayon etc for centuries. An early description of flame retardant cellulosic materials has been found in a British patent[111] granted to Obadiah WYLD IN 1735. This patent described the use of alum, borax and vitriol to prevent the flaming of paper, pulp or textiles. Nearly all successful flame resistant finishes depend upon the application of compounds containing phosphorus to the cellulose. It is know that on combustion of cellulose of cellulose molecules breaks down into a solid carbonaceous char accompanied by the formation of volatile liquids, gas and tarry substances. Anything which reduces the formation of volatile products of combustion will retard the rate of propagation of the flame.

However for ligno-cellulosic fabrics like jute, it is necessary to standardize the recipe and methods separately.

Polymer combustion is a complex process involving a multiple of steps. Figure 1.7 is a schematic diagram of the various steps. The three essential stages require to initiate the combustion are heating, thermal decomposition or pyrolysis and ignition. Ignition occurs either spontaneously (auto ignition) or due to the presence of an external source such as a spark or flame. Figure 1.8 demonstrates the mechanism of chain reaction of pyrolysis of cellulose.

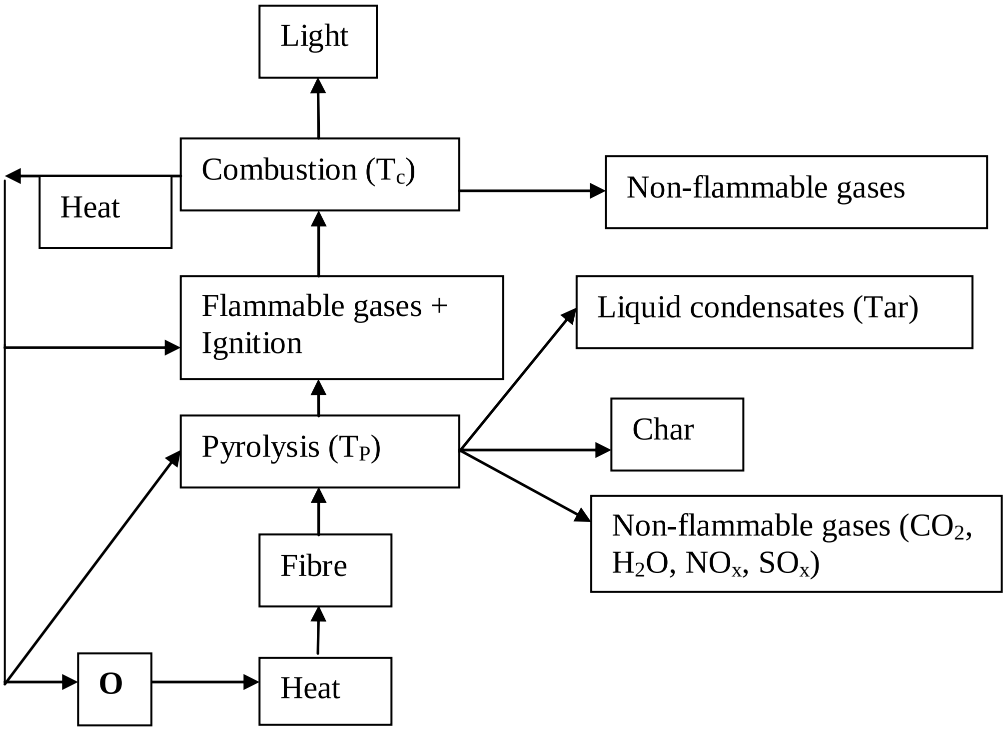


Fig 1.7 Schematic diagram of the Combustion cycle for fibres[112].

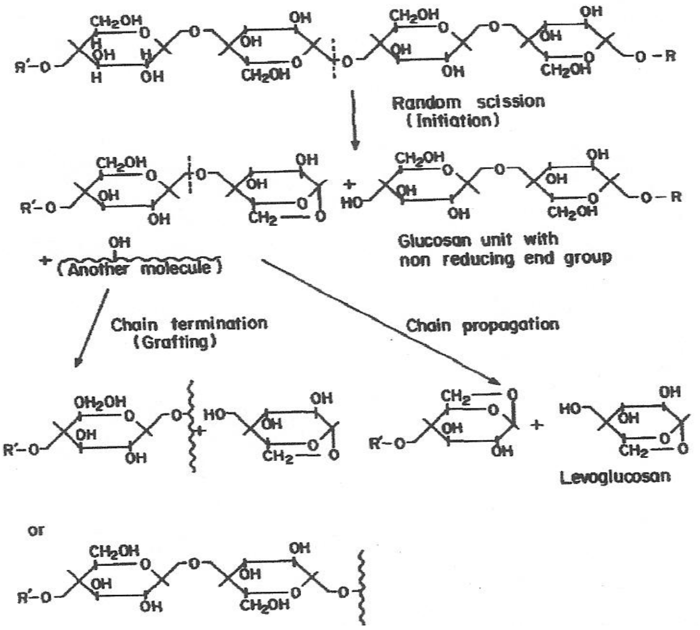


Fig 1.8 Mechanism of chain reaction of pyrolysis of cellulose[112]

As mentioned earlier one of the earliest significant contributions in history of flame retardant finishing of textiles was Wyld's patent of 1735 [111]. This describes a finishing treatment for cellulosic textiles with chemicals based on alum, ferrous sulphate and borax[111]. Almost a century later, in 1821, Gay-Lussac [113] published perhaps the first systematic study on the use of flame retardants. This work indicated that the most effective flame retarding inorganic salts both having low melting points and so formed glassy deposits over the fibre surface or decomposed into non-flammable gases derivable from the cellulose macromolecules. These ideas laid the foundation for the pioneering theories of flame retardancy of textiles. Some early references on flame retarding treatment of textiles are cited by Little [114] and Ramsbottom [115].

Tesoro [116] has compiled a whole series of definitions of terms associated with flammability. However some common terms related to flame retardancy of textile as per textile terms and definitions are given hereunder for better understanding: -

Definitions of some common terms [117]

1. Flame retardant treatment: - chemical process or treatment whereby improved flame resistance is imparted to a material. [Note- 1: This definition is published in ISO 4880-1984]

2. Flame retardant:-A chemical used to impart flame resistance.

3. Flame spread: - Propagation of a flame away from the source of ignition.

4. Flame spread time: - The time taken by a flame on a burning material to travel a specified distance under specified test condition. [Note – this definition is published in ISO 4880-1984]

5. Flame spread rate: - Distance travel, per unit time by a flame during its propagation under specified test condition. [Note – this definition is published in ISO 4880-1984]

6. Flammability: - The ability of a material or product to burn with a flame.

7. Flammable: - Capable of burning with a flame under specified test condition.

8. Flame resistance flame retardancy: - the property of a material whereby flaming combustion is slowly terminated or prevented. [Note –1: this definition is published in ISO 4880-1984]

9. Flame retardant :- a substance added or a treatment applied to a material in order to suppress significantly or reduce or delay the combustion of the material.

10. Limiting oxygen index: - the minimum concentration of oxygen in a mixture of oxygen & nitrogen that will just support combustion of a material under specified condition.

11. After flame: - continuous flaming of a material after removal of the ignition source.

12. After flame time duration of flaming: - the length of time for which a material continues to flame under specified test condition, after the ignition source has been removed.

13. Afterglow:-glow of material after the removal of an external ignition source or after the cessation (natural or induced) of flaming of the material.

14. Afterglow time duration of a glow: - the time for which a material continues to glow, under specified test condition after cessation of flaming or after removal of the external ignition source.

15. Char length: - the maximum extent in a specified direction of the damaged area of a material under specified combustion test condition.

16. Combustion textile: - a textile that will ignite & burn or that will give off vapour that ignite & burn when subjected to external sources of ignition specified test conditions.

Natural and synthetic polymers will decompose evolving flammable volatiles when exposed to a source of sufficient heat. These mix with the air shall ignite if, temperature is high enough. Table 1.8 provides a listing of decomposition and ignition temperature and Table 1.9 provides a listing of thermal transitions of fibres for a range of common polymers.

Table 1.8 Decomposition and ignition temperatures (determined by ASTM D 1929) together with heat of combustion of some common thermoplastic polymers and cellulose (cotton)

Polymer	**Decomposition Range/ ^oC**	**Flash Ignition Temperature/ ^oC**	**Auto ignition Temperature/ ^oC**	**ΔH_c/KJKg^{-1}**
LDPE	340-440	340	350	46.5
Poly propylene	330-410	350-370	390-410	46.0
Polystyrene	300-400	345-360	490	42.0
PVC (Rigid)	200-300	390	455	20.0
Polymethyl methacrylate (PMMA)	170-300	300	450	26.0
Cellulose (Cotton)	280-380	210	400	17.0

Table 1.9:- Thermal transitions of Fibres

Fibres	**TG(°C)**	**TM (°C)**	**TP(°C)**	**TC(°C)**	**LOI ***
Wool	-	-	245	600	25
Cotton	-	-	350	350	18.4
Viscose	-	-	350	420	18.9
Nylon-6	47-50°C	215	431	460	20-21.5
Nylon-66	50°C	265	403	530	20-21.6
Polyester	78-80 or 80-90	255	420-447	480	20-21
Acrylic	100	>320	290^{+}	>250	18.2
Polypropylene	-20	165	469	550	18.6
Nomex	275	375	410	>500	28.5-30
Kevlar	340	560	>590	>550	29.0
Jute	-	-	HC – 290°c $^{+}$ lignin – 425°c^{+} Cellulose– 360°c^{+}		

* Fibres having $<$ 21 LOI, readily burns in air, ad fibres having $\geq$ 27 LOI is considered to be

Flame retardant.

To fully understand the mechanisms by which flame retardants function requires knowledge of the followings;

i) Thermal degradative or pyrolytic behaviors of fibrous material

ii) Complex chemistry of flame retardant formulation.

iii) Mode of application of flame retardants.

iv) Interaction of flame retardants with the fibres.

During the initial exposure to heat thermoplastic polymers/fibres which have a linear chain structure, soften or melt starts to flow. On the other hand, on initial heating, thermoset polymers which have a three dimensional cross-linked structure, on non-thermoplastic fibres (cotton/jute/silk/wool etc) which prevents softening or melting and ultimately developed. Additional heat causes both types of polymer to pyrolyse and evolves smaller volatile molecular species. Because of their structure this occurs at high temperature for thermosets or non-thermoplastic natural fibres as opposed to that for thermoplastics. Pyrolysis is an endothermic process which requires the input of sufficient energy to satisfy the dissociation energies of any bonds to be broken (200-400 $KJmol^{-1}$) plus any activation energy requirements of the process. As individual polymers differ in the structure their decomposition temperature ranges vary within certain limits. The rate of pyrolysis will be accelerating leading to an increasing supply of fuel to the flame which then spreads over the polymer surface. Major interest for flame retardancy of textile is the fact that when the textile products burn how to render them less likely to ignite and if they are ignited, to burn much less efficiently. This phenomenon is termed as "Flame Retardancy".

Flame retardant act is to break the self-sustaining polymer combustion cycle and thus extinguish the flame or reduce the burning rate in a number of possible ways as follows:

a) To use such flame retardant materials that shall thermally decompose through strongly endothermic reactions, such that, heat required for thermal decomposition is not achieved easily. Further T_p of the fibre should not be attained and no combustion takes place easily. For this purpose Aluminium hydroxide or Alumina trihydrate and Calcium carbonate and even chaina-clay/alumina etc. is incorporated as filler in polymers and coatings.

b) To apply a material that forms insulating layer around the temperature below the fibre T_p of the fibres. Boric Acid and its hydrate salts→ when heated the low melting compounds release water vapour and produce a foamed glassy surface on the fibre insulating the fibre from the applied heat and oxygen.

c) To influence the pyrolysis reaction to produce less flammable volatile and more residual char to achieve fire retardancy of textile. This 'condense phase' mechanism is in the action by phosphorous-containing flame retardant, which after having produced phosphoric acid through thermal decomposition, crosslink with hydroxyl-containing polymers→ altering the pyrolysis pattern to yield less flammable by-products. Another explanation→ is the blocking of primary hydroxyl group in the C-6 position of the cellulose units, preventing formation of flammable by products (levo-glucosan) these phosphates catalyse the dehydration and promotes char formation and prevent the formation of levo-glucosan, the precursor of flammable volatiles.

d) To prevent combustion by erecting interference with the generated free radicals ($Br^{\cdot}$ / $Cl^{\cdot}$) from flame retardant agents reducing available heat. Such materials act in 'gas phase' mechanism, which includes halogen containing flame retardant compound, which during combustion, yield relatively long lived hydrogen halides, less reactive free radicals, for effectively reducing the heat available for perpetuating the combustion cycle and which decreases the oxygen content in the surrounding air by halogen/hydrogen halide gas generation.

e) To enhance T_c (Combustion Temperature), the temperature at which flammable bye products/fibre-fuel reduces, interference with the flame retarding agent during burning.

f) To modify/enhance the initial decomposition temperature, i.e. temperature of pyrolysis (T_p), at which it prevents/reduces significant volatile formation and increases char formation/non-flammable gaseous volatile formation.

The earlier ideas of flame retardancy, reviewed by Reeves et al. [118] are often defined in terms of coating, gas, thermal and catalytic dehydration theories. The coating theory may operate by (a), (b) and (c) functioning singly or in combination. The gas theory considers retardants which cause gas formation at temperatures below their ignition temperature (mode (c)) and/or the gases produced which do not burn at normal flame temperatures but merely dilute the flame (e.g. CO_2, HCl, H_2O, SO_2 operate by mode (b).the thermal theory describes retardants which function in terms of (c) and often these agents undergo endothermic changes such as fusion, sublimation or loss of water of crystallization. Obviously release of non-flammable volatiles here will involve pathway (b). Catalytic degradation describes flame retardants which promote char and water vapour formation and so involve functions (b) and (c).

Rarely do flame retardants operate by a single mode and it is more common to refer now days to their retardant activity functioning in the condensed phase (modes (a), (f), (c)), in the vapour (or gas) phase (modes (b) and (e)) or both. For instance, the traditional borax and boric acids/borates mixtures and similar acid generating salt systems function in the condense phase by promoting char formation and, in some cases, impart a glassy impervious coatings in front of the advancing flame [119,120]; their action has been fully reviewed by Pitts [121] More recently Nakanishi [122] has demonstrated that of a variety of commonly available flame-retardants for cellulose, the boric acid-borax system is the safest with regard to carbon monoxide and smoke production during burning.

1.3 Introduction to Nanotechnology

The progress of technology and quality of life of mankind has always been closely knit with the progress in material science and material processing technology. Most material processing techniques are based on breaking up large chunk of a material into desired shapes and sizes, inducing strain, lattice defects and other deformations in the processed material. Recent developments in nanotechnology and the demonstration of various quantum size effects in nanoscale particles, implies that most of the novel devices of the future will be based on properties of nanomaterials.

Nanostructure materials are single phase or multiphase polycrystalline solids with a typical average size of a few nanometers (1nm = 10^{-9}m).Basically, the range from (1-100)nm is taken as nano-range for convention as per National Nanotechnology Initiative in the US., and the size of hydrogen atom is considered as the lower limit of nano whereas upper limit is arbitrary. The grain sizes are so small that a significant volume fraction of the atoms resides in grain boundaries. Material is characterized by a large number of interfaces in which the atomic arrangements are different from those of crystal lattice[125-129]. Each nanoparticle contains only about 3-107 atoms/molecules. Lattice defects and other imperfections induced by the traditional material processing techniques will no longer be diluted by sheer number of atoms, when used for synthesizing nanoparticles. Furthermore, it is difficult to achieve size selective synthesis of such small particles by using the traditional approach.

The synthesis of nanomaterial can be well accomplished by two approaches. Firstly, by “Bottom Up” method where small building blocks are produced and assembled into larger structures. Here the main controlling parameters are morphology, crystallinity, particle size, and chemical composition. Examples: chemical synthesis, laser trapping, self-assembly, colloidal aggregation, etc and secondly, by “Top Down” method where large objects are modified to give smaller features. For example: film deposition and growth, nano imprint /lithography, etching technology, mechanical polishing etc. the main reason of alteration in different mechanical, thermal and other property is due to increase in surface to volume ratio.

Synthesis of nanomaterial is most commonly done based on three strategies[123] i.e.

- Liquid-phase synthesis.
- Gas-phase synthesis.
- Vapour-phase synthesis.

LIQUID-PHASE SYNTHESIS

Under liquid phase synthesis the techniques used for synthesis are:

- Co-precipitation.
- Sol-gel Processing.
- Micro-emulsions.
- Hydrothermal/Thermal Synthesis.
- Microwave Synthesis.
- Chemical Synthesis.
- Template Synthesis.

GAS-PHASE SYNTHESIS

- Supersaturation achieved by vaporizing material into a background gas, then cooling the gas.

VAPOUR-PHASE SYNTHESIS.

- Chemical Vapour Synthesis
- Spray Pyrolysis
- Laser Pyrolysis/ Photochemical Synthesis
- Thermal Plasma Synthesis
- Flame Synthesis
- Flame Spray Pyrolysis
- Low-Temperature Reactive Synthesis

Nano structured materials can have significantly different properties, depending on the chosen fabrication route. Each method offers some advantages over other techniques while suffering limitation from the others.

Due to the advancement of nanotechnology in the manufacturing of fibers/yarns including the development of fabric finishes, the applications and scopes are widespread in the area of textiles for the last few decades. By combining the nanoparticles with the organic and inorganic compounds [124], the surfaces of the fabrics treated with abrasion resistant, water repellent, ultraviolet (UV), electromagnetic and infrared protection finishes can be appreciably modified. In the most recent age, Titanium-dioxide (TiO_2) nanoparticles have been utilized for the UV protection. The usage of nano engineered cross-link agents during finishing process enhances the wrinkle resistance of cotton fabrics. The newly developed micro encapsulation technique is being used in textile industry for flame or flame retardant agents. Microcapsules using silver nanoparticles (Silver Cap) have been developed for providing anti-microbial effects and for odor control. A list of different type of nano particle finished functional textiles are given in Table 1.10

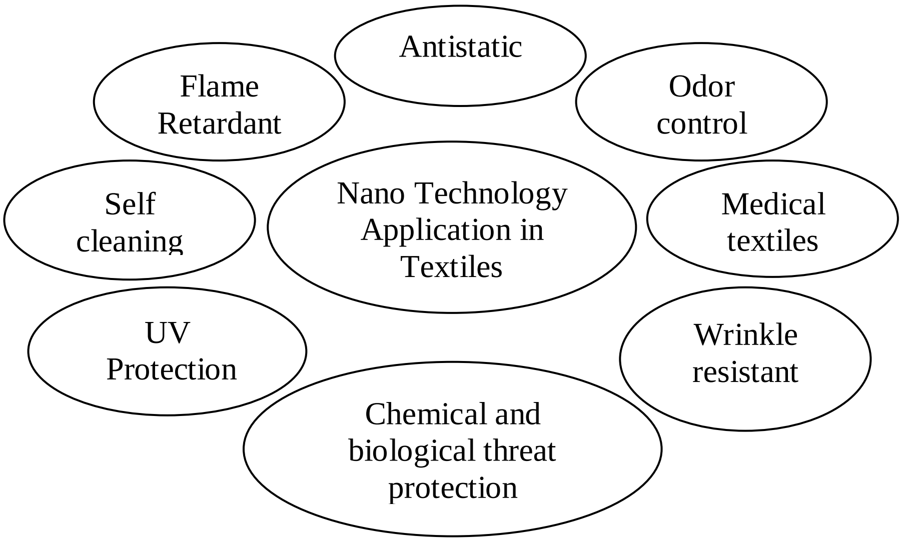
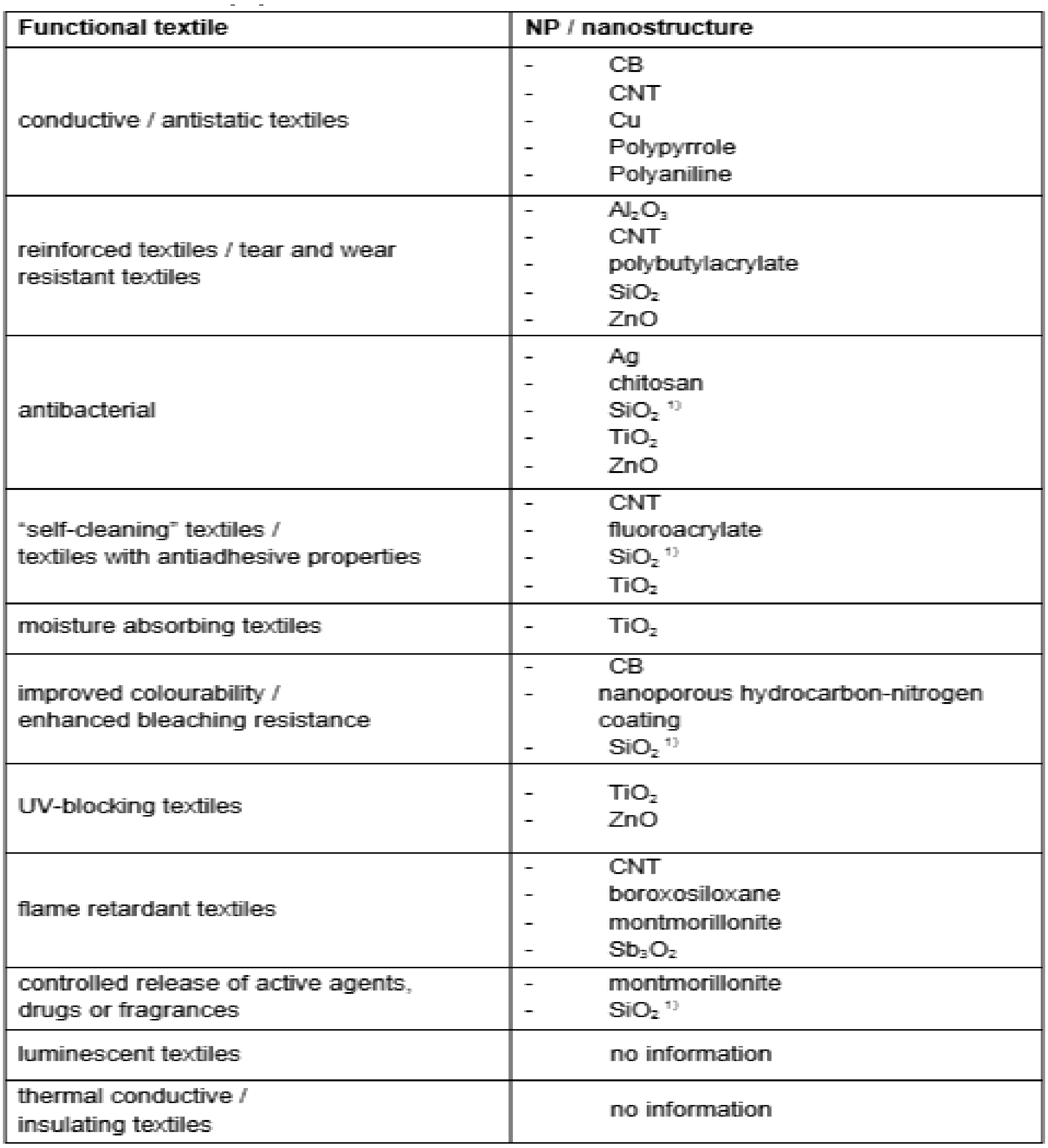


Figure 1.9 : Applications of Nano Technology in textiles.

Table1.10: Overview over functional textiles and the nanoparticles used



Functional textile	**NP / nanostructure**
conductive / antistatic textiles	- CB - CNT - Cu - Polypyrrole - Polyaniline
reinforced textiles / tear and wear resistant textiles	- Al_2O_3 - CNT - polybutylacrylate - SiO_2 - ZnO
antibacterial	- Ag - chitosan - SiO_2 1) - TiO_2 - ZnO
"self-cleaning" textiles / textiles with antiadhesive properties	- CNT - fluoroacrylate - SiO_2 1) - TiO_2
moisture absorbing textiles	- TiO_2
improved colourability / enhanced bleaching resistance	- CB - nanoporous hydrocarbon-nitrogen coating - SiO_2 1)
UV-blocking textiles	- TiO_2 - ZnO
flame retardant textiles	- CNT - boroxosiloxane - montmorillonite - Sb_3O_2
controlled release of active agents, drugs or fragrances	- montmorillonite - SiO_2 1)
luminescent textiles	no information
thermal conductive / insulating textiles	no information

The commercial application of nanotechnology has already been introduced in many prospect of textile arena. To create, alter and improve textiles at the molecular level and increase durability and performance beyond that of normal textiles are possible now. To continue this favorable trend also in jute sector it has been tried to get the flame retardant property using application of nanotechnology. With the changing trends and demands of the customer, it is the need of the age to make use of the technology available today.

1.3.1 Introduction on use of Zinc Oxide Nano-Particles for different purpose

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, flame retardants, etc. ZnO is present in the Earth crust as a mineral zincates; however, most ZnO used commercially is produced synthetically.

The biggest advantages of ZnO are low price, good gas sensing properties, photo catalytic activity, antibacterial activity, possibility to prepare structures with interesting optical properties like photonic crystals, catalytic materials in small amounts ZnO is not toxic.

.Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but it is soluble in(degraded by) most acids, such as hydrochloric acid:

$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$

Bases also degrade the solid to give soluble zincates:

$ZnO + 2NaOH + H_2O \rightarrow Na_2(Zn(OH)_4)$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such oxalate or stearate. ZnO decomposes into zinc vapor and oxygen only at around 1975 °C, reflecting its considerable stability. Heating with carbon converts the oxide into zinc vapor:

$ZnO + C \rightarrow Zn + CO$

Zinc oxide reacts violently with aluminum and magnesium powders, with chlorinated rubber and linseed oil on heating causing fire and explosion hazard.

ZnO nanoparticles as one of the multifunctional inorganic nanoparticles has many significant features, such as, chemical and physical stability, high catalysis activity, effective antibacterial activity as well as intensive ultraviolet and infrared adsorption with broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, etc. [125]. ZnO nanoparticles can be prepared by different methods like hydrothermal, chemical precipitation, sol-gel, spray-pyrolysis, solid state reaction; laser induced chemical method, etc. [126,127]. The shape and size of the nano particles depend upon various factors like method of synthesis, reaction time and temperature, type of the precursor and its concentration, etc.

Contradictory reports were revealed by researches regarding toxicity of the nano particles. A large number of materials which were considered to be safe develop toxicity at nano size ranges which is mainly related to the increased specific surface area and high reactivity of nano size materials [128]. Zinc is an essential element in human body and ZnO nanoparticles are considered to be non-toxic. Toxicity studies have shown that zinc ions do not cause any damage to the DNA of human cells [129]. Several recent investigations have reported that ZnO nanoparticles do not penetrate into the dermis [130]. Mean time increased amount of Zinc has been reported in blood and urine after exposure to Zn-enriched zinc oxide-containing sunscreens [131]. Reddy et al. [132] reported the toxicity of ZnO nanoparticles to gram-negative and gram-positive bacteria, and primary human immune cells. However working with ZnO nano particles are generally considered to be not harmful to human being.

Hady et al [133] investigated the action of sodium hypophosphite as a flame retardant in the presence of nano-ZnO, to cotton and cotton/polyester blend fabrics and reported nano ZnO as an effective compound for increasing the char formation. Table 1.12 shows some application of ZnO nanoparticle along with its production method.

Table 1.11: ZnO-NP, textile matrices and production methods reported in some of the research reports for flame retardant textiles

Nano Particle/ Nanostructure	Textile material	Production method	Integration into the textile matrix
ZnO	cotton	coating of finished fabric by dip pad dry cure method [134]	ZnO NP coating
ZnO	cotton	coating of finished textile by dip-pad-dry-cure method [134]	Starch matrix coating with ZnO NP
ZnO	cotton	coating of finished fabric by dip-pad-dry-cure method [134,135]	no information

There are many reports on flame retardant finish of cellulosic textiles but most of the earlier developed process is based on such chemical formulations which are not fully eco safe or ecofriendly in nature. Hence, the present work undertaken is an endeavour towards this direction of finding newer chemical formulations and methodology to be adopted for fire protective chemical finishes for jute fabrics. So, in the present work, (1) uses of phosphorylated polyvinyl alcohol (proved to be ecosafe and already used in dental treatment), (2) Ammonium Sulfamate, Sulfamic Acid and Urea individually and in combination and (3) use of normal ZnO powder and ZnO nano particle a to be applied on jute in the present work, to achieve the desirable degree of flame retardant performance on jute fabrics.

So, with this background, in the present work following flame retardant materials have been chosen for detailed study of their FR performance on jute and optimization of their recipe to get desirable level of FR finish and other mechanical properties.

1. Preparation of phosphorylated polyvinyl alcohol (P-PVA) and treatment of jute fabric with P-PVA for obtaining durable flame retardant performance.
2. Use of Ammonium sulfamate , Sulfamic acid and urea for obtaining FR perfprmance on jute.
3. Preparation and application of low degree of nano-ZnO with silicone emulsion for obtaining desired level of FR performance on Jute.

However before discussing these it is better to review the literature already available in these aspects.

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Chapter II

REVIEW
OF
LITERATURE

2.1 An Introduction to the Flame retardancy of Textiles

The initial work for making flame retardant fabric was started in 1735 in England [1]. Cellulosic fabrics can be made fire-resistant by treatment with different non-durable and durable flame retardant formulations, which are readily available in a comprehensive review made by Horrocks [2]. Some preliminary studies on temporary flame retardancy of jute have been also reported earlier by Banerjee et.al. [3] using borax-boric acid and diammonium phosphate. Sharma [4] suggested potassium-sodium tartarate (Rochelle Salt) as one of the flame retardant agent for jute fabric. A short review on fire retardancy finishing of jute is also available in a review paper of Samanta[5]. Today, flame retardant textiles finds application in different fields like floor coverings, floor mats, carpets, Brattice cloth in mines, military garments, hospital furnishings in public place, kitchen apron and gloves etc. [6-8]. Different flame retardant chemicals act in different way by manipulating pyrolysis, prevention of flammable gases, less or more char formation, controlling combustion , protecting from heat/oxygen and fuel etc. [8]. Now a days to avoid toxic flame retardant chemicals, extensive research has been going on to develop newer flame retardant products to enhance flame retardant property in eco-friendly system, which may be non-durable, semi durable or durable. An ideal FR fabric for textile applications must be comfortable, eco-friendly, semi-durable, durable and cost effective.

Gay Lussac [9] and Horrocks[10] have given an overview of different FR chemicals applied in textiles. The pyrolysis of cellulose has been reviewed by Kilzer[11] Lewin et.al[12] Shafizadeh[13] Davies[14]. Also few review articles have discussed the pyrolysis of wool; Benisek[15] has briefly reviewed the important thermal degradation actions which influence burning behavior of wool whilst Slater[16] has reviewed the thermal degradation behaviour of wool, cellulose and synthetic fibres up to 1975. Peters and Still [17] has reviewed the chemistry of pyrolysis of the major fibre forming polymers, including cellulose, polyester, polyamide and poly(acrylonitrile). The thermal and thermal oxidative mechanisms of degradation which essentially lead to the formation of flammable volatiles generated from polyamide and polyester fibres has been described by Pearce et al. [18] , D'Alo and Ciaperoni respectively[19] .Recently, a general review by Lewin [20] also contained flame retardant mechanism and systems of most common fibres upto 1984. A short review on fire retardancy of jute is also available in the review paper of Samanta.[5] The important properties of textile materials that determine the extent of fire hazard are[21]

a. Ease of ignition
b. Rate of burning
c. Heat release rate
d. The other factors that influence the thermal protection level include :-

-Melting and shrinkage characteristics of synthetic fabrics.

-Emission of smoke and toxic gases during burning

-Physical and chemical changes of thermoplastic materials

A general review of the action of non-durable, semi-durable and durable flame retardants has been carried out by Reeves et al. [22] and Kasem and Rouette [23]. The most important group of flame retardants are those containing phosphorus in most 0f the fibre/ polymer subtrates, which functions in the condensed phase as char promoters. Weil [24] and Aenishaenslin [25, 26] have comprehensively discussed available types of such agents and their mechanisms of action. Phosphorous-based flame retardants function only if the fibre structure is capable of under going transformation to char. In the case of thermoplastic fibres like polyamide and polyester, melt and drip are the key factor for such action.

In many flame retardants the presence of nitrogen has an additive and in many cases a synergistic effect on the performance of phosphorus containing flame retardants. Consequently, many commercially available flame retardant contain both phosphorous and nitrogen together, this interaction has critically reviewed by Weil [27], Khanna and Pearce [28] and by Einsele[29] who specially refers to their activity including synthetic fibres. Those organophosphorous flame retardants containing synergistically active nitrogen (which are particularly suitable for use on cellulosic textiles) functions in more than one way. Barker and Hendrix [30] suggest that the nitrogen acts as a nucleophile with respect to the phosphorous entity thereby facilitating to form polar P-N bonds in polymeric species.

The enhanced electrophilicity of the phosphorous increases its ability to phosphorylate the C-6 primary hydroxyl group on anhydroglucopyranose repeat unit of the cellulose molecule. This prevents the intramolecular C(6)- C(1) laevoglucosan-forming reaction to occur, which is the main volatile fuel formed during pyrolysis of cellulose. Simultaneously, the Lewis acidicity of the electrophilic phosphorous promotes dehydration and char formation [25]. The main actions of such retardants may be summarized as [31]

i) Nitrogen-synergized phosphorylation of cellulose to block laevoglucosan formation

ii) Lewis acid-catalyzed dehydration plus some chain dehydration to short chain oligomers not conducive to laevoglucosan formation and

iii) Cellulose cross-linking following phosphorylation which promotes both char formation and its consolidation.

Thermal degradation of jute containing 54-62% cellulose and its flame retardant finishing have been described by some earlier researcher in different reports.[32-40]

Whewell [41] has surveyed flame retardants treatment within the wider context of fabric finishing up to 1970. Similar studies have been made by Brukitt and Heap [42] in 1971 and Smith [43] in 1975. Mehta [44] more briefly has considered the aspects of flame retardant finishing with special reference to polyester and cotton, while Sello [45] more generally reviewed the flame retardant finishes in brief for both natural and synthetic fibres.

Specific reviews of flame-resistant or flame retardant finishing (FR) are also made available earlier by Hangte [46] and Einsele [47] considering all the general aspects up to 1970. Most recently, Meheta [48], Mukle [49] and Glass [50] considered FR finishing developments between 1978 and 1981. The most recent reviews on this subject is cited by Zhuk Y. [51] which have introduced bromine free flame retardant materials and additives without causing changes in handle and the porosity of the treated fabric. Miller T. [52] has studied the mechanism of flame retardants, methods of flame retardant finishing including flammability tests which are discussed, in terms of non-durable, semi-durable and durable flame retardant finishing systems. Horrocks [53] have discussed a comprehensive revew of different flame retardant formulation in terms of their flame retarding and char forming characteristics as well as their end use applications.

Whilst specific flame retardant chemicals and treatment methods have been covered in the reviews available in few recent references [41-48] , [54] mentioning specific flame retardant agents covered by Kuryla [55] . These references not only lists the chemical structures of flame retardant agents based on inorganic, phosphorous, halogen and nitrogen compounds but also indicates and states the manufacturers and suppliers of these agents in USA and Europe. As previously cited, Weil [27] specifically collates and reviews the phosphorous-based flame retardants, whilst Reeves et al. [56] has made a survey of non- durable, semi- durable and fully durable flame retardants for cellulose and manmade fibres based textiles. Another publication [57] summarizes the availability of natural flame retardants for textiles. Horrocks et al. [58] have studied a series of phosphorous containing flame retardants including some in the formulation with selected resins and applied as back-coating to both cotton and cotton-polyester (35:65) blended fabrics, where all these formulations raise the LOI value, but only those based on the Ammonium phosphate and a cyclic phosphate which has enabled samples to pass a small-scale version of the simulated match test BS5852:1979. Flame retardant back coating promoted higher level of char formation but, this do not reflect on their performance to the match test BS5852:1979. Thermo gravimetric analysis (TGA) study suggests that the more effective flame retardant (amongst different types of phosphates), is $(NH_4)_2PO_4$ which liquify by melting and/or decomposition well below 300^{o}c. It is proposed that this liquification enables wetting of the back face of the fabric and diffusion to the front face whereas the temperature rises towards char formation which occurs before ignition can take place. Nair G P[59] has introduced new stannate based phosphate process. The stannate step involves padding with sodium stannate followed by Ammonium-phosphate treatment which partly counters fabric flaming. However flameless combustion through the afterglow effect is obtained, when the same is passed through the phosphate step which includes further padding with DAHP and urea. This process is said to give good flame retardant results up to 25 washes. The study by Stowell J. K & Yang C. Q [60] details the development of a new phosphorus based technology for flame retardancy which is easy to apply and are durable to numerous home launderings and in some cases even enhance the physical properties of the fabrics. A study[61] on fluro-chemical treatments was produced durable fabrics that are simultaneously flame retardant and water and oil repellent and the effect of fluro-chemicals on the thermal chemistry of inherently flame retardant fibres was studied using thermo gravimetric analysis(TGA). Extended study on the same covers the use of metal salt and especially copper nitrate as a bath salt stabilizer which confirms durable flame retardant properties and rot resistant protection of fabric [62].

2.2 Brief Review on Different type of Flame retardant Agents

The flame retardant agents available and their modes of application have been partly reviewed by Lyons [63] and also by Tesoro [64] chronologically. More comprehensive studies are also made available by Drakes and Reeves [65], Lewin and Sello [66] and very recently by Barker and Drews [67]. Sanghvi [68] has surveyed those flame retardants which are of specific use in the Indian textile industry. Very few literature are available which relates FR finishes to natural cellulose other than cotton.Specially to nmention, the work by Haszczynska [69] is on linen and the work of Mehta and Hoque [70] concern the flame retardant finish of jute besides some scanty work by other researches on jute. However, the different FR agents can be discussed in three different categories viz., non-durable, semi-durable and durable type.

2.2.1 Non-Durable Flame retardants

The chemistry of non-durable and semi-durable inorganic flame retardants for cellulose have changed little since the reviews of Little [71,72] and Lyons [63]. Little's classification of non-durable flame retardants in three groups still holds true. Group I flame retardants are those which have relatively low melting temperatures and so produce a glassy melted film or foam in contact with decomposition products and the glassy melted film or foam provides a barrier between flame and substrate. Notable examples here are boric acid, its sodium salts and mixtures with borax . Group II FR agents are inorganic acids and acidic salts or salts releasing acids on heating and thereby cause dehydration and promotes char formation, e.g. Sulphamic acid, ammonium sulphate, phosphoric acid and its salts and other lewis acids such as copper nitrate, zinc chloride etc. occupy this group. Compounds which sublime or release non-flammable vapours such as carbonates, halides, hydrated salts and ammonium salts, constitute the Group III flame retardants amongst all non-durable type FR agents.

The following non-durable flame retardants may be regarded effective for imparting non-durable flame retardant finishes on cotton or jute.

Borax-Boric Acid Mixture

This retardant formulation is made by preparing a paste of seven parts of boric acid in a minimum amount of water, then adding this to a water solution of three parts of borax. About 10 per cent add-on for cotton and minimum 12% add-on for jute by weight is adequate for a medium weight cotton or jute fabrics. Fabrics treated with this retardant are flame resistant but have afterglow, which can persist from 30 sec to several minutes.

Borax- Diammonium Phosphate

This flame retardant formulation is made by dissolving equal parts of borax and diammonium phosphate in water. However, the presence of the phosphate provides glow resistance. Borax-diammonium phosphate can cause some corrosion of metals of the application bath for applying this flame retardant formulation.

Diammonium Phosphate

The fire retardancy imparted by diammonium phosphate is about equivalent to that of borax and diammonium phosphate mixture.Diammonium phosphate provides both flame and glow resistance.

Ammonium Sulphate

Ammonium sulphate is dissolved in water· to form a clear solution, then ammonium hydroxide is added to give a faint odour of ammonia. This formulation also provides flame and glow resistance. It may cause a slight reduction in the strength of treated fabric.

Others

Many additional non-durable flame retardants are available. Some are based upon alkyl and aryl phosphates of various types. Others are based upon the products obtained by reacting urea or other amides with phosphoric acid and various phosphoric acid derivatives are known to produce a complex water-soluble flame retardant formulation. These are applied to cotton and rayon fabrics from a water solution by pad-dry-curing technique.

Where aesthetic properties of the fabric, such as, handle and drape are not that important for such fire-retardant fabrics, but a level of durability commensurate with that required for outdoor weathering as per end use is necessary.

2.2.2 Semi-Durable Flame Retardants

Semi-durable flame retardants may be defined as those which withstand a few (one or more) laundry cycles, the upper limit being about 15 mild laundry cycles. Flame retardants of this class are useful for draparies, party dresses and other items which will not be laundered several times frequently.

The use of semi-durable, insoluble metallic agents and, in particular, those with titanium and antimony compounds which function together in a mutually advantageous manner, are well documented [65-67], of specific interest is the proposal [73] of an effective durable flame retardant based on titanium (IV) chloride, antimony (III) oxide suitable resin for some enhanced durability(as semidurable).

For example, use of Sb_2O_3 in synergistic combination with halogenated organic species is commonly used for synthetics, while, simultaneous use of chlorinated paraffins offers a combination of water repellency and consequent flame retardancy durability for outdoor use of such fabrics in tentage and other outdoor applications.

The efficiency of molybdenum compounds has been studied by Trask et al. [74] and they report that combinations of diammonium molybdate with either Tri methyl melamine(TMM) or poly(vinyl bromide) are synergistic in their promotion of flame-retardant behaviour on cotton, Their treatments show good outdoor and weather durability and so is recommended for tents and sleeping bags.

Use of poly(vinyl chloride)-Sb_2O_3 combinations has been investigated but has received little interest since the 1960s until perhaps in 1975 when LeBlanc et al. [75] reported a novel, low cost, flame-retardant system for industrial cottons by a synergistic combination of urea, diammonium phosphate and antimony (III) oxide applied in mixed vinyl chloride copolymer and acrylic latex after curing, gives a semi-durable, effective FR finish. This combines a phosphorylated finish with an Sb-Cl synergistic system which acts in both' the condensed and vapour phases and is most suitable for synthetics like polyester and polyamides but may also be applied on cotton as well.

During the last 15 years, there has been some drive toward the use of synergistic combinations of antimony(III)oxide and brominated aromatic hydrocarbon derivatives applied in the presence of a synthetic resin Mischutin [76] has reviewed the use of decabromo-diphenyl oxide- Sb_2O_3 finishes for both cotton and Cotton/polyester blends. These finishes also function well on synthetic blends with cotton. Whilst halogen and phosphorus-halogen flame retardant combinations are commonly used for synthetic polymers as successful flame retardants. Timpa [77,78] have synthesised and applied the phosphorus-free compound tetramethylol 2,4. diamino-6- (3,3,3-tribromo-1 -propyl) -1, 3,5-triazine to cotton at add-on about 13% for desirable level of flame retadancy.

Whilst the nitrogen-bromine-containing finish requires no catalyst and gives good handle and also an enhancement of crease recovery. An improved FR performance followed if the methylated derivative was used in its place. However, both these finishes are a combination of nitrogen with halogen[79].

An interesting finish which combines nitrogen, halogen and phosphorus is the prepolymeric finish prepared from tris (1,3-dichloro-2-propoyl)phosphate and poly (ethylene imine)[80]. Whlist Bertoniere and Rowland found this finish conferred acceptable flame retardancybut its durability was low; this caused them to modify the formulation to replace the chlorinated phosphate by a chlorinated phosphonate derivative, as previously discussed. [81]

No work has been cited for phosphorus-halogen systems for cotton since the review by Liu[82] in 1973

2.2.3 Durable Flame Retardants

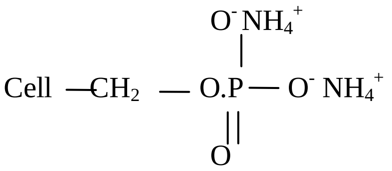
There are two general types of durable flame retardants for cotton: (a) those used on apparel and household fabrics, and (b) those used on industrial fabrics. Flame retardants of the first group for apparel and household fabrics, should be unaffected by washing and cleaning processes and should provide a supple fabric and should have no adverse effect on textile related properties. Phosphorus-containing compounds and polymers are the most important materials in this group. Retardants for industrial textile fabrics should be resistant to sunlight, rain and outdoor weathering conditions. A combination of antimony oxide (Sb_2O_3) and halogen provides the most suitable type of fire- retardant for such industrial fabrics.

Three important techniques/methods have been used in the application of durable flame retardants to cotton and related fabrics for apparel and household uses: (1) permanent coating of flame retardant chemicals on cellulosic fibres/fabrics, (2) chemically fixing flame retardant chemicals with cellulose, and (3) polymer film (flame retardant) formation by suitable FR agent on the fabric surface. A few of the preferred processes are reviewed in this section. However, chemical fixing of flame retardant chemical is the only concern of the present work. Hence a brief review on chemical fixing of flame retardant chemical is discussed below.

Reference to the work of Lewin and Sello [66,67] and Weil [85] , it appears that for two decades since 1950 were the ‘golden age’ of the developments in synthetics and development of durable phosphorus containing flame retardants and in particular, those for cellulosic substrates. Since the mid- 1970s, very few new developments have taken place and most currently available and successful commercial durable retardants were discovered during the said former period; some of the important developments of which are discussed below.

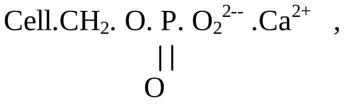
2.2.3.1 Phosphorous containing Flame retardants

Before discussing the important durable flame retardant system containing phosphorus, it is worth considering that the simplest durable flame retardant cotton was derived from its phosphorylation as described in the classic work of Little [71] and more recently by Lewin and Sello [66,67]. Phosphoric acid and its derivatives in the presence of a nitrogenous buffer will esterify cellulose under elevated temperature (curing conditions) with minimum acceptable degradation. An early review of phosphorylation of cellulose is that described by Reid and Mazzeno [86] . Such phosphoric esters of cellulose having the typical formula as follows: -



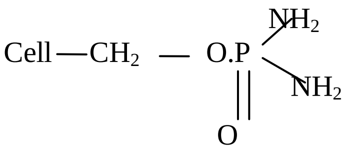
$$\text{Cell}—CH_2—O.\overset{O^-NH_4^+}{\underset{O}{P}}—O^-NH_4^+$$

Unfortunately by exchange of cations Ca^{2+} ions of hard water give the respective salt



$$\text{Cell}.CH_2.\ O.\ \underset{O}{P}.\ O_2^{2--}.Ca^{2+}\ ,$$

which is stable and prevents release of free phosphoric acid on heating and so reduces the flame retarding character of the finish. Nuessle et al. [85] however showed that phosphorylation by means of cellulose-diammonium phosphate reaction in the presence of urea gave rise to a finish which resists simple Ca^{2+} ion exchange. Although it is saponified by alkaline washes. Below 170°C, or after prolonged curing at 170°C, formation of the respective amido phosphate occurs:



$$\text{Cell}—CH_2—O.\underset{O}{P}\begin{matrix}NH_2\\NH_2\end{matrix}$$

The role of urea was considered to be that of a solvent which dissolves released H_3PO_4 and swells cellulose to enhance penetration although above 170°C, some cellulose-urea interaction occurs, possibly forming cellulose carbamate, $\text{Cell}.CH_2.O.CO.NH_2$.

In 1968, an improved flame retardant for cellulosics was reported; it is based on cyanamide and phosphoric acid[86]. For best results, the cellulosic material is treated with an aqueous solution containing about three moles of cyanamide per mole of phosphoric acid, and then dried and cured. Cotton fabric treated by this process has good flame retardancy and better physical properties than· cotton subjected to earlier techniques. However, the loss in tensile strength is considerable and there is some ion exchange during laundering.

The actions of urea and the other organic nitrogen compounds, including guanidine and melamine derivatives, are partly those of pH buffering system to reduce cellulose degradation which accompanies the esterification; the considerable work in this area were reviewed in

1975 [66] is supplemented by the more recent studies by Muniswamy et. al. [87] showing the effects of finishing variables on fabric properties subjected to combined urea-phophate-formaldehyde (N-methylolated) resin treatment. The low cost of such flame retarding systems has attracted considerable recent research[88] interest in India and not only has comparison with THPC-amide systems and modes of increasing the efficiency of such fire-retarding agents have been studied. Iyer et. al. [89] has noted that use of certain resin formulations can enhance durability and crease resistance on urea-diammonium phosphate finished cotton fabrics. A subsequent report by Nonsiainen [90] has completed review for both durable and non durable urea-phosphate finishes for cotton and other cellulosics.

A compound closely related to phosphoryl amide imparts durable flame retardancy to cellulosic fibrous materials. This compound viz., chloromethyl phosphonic diamide [$ClCH_2P(O)$ (NH_2)], is prepared .by the reaction of chloromethyl phosphonic dichloride with· ammonia[91]. It is applied from water solution by a pad-dry-cure method. During the reaction some ammonia and chlorine are eliminated, but the finished fabric also contains nitrogen and chlorine and much larger quantities of phosphorus. Presumably, some polymerization takes place within the fibres, but it is highly probable that esterification is extensive. Esterification results in the loss of ammonia. Fabric containing 3·2 per cent phosphorus passes the vertical flame test after three washes for 30-min soap-soda washings at the boiling temperature. Apparently, this finish is more stable to hydrolysis than that produced by reacting phosphoryl amide with cotton.

More recently the after treatment of phosphorylated cotton with antimony (III) oxide and zirconium oxychloride [92,93] and precipitated stannate salts [94] have been studied with the aim of improving lauder ability of such FR finish.

A final interesting variation of the phosphorylation reaction is the observation by Issac et al.[95,96] , that if phosphorylation is undertaken simultaneously with sulphamation, ion exchange problems are rendered tolerable. In this system sulphamation by ammonium sulfamate, NH_2SO_3H is enhanced, if phosphorylation is carried out with phosphoric triamides; (diammonium phosphate may not be used because it cannot suppress the afterglow associated with the cellulose sulphate groups) and the phosphorylation itself is associated with sodium ion exchange from soft water used in laundering liquors and in this system minimal afterglow and acceptable durability is achieved, if sulphur is present at about the 2% level and a P/S mass ratio of 1.3-2.0 on cellulose is maintained.

2.2.3.2 Tetrakis (hydroxymethyl) Phosphonium Derivatives

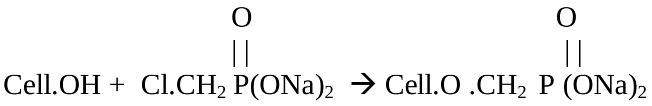
Tetrakis (hydroxymethyl) phosphonium chloride, THPC, a most popular FR agent for cotton is a water-soluble, crystalline compound produced in high yield by reaction of formaldehyde with phosphine and hydrochloric acid [97]. The methylol groups in THPC react with amides and amines to form highly insoluble polymers when the nitrogenous compound are di- or polyfunctional. Although the phosphonium structure exists in THPC, the final product is in the form of a phosphine oxide. This phosphine oxide structure is very stable to hydrolysis. The ionic chlorine in THPC is lost during reaction and is not present in the final product. The methylol groups of THPC react with amines and amides much as N-methylol compounds react with the same amines and amides. THPC also reacts with cellulose, but the reaction is very slow under the usual conditions of producing flame resistant finish of cotton.

In THPC-Amide Process, *w*hen THPC-based amides are formed inside the fibres of cellulosic fabrics in suitable concentrations, the fabric renders a good flame retardancy[98]. The first method for using these polymers in the production of flame resistant cotton is now referred to as the THPC-amide process. A typical formulation contains 17 per cent THPC, 10 per cent methylol melamine, 10 per cent urea, and 1 to 4 per cent of a base (amide). The formulation is applied to fabric in a pad-dry-cure method. This process (and slight modifications of it) has been used commercially in the U.S. for several years. .

The original THPC-amide flame retardant formulation has been modified to reduce cost and improve the properties of the treated fabric. Some of the more important modifications are described below.

2.2.3.3 Phosphonic Acid Derivatives

Whilst phosphorylation with phosphonic acids and derivatives gives rise to hydrolytically unstable P-O ester bonds, this is not so if, phosphorylation occurs via the P-C moiety of a phosphonic acid derivatives.It was at this time that Drake et al[99] disclose the following reaction for the preparation of phosphono methyl cellulose from chloromethyl phosphonic acid as the di sodium salt:



$$\mathrm{Cell.OH} + \mathrm{Cl.CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(ONa)_2} \rightarrow \mathrm{Cell.O\,.CH_2}\ \overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\ \mathrm{(ONa)_2}$$

Other phosphonate derivatives of cellulose developed during this period are reviewed by Lewin and Sello[66]. One interesting later development by Tesoro [100], demonstrated the presence of nitrogen-phosphours synergism in durable flame retardant formulations based on amination of the halogenated polyphosphonate (phosgard C-22 R, Monsanto) condensed to cellulose via a suitable bridging reactant such as APO(Aziridinyl phosphine oxide).

Subsequent work[101], demonstrate that amido derivatives of methyl phosphonic and chloromethyl phosphonic acid. Sanderson et al. [102] had demonstrated earlier that the methyl phosphonic acid was condensed to cellulose in the presence of cyanamide, the simple cellulose ester was obtained which was effective at low phosphorus levels of 1.5-2.0 % which was surprisingly resistant to 50 washes.Whilst Tesoro et al. showed that phosphonoacetamide derivatives of cellulose confer acceptable flame retardancy[103,104]. Most commercially successful phosphonates are the N-methylol dialkyl phosphonopropionamides from which Pyrovatex CP (CGY) is derived and are effective on all cellulosic fibres [105,106]. Use of this flame retardant was made by Willard and Wondra[107] to quantify the flame retarding behaviour of such FR finish, in terms of oxygen index measurements, as functions of both nitrogen and phosphorous concentration. This function is a condense phase retardant and promotes char formation[108]. Ohe and Fujii[109] have recently compared the behaviour of phosphonopropionamide finishes with the flame retarding character of THPC and especially the influence that melamine derivatives have on their effectiveness, Mehta [110] has, shown that by applying Pyrovatex CP to cellulose modified with-$CONH_2$ and/or -NH_2 groups, 30-50% reduction of finish concentrations may be made without loss of flame retardancy. However, as with THPC finishes, so too with this type, free formaldehyde may be a problem and is not considered now as eco-friendly. Sanuki et al. [111] demonstrate the need to soap finish of the fabrics to minimize this hazard. Recent studies by Ball and van der Walt [112] have shown that compatible direct and reactive dyes may be applied simultaneously with Pyrovatex CP although shade depths are less than normally expected. Subsequently, the effects of varying resin and catalyst types on both flame retardancy and colour fastness were investigated [113]. As an alternative to Pyrovatex CP, Bandyopadhay et al. [114] have later considered the effect of varying the resin finish on the flame retarding behaviour of N-methylol diethyl phosphonopropionamide. The whole range of Fyrol oligomeric phosphonic ester flame retardant finishes designed to suit different substrate has been described in a literature [115]. However Fyrol 76 has since been withdrawn for suspected toxicological reasons.Very recently, Sanuki et al. [116,117] have replaced the persulphate initiator by cerium (IV) ammonium nitrate which can function at temperatures as low as 40°C. They found that better flame retardancy resulted from a given level of phosphorus nitrogen and that enhanced fabric whiteness and strength retention followed by the low temperature cure.

2.2.3.4 Other phosphorus containing Finishes

As phosphates are also not considered as eco-friendly or skin friendly, attempt has been made recently to produce polymeric phosphates that are eco-safe, e.g. is phosphorylated polyols that are used in replacement of teeth etc. in dental/medicenary field [118]. So, considering ecofriendliness, many researchers has started searching effective polymeric phosphates derivatives for FR finish that are eco-safe. Hence, phosphorylation of polyols though they are not always exactly related to textile applications has become an interesting subject of research now a days. Ying-Ling Liu et al. [119] have reported the chemical modification of poly (vinyl alcohol) (PVA) through its initial oxidation followed by nucleophilic addition by suitable agents. PVA was oxidized by $KMnO_4$ to forn vinyl ketone units along the polymer backbone. The chemical modification of PVA was then conducted through the reaction of the carbonyl group of the vinyl ketone unit with 9,10-dihydro-9 oxa-10-phosphaphenanthrene-10-oxide (DOPO) as a neucleophile. Through this approach the phosphorous DOPO group was attached onto the carbon atom of the polymer main chain rather than onto the pendent hydroxyl group of PVA. This DOPO containing modified PVA showed improved thermal stability, organic solvent solubility, and flame retardancy on textiles. Suzuki et al reported [120] polymer films of partially phophorylated poly (vinyl alcohol) (P-PVA) with dipotassium salts that have been prepared and characterized, and the effect of phosphorylation on the ionic conduction in the mixed film of P-PVA and poly ethylene glycol (PEG: avg. MW=200), P-PVA /PEG film, have been investigated thoroughly. The glass transition temperature (Tg) was significantly decreased by phosphorylation and it decreased with increasing degree of phosphorylation indicating an increase in amorphous part of the polymer for P-PVA and PEG combined systems, the ionic conductivity increased and the activation energy of the ionic conduction decreased with increase in DP, which agreed with the result of Tg.

Koyarna et al.[121] have reported the preparation of new anionic gels by the chemical cross linking reaction of highly phosphorylated poly (vinyl alcohol) with gutaraldehyde. The various type of poly-anionic gels having high or low swelling characteristics and different degrees of hardness were prepared for using the crosslinking reaction under different reaction conditions. The thermal properties of the chemically crosslinked P-PVA were also investigated. F. A. Abdel-Mohdy[122] has reported phosphoramide containing an active vinyl group (P-III). Its structure was confirmed by elemental analysis and Fourier transforms infrared, nuclear magnetic resonance, and mass spectroscopy.

2.3 Important Research works on flame retardancy treatments on cotton and other fibres and their blends including its testing.

Menezes et.al.[123] have discussed the role of fire safety regulations, tests, the fire risk of materials and different flame retardants agents, which may be a guidline to the present researchers.

Eaton et.al [124] gave a comprehensive description on various test methods aimed at different sectors of industry to produce the wide range of flame retardancy test methods and standards. Ozcan et.al [125] found that fabrics produced from coarse yarns will burn more easily than those from fine yarn because of their loose structure of former. Yarn count and twist factor made an influence on ignition time for the knitted fabrics where, increasing yarn counts decrease the ignition time and the best ignition time is obtained for yarns with a 3.6 twist coefficient.Mehta [126] has briefly considered different aspects of flame retardant finishing with special reference to cotton and polyester also.

Benisek et.al [127] showed how different fabrics and finishes behave in fire protective clothing designed to resist radiative, convective and conductive heat. Dawn et.al [128] analysed the provision and properties of cotton based fire protective apparel designed for the US Space Shuttle. They thoroughly assess the acceptability of cotton finished with tetrakis (hydroxymethyl) phosphonium sulphate – urea-ammonia cure system for this most stringent end use specifications. Stephenson et.al [129] surveyed both non-durable and durable FR treatments for non-woven products with special reference to cellulosics and polyester too.

Mehta et.al [130] reviewed the toxicological hazards of flame retardants which are often questioned in terms of the toxicity of the basic flame retarding chemicals used and the chemical hazards occur during applicat during specific and end use. They studied for commonly available cellulosic flame retardants and mentioned agent like tris (aziridinyl) phospine oxide (APO) and antimony oxide which are considered to be toxic and hence are not eco-friendly.

Nuessle et.al [131] showed that phosphorylation by means of cellulose-diammonium phosphate reaction in the presence of urea gave rise to a flame retarding finish to a reasonable extent, but the same is not considered as eco-friendly too.

Kaushik, et.al [132] have studied that a THPC-Thiourea based formulation, which is applied to the polyester-viscose blended fabrics by pad-dry cure procedure followed by washing to produce. FR P/V fabrics, which retain their retardancy, offer as many as fifty thorough laundering and trumble drying, but THPC is susceitible to formaldehyde release problem. THPC-Thiourea finish imparts the durable flame retardancy by crosslink-OH Group of cellulose portion of viscose fibres in polyester/viscose blended fabric due to which about 15% loss in tensile strength of treated fabrics occur. Comparative studies of flammability behaviour and physical properties of controlled, treated and washed fabrics are reported under the different conditions of treatment.

Ramchandran et.al [133] studied two different methods for flame retardant finish applied to cellulosic fabrics. Between two different this novel methods, the observed results proves that Urea-phosphoric acid combination is found to be the best for imparting a durable flame retardant finish to cellulosic fabrics even better than stannate-phosphate step method in terms of higher flame resistance and better tensile properties retention with and also reduced stiffness character for the former than the later.

Blanchand et.al [134] stated that cut pile cotton/polyester carpets burns over the entire area upon ignition if, the pile density of the carpet is sufficiently low. Specific chemical modification of cotton part by esterification of cellulosic fibres results reduced and restricted combustion behaviour. This type of chemical treatment allows such substrates to pass the standard flammability test for carpets and rugs. This, cotton containing such carpet PET/Cotton is when spray treated with only 5-10% polycarboxylic acid and suitable catalyst, it exhibits satisfactory flame suppression properties. Such polycarboxylic acids i.e. 1,2,3,4 – butane tetra carboxylic acid (BTCA), Citric Acid and maleic acid or anhydride when is treated with catalyst such as Sodium hypophosphite, sodium phosphate it achieves required FR properties too.

Domobrowski[135] discussed that there is a common assumption about the dangers of decabromodiphenyl Ether (DECA). The said work to presents an alternative view regarding to the use of such halogenated flame retardant (FR). Brominated FRs such as DECA inhibits the chemical reaction between oxygen and fuel, preventing a fire to develop or propagate.

Indushekar et.al [136] studied the development of flame, water and oil repellent properties of fabrics produced by three different techniques (a) fabric treatment (cotton and nylon) (b) incorporation of FR as additives before melt or solution spinning of the synthetic fibre followed by application of water and oil repellent treatment at the fabric stage (TR polyester) (c) introduction of water and oil repellency in a blend of inherently FR fibre to produce dope treated FR man-made fibre (KRVR).

Horrocks [137] discussed the burning behaviour of polyester/cotton blended fabrics in a comprehensive way in relation to their FR finishes. Particular attention is paid to the effectiveness of phosphorous, nitrogen and antimony (III) oxide/halogen flame-retardant systems. Relatively recent developments in UK suggests that phosphonium salt based condensate FR finishes are effective on cotton-rich blends and antimony-halogen systems may be used on all polyester/cotton blend compositions. Both types of flame retardants are acceptable considering its durability to laundering.

Bajaj et.al [138] reported that Diammonium Hydrogen phosphate (DAP) and N-methylol resins were applied in combination to cotton and polyester/cellulosic blends using one step method and also by two step sequential pad-dry-cure process. Amongst different types of N-methylol resins used, only urea formaldehyde (UF) resin treatment on phosphorylated cotton demonstrated the phenomenon of N-P synergism action in terms of Limiting oxygen index(LOI), while no clear trend of results could be established in such blends.

Nakanishi et.al [139] studied the flame retardant of cotton fabric with nitrogen, phosphorous, sulfur, halogen and boron based compound individually and also in combination with two components at a time as a binary mixtures which showed sufficient flame retardancy to cotton fabric and the flame retardant samples exhibited clear differences in thermal degradation behavior after the treatments compared to the corresponding untreated fabric.

Blanchard et.al.[139] studied phosphorylation of cellulose with phosphonic acid derivatives for flame retardant finish of cotton and investigated the changes in physical properties of such fabrics. Discolouration upon curing of phosphorylated cotton is reduced by incorporation of 1-4% of dicyandiamide.

Mamalis et.al[140] mentioned that the flame retardant finishing of cotton affected some of the textile related mechanical properties e.g. tensile, bending, shear, compression and surface properties. House et.al.[141] studied the effectiveness of commercial flame retardant Proban-210 on cotton clothing and concluded that Proban-210 as FR agent. Giraud et.al [142] studied the flame retarding behavior of cotton coated with polyurethane containing microencapsulated flame retardant agent.

Synergism behaviour of P-Br in polyester-cotton fabric treated with tetra bromo bisphenol (TBBA), TBBA- DAP was also studied[143] and maximum synergism was obtained when the concentration of TBBA was equal to DAP. Garba et. al.[144] reported that some degree of flame retardancy on cellulosic material is achievable with crosslinking agents such as dimethyl dihydroxy ethylene urea or even by di methylol urea.

Post grafting reaction of glicidylmethacrylate (GMA) grafted cotton fabric with ethylene diamine followed by treatment with orthophosphoric acid were carried out by Reddy et.al.[145] to produce flame retardant cotton fabric. FTIR analysis of gases evolved from cotton and flame retarded cotton fabric pyrolysed in air was carried out by Horrocks et.al.[146]

Kandola et.al.[147] studied the influence of treatment of flame retardant to cotton on the mechanism of cotton pyrolysis. Also Photochemical grafting of 4-vinyl pyridine onto cotton fabric helps for imparting flame retarding properties on cotton[148].

Nakanishi et.al.[149,150] studied thermal degradation of cotton as well as flame retardant cotton and revealed that flame retardant cotton samples show extremely reduced amount and fewer numbers of gas products when compared with untreated samples.

Rearick et.al [151] have studied the flammability considerations for textiles having raised-surface apparel. The applications of poly-carboxylic acid look promising even though there are some serious concern related to the pH of the treated samples and its effect on shade of dyed fabrics as well as possible strength loss.

2.4 Effect of heat/fire on ligno-cellulosic fibres

Ligno-cellulosic fibres like, jute, flax, hemp, kenaf, roselle (karkadeh) & others viz., sisal, grass like Miscantus, grain straw reed, bagasse, bamboo, curava etc, recently have found use in extended areas of diversified applications which include different technical textiles, geotextiles, furnishings, building/structural and automobile textile components in the form of rigid or fexible composites, which are therefore essentially need flame retardant property for specific end uses.

According to one report [152] followings are the general stages of action of heat on ligno-cellulosic natural polymers & woody substance (though it may vary from fibre to fibre depending on the composition and inter unit linkages): -

Upto 105°C→ Removal of absorbed moisture

150-200°C→ Slow start of thermal decomposition of the low molecular weight compounds of natural polymers.

160°C→ Part decomposition of small molecular weighted/low DP encrustant begins [it yields phenols from cleavage of ether and C-C linkages resulting in more char than in case of cellulose]

> **180°C→** Hydrolysis or pyrolysis of low molecular weight polysaccharides (hemicellulose) begins [Hemicellulose releases more incombustible gasses & fewer tarry substance. According to Saunders and Allcorn gasses released most frequently contain about 70% of incombustible CO_2 and about 30% of combustible CO.]

200-260°C→ Exothermic reaction begins for decomposition of free (uncrosslinked/unesterified) hemicellulose of relatively low to medium molecular weight. [Characterized by increased emission of gaseous products of decomposition, release of tarry substance and appearance of local ignition areas of hydrocarbons with low boiling points]

260-300°C→ Initial decomposition of low molecular weight of cellulose along with higher molecular weight and crosslinked or esterified hemicellulosebstrats.[Primarily responsible for the formation of flammable volatile compounds. i.e. General thermal decomposition of wood substance starts with uncontrolled release of considerable quantities of heat begins and increased amount of liquid and gaseous products (including methanol, ethanoic acid) formed.

300-450°C→ Active process of decomposition major cellulose components starts. [Ignition of thermal decomposition products, flame spread by combustible gases and increase in heat release and mass loss rates]

Above 500°C→ Formation of combustible compounds is small, the formation of charcoal increases and mineral materials remains as residue.

It is also reported [153] that moisture is evaporated from jute in between 30-110°C, jute-hemicellulose show exothermic reaction at around 260-300°C (showing a broad hump for DSC peak having maxima at 293°C), though 10% weight loss is obtained in jute at >100°C, after which decomposition rate accelerates; while the jute-cellulose decomposes at around 300-380°C (Showing sharp endothermic peak at 360-365°C) and lignin decomposition nearly occur at 400-450°C (Showing exothermic reaction peak/Hump at 420-450°C).

2.5 Important research work on Flame retardant finishing of jute

Jute brattice cloth used in coal mines, jute based tent-fabrics, pandal fabrics and jute cotton union or jute based upholstery fabrics need fire –safety and essentially to be finished with a suitable flame retardant finish.

It is reported[154] that the treatment with 6.75% potassium sodium tartarate (PST) on jute results in a complete self-extinguishing property. But, this is not durable but it can withstand steaming and brushing. However, alkali pre-treated jute shows a significant improvement in flame retardancy[155]

There are several non-durable flame retardant chemicals for cellulosics which was also be applied to jute, such as –Borax, Di-Ammonium Phosphate, Borax:Boric acid(7:3) mixture, Ammonium sulphamate : Ammonium phosphate(85:15), phosphoric acid etc. which if applied in conjunction with resin finish and silicone emulsion finish, the non-durable flame retardant is mechanically entrapped or anchored into the fabric surface and thus, becomes some what semi-durable. The jute fabric if padded with 5% polyacrylate emulsion (Primol-HA) along with any flame retardant chemicals, such as a combination of Borax, Boric acid, Di-Ammonium hydrogen Phosphate = 7:3:5 ratio in proportion of 1:1 followed by drying at 100°c for 10 minutes and cured at 130°c for 3 minutes shows reasonable flame retardant property[156].

Amongst several durable flame retardants, available for cellulosics, the most widely used FR agent for cotton may be equally be effective on jute fabrics, such as application of Antimony oxychloride/Antiminy oxide. Tetrakis hydroxyl methyl phosphonium chloride (THPC), Tris-1-aziridinyl phosphine oxide (APO), APO-THPC combination APO-Zn $(BFn)_2$ or THPC-

Thiourea or APO-Thio-urea combinations, THPC-antimony oxide combination etc. in suitable proportion but none of these are ecofriendly in today's context and should be avoided.

Use of phosphate compounds with melamine-formaldehyde resin has been found to be another alternative method for fire proofing jute goods as reported by BJRI, Dhaka[157], but this has significant formaldehyde release problem and is not eco-friendly. So, with the above mentioned scanty woirk on FR Finishing of jute fabrics it is felt essential to undertake the present work for trying new FR formulations for jute with ecofriendly and low budget elements.

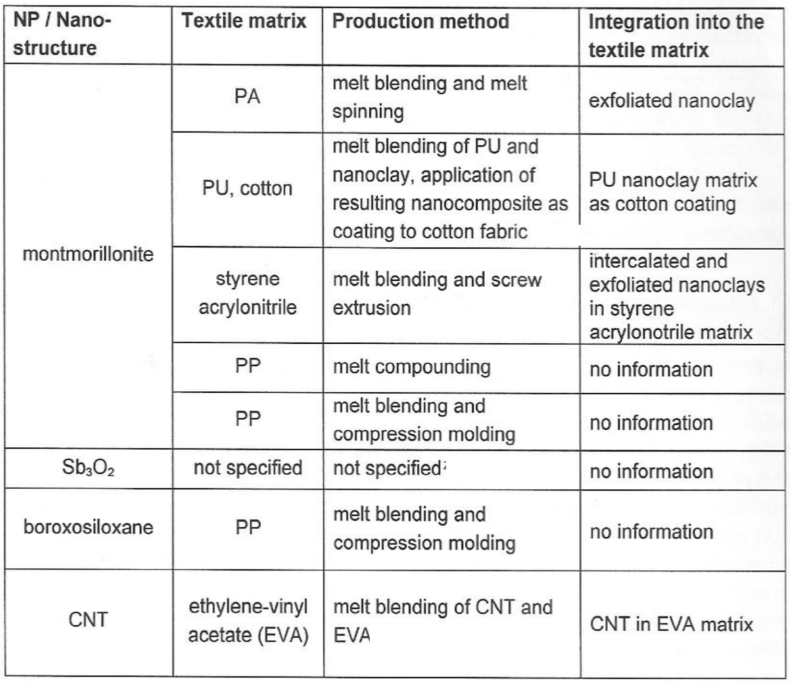
2.6 Thermal Behavior of treated and untreated Jute

Basak et al. [158] has studied the thermal behavior of flame retardant jute fabrics impregnated with Diammonium hydrogen phosphate (DAP) and Urea (1:2) solution using differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) under nitrogen and air atmosphere. Thermal suitability for flame retardant treated jute fabrics is gradually decreased as chemical add-on is increased. Weight loss after pyrolysis is decreased, and a much larger carbon (char) residue remained when pyrolysis is completed. The Limiting Oxygen Index (LOI) value is found to be also increased with increasing chemical add-on. The thermal properties of jute and its major components i.e. holocellulose (hemicellulose+α cellulose) and lignin have been investigated to interpret the results by thermal degradation behavior of untreated and flame retardant finished jute fabrics. In 1993 Pandey et al.[159] have studied DSC and TGA of jute treated with some other flame retardant formulation viz., borax-formaldehyde-sodium hydrosulphite combination. A comparison[159] of thermograms for treated fibres with that of control (untreated) jute showed the differences in the characteristic of DSC peaks and patterns due to the said FR treatment. Samanta et al.[160] have also analyzed and reported the thermal degradation behavior of all the major constituents of jute namely hemicellulose,α cellulose and lignin reacted with the Acrylamide formaldehyde(AMF) resin system and that resin finish turned jute thermally more stable. Samanta et al.[161] have studied the thermal behavior of chemically modified jute by low degree of aerial graftcopolymerization of acrylamide and its mixtures with ethylene glycol and aminosilicone using $K_2S_2O_8$ pre-treatment technique under limited aqueous system. Samnta and Singhee et al.[161] have studied the effect of NaOH treatment, conventional hot H_2O_2 bleaching and H_2O_2 + $K_2S_2O_8$ combined leaching system at room temperature as well as effect of mixed enzyme treatment and for treatment with N-methylol resins (i.e. Acrylamide formaldehyde) finishing for understanding the changes in thermal behavior for treated jute as compared to untreated one using DSC, which reveals distinct peaks of thermal degradation for hemicellulose, cellulose and lignin of chemically and bio-chemically modified jute, showing some positive or negative shifts of thermal degradation temperature for each of the three major constituents of jute owing to alkaline/oxidative or enzymatic degradation or resinification of jute components. ; where Thiourea formaldehyde(TUF) resin produce most thermally stable jute.

2.7 Production of Flame retardant textiles using Nano-technology

The integration[162] of several kinds of nano-composites using nano-clay without or with combination of different FR agents have been found to cause flame retarding effects on different subatrate. Due to its low price, many research projects are focused on the production of montmorillonite-nanoclay containing composites to achieve such flame retardant and other properties [163-167], while use of boroxosiloxanes or Sb_2O_3 containing nano-composites are also reported to inhibit the combustion process [162]. A further possible method seems to be the use of carbon nanotubes which led to enhanced flame retardancy when incorporated into a ethylene-vinyl acetate (EVA) polymer-matrix [168]. The exact mechanism[162] of the combustion inhibition caused by the nanoclay is not yet clear, but it is presumed that while the polymer matrix is burnt and gasified during combustion, the incorporated nanoclays accumulate at the surface and form a barrier to oxygen diffusion, thereby slowing down the burning process. According to Horrocks et. al.[162], the integration of nanoclay-composites alone is not sufficient to provide a textile fabric to be desirable level of reliable combustion flane protection: The nanoclays do slow down the burning process and enhance the char formation but, they have no effect on the ignition behaviour of the materil including afterglow properties. RelativelyRecent research indicates that, optimized properties can be achieved by combining the nanocomposites with low concentrations of conventional flame retardants [164,167]. For the integration of the described nanocomposites for textile fabrics, mainly two process pathways are possible[165]. For both application pathways, the nanoclay or nanoparticle with out or with combination or other FR agents is melt blended with the polymer material [163-167]. Before this process, the nanoclays have to be modified by replacing the (sodium-cations) cations found between the clay layers with other materials used to crate the substrate, sufficiently organophilic (ions) to make the integration and dispersion of the nanoclays in the polymer matrix possible [162]. One possibility to incorporate these nanocomposites into textile materials during melt spinning them into filament yarns which can subsequently be knitted or woven to textile fabrics .The second possibility is to apply the produced[165, 166] polymer-nanoclay composite as a coating to the surface of the textiles as coated finish on cotton or polyester or any other fabrics or their blends. Following are some of the examples cited in Table 2.1.

Table 2.1: Some examples of Nano Particle (NP) used in , textile matrices for production for flame retardant textiles:-



NP / Nano-structure	Textile matrix	Production method	Integration into the textile matrix
montmorillonite	PA	melt blending and melt spinning	exfoliated nanoclay
	PU, cotton	melt blending of PU and nanoclay, application of resulting nanocomposite as coating to cotton fabric	PU nanoclay matrix as cotton coating
	styrene acrylonitrile	melt blending and screw extrusion	intercalated and exfoliated nanoclays in styrene acrylonotrile matrix
	PP	melt compounding	no information
	PP	melt blending and compression molding	no information
Sb_3O_2	not specified	not specified	no information
boroxosiloxane	PP	melt blending and compression molding	no information
CNT	ethylene-vinyl acetate (EVA)	melt blending of CNT and EVA	CNT in EVA matrix

* The last column shows the form in which the Nano Particle (NP) occurs in the finished fabric.

2.8 Use of Zinc-oxide nano-particles in different fields

It is known from different literature that ZnO nanoparticles can be used[169] for antibacterial and UV-blocking properties, since, the inorganic UV blockers has additional preferable properties[170] than organic UV blockers for higher tharmal stability at high temperature and non-toxicity of the former. Moreover, nanoparticles have great effect for having a large surface area to volume ratio that results in a major increase of the effectiveness in blocking UV radiation when compared to bulk materials [169].Therefore, nanoparticles could grant high durability for finished fabrics with respect to conventional materials as because, they have large surface area and high surface energy that ensure enhanced affinity for textile fabrics and lead to an increase in durability. Hence it is observed that textile fabrics treated with ZnO nanoparticles have excellent UV blocking properties[169] even after 55 home laundering [171]. Most important textile related fabric properties like tensile strength, bursting strength, bending rigidity, air permeability, dyeing capacity, and abrasion resistance that play a vital role to textile consumers are not muched affected after nanoparticle coating process [169] while air permeability of the fabric is reduced after coating process with normal bulk-ZnO [169], while it is improved when nano-ZnO particle is used. Compared to normal bulk-ZnO treated fabric, fabric treated with nano-ZnO particle result in lowering of the surface friction [172]. Zinc oxide is a wide-bandgap semiconductor (3.3 eV) with a large exciton binding energy (60 meV) at room temperature [173] and hence is considered as one of the best biofriendly absorbers of UV radiation[174]. Moreover, it has been widely used in different fields of application because of its unique dermatological, photocatalytic, electronic, optical, electrical, UV protective and antibacterial properties,[175-178]. Also, it is one of the few oxides that within the quantum property, allowing variation of the location of the electronic bands in an experimentally available size range [179]. Different methods have been reported for the preparation of ZnO nanoparticles with different size and shape, such as sol-gel method [180], spray pyrolysis [181], pulsed laser deposition[182], template method [183], vapour synthesis[184], wet chemical route [185], emulsion/ micro-emulsion [186], hydrothermal[187], polymer precursor (so-called Pechini method)[188], thermal decomposition[189], microwave methods[190] etc. Zinc oxide particles have been synthesized under different synthesis method and condition with abundant morphologies e.g. individual ZnO nanoparticles [189,191] , nanowires[187] and dendritic nanowires [192], nanobelts [193], nanorods [194], nanotubes[195], and nano cantilevers [196]. Also as antibacterial agent, there are many studies investigating the antibacterial effect of ZnO nanoparticles. For example, some of the authors reported that nano-ZnO particles is considered to have antibacterial activity against both Gram-positive and Gram-negative bacteria [178]. Also at high pressure and temperature, it has antibacterial activity against spores, while higher temperature leads to lower this activity [197-199]. Yamamoto et al.[200] reported that the surface area and the concentration play an important role in the antibacterial activity consideration for nano-ZnO particles, while the particle shape and crystalline structure have lower impact on it. Yamamoto [201] also reported that the antibacterial activity increased as the particle size decreased. Adams et al.[202], Brayner et al.[203] and Jeng et al.[204] reported that ZnO behaves in a different way towards microorganisms rather than other metal oxides such as SiO_2, MgO, TiO_2 and CaO etc. . All observations reported by the researchers were explained by a number of mechanisms, these mechanisms and include production of active oxygen species due to the existence of the nanoparticles[205], damage of membrane cell wall because of the binding of the particles on the bacteria surface due to the electrostatic forces [206], penetration through the cell membrane [187], interaction between the active oxygen species and the cell [207], both the direct nanoparticle-cell membrane interaction and generation of active oxygen species (all the antibacterial tests of this work were done under dark condition) [208], and cellular internalization of ZnO nanoparticles. Some study suggests that small nano-particles are able to penetrate and accumulate in the bacterial membrane and cytoplasm region of the cell [203]. In another study, Hydrophobic modification of nano-ZnO films has been carried out with applying long-chain fatty acids or their sodium salts [204]. Tang et al.[209] have modified ZnO nanorods using sodium oleate as the capping agent, hydrophobicity of ZnO nanorods was found to increase with increase in the amount of sodium oleate. Wu et al [210] studied the surface wettability of micro-structured ZnO surfaces with different alkanoic acids (C8–C18) and found that, greater the chain lengths of fatty acids, more is the stability of super hydrophobic surface obtained by ZnO nano particles. Badre et al. have studied the super hydrophobicity of electrochemically deposited ZnO films [211]. They found that after treating the ZnO nanorod films with a linear saturated long-chain fatty acid like stearic acid, higher contact angles were obtained compared to the treatment with other unsaturated fatty acids of the same chain length. Electrodeposited ZnO nanowire array film has a highly water-repellent surface when treated with stearic acid [212]. Modification of ZnO films with compounds other than fatty acids has also been reported [213,214]. Guo et al. have reported the superhydrophobicity of ZnO nanorod array films obtained by a hydrothermal method after surface modification using octadecanethiol. Li et al. [214] have prepared conductive as well as hydrophobic ZnO thin films by electrochemical deposition and finish hasmade it superhydrophobic by fluoro-alkyl silane modification.

The control over the size and morphology of nanometer- or micrometer-sized ZnO particless represents a great challenge to realize the design of novel functional effects. This is because the optical and electronic properties of ZnO particles, which finally determine practical applications, can be modulated by varying their size and morphology. Recently, the synthesis of one-dimensional ZnO nano- or microstructures in shapes including wires,[215] rods,[216,217] tubes,[218,219] needles[220], columns[221], towers[222,223], belts[224], nails[225], helices[226], branches[227], combs[228], tetrapods[229], and dumbbells[230-233] has been of increasing interest because of their promising applications in optoelectronic devices and functional materials. Different methods (including calcination process) such as vapor-liquid-solid growth, thermal evaporation, thermal decomposition, electrochemical deposition, and solution-phase processes have been introduced to prepare one-dimensional ZnO nano- or micro-structured materials with various morphologies. Large scale use will require the development of simple low-cost approaches to the synthesis of this nano-ZnO by suitable process to produce different sizes of nano-ZnO as inorganic functional nanomaterials. Recently, dumbbell-like ZnO microcrystals were prepared by a hydrothermal process [230,231] but, the morphologies of the ZnO micro-crystals were controlled by additives. Subsequently, Wang and co- workers also fabricated dumbbell-like ZnO microcrystals by an ambient pressure and low temperature zerogel-seeded opening crystallization approach[232], and dumbbell-like ZnO microcrystals were prepared on the ZnO nanorod-built on surface of cotton fabrics.

2.9 Application of ZnO Nanoparticles as Flame-retardant

The research of El-Hady et. al.[234] mainly deals with a novel flame-retardant and UV-protection for cellulosic fabrics using different polycaboxylic acid, sodium hygrophosphite in presence of ZnO nanoparticles as an effective flame increasing char formation. The application of nano ZnO on cellulosic fabrics (cotton 100% and cotton/cotton polyester 65/35%) was achieved by using different polycarboxilic acids (succinic acid [SA] and 1,2,3,4-butane tetracarboxilic acids [BTCA]) with sodium hypophosphite (SHP), through conventional pad-dry-cure method. The effect of concentration of SHP on the physical properties, flammability and UV-protection of cross-linked fabrics are investigated.

Another research of Lam et. al. [235] states an organic phosphorus compound (flame retardant agent, FR) in combination with a melamine resin (crosslinking agent, CL), phosphoric acid (catalyst, PA) and zinc oxide (ZnO/nano-ZnO) applied on cotton also imparted effective and durable flame retardant properties. Moreover, above said ZnO or Nano-ZnO FR-CL-PA-system treated specimens showed further improvement in flame retardant property if the said treatment is done after plasma pre-treatment. However, this flame-retardant-treated cotton specimens had poor mechanical strength when compared with control sample, due to the acidic degradation and the side effects of the crosslinking agent used, while plasma pre-treatment and ZnO/nano-ZnO (co-catalyst) may compensate a part of the reduction in tensile and tearing strength.

Lam et. Al [236]. Also studied, application of a combination with N-Methylol dimethyl phosphonopropionamide (FR) with melamine resin (CL), phosphoric acid (PA) catalyst and zinc oxide (ZnO) or nano-ZnO co-catalyst i.e (FR-CL-PA-ZnO or nano-ZnO system) to impart flame-retardant property on cotton fabrics. By using 0.2% and 0.4% of ZnO or nano-ZnO as co-catalyst, the flame spread rate of neutralized and/or laundered test specimens decreased, and the specimens can withstand atleast 10 home laundering cycles.

Guodong Zhao et. al[237] investigated the influence of micrometeric zinc oxide (micro-ZnO) and nanostructured zinc oxide (nano-ZnO) on the flammability and thermal properties of acrylonitrile–butadiene–styrene (ABS)/(polyethylene terephthalate)/ammonium polyphosphate (APP) systems. When 1 wt % micro-ZnO (or nano-ZnO) was incorporated into the ABS/PET/APP systems, the best flame-retardancy rating was achieved during UL94 tests, and the limiting oxygen index value was 30-31.

Sertsova et. al. [238] reported the fire-resistant properties of polymer nanocomposites based on polyvinylchloride and nanoparticles of metal compounds. The size of the nanoparticles of magnesium hydroxide was equal to 50–100 nm; iron oxide, 25–50 nm; and zinc oxide, 50–100 nm. Another type of flame retardant used in the work was aminotrimethylenephosphonic acid ammonium salt (AMPAS); however, the total content of the different additives did not exceed 15%.

2.10 Flame retardant performance and fabric properties

Effects of THPOH, NH_3, POH-urea- TMM, THPC-urea-NH_3 (Proban), PC-urea (catalysed by Na_2HPO_4), (Fyrol 76) and (Pyrovotex CP) on fabric tensile property and crease-resistant property have been studied by Rowland and Mason [239]. In the presence of the crease-resistant finish DMDHEU [240], the normally expected inverse relationship between crease resistance or resilience and abrasion resistance demonstrated by such finishes when applied alone was not as clearly observed for above said flame retardant combined finishes. Moisture properties of flame-retardant cotton were found to be dependent on proportion to the finish level on the fabric; for THPOH-amide and THPC-urea and Pyrovatex CP or THPOH-NH_3 FR finish because of the lower degree of cross-Iinking [241]. Later work [242] showed that the mechanism of sorption in THPOH-NH_3-finished cotton. The associated hazard of static generation has been shown to be a problem for most flame-retardant cottons at or below 42% RH [243] with the hazard increasing after laundering. Carefully selected anionic and cationic antistatic finishes has to be included which has negligible effect on flammability. Lowering of LOI .values, however, may occur if, such finishes are applied for to flame-retardancy for synthetic fibres.

The cross-.Iinked structures of durable flame retardants for cotton have been shown to block the enzyme activity of micro-organisms [244] and, consequently, enhance the fibre rot resistance [245]. Susceptibility to mildew growth depends on the finish type, for example, pyrovatex CP being less prone to mildew attack than THPC-urea or THPOH-NH_3 [246].

The general success of any flame retardant fabric is further influenced by its compatibility with dyes and other finishes. The multipurpose finishes for wool have been extensively discussed in literature[245-263]. It seems that less interest has been shown in such finishes for cotton, although flame retardancy combined with soil-resistant. [264,265], water-repellent [266], antibacterial [267] and weather-resistant [264] finishes have been described in addition to the aforementioned crease-resistant treatments [240] with flame retardancy finish on cotton .

Surprisingly, the influence of flame-retardant finishes on dyeing behavior and subsequent fastness properties has received little attention. Timpa et al. [268] showed that for THPOH- and THPC-finished FR cotton, by dyeing followed by flame-retardant treatment gave better flame retardant behaviour and that dyes leads to show somewhat reduced LOI. values compared to undyed control samples. Kullman and. Vail [269] demonstrated that, these FR finishes can influence shade changes especially for vat dyes and that light fastness is significantly reduced when dyeing is followed by flame retarding treatment. UV exposure of THPOH-finished cotton dyed with a specific certain vat dye produced significant concentrations of free radicals, deteriorating light fastness. More recent work [270] for similar flame retardant finishes relating to cotton and wool produced a similar findings.

The photosensitivity of flame retardant treated cottons has been studied [271-273] and the use of light screening pigments has proved to be effective in enhancing their stability to daylight exposure [271]. Slightly improved weather resistance has been observed for oxidised THP based finishes [274] as well as by the use of screening pigment like titanium dioxide[275]. Yeadon and Harper[276] intensively investigated the behaviour of THPOH - THPS-urea and THPC-urea-NH_3 finishes when exposed to both natural daylight and xenon arc radiation. Following the above study[275], all samples were topped with a light-screening TiO_2 pigment and fluorocarbon for water-repellent finish and found that after one year's outdoor exposure or 500h xenon arc exposure, THPOH-NH_3 treated cotton fabrics showed little change in LOI values and char lengths but associated with loss in tensile properties similar to those of a TiO_2 pigment and topped unfinished (without FR finish) control fabric. Both THPS and THPC-urea-NH_3-treated fabrics showed comparable retention of flame retardancy with greater retention of elemental phosphorus and nitrogen and tensile properties. Whilst the presence of the TiO_2 water-repellent finish enhances weather resistant, where, both these agents lower the fabric LOI values, although this may be partly offset by including the nitrogen-rich trimethylol melamine in the topping.

A concurrent research work by Slaten et al.[277] investigated the effect of xenon arc irradiation on cotton treated with THPOH-NH_3 and Pyrovatex-3805 (a modification of pyrovatex-CP) in SO_2 NO_2 and O_3 atmospheres. Both these two finishes moderated the finished fabric shows changes in chemical and physical properties for Pyrovatex exerting a protective effect with respect to the untreated control exposed in air and the aforementioned gases. The THPOH-NH_3-finished sample showed little change in flame-retarding behaviour during exposure, however, but Pyrovatex-treated cotton showed a decreased in LOI value, at least, two index lower during 150h exposure in each gas.

2.11 Aims and objectives of the thesis

The present work embodied in this thesis was initiated with the following objectives-

i) To develop suitable eco-friendly fire resistant chemical finishing for jute fabrics.

ii) To study the efficacy of fire-resistant finishing action of jute with the use of common chemicals (available easily) to broaden the scope of using jute based fabrics in the field of fire-protective textiles (like brattice cloth used in mines) and home textiles (as flame

retardant furnishing fabrics, kitchen apron etc.) having required level of Limiting Oxygen Index (LOI >>27) for specific end uses as flame retardant textiles.

iii) To study the low add on application of flame retardant finish by use of nanotechnology (i.e. application of suitable flame retardant chemicals in nano material form).

2.12 Sheme of the present work embodied in this thesis

The background information detailed in the introductory chapter and review of literature highlighting the chemistry and properties of jute fibre and the scope of fire protective chemical finishing of jute fabrics as well as scope of further research on flame retardancy finish of jute fabrics aimed at making jute widely useable, acceptable and more competitive with regard to quality and cost effectiveness. Non-traditional areas of application of jute textile still remains a challenging task for modifying jute textiles by eco-friendly chemical finishes particularly in view of ever growing awareness to preserve and sustain the environment. It has become extremely urgent to look for newer, simpler, low cost and improved method for fire-protective chemical finishing of jute textiles, so that, demand for jute products in diverse application areas could be increased. The present work therefore envisages to find a viable and eco-friendly chemical finishing process for fire protective chemical finishing of jute textiles without much affecting the desirable textile related properties of the treated jute fabric. Moreover, in today's context, finishing chemicals to be used are to be eco-safe for the environment. For literature review prt of this thesis, it has been mentioned that studies on the flame retardancy and thermal behavior of either cotton or viscose rayon are widely available in literature, while such studies are scanty for jute and lignocellulosic fibres where not much work has been done except few works cited in the review literture.

Many of the popular flame retardant chemicals having formaldehyde release problems, are not eco-safe and has been banned now a days or restricted due to environmental safety reasons. Some flame retardant agents like e.g. halogen based flame retardant, APO, THPC (HCHO) based flame retardant etc are not eco-safe. Most of the flame retardant treatment so far developed for jute fabric using borax-boric acid or Rochelle’s salt showed medium level of fire retardancy, high strength loss and affects some other textile related properties. The present work therefore aims at to study the effect of unique newer type of flame retardant chemical treatments on flammability properties(flame retardant performances) and all important textile related properties e.g. tensile strength, tear strength, abrasion resistance, stiffness, brightness, whiteness etc. of jute fabrics. The normal requirement of dosages and add-on of flame retardant chemicals to be applied on jute fabrics so far reported on jute is relatively much higher as compared to cotton fabrics and hence should be separately optimized. Flame retardant chemicals treated jute fabrics having different add-on for selective flame retardant need to be been subjected to all important textile testing regarding its important textile related properties and flame retardant performances in terms of ignition time /flames spread time ,after glow time ,char length and limiting oxygen index value. With this background information from general introduction and literature review, the present work was undertaken for applying ecosafe FR finishing of jute fabrics and thus to create suitable knowledgebase and database for flame retardant treatment to jute based fabrics and their performance analysis. Following research plan and scheme of work has been executed and embodied in the present thesis:

(1) Effects of phosphorylated poly vinyl alcohol (PVA) and oxidized form of phosphorylated polyvinyl alcohol (oxy-P-PVA) treatment on the flame retardant performance of bleached jute and oxy-jute fabrics.

Though phosphate compounds are not fully ecosafe, but some of the stable phosphate derivatives like phosphorylated polyvinyl alcohol (P-PVA) or phosphorylated oxy PVA may be used as ecosafe materials, which is also being used in artificial teeth replacement and other dental application as ecosafe medical use. Hence, in the 1st part of the present work, polyvinyl Alcohol (PVA, Textile sizing grade) which is commonly used in textile industry as a sizing agent as well as Stiffener for some specific end-uses have been modified by phosphorylation to produce P-PVA or P-oxy-PVA. An effort has been made to use this commonly available chemical (PVA) to develop an eco-friendly aqueous solution based flame retardant formulations based on phosphorylated polyvinyl alcohol (P-PVA) and oxidized P-PVA [i.e. O(P-PVA)], as these two derivatives of polymeric phosphate are ecosafe and can be readily synthesized from PVA in any textile industry or even in jute industry. Hence, PVA is made phosphorylated under a specific condition of treatment and effect of the treatment on jute fabric with this P-PVA and oxy-P-PVA formulations on the flammability in terms of LOI, Char Length, Flame spread time and on the other textile related properties in terms of Loss in tenacity, Bending Length, Whiteness Index of such treated jute fabric have been investigated. The thermal behaviour of untreated and P-PVA and oxy-P-PVA treated jute fabrics have been investigated by study of DSC & TGA for such phosphorylated Polyvinyl Alcohol (P-PVA) or oxy P-PVA treated jute fabric (chemically modified) as a flame retardant textiles. This study of thermal behavior of P-PVA and oxy-P-PVA treated jute fabrics is thought to be useful for understanding the mechanism of thermal degradation behaviour of the chemically modified jute under different temperature ranges. Partially phosphorylated PVA (P-PVA) has recently attracted considerable interest to present researchers because of its nonflammable and eco-safe character. In the present work both P-PVA and Oxy-P-PVA were used as potential flame retardant chemical on jute and oxidized jute (oxy-jute) fabrics. The FTIR and SEM studies of such P-PVA or oxy-P-PVA treated jute fabrics are also carried out for more intense understanding of the chemical bond and surface characteristics for better interpretation of the observations/ results. This will probably explore the new rate of FR-treatments on jute

(2) Effect of treatment with ammonium sulfamate, sulphamic acid, urea flame retardant finish of bleached jute fabrics.

Instead of inorganic phosphates like Diammonium Phosphates, Ammonium phosphates and sodium hydrogen phosphates etc finish to be skin irritating and ecosafe, the present work attempted use of ammonium sulphamate, sulfamic acid and urea etc. for obtaining a reasonable level of fire retardancy of jute fabrics. Several types of flame retardants such as halogen based FR agents and phosphorous based FR agents with or without nitrogenous compound, have been used to improve the flame retardancy of cotton and synthetic textiles which are not eco-safe industry’s context. However the application of halogen based FR is being greatly limited due to the possible production of dioxin, large amount of smoke and corrosive gases during the combustion of the halogen flame retarded materials. Phosphorus based FR also has some drawbacks such as human skin irritating toxicity and high exudation. Hence, Sulfur based flame retardants such as sulfamic acid and ammonium sulfamate etc may be an attractive eco-safe fire retardant, as used in the past for developing the flame retardancy of cotton, paper and wood. Sulfamates have been used in designs of many antibiotics, anti-cancer drugs, antiseptic drugs and weight loss drugs and other medical purposes, besides its renewed applications in flame retardant textiles as an eco-safe material. Ammonium Sulfamate decomposes at elevated temperatures and releases some non-combustible gases, such as NH_3 and H_2O as this reduces fire.

Somework with cotton and nylon-6 (polyamide-PA6) using ammonium sulfamate with other additive and co-additives are found in earlier literature, as mentionaed in the review of literature part of this thesis. Considering these background information, the present work was aimed to develop a suitable ecosafe flame retardant formulation for jute fabric using ammonium sulphamate, sulfamic acid and urea as commonly available chemicals by their suitable optimized combination. The above said three chemicals were applied on bleached jute fabrics individually and in different binary mixture/combination at specific and varying conditions of treatment to optimize the same initially by unitary method and later by Response surface methodology using UDQM statistical model or technique. FR performance for use of different concentration of FR chemicaland arying conditions of treatment etc were investigated in terms of LOI value, flame spread time, afterglow time, char length (on the basis of vertical flammability test) and changes in tenacity, bending length and surface appearance in terms of whiteness index to get an optimized FR formulation for jute fabrics . Finally, the thermal decomposition and functional pattern of such FR treated jute fabrics have been investigated using TGA/DSC and FTIR spectroscopy, SEM analysis. Was stability of such FR finish was also investigated and reported.

(3) Effect of low Add-on treatment with ZnO nano-particles in presence of silicone emulsion (Formulation Code J-ZnO NP) on bleached jute fabrics for improved flame retardancy of bleached jute fabric.

With the advent of nanotechnology, some studies made for nano sized zinc oxide (ZnO) particle (as a nano semi-conductor, solar energy conserver, electrostatic dissipative coating, UV-protective coating, and chemical sensor) are available in literature, as mentioned in the review of literature of this thesis. One or two discrete studies for nano-ZnO application as . ZnO flame retardant surface finish on cotton coating has been reported. However, there is no such studies available on jute. Hence, nano-ZnO application with this background information, it was thought to be appropriate to study this for developing a low add-on flame retardant finish on jute fabrics. The major problem with common flame retardant chemicals applied on of jute are higher chemical add-on, noticeable strength loss, yellowing of fabric, higher fabric stiffness, etc. An ideal FR fabric for textile applications must not loose its drape, comfort and major physical properties and at the same time it should be eco-friendly, cost effective and non-leached off after laundering.

Nano sized particles (1nm= 10^{-9}m) as textile auxiliaries, chemicals and finishes are a special group of materials having high surface are, low weight etc as leading to extensive applications in diverse fields. The particles having size ranging from around 30-100 nanometers and sometimes upto 500 nm are considered to be mostly used nano particles for textile finish application. The formation of nano particles changes the properties of many conventional materials. Recent advances in the field of nanotechnology, leads to the preparation of highly ordered nano particulates of any size and shape. Nano particle of different metal oxides are an emerging area in research in different fields including health-related as well as textile applications. Among metal oxide nano particles, ZnO nano particles are as one of the multifunctional inorganic nano particles which has many significant features such as chemical and physical stability, high catalysis activity, effective antibacterial activity intensive ultraviolet and infrared adsorption protective material with broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, etc. including possible applications as FR coatings in association with additives or co-additives. Hence nano-ZnO. Particle are prepared byone of the technique used after dispersing the sme in non-flammable dispersing media of silicone emulsion. Nano ZnO is also effectively used in various materials and products, including dental clinics, cosmetics, solar cells, foods and recently applied on even on textiles. Hence an attempt has been made in the present work to apply nano ZnO dispersed in silicone emulsion on jute fabric to evaluate the changes on its textile related physical and flame retardant performance using AaS FTIR, XRD, EDX SEM, particle size analyser as well as evaluation of tensile strength, fabric stiffness, whiteness index, vertical flammability test and LOI value etc.

Initially preliminary expt, a general optimization of concentration of nano-ZnO and silicone emulsion treatment time and temperature for curing and later final optimization was arrived following statistical response surface methodology (RSM using UDQM technique.

It is thought, that the results obtained from the above mentioned investigations on efficacy of selective flame retardant finishing chemicals and their optimed dosages and conditions of treatment for applicationon jute, would be very useful in building a knowledge base and data base in this field of textile chemical processing technology for further researchers. These techniques may also be used to promote the uses of commercially FR finish jute fabrics in diversified areas of application as improved FR finished home textiles/ fire protective jute textiles as flame retardant sheets for mines and fire-retardant jute cotton union fabric as kitchen apron etc.

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Chapter III

MATERIALS AND METHODS

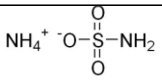
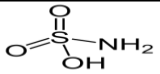
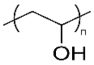
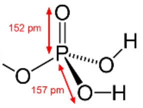
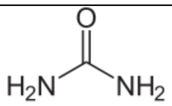
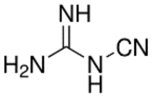
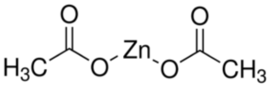
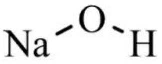
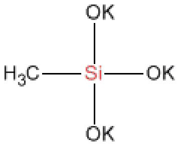
3.1 Materials

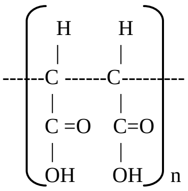
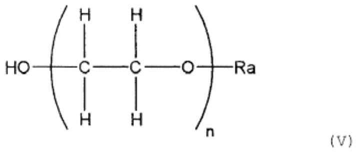
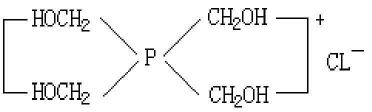
3.1.1 Fabrics

Conventional 3% H_2O_2 bleached plain weave jute fabrics having 63 ends/dm, 59 picks/dm, 220 g/m^2 (area density), 195 tex warp, 214 tex weft, and 0.80 mm thickness were used for the present study.

3.1.2 Chemicals

<u>Fire Retardant Chemicals Used</u>

Chemical Used	Chemical Character	Chemical Manufacturer
Ammonium Sulfamate	 $NH_4^+ \; {}^-O-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-NH_2$	Loba Chemicals
Sulfamic Acid		Loba Chemicals
Polyvinyl alcohol		Loba Chemicals
Orthophosphoric Acid		E-merck India Pvt Ltd
Urea		Loba Chemicals
Dicyandiamide		Loba Chemicals
Zinc Acetate		Loba Chemicals
Sodium Hydroxide		Loba Chemicals
Potassium Methyl Siliconate (PMS)		Wacker Silicones

Arkofix NEC Plus Liq (Modified polycarboxylic Acid based)		Clariant India Pvt. Ltd.
Ceralube HD.IN Liq (poly oxo ethylene Dispersion)		Clariant India Pvt. Ltd.
Saraflam CWF (THPC based)		Sarex Chemicals

3.2 Experimental Methods

3.2.1 Application Methods for Fire-retardant formulation with phosphorylated polyvinyl alcohol[14-16]

Preparation of Phosphorylated PVA Salt

10% aqueous Poly vinyl alcohol (PVA) solution was prepared by boiling PVA in requisite water at 100^0C for 30 mins. When a clear jelly like suspension of PVA was formed the heating was discontinued and cooled to a room temperature. The clear 10% PVA solution thus formed was then mixed with Dicyandiamide and Urea in the proportion of the ratio 1:0.5:0.5 (PVA: Dicyandiamide: Urea). The sample solution was then mixed with 10% H_3P0_4 solution and heated at a temperature of 100^0C for 30 min. After cooling the solution, KOH aqueous solution was added slowly into it until pH 11 is reached and precipitate is formed. The total precipitated mass was then separated subjecting the whole matter to filtration process to obtain the solid residual mass. It was then dried at 100^0C for 1-2 hrs. This residual solid mass thus obtained is phosphorylated PVA (P-PVA).

Application of P-PVA on Jute Fabric

The bleached jute fabric is padded with the P-PVA solutions in presence of 5% Al_2SO_4 as the catalyst (100% weight pick-up) and cured at 140 ^{o}C for 5 min and consequently padded

(100% weight pick-up) with KOH aqueous solution of pH 11. Then the fabric is dried at 100^{o}C for 5 min. Then the fabric was washed with the old water.

Preparation of pre-oxidised jute fabric (P-Oxy-PVA or Oxy-P-PVA)

Oxidation of bleached jute fabric was carried out, by padding the fabric with 1% (owf) $K_2S_2O_8$ solution at room temperature followed by 2 hr batching. Then the jute fabric is washed and air dried.

Preparation of pre-oxidised P-PVA

The aqueous solution of PVA was initially treated with $NaIO_4$ at a dose level of 2% of PVA taken. Then this periodate treated PVA is phosphorylated following the same method mentioned above to obtain the phosphorylated-pre-oxidised PVA (P-oxy-PVA) or also called as oxy-P-PVA.

Application of periodate treated P-PVA on normal jute and Oxy-Jute Fabric

The bleached jute fabric is padded with the P-Oxy-PVA or Oxy-P-PVA solutions in presence of 5% Al_2SO_4 as the catalyst (100% weight pick-up) and cured at 125^{o}C for 5 min and consequently, padded (100% weight pick-up) with KOH aqueous solution of pH 11. Then the fabric is dried at 100 ^{o}C for 5 mins. Then the treated jute fabric wash washed with the cold water.

3.2.2 Application Methods using sulfamate and urea based Fire-retardant formulation [17-19]

Bleached jute fabrics were padded (100% weight pick-up) with following flame retardant formulations in various concentrations as given below followed by drying at 100 ^{o}C and curing at 130^{o}C for 3 min.

Sl. No.	Formulation Description	Formulation Code
1	Urea + Ammonium Sulfamate with varying concentration	J-UAS
2	Urea + Sulfamic Acid with varying concentration	J-USA
3	Urea + Ammonium Sulfamate + Arkofix NEC Plus Liq + Ceralube HD.IN Liq + Magnesium Chloride (as catalyst)	J-UAS-AC
4	Saraflam-CWF (Commercial Fire-retardant)	J-S-CWF

Fire retardant finishing treatments of jute fabric with the above formulations 1-4 was optimised by treating the jute fabric separately with all the individual chemicals and in combination as stated with varying concentration levels respectively by the same procedure and conditions of pad-dry-cure technique for understanding the effect of individual chemicals on evaluating the fire retardant performance and textile related properties of such fire-retardant finished jute fabric.

3.2.3 Application Methods for Fire-retardant formulation with Zinc Oxide nano Particles Preparation of Nano Zinc Oxide

The zinc acetate dehydrate and sodium hydroxide were purchased from Loba Chemicals. ZnO nano powder was prepared by co-precipitation method. 50 gm of zinc acetate dihydrate was put into 1000 ml of distilled water under vigorous stirring. After 10 min stirring, 2 M NaOH aqueous solution was introduced into the above aqueous solution, resulting in a slurry like white solution, which was then placed on magnetic stirrer for stirring for 2 hr. The precipitate was then taken out and washed repeatedly with distilled water followed by ethanol to remove the impurities for the final products. Then a white powder was obtained after drying at 100^0C in vacuum oven for 6 hrs. The white precipitate is then calcinated at 600^0C for 4 hrs in Muffle furnace in order to get purified Zn nano powder.[1]

The overview of the synthesis of ZnO-np can be summarized as below.

$Zn(O_2CCH_3)_2.2H_2O(s) \rightarrow Zn^{2+}(aq) + 2(ClO_4)^-(aq)$

$Zn(ClO_4)_2(aq) + 2NaOH\ (aq) \rightarrow Zn(OH)_2(s) + 2Na(ClO_4)(aq)$

$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O\ (aq)$

Application of ZnO Nano particles[20]

As ZnO nano particles has tendency to agglomerate, it is wise to use freshly prepared nan ZnO particle dispersed in a dispersive media like Potassium methyl siliconate emulsion (BS-16) 0.01gm ZnO nano powder was weighed and made dispersion with 10 ml PMS. Distilled water is added in this and the value of the emulsion is made up to 100 ml. The bleached jute fabric is dipped/soaked in this liquor/emulsion of nano-ZnO and PMS in different concentrations and ratio for 30 minutes. Then the fabric is padded through the padding Mangle for maintaining with 100% expression .The treated fabric is then taken out and dried at 100^0C and cured at 120^oC for 3 minutes and also at varying conditions of treatment curing for optimizing the formulations**.**

3.3 Testing Methods

3.3.1. Vertical Flammability Test

This test has achieved the widest acceptance for determining the fire resistance of fabrics. It was designed specifically to measure the fire resistance of cellulosic textiles in which a flame is allowed to impinge on the bottom edge of the textile held in vertical position. In this test the selected untreated and treated jute fabric specimens, 2.75 x 10 inch, are conditioned by exposure to an atmosphere of 65± 2percent relative humidity for at least 8 hr before testing. The conditioned fabric specimen is then mounted in a suitable clamp and placed in a standard cabinet, and the bottom edge of the fabric is exposed to a standard flame for exactly 12 sec under controlled conditions. After removal of the flame, time of flaming and afterglow are observed. ASTM D6413 / D6413M - 13b Standard Test Method for Flame Resistance of Textiles (Vertical Test) has been followed. This test method determines the response of textiles to a standard ignition source, deriving measurement values for afterglow time, and char length.

After glow time was measured with a stop watch and char length was physically measured by a scale.

3.3.2 Optimization of Fire retardant formulation using Response surface methodology (RSM)

Response surface methodology (RSM) has recently emerged as useful mathematical and statistical tools for empirical model building for evaluation of interactive effects amongst process factor, process variables for assessing the optimal process conditions[13]. In statistics, response surface methodology (RSM) explores the relationships between several explanatory variables and one or more response variables. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. By careful selection of suitable design of experimental model like Box and Benkan or UDQM (user defined quadratic model), the objective is to generate useful equations to optimize the response (output variable) by using Response surface methodology (RSM), which is influenced by several independent process variables (input variables). Design of experiment is a series of experimental tests, called runs, designed in a planned scientific manner in which equal differences of variables are changed in the input variables in order to identify assessment of corresponding changes in the output response. As revealed by a series of preliminary experiments, the required average dosages of flame-retardant chemicals and additives/binder etc. and average conditions of treatment etc. are identified as initial set of experiments, before use of this response surface methodology (RSM) with UDQM technique of design of experiment for finding the optimized process variables for optimizing output process variables like Limiting oxygen Index (LOI) value, Char Length and Loss of Tenacity of corresponding fabrics etc. for all the two types of flame retardant agents and additives (experiment 1: For Ammonium Sulphamate and Urea combination and experiment 2(A+B) for normal ZnO or Nano-ZnO powder as flame retardant coating and potassium methyl siliconate (PMS) as dispersing media of ZnO) are finalized.

Thus all the fire retardant formulation applications on bleached jute fabric were performed in accordance with User defined quadratic model design (UDQM) as shown in Table 3.1 in which Limiting Oxygen Index in % (R1), Char Length in mm (R2) and Loss in Tenacity in % (R3) were selected as response or dependant variables while Concentration of Urea, Ammonium Sulfamate for expt. Set -1, Normal ZnO and Potassium methyl siliconate (PMS) for expt-set-2, ZnO Nanoparticles and Potassium Methyl Siliconate (PMS) for expt-set-3 were chosen at five different level (-2, -1, 0 +1, +2) i.e. ± 2 levels to perform RSM using Design expert software as the operating (independent) variables with fixed curing condition (i.e 120^{o}C for 3 minutes) as treatment conditions. The effect of these variables on LOI value, char length & loss in tenacity were optimized.

Table3.1 Experimental Design matrix with ranges and levels of the process variable for Response Surface Study

Chemicals Used	Coded Factors	Units	Uncoded Values	Coded Values
Urea	A	g/l	50.00	-2
			87.50	-1
			125.00	0
			162.50	+1
			200.00	+2
Ammonium Sulfamate	B	g/l	50.00	-2
			100.00	-1
			150.00	0
			200.00	+1
			250.00	+2
Normal ZnO	A	g/l	0	-2
			0.05	-1
			0.1	0
			0.15	+1
			0.2	+2
Potassium Methyl Siliconate (PMS)	B	g/l	50	-2
			75	-1
			100	0
			125	+1
			150	+2
ZnO Nanoparticles	A	g/l	0.00	-2
			0.05	-1
			0.10	0
			0.15	+1
			0.20	+2
Potassium Methyl Siliconate (PMS)	B	g/l	10	-2
			45	-1
			80	0
			115	+1
			150	+2

The present work therefore attempts to optimize the input variables of different flame retardant chemical dosages for obtaining maximum LOI, minimum char length and minimum loss of fabric tenacity. The curing condition was kept constant as increase of the time or temperature causes yellowing and degradation of Jute fabric as revealed from the preliminary study. As per the RSM design layout UDQM experimental design technique was used to vary one parameter at a time while keeping the other constant as given in table 3.1 and all the experiments are repeated three times and data represented for the response variables (in Results and discussion) are the average value of those three repeat test results in each case.

The following second order response surface equation[13] for all three response variables following a quadratic polynomial form for analysis of UDQM rotable second order design were generated by the Design Expert Software 8.0.7.1 for the User Defined Quadratic Model design of experiment of set (as given in table 3.1):-

$R= a_1 + b1*A + b_2*B+ b_3*A*B- c_1*A^2 - c_2*B^2$……………eq 1

i.e. $R= a_1 + \sum b1*A + \sum b_2*B+ \sum b_3*A*B- \sum c_1*A^2 - \sum c_2*B^2$

Where a_1, is constant intercepts b_1, b_2, b3, c_1 and c_2 are correlation regression co-efficient, generated by the statistical software and are different for each equation and A and B are corresponding process/operating in dependent variables (as mentioned in Table 3.1 in the coded form). After establishing eq. 1, it was used for simultaneous maximitization of R_1 (LOI value) and minimization of R_2 (char length) and R_3(Loss of Tenacity) by RSM. The results obtained are discussed in R & D Section.

3.3.3 Determination of Limiting Oxygen Index

Considerable attention has been given to the interpretation of flammability in the terms of the Oxygen Index (LOI). Limiting Oxygen Index (LOI) is the critical oxygen index value indicating the relative measure of flammability of any materials or textiles. If LOI values are above certain critical limit (say >27), there is hardly any chance of fire propagation. The apparatus consists of two sections, a gas metering system the volumetric flow of gas in each line is accurately determined before the streams are mixed and fed into the base of the test column. In the test column the gas mixture flows upward past the burning specimen, which is ignited at the top to burn in a candle like manner. By adjusting the flow in each line to vary the oxygen concentration which will just support combustion of the material. LOI testing instrument thus provides a precise method for determining the critical oxygen index of the sample by measuring the minimum volume concentration of oxygen gas in a flowing stream of mixture of oxygen and nitrogen gases (mixed in different volume ratio) required to maintain candle like burning of a sample for a specified time.

LOI values of selected untreated and treated jute fabric samples were determined by a standard LOI tester (Make: S C Dey & Co. , Kolkata) as per ASTM-D-2863-77 method [2] by using the following formula.

$$\text{Limiting Oxygen Index (n)} = \frac{100 \text{ x Volume concentration of } O_2}{\text{Volume concentration of } N_2 + \text{Volume concentration of } O_2}$$

3.3.4 Measurement of Tensile Properties

Tensile strength of selected fabric samples were measured by the raveled strip method as per IS-1969-1968 method using an Instron (Model-1445) CRT-Universal tensile tester with a traverse speed of 100 mm/min and a pretension of 0.5 N. The final gauge length (sample size) of the fabric sample was 50 mm. x 20 mm. under the jaws.

Warp-way breaking tenacity (cN/tex) of selected fabric samples were measured by the raveled strip method as per IS-1969-1968 method[3] using an Instron (Model-1445) CRT-Universal tensile tester with a traverse speed of 100 mm/min and a pretension of 0.5 N. The final gauge length (sample size) of the fabric sample was 50 mm.x 20 mm. after raveling.

3.3.5 Measurement of Bending Length

The bending length of the selected fabric samples was measured as per IS-6490-1971 method[4] using Cantilever type Sasmira fabric stiffness tester with a specimen size of 200 mm × 25 mm.

In this test, the rectangular strip is extended beyond the edge of the platform of the stiffness tester and the free edge of the fabric is allowed to bend under its own weight until the free edge makes an angle of 41.5^0 (already marked in the instrument) with the horizontal platform. The bending length was assessed from the observed length of the fabric required to bend to a particular angle. Higher the bending length, stiffer is the fabric. The test results reported are an average of 5 tests in each case.

3.3.6 Measurement of Whiteness

Whiteness index as per Hunter Lab-Scale formula,[5] of the selected jute fabric samples were directly evaluated using a computer aided Macbeth 2020 plus reflectance spectrophotometer (with D_{65} standard illuminant and 10^o standard observer setting) and associated colour measurement software , using following relationship.

Whiteness Index (Hunter Lab-Scale) = $L - 3b = 10\sqrt{Y} - [21(Y–Z\ \%)] / \sqrt{Y}$

where, X, Y and Z are the tristimulus values of the sample, L is the lightness/darkness indicator in CIE Lab-Scale [L^* or simply $L = 16\ (Y/Y_o)^{1/3} - 16$ as per CIE Lab-1976 formula [6]], b is the blueness/yellowness indicator in the CIE Lab-Scale[6]{b^* or simply $b = 200\ [\ (Y/Y_o)^{1/3} – (Z/Z_o)^{1/3}]$}, $B = Z/1.181 = 0.847\ Z$, $G = Y= L^2/100$ and X_o, Y_o and Z_o are the CIE-tristimulus values[7] for D65 standard illuminant and 10^o standard observer.

3.3.7 Study of Thermal Behaviour by TGA and DSC Thermograms

Differential Scanning Calorimetric (DSC) thermogram indicate different thermal transitions and thermal decomposition temperatures of the constituting materials of the polymer fibre sample in certain temperature range. In Thermo-Gravimetric Analyser (TGA), with constant heating from ambient to any limiting temperature range, the change in sample weight due to thermal degradation ,evaporation and dehydration are measured. This technique is effective for quantitative analysis of thermal degradation at any or at use temperature , rate and type reactions that are accompanied by mass change due to thermal decomposition, evaporation, gas adsorption and dehydration etc..The TGA and DSC thermograms of jute not only give an indication of its thermal behaviour, but also give a clear reflection regarding the degree of chemical changes/interaction of the major constituents of jute after chemical treatments and modifications, altering the rate of mass loss on heating (in TGA) and also showing relative thermal changes in degradation temperatures (in DSC) for major jute constituents.

TGA and DSC thermograms of untreated and treated jute fibre samples (finely crushed) after being taken out from the corresponding untreated and treated jute fabrics were obtained from the Q600 provides simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample at heating rate of 10°C/min, using a pre-fixed sample weight over a temperature range from 30°C (ambient) to 500°C, following usual procedure [8-10] from ambient to 500 ˚C. It features a field-proven horizontal dual beam design with automatic beam growth compensation, and the ability to analyze two TGA samples simultaneously. DSC heat flow data is dynamically normalized using the instantaneous sample weight at any given temperature.

3.3.8 Scanning Electron Microscopy (SEM)

Surface morphology of untreated and treated jute fibre samples taken out from the corresponding raw and treated fabrics were examined according to the prescribed procedures using a scanning electron microscope (Model: FEI Quanta 200 Scanning Electron Microscope). Jute fibre samples taken out from the relevant fabric sample were mounted on a specimen stub with double sided adhesive tape and then subjected to coating with gold using a sputter coater to avoid charging of the specimen [11,12]. The observations were made at an operating voltage of 15 KV using usual magnification of 6 000, or using a higher or lower magnification wherever specifically required.

3.3.9 Fourier Transform Infrared Spectroscopy (FTIR)

Selected jute fibre (finely crushed) samples are taken out from untreated and treated fabrics were examined in Bruckner Alpha FTIR Spectrophotometer using ATR attachment which is an easy to use FT-IR sampling method and does not require any sample preparation.

3.3.10 XRD (X-ray Diffraction)

As the atomic distance in matter is comparable with the wavelength of X-ray, the phenomenon of diffraction find its way through it and gives many encouraging results related to the crystalline structure. The unit cell and lattices which are distributed in a regular three-dimensional way in space forms the base for diffraction pattern to occur. These lattices form a series of parallel planes with its own specific d-spacing and with different orientations exist. The reflection of incident monochromatic X-ray from successive planes of crystal lattices when the difference between the planes is of complete number n of wavelengths lead to famous Bragg’s law: $n\lambda=2d\sin\Theta$

Where n is an integer 1, 2, 3….. (Usually equal 1), λ is wavelength in angstroms (1.54 Å for copper), d is interatomic spacing in angstroms, and θ is the diffraction angle in degrees. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample.

X-ray powder diffraction (XRD) pattern of the samples were analysed on PAN analytical X'PERT PRO system with Bragg-Brentano geometry using Cu K1 radiation, operating at 40 kV and 30 mA, whereas = 1.54 ˚A for the Cu Kα1 line.

3.3.11 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample.

In order to quantify the amount of ZnO and PMS present on the fibre surface, Energy Dispersive X ray (EDX) spectroscopy analysis was performed with the SEM instrument (Tescan SEM VEGA 3 XM) with a separate EDS detector connected to that instrument.

3.3.12 Particle size analysis

The size of the nano particles were analysed by using Malvern Mastersizer 2000(available at BTRA Mumbai) by making dispersion with distilled water.

3.3.13 Atomic Absorption Spectroscopy (AAS)

In order to quantify the amount of Zinc present in the jute fibre after treatment with ZnO (Normal and Nano ZnO), Atomic Absorption Spectroscopy (AAS) was performed on nano ZnO treated jute sample using GBC-Avanta spectrophotometer (available at BTRA, Mumbai).

3.4 Method of Ranking by comparing observed data and assigned score ranking for three different process and techniques for imparting Fire-retardant finish to the bleached jute fabric

For ranking the three treated fabric at corresponding optimized conditions a method of data and score analysis was done based on weighted average. Following seven (7) properties are incorporated in this analysis, which was thought to be important for the optimization purpose.

Among these 7 properties properties three (Loss in Tenacity , Char Length , Bending Length) are inversely proportional to the desired textile property parameters hence, its effect in weight average score endorsed as negative, while all other are considered positive. Also the first three properties are allotted maximum weightage i.e. double (20) than weightage of other parameters (10) has been apportioned depending upon the much higher importance of these parameters than the other properties. The following table shows the example how the score for a particular formulation is derived based on their data following simple weighted average method by calculating weighted average score = ±(Data X Weightage) / 100. The reason for double weightage of the three important parameter as compared to others, are passed on opinion poll results of possible users industry dealing customers for such FR jute fabrics- as given in Table 3.3.

Table 3.2: Calculation of Weightage Average Score for each Parameter studied.

Sl. No.	**Properties & Parameter Code**	**Full Marks**	**Data**	**Score** = ±(Data X Weightage) / 100
1	Loss in Tenacity * (P1)	20 (20 marks for no loss in tenacity)	A	-(A x 20) = -a
2	LOI (P2)	20 (20 marks for 40)	B	(B x 20) = b
3	Char Length * (P3)	20 (20 marks for 1 cm)	C	-(C x 20) = -c
4	Whiteness Index (P4)	10 (10 marks for 75)	D	(D x 10) = d
5	Bending Length * (P5)	10(10 marks for 3.5)	E	-(E x 10) = -e
6	Wash Stability (P6)	10 (10 marks for no loss in LOI value)	F	(F x 10) = f
7	Residue left at 500^{O}C (P7)	10 (10 marks for 40)	G	(G x 10) = g
			Total	Sum of the all score (i.e. Sum of –a+b-c+d-e+f+g)

Table 3.3: Basis of weightage Average Score different for different parameters studied for study of Flame Retardant Performance for Jute

Sl. No.	**Code of Mill/ Industry where opinion pole was taken**	**Rating (0-20 Scale) of parameter by opinion pole**						
		P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**
1	Mill-P	20	20	20	11	9	11	9
2	Mill-Q	21	19	20	11	11	10	8
3	Mill-R	19	22	21	10	11	9	12
4	Mill-S	19	19	21	8	9	11	10
5	Mill-T	20	20	20	10	11	8	12
(A) Sum of 5 set of results for weightages of parameters obtained by opinion pole		99	100	102	50	51	49	51
(B) = (A/5) Avg. Weightage for each parameter		19.8	20	20.4	10	10.2	9.8	10.2
Final nearest rounded weightage taken for each parameter		20	20	20	10	10	10	10

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Sl. No. Description

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Chapter IV

RESULTS
AND
DISCUSSION

4. Result and Discussion

Introduction:

There is high demand for flame retardant textiles for protection against catching fire in variety of end-uses. For jute based fabrics to be used in mines, car upholstery and as furnishing/upholstery in home textiles as well as for kitchen apron and gloves etc., it should be fire resistant. Cellulosic fabrics can be made fire-resistant by treatment with different non-durable and durable flame retardant formulations, which are readily available in literature[1]. However for ligno-cellulosic fabrics, it is necessary to standardize the formulation (recipe) and methods for application of flame retardant finish separately for jute and jute/cotton union fabrics.

Most of the conventional processes found in literature [2-5] for obtaining fire retardancy on jute fabric is based on application of a combination of borax and boric acid (7:3) with suitable proportion of organo-phosphate compound etc. Some details are available in review[2,3] literature on chemical finishing of jute. Borax-boric acid mixtures are being used for a long time to impart temporary fire retardancy to jute substrate. Some preliminary studies on temporary flame retardancy of jute has been reported earlier by Banerjee[4] and others[5] by treatment with borax- boric acid/ di-ammonium phosphate and potassium-sodium tartarate (Rochelle Salt). Preliminary study of thermal behaviour of jute fibre and its components for different chemical treatments has been reported[6-11] earlier for understanding its thermal degradation behaviour. Phosphorus based flame retardant treatment on jute fabric has been recently reported by Samanta and Bagchi.[12]

With the aforesaid information , it may be said that for ligno-cellulosic fibres like jute, not much work has been done except the works cited above. The work done so far on flame retardancy of jute fabric are mainly of temporary type and using only limited number of flame retardant chemicals. There are ample scope to work on development of better level of fire retardancy for non-durable, semi-durable and durable flame retardant finishing of jute fabrics. It is also essential to study the thermal behaviour of such chemically modified flame retardant jute based fabrics for understanding the mechanism of thermal degradation under different temperature ranges.

Hence in the present study, efforts are being made to develop semi-durable water based flame retardant treatment formulations based on eco-friendly compounds like phosphorylated polyols, Ammonium sulfamate based compound and ZnO nano-particles. Hence the present work embodied in this thesis has been presented into three major sub-sections as follows:-

4.1 Effects of treatment with phosphorylated polyvinyl alcohol (P-PVA) treatment on the flame retardant performance of bleached jute and oxy-jute fabrics.

4.2 Effects of treatment with ammonium sulfamate / sulfamic acid / urea individual FR chemicals and their mixtures on the flame retardant performance of bleached jute fabric.

4.3 Effect of the treatment with combination of zinc oxide nano-particles and silicone emulsion for improved flame retardant performance of bleached jute fabric.

Section 4.1 Effects of treatment with phosphorylated polyvinylalcohol (P-PVA) on the flame retardant performance of bleached jute and oxy-jute fabrics.

Introduction

There are several non-durable flame retardant formulations for cellulosics[2-4] such as –Borax, Di-Ammonium Phosphate, Borax:Boric acid(7:3) mixture, phosphoric acid etc. which if applied in conjunction with resin finish, the non-durable flame retardant is mechanically entrapped into the textile matrix of the fabric and thus, becomes somewhat semi-durable. Also the use of such phosphate compounds with melamine-formaldehyde resin has been found to be another alternative method for fire proofing jute goods as semi-durable FR finish of jute as studied in BJRI, Dhaka[13]. Among several durable flame retardants, available for cellulosics, the important ones are Antiminy oxy-chloride/Antimony oxide. Tetrakis hydroxyl methyl phosphonium chloride (THPC)[14], Tris-1-aziridinyl phosphine oxide (APO), APO-THPC combination APO-Zn $(BFn)_2$ or THPC-Thiourea or APO-Thio-urea combinations, THPC-antimony oxide combination etc. But none of these are ecofriendly in today's context for problem of formaldehyde release.

The toxicological hazards of conventional and commercially available THPC based flame retardants are often questioned in terms of the toxicity of the basic FR-retardant chemicals and chemical hazards during its application. These questions have been studied and reviewed by Mehta and Sharma[15] for the commonly available such flame retardants for cellulosics. Moreover, agents like tris (aziridinyl) phosphine oxide (APO) and antimony (III) oxide are also proved to be extremely toxic. Of all the phosphorus-containing flame retardants, including phosphonium, phosphine, phosphine oxide and phosphonate derivatives, all were found to be non-mutagenic. However, toxicity of two of the three bromo-alkyl substituted triazines (APO etc.) was investigated and it did exhibit mutagenic activity. THPC based flame retardants are though proved to be much efficient flame retardant agent, but this is not free from releasable formaldehyde toxicity and hence, is not eco-friendly. Hence the interest of the present researcher, has been revised/renewed recently to find eco-friendly flame-retardant for cellulosics and lignocellulosic textiles. For protection of consumers from unsafe fire hazards, flame retardant finishing of jute furnishing is considered to be very important especially for floor coverings, upholstery and draperies as well as for brattice cloth in mines, kitchen apron etc. So, it may be said that for ligno-cellulosic fibres like jute, the works done so far on flame retardancy finish of jute fabric are mainly of temporary [4, 5] in nature and that too is scanty all limited in number. Hence it was understood that, there are ample scope to work on development of different level of flame retardant finish for non-durable, semi-durable and durable flame retardant finishing of jute fabrics. Now a day even phosphates are being avoided as flame retardant agent. But, phosphorylated polyols as for its skin-unfriendliness and toxicity in question. Polyionic hydrogels with varying degree of hardness is found non-toxic and being used as a artificial teeth[16] (calcium complex of the same) etc. So present researchers have been attracted towards the use of phosphorylated polyols like phosphorylated poly-vinyl alcohol (P-PVA) or oxidized (i.e.oxy-P-PVA) as flame retardant chemicals for cellulose may also used ligno-cellulsic fibres like jute. Hence, in the present work, P-PVA and oxy-P-PVA was prepared and applied on jute fabric to get reasonable flame retardancy on jute fabric. Analysis of changes in textile related properties and flame retardant performance were studied after treating jute with P-PVA & oxy-P-PVA. Moreover, for understanding the changes in thermal behavior of jute constituents, after treatment jute with P-PVA and oxy-P-PVA under different temperature ranges have investigated by DSC and TGA study. Recently, partially phosphorylated P-PVA has attracted considerable interest because of its non flammability[17-19]. Hence in the present study attempts have been made to develop ecofriendly water based flame retardant treatment formulations based on phosphorylated polyols to study the efficacy of this formulation on the flammability and related properties of such jute based fabric.

4.1.1 Flame retardant performance of bleached jute with and without phosphorylated Poly-vinyl Alcohol treatment

Jute is a highly combustible material and the ignition time is ≥10 sec, LOI value of untreated bleached jute fabric is found to be 20.5 (as shown in Table 4.1), flame spread time to be 49 sec for the entire test length (12.5 cm) of jute fabric which burns the entire length in 49-50 sec and duration of afterglow is 55 sec (as per test result obtained from standard vertical flammability tester).

Polyvinyl Alcohol (PVA, Textile sizing grade) is commonly used in jute and textile industry as a sizing agent as well as stiffener for some specific end-uses. Therefore an effort has been made in the present work, to use this common chemical to develop an eco-friendly aqueous solution based flame retardant formulations based on phosphorylated polyvinyl alcohol (P-PVA) and oxidized P-PVA [i.e. O(P-PVA)], as P-PVA is proved to be toxicity free and is being used dental clinics as artificial teeth etc. Moreover, PVA is readily available at reasonable lower price. Hence, PVA is after phosphorylation under a specific condition effect of the treatment of jute fabric with this P-PVA or oxy-P-PVA formulation on the flammability performance and major textile related properties of such jute based fabric have been investigated. The thermal behaviour by study of DSC & TGA for such phosphorylated Polyvinyl Alcohol (P-PVA) treated jute fabric (chemically modified) as a flame retardant textiles have been studied for understanding the mechanism of thermal degradation behaviour of the chemically modified jute under different temperature ranges. Partially phosphorylated PVA (P-PVA) has recently attracted considerable interest to present researchers because of its nonflammable as well as eco-friendly character.[17-19] In the present work, both P-PVA and Oxy-P-PVA were used as potential flame retardant chemicals for jute and oxidized jute (oxy-jute) fabrics.

4.1.2 Analysis of Flame retardant performance and textile related properties:

Major textile related mechanical properties and flame retardant performances of untreated jute fabric (untreated bleached-control jute fabric) and jute fabric (bleached or otherwise pre-oxidised) treated with P-PVA and periodate treated P-PVA(oxy-P-PVA) have been evaluated and the respective results are shown in Table 4.1. Relevant data in Table 4.1 indicate that there is a trend of obtaining higher LOI values, for oxy-P-PVA treatment than un-oxidised normal P-PVA on jute and oxy-jute and shows LOI value approx. 30-32. Maximum LOI of 32 is obtained for treatment “OJ-O(P-PVA)” with loss of tenacity around 33%. The loss of strength is expected due to acidic degradation by $Al_2(SO_4)_3$, degrading jute cellulose and hemicelluloses part when heating and curing conditions. As the combination of jute or oxidised jute (oxy-jute) and periodate treated P-PVA i.e. O(P-PVA); imparts higher and easier accessibility than ordinary P-PVA there is a possibility of higher rate of reaction and hence, the LOI values are found to be also higher for oxy P-PVA than oxy-P-PVA treatments on jute. But at the same time, it is also observed that the third treatment "J-O(P-PVA)" i.e. treatment with O(P-PVA) on bleached jute showed somewhat the same level of flame retardant performance it is proved that the efficacy of O(P-PVA) is superior than the efficacy of only P-PVA irrespective of the use of oxidised jute or un-oxidised jute as substrate. Moreover there is no possibility of anchoring of oxy-P-PVA on oxy-jute, both having same –CHO functionality destroying the chances of possible hemiacetal formation (4.1.3 Reaction Scheme shown later). While $–CH_2OH$ group of jute and –CHO group of O(P-PVA) may be adhered well due to the hemiacetal formation (4.1.30Reaction Scheme). Thus either, jute fabric treated with O(P-PVA) (LOI-31.5) or oxy jute treated with P-PVA (LOI-30) show a better balanced flame retardant performance (in terms of LOI value) with loss of tenacity around 25-30% having char length within 5cm/6cm for jute treated with oxy-P-PVA (10% owf) or P-PVA(10%). Therefore, oxidation of both the reactants (jute fabric and P-PVA) is not recommended or the same is to be avoided. However, afterglows in each case are within 15-20 sec, much less than untreated jute showing afterglow for 55 sec.

The bending length values are found to be increased for treatment on both jute and oxy-jute fabric with P-PVA but this increase in bending length is found to be diminished when jute and oxy jute fabric is treated with periodate treated P-PVA, as because preoxidised P-PVA do not act as stiffening agent. An earlier study by Ghosh et al[20] reported that, prior periodate treatment of PVA gives higher wrinkle resistance with somewhat lower stiffness character (bending length) for the treated jute fabric which confirms the present finding of lower bending length value of O(P-PVA) treated jute fabric than that for P-PVA treated jute fabric. In poly vinyl alcohol the termination of polymerization is most likely to appear in the middle of the chain molecules as a 1,2 glycol moiety which is vulnerable to periodate attack, leading to chain breakage at the middle with the formation of aldehyde (-CHO) end groups. This chain breakdown leads to an abrupt drop in the viscosity of P-PVA, which may cause the improvement in bending length. For the surface appearance properties it is noticed that whiteness index are slightly decreased with these selective P-PVA or O(P-PVA) as flame retardant treatments on jute, while reduction in whiteness index, however, are found much predominant for oxy-P-PVA treatment than P-PVA treated maximum reaction is observed when both jute and P-PVA, both are pre-oxidised for such treatment and is not recommendable.

Table-4.1 Flame retardant performance of jute fabric and pre-oxidised jute fabric treated P-PVA and Periodate treated P-PVA

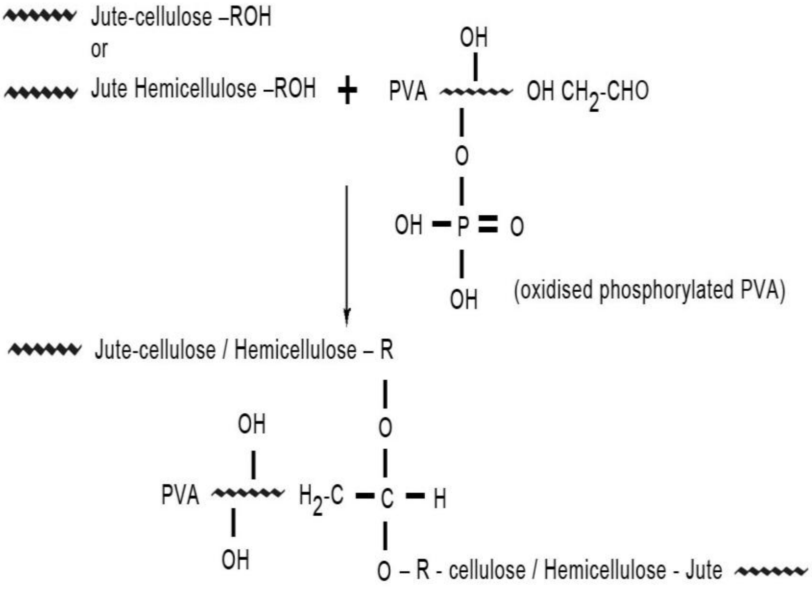
Type of fabric and treatments	Expt .No.	Treatment Code	Physical Properties				Flammability Properties			
			Loss in Tenacity (%)	Breaking Elongation (%)	Bending Length(cm)	Whiteness Index	Flame Spread Time (sec)	After Glow Time (sec)	Char Length (cm)	Limiting Oxygen Index(%)
Untreated bleached jute	--	---	-	5.0	3.8	75.20	49	55	12.5	20.5
Jute treated with 10% P-PVA	1	J-P-PVA	25	5.17	4.2	69.75	55	20	8	28.5
Oxy-Jute Treated with 10% P-PVA	2	OJ-P-PVA	32	6.24	4.1	62.16	60	15	6	30
Jute treated with Periodate treated 10% P-PVA	3	J-O(P-PVA)	30	8.24	4.5	67.24	65	15	5	31.5
Oxy-Jute Treated with Periodate treated 10% P-PVA	4	OJ-O(P-PVA)	33	8.01	3.8	59.23	69	10	4	32

4.1.3 Reaction Mechanism

The effect may be better understood if the possible reaction mechanisms are discussed here before proceeding for further evaluation of fabric property parameters and fire–retardant performance on application of the said newer generation flame retardant chemicals (P-PVA or O(P-PVA)) on jute textiles. So, the possible reaction mechanisms are given below:-

A. Reaction Scheme 4.1A (Pre oxidation of Jute)

B. Reaction Scheme 1.2 (Reaction[hemi-acetal formation] between jute and oxidised phosphorylated PVA)



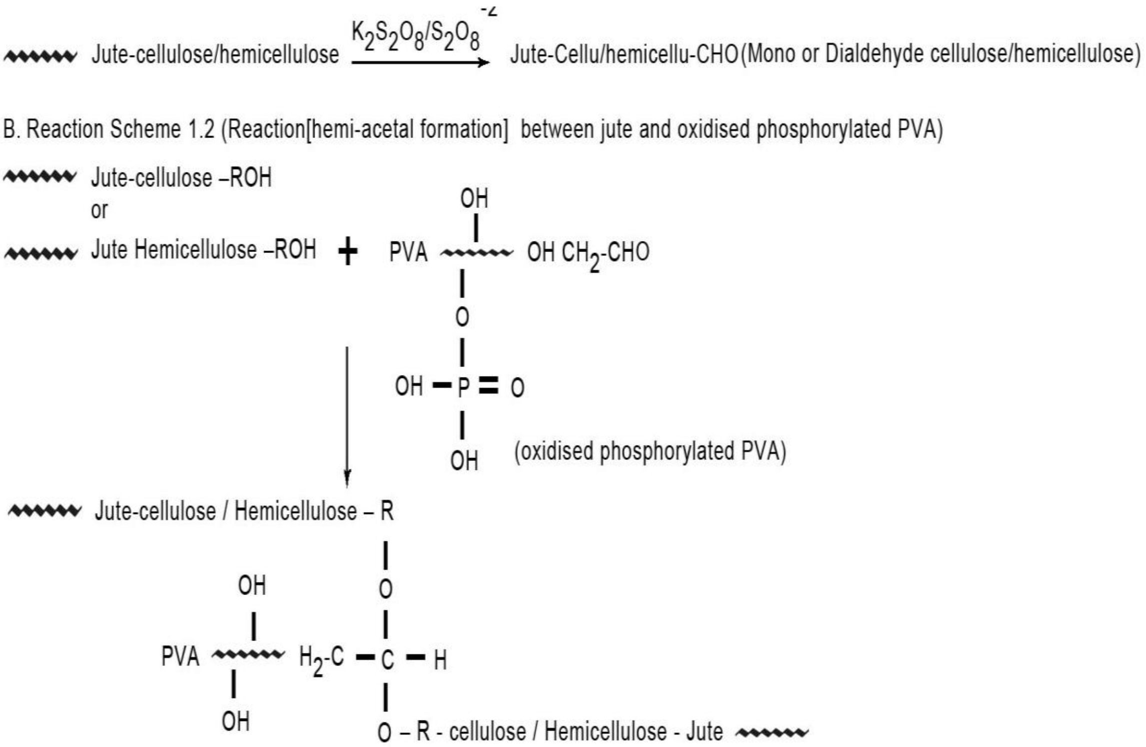
[Hemi-acetal Formation in acidic environment through –CHO group of oxidised phosphorylated PVA (Oxy(P-PVA)]

Reaction Scheme 4.1A shows pre-oxidation of jute cellulose/hemicelluloses to form/generate –CHO group in jute cellulose/hemicelluloses by potassium persulphate treatment at room temperature for 30 min.

Reaction Scheme 4.1B shows reaction between jute-cellulose-OH and hemicelluloses-OH and oxidized-P-PVA, forming cross linked product by forming phosphorylated crosslinked products of jute cellulose/hemicelluloses and oxy-P-PVA in presence of $Al_2(SO_4)_3$ as acidic catalyst.

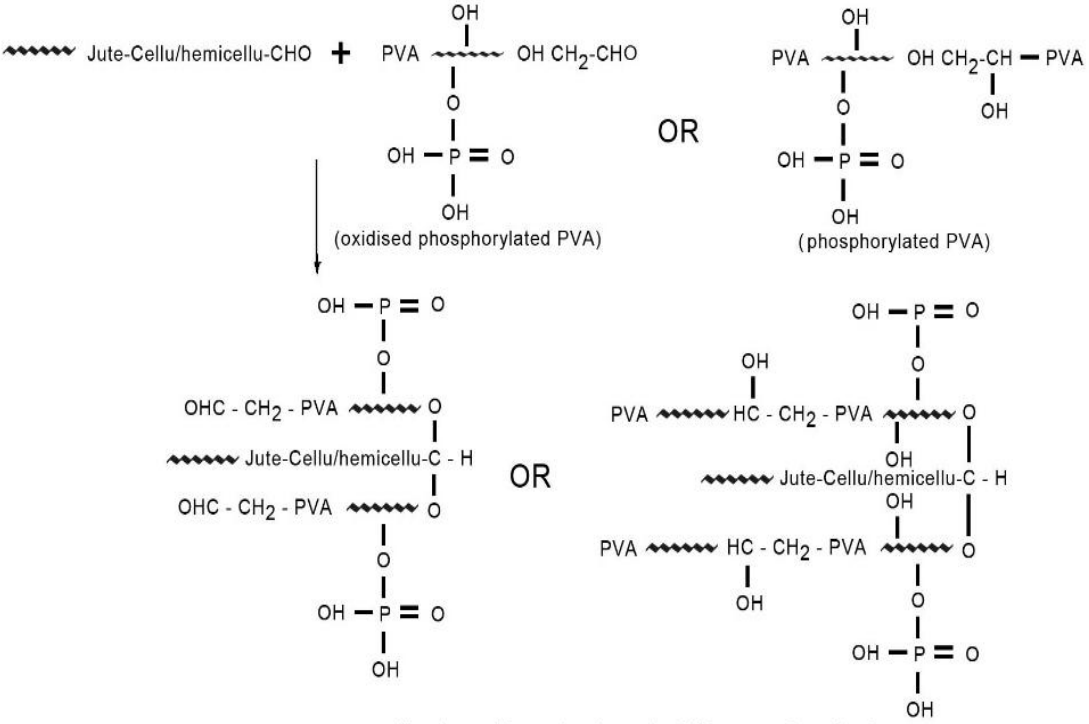
Reaction scheme 4.1C shows reaction between oxidized jute (i.e. jute cellulose/hemicelllose-CHO with phosphorylated P-PVA and/or with P-PVA, forming cross linked jute cellulose/ hemicelluloses with P-PVA and oxy-P-PVA, in presence of acidic catalyst.

Reaction Scheme 4.1 D shows reaction between oxidized jute cellulose/hemicelluloses-CHO functional groups with P-PVA which are more stable form of hemiacetal formation.4.1A, 4.1B and 4.1D being more stable may be a predominant reaction to occur in this case, need to be confirmed by FTIR etc.


B. Reaction Scheme 1.2 (Reaction[hemi-acetal formation] between jute and oxidised phosphorylated PVA)

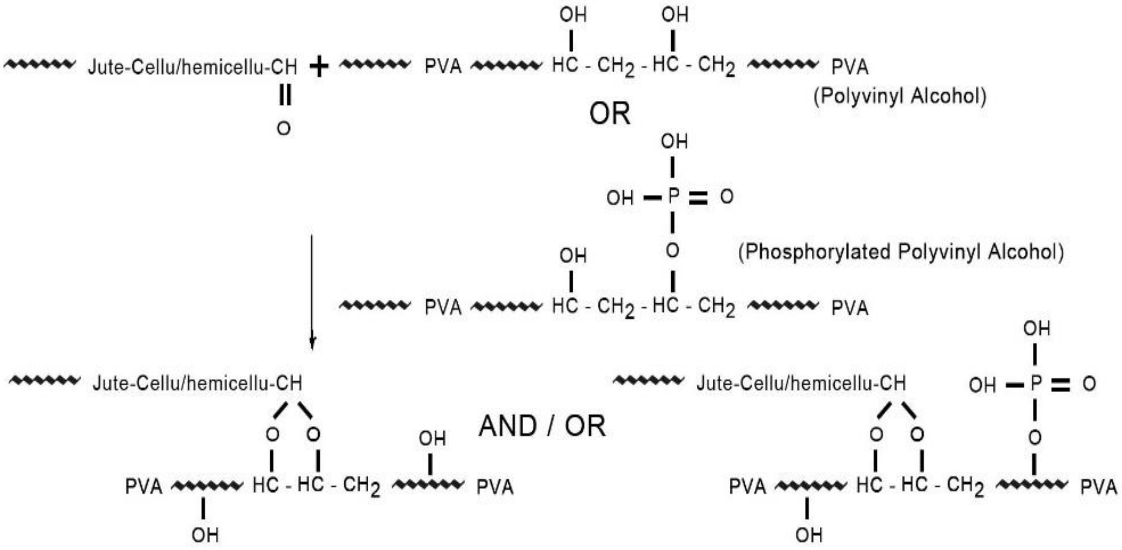
[Hemi-acetal Formation in acidic environment through –CHO group of oxidised phosphorylated PVA (Oxy(P-PVA)]

C. Reaction Scheme 1.3 [Reaction between oxidised jute and phosphorylated PVA (P-PVA) and/or oxidised phosphorylated PVA(o(P-PVA)]



[hemiacetal formation through –CHO group of oxy-jute]

D.Reaction scheme 1.4: [Reaction Between Oxy - Jute and PVA or P - PVA by hemiacetal formation]



4.1.4 FTIR studies of Untreated & flame retardant treated jute Substrate

FTIR spectra of Fig 4.1(a) Controlled bleached Jute; (Fig 4.1b) FTIR Spectra of J-(P-PVA) treated jute fabric ; (Fig 4.1c) FTIR Spectra of OJ-(P-PVA) treated jute fabric; (Fig 4.1d) FTIR Spectra of J-O(P-PVA) treated jute fabric; (Fig 4.1e) FTIR Spectra of OJ-O(P-PVA) treated jute fabric are shown in Fig 4.1 (a) to (e) from wave no. 4000 cm^{-1} - 500 cm^{-1}. The characteristic features of the FTIR spectrum of jute are due to different unit and inter unit linkages/bonds of its three major constituent alpha-cellulose, hemi-cellulose and lignin and also flame retardant chemicals anchored/fixed, wherever applicable.

Common FTIR transmittance peaks corresponding to 550 cm^{-1} (for −OH out of plane bending), 890 cm^{-1} (for β-glycosidic linkage), 1030 cm^{-1} (assigned to aromatic C-H in plane deformation & C-o deformation for primary alcohol in lignin), 1245cm^{-1} (for −C−O−C and −C=O stretching in xylan side substituent and lignin aromatic C=O stretching), 1335 cm^{-1} (for −OH in plane bending), 1370 cm^{-1} (for C-H deforming (symmetric) may be attributed to cellulose, hemicellulose and lignin), 1446 cm^{-1} (for C-H deforming (asymmetric) may be attributed to lignin) 1508 cm^{-1} (for lignin aromatic ring vibration and stretching), 1596 cm^{-1} (for C=C stretching in lignin olefinic units), 1735 cm^{-1} (for C=O stretching of ester group), 2355 cm^{-1} (for C−H stretching in polysaccharide chains), and 2905-2920 cm^{-1} (for C−H stretching vibrations of aliphatic methylene groups), 3350 cm^{-1} (for H bonded H-O Stretching) are found in all the FTIR-spectra including untreated jute Spectrum (a), Fig. 4.1] and jute fabrics treated in different manner [21,22] [Spectrum (b) and Spectrum(e), Fig. 4.1].

$K_2S_2O_8$ treated oxy-jute fibre shows in its FTIR spectrum (b) in Fig 4.1 a broad sharp peak at 1715-1735 cm^{-1} including >C=O stretching vibration of quinone formed in lignin by oxidation and 2100-2300 cm^{-1} (peak at 2345^{-1}) including –CHO group vibration for DAC (Di-aldehyde cellulose) or MAC (Mono-aldehyde cellulose) formed by oxidation J-(P-PVA) treated jute [Spectrum (b), Fig. 4.1] , by and large retain similar characteristics in their FTIR spectra as that obtained for the bleached $K_2S_2O_8$ treated oxy-jute however, showing some minor changes in functional group pattern by the said treatment, with decrease / increase or weakening / strengthening of some FTIR peaks / bands showing one or two additional small peaks.

FTIR analysis was done to understand the changes in chemical structures of jute after reacting with phosphorylated PVA or oxy P-PVA. FTIR spectra of phosphorylated PVA treated jute and oxy-jute and also oxidised P-PVA [Spectrum (b-e), Fig. 4.1], all of them shows sharp peaks in the range 3310–3340 cm^{-1} for hydrogen bonded –OH stretching. Intensity of peak decreases and broadens when the jute or the PVA is oxidized prior to application. This may be due to decrease in -OH groups in oxidized jute cellulose and PVA. This may be due to decrease in intermolecular hydrogen bonding due to phosphate ester formation. FTIR spectra of phosphorylated PVA treated jute and oxy-jute and also oxidised P-PVA [Spectrum (b-e), Fig. 4.1] show few small and sharp extra peaks at the region of 1100 -1500 cm $^{-1}$ for asymmetric stretching of –CH_2– vibration in –CH_2OH of jute cellulose and hemicellulose. In case of all jute fibre treated with the said flame retardant chemicals shows reduction of peak size for incorporation of phosphate groups with CH_2-OH or aldehyde group of cellulose and oxy-cellulose. These spectra also show small minor peaks in the range 1735–1745 cm–1 for>C=O stretching of acetate/ester group in PVA. Phosphorylated PVA–cellulose show peaks at 1021 cm^{-1} for P–O-alkyl stretching. Phosphorylated PVA–cellulose also show peaks at 707 cm–1, respectively for P–O stretching. These observations support the formation of intermolecular phosphate di-ester linkage amongst respective polymer chains in these flame retardant treated jute fabrics (treated with P-PVA or O(P-PVA)).

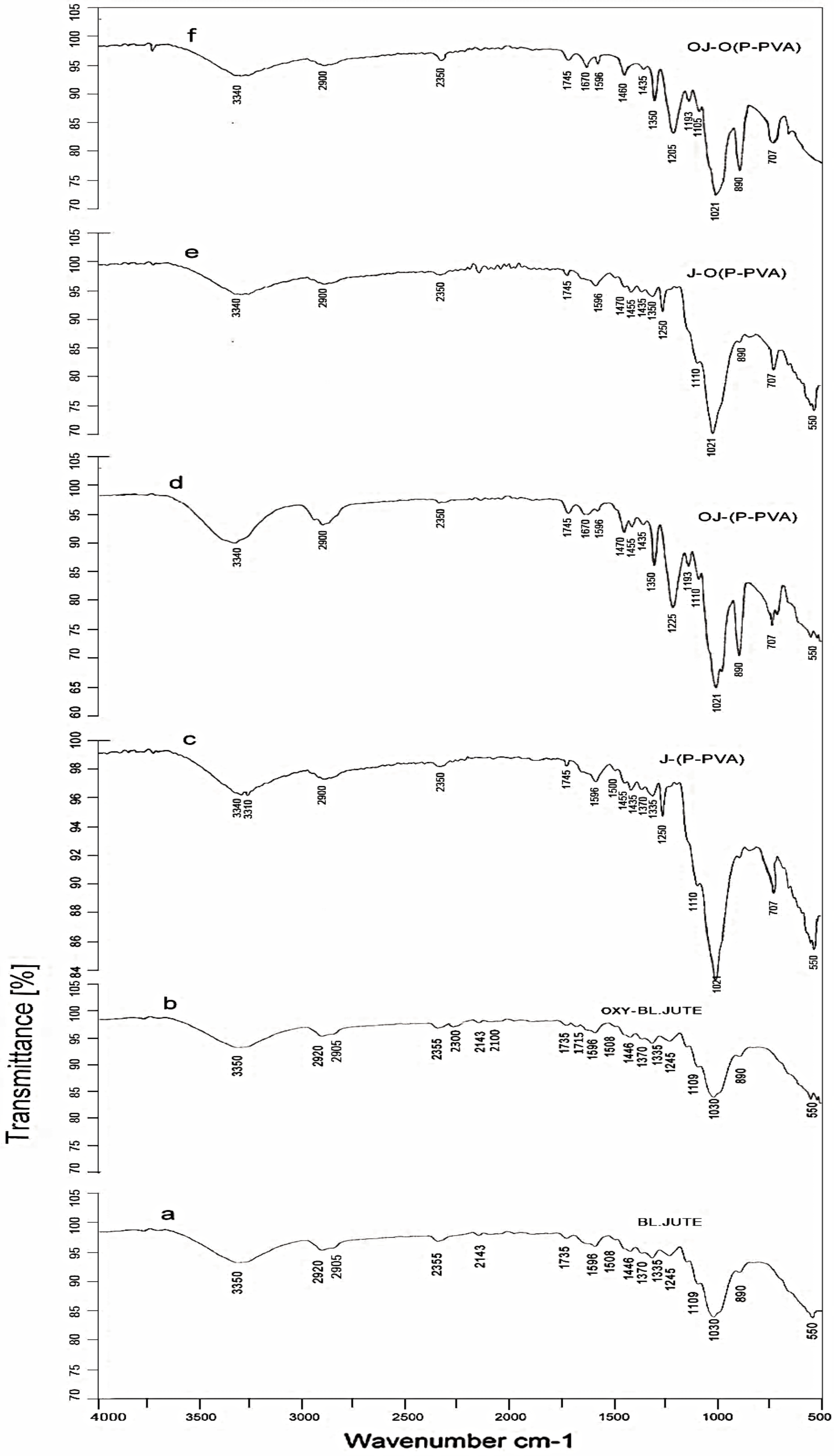


Fig 4.1: FTIR of untreated and treated Jute Fabric

4.1.5 Thermal analysis of bleached jute fabric and oxy-jute fabric treated with P-PVA and periodate P-PVA

Jute fabrics untreated and jute fabrics treated with P-PVA or oxy-P-PVA are subjected to TGA and DSC analysis from ambient to 500^0C. The TGA analysis data (in Table 4.2) of controlled jute and oxy jute fabric treated with P-PVA and periodate P-PVA (i.e. O(P-PVA)) shows that residue(ash) left at 500^0C is always more than that of untreated jute and is therefore more stable thermally.

Thus the untreated jute fabric shows negligible or no residue for heating at 500^oC while all other treated jute fabric shows a residue left for 8-3.5% for heating the same upto 500^oC showing higher stability, than untreated jute. Oxidized jute is thus more vulnerable on heating causing higher and quicker degradation at the same temperature.

Amongst the different TGA thermograms of jute or oxy-jute fabrics treated with P-PVA or oxy-P-PVA in the same conditions of treatment as compared with untreated jute as shown in (Fig: 4.2) periodate P-PVA treatment on Jute leaves highest residue (38%, Table 4.2) whereas, the weight loss is minimum. Therefore, the 3rd formulation [J-O(P-PVA)] gives somewhat good flame retardant property than other formulations used here. The LOI value and vertical flammability test results also confirm this observation.

P-PVA treatment on controlled jute also leaves a residue of 35% (2nd highest) at 500^0C as shown in Table 4.2, which is also matches with the observed higher flame retardant properties for this treatment.

However, in both the cases of oxy jute treated with only P-PVA and periodate P-PVA leaves a much less residue of only 8% and 11% respectively for heating upto 500^0C. Due to oxidation treatment on jute fabric it became mere susceptible to easy thermal degradation and hence leaves fewer residues at 500^0C. So, oxidized jute (oxy-jute) treated with P-PVA can form more stable and less hydrolysable hemiacetal, but thermal residue left at 500^oC is lesser than jute treated P-PVA or jute treated with oxy-P-PVA samples.

Table 4.2: Weight loss % of treated and untreated jute fabrics subjected to heating in varied temperature, indicating nature of thermal decomposition

Temperatures Formulation	Approximate Residue Left (in %) at respective temperatures (^oC)						
	80	**200**	**250**	**350**	**400**	**450**	**500**
Controlled Jute	92	88	86	38	29	13	Nil
J-P-PVA	92	88	77	41	36	34	35
OJ-P-PVA	92	88	83	43	37	25	8
J-O(P-PVA)	92	89	79	41	39	34	38
OJ-O(P-PVA)	93	90	81	41	39	31	11

While-analysis of DSC thermograms(Fig 4.3) for untreated jute fabric shows moisture evaporation endotherm at near about 60^{o}C onwards to 80^{o}C and thermal degradation of jute hemi-cellulose part occurs at 290^o to 320^{o}C by a broader but small exothermic hump having peak at 320^{o}C, while major cellulosic degradation occurs at 370^{O}C by a endothermic trough and a small sharp bilobal (duplet) trough showing bilobal endothermic trough and finally thermal degradation of lignin part occur at about 450^{0}C - 470^{0}C with sharp exothermic hump/peak. These findings are more or less at par with or nearly same with the similar observations made and reported by earlier researchers [21]. However, selective treatments with P-PVA and O(P-PVA) on jute show an early hemicellulose degradation at around 300^{o}C (in all cases the thermal degradation of hemicelluloses or cellulose occurs) and cellulose degradation occur showing a flat endothermic trough in between 320^{0}C to 400^{0}C and finally thermal degradation of lignin part of treated jute occurs at 440^{o}C -460^{o}C (particularly observed for DSC curve c) while DSC curves b, d, e in Fig 4.3 show similar nature of peaks for those corresponding thermal degradations of cellulose and lignin at slightly higher or lower temperature finally showing the thermal stability of ‘d’ appearing to be more than all other treatments reported here. DSC thermograms‘d’ thus just confirms better thermal stability with better balance of flame retardant performance.

Fig 4.2 TGA Thermograms of treated and untreated jute fabric

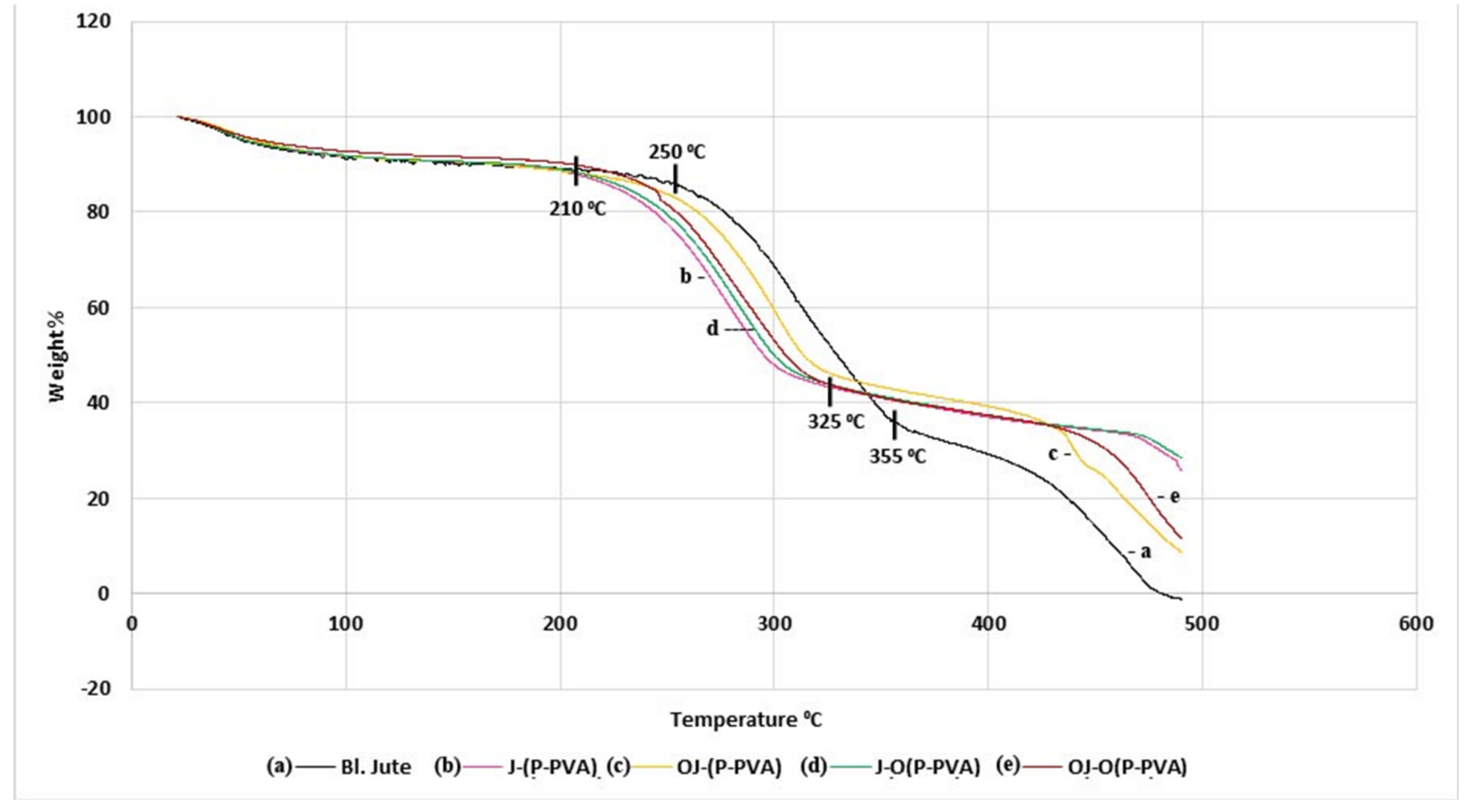
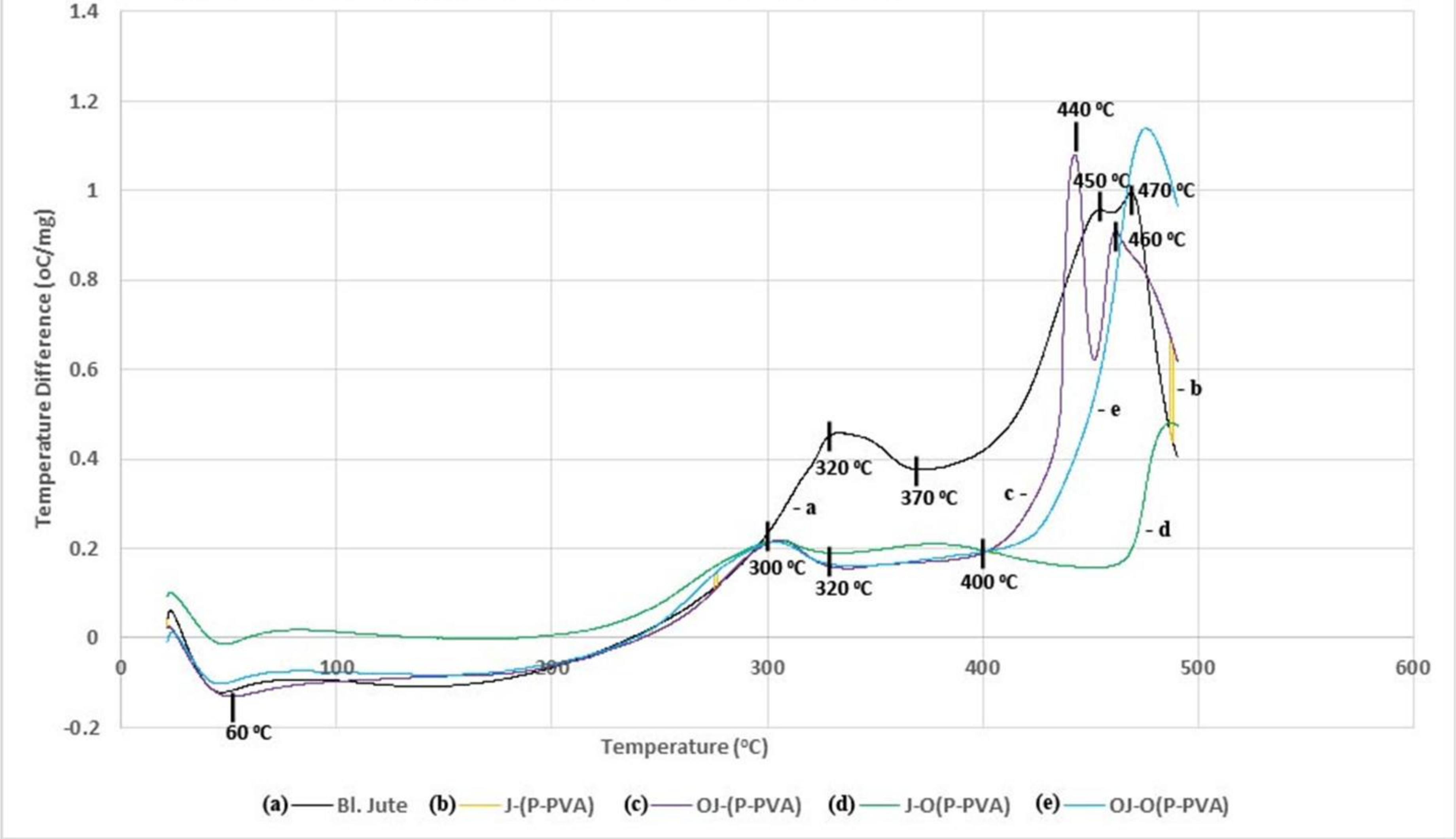


Fig 4.3 DSC Thermograms of treated and untreated jute fabric



4.1.6 Study of Surface Morphology of Untreated & flame retardant jute fibres

The scanning electron micrographs showing the surface appearance of bleached and different flame retardant chemical treated jute fabrics (after thorough washing with water and alcohol) are shown in Fig.4.4 (a-e). SEM – micrograph 3a of bleached jute fibre from corresponding fabric show the multicellular smooth surfaces with serrations and 1% $K_2S_2O_8$ treated jute fabric (fig 4.4b) shows the similar multi cellular structure with some oxidational damage on the surface , whereas all the flame retardant treated jute fibres taken out from corresponding fabrics amongst all the flame retardant treated jute and oxy-jute Fig 4.4c shows a tacky and gritty film of P-PVA over jute fabric surface making up the serrations. SEM micrographs in Fig4.4d shows some uneven powdery deposition of PVA film on oxy-jute whereas the SEM micrographs in Fig4.4e shows a smooth ,glossy and uniform coated film of oxy P-PVA which is obtained probably due to better flow and film forming nature of oxidized P-PVA than unoxidised P-PVA with higher viscosity. The SEM micrograph Fig 4.4f shows lesser deposition of FR chemicals on the oxy-jute fibre surface, when both fabric and P-PVA are oxidised, partly showing open serrations of multicellular nature of jute i.e. when both are oxidised, the anchoring of O(P-PVA) is much lesser on oxy-jute (SEM micrograph -4d) than when O(P-PVA) is applied on un-oxidised jute (SEM Micrograph 4c)..

Thus this SEM study reveals that the application of flame retardant recipe with P-PVA and Oxy- P-PVA are more uniform on un-oxidised jute than oxy-jute fabric probably due to the oxidation damage caused on the surface of the oxy-jute fabric.

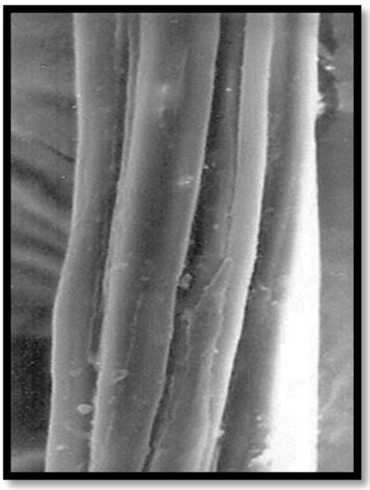
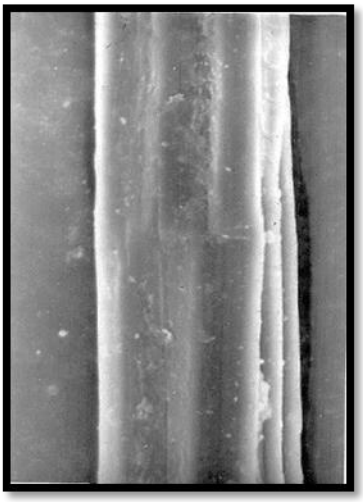
	

Fig 4.4a: Bleached Jute	Fig 4.4b:Oxy-Bl. Jute

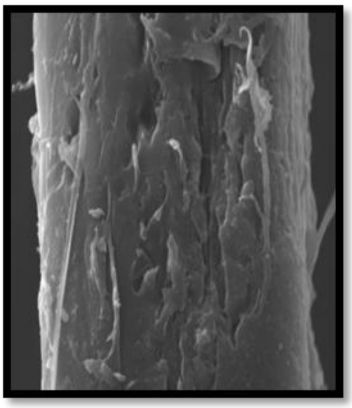
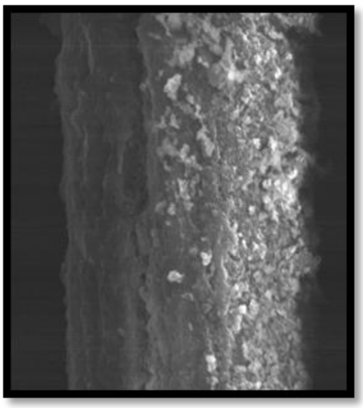

	

Fig 4.4c:J-P-PVA	Fig 4.4d:OJ-P-PVA

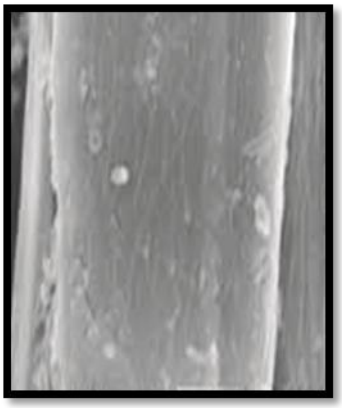
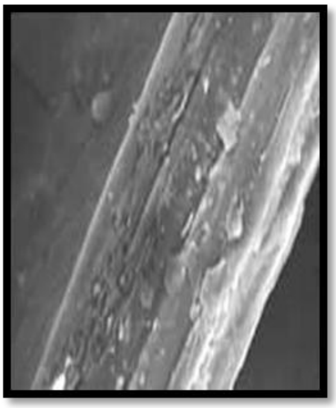

	

Fig 4.4e:J-O(P-PVA)	Fig 4.4f:OJ-O(P-PVA)

Fig 4.4 SEM Micrographs of controlled and treated jute fabric.

4.1.7 Wash stability of different flame retardant treated jute fabrics

Jute fabrics used as brattice cloth in mines are never washed jute based furnishings are washed very seldom – say once in a year/semester and hence, the wash stability for 1-5 cycles are sufficient considering its life 2-3 years only. After conventional normal washing of this flame retardant treated jute fabrics with 0.1% (1 gpl) non-ionic detergent/soap solution for 30 minutes at normal room temperature (jute is not washed with hot water or alkaline soap), the flame retardant performance is found to be decreased to some extent after 1-5 cycles of washing and the observed results are shown in Table-4.3. It is observed that in case of the treatments with the formulations J-P-PVA; OJ-P-PVA; OJ-O(P-PVA) the flame retardant property to some extent diminishes after 3rd and then also at or after 5th wash for all the formulations used, while for formulation 3 i.e. Jute treated with Periodate treated 10% P-PVA (i.e oxy-P-PVA) shows a little bit better retention of the flame retardant property even after 5th wash cycle retaining the LOI value of 27 or so. The higher loss of LOI value in all the cases except formulation 3 may be due to (1) less non-anchoring of the FR chemicals applied (2) or due to more amount of hydrolysis of the already fixed P-PVA or oxy-P-PVA flame retardant chemicals etc., and probably the later (reason 2) is pre-dominating for higher no. of wash cycle (5th wash cycle) for oxy-jute treated with oxy-P-PVA and retention of flame retardancy is relatively better for jute treated with oxy-P-PVA, due to more cross-linking (4.1.3 Reaction Scheme) than even was stable hemiacetal formation for oxy-jute treated with P-PVA (4.1.3 Reaction Scheme). These results are well understood from the data shown in table 4.3.

Table-4.3: Flammability property of the different flame retardant treated fabric at the optimized level after soap washing

Formulation Code	Treatment	LOI-value Before Soap Washing	LOI –value after Soap Washing		
			1st wash	3rd wash	5th wash
J-P-PVA	Jute treated with 10% P-PVA	28.5	27.5	26	25
OJ-P-PVA	Oxy-Jute Treated with 10% P-PVA	30	29	26	26
J-O(P-PVA)	Jute treated with Periodate treated 10% P-PVA	31.5	30	29	27
OJ-O(P-PVA)	Oxy-Jute Treated with Periodate treated 10% P-PVA	32	29	28	26.5

Section4.2 Effects of treatment with Ammonium sulphamate / Sulphamic acid / Urea as individual flame retardant chemicals and their mixtures on flame retardant performance of bleached jute fabrics

Introduction

Several types of flame retardants such as halogen based flame retardant (FR) agents and phosphorous based flame retardant (FR) agents with or without nitrogenous compound, have been used to improve the flame retardancy of cotton and synthetic textiles. However the application of halogen based FR is being greatly limited due to the possible production of dioxin, large amount of smoke and corrosive gases during the combustion of the halogen flame retarded materials. Phosphorus based FR with some exception for polymeric phosphates also has some drawbacks such as toxicity and high exudation [23-25].Sulfur based flame retardants such as sulfamic acid and sulfamate was used in the past for developing the flame retardancy of cotton, paper and wood. [26-28]. Sulfamate have been used in designs of many antibiotics, anti-cancer drugs, antiseptic drugs and weight loss drugs and other medical uses and hence is eco-safe. Considered as Ammonium sulfamate decomposes at elevated temperatures and releases some non-combustible gases, such as NH_3 and H_2O as this reduces fire. Lewin et al. [29,30] reported indeed that the use of ammonium sulfamate (AS) combined with dipentaerythritol improves the reaction to fire of PA6 (Nylon 6) in terms of LOI value. Menachem Lewin [31] has also reported that cotton fabrics are rendered flame retardant upon treatment with ammonium sulfamate (AS) with urea or a urea-based cross linking agent, as co-additive, in the pad-dry-cure finishing treatment, with curing at 180-200°C for one to three minutes.

Considering all these as background information, the present work was aimed to develop sulfamate based flame retardant formulations for Ammonium sulfamate or sulfamic acid along with urea as easily available common chemicals to apply on jute fabrics.

4.2.1 Preliminary study on Flame retardant performance of bleached jute treated with Urea / Ammonium sulfamate / Sulfamic acid individually.

It is already mentioned in section 4.1.1 that jute is a combustible material having LOI value 20.5 and the ignition time is 10 sec, LOI value of untreated bleached jute fabric is found (as shown in Table 4.1) to be 20.5, flame spread time to be 49 sec for the entire test length (12.5 cm) of jute fabric which burns the entire length in 49-50 sec and duration of afterglow is 55 sec (as per test result obtained from standard vertical flammability tester). The main aim of this present work is to find a suitable recipe for flame retardant finish of jute fabric using Ammonium Sulfamate, Sulfamic Acid, Urea. Therefore, the effects of these individual FR compounds on jute fabric viz a viz application of their mixtures on bleached jute fabric to evaluate their flame retardant performance. A commercial flame retardant finishing agent for cellulosic materials, i.e. Saraflam-CWF (THPC based FR agent) is also taken to apply on the same jute fabric for comparative study. From earlier studies on flame retardant treatment of cellulosics, using sulfamate [23-31] it is known that sulfamate based compounds are also very effective for flame retardants for cellulosic materials. So, Sulfamic acid and Ammonium sulfamate along with Urea have been applied on jute (ligno cellulosic fibre having 58-64% cellulose) fabric at different concentrations to achieve a certain level of flame retardant property. Bleached jute fabric was therefore individually treated with 5-20% Sulfamic acid and 5-20% Ammonium sulfamate and 5-20% Urea and their suitable mixtures to obtain desired flame retardant property and the observed results are shown in Table 4.4.

It was observed from the data given in Table 4.4 that said flame retardant agent (Sulfamic acid / Ammonium sulfamate / Urea) treated jute fabric achieved a reasonable level of flame retardancy with considerable loss of tensile strength. The loss of tensile strength assumed to be due to acidic degradation of jute fabric constituents during curing. LOI value observed for application of 15% and 20% Sulfamic Acid treatment is around 30 and above. while, for use of above 10% concentration level of Sulfamic Acid (SA), it causes noticeable loss in tensile strength in treated jute fabric. 15-20% Sulphamic acid causes 41-51% loss of fabric tenacity. While, 15-20% Ammonium sulfamate treated jute fabric shows good degree of flame retardancy with 30-32 LOI value and 4-4.5 cm char length. 20% Ammonium Sulfamate treated jute shows LOI value of 32 and also reduces the char length to 4 cm minimum. But, use of more than 15% Ammonium Sulfamate causes more than 30% loss in fabric tenacity.

Further, for identification of suitable combination of flame retardant formulations such FR compounds may be applied with nitrogen based compound e.g. Urea (5-20%). Application of urea on bleached jute fabric has been found also to render some degree of flame retardant property for using a level of concentration individually. It was observed that urea at higher concentration (20%) imparts moderate level of fire retardancy to jute (showing LOI value 25 from 20.5 LOI value for bleached jute).

So, it is imperative that use of suitable and judicious mixture of such flame retardant compounds in different ratio with or without other additives is expected to give better results than that obtained by individually application of them in flame retardant performance with least affecting the desirable textile related properties. So as next experiment suitable mixture of these three FR compounds were applied on bleached jute fabrics.

Table 4.4. Flame retardant performance of bleached jute fabric treated with individual chemicals.

Treatments	Physical properties				Vertical flammability test			LOI %
	% Loss in Tenacity	Elongation (%)	Bending Length (cm)	Whiteness Index (Hunter)	Flame Spread Time (sec)	After Glow Time (sec)	Char Length (cm)	
Untreated jute	-	3.1	4. 0	62.03	49 (BEL*)	55.0	-	20.5
Sulfamic Acid 5%	21	3.4	4.2	59.26	30 SE *	40	8	21
Sulfamic Acid 10%	35	3.5	4.2	58.63	28 SE	33	7.5	27
Sulfamic Acid 15%	41	3.9	4.6	53.65	21 SE	28	5.5	30
Sulfamic Acid 20%	51	4.1	4.4	48.15	20 SE	25	5	30.5
Ammonium Sulfamate 5%	18	3.3	4.5	59.71	28 SE	38	6	23
Ammonium Sulfamate 10%	24	3.6	4.4	57.95	20 SE	30	5.5	28.5
Ammonium Sulfamate 15%	29	3.5	4.2	55.68	15 SE	24	4.5	30
Ammonium Sulfamate 20%	36	4.0	4.9	55.63	18 SE	20	4	32
Urea 5%	8	3.6	4.3	60.34	45 (BEL)	-	BEL	20
Urea 10%	13	3.7	4.6	59.21	50 (BEL)	-	BEL	21
Urea 15%	18	3.9	4.9	58.36	56 (BEL)	-	BEL	23.5
Urea 20%	20	4.2	4.8	57.69	59 (BEL)	-	BEL	25

***BEL: Burned entire length : S.E.; Self extinguishing**

4.2.2 Effect of treatment with combination of Urea and Ammonium Sulfamate (Formulation –1; Code J-UAS)

In this experiment, Ammonium sulfamate and Urea mixture was used as FR agents and was considerably applied on bleached jute fabric in different proportions by pad-dry-cure method to measure its flame retardant performance.The superiority of sulfamate compounds for flame retardancy almost all over nitrogen compound is known [23-31] for long time. However, Ammonium Sulfamate(AS) is the main flame retardant agent, this is when applied in combination with Urea as a nitrogeneous compound, it may have some synergistic effect for flame retardancy. The function of urea is manifold e.g. moderate flame retardancy, to have some buffer action, facilitates formation of sulfonate ester with cellulose, to reduce acidity of the formulation so that it reduces loss in tenacity and to swell cellulose to enhance penetration of the applied chemicals etc. So, use of Ammonium sulfamate and urea in combination is thought to be useful and attempted in the present work.

The changes in flammability and related textile properties of jute fabrics after being treated with combination urea (10%,15%) and ammonium sulfamate in varying amount (viz. 10%,15%.20%) under specific controlled conditions of treatment have been assessed and the results are shown in Table 4.5, for formulation 1.

Relevant data in Table-4.5 thus indicate that for formulation (a-f) with the application of 10-20% ammonium sulfamate (AS) alongwith 10% & 15% urea, LOI value is found to be nearly to 31-38 (from original LOI value 20.5 for untreated jute) with simultaneous loss (28-37%) in jute fabric tenacity. This preliminary study shows that use of 15% urea and 15% AS combination (formulation 1e) gives more or less near optimum flame retardancy of jute fabric with LOI value of 38 and char length of 1 cm, which is even better than the results of earlier chapter 4.1 using P-PVA or oxy-P-PVA treatment on bleached jute fabric. It may also be noted that 10 % Urea and 15% combination (formulation 1b) AS treatment shows almost at per results with formulation 1e showing a bit lower LOI 35 and char length 2.5 cm whereas application of 10 % urea and 20% AS combination (formulation 1d) treatment causes 37 % loss of tenacity of jute fabric with no further significant improvement in LOI value. With increase in ammonium sulfamate (10-20%), the increase in LOI value upto a certain level (31 to 38) may be explained by increased blocking of C_6 position of jute cellulose preventing levo-glucosan (the flammable gas produced by burning of cellulose).

The effect may be better understood if the possible reaction mechanism is discussed here before proceeding for the analysis of property parameters and fire–retardant performance on application of these chemicals. Hence, the following postulations were made for possible reaction mechanism

4.2.2.1 Reaction Mechanism-:

The cellulose of jute may react with ammonium sulfamate at elevated temperature possibly in the following manner. AS at high temperature reacts with the hydroxyl groups of jute fibre. Based on reported literature [32] the following structure for treated jute is given. According to reports in earlier literature reported [33] there might be the following chemical reactions when urea and ammonium sulphamate applied together on cellulosic textiles and cured at a temperature of 140°C for few minutes.

$Cell\text{-}CH_2OH + NH_4OSO_2NH_2 \rightarrow Cell\text{-}CH_2OSO_2NH_2 + H_2O + NH_3$ ……………………..Eq 1

Ammonium Sulfamate

$NH_2CONH_2 + H_2NOSO_2NH_4 \rightarrow NH_2CONHSO_3NH_4 + NH_3\uparrow$ ……………….Eq 2

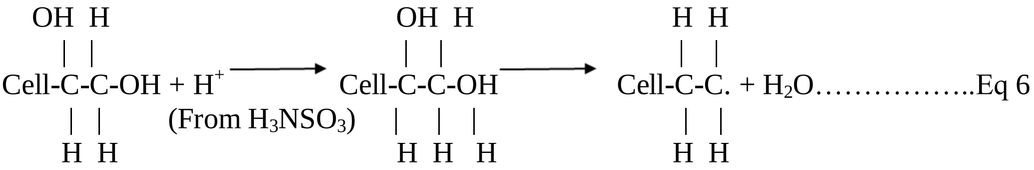
Urea Ammonium Sulfamate Ammonium Ureasulfonate

$Cell\text{-}CH_2OH + NH_4OSO_2NHCONH_2 \rightarrow Cell\text{-}CH_2OSO_2NHCONH_2 + H_2O + NH_3\uparrow$ ……………..Eq 3

Cellulose Ureasulfonate

$NH_4OSO_2NH_2 \xrightarrow{H_2O} H_2N\text{-}OSO_2H + NH_4OH$ ……………..Eq 4

$NH_4OSO_2NH_2 \xrightarrow{\triangle} H_3N\text{-}SO_3 + NH_3\uparrow$ ……………..Eq 5



$$Cell\text{-}\overset{OH}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}OH + H^+ \xrightarrow[\text{(From } H_3NSO_3)]{} Cell\text{-}\overset{OH}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}\text{-}\underset{H}{OH} \longrightarrow Cell\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}. + H_2O$$ ……………..Eq 6

(Dehydration Promoting char formation)

groups by forming urea sulphonate complex in 4.2.3 reaction mechanism shown above. Moreover, higher AS produces higher amount of sulfamic acid (SA) (eq. 4) where H^+ ion (proton) of SA promotes char formation in jute cellulose (eq. 5) and improves flame retardant performance and increases LOI value of the AS-urea treated jute fabric sample.

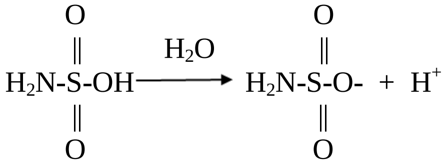
The bending length of these flame retardant treated jute fabrics are found to be increased with the increase in concentration of AS causing the fabric handle to become slightly stiffer and hence this treatment may need to be combined with application of some chemical softener , if required. For the surface appearance properties, it is noticed that whiteness indices are found to be decreased with increase in concentration of AS , irrespective of concentration of urea used.

4.2.3 Effect of treatment with combination of Urea and Sulfamic Acid (Formulation –2, Code J-USA)

As sulfamic acid produced ammonium sulfamate, promotes char formation for developing flame retardancy, it is thought appropriate to use sulfamic acid instead of sulfamates which may give rise to similar flame retardancy at lower cost.

4.2.3.1 Reaction Mechanism:

Hence, Jute cellulose may react with sulfamic acid (H_3NSO_3) at much higher and elevated temperature (>200°C) possibly in the following manner as shown in eq. 8 which is predominating if the higher temperature of reaction (more than 205°C, its decomposition temparature) is assumed to block C_6 position- of primary hydroxyl groups of jute cellulose. Hence, actually as jute fabrics cannot be treated above 130-140°C that too for 4-5 mins eq. 8 cannot be generated. So, following reaction as shown in eq. 9 and 10 may occur when urea and Sulfamic Acid are applied together in a combination at a temperature of 140°C for 4 min. Sulfamic acid may be hydrolysed in presence of water as shown in eq. 7. H^+ liberated from sulfamic acid then may follow the equation 6 in reaction mechanism 4.2B for promoting char formation in jute cellulose and hemicelluloses when burns and thus became flame retardant to a desired level:-



$$H_2N\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}OH \xrightarrow{H_2O} H_2N\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}O^- + H^+$$ ……………..Eq 7

Sulfamic Acid

$Cell\text{-}CH_2OH + H_3NSO_3 \rightarrow Cell\text{-}CH_2NH_2SO_2 + H_2O$ ………………..Eq 8

The changes in flammability and related textile properties of jute fabrics after being treated with combination urea (10%,15%) and sulfamic acid in varying amount (viz. 5%,10%,15%) under specific controlled conditions of treatment, the treated jute fabrics have been assessed for changes in texture related properties and flame retardanct performance and observed results are also shown in Table 4.5, formulation 2.

Superiority of sulfamate compounds in medical industry and also for flame retardant agent almost over nitrogen compound is already reported. Hence, in this part of the present work sulfamic acid is used as main flame retardant agent and the function of urea is manifold e.g. moderate flame retardancy, have some buffer action, facilitates formation of sulfonate ester with cellulose, reduces acidity of the formulation and thus, reduces loss in tenacity and swells cellulose to enhance penetration of the chemicals to jute cellulose, as told earlier.

By this preliminary experiment, as per relevant results shown in Table-4.5 for formulation 2, it indicate that with the application of 5-15% sulfamic acid along with 10% & 15% urea, LOI value is found to increase to 26-35(from original LOI value 20.5) with some loss in tenacity (30-47%) in treated fabric. 15% urea and 10% sulfamic acid combination (formulation 2e) showed near optimum results of flame retardant performance for treated jute fabric showing LOI value of 35 and char length of 2cm. While, it may also be noted that 10 % urea and 10% sulfamic acid combined treatment shows less LOI value 28.5 associated approx-36% with loss of fabric tenacity, whereas application of 10 % Urea and 15% Sulfamic Acid treatment causes 47% loss of tenacity of jute fabric rendering LOI value upto 33. Thus with increase in concentration of urea from 10% to 15% keeping SA concentration same (10%) the LOI value increases from 28.5 to 35 due to a synergistic characteristics of both urea and SA in combination, i.e. that its amino groups present in both are linked to electron withdrawal nature and hence can participate easily in delocalized bonding with jute cellulose for blocking of C_6-CH_2OH group. However urea is basic in nature and SA is acidic in nature and hence, SA in combination with urea neutralizes some of the strong acidic degradation action of SA acids during curing and reduces strength caused for such acidic degradation. However flame retardant performance for formulation 2a-2f with direct sulfamic acid than ammonium sulfamate causes higher loss in tenacity and lower LOI value than formulations (1a-1f), due to more acidic degradation by sulfamic acid causing chain scission cellulose/hemicellulose moities of jute rather than complexing between cellulose and Ammonium sulfamate plus Urea combination while use and consumption of Urea is more in this case for neutralizing acidity of SA rather than forming a coordinate complex for blocking of C_6-CH_2OH group attaching to cellulose of Jute.

However it may be better understood if, possible reaction mechanism is given before proceeding to the discussion on the effect on FR performance and important textile related properties. Hence, different properties of Sulfamic acid + Urea was applied on bleached jute fabric by pad-dry-cure technique, cured at 140 degree Celsius for 4-5 min.

$NH_2CONH_2 + H_3NOSO_2 \rightarrow NH_2\,CO\,NHSO_3H + NH_3$ ……………….Eq 9
Urea Sulfamic Acid Sulfonated Urea

Cell-CH_2OH + $NH_2\,CO\,NH_2SO_3 \rightarrow$ Cell-$CH_2\,OSO_2\,CONH_2 + H_2O + NH_3$ ………..Eq 10

As the eq. 8 has limited possibility to occur eq. 9 & eq. 10 are the most possibilities.

The bending length of these flame retardant treated jute fabrics are however found to be increased to some extent with the increase in concentration of sulfamic acid causing the fabric handle to become slightly stiffer, as was also observed sulfamate + urea combination and hence should be post treated or simultaneously treated with some chemical softener for reducing the stiffness. For the surface appearance properties, it is noticed that whiteness indices are found to be decreased with increase in concentration of sulfamic acid, irrespective of concentration of urea used, caused to more acidic degradation of major jute constitutents by sulphamic acid.

Table 4.5. Flame retardant performance of bleached jute fabric treated with FR-formulations 1-4.

Treatments	Physical properties				Vertical flammability test			LOI %
	% Loss in Tenacity	Elongation (%)	Bending Length	Whiteness Index (Hunter)	Flame Spread Time (sec)	After Glow Time (sec)	Char Length (cm)	
Untreated jute	-	3.10	4. 0	62.03	49.0 BEL*	55.0	-	20.5
Formulation 1; Code J-UAS (Urea & Ammonium Sulfamate)								
Formulation 1a U 10% ; AS 10%	28	4.12	4.1	59.61	25 SE	30	3.5	31.0
Formulation 1b U 10% ; AS 15%	30	4.31	4.2	58.38	15 SE	23	2.5	35.0
Formulation 1c U 10% ; AS 20%	37	4.53	4.5	57.46	8 SE	11	2	36.0
Formulation 1d U 15% ; AS 10%	25	4.41	4.6	55.73	10 SE	7	2.5	32.0
Formulation 1e U 15% ; AS 15%	28	4.62	4.8	56.42	5 SE	3	1	38.0
Formulation 1f U 15% ; AS 20%	35	4.73	5.0	58.31	5 SE	3	1	38.5
Formulation 2; Code J-USA(Urea & Sulfamic Acid)								
Formulation 2a U 10% ; SA 5%	31	4.81	4.0	58.24	24 SE	30	4.0	26.0
Formulation 2b U 10% ; SA 10%	36	4.31	4.1	56.87	14 SE	25	3.5	28.5
Formulation 2c U 10% ; SA 15%	47	4.81	4.2	54.12	9 SE	11	2.5	33
Formulation 2d U 15% ; SA 5%	30	4.50	4.3	57.56	13SE	9	3.0	26.5
Formulation 2e U 15% ; SA 10%	34	4.90	4.1	55.34	7 SE	5	2.0	35
Formulation 2f U 15% ; SA 15%	42	4.87	4.2	54.91	6 SE	5	2.0	34.5
Formulation 3; Code J-UAS-AC(Urea & Ammonium Sulfamate with commercial								
Formulation 3 U 15% ; AS 15%; Arko 50gpl ; Celu 30gpl ; $MgCl_2$	32	4.1	5.3	54.53	4SE	2	1.5	38.0
Formulation 4; Code J-S-CWF(commercial Flame retardant chemical SARAFLAM-								
Formulation 4a S-CWF 10%	23	4.1	4.5	59.01	16 SE	10	5.0	29.5
Formulation 4b S-CWF 20%	28	4.4	4.7	57.52	11 SE	8	4.5	30.0
Formulation 4c S-CWF 30%	33	4.3	5.0	56.46	8 SE	5	3.8	33.5
Formulation 4d S-CWF 40%	35	4.5	5.2	55.84	8 SE	5	3.2	35.0

***BEL: Burned entire length : S.E.; Self Extinguishing**

4.2.4 Effect of treatment with combination of Urea and Ammonium Sulfamate with binder (Formulation –3, Code J-UAS-AC)

The wash stability (upto 1-5 wash cycle) of Urea + Ammonium Sulfamate treated jute fabric is marginally better than Urea-Sulfamic acid treated jute fabric as detailed later in Table 4.6. Hence, to make the formulation wash stable to some extent a commercial binder (Arkofix) treatment was tried (formulation 3) along with urea-ammonium sulfamate formulation under specific controlled conditions of treatment and the observed results are shown in Table 4.5.

Relevant results in Table 4.6 indicate that the changes in flame retardant performance after 1,3 and 5 cycle of washes following standards have been assessed for jute fabrics after being treated with combination of urea (15%) and ammonium sulfamate (15%) with or without any binder, after 1-5 was cycle as detailed in table 4.6. The reduction of LOI value in this case (urea (15%) and ammonium sulfamate (15%) combination) is almost 2 unit per wash cycle and after 5 wash the LOI value become 29-30 (which was 38 before wash). However detailed wash stability study was explained later considering all types of treatment and experiment.

Relevant data in Table-4.5 also indicate that with the application of urea (15%) and ammonium sulfamate (15%) along with Arkofix NEC Plus Lid (50gpl) & Ceralube HD.In Lid (30gpl) with magnnesium chloride as catalyst (10gpl), LOI value is found to remain almost same as without binder, i.e 38 (from original LOI value 20.5) associated with the char length of 1.5 cm with a little higher loss in tenacity (32%) with binder as said above. The reduction of LOI value in this case (Urea (15%) and Ammonium Sulfamate (15%) combination with binder) is almost 0.5to 1 unit per wash cycle and after 5 wash the LOI is 36 (which was 38 before wash). Thus the effectiveness of this binder is proved to be important but still not highly satisfactory and need more research for obtaining maximum wash durability for more no. of wash cycle. However as jute fabric used in mines as brattice cloth is never washed and furnishing fabrics for jute is generally washed seldom, hence this much wash stability is thought to be sufficient.

4.2.5 Effect of treatment with combination of varying concentration of Saraflam-CWF (Formulation 4, Code J-S-CWF)

Saraflam-CWF, a commercial grade flame retardant agent based on THPC, (Tetrakis Hydroxy methyl phosphonium chloride) has been obtained from local supplier to provide reasonable flame retardant performance on cellulosics by the said commercial agent, so that it can be compared. To understand the rating of flame retardant performances of different combination of flame retardant chemicals (Ammonium Sulfamate, Slfamic Acid, Urea) used in this present work was compared to the flame retardant performance obtained by Saraflam-CWF. Additional experiments were carried out by applying varying concentration of Saraflam-CWF on same bleached jute fabric. The changes in important textile related properties of Saraflam-CWF treated jute fabrics after being treated with formulation-4 [Saraflam-CWF in varying amount viz.10%,20%,30%,40%] have been assessed and relevant results shown in Table 4.5. Results for formulation 4 (in Table 4.5) indicates that there is medium to good improvement in flame retardant performance by almost all the varying concentration level for application of Saraflam-CWF (Formulation 4) as indicated in terms of LOI values, flame spread time, after glow time and char length (though char length did not reduces below 3.2 cm). The flame retardant performance is also found to be increased with increase in concentration of Saraflam-CWF from 10% -40% in Formulation 4. Highest value of LOI 33-35 is achieved with 30%-40% application of Saraflam-CWF as compared to LOI value 38 obtained in case of formulation 1e with ammonium sulfamate and urea. The flame spread time, after glow time and char length for 30-40% saraflam-CWF treated jute fabric are also found to be higher than the corresponding formulation 1e it is found that strength loss is to some extent higher (approx 5% higher) in case of formulation 4c than that of Formulation 1e. Though there is always some loss in tensile strength for all the flame retardant agent applied here. The loss of tensile strength is found to increase with the increase in the percentage application of Saraflam -CWF. For all the treatment with Saraflam-CWF formulation 4, the bending length values are found to be increased as usual with the increase in percentage application of

Saraflam-CWF in Formulation 4. Also whiteness indices deteriorated to some extent with Saraflam-CWF treatment in Formulation 4 for jute fabrics.

The higher loss of tensile strength and lower reduction in flame spread time, char legth and to some extent overall lower value of LOI, obtained for 20-30% saraflam-CWF, may be viewed as an effect of higher degradative action of THPC based chemicals, while it is found to be better improved for formulation 1e showing higher LOI(38), lower char length (2 cm)etc. due less degradative action of Ammonium sulfamate and Urea combination.

Thus it is evident from this preliminary experimental data that the flame retardant performance of 15% urea and 15 % AS treated jute fabric is found to be superior even as compared to same or higher dosages commercially available / non-ecofriendly flame retardant formulations (Saraflam-CWF). To establish this combination as a specific flame retardant formulation for jute, it is need to be analysed and optimized by statistical experimental design technique.

Hence, study of wash stability, study of thermal degradation by DSC & TGA, study of changes in functional groups etc. by different treatments-by FTIR analysis and changes in surface morphology by SEM analysis and finally statistical optimization was done by Response surface methodology statistical software using User defined quadratic model.

4.2.6 Detailed study of wash stability of all flame retardant treatment experiments done on bleached jute fabrics

After normal washing of this flame retardant treated jute fabrics with 0.1% non-ionic detergent solution for 30 minutes at room temperature, the flame retardancy performance is found to be decreased to some extent after 1-5 cycles of washing and observed results are shown in Table-4.6 (as mentioned earlier). It is observed that for the formulation 1e (J-UAS) the reduction in LOI value per cycle is almost 2 unit and for the formulation 2e (J-USA) the reduction in LOI value is almost the similar, while formulation 3 i.e. Modified formulation 1e after admixing the specific non-washable of a binder (Arkofix NEC Plus) show somewhat higher wash stability of the modified formulation1e up to 5 wash cycles and the reduction in LOI value per cycle is 1 unit in this case. The higher loss of LOI value in all the other cases except formulation 3 is due to the unfixed water soluble flame retardant chemicals applied on jute fabric are susceptible to readily hydrolysis of these FR chemicals even already fixed. However, the rate of reduction of LOI value is not so rapid after 3rd or 5th wash because such unfixed chemicals are already washed out during 1st and 2nd washes (separate data for 2nd wash not shown). Moreover, the changes of LOI value observed in 3rd& 5th wash is mainly due to the hydrolysis of the already fixed chemicals and is therefore lesser extent of reduction of LOI value is obtained in all the cases in 3rd & 5th washcycle, as shown in data table 4.6. However, use of binder, Arkofix shows much improvement in wash stability for formulation 3 (modified formulation 1e) as the binder prevents the contact of water and flame retardant chemicals in the jute fabric.

Table-4.6: Flammability property of the different flame retardant treated fabric at the optimized level after soap washing

Formulation Code	**Treatment**	**LOI-value Before Soap Washing**	**LOI –value after Soap Washing**		
			1st wash	**3rd wash**	**5th wash**
J-UAS (1e)	Urea –15%, Ammonium Sulfamate – 15%	38	34	30	29
J-USA (2e)	Urea –15%, Sulfamic Acid – 15%	35	29	28	27
J-UAS-AC (3)	Urea (15%) and Ammonium Sulfamate (15%) , Arkofix NEC Plus Lid (50gpl) & Ceralube HD. In Lid (30gpl) & Magnesium Chloride as catalyst (10gpl)	38	37	36.5	36
J-S-CWF (4c)	Saraflam CWF -30%	33.5	31	29	28

4.2.7 Analysis of the thermal decomposition of treated and untreated jute fabric

The thermal degradation behaviour is extremely important for flame retardant materials [33]. Thermo-Gravimetric Analysis (TGA) in air and Differential Scanning Calorimetric (DSC) study in air of jute and chemically treated jute samples are shown in Fig 4.5 & Fig 4.6

respectively. The effectiveness of the said flame retardant chemicals on cellulosic material may be indicated by substantial lowering of the decomposition temperatures of major jute constitutents as well as higher char formation (leaving higher residue at max. temp.) of treated jute fabrics as compared to the untreated jute fabric.

TGA analysis of jute fabric treated with sulfamate/sulfamic acid based flame retardant chemicals with or without additives binders (formulations 1 to 3) show that residue left at 500^0C is more in these cases than that of untreated jute as shown in Table 4.7. Amongst all the differently flame retardant treated jute fabric, it is observed that the treatment with formulation 3 leaves highest residue (25.5% at 500^oC) or min. weight loss, whereas, residue of untreated jute is almost nil at 500^oC. Therefore, the formulation 3 is expected to give best flame retardant property. The LOI value and vertical flammability test and other flammability performance also confirm this observation as shown in Table 4.5 earlier. Treatment with formulation 1e also leaves a residue of 20.5% (2nd highest) at 500^0C which is also matched with the observed higher flame retardant properties amongst other treatments and is 2nd best after formulation 3. Residue left for formulation -4c (with 30% Saraflam CWF) treatment is approx. 18% at 500^0C which indicate also a higher level of flame retardancy for this commercial FR agent (Saraflam-CWF a THPC based FR agent). However, jute fabric treated with Formulation 2e showed residue of 15% at 500^0C which is somewhat lesser than other treatments. This can be explained by lesser extent of sulfonation to jute cellulose as compared to other treatments on jute cellulose.

Table 4.7: Weight loss % of treated and untreated jute fabrics subjected to heating in varied temperature, indicating nature of thermal decomposition

Temperatures / Formulations	Approximate Residue Left (in %) at respective temperatures (^oC)						
	80	**200**	**250**	**350**	**400**	**450**	**500**
Untreated Jute	92	88	86	38	29	13	Nil
J-UAS (1e)	94	90	63	45	37	28	20.5
J-USA (2e)	92	87	59	40	31	22	15
J-UAS-AC (3)	97	89	74	43	36	28	25.5
J-S-CWF (4c)	96	89	64	25	22	19	18

From the Thermo-gravimetric Analysis (TGA) curves (Fig 4.5), the Initial Weight loss Temperature (T_{onset}) of untreated jute and treated jute can be found. Formulation- 1-4 shows the T_{onset} as 245^0C, 270^0C respectively which are 35-10^oC lower than that of untreated jute (280^oC). This indicates that sulfamate based formulations facilitate the degradation of jute forming lesser amount of volatile product with increasing char formation giving rise to higher LOI values.

All the DSC thermograms for 4 types of flame retardant agent treated jute fabrics and also untreated jute fabric are shown in Fig 4.6. DSC thermogram for bleached jute shows broad endothermic peak at 50^0C (for evaporation of moisture present in jute), a broad exotherm with a hump at 325^0C (for degradation of hemicellulose part of jute), a sharp endotherm i.e. peak at 364^0 C (for degradation of cellulose component of jute) and a broad exotherm with two small hump at 450^0C & 460^0C (for degradation of lignin part of jute) which corroborates earlier findings of thermal behaviour study of control jute by DSC [20]. The thermal decomposition temperatures in treated jute fabrics are found to be gradually decreasing for all four formulations. In DSC Thermograms for all these four treatments the thermal decomposition rate is found to be highest in case of formulation 3 followed by formulation 2e followed by the next increase in formulation 1e.

All these DSC thermograms as presented in Fig 4.6 for FR treated jute fabrics, the changes in pattern of thermal degradation showing only one broad hump instead of two different exotherm & one endotherm at specific temperature as shown in bleached jute fabrics for degradation of major 3 constituents of jute (hemicellulose degradation at 325^oC, cellulose degradation at 364-365^oCand lignin degradation at 450-460^oC) indicate that all these FR chemicals perhaps chemically attached with both cellulose, hemicellulose and lignin, changes the thermal degradation behavior with early degradation of all these components within 250 ^{o}C -400 ^{o}C /425^oC by showing a bigger combined exothermic hump.

Fig 4.5. TGA Thermograms of Treated & Untreated Jute Fabric

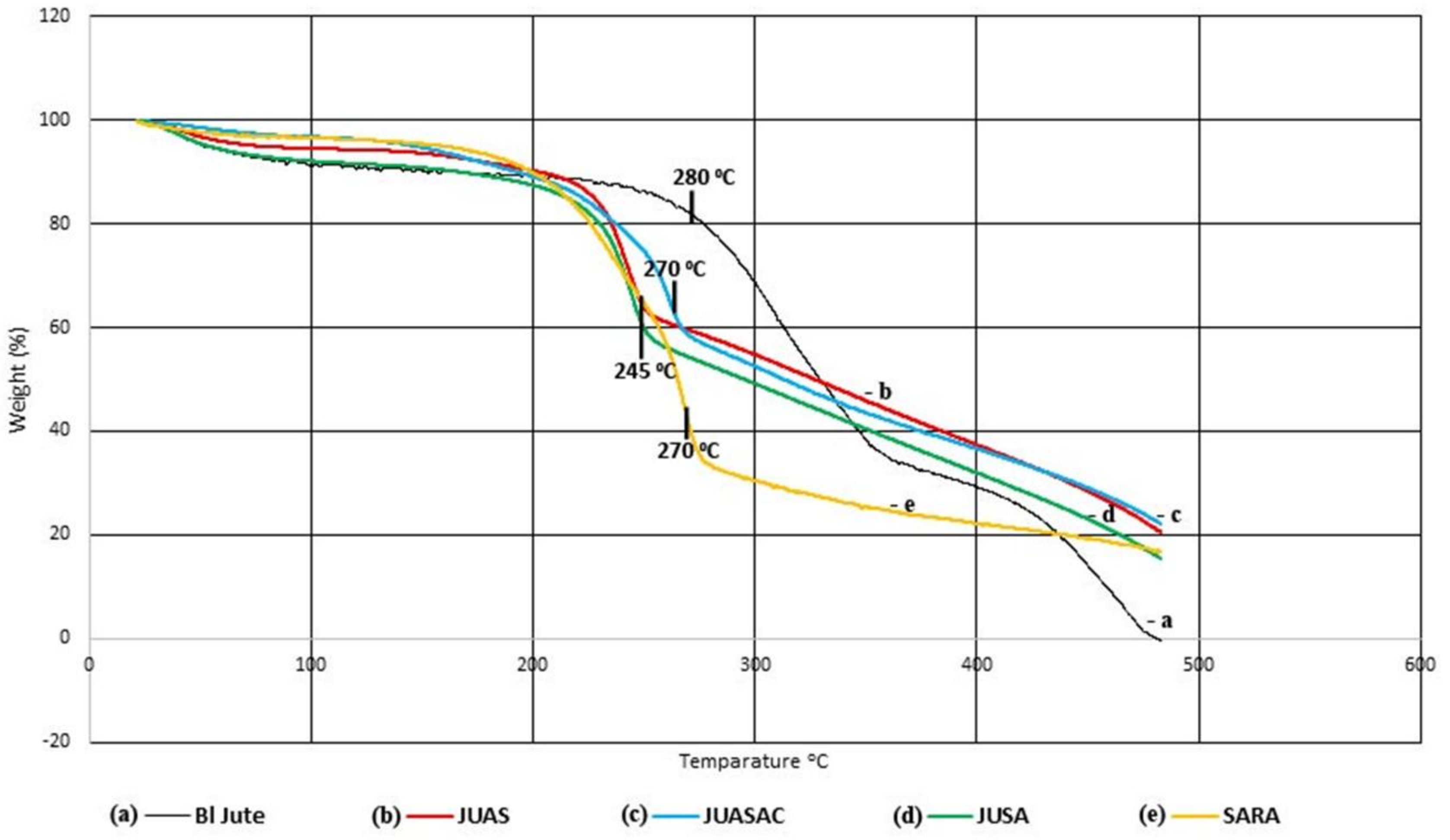
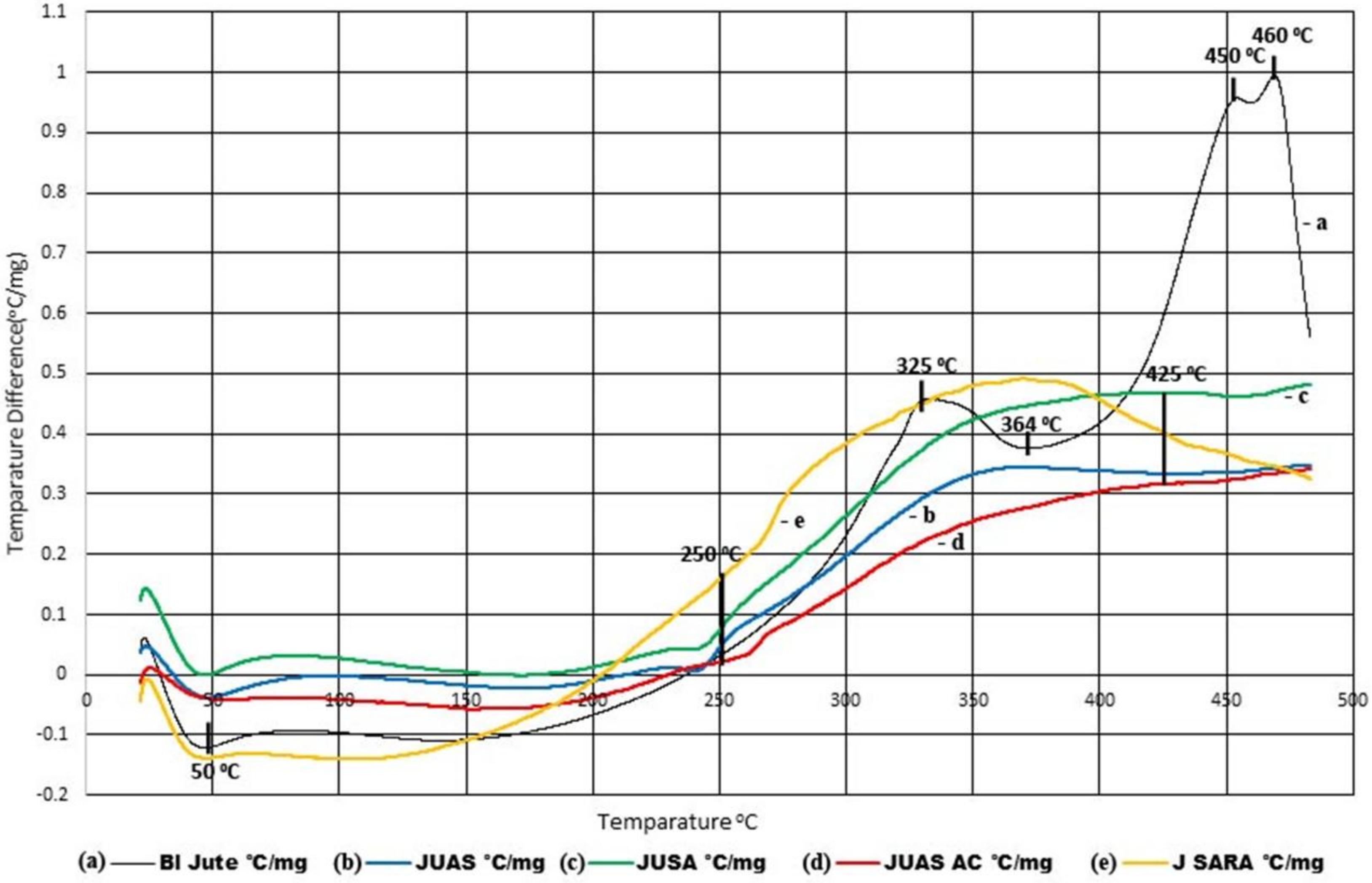


Fig 4.6 DSC Thermograms of Treated & untreated jute fabric



4.2.8 FTIR studies of Untreated & flame retardant jute fibres

FTIR spectra of (a) Untreated Jute; (b) J-UAS-Formulation 1e; (c) J-USA- Formulation 2e; (d) J-UAS-AC- Formulation 3; (e) J-Sara-Formulation 4c are shown in *Spectra* (a) to (e) in *Fig*.4.7 from wave no. 4000 cm^{-1} - 500 cm^{-1}. For all the five FTIR spectra there are some common characteristic features due to its three major constituents alpha-cellulose, hemi-cellulose and lignin which is already discussed in the section 4.1.5 and also stated once again in tabular form in the following Table no 4.8[20,21]:

Table no 4.8: Common Transmittance peaks with their significance of untreated and treated jute fabric

Sl. No.	Transmittance Peaks in FTIR Spectra	Significance
1	550 cm^{-1}	for −OH out of plane bending
2	890 cm^{-1}	for β-glycosidic linkage
3	1030 cm^{-1}	assigned to aromatic C-H in plane deformation & C-o deformation for primary alcohol in lignin
4	1245cm^{-1}	for −C−O−C and −C=O stretching in xylan side substituent and lignin aromatic C=O stretching
5	1335 cm^{-1}	for −OH in plane bending
6	1370 cm^{-1}	for C-H deforming (symmetric) may be attributed to cellulose, hemicellulose and lignin
7	1446 cm^{-1}	for C-H deforming (asymmetric) may be attributed to lignin
8	1508 cm^{-1}	for lignin aromatic ring vibration and stretching
9	1596 cm^{-1}	for C=C stretching in lignin olefinic units
10	1735 cm^{-1}	for C=O stretching of ester group
11	2355 cm^{-1}	for C−H stretching in polysaccharide chains
12	2905-2920 cm^{-1}	for C−H stretching vibrations of aliphatic methylene groups
13	3350 cm^{-1}	for H bonded H-O Stretching

J-UAS-Formulation 1e treated jute [Spectrum (b), Fig. 4.7] , by and large retain similar characteristics in their FTIR spectra as that obtained for the bleached jute , thereby showing some change in functional group pattern by the said treatment, though show some minor decrease / increase or weakening / some additional peaks observed. In *Spectrum* (b), *Fig*. 4.7, for J-UAS-Formulation 1e treated jute, there is introduction of a new peak at 810 cm^{-1} (indicating the presence of $–HSO_4$) and there is a minor increase in band intensity at 1030 cm^{-1}(due to $–OSO_3$-) and appearance of – SO_4^{2-}stretching vibration of sulfamate salt at 1109 cm^{-1} due to sulphamation of ester groups during the treatment. Additional appearance of transmittance peaks between 1300 cm^{-1} to 1400 cm^{-1} is attributed to C-N stretching vibration in primary and secondary amines due to incorporation of urea in the formulation, increase in the band intensity of the peak at 1446 cm^{-1} is ascribed the presence of $N-CH_2$ component [34] in the treated jute. Transmittance peaks corresponding to 1681 $cm^{-1}$is attributed to C=O stretching vibration in intra-molecular H bonded acids. Another huge peak at 1681 cm^{-1} is attributed to NH^+ stretching vibration in C= NH^+ . The treatment results in some modification of both hemicellulose and cellulose is evident from FTIR *Spectrum* (b), *Fig*. 4.7, which shows some decrease in band size at 2920 cm^{-1} and 4000 cm^{-1} as compared to the corresponding bands in FTIR *Spectrum* (a),*Fig*. 4.7 for bleached jute. Also the new sharp peak in this *Spectrum* (b), *Fig*. 4.7 at 2370 cm^{-1} is observed for N-H vibration of urea present in the formulation.

J-USA-Formulation 2e treated jute [Spectrum (c), Fig. 4.7], is showing some minor changes in functional group pattern by the said treatment when compared to the Spectrum (b), Fig. 4.7, discussed earlier though some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed. In *Spectrum* (c), *Fig*. 4.7, for J-USA-Formulation 2e treated jute, there is difference in the band intensity at 810 cm^{-1} (indicating the presence of $–HSO_4$) and a duplet arrived at 989 cm^{-1} near 1030 cm^{-1} (due to $–OSO_3$-) The increase in band intensity of the transmittance peaks between 1700 cm^{-1} to 1400 cm^{-1} is attributed to more reaction (in more acidic condition partial loss of hemicellulose and cellulose) as compared to ammonium sulfamate in the treated jute. Also the new sharp peak in this *Spectrum* (b), *Fig*. 4.7 at 2370 cm^{-1} is observed for N-H vibration of urea present in the formulation. Transmittance peaks corresponding to 3800 cm^{-1} to 3500 cm is attributed to O-H stretching free OH and increased H bonded OH for incorporation of these chemicals.

J-UAS-AC Formulation 3 treated jute [Spectrum (d), Fig. 4.7] , is modified formulation of J-UAS- Formulation 1e treated with a commercial binder for improving the durability of the treatment it largely retain similar characteristics in their FTIR spectra as that obtained for the J-UAS- Formulation 1e treated jute Spectrum (b), Fig. 4.7, thereby showing some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed. Only the major change is appearance of a duplet at 3000cm^{-1} - 2750 cm^{-1} spectral region denotes the presence of polyolefin attributed to -CH_2- asymmetric and symmetric stretching vibration (as additional polyolefin characteristics for incorporation of PE-emulsion softener along with the fixing binder to improve the stability of this flame retardant formulation).

For comparison purpose the jute is treated with a THPC based chemical commercially available chemical SARAFLAM-CWF. Thus, J-SARA Formulation 4c treated jute FTIR spectra [Spectrum (e), Fig. 4.7] as compare to the FTIR spectra as that obtained for the bleached jute , and thereby showing some change in functional group pattern by the said treatment, despite showing some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed here. In Spectrum (e), Fig. 4.7, there is introduction of a new peak at 1646 cm^{-1} (indicating –C-O stretching vibration) and there is a increase in band intensity at 2355 cm^{-1} (due to N-H stretching vibration for associated amines) and appearance of a duplet in the region 2839 cm^{-1} with 2920 cm^{-1} signifies C-H stretching and deformation vibration of CHO due to the oxidation of hemicellulose and cellulose during the phosphorylation treatment. The treatment results in blocking of some-OH-group due to Phosphorylation which is evident from FTIR *Spectrum* (b), *Fig*. 4.7, which shows some decrease in band size at 3350 cm^{-1}as compared to the corresponding bands in FTIR *Spectrum* (a) ,*Fig*. 4.7 for bleached jute.

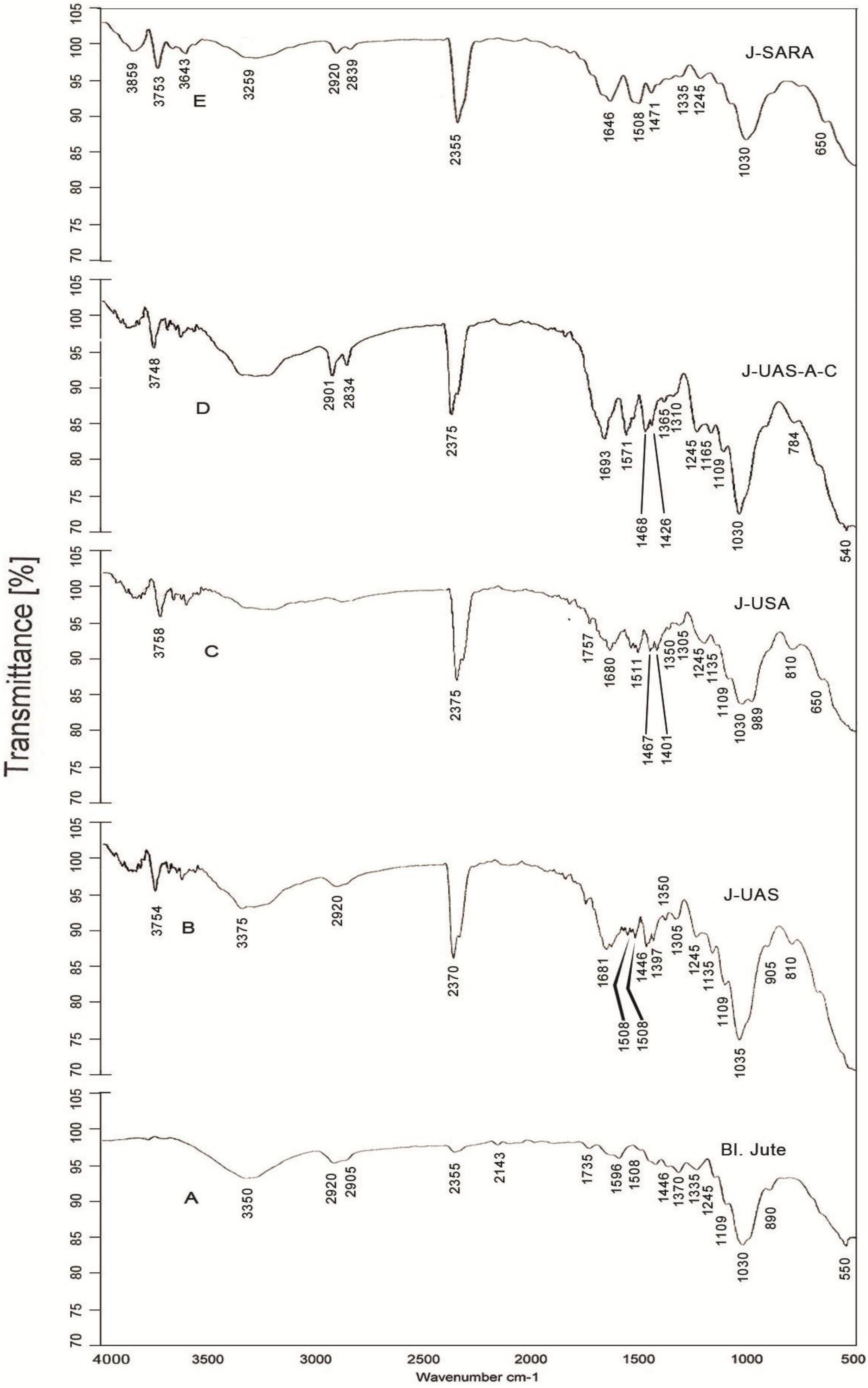


Fig 4.7 FTIR Spectra of treated and untreated jute

4.2.9 Study of Surface Morphology of Untreated & flame retardant jute fibres

The scanning electron micrographs showing the surface appearance of bleached and different flame retardant chemical treated jute fabrics (after thorough washing with water and alcohol) are shown in Fig.4.8 (a-e). SEM – micrograph 4.8a of bleached jute fabric show the smoother surfaces with small serrations, smooth whereas all the flame retardant treated jute fibres (for formulation 1-4) show that there are some distinct surface deposition having varying degree of uniformity and non-uniformity with extraneous deposition of anchored flame retardant compounds on the fibre surface. Amongst all the FR treated jute fibres SEM micrograph 4.8d shows a coated surface appearance having almost an irregular but continuous coating of specific FR chemical in presence of a binder resin applied on it ,making the serrations of multi-cellular jute while SEM micrograph 4.8e also shows a similar look of continuous coating, on surface of jute fibre making the serrations of multi cellular jute. But SEM micrograph 4.8b also shows lesser deposition of FR chemicals on the fibre surface, partly keeping serrations of multi cellular jute visible. Thus the SEM – micrographs clearly indicate the surface deposition of Flame retardant chemicals with or without additional binder applied, even after washing the samples in water followed by alcohol & acetone, indicating the firm anchorage of the deposited chemicals on jute.

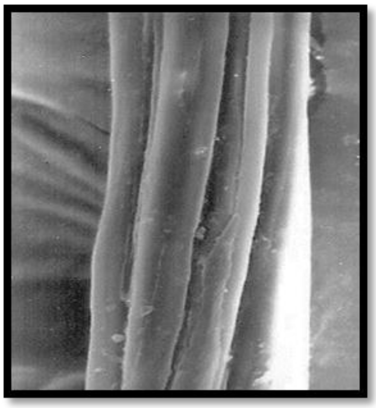
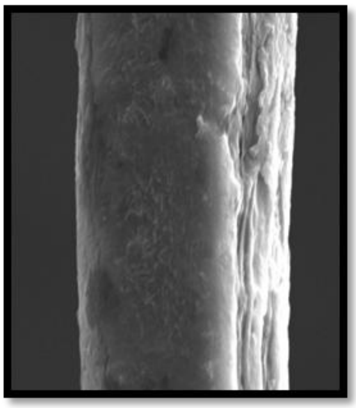
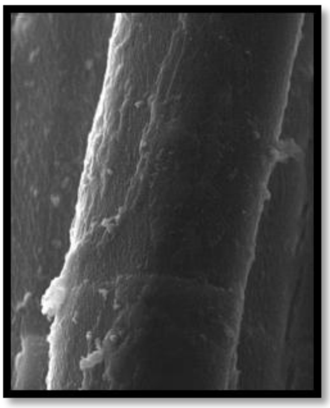
		

Fig4.8a: Bleached Jute	Fig4.8b:J-UAS	Fig4.8c:J-USA

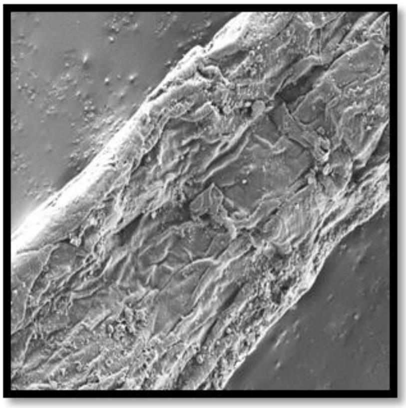
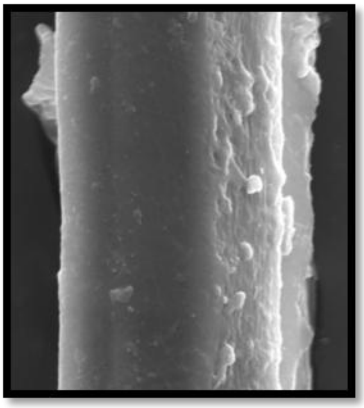
	

Fig4.8d:J-UAS-AC	Fig4.8e:J-SARA

Fig 4.8: Scanning Electron Micrographs of Untreated and Treated Jute Fibres

4.2.10 Optimisation of the Flame retardant formulation using Urea and Ammonium sulfamate combination by using the statistical software following UDQM (user defined Quadratic Model) of experimental design following Response Surface Methodology.

Response Surface Methodology (RSM) has recently emerged as a useful tool for evaluation of mutual-interactive effects among process factors and for assessing the optimal process condition. It is customary to get the optimal conditions from the RSM design software following a particular model of experimental design and compared the results obtained selecting process variables data based on the experience and results of the preliminary study (as detailed in 4.2.1 to 4.2.5). The User Defined Quadratic Model (UDQM) was followed to determine the statistically optimised Flame retardant formulations to predict the optimum (i.e maximum level of LOI, minimum level of Char Length and maximum reduction in Loss in Tenacity value.

Preliminary studies done and discussed in 4.2.1 to 4.2.5 for varying percentage of Urea (50-200g/l) and Ammonium Sulfamate (50-250g/l) to reveal the applicable ranges of chemical dosage for further optimisation of the above said flame retardant chemicals and their combinations for obtaining desirable range of Flame retardant performance. Table 4.9 represents the values of response variables (R1- LOI, R2- Char Length, R3- Loss in Tenacity) against the respective independent process variables A (Urea) and B (Ammonium Sulfamate) selected at five levels (-2, -1, 0, +1 and +2) as per the UDQM model derived to statistical experimental the design technique by specific Design expert software as detailed in material and Method section in item no 3.3.2 in Table 3.1. Table 4.9 shows the resultant response surface variables for corresponding variation in process variables A and B.

Table 4.9: Values of response variables against the respective independent process variable as per the UDQM model

Independent Process Variables		**Response Variables**		
UREA(g/l) (A)	**AMMONIUM SULFAMATE (g/l) (B)**	**LOI (%)(R1)**	**CHAR LENGTH (mm) (R2)**	**LOSS IN TENACITY (%)(R3)**
125	50	27.5	51	16
200	50	28.3	43	18
50	50	24.5	56	13
162.5	100	32.8	36	26
125	100	32	35	28
125	150	37.5	15	30
50	150	35.6	22	26
200	150	39.3	9	29
162.5	150	39.2	10	28
87.5	150	35.4	21	27
87.5	200	35.5	22	30
87.5	200	35.3	21	31
162.5	200	39.5	9	33
125	200	38.4	11	32
200	250	39.5	10	36
125	250	38.6	10	34
50	250	33.9	19	36

The corresponding Annova table for LOI is shown in Table 4.10, Annova Table for char length is shown in Table 4.11 and Annova Table for Loss in Tenacity is shown in Table 4.12.

Table 4.10 ANOVA Table for Response Surface Quadratic Model for LOI (R1)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	335.61	5	67.12	60.5	< 0.0001	significant
A-A	43.2	1	43.2	38.94	< 0.0001	
B-B	217.62	1	217.62	196.16	< 0.0001	
AB	1.36	1	1.36	1.22	0.2926	
A^2	0.11	1	0.11	0.095	0.7634	
B^2	64.8	1	64.8	58.41	< 0.0001	
Residual	12.2	11	1.11			
Cor Total	347.81	16				

Table 4.11 ANOVA Table for Response Surface Quadratic Model for Char Length (R2)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	3650.88	5	730.18	43.98	< 0.0001	significant
A-A	282.13	1	282.13	16.99	0.0017	
B-B	2745.63	1	2745.63	165.36	< 0.0001	
AB	0.13	1	0.13	7.97E-03	0.9305	
A^2	4.59	1	4.59	0.28	0.6093	
B^2	591.7	1	591.7	35.64	< 0.0001	
Residual	182.65	11	16.6			
Cor Total	3833.53	16				

Table 4.12 ANOVA Table for Response Surface Quadratic Model for Loss in Tenacity (R3)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	600.43	2	300.22	44.03	< 0.0001	significant
A-A	10.8	1	10.8	1.58	0.2288	
B-B	589.63	1	589.63	86.48	< 0.0001	
Residual	95.45	14	6.82			
Cor Total	695.88	16				

Annova table for all the three response variables (R1 , R2 & R3) against A and B as process variables elucidates the lack of fit in terms of p value (p>0.05), which are therefore neglected and used to generate the resultant model equation in coded form as expressed below in following-equations 11,12,13 for R1 (for LOI), R2 (for Char Length), R3 (for Loss in

Tenacity) showing the value of corresponding coefficient for predicting the resultant respective variables:

$$R1= 14.74+0.03*A+0.19*B+7.53*10^{-5}*A*B-3.47*10^{-5}*A^{2}-4.83*10^{-4}*B^{2} \qquad \text{eq 11}$$

$$R2= 87.05-0.03*A1-0.63*B1+2.35/100000*A1*B1-2.29/10000*A1*A1+1.46/1000*B1*B1 \qquad \text{eq 12}$$

$$R3 =12.35+0.02*A1+0.09*B1 \qquad \text{eq 13}$$

It is apparent from the tree above three annova tables (Tables 4.9, 4.10, 4.11) that B (Ammonium Sulfamate) is the most prominent factor followed by A (Urea) affecting the three response variables. Both the two factor A & B have synergetic effects on the three response variables (R1- LOI, R2- Char Length, R3- Loss in Tenacity). Three contour plots for three different response variables (R1- LOI, R2- Char Length, R3- Loss in Tenacity) are shown in Fig 4.9 , 4.10 and 4.11 respectively.

Table 4.9 shows the values of the process variables (A & B) used in the statistical experimental design with user defined quadratic model (UDQM) run in Design expert software and the corresponding resultant response variables (R1, R2, R3) obtained from the test results of those treated fabrics under the corresponding experimental set for each case.

These results are then processed for analysis of variance (ANNOVA) obtain the F value and p values (as shown in Table 4.10, 4.11, 4.12) for R1- LOI, R2- Char Length, R2- Char Length.

To establish the relationship between the variables, analysis of variance (ANNOVA) and regression analysis were done. The coefficient generated by ANNOVA by design expert software, to determine the RSM equations as shown in eq. 11 for R1 (LOI) eq. 12 for R2 (Char Length) eq. 13 for R2 (Char Length) for determination of predicted values of particular response variables. The plots of the effects of independent process variables individually or in combination on the resultant values of LOI (Fig-4.9), Char length (Fig 4.10) and loss of tenacity (Fig 4.11) are given here for understanding both the effects of one single process variables and also for effect of combinations (AA, AB, BB) i.e. interdependent factors also .

The coefficient obtained from optimization by design expert software following RSM technique either have positive or negative values and so have positive or negative effects on the experimental results (for the properties selected and studied). For a process variable to have a significant effect, the coefficients must be greater than twice of the standard error. However, non significant coefficient also have some inputs and is not useless or not to be dismissed, as there me be some small effect, but is important too. Thus from these three plots, it can be said that the effects of independent process variables or their combined interrogative effects on R1 (LOI), R2 (char length) and R3 (Loss of Tenacity), can be effectively be now interpreted easily and can be explained/ understood from the corresponding plots (Fig 4.9, 4.10, 4.11).

Plots in Fig 4.9 shows that variable A (i.e Urea) has less positive effect on increase of LOI value ; showing increase in LOI value with increase in concentration of AS (B), which however is not that significant after 87.5 gpl while the effect of variable A is not much after increasing it to 147.8 gpl.

Thus corresponding RSM equation-11, generated for predicting the value for R1(LOI) for specific dosages of A(Urea) and B(AS) indicate that the positive values of both (A) and (B) has positive effect, while negative values of the coefficients for both A^2 and B^2 terms, meant that further increase of the dosages for both the chemicals (urea+ AS) will reduce or have no effect on increasing LOI value, rather may reduce or remain same. Positive and higher value of coefficients for the interactive effect between AS (B) and Urea (A) meant the effect is to be positive and significantly higher i.e. there will be much higher effect obtained for using combination of Urea and AS than the use of AS individually and use of Urea individually, for increase in LOI value. So, it may be mentioned here that both the chemicals are required to get an optimum value of LOI.

Plot in Fig 4.10 shows that char length (one of the major 2nd important criteria for flame retardant performance of textiles) is reduced by increasing both the process variables (A) and (B) upto a certain dosages and then further increases above a certain dosages. However the effect of variable (A) i.e. Urea is found to be lower than the effect of variable (B) i.e Ammonium Sulphamate.

Corresponding RSM equation 12 generated for predicting values of R2 (Char length) for specific dosages of Urea (A) and Ammonium Sulphamate (B) indicate negative value of coefficient for A and B and A^2 term, i.e both increase of A & B cause a good reduction in char length but very high increase in A (Urea) did not show much reduction in R2(Char Length). Hence, it can be said that Ammonium sulfamate is much more important and is essentially required to reduce char length along with urea. So, determination of optimal values for combination of Ammonium Sulfamate and Urea is essential in this case.

Plot in Fig 4.11 shows that loss in fabric tenacity of treated jute fabric is increased with increase in variables B (Ammonium Sulfamate) to a large extent than the effect of variable A i.e Urea. Increase in concentration of Urea has minimum or very less effect on loss of fabric tenacity. Ammonium Sulfamate produces sulphamic acid during heating (curing stage) and hence there is probable acidic degradation of jute cellulose/hemicelluloses chain, causing the loss in fabric tenacity.

Corresponding RSM equation -13, generated for predicting resultant values of R3 (loss in tenacity) for specific dosages of Urea (A) and Ammonium sulfamate (B) indicate the positive value of coefficient, for both variables A and B showing coefficient of variable –B is higher than coefficients A , meant the effect of increase of Ammonium sulfamate is much higher than the said effect of increase of variable A i.e. Urea. Hence, Dosages of AS is to be restricted to avoid with loss in tenacity. So there is no question of Urea and AS to a much higher dosage i.e A^2 & B^2 terms.

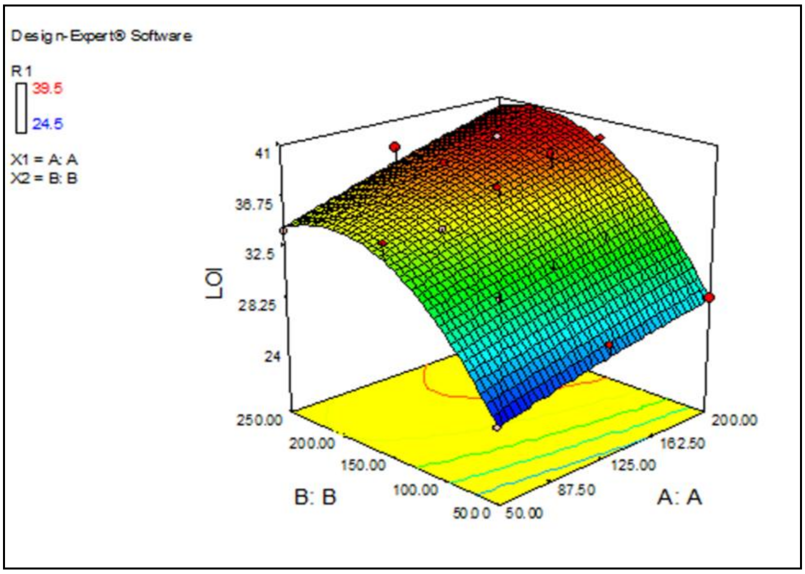


Fig 4.9 RSM Plot in respect to LOI

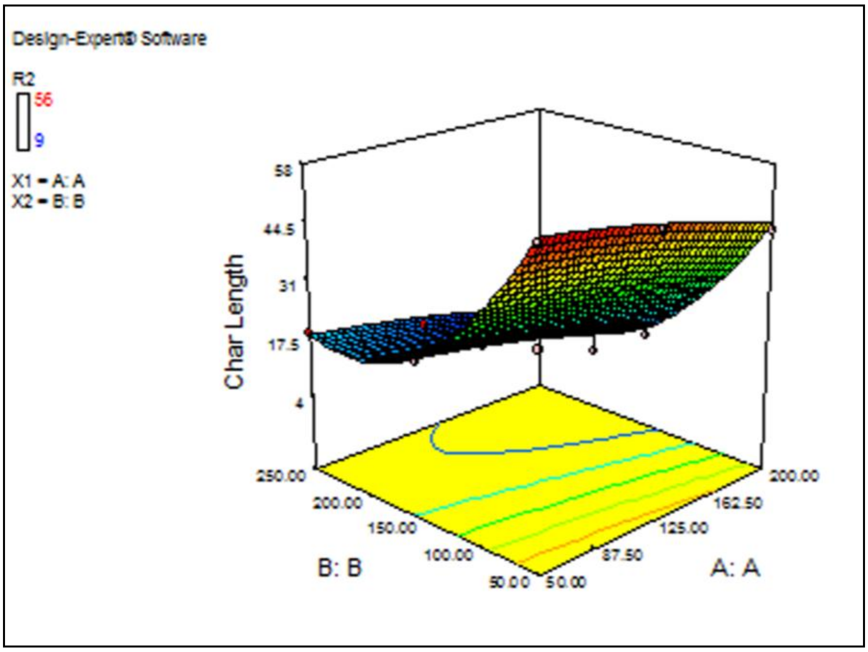


Fig 4.10 RSM Plot in respect to Char Length

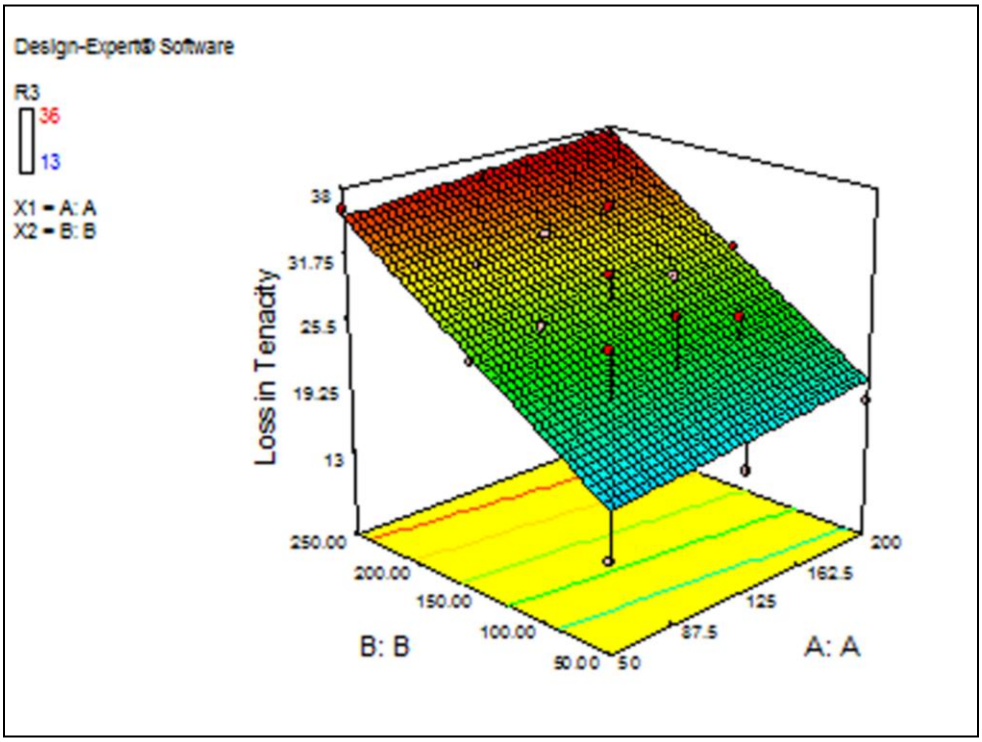


Fig 4.11 RSM Plot in respect to Loss in Tenacity

Finally, the numerical optimisation program was run in the design expert software to evaluate the optimal parametric values which are correspondingly represented in the three respective contour curves in plots given in Fig 4.9, 4.10 and 4.11 presenting the above stated results discussed above.

The optimal value of A and B as generated by RSM technique by UDQM model i.e A (Urea)= 147.80 and B (Ammonium Sulfamate)=87.90 for which the resultant optimal values of R1(LOI), R2(Char length) and R3(Loss of tenacity) respectively are 32.36% LOI, 33.82mm Char length and 23.21% Loss in Tenacity as predicted values of three response variables against the actual vales for varying parameters as shown in Table 4.8.

So, optimum dosages of ammonium sulfamate is 14.76% and urea is 8.79% much closer to the values of semi optimal dosages of these two chemicals obtained in preliminary experiment i.e. 15 % Urea and 10% Ammonium Sulfamate for which LOI was 32, Char length was 2.5 cm and Loss in tenacity value is 25%. However, considering the interactive effect of these two chemicals the finally optimized results for determining optimum dosages of these two chemicals are finally arrived at 14.78% of Urea and 8.79% AS for obtaining LOI 33, char Length 3.38cm and much lower tenacity loss of 23.21% (instead of 47% as was in formulation 2c in preliminary experiment (shown in table 4.5). So, to get much reduced strength loss in treated fabric, this optimized result have been accepted and finalized.

Section 4.3 Effect of treatment with combination of ZnO nano-particles and Polymethyl siliconate (PMS) emulsion for improved flame retardancy of bleached jute fabric.

Introduction:

With the advent of nanotechnology, nano zinc oxide (ZnO) particle; as a nano semi-conductor, solar energy conserver, electrostatic dissipative coating, UV-protective coating, chemical sensor have been studied [32,33]

ZnO flame retardant coating has been reported by different researchers. However, studies on jute are very few. Fire protection for cotton has been reported during last 10 yrs by many researchers. Recently some references have been found in the literature of Samanta & Bagchi et.al.[12] on jute. The major problems associated with flame retardant of jute are higher chemical add-on, noticeable strength loss, yellowing of colour, fabric stiffness, etc. Moreover Fire retardant formulations developed for jute were non-durable or semi durable. So it is found highly essential to find a solution to obtain a durable flame retardant formulation for jute. The durability of a flame retardant formulation with substrate and whether it is hydro soluble or not, when it is subjected to laundering. Large volumes of FR chemicals used in textile industry are nondurable, which wash off completely or partially after washing. If a fabric can survive water soaking to various degrees this is called a semi durable flame retardant. This type of treatment loses its effectiveness with alkaline detergent or hard water. An ideal FR fabric for textile applications must be comfortable, eco-friendly, cost effective as well as not to be leached off after laundering.

Nano particles (1nm= 10^{-9}m) are special group of materials with unique features and extensive applications in diverse fields [34]. The particles having size ranging from around 30-100 nanometers is considered to be nano particles for textile application. The formations of nano particles change the properties of many conventional materials [35]. Recent advances in the field of nanotechnology, leads to the preparation of highly ordered nano particulates of any size and shape. Nano particle metal oxides are an emerging area in research in different fields including health-related as well as textile applications. Amongst metal oxide nano particles, ZnO nano particles as one of the multifunctional inorganic nano particles which has many significant features such as chemical and physical stability, high catalysis activity, effective antibacterial activity as well as intensive ultraviolet and infrared adsorption with broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, etc. including application as FR coatings [36]. Due to the above mentioned noble properties nano ZnO could be effectively used in various materials and products, including medicine, cosmetics, solar cells, rubber and concrete, foods and textiles [37].

4.3.1 Reaction mechanism showing the preparation of ZnO nano-particles:

Before discussing the fire retardant performance and changes in important physical properties of jute fabric after nano ZnO treatment, it is appropriate to study the possible reaction mechanism for preparation of nano ZnO powder is discussed as below.

Reaction Mechanism showing the preparation of ZnO nano-particles

ZnO nano particle, for the application to jute fabric was generated by co-precipitation method. Zinc acetate dihydrate and NaOH were used as a precursor for generating ZnO nano particle by co-precipitation method followed by calcinations at higher temperature (600oC). The growth of ZnO by this method undergoes the following steps of reactions[38]

$$Zn(CH_3COO)_2 + NaOH \rightarrow Zn(CH_3COO)(OH) + Na(CH_3COO)$$

$$Zn(CH_3COO)OH + NaOH \rightarrow Zn(OH)_2 + Na(CH_3COO)$$

$$Zn(CH_3COO)OH + NaOH \rightarrow ZnO + Na(CH_3COO) + H_2O$$

$$Zn(OH)_2 \rightarrow Zn_2+ \ + OH- \rightarrow ZnO$$

The conversion of normal ZnO to powdered ZnO nano particles was made by calcination at 600°C. However, any nano particles, including nano ZnO suffer agglomeration Luo et al [39] and hence use of dispersing medium is preferred. That is why; PMS dispersion is used in the present work as a dispersive medium to apply nano ZnO on jute fabric.

4.3.2 Characterisation of ZnO nano particle by XRD Analysis

Figure 4.12 shows the XRD spectrum of synthesized nano ZnO produced from Zinc acetate by co-precipitation method. All the diffracted peaks are well assigned as hexagonal (Wurtzite) ultra nano crystalline phases of ZnO. Phase peaks corresponding to the

JCPDS card number 01-089-0511 with lattice constants of a = 3.245 Å and c = 5.205 Å. The XRD indicates that the ultra crystalline ZnO particles are highly pure and are free from the impurities viz., Zn $(OH)_2$ and zinc acetate. From XRD spectrum, the characteristic peaks with high intensities corresponding to (100), (002), (101) planes and lower intensities corresponding to (102), (110), (103), (200), (112) and (201) planes indicate that this nano ZnO product produced as above is of high-purity hexagonal ZnO quartzite structure. The sharpness of the peaks point out that ZnO is well crystalline in nature[39]. The broadness of these peaks shows the low crystallite size for the synthesised ZnO. The crystallite diameter was calculated using well known Scherrer equation: $D = (k\lambda) / (\beta \cos \theta)$, where D is mean crystallite size of the powder, λ is the wavelength of Cukα , β is the full width at half-maximum, θ is the Bragg diffraction angle and k is a constant. The average size of one such crystallite particle of nano ZnO obtained for its prominent peak in (101) plane is ~36.4 nm, confirmed the presence of nano sized crystalline ZnO particle, which is obviously much lower than the particle size of commercially available bulk ZnO[40] .

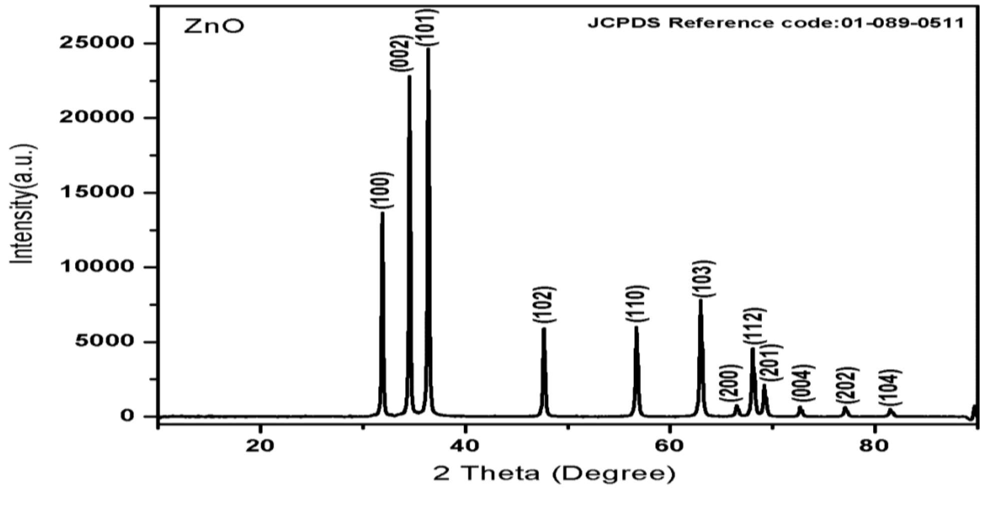


Fig. 4.12 XRD of Nano ZnO powder

4.3.3 Effect of application of nano ZnO particles on the changes in the textile related properties of jute fabric

To understand the effects of application of ZnO nano particle (in presence of PMS as a dispersing medium as well as a binder) coating on the changes of important textile related properties of the jute fabric viz., tensile strength, stiffness, and whiteness index of treated and untreated jute fabric were evaluated. Table 4.13 shows the effects of nano-ZnO particle coating treatment on important physical properties of jute fabric, in comparison with that of untreated jute fabric.

Tensile strength of jute fabric was found to be reduced to an extent of 10 – 20 % after different dosages of treatment of nano particles in presence of required amount of PMS. This reduction in fabric tenacity may be considered due to the alkaline degradation of major jute constituents by alkaline PMS dispersion, particularly during pad-dry process. Due to the alkalinity of PMS, partial removal of hemicellulose and a small part of removal of the lignin takes place, which ultimately results some reduction in the tensile strength of treated jute fabric. The initial bending length of untreated jute fabric was 3.8 cm, which was found to be increased up to 4.8 cm, showing increased stiffness after different dosages of treatment with ZnO nano particles. This may be due to the effect of coating of the binder polymer (PMS) over the fabric. It is also observed that the bending length reduces after five cycles of washing of the treated fabric, which indicates the partial removal of PMS binder coating from the treated jute fabric. It is there for clear that the ZnO nano particle does not contribute towards the loss in tenacity and an increase in bending length. The initial Hunter whiteness index of untreated bleached jute fabric was measured as 75.20, after nano ZnO particle coating formulation of 10% PMS+ 0.01% ZnO, it decreased to 60.25 and it shows increase up to 67.35, after five cycles of washing. The reduction of whiteness index may be caused due to the drying of treated fabric at a higher temperature at alkaline pH (in presence of PMS, which has alkaline pH). Thus, treated jute fabric shows slight yellow shade after treatment with 10% PMS +0.01% nano ZnO powder applied by pad dry method. Thus, the formulation having Sl. No. 8 (0.01% nano ZnO + 10% PMS) applied on jute fabric appeared to be better option if it passes fire retardant performance criteria, as discussed below:

Table 4.13 Physical properties of PMS and Nano ZnO coated jute fabrics

S.No	Treatments	Physical properties		
		% Loss in Breaking Tenacity	Bending Length (cm)	Whiteness Index (Hunter)
1	Untreated (control)	-	3.8	75.20
2	1% PMS	5	3.9	70.06
3	5% PMS	8	4.0	62.16
4	10% PMS	10	4.2	59.24
5	15% PMS	20	4.7	58.32
6	1% PMS + 0.01% nano ZnO	5.5	4.0	70.68
7	5% PMS + 0.01% nano ZnO	8	3.9	63.52
8	10% PMS+ 0.01% nano ZnO	10	4.5	60.25
9	15% PMS + 0.01% nano ZnO	21	4.8	58.96
10	10% PMS + 0.005% nano ZnO	10	4.4	60.32
11	10% PMS + 0.02% nano ZnO	10	4.7	61.64
12	10% PMS+ 0.01% nano ZnO (After 5 cycle of washing)	10	4.0	67.35
13	20 % SARA Flame CFW	28	4.7	67.52

4.3.4 Effect of application of nano ZnO particles on fire retardant performance for jute fabrics

Results of fire retardant performances for experiment SI.No.2 to 11 are shown in Table 4.14. Corresponding data in Table 4.14 for SI. No. 8 formulation (10% PMS+ 0.01% ZnO) show that in this case the char length was found to be 1.0 cm and flame does not spread at all and afterglow remained for 37 seconds. The presence of silica metal (from PMS) as a metallic residue on the fabric surface is causing this afterglow on the treated jute fabric. The measurement of char length is an important factor too in order to study the influence of any flame retardancy[33]. The maximum LOI value was found to be 35, among all the formulations used, where LOI value for experiment in SI. No. 8 (10% PMS+ 0.01% ZnO) were also 35. Data of LOI values for experiment SI. No. 8, 9 and 11 shows that an increase in the concentration of nano ZnO particles from 0.01 to 0.02% does not increase the LOI value any more, but experiment No. 10 with a reduction of nano zinc oxide to 0.005% shows a reduction in LOI value to 29. After 5 cycles of washing, there is a marginal decrease in fire retardant performances, showing an adverse decrease in LOI value (30 from 35), decrease in afterglow time (30 s from 37 s), adverse increase in char length (2 cm from 1 cm) and adverse effect showing flame spread time to be 5 s instead of nil / no flame spread though the flame still remains self-extinguishing in nature. This may be due to the partial removal of the PMS binder along with nano ZnO from jute fabric by 5 wash cycles. Generally, a fabric is said to be flame retardant, if its LOI value is above 27. This result was comparable with commercial fire retarding chemicals (result of application of 20% SARA Flame - CFW as commercial fire retardant, as shown in SI. No. 13 in Table 4.14. For a commercial fire retardant formulation, for getting LOI value of 30 to 35, around 200-300 gpl (i.e. 20% to 30%) concentration may be needed, while for application of this nano zinc oxide, much lower concentration is sufficient. For 0.01% ZnO nano particle along with 10% PMS (silicone emulsion) treated jute fabric, the LOI value was found to be maximum (35), which indicates that the treated jute fabric has very good fire retardant property even with much lower % of application of zinc oxide in nano form. Since PMS forms a binder coating over the fabric, the fabric coated with PMS even without ZnO nano particles (only 10% PMS treated jute fabric), shows LOI value of 22 (LOI value of untreated jute is 20.5). In the case of formulation 0.01% ZnO nano particle along with 10% PMS, even after 5 cycles of washing, LOI value is still around 30, which can also be considered good flame retardant in terms of LOI value for moderate to good flame retardancy for jute fabric, as jute fabric or flame retardant treated jute fabric are seldom washable. This show the ZnO nano particles along with the silicone binder emulsion are fairly adhered on the jute fabric surface. However, on repeated 5 cycles of washing, some loosely held ZnO nano particle with the silicone emulsion are washed out from the surface of the treated jute fabric. A treatment with a commercial flame retardant agent like, SARA Flame – CFW, applied in 20% concentration on jute fabric shows LOI value of 30. Thus, experiment SI. No. 8 can be considered as the best option to be optimum for imparting semi-permanent and reasonably wash stable flame retardant jute fabric using .01% nano zing oxide particle dispersed in 10% PMS applied by pad dry method. However, for the scientific understanding of the changes on thermal behaviour and surface character as well as structural changes in chemical functionality, etc. the treated jute fabric was subjected to analysis with DSC, TGA, EDX, AAS, SEM and FTIR Spectroscopic analysis as discussed below:

Table 4.14 Flammability properties of ZnO coated jute fabric

S.No	Treatments	Vertical flammability test			Limiting Oxygen Index (%)
		Flame Spread Time(s)	After Glow Time (s)	Char Length (cm)	
1	Untreated	49.0 (BEL*)	55.0	12.5 (BEL)	20.5
2	1% PMS	28	20	BEL	21
3	5% PMS	26	22	BEL	22
4	10% PMS	25	23	BEL	22
5	15% PMS	26	23	BEL	24
6	1% PMS + 0.01% ZnO	5,SE*	35	2.2	30
7	5% PMS + 0.01% ZnO	7,SE	35	1.3	32
8	10% PMS+ 0.01% ZnO	Nil,SE,NFS	37	1	35
9	15% PMS + 0.01% ZnO	Nil, NFS	37	1	35
10	10% PMS + 0.005% ZnO	10,SE	40	2	29
11	10% PMS + 0.02% ZnO	Nil, NFS	45	1	35
12	10% PMS+ 0.01% ZnO (After washing)	5, SE	30	2	30
13	20 % SARA Flame CSW	11, SE	8	4.5	30

BEL – Burnt entire length, SE- Self extinguished, NFS - No flame spread

4.3.5 Study of analysis of the thermal decomposition of ZnO nano particle treated jute fabric using DSC & TGA thermograms

The thermal degradation behaviour is extremely important for flame retardant materials. Thermo-Gravimetric Analysis (TGA) in air and Differential Scanning Calorimetry (DSC) study in air for untreated jute and nano ZnO particle coated with PMS binder jute samples are shown in Fig 4.13 and Fig 4.14 respectively. The effectiveness of fire retardant chemicals in lignocellulosic material is generally indicated by somewhat lowering of the thermal decomposition temperature of individual major jute constituents. It was found in both Fig 4.13 and Fig 4.14 that there is an early thermal decomposition of hemicellulose part of jute along with indicating higher char formation (leaving higher residue at 500°C max. temp studied) by nano ZnO treated jute substrate as compared to the untreated jute substrate. Untreated jute fabric in fig 4.13 shows its 1st thermal degradation at 280°C-310°C for hemicellulose and 2nd thermal degradation at 360°C-380°C for cellulose and 3rd thermal degradation at about 430°C - 450°C for lignin, indicating a change in slope at those temperatures[21], as shown in fig 4.13 (TGA). While, TGA thermogram of ZnO nano particle (0.01 %) along with 10% PMS treated jute sample also shown in fig 2 shows its 1st thermal degradation at about 250 - 280°C for hemicellulose and 2nd thermal degradation at about 330 to 350°C and 3rd thermal degradation occur at about 430 - 450°C showing marginally more residue (5% difference) left at 400°C-500°C. This indicates a marginally early thermal degradation of hemicellulose and cellulose part, but not in the lignin part. Moreover, it is revealed by the observation that the said treated jute sample render more residue left at 400-500°C causing more char formation (showing 5% higher amount of residue left at 400 – 500°C. This may be due to early dehydration of cellulose and hemicellulose part showing early degradation with more char formation probably resulting less formation of flammable (levo-glucosan) gases.

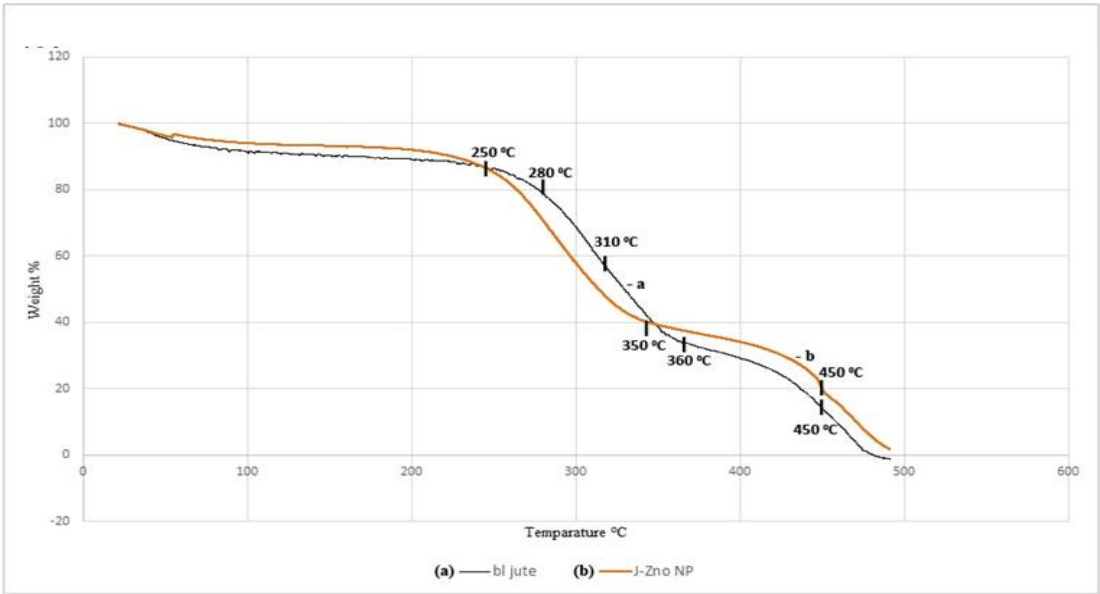


Fig. 4.13 TGA Thermograms of nano ZnO treated and untreated jute

The weight loss at different temperature zones during TGA analysis is shown in Table 4.15. It is observed from both the thermograms and the data given in Table 4.15 that the nano ZnO treated jute fabric leaves 5% higher residue than the untreated one at the temperature zone of 400°C -500°C. The results of LOI value, vertical flammability test and other flame retardancy performance for treated jute also supports this observation.

Table 4.15 Weight loss % of nano ZnO treated and untreated jute fabrics subjected to heating in varied temperature, indicating the nature of thermal decomposition

Sample	Approximate residue left (%) at respective temperatures (°C)						
	80	**200**	**250**	**350**	**400**	**450**	**500**
Untreated jute	92	88	86	38	29	14	Nil
10% PMS+ 0.01% nano ZnO treated jute fabric	94	91	85	39	34	19	5

ZnO nano particle coated jute fabric shows marginal early degradation of hemicellulose and cellulose part of jute forming lesser amount of volatile product leading to less levo-glucosan formation and higher LOI values (Table 2) with higher residue left after heating up to 500°C (Table 3).

DSC thermograms of untreated jute and treated jute (with 0.01% ZnO nano particle along with 10% PMS) are shown in Fig. 3. DSC thermogram (a) of untreated jute as shown in Fig 3 shows moisture evaporation at 50-60°C, thermal decomposition of hemicellulose part at around 335°C (with an exothermic hump at 325-350°C). It can also be seen that the thermal decomposition of cellulose part occurs at around 390°C (with an endothermic crest at 360-420°C) and thermal decomposition of lignin part occur at with two exothermic duplet at 450°C and 460°C. While in Fig 4.14, the DSC thermograms (b) for 0.01% ZnO nano particle along with 10% PMS treated jute substrate shows moisture evaporation at 50-60°C (showing no change); but thermal degradation of hemicellulose part of the said treated jute occur at around 300°C (showing exothermic hump at 250-325°C, i.e. much earlier than 325-340°C, as observed in untreated jute). This indicates an observed lowering of thermal decomposition temperature of hemicellulose part of treated jute. The said DSC thermogram (b) in Fig 4.14

also shows a broad trough for the thermal degradation at 325 - 420°C for cellulose part i.e. cellulose part also starts thermal degradation early at 325°C but otherwise thermal behaviour of the cellulose part of the nano ZnO treated jute remains almost same with said minimum changes requiring much less ΔH, showing less heat consumption. But the thermal degradation of lignin part of the nano ZnO treated jute occurs at same temperature showing a much sharper duplet peaks at the same temperature zone as shown for untreated jute lignin part at 450°C - 460°C. This DSC study thus reveals that the treated jute fabric, due to the presence of nano ZnO powder and PMS lowers the thermal degradation temperature of mainly for hemicellulose part and partially for cellulose part, while lignin part remains unaffected. Presence of ZnO nano particle with PMS over the treated jute is also thus evidenced by changes of DSC and TGA thermograms.

Moreover, comparing the two DSC thermograms of treated and untreated jute in Fig 4.14, it may be concluded that the effect of the nano ZnO with PMS treatment is much more localized and probably restricted to the hemicellulose part predominantly than the cellulose part (which is less affected) and have almost no effect on lignin, so far their thermal degradation temperatures for nano ZnO particle with PMS treated jute fabrics.

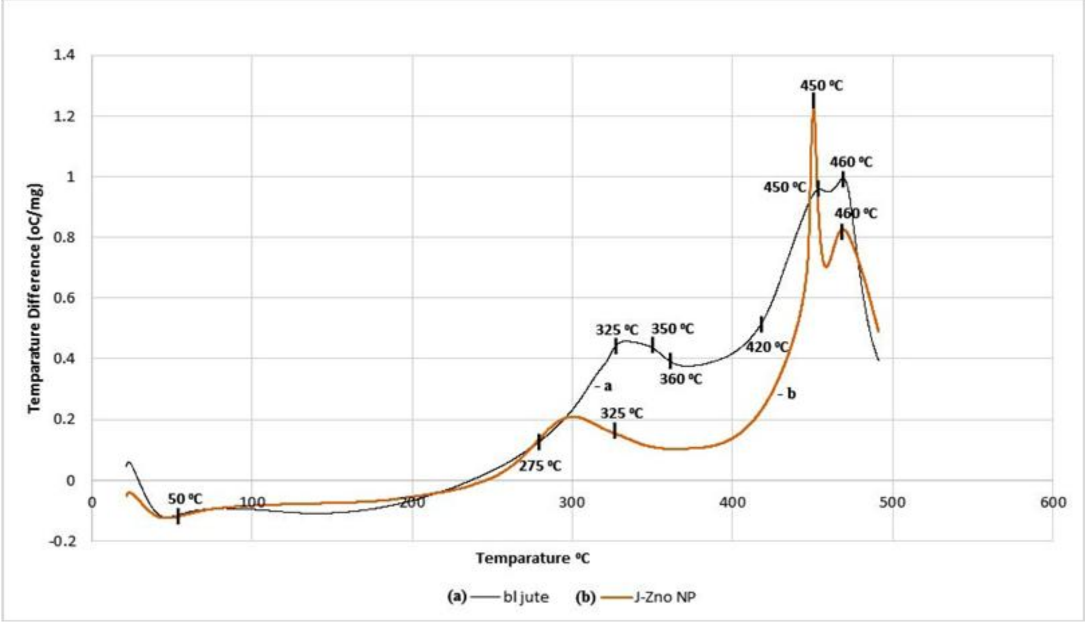


Fig. 4.14 DSC Thermograms of nano ZnO treated and untreated jute

4.3.6 FTIR analysis of untreated and ZnO nano particle treated jute fabric

To investigate the molecular interaction of ZnO nanoparticles with jute, FTIR spectroscopic analysis of PMS , ZnO nano powder, untreated jute (bleached control sample), PMS + nano ZnO particle treated jute fabric was performed (after washing the samples in water and alcohol followed by drying) and the said four (4) FTIR Spectra are shown in Fig. 4.15. FTIR spectrum of ZnO nano particles (Fig 4.15) shows significant peaks at 3800, 2325, 1600 and below 500 cm^{-1}. The peak below 500 cm^{-1} show the distinct lattice vibrations of ZnO and the band at 760 cm^{-1} attributed to the asymmetric stretching vibration of Zn-O-Zn bridging evidencing some agglomeration of nano ZnO. The broad peak at 3800 cm^{-1} of the OH stretching and a peak at 1600 cm^{-1} for OH bending suggests also the presence of moisture absorbed by $Zn(OH)_2$ produced by a combination of aerial moisture and nano ZnO.

The common FTIR transmittance peaks corresponding to 550 cm^{-1} (for −OH out of plane bending), 890 cm^{-1} (for β-glycosidic linkage), 1030 cm^{-1} (assigned to aromatic C-H in plane deformation and C-O deformation for primary alcohol in lignin), 1245cm^{-1} (for −C−O−C and −C=O stretching in Xylan side substituent and lignin aromatic C=O stretching), 1335 cm^{-1} (for −OH in plane bending), 1370 cm^{-1} (for C-H deforming (symmetric) may be attributed to cellulose, hemicellulose and lignin), 1446 cm^{-1} (for C-H deforming (asymmetric) may be attributed to lignin), 1508 cm^{-1} (for lignin aromatic ring vibration and stretching), 1596 cm^{-1} (for C=C stretching in lignin olefinic units), 1735 cm^{-1} (for C=O stretching of ester group), 2355 cm^{-1} (for C−H stretching in polysaccharide chains), 2905-2920 cm^{-1} (for C−H stretching vibrations of aliphatic methylene groups), and 3350 cm^{-1} (for H bonded H-O Stretching) were observed in both the FTIR-spectra of untreated and ZnO nanoparticles treated jute fibres[22].

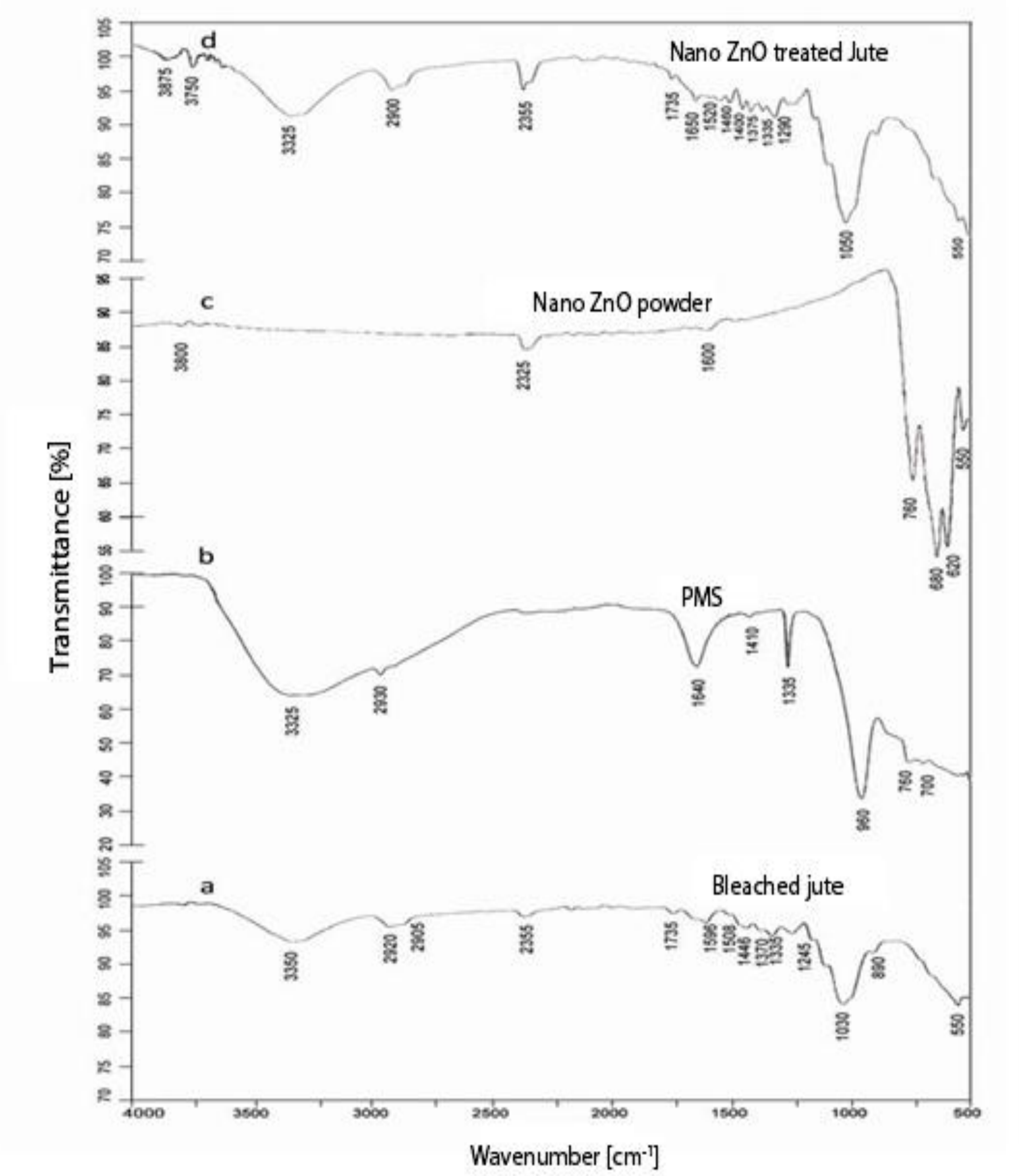


Fig.4.15 FTIR spectra of PMS, nano ZnO powder , untreated jute and nano ZnO particles along with PMS treated jute samples

The FTIR spectrum of the jute fabric treated with ZnO nano particle with PMS (silicone binder dispersion) shows broadening of some of the FTIR peak present jute like peaks at 1335cm^{-1} - 2355 cm^{-1}, 2905 cm^{-1} and also at 3350 cm^{-1} while peak at1735 cm^{-1} is reduced in the treated jute. Also, presence of PMS is indicated by few additional small peaks at 1290 cm^{-1}- 1300 cm^{-1} corresponding to Si-C in the silicone compound (original FTIR curve for PMS show the peaks at 1260 cm^{-1}, which on jute after application shifted to1290 cm^{-1} -

1300 cm^{-1} showing small peaks which was absent in bleached jute). Si-O stretching vibration of silicone which usually occur at 960cm^{-1} at FTIR peak of PMS (spectrum b) is when applied on jute merge with the peak already present in the jute at 1030 cm^{-1} and shows a sharper peak at 1050 cm^{-1}(spectrum b). The additional very small peak observed at 550 cm^{-1} indicates the presence of ZnO in the coated jute fibre (which is also shown in FTIR spectrum c for ZnO nano particle powder).

4.3.7 Elemental analysis of Zn and Si of the treated jute fabric by EDX and AAS study

EDX analysis was performed on the optimized formulation (10% PMS+ 0.01% ZnO) treated jute fabric for the quantitative estimation of Zn from nano ZnO and Si from PMS present on the treated jute fibre surface and is shown in Figure 4.16. The EDX analysis shows distinct peaks for O, C, Si, K and Zn. The elemental content of the above said elements as per EDX result is as tabulated in the Table 4.16.

Table 4.16 Element content as per EDX analysis of nano ZnO and PMS coated jute fabric

Element	O	C	Si	K	Zn	Cl	Total
Atomic Wt %	55.46	20.79	13.32	8.47	1.05	0.91	100

The presence of Zinc along with its qualitative content on treated fabric was confirmed from EDX analysis and as per EDX analysis the atomic wt % of Zn was found to be 1.05 (atomic weight %) for 0.01 % nano ZnO + 10% PMS treated fabric, which may be converted to 0.0093% by molecular weight percentage. Since EDX analysis gives quantitative estimation of Zn content in the jute fabric surface only, the total quantity of zinc in nano coated fabric was further estimated by AAS spectrophotometry and is found to be 588.4 mg per kg, which is equivalent to 0.0588% in wt % of fabric weight (against the application of 0.01% nano ZnO particle along with 10 % PMS). The variation / difference in the data of Zn content (as element not as ZnO) as observed by EDX analysis and by AAS analysis, may be because of the reason that EDX measures Zn content on the surface of the treated jute fabric, whereas AAS data show Zn content in the bulk of treated fabric on fabric wt %. EDX data also show Si content (from 10 % PMS application) to be 13.32 % as atomic wt %, which is equivalent to 6.66 % by molecular wt % of Si present on the fabric surface and rest may be in the bulk.

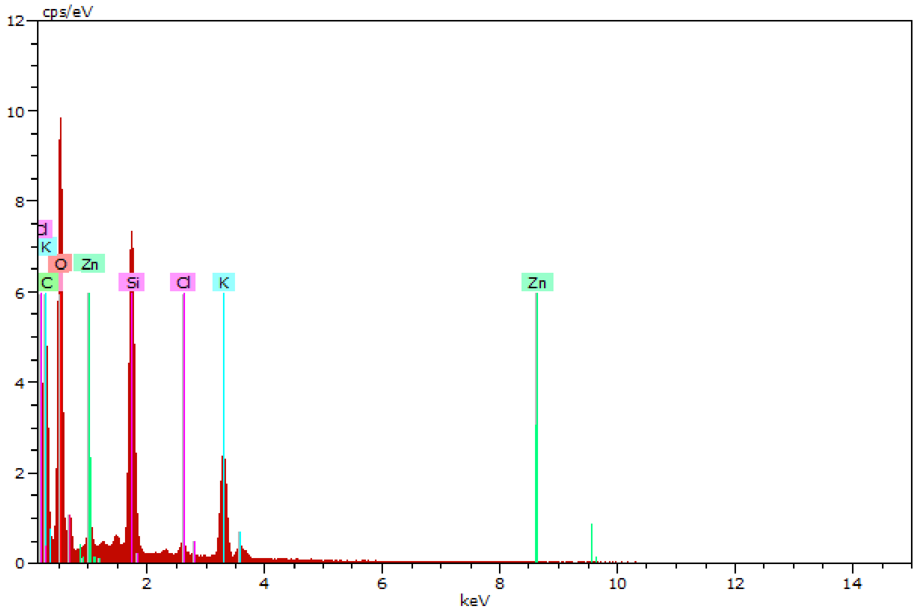


Fig.4.16 EDX spectrum of nano ZnO + PMS treated jute fabric

4.3.8 Study of Surface Morphology of Untreated & ZnO nano particle treated jute fabric

SEM investigates the changes in the topography of the nano ZnO treated jute fabrics in comparison with untreated jute fabric. The corresponding SEM micrographs are shown in Fig.4.17. The scanning electron micrographs (4.17a) & (4.17c) shows the surface appearance of bleached jute and ZnO nano particle treated jute fibre surface. SEM micrograph (4.17b) shows the microscopic view of the calcinated ZnO nano particle deposited on the surface of the jute fibres. SEM micrograph (4.17a) of bleached jute fibre (from fabric) shows the smoother surfaces with small serrations of untreated jute fibre, while the nano ZnO treated jute fibre shows that there are some distinct surface deposition having varying degrees of uniformity with extraneous deposition of anchored ZnO nano particle embedded in the PMS dispersion on the surface of treated jute fibre. The agglomeration of nano ZnO particles over the fibre surface is also partly understood from the SEM micrographs of treated jute fibre. The surface deposition on jute fabric in a higher magnification is shown in SEM micrograph (4.17d). The size of the nano ZnO particles analysed from SEM picture on the treated jute fibre surface was found to be in between 38 nm - 60 nm by the measurement of average dimension of the few such nano ZnO particles chosen from magnified images of SEM picture. However, to understand the actual average size and distribution of size of nano ZnO, the particle size analysis of nano ZnO powder produced in the present work is felt essential, as some agglomeration of nano ZnO particles are also visible in the magnified SEM micrograph of treated jute fabric. (SEM micrograph 4.17d in Fig 4.17)

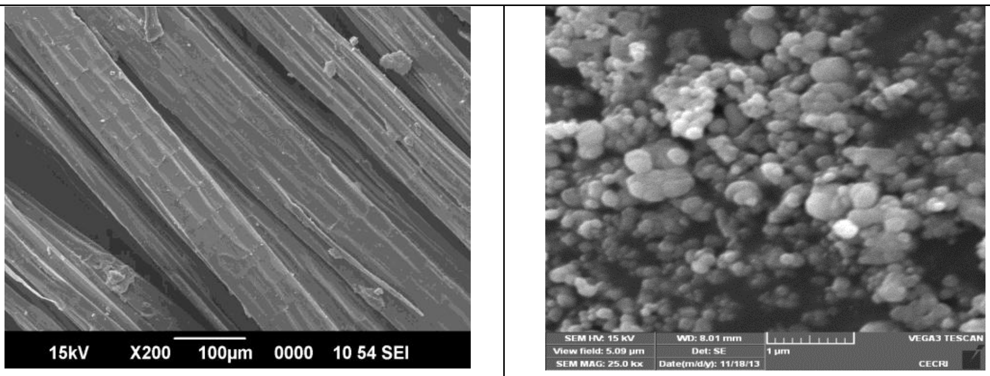


Fig 4.17 a Bleached jute

Fig 4.17b ZnO Nano particles

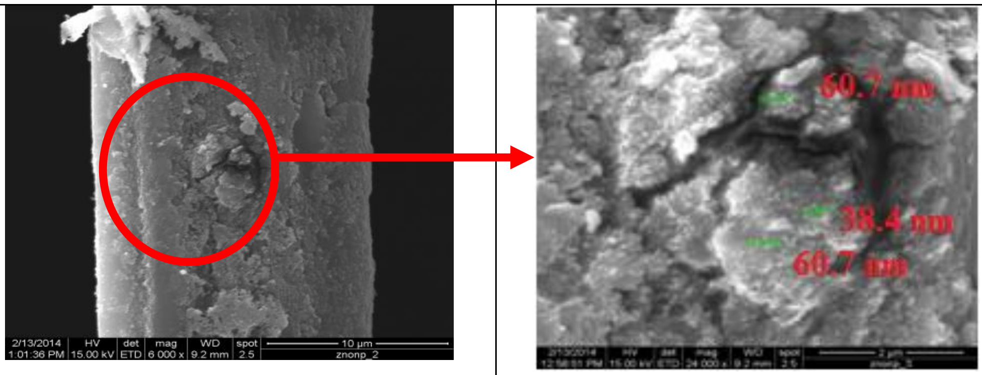


Fig 4.17c Bleached jute fibre with nano ZnO coating

Fig 4.17d magnification of Fig 6c indicating the nano particle size

Fig.4.17 SEM micrographs of untreated and nano ZnO particle + PMS treated jute samples

Hence, analysis of size profile of nano ZnO powder produced and the distribution of size of nano ZnO particles in water was analyzed by using particle size analyzer and the size distribution is shown in Fig. 4.18, which indicates a majority (60%) of the particles are below 0.5 µm (i.e. within 500 nm) and the rest are bigger or agglomerated producing micro particle by agglomeration in nano ZnO powder. This shows somewhat poor dispersibility of nano ZnO powder dispersed in water. The size and quality of the nano particles have effect on particle's settling velocity in dispersion medium. The larger the particle, higher is its settling velocity. Nano particles owe to the properties of small dimension, large specific surface area and high surface activity, which may lead also to obvious agglomeration. The results indicate that, for better nano coating, one must use some better dispersing media for breaking/preventing the agglomeration of nano ZnO particles. This is the one of the reasons for the selection of PMS dispersion as application media in which nano ZnO particles are dispersible and help to restrict the agglomeration of nano ZnO, resulting in the formation of uniform dispersion of nano ZnO crystallites having the size 38 - 60 nm. However, considering this as a textile finish application, as 60% of the nano ZnO are within the desired range of common nano textile finish application, i.e. within 30 to 500 nm average size of the nano finish application usually used for textile finishing, this experiment is considered acceptable as the nano fire retardant finish.

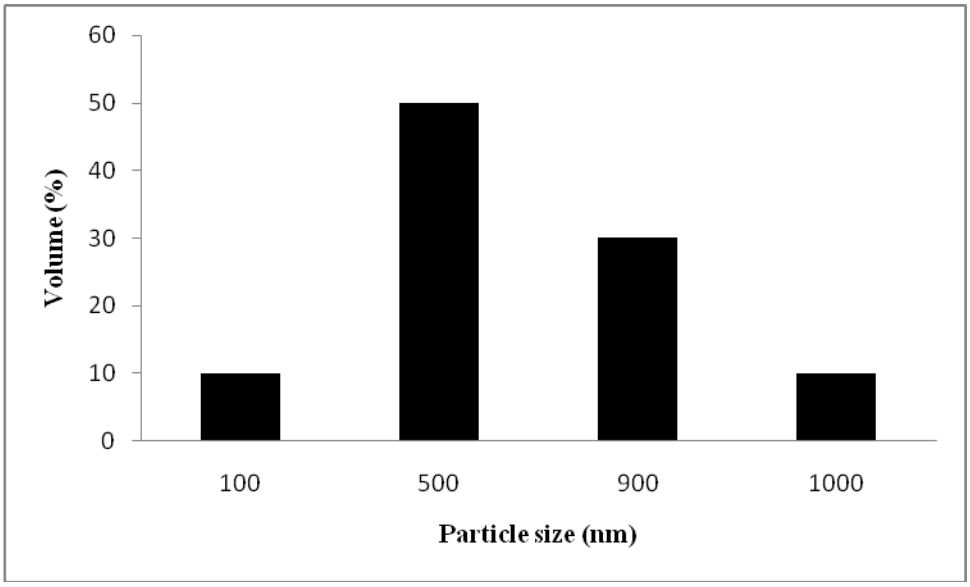


Fig.4.18 Particle size distribution of nano ZnO particle in water

In the present study, ZnO nano particles were generated by co-precipitation method followed by its application on bleached jute fabric using 0.01 % nano ZnO particles in a dispersion of 10 % Potassium Methyl Siliconate (PMS), which shows a good level of fire retardancy comparable with a commercial flame retardant formulation SARA-Flame CWF (THPC based) applied on the same jute fabric to achieve the same level of LOI value. The nano ZnO treated fabric shows LOI value 35 and minimum char length of 1 cm with satisfied level of washing fastness for five cycles of wash. TGA and DSC analysis reveals that the nano ZnO treated jute fabric produced more char than untreated jute fabric, with 5% higher residue (char) at 400^{O}C - 500^{O}C. The presence of nano ZnO in jute fabric was also confirmed by EDX, AAS and FTIR analysis. The particle size of ZnO nano particles was confirmed by particle size analysis showing 60% of the particles are within 30 - 500 nm, with some agglomeration of the rest of the nano ZnO particles as micro particles. FTIR studies indicate that the nano ZnO has not reacted with jute, while SEM studies indicate that it has adhered/deposited on the jute fibre surface with the help of PMS as a binder, which also act as a dispersive medium for the application of nano ZnO on jute fabric. The high crystalline nature of nano ZnO was confirmed by XRD analysis, determining also the average crystalline size being 38 – 60 nm. Thus 0.01 % nano ZnO+ 10 % PMS formulation can be a better economic alternative for commercial fire retardant formulations for jute fabric since other commercial fire retardant formulations like SARA Flame CWF need very high pick up (at least 20% i.e. 200 gpl) for obtaining the same level of fire retardancy performance (i.e. LOI value and char length etc.). Thus, with very low concentration of 0.01 % nano ZnO in combination with 10% Potassium methyl silicate application for jute fabric renders acceptable level of fire retardant performance, which could be considered as a better option for commercial applications for producing various domestic and industrial jute based fire protective technical textiles.

4.3.9 Optimisation of the Flame retardant formulation using Nano ZnO with Potasium methyl Siliconate (PMS) by using the statistical software (Response Surface Methodology)

Response Surface Methodology (RSM) is used here as a useful tool for optimization by determining the interactive effects between and among process variables for assessing the optimal process conditions, as was done in earlier chapter, it is customary to get the optimal formulations using statistical experiment of design with the RSM design on the basis of choosing process variables from the results of the preliminary study conducted. The User Defined Quadratic Model (UDQM) of experimental design used was devised to determine the statistically optimised, Flame retardant formulations with nano-ZnO application to predict the the optimum level of LOI, Char Length and Loss in Tenacity for treated jute fabrics.

Preliminary studies made here (Table no. 4.13 and 4.14) indicate the percentage application with varying percentage of Nano ZnO (0.00-0.20g/l) and PMS (10-150g/l) for further optimisation of the above said chemicals for obtaining best optimum of Flame retardant performance in terms of maximum LOI, minimum Char Length and minimum loss in fabric tenacity. Data in Table 4.17 represents the values of response variables R1 (LOI), R2 (Char Length) and R3 (loss in fabric tenacity) against the respective independent process variables A for Nano ZnO and B for PMS as per the UDQM model generated by the design expert software.

From the preliminary study for knowing the better application ranges of nano Zno particles and PMS emulsion used, keeping other process parameters constant / fixed, to get optimum LOI (R1), char length (R2), loss in tenacity (R3), after optimizing in varying percentage using statistical experimental design (UDQM model) to get RSM responses.

Table 4.17 given below shows the value of resultant response variables (R1, R2, R3) against the respective dependent process variables like A (for nano ZnO) and B for Poly methyl siliconate (PMS) emulsion is selected at five level (i.e -2, -1, 0, +1, +2 level) for statistical experimental design technique. Table 4.17 shows the results of response surface variables (R1, R2, R3 i.e LOI, Char Length and Loss of fabric Tenacity respectively) against the independent process variables (A and B i.e concentration of nano ZnO and PMS) as given by the RSM software.

Table 4.17: Values of response variables against the respective independent process variable as per the UDQM model of experimental design run in RSM Technique

NANO ZnO(g/l)	POTASIUM METHYL SILICONATE (g/l)	LOI (%)	CHAR LENGTH (mm)	LOSS IN TENACITY (%)
A	B	R1	R2	R3
0	80	22	125	6
0	10	21	125	10
0	150	24	125	22
0.05	115	29	20	11
0.05	45	25	100	5
0.05	80	28.8	25	11
0.1	45	32	13	8
0.1	115	35.4	10	10
0.1	80	35	12	9
0.1	10	30	22	5
0.1	150	35.2	11	21
0.15	115	35.2	10	11
0.15	80	34.9	10	10
0.15	45	30.5	55	6
0.2	80	33.8	35	10
0.2	10	30.4	49	6
0.2	150	35	11	23

The corresponding Annova table for LOI is shown in Table 4.18, Annova table for char length is shown in Table 4.19 and Annova table for Loss in Tenacity is shown in Table 4.20.

Table 4.18 ANOVA Table for Response Surface Quadratic Model (LOI) R1

Analysis of variance table [Partial sum of squares - Type III						Remarks
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	358.42	5	71.68	34.18	< 0.0001	significant
A-A	225.23	1	225.23	107.4	< 0.0001	
B-B	47.38	1	47.38	22.59	0.0006	
AB	0.74	1	0.74	0.35	0.5642	
A^2	74.1	1	74.1	35.34	< 0.0001	
B^2	0.26	1	0.26	0.12	0.7309	
Residual	23.07	11	2.1			
Cor Total	381.49	16				

Table 4.19 ANOVA Table for Response Surface Quadratic Model (Char Length) R2

Analysis of variance table [Partial sum of squares - Type III]						Remarks
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	26982.05	5	5396.41	11.62	0.0004	significant
A-A	13230	1	13230	28.48	0.0002	
B-B	1702.53	1	1702.53	3.66	0.0819	
AB	201.31	1	201.31	0.43	0.5239	
A^2	10650.97	1	10650.97	22.93	0.0006	
B^2	1.57	1	1.57	3.37E-03	0.9547	
Residual	5110.07	11	464.55			
Cor Total	32092.12	16				

Table 4.20 ANOVA for Response Surface Quadratic Model (Loss in Tenacity) R3

Analysis of variance table [Partial sum of squares - Type III]						Remarks
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	476.31	5	95.26	20.09	< 0.0001	significant
A-A	0.13	1	0.13	0.028	0.8699	
B-B	353.63	1	353.63	74.58	< 0.0001	
AB	5.31	1	5.31	1.12	0.3127	
A^2	4.72	1	4.72	1	0.3397	
B^2	88.88	1	88.88	18.74	0.0012	
Residual	52.16	11	4.74			
Cor Total	528.47	16				

Annova table for all the three response variables R1, R2, R3 elucidates the model the lack of fit in terms of terms p ($p>0.05$), which are therefore neglected and used to generate the resultant model equation in coded form as expressed bellow in following equations 14, 15 and 16 for R1(LOI), R2 (Char Length) and R3 (Loss of Fabric Tenacity) showing the corresponding values of response coefficients for predicting the resultant response variables:

$R1=19.40+153.33*A+0.04*B+0.60/100000*A*B-516.54*A*A-6.26*B*B$ eq 14

$R2=131.20-1579.90*A1-0.14*B1+0.98*A1*B1+6192.76*A1*A1+1.53/10000*B1*B1$ eq 15

$R3=9.74-37.52*A1-0.10*B1+0.16*A1*B1+130.43*A1*A1+1.15/1000*B1*B1$ eq 16

It is apparent from the first two annova tables (4.18 & 4.19) that A (Nano ZnO) is the most prominent factor followed by B (PMS) affecting the first two response variables. But Annova table4.18 also indicates that B is the most prominent factor followed by A affecting R3 (Loss of fabric Tenacity) as response variables. Both the independent process variables A & B have thus synergetic effects on these response variables. Corresponding three contour plots for three different response variables (R1, R2, R3) are shown in fig 4.19, 4.20 and 4.21.

Table 4.17 shows the values of process variables (A and B)used in statistical experimental design with UDQM model run in Design expert Software and the corresponding response variables (R1, R2, R3) obtained from the test results of these treated fabrics under the corresponding experimental set for each case.

These results were then processed for analysis of variance (AnnovaTable) to obtain the F-values and P- Values (as shown in Table no. 4.18, 4.19, 4.20). To establish relationship between the variables, analysis of variance and regression analysis were done. The coefficient generated by annov to determine the RSM equation as shown in equation 14 for R1 (LOI), equation 15 for R2 (Char Length), equation 16 for R3 (Loss in fabric tenacity), for determination of predicted values of that particular property (response variables). The significance of the effect of the variables were treated by F values. These quadratic second order equations generated by response surface methodology analysis using design expert software were used to get the best possible treatment conditions for achieving each response variables to a minimum or maximum desired value suitable for its textile application.

The plots shows the effects of independent process variables individually or in combination on the resultant value of LOI (Fig 4.19), char Length (Fig 4.20) and loss in fabric tenacity (fig 4.21) are given here for understanding both the effects of single process variables (A & B) and also for effect of combination (AA, BB, AB) i.e. interdependent factor also. The coefficient obtained from optimization by the software either have positive or negative values so have a positive or negative effects on experimental results. For a process variable to have a significant effect, the coefficient must be greater than twice of the standard error. However non-significant coefficients also have some inputs and not to be dismissed, as there was a very small effect but is important too.

Thus for these three plots it can be said that the effect of the independent process variables or their interactive effects on R1 (LOI) R2 (Char length) and R3 (Loss in fabric tenacity) can be interpreted easily and can be explained from corresponding plots 4.19, 4.20, 4.21.

Plots in 4.19 shows that the variable A (Nano- Zno) has much more and higher positive effect on increase of LOI than the effect of variable B (PMS) showing sharper steep increase in LOI value for increase of nano-Zno from 0.05 to 0.15 gpl application. The effect is flattened after 0.15gpl value of variable A and starts declining o LOI at 0.20 gpl of Nano-Zno application while variable B also show gradual marginal increase in LOI with increase in PMS percentage steadily from 10 to 150 gpl.

Thus corresponding equation 14 generated for predicting the values of R(LOI) for specific dosages of A (Nano ZnO) and B (PMS) indicate that positive value of both A and B individually and in combinations for increase in dosages of A (Nano ZnO) and B (PMS) upto a certain limit and showing positive impact for interactive effect of A and B applied in combination. While negative values of both the coefficients of AA and BB indicates in this case shows that further very high increase in concentration of both A & B either reduce or have less or no impact as can be seen in the plot (fig 4.19). So it may be predicted that Nano ZnO is more important variable in this case and PMS also has less but positive effect on LOI and hence both chemicals are interactively required for this finish.

Plot in Fig 4.20 shows that the char length is shortly reduced by increase in A (Nano-ZnO) from 0.05 to 0.15gpl and therefore it further starts increasing upto 0.20 gpl of Nano-ZnO, while char length is remains almost same or marginally reduced only showing a very less small insignificant effect but is important too considering o its ability to increase in LOI to some extent for the binder coating of PMS restricting the textile surface for catching fire.

Corresponding RSM equation 15 generated for predicting the resultant values of R2 (Char length) response variable for use of specific dosages of A(Nano ZnO) and B (PMS) indicate that both the coefficients of individual A and B are negative, and amongst A and B, A variable shows very high negative value coefficient and B shows very low negative value i.e. there is much higher reduction in char length for increase in dosages of A (Nano ZnO) and there is very less reduction on char length for increase in B (PMS concentration). While positive values of coefficients for interactive efforts of A and B (AB) and also for higher increase in A (A^2 term) and higher increase in A (Nano ZnO) may lead to further reversing the trend i.e. it may increase the char length above a certain level and so is the indication in Fig 4.20. Thus Nano-ZnO would not be used above 0.15gpl or so with approximate 115-150 gpl of PMS.

Plot in Fig 4.21 shows that for loss in fabric tenacity (one of the side effects of fire retardant chemical treatment) of treated jute fabric dosage of B (PMS) is most prominent factor and with increase in dosages of B(PMS) loss in fabric tenacity is increased significantly, which is considered to be alkaline degradation of hemi cellulose and lignin partially from jute, due to the alkalinity of PMS emulsion. While the increase in dosages of nano ZnO (A) individually has little or small effect on loss of fabric tenacity. But the interactive effect of A and B (AB) is understood from the fig. 4.21 from the contour curve shown in this plot, which has also positive interactive effects in this, while further high increase of A(A^2 term) and B (B^2 term) are found to have small positive effect including that high increase in PMS or Nano ZnO had not further much degradation effect of treated jute fabric.

Corresponding RSM equation 16 generated for predicting the resultant values of R3 (Loss in Tenacity) response variable for use of specific dosages of A(Nano ZnO) and B (PMS) indicates that both the coefficients of individual A and B are negative, and amongst A and B, B variable shows higher effect than A variable including the coefficient of AB term interactive effects is found to be positively small. Values of coefficients A^2 and B^2 term also found to be small but positive. Thus the loss in fabric tenacity is increased by increase in PMS and upto a certain level of Nano-ZnO as per the coefficient found for the equation 16.

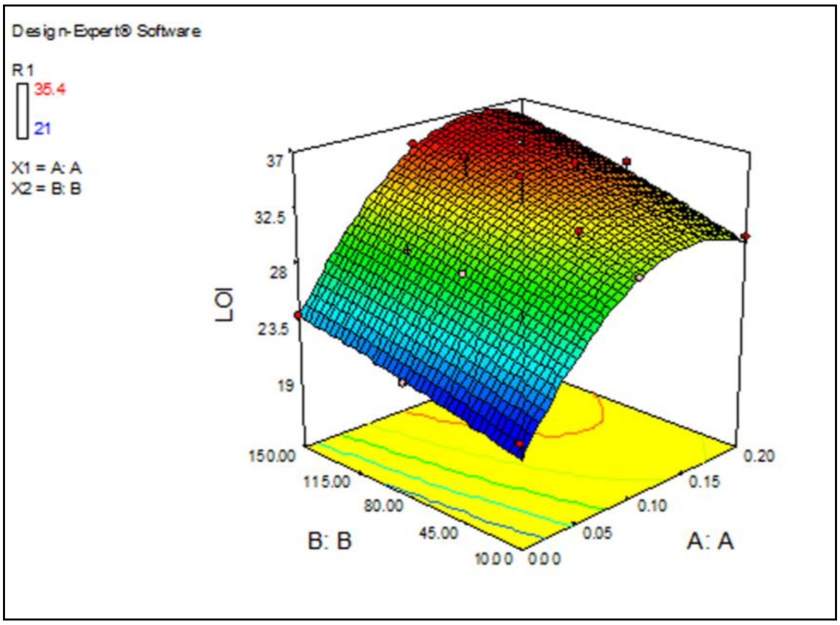


Fig 4.19 RSM Plot in respect to LOI

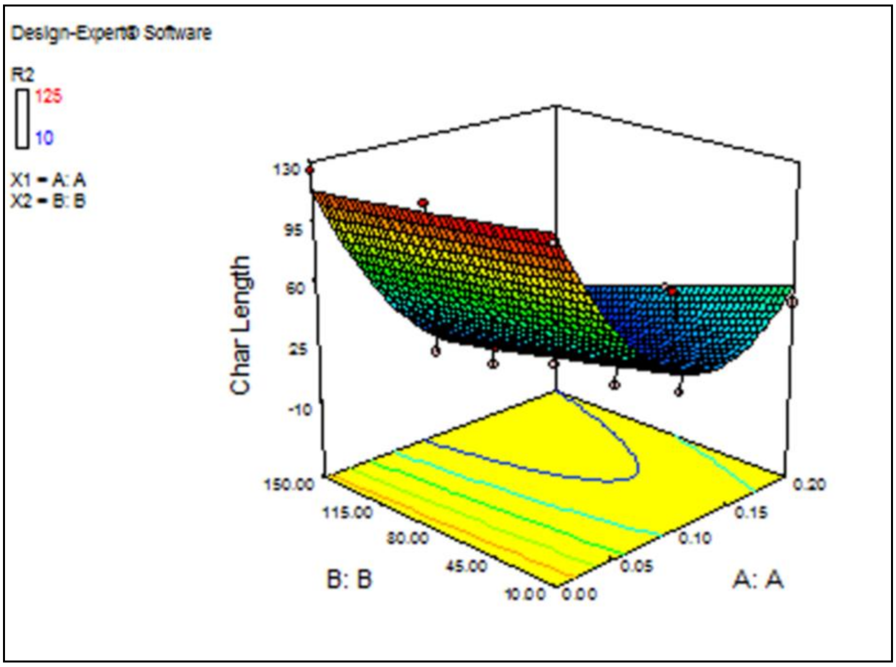


Fig 4.20 RSM Plot in respect to Char Length

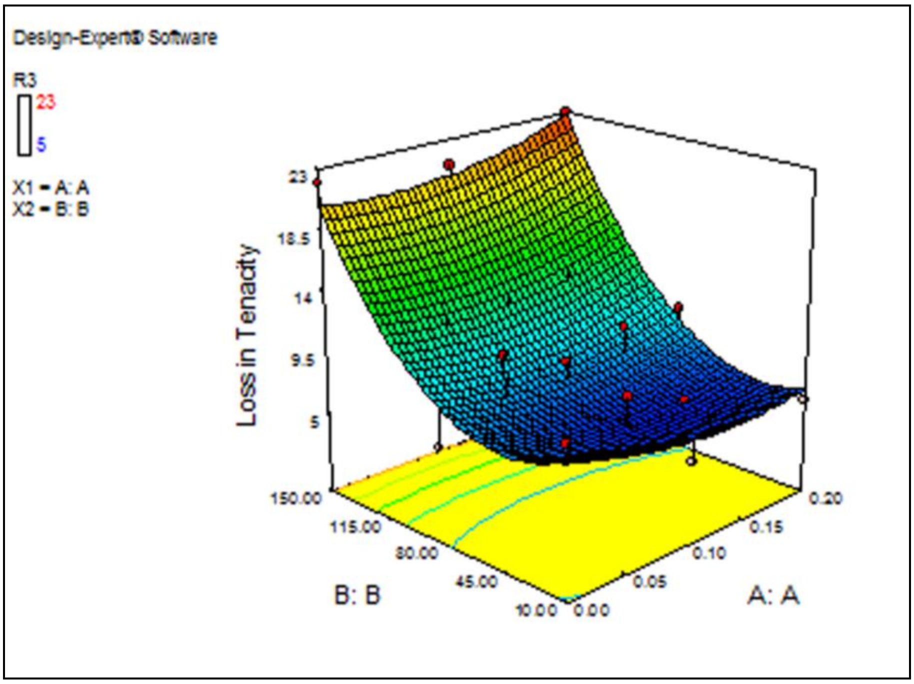


Fig 4.21 RSM Plot in respect to Loss in Tenacity

The numerical optimisation program was run to evaluate the optimal parametric values which are correspondingly represented in the three respective contour curves in fig 4.19 , 4.20 and 4.21 corresponding the above stated results discussed.

At the optimal value of A and B as generated by the software i.e A (Nano-ZnO) = 0.07gpl and B (PMS) =137.80gpl , the optimal value of R1 (LOI), R2(Char length) and R3(Loss in Tenacity) respectively showing 37.71% LOI, 44.01mm Char length and 17.35% Loss in Tenacity, as predicted values of three response variables, against actual values for varying parameters, which are given in Table 4.17. Thus this optimum values of process variables for dosages of nano ZnO and PMS obtained by using experimental design are found to be nearer to these earlier found in preliminary experiment done here. Nano ZnO dosages is 0.07% (as per experimental design) instead of 0.1% (in preliminary experiment) and PMS dosages is 13.7% (as per experimental design) instead of 15% (in preliminary experiment). Thus these optimal results indicate close values of optimized dosages of independent variables found in the preliminary experiment confirming the efficacy of this UDQM model of RSM software for optimization of this experimental work.

4.4 Comparison of Similar dosages of Normal ZnO Particle and Nano ZnO particle application on jute fabric.

Additional experiments are carried out with similar dosages of normal bulk ZnO powder application to understand the differences between the effect of application of normal ZnO and Nano ZnO on Jute fabric. Optimisation of the Flame retardant formulation using normal ZnO with Potasium methyl Siliconate (PMS) was also carried out by using the same statistical experiment of design software Response Surface Methodology technique by applying the similar dosages of both normal ZnO and ZnO nanoparticles for comparing their Flame retardant performances .

Table 4.21 represents the values of three response variables R1 (LOI), R2(Char length) and R3(Loss in Tenacity) against the respective independent process variable A (Normal ZnO) and B (PMS) as per the UDQM model generated by the design expert software.

Table 4.21: Values of response variables against the respective independent process variable as per the UDQM model

Normal ZnO	PMS	LOI %	Char Length	Tenacity
0	50	21	125	6
0	100	22	125	11
0	150	24	100	22
0.05	75	24	125	28
0.05	100	23	114	31
0.05	125	25	91	33
0.1	50	21	88	30
0.1	75	23	85	33
0.1	100	21	91	33
0.1	125	24	77	35
0.1	150	24	78	39
0.15	75	23	85	28
0.15	100	24	80	30
0.15	125	24	79	31
0.2	50	25	80	23
0.2	100	25	77	27
0.2	150	24	81	41

Corresponding Annova Table for R1(LOI) is shown in Table 4.22, Annova Table for R2(Char length) is shown in Table 4.23 and Annova Table for R3(Loss in Tenacity) is shown in Table 4.24.

Table 4.22 ANOVA for Response Surface 2FI Model (LOI)

Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	15.03	3	5.01	4.39	0.0243
A-A	5.63	1	5.63	4.93	0.0448
B-B	5.63	1	5.63	4.93	0.0448
AB	3.76	1	3.76	3.3	0.0926
Residual	14.85	13	1.14		
Cor Total	29.88	16			

Table 4.23 ANOVA for Response Surface Quadratic Model (Char length)

Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	4435.5	5	887.1	13.89	0.0002
A-A	3203.33	1	3203.33	50.16	< 0.0001
B-B	448.53	1	448.53	7.02	0.0226
AB	256.24	1	256.24	4.01	0.0704
A^2	494.78	1	494.78	7.75	0.0178
B^2	150.38	1	150.38	2.35	0.1532
Residual	702.5	11	63.86		
Cor Total	5138	16			

Table 4.24 ANOVA for Response Surface Cubic Model

Analysis of variance table [Partial sum of squares - Type III]					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	1264.946	9	140.5496	114.6233	< 0.0001
A-A	14.81026	1	14.81026	12.0783	0.0103
B-B	3.510256	1	3.510256	2.862741	0.1345
AB	0.529412	1	0.529412	0.431754	0.5321
A^2	457.9962	1	457.9962	373.5124	< 0.0001
B^2	18.34511	1	18.34511	14.9611	0.0061
A^2B	22.33846	1	22.33846	18.21782	0.0037
AB^2	1.312821	1	1.312821	1.070653	0.3352
A^3	82.68478	1	82.68478	67.43242	< 0.0001
B^3	3.191946	1	3.191946	2.603147	0.1507
Residual	8.583311	7	1.226187		
Cor Total	1273.529	16			

Annova tables 4.20, 4.21, 4.22 for all the three response variables elucidates the model lack of fit for P value ($p>0.05$), which are neglected and run to generate the resultant model equations in coded form as expressed below in equation 17 for R1 (LOI), equation 18 for R2 (Charlength) and equation 19 for R3 (loss in fabric Tenacity):

$R1=18.87+27.49 * A+0.036 * B-0.19*A*B$ eq 17

$R2=125.93-628.91*A+0.28*B+1.55*A*B+1334.74*A1*A1-2.94/1000*B1*B1$ eq 18

$R3 = -12.4399+776.3727*A+0.565265*B-2.34172*A* B-5766.22*A*A-0.00513*B*\mathbf{B}+ 8.123077*A*A*B+0.003938*A*B*B+12232.48*A*A *A +1.92/100000*B*B*B$ eq 19

It is apparent from the all the three annova tables 4.22, 4.23, 4.24 that A (Normal ZnO) is the most prominent factor followed by B(PMS) affecting the three response variables. Both the two factor A & B have synergetic effects on the response variables. Three contour plots for three different response variables are shown in fig 4.22 , 4.23 and 4.24 which indicate the optimal values for these two chemicals to find the optimum results.

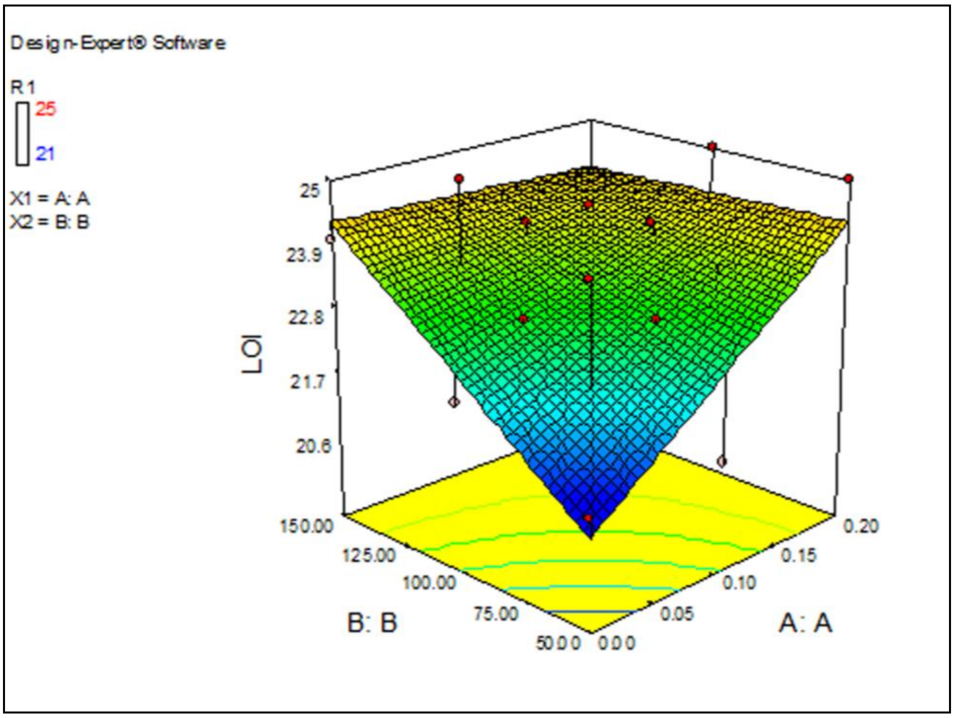


Fig 4.22 RSM Plot in respect to LOI

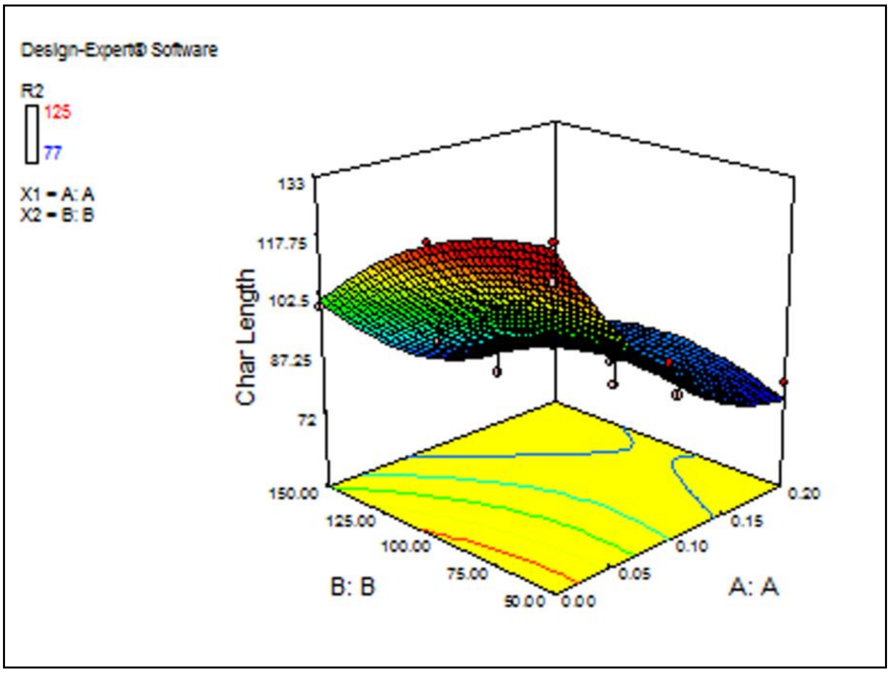


Fig 4.23 RSM Plot in respect to char Length

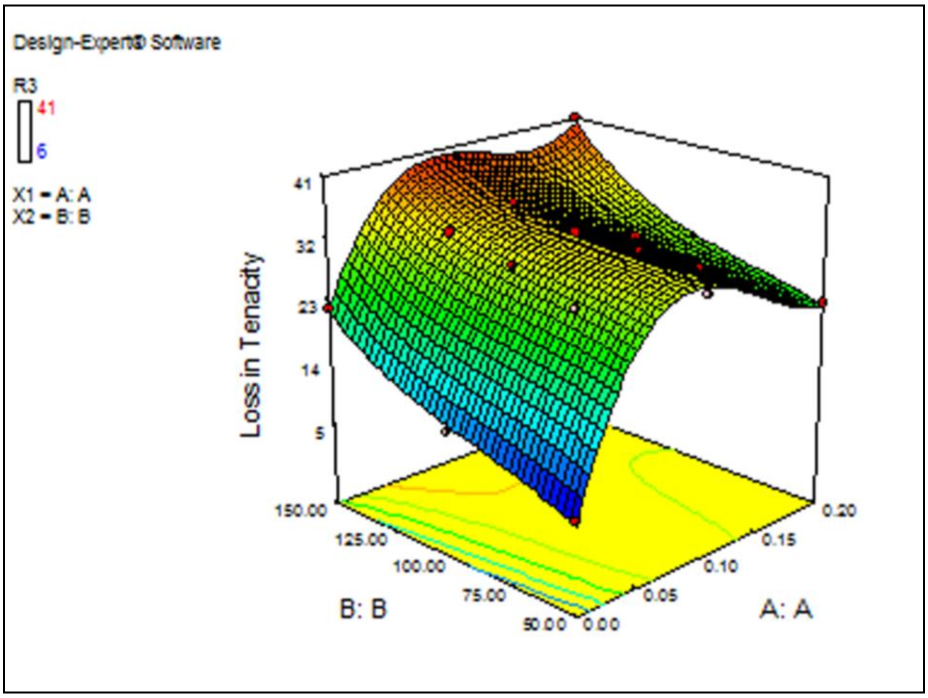


Fig 4.24 RSM Plot in respect to Loss in Tenacity

The numerical optimisation program was thus run in statistical design expert software to evaluate the optimal parametric values which are correspondingly represented in the three respective contour curves in fig 4.22 , 4.23 and 4.24.

The optimal values of A (Normal ZnO) and B(PMS) as generated by the design expert software were found to be A= 0.03 and B=117.45 , the predicted optimal value of R1 (LOI), R2(Char length) and R3(Loss in Tenacity) respectively 23.25% LOI, 106.05mm Char length and 26.96% Loss in Tenacity. These results are found to be much inferior to those obtained by application of Nano ZnO, which thus proves to be much superior technique for developing semi-permanent flame retardancy of jute fabric.

It is very much evident from the optimum values of Normal ZnO treated fabric , that for application of the same range of concentration as normal ZnO particle did not show good flame retardant property as char length is 10.6 cm and LOI became 23 (<27) and hence flame retardant property is not imparted by same dosages of normal ZnO application with same amount of additives(PMS). However, on further trial it was observed that 80 g\l normal ZnO i.e. 8% normal ZnO with 100 g\l of PMS i.e. 10% of PMS is atleast required for achieving the same level of flame retardant performance as was obtained in case of 0.01%nano ZnO particle with 10% PMS. The good flame retardant performance of Nano-ZnO as compare to the same dosages of Normal ZnO may be attributed by the better coated film of Nano-ZnO with PMS rendering more surface area and better coverage of the Nano-ZnO particles than the normal ZnO particles. Thus the superiority of Nano-ZnO along with PMS is found to be encouraging.

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Chapter V

SUMMARY AND CONCLUSION

5.1 Conclusions of Section 4.1 Effects of phosphorylated poly vinyl alcohol treatment on the flame retardant performance of bleached jute and oxy-jute fabrics.

The followings can be concluded from the study on the effect of phosphorylated poly vinyl alcohol (P-PVA) treatment on jute fabric for obtaining the flame retardant performance of bleached jute and oxy-jute fabrics.

5.1.1 Polyvinyl alcohol after phosphorylated i.e. P-PVA can be made anchored to jute or persulphate initiated pre-oxidised jute (oxy-jute) for obtaining moderate to good flame retardant performance achieving LOI value of 30-32 at the cost of 25-30 % loss in tenacity.

5.1.2 When both P-PVA and Jute fabric are peroxidised with persulphate and than applied on oxidised jute fabic, the results are not that much improved much while strength loss become much higher and hence is not recommended. Rather application of oxy-P-PVA on jute fabric (J-O-P-PVA) gives a better balance between the flame retardant performance and impotant textile related properties.

5.1.3 Analysis of DSC and TGA for P-PVA or oxy-P-PVA treated jute or oxy-jute fabrics show early degradation of hemicellulose and cellulose component of such treated jute fabrics with higher char residue for heating up to 500 degree centigrade. The maximum thermal stability is obtained for jute fabric treated with oxy-P-PVA.

5.1.4 FTIR spectra for differently treated jute also confirm incorporation of Phosphate group (from P-PVA) in P-PVA or oxy-P-PVA treated jute fabrics where formation of intermolecular phosphate di-ester linkage amongst respective cellulose polymer chain of jute (after treatment of jute or oxy-jute with P-PVA or oxy-P-PVA) is also confirmed.

5.1.5 Scanning electron micrographs of untreated and treated jute fabrics before and after treatment with P-PVA or oxy –P-PVA on jute or oxy-jute fabrics reveals that amongst all these treatment combinations (with P-PVA or oxy-P-PVA on jute or oxy-jute fabrics), Jute fabric treated with Oxy-PVA forms a much smoother P-PVA or oxy-P-PVA film over the surface of jute fabric, showing more uniform film formation/ anchoring on surface to jute as compared to other combination like oxy-jute fibres when treated with P-PVA.

Finally it is concluded that Jute Treated with Oxy-P-PVA show best all round results showing better balance between flame retardant performance and less deterioration of important textile related properties.

5.2 Conclusions of Section4.2 Effect of various individual flame retardant chemicals and their mixtures on bleached jute fabrics

The followings can be concluded from the study on application of Ammoniu Sulfamate / Sulfamic acid with Urea as individual flame retardant chemicals as well as their mixtures applied on bleached jute fabrics for achieving moderate to good flame retardancy of jute fabric.

5.2.1 Application of Sulfamic acid, Ammonium sulfamate and urea on jute fabric individually renders treated jute fabric to a reasonable degree of flame-retardancy achieving LOI value from 30-32 associated with noticeable loss of tenacity in all the cases, finally showing somewhat better results by the treatment done with 20% Ammonium sulfamate but associated with high loss of fabric tenacity.

5.2.2 Application of combination of 15% urea and 15% ammonium sulfamate shows however a synergistic effect resulting a LOI value upto 38 with char length of 1 cm only at the cost of 28% loss in tenacity of treated jute fabric. This particular combination is found to be a better option than an equivalent dose of application of 15% urea and 15% sulfamic Acid achieving LOI upto 34.5, char length 2 cm and 42% loss of tenacity in treated jute fabric.

5.2.3 Test of wash stability indicates that though, the application of above said combination of i.e. 15% urea and 15% ammonium sulfamate applied on jute fabric gives LOI value up to 38 but the effect is gradually reduced with the no. of wash cycle and become 30 from 38 after 5 wash cycle. Hence the use of 5% Arkofix commercial binder (Polycarboxylic Acid based) along with 3% Ceralube (Polyethylene based softener) shows much better wash fastness and better retention of LOI value around 36 (from 38) after 5 wash cycle for application of 15% urea and 15% ammonium sulfamate + 5% Arkofix commercial binder + 3% Ceralube (a softener).

5.2.4 A comparison with commercially available flame retardant agent for cellulose at the equivalent doses i.e 30% of SARAFLAM-CWF (THPC based) as compared to application of 30% flame retardant chemical as stated in 5.2.2 (i.e. 15% urea and 15% ammonium sulfamate), reveals that the LOI value is 4.5% higher and tenacity loss is 5% lower for application of 15% urea and 15% ammonium sulfamate combination than those obtained for SARAFLAM-CWF (a commercially available flame retardant agent).

5.2.5 Analysis of DSC & TGA also show earlier degradation of hemicellulose and cellulose component of urea and ammonium sulfamate combined treated jute substrate with or without binder, with higher residue for heating up to 500^{O}C than untreated jute and SARAFLAM (a commercial Flame retardant agent) treated jute. The maximum thermal stability is obtained with 15% Urea and 15% ammonium sulfamate with binder confirming better flame retardant performance with this treatment.

5.2.6 FTIR spectra for differently treated jute for the above said treatment (urea, ammonium sulfamate, sulfamic acid with binder in different combination) confirms in corporation of $O-SO_3$ group by a duplet at 810 cm^{-1} and 905 cm^{-1} as well as 1681 cm^{-1} is attributed to NH^+ stretching vibration in $C= NH^+$ and 1300 cm^{-1} to 1400 cm^{-1} is attributed to C-N stretching vibration in primary and secondary amines due to incorporation of urea proving the chemical anchoring of both urea and ammonium sulfamate to jute for the observed flame retardant effect, moreover appearance of a duplet at 3000-2750 cm^{-1} spectral region denotes the presence of polyolefin attributed to $-CH_2-$ asymmetric and symmetric stretching vibration for incorporation of PE-emulsion softener another peak at 1681 cm^{-1}is attributed to C=O stretching vibration for the polycarboxyl based binder Arkofix which is incorporated to improve the wash stability of the formulation.

5.2.7 Scanning Electron Micrographs of untreated and treated jute fabric before and after treatment with urea, ammonium sulfamate, sulfamic acid and the commercial binder in different combination show that all the treatments show some masking effect by deposition of the Flame retardant chemicals to a large extent amongst all the said treatment the deposition of Flame retardant chemical appears to be maximum in the case of jute treated with optimum application of urea and 15% ammonium sulfamate with binder shows better physical coverage and perhaps better anchoring of the said flame retardant chemicals.

5.2.8 A study on optimization by using statistical experimental software (UDQM Model) for obtaining the optimum concentration of the independent variables (urea and Ammonium Sulfamate) for getting optimum values to the dependant variables (LOI, Char Length, Loss in Tenacity) The optimal value of A and B as generated byRSM technique by UDQM model i.e A (Urea)= 147.80 and B (Ammonium Sulfamate)=87.90 for which the resultant optimal values of R1(LOI), R2(Char length) and R3(Loss of tenacity) respectively are 32.36% LOI, 33.82mm Char length and 23.21% Loss in Tenacity.

Finally it is concluded that jute treated with 14.78% Urea and 8.79% Ammonium sulfamate + 5% Arkofix commercial binder + 3% Ceralube may be used to obtain a good degree of flame retardant performance obviously with some loss of fabric tenacity with minimum deterioration of other textile related properties achieving LOI value up to 38 with 1 cm char length and also reasonably stable upto five nos. of normal wash cycle may be achieved. The obtained flame retardant performance with minimum deterioration of other textile related properties was obtained from the RSM technique of Statistical design expert software At the optimal value of Urea(A) and Ammonium Sulfamate(B) as generated by the software i.e A(Urea)= 147.80 and B(Ammonium Sulfamate)=87.90 for predicted response variables like 32.36% LOI, 33.82mm(3.4cm) Char length and 23.21% Loss in Tenacity, which however consider to be a best optimum results obtained from the present work.

5.3 Conclusions of Section4.3 Effect of treatment with combination of ZnO nano-particles and silicone emulsion (Formulation Code J-ZnO nano-particle) for improved flame retardancy of bleached jute fabric.

The followings can be concluded from study on application of ZnO nano-particles with poly methyl siliconate(PMS) emulsion on bleached jute fabrics.

5.3.1 ZnO nanoparticle (ZnO-NP), prepared by precipitation method using zinc acetate dehydrate and NaOH followed by calcination at 600^{o}C. Application of 0.01% ZnO-NP on jute fabric (by pad-dry-cure method) using 10% PMS emulsion as a dispersing medium (readily available in the market) at pH 14 (PMS is alkaline in nature) shows a good level of fire-retardancy achieving LOI value 35 and char length 1 cm having nearly 10 % loss in fabric tenacity and reduction of 15 unit loss in hunter whiteness index along with some stiffening effect.

5.3.2 However statistical design expert software using UDQM modelfollowing RSM technique optimum value of ZnO-NP and PMS is found to be 0.007% and 13.7% which offers a better option to get the optimum results of response variables like 37.71% LOI, 44.01mm Char length and 17.35% Loss in Tenacity.

5.3.3 Test of wash stability of ZnO-NP coated jute fabric indicate that the LOI value become 30 from 35 after 5 normal wash cycle indicating reasonably good to medium wash stability.

5.3.4 Analysis of DSC & TGA thermograms reveals that there is early degradation of cellulose and hemicellulose component forming lesser amount of flammable volatiles like levoglucosan (giving rise to higher LOI values) showing higher residue left while heating up to $500^{O}C$ than that of untreated jute substrate. Moreover, in this case it has been observed that the effect of the said ZnO-NP along with PMS is preferentially more restricted probably to hemicellulose part rather than the cellulose and there is almost no effect on lignin.

5.3.5 pXRD spectrum of ZnO-NP generated from zinc acetate is found to be highly crystalline showing size of nano particle to be around 38-60nm particle size though distribution of the particle size shows 10% particles within 100 nm, rest are within 500nm i.e. total 60% are around 30-500nm and rest are agglomerated .

5.3.6 FTIR spectrum of ZnO-NP shows the peak below 500 cm^{-1} due to the distinct lattice vibrations of ZnO and the band at 842 cm^{-1} attributed to the asymmetric stretching vibration of Zn-O-Zn bridging. The broad peak at 3400 cm^{-1} of OH stretching and a peak at 1550 cm^{-1} OH bending suggests the presence of $Zn(OH)_2$/ physically absorbed moisture. FTIR analysis of untreated bleached jute and treated jute with ZnO-NP in PMS are when compared shows few additional small peaks at 1290 cm^{-1} – 1300 cm^{-1} corresponding to Si-C in the silicone compound and also Si-O stretching vibration of silicone which occurred at 960cm^{-1}in FTIR peak of PMS when applied on jute merge with the peak already present in the jute at 1030

cm^{-1} and shows a sharper peak at 1030 cm^{-1}. The additional very small peak observed at 500 cm^{-1} -505 cm^{-1} indicates the presence of ZnO in the coated jute fibre.

5.3.7 Comparison of SEM micrographs of untreated bleached jute and treated jute with0.007 to 0.01% ZnO-NP in 10% to 11.74% PMS reveals that the serrated surface structure of jute is finally covered with the applied chemicals.

5.3.8 By using the statistical design expert software following Response surface Methodology the optimal value of Nano ZnO and PMS as generated by the software which is for Nano ZnO(A) = 0.007% and the optimal value for PMS(B)=13.78% predicting value of R1, R2 and R3 respectively 37.71% LOI, 44.01mm (4.4cm) Char length and 17.35% Loss in Tenacity which are definitely better results than that was obtained in preliminary studies.

5.3.9 From AAS study and EDX Study of Nano ZnO particles with PMS treated jute confirms presence of both zinc and silicone content in the treated (with optimum dosages of Nano ZnO particles and PMS) jute fabric.

5.3.10 Additional experiments are carried out to compare the effects of same dosages of normal ZnO and Nano ZnO particle on Jute and the results were finally compared and found that the same dosages of normal ZnO (with 10% PMS) cannot render required flame retardancy showing LOI below 23, Char length near about 10 cm with reasonable loss in tenacity.

For obtaining same level of flame retardancy that was obtained by 0.007-0.01% Nano-ZnO particle with 10% PMS, it is required to use 8% normal ZnO with 10% PMS.

Finally a relative comparison amongst the three types and category of chemical formulations optimized and used in the present research, is made by comparing the effects of these three optimal formulations/ processes/ techniques developed , which may be therefore be useful for understanding the relative performance of one over other. Hence the three category of formulations treated fabric (at the corresponding optimised conditions) are ranked below as per the following weighted average ranking method as given below in Table. 5.1.

Table-5.1: Data and Score for ranking three different process and techniques for imparting Flame retardant finish to the bleached jute fabric

Sl. No.	Properties	Full Marks	Optimised FR Formulations					
			J-O-P-PVA		J-UAS-AC		J-ZnO-NP	
			Data	Score	Data	Score	Data	Score
1	Loss in Tenacity *	20 (20 marks for no loss in tenacity)	30	-6	22	-4.4	10	-2
2	LOI	20 (20 marks for 40)	31.5	6.3	38	7.6	35	7
3	Char Length *	20 (20 marks for 1 cm)	5	-1	1.5	-0.3	1	-0.2
4	Whiteness Index	10 (10 marks for 75)	58.12	5.8	64.35	6.4	60.25	6.02
5	Bending Length *	10(10 marks for 3.5)	4.5	-0.45	5.3	-0.53	4.5	-0.45
6	Wash Stability	10 (10 marks for no loss in LOI value)	27	2.7	36	3.6	29	2.9
7	Residue left at 500^{O}C	10 (10 marks for 40)	38	3.8	25.5	2.5	5	0.5
Total				**11.16**		**14.95**		**13.77**

* WA Score= Weighted Average Score = +/- (Data x Weightage/100) for each case.

***** As these properties are inversely proportional to the desired textile property parameters its effect in weight average score endorsed as negative, while all other are considered positive.

\# Maximum weightage i.e. double (20) than weightage of other parameters (10) has been apportioned depending upon the much higher importance of these parameters than the other properties.

So, for the relative it is concluded that 0.007- 0.01% ZnO-NP in 10% PMS render jute fabric a good level of flame retardant achieving LOI value up to 30-35 and char length 1-4 cm with the loss of tenacity around 10%-17.35% is most equally good as compared to the other two optimised treatments with 8-10% Urea and 14.78-15% ammonium sulfamate + 5% Arkofix commercial binder + 3% Ceralube showing LOI value though up to 32-38,char length 1-3.38cm, at the cost of 20-23.2% loss in tenacity followed by another treatment with 10% Oxy-P-PVA on bleached jute rendering LOI value up to 30-31.5 with nearly 30% loss in tenacity.

However, considering finer differences, the above ranking indicate the decreasing order of overall flame retardant performance of these three categories of processes are as follows: J-UAS-AC(Total Score 14.95)>J-ZnO-NP(Total Score 13.77)>J-O (P-PVA) (Total Score 11.10) vide data and score in Table 5.1(based on weighted average ranking as above).

SUGGESTION FOR FUTURE WORK

1. Effect of different common additives in these techniques presently studied for further enhancing its Fire-retardant performance.

2. Study of simultaneous dyeing and fire-retardant finishing of jute.

3. To explore the possibility of multiple finishing in one stage i.e. simultaneous fire-retardant, crease resistance and rot resistance finish application.

4. To study different fire-retardant finishing by cold pad-batch or spraying technique at room temperature so that jute fibre can be made fire-retardant for loose stock of fibre with an aim to make FR-composite.

5. Identification use of natural & eco-friendly fire-retardant chemicals (like extracted juice of banana) stem etc.

REPRINTS

International Journal of Applied Engineering Research
ISSN 0973-4562 Volume 9, Number 4 (2014) pp. 439-450

http://www.ripublication.com

Eco-friendly Fire Retardant Finishing of Jute Fabric by Impregnation or Coating Phosphorylated PVA and its Effect on Physical Properties and Thermal Behaviour of Treated Jute Fabric

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Abstract

There are commercially available permanent fire-retardant formulations based on hydroxy-methyl i.e. methylol group based chemicals like THPC, (commercially known as Pyrovatex CP or Pekoflame DPN) for cellulosics. These are not eco-friendly for chances of release of formaldehyde. Hence, it is attempted in this work, to findnewer eco-friendly FR-formulations for cellulosics and jute fabrics. In the present work, Polyvinyl alcohol is phosphorylated in a controlled condition in the laboratory and the bleached jute fabrics have been subjected to treatment with phosphorylated polyvinyl alcohol by pad-dry process for imparting ecofriendly fire retardant finish on it. The fire retardant performance of the said newer FR-formulation is investigated in terms of LOI value, flame spread time, afterglow time, char length and changes in tenacity, breaking elongation, bending length, flexural rigidity, and surface appearance properties (in terms of K/S value, whiteness index, yellowness index and brightness index). The said fire retardant formulation showed moderate fire retardant performance when applied on bleached jute fabrics showing 28.5-32 LOI value and char length with in 2 cm. However, the said fire retardant finished jute fabrics showed loss of nearly 15-20% of LOI value. on washing. Loss of tenacity on such fire retardant treatment was around 15-40%. Thermal behavior of phosphorylated PVA treated jute by TGA thermograms of the experimental fabrics showed that minimum weight loss occur during its heating at ambient to 500^0C at different temperature zones as well as somewhere the thermal degradation a bit early and somewhere occur a bit delayed showing somewhat different pattern of thermal degradation/pyrolysis of major jute constituents than that occur for control bleached jute fabric. FTIR analysis proved that phosphorylated PVA reacts with bleached jute fabrics in such newer chemical finishing.

Keywords: Fire-retardant finish, Jute fabric, Limited oxygen Index, Thermal Degradation Behavior, Phosphorylated PVA, Thermo-gravimetric Analysis.

1. INTRODUCTION

There are several non-durable flame retardant formulations for cellulosic's [1-4] such as –Borax, Di-Ammonium Phosphate, Borax:Boric acid(7:3) mixture, , phosphoric acid etc. which if applied in conjunction with resin finish, the non-durable flame retardant is mechanically entrapped into the textile matrix of the fabric and thus, becomes somewhat semi-durable. Also the use of such phosphate compounds with melamine-formaldehyde resin has been found to be another alternative method for fire proofing jute goods as semidurable FR finish of jute as studied in BJRI, Dhaka.[5]Among several durable flame retardants, available for cellulosics, the important ones are Antiminy oxychloride/Antiminy oxide. Tetrakis hydroxyl methyl phosphonium chloride (THPC)[6], Tris-1-aziridinyl phosphine oxide (APO), APO-THPC combination APO-Zn $(BFn)_2$ or THPC-Thiourea or APO-Thio-urea combinations, THPC-antimony oxide combination etc. But none of these are ecofriendly for chances of problem of formaldehyde release in today's context.

The toxicological hazards of conventional and commercially available THPC based flame retardants are often questioned in terms of the toxicity of the basic FR-retardant chemicals and also the hazards during the application and its end-use. These questions have been studied and reviewed by Mehta and Sharma[7] for the commonly available such flame retardants for cellulosics. Whilst agents like tris(aziridinyl) phosphine oxide (APO) and antimony (III) oxide are also proved to be extremely toxic. In a concurrent paper by Macgregor et al. [8] investigate the potential mutagenicity of a no. of common flame retardants for cotton. Of all the phosphorus-containing flame retardants, including phosphonium, phosphine, phosphine oxide and phosphonate derivatives, all were found to be non-mutagenic. However, toxicity of two of the three bromo-alkyl substituted triazines (APO etc.) were investigated and it did exhibit mutagenic activity. THPC based flame retardants are though proved to be much efficient flame retardant agent, but this is not free from formaldehyde toxicity and hence, is not eco-friendly. Hence this interest of researcher, have been revised/renewed recently to find eco-friendly flame-retardant for cellulosics. For protection of consumers from unsafe fire hazard flame retardancy finishing of jute furnishing is considered to be high important especially for Floor coverings, upholstery and draperies, So, it may be said that for ligno-cellulosic fibres like jute, the work done so far on flame retardancy finish of jute fabric are mainly temporary [4, 5] types and that too is only limited in number as fire retardant chemicals. Henceit was understood that, there are ample scopes to work on development of better level of fire retardancy finish for non durable, semi-durable and durable flame retardant finishing of jute fabrics. It is also felt essential to study the thermal behaviour of the

Phosphorylated Poly(Vinyl Alcohol) salt and such chemically modified flame retardant jute based fabrics for understanding the mechanistic of thermal degradation under different temperature ranges. Partially phosphorylated P-PVA has attracted considerable interest because of its non flammability[9]. Hence in the present study efforts are have been made to develop ecofriendly water based fire retardant treatment formulations based on phosphorylated polyols to study the efficacy of this formulation on the flammability and related properties of such jute based fabric.

2. MATERIALS AND METHODS

2.1 Materials

Fabrics

Conventional H_2O_2 bleached plain weave jute fabrics having 65 ends/dm, 60 picks/dm, 270 g/m^2 (area density), 214 tex warp, 241 tex weft, and 0.80 mm thickness were used for the present study.

Chemicals

Laboratory reagent grade Polyvinyl alcohol, Dicyandiamide from LOBA, Urea from NICE, Ortho-phosphoric acid from RFCL, Potassium Hydroxide from Quligence Fine chemicals, India, were used.

2.2 Methods

2.2.1 Preparation of Phosphorylated PVA Salt

10% aqueous PVA solution was prepared at 100^{0}C for 30 mins. When a clear jelly like suspension was formed the heating was discontinued and cooled to a room temperature. The clear 10% PVA solution thus formed was then mixed with Dicyandiamide and Urea in the proportion of the ratio 1:0.5:0.5 (PVA: Dicyandiamide: Urea). The sample solution was then mixed with 10% H_3P0_4 solution and heated at a temperature of 100^{0}C for 30 min. After cooling the solution, KOH aqueous solution was added slowly into it until pH 11 is reached and precipitate is formed. The total mass was then subjected to filtration process to obtain solid residual mass. It was then dried at 100^{0}C for 1-2 hrs. This residual solid mass thus obtained is phosphorylated PVA (P-PVA).

2.2.2 Application of P-PVA on Jute Fabric

The bleached jute fabric is padded with the P-PVA solutions in presence of 5% Al_2SO_4 as the catalyst [10] (100% weight pick-up) and cured at 140 ^{o}C for 5 min and consequently padded (100% weight pick-up) with KOH aqueous solution of pH 11. Then the fabric is dried at 100 ^{o}C for 5 min. Then the Fabric wash washed with the cold water.

2.2.3 Preparation of pre-oxidised jute fabric

Oxidation of bleached jute fabric was carried out, by padding the fabric with 1% (owf) $K_2S_2O_8$ solution at room temperature followed by 2 hr batching. Then the jute fabric is washed and air dried.

2.2.4 Preparation of pre-oxidised P-PVA

The aqueous solution of of PVA was initially treated with $NaIO_4$ at a dose level of 2% of PVA taken. Then this periodate treated PVA is phosphorylated following the same method mentioned above.

2.2.5 Application of periodate treated P-PVA on normal jute and Oxy-Jute Fabric

The bleached jute fabric is padded with the periodate treated P-PVA solutions in presence of 5% Al_2SO_4 as the catalyst [10] (100% weight pick-up) and cured at 125 ^oC for 5 min and consequently padded (100% weight pick-up) with KOH aqueous solution of pH 11. Then the fabric is dried at 100 ^oC for 5 min. Then the Fabric wash washed with the cold water.

2.2.6 Measurement of Breaking Tenacity and Breaking Extension

Warp-way breaking tenacity (cN/tex) and the breaking extension (%) of selected fabric samples were measured by the ravelled strip method as per IS-1969-1968 method[11] using an Instron (Model-1445) CRT-Universal tensile tester with a traverse speed of 100 mm/min and a pretension of 0.5 N. The final gauge length(sample size) of the fabric sample was 50 mm.x 20 mm. after raveling.

2.2.7 Measurement of Bending Length and Flexural Rigidity and Bending Modulus

The bending length of the selected fabric samples in both warp and weft directions was measured as per IS-6490-1971 method[12] using Cantilever type Sasmira fabric stiffness tester with a specimen size of 200 mm × 25 mm. From bending length data, flexural rigidity and the bending modulus were calculated using the following relationships [13]:

Flexural Rigidity of the Fabric in the Warp Direction (G_1) = $MC_1^3 \times 10^3$ mg.cm

Flexural Rigidity of the Fabric in the Weft Direction (G_2) = $MC_2^3 \times 10^3$ mg.cm

Overall Flexural Rigidity (F) of the Fabric = $\sqrt{G_1 \times G_2}$ mg.cm

Where, M= fabric weight (g/cm^2), C_1 = bending length (cm) in warp direction, C_2 = bending length (cm) in weft direction.

2.2.8 Measurement of Surface Colour Strength (K/S Values)

Surface colour strength in terms of *K/S* value was determined by measuring reflectance value of the textile substrate using a computer aided Macbeth 2020-plus reflectance spectrophotometer under D_{65} standard illuminant and 10^o standard observer setting using the following relationship(Kubelka Munk-Function) [14] .

$$K/S_{\lambda max} = \frac{\text{Co-efficient of absorption}}{\text{Co-efficient of scattering}} = \frac{(1 - R_{\lambda max})^2}{2 R_{\lambda max}}$$

Where K= the co-efficient of absorption, S = the co-efficient of scattering, C_d = the concentration of dye, $R_{\lambda max}$ = the surface reflectance value at maximum absorbance wave length (λmax) .

2.2.9 Measurement of Whiteness, yellowness and Brightness Indices

Whiteness index as per Hunter Lab-Scale formula, [15] yellowness index as per ASTM-E-313 formulla [16]and brightness index as per ISO-2470-1977 formula[17] of the selected jute fabric samples were directly evaluated using a computer aided Macbeth 2020 plus reflectance spectrophotometer (with D_{65} standard illuminant and 10^o standard observer setting) and associated colour measurement software, using following relationship.

$$\text{Whiteness Index (Hunter Lab-Scale)} = L - 3b = 10\sqrt{Y} - [21(Y-Z\ \%)] / \sqrt{Y}$$

$$\text{Yellowness Index (ASTM-E313/1973)} = 100\,(1-B/G) = 100\left[1 - \frac{0.847Z}{Y}\right]$$

$$\text{Brightness Index (ISO-2470-1977)} = \frac{\text{Reflectance value of the substrate at 457nm}}{\text{Reflectance value of the standard white diffuser/ white tile at 457nm}} \times 100$$

where, X, Y and Z are the tristimulus values of the sample, L is the lightness/darkness indicator in CIE Lab-Scale [L* or simply $L = 16\,(Y/Y_o)^{1/3} - 16$ as per CIE Lab-1976 formula [13]], b is the blueness/yellowness indicator in the CIE Lab-Scale[13]{b* or simply $b = 200\,[\,(Y/Y_o)^{1/3} - (Z/Z_o)^{1/3}]$}, $B = Z/1.181 = 0.847\,Z$, $G = Y = L^2/100$ and X_o, Y_o and Z_o are the CIE-tristimulus values[13] for D65 standard illuminant and 10^o standard observer.

2.2.10 Testing of Flammability Performances

Selected untreated and treated jute fabric samples of specified length (15cm length and 5cm wide) were exposed to a standard flame for a specified time (for cotton it is 1sec, for jute it is 10 sec, standardized in this laboratory) and was allowed to burn in an inclined plane (45^0 inclined) Standard flammability tester (Make: Paramount, India,) following ASTM-D-1230-94 standard method[18]. The fabric samples was mounted at 45 ^{0} angle in a specimen holder and was then exposed to a standard flame of specified height exposed at 90 ^{0} with the specimen for 10 second and is left for burning, to note flame spread time, afterglow time, and char length (in cm) after the burning. The time taken (t in seconds) for the flame to travel 12.5cm of the fabric sample mounted in the frame at 45 ^{0} angle for the fabric of specified length and width to burn was recorded on digital timer provided in the instrument. After glow time was measured with a stop watch and char length was physically measured by a scale.

2.2.11 Determination of Limiting Oxygen Index

Limiting Oxygen Index (LOI) are critical oxygen index values indicating the relative measure of flammability of any materials or textiles. If LOI values are above certain critical limit (say 27), there is hardly any chance of fire propagation. LOI testing instrument thus provides a precise method for determining the critical oxygen index of the sample by measuring the minimum volume concentration of oxygen gas in a flowing stream of mixture of oxygen and nitrogen gases (mixed in different volume ratio) required to maintain candle like burning of a sample for a specified time. LOI values of selected untreated and treated fabric samples were determined in an standard

LOI tester (Make: S C Dey & Co., Kolkata) as per ASTM-D-2863-77 method [19] by using the following formula.

$$\text{Limiting Oxygen Index (n)} = \frac{100 \times \text{Volume concentration of } O_2}{\text{Volume concentration of } N_2 + \text{Volume concentration of } O_2}$$

2.2.12 Study of Thermal Behaviour by TGA Thermograms

In Thermo-Gravimetric Analyser (TGA), with constant heating from ambient to any limiting temperature range, the change in sample weight due to thermal degradation, evaporation, dehydration is measured. This technique is effective for quantitative analysis of thermal degradation at any or at use temperature, rate and type reactions that are accompanied by mass change due to thermal decomposition, evaporation, gas adsorption and dehydration etc..The TGA thermograms of jute not only give an indication of its thermal behaviour, but also give a clear reflection regarding the degree of chemical changes/interaction of the major constituents of jute after chemical treatments and modifications, altering the rate of mass loss on heating (in TGA).

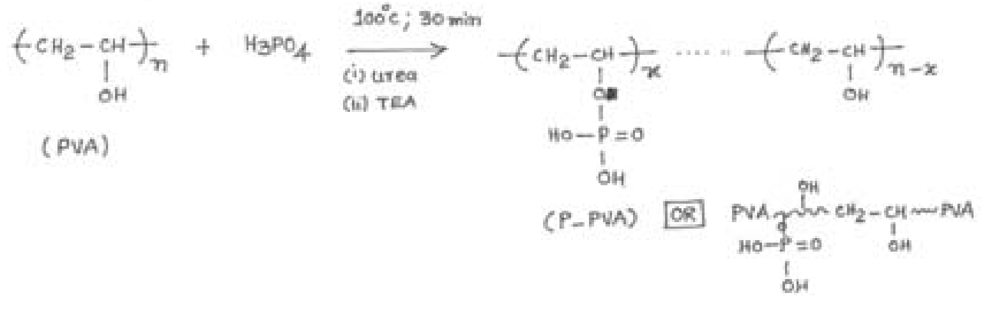
TGA thermograms of untreated and treated jute fibre samples (finely crushed) after being taken out from the corresponding untreated and treated jute fabrics were obtained from a Shimadzu Thermo-Gravimetric Analyser (Model –TGA-50) under atmospheric air (for TGA) at a heating rate of 10°C/min, using a pre-fixed sample weight of exactly 2 mg over a temperature range from 30°C (ambient) to 500°C, following usual procedure [20] .

3.0 RESULTS AND DISCUSSION

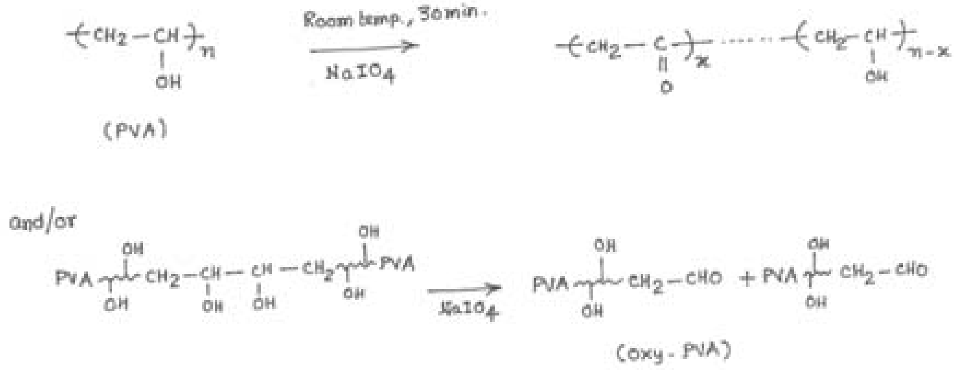
Before discussing the results of the fabric performances after these chemical modifications/ Finishing treatments on these two types of fabrics, it will be appreciated to look into the possible reaction mechanism and types of chemical changes envisaged, which are given below :-

Postulated Reaction Mechanism :

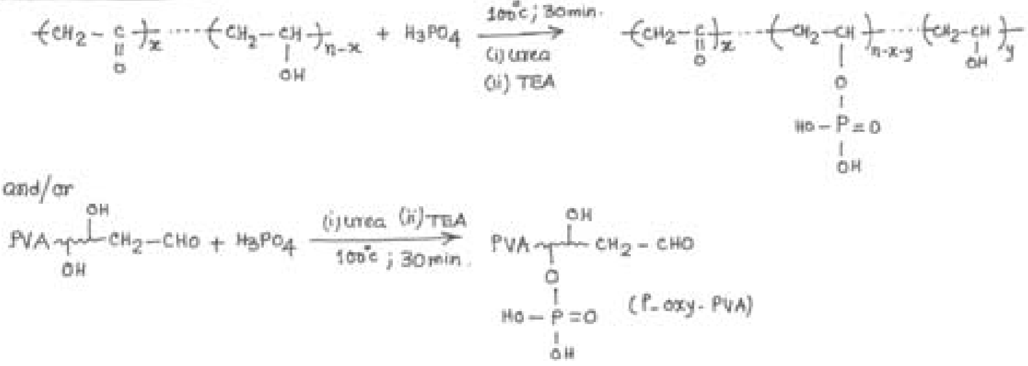
(1) Reaction Scheme - 1 (Phosphorylation of PVA)



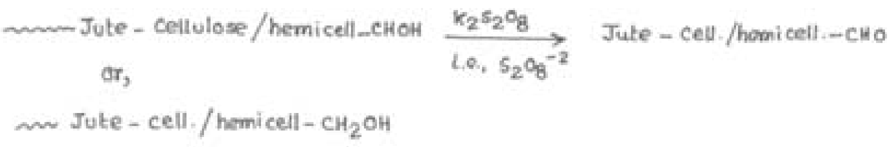
(2) Reaction Scheme - 2 (Pre Oxidation of PVA)



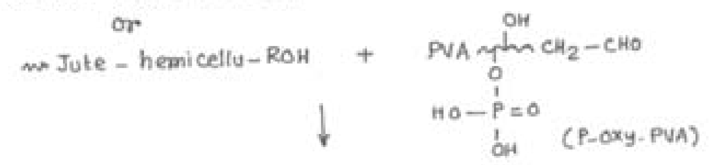
(3) Reaction Scheme - 3 (Phosphonylation of Oxy-PVA)

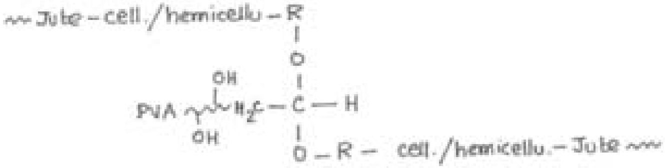


(4) Reaction Scheme (4) (Pre Oxidation of Jute)



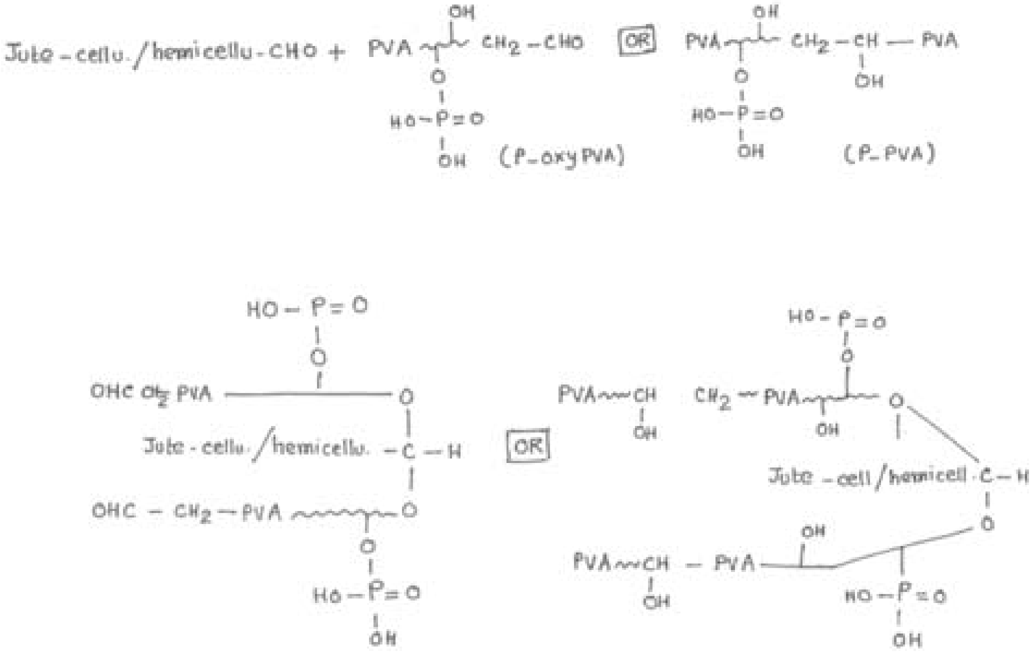
(5) Reaction Scheme (5) (Reaction [Hemi-acetal formation] between Jute and P-Oxy-PVA]





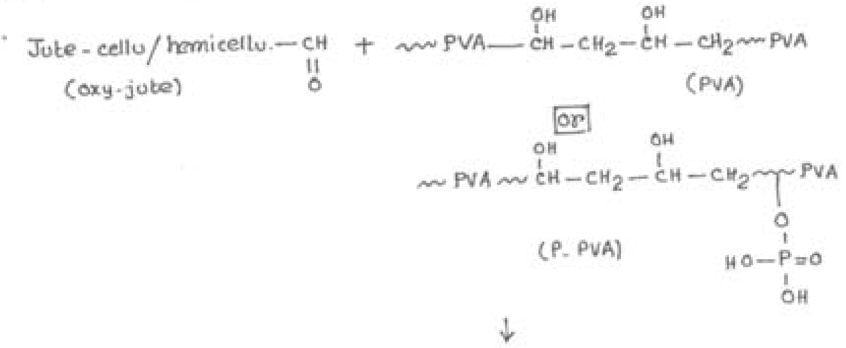
[Hemiacetal formation in acidic environment through –CHO group of PVA]

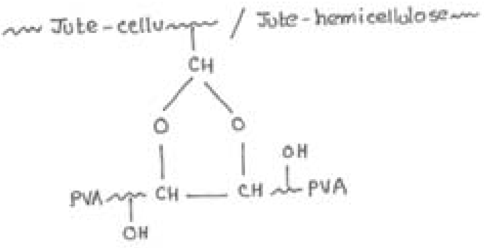
(6) Reaction Scheme (6) [Reaction between Oxy-Jute and P-PVA or P-oxy-PVA]



[Hemiacetal formation through -CHO group in oxy-jute]

(7) Reaction Scheme (7) : [Reaction between Oxy-jute and PVA or P-PVA by hemiacetal formation]





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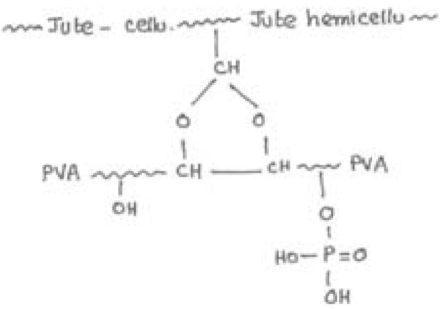

Table-1. Fire Retardant performance of jute fabric and pre-oxidised jute fabric treated P-PVA and Periodate treated P-PVA

Type of fabric and treatments	Treat--ment Code	Physical properties					Surface Appearance				Flammability			
		Tensile Properties		Bending Properties										
		Tenacity(cn/tex)	BreakingElongation(%)	BendingLength(cm)	Flexural Rigidity(mg.cm)	BendingModulus(kg/cm²)	K/S	WhitenessIndex	YellownessIndex	BrightnessIndex	Flame Spread Time (sec)	After Glow Time (sec)	CharLength(cm)	LimitingOxygenIndex
Untreated bleached jute	---	5.78	5.0	3.8	1408	16.89	.34	36.92	17.72	52.04	49	55	12.5	20.5
Jute treated with 10% P-PVA	A	3.7	5.17	3.2	2451.26	57.45	.62	22.63	25.81	41.75	55	20	8	28.5
Oxy-Jute Treated with 10% P-PVA	B	3.5	6.24	4.1	2053.21	47.25	.56	25.15	24.47	44.08	60	15	6	30
Jute treated with Periodate treated 10% P-PVA	C	3.67	8.24	4.5	1853.41	43.44	.56	25.44	24.24	44.25	65	15	5	31.5
Oxy-Jute Treated with Periodate treated 10% P-PVA	D	3.3	8.01	3.8	1476.06	34.59	.56	22.07	26.75	42.88	69	10	4	32

Fire retardant performance of jute fabric and pre-oxidised jute fabric treated with P-PVA and periodate treated P-PVA has been evaluated and the results are shown in Table 1. Relevant data in Table 1 indicate that there is an increasing trend of LOI values, according to the treatements. Maximum LOI of 32 is obtained for treatment “D” with loss of tenacity within 40%. However, It is observed that Treatment “A, B, C” showed somewhat lesser fire retardancy property than Treatment “D” but strength retention is better . Loss of tenacity of P-PVA treated jute fabric is 35%. Overall, jute fabric and pre-oxidised jute fabric treated with P-PVA and periodate treated P-PVA showed balanced fire retardance property(LOI value 28-32) with loss of tenacity within 30-40%.

The bending length values are increased in case of treatment with P-PVA but improved by treating the jute and oxy jute fabric with periodate treated P-PVA. For the surface appearance properties it is noticed that whiteness index are slightly decreased with the different treatments.

Analysis of TGA Thermograms:

TGA analysis of jute fabric treated with P-PVA and periodate P-PVA shows that residue left at 500^0C is more than that of untreated jute.

Among the different treated fabric, lt can be shown periodate P-PVA treatment on Oxy Jute leaves highest residue(35%) or weight loss is minimum where as untreated jute leaves a residue of only 10%. Therefore, this combination is expected to give best fire retardant property. The LOI value and 45^0 flammability test results also confirm this observation.

P-PVA treatment on Oxy Jute also leaves a residue of 34.5% (2nd highest) at 500^0C which is also matched with the observed higher flame retardant properties.

However, jute fabric treated with P-PVA treatment on Jute showed residue of 30% which is somewhat lesser than other treatments. This can be explained by lesser extent of phosphorylation occurred as compared to other treatments.

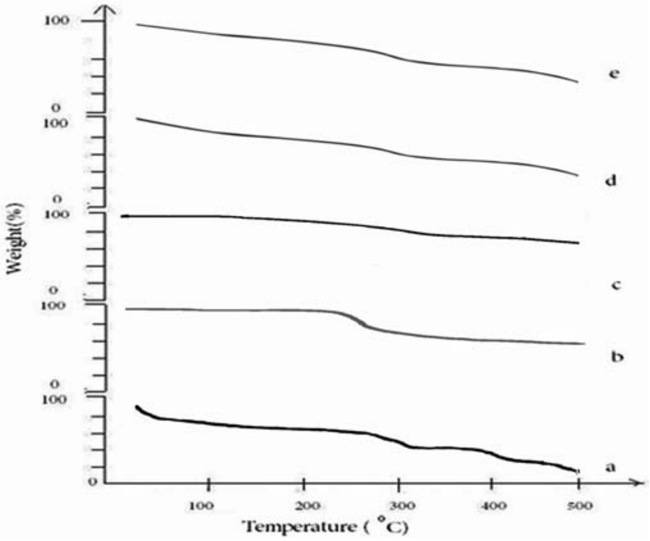

Fig.1. Thermogravimetric analysis Thermograms of (a) Untreated Jute (b) Normal PVA (c) P-PVA (d) Jute Treated with P-PVA (e) Oxy-Jute Treated with periodate treated P-PVA

Acknowledgements:
The authors express their sincere thanks to Prof.(Dr.) S.K.Sett, Head of the Department, Department of Jute and Fibre Technology, Institute of Jute Technology, Calcutta University for all sorts of administrative support to carry out this work. The authors are also thankful to AICTE, New Delhi for the grant-in-aid received for the AICTE-NCP-II project (Ref. File No. 8023/RID/BOIII/NCP/10/2005-06) during 2007-11 and also to National Jute Board, Ministry of Textiles, Govt. of India for sponsoring another research project under Jute Technology Mission –MM-IV-scheme 7.1 as project no. 10 on 'Development of fire retardant jute fabric' during 2008-2011.

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AASCIT Journal of Materials
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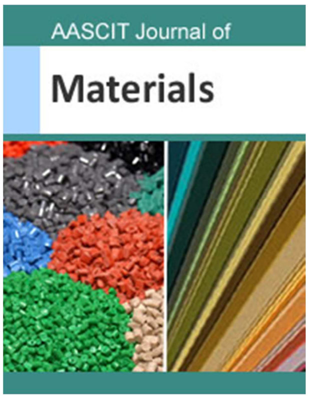

Fire-retardant Chemical Finishing of Jute Fabric Using Sulfamate and Urea Mixture

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Citation

Ashis Kumar Samanta, Reetuparna Bhattacharyya (Roy), Ranjana Chowdhury. Fire-retardant Chemical Finishing of Jute Fabric Using Sulfamate and Urea Mixture. *AASCIT Journal of Materials*. Vol. 1, No. 4, 2015, pp. 98-110.

Keywords

Sulfamates,
Urea,
Fire - Retardant Finish,
Jute Fabric,
Limiting Oxygen Index,
Char Length,
Fire Protective Textiles

Received: August 31, 2015
Revised: September 23, 2015
Accepted: September 25, 2015

Abstract

Most of the commercially used fire-retardant agents like THPC/APO etc., are not eco - friendly for release of formaldehyde or other toxicity. Hence, an attempt is made, to find newer eco-friendly fire-retardant formulations for jute fabrics. The effect of ammonium sulfamate alone & in presence of urea was studied for the fire-retardant performance of the jute fabric as protective textiles. It is found that the Limiting Oxygen Index (LOI) of Jute Fabric is significantly improved by application of these simple fire-retardant agents. The fire-retardant performance of each formulation is investigated at different concentration levels in terms of LOI value, flame spread time, afterglow time, char length (on the basis of vertical flammability test) and changes in tenacity, bending length etc.. Most of the fire-retardant formulations showed high fire-retardant performance showing LOI value in the range of 35 - 38. However, all the above fire-retardant finished fabric showed loss of nearly 20 - 30% of LOI value on repeated soap washing. So the use of acrylic/Poly - carboxylic binder like Arkofix NEC Plus Liq. (from Clariant India Pvt. Ltd) was studied which improves its wash stability upto 5 wash cycles. Loss of tenacity on such fire-retardant treatment was around 15 - 50% in different cases. DSC & TGA analysis of untreated and said chemically treated jute fabric with different fire - retardant formulations show that residue left at 500°C is more than that of untreated jute indicating higher thermal protection. FTIR analysis and SEM - study of fire-retardant treated jute fabric were also studied and reported. These fire-retardant jute fabrics has industrial protective textile application as Brattice Cloth in mines and many other potential field of applications, such as fire-retardant kitchen apron, furnishings for public Hall/Theater/Hospital etc.

1. Introduction

Jute, like all natural textile fibers has a higher proneness to burning, though LOI value of untreated jute (20.5) is higher than the LOI value of cotton (15.5). So jute based home furnishings/ Pandal clothes, wrapping hessian cloth and brattice cloth for mines which are made up of jute can ignite slowly (slower than cotton) and enhance development of fire by burning its cellulose part forming higher Levoglucosan, a flammable compound. Jute is a ligno-cellulosic fibre with hemicellulose (22 - 24%), α - cellulose (58 - 60%)

and lignin (12 -14%) as the main constituents with other minor constituents as well. The thermal behaviour of these components differs due to differences in their chemical nature. Some preliminary work on the thermal behavior of jute has been reported earlier [1, 2]. Jute carpet backing, decorative jute furnishing fabrics, brattice cloth for mines have been made fire-retardant to reduce casualties and injuries caused by fire. Brattice Cloth is basically a Hessian fabric which after rot and fire - proofing treatment used in mines as windscreens for ventilation purposes.

The initial works for making fire-retardant fabric was started on 1735 in England. Cellulosic fabrics can be made fire-retardant by treatment with different non-durable and durable fire-retardant formulations, which are readily available in the review literature by Horrocks [3]. There are many reports on fire retardancy of cotton, but similar study on jute is scanty. Some preliminary studies on temporary flame retardancy of jute has been also reported earlier by Banerjee et. al. [4] using borax-boric acid and di-ammonium phosphate. Sharma [5] suggested potassium-sodium tartarate (Rochelle Salt) as a fire-retardant agent for jute fabric. A short review on fire-retardant finishing of jute is also available in a review paper of Samanta [6]. Today, fire-retardant textiles finds application in different fields like floor coverings, floor mats, carpets, military garments, hospital furnishings, hospital drapery and industrial ventilations etc. [7, 8]. The application of suitable fire-retardant chemicals on different type of textile material and its end use requirements [9]. Different fire-retardant chemicals act in different way by manipulating pyrolysis, prevention of flammable gases, less or more char formation, controlling combustion, protecting from heat/oxygen and fuel etc. [10]. However, to avoid toxic fire-retardant chemicals, extensive research has been going on to develop newer fire-retardant products to enhance fire-retardant property in eco-friendly system, which may be non-durable, semi-durable or durable. An ideal fire-retardant fabric for textile applications must be comfortable, eco-friendly, semi-durable and durable & cost effective.

Several types of fire-retardant agents such as halogen based fire-retardant agents and phosphorous based fire-retardant agents with or without nitrogenous compound, have been used to improve the flame retardancy of cotton and synthetic textiles. However the application of halogen based fire-retardant is being greatly limited due to the possible production of dioxin, large amount of smoke and corrosive gases during the combustion of the halogen fire-retardant materials. Phosphorus based fire-retardant also has some drawbacks such as toxicity and high exudation [11-13]. Sulfur based flame retardants such as sulfamic acid and sulfamate was used in past for developing the flame retardancy of cotton, paper and wood. [14-16]. Sulfamates have been used in designs of many antibiotics, anti-cancer drugs, antiseptic drugs and weight loss drugs and other medical uses, besides are of its newer application in fire-retardant textiles. Ammonium Sulfamate decomposes at elevated temperatures and releases some non-combustible gases, such as NH_3 and H_2O as this reduces fire. Lewin et al. [17, 18] reported indeed that the use of Ammonium Sulfamate (AS) combined with dipentaerythritol improves the reaction to fire of PA6 (Nylon 6) in terms of LOI. Menachem Lew in [19] has also reported that Cotton fabrics are rendered flame retardant upon treatment with ammonium sulfamate (AS) with urea or a urea based cross linking agent, as co-additive, in the pad-dry-cure finishing treatment, with curing at 180-200°C for one to three minutes.

Considering all these as background information, the present work was aimed to develop a fire-retardant jute fabric using common chemical combination of Urea & Ammonium sulfamate on the basis of Lewin's work for PA6 (Nylon 6). The fire-retardant performance of each formulation is investigated at different concentration in terms of LOI value, flame spread time, afterglow time, char length (on the basis of vertical flammability test) and changes in tenacity, bending length and surface appearance in terms of whiteness index The assessment of LOI and Flammability tests were conducted to meet the fire - retardant specification for brattice cloth as per IS: 11884 - 1986. Finally the thermal decomposition pattern of treated jute fabric has been investigated using TGA/DSC coupled with FTIR. A commercial fire-retardant finishing agent for cellulosic materials, Saraflam - CWF (THPC based FR agent) is also studied for the same jute fabric for comparison. The fire-retardant performance of the developed formulations applied on jute fabric are compared with the fire - retardant performance of commercial fire-retardant finishing agent applied on the same fabric.

2. Experimental

Material used: Bleached jute fabric – Hydrogen peroxide bleached plain weave jute fabrics having 63 ends/dm (count 256 tex), 55 picks/dm (count 256 tex), 275 g/m^2 (area density).*Chemicals Used:* Laboratory grade Ammonium Sulfamate (AS) (Loba Chemicals), Laboratory grade Sulfamic Acid (SA) (Loba Chemicals), Laboratory grade Urea (Loba Chemicals), Arkofix NEC Plus Liq (Clariant India Pvt. Ltd), Ceralube HD. IN Liq [Polyolefin dispersion] (Clariant India Pvt. Ltd), Laboratory grade Magnesium Chloride (Loba Chemicals), Saraflam - CWF (a Commercial FR chemical from Sarex Chemicals, Mumbai, India)

Methods

Table 1. *List of the formulation and their code.*

Sl. No.	Formulation Description	Formulation Code
1	Urea + Ammonium Sulfamate	J - UAS
2	Sulfamic Acid	J - USA
3	Urea + Ammonium Sulfamate + Arkofix NEC Plus Liq + Ceralube HD.IN Liq. + Magnesium Chloride (as catalyst)	J - UAS - AC
4	Saraflam - CWF (Commercial Fire - retardant)	J - S - CWF

Bleached jute fabrics were padded (100% weight pick - up) with following fire-retardant formulations as given below followed by drying at 100°C and curing at 130°C for 3 min.

Fire-retardant finishing treatments of jute fabric with the above formulations 1 - 4 was optimised by treating the jute fabric separately with all the individual chemicals and in combination with varying concentration levels respectively by the same procedure and conditions of pad-dry-cure technique for understanding the effect of individual chemicals on achieving the fire-retardant performance on jute fabric.

2.1. Evaluation Methods

2.1.1. Fabric Stiffness (Bending Length)

The bending length of the selected fabric samples were measured as per IS-6490-1971 method using Cantilever type Sasmira fabric stiffness tester.

2.1.2. Measurement of Tensile Properties (Tenacity)

Breaking tenacity (cN/tex) of selected fabric samples were measured by the raveled strip method as per IS-1969-1985 method using an Instron (Model-1445) CRT-Universal tensile tester with a traverse speed of 100 mm/min and a pretension of 0.5 N. The final gauge length (sample size) of the fabric sample was 50 mm. x 20 mm. under the jaws.

2.2. Vertical Flammability Test

The Selected untreated and treated jute fabric specimens are tested as per IS-11884-1986, 2.75 x 10 inch, are conditioned by exposure to an atmosphere of 65+2 percent relative humidity for at least 8 hrs. before testing. The conditioned fabric specimen is then mounted in a suitable clamp and placed in a standard cabinet, and the bottom edge of the fabric is exposed to a standard flame for exactly 12 sec under controlled conditions. After removal of the flame, flame spread time, char length and afterglow were observed.

2.3. Determination of Limiting Oxygen Index

Limiting Oxygen Index (LOI) is the critical oxygen index value indicating the relative measure of flammability of any materials or textiles. If LOI values are above certain critical limit (say 27), there is hardly any chance of fire propagation. LOI testing instrument thus provides a precise method for determining the critical oxygen index of the sample by measuring the minimum volume concentration of oxygen gas in a flowing stream of mixture of oxygen and nitrogen gases (mixed in different volume ratio) required to maintain candle like burning of a sample for a specified time.

LOI values of selected untreated and treated jute fabric samples were determined by a standard LOI tester as per ASTM-D-2863-77 method by using the following formula.

$$\text{Limiting Oxygen Index (n)} = \frac{100 \text{ x Volume concentration of Oxygen}}{\text{Volume concentration of Nitrogen} + \text{Volume concentration of Oxygen}}$$

2.4. TGA and DSC Analysis

TGA and DSC thermograms of untreated and treated jute fibre samples (finely crushed) after being taken out from the corresponding untreated and treated jute fabrics were obtained from the Q600 provides simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample at heating rate of 10°C/min, using a pre- fixed sample weight over a temperature range from 30°C (ambient) to 500°C, following usual procedure [20, 21, 22] from ambient to 500°C. It features a field - proven horizontal dual beam design with automatic beam growth compensation, and the ability to analyse two TGA samples simultaneously. DSC heat flow data is dynamically normalized using the instantaneous sample weight at any given temperature.

2.5. Scanning Electron Microscopy (SEM)

Surface morphology of untreated and treated jute fibre samples taken out from the corresponding raw and treated fabrics was examined according to the prescribed procedures using a scanning electron microscope (Model: FEI Quanta 200 Scanning Electron Microscope). Jute fibre samples taken out from the relevant fabric sample were mounted on a specimen stub with double sided adhesive tape and then subjected to coating with gold using a sputter coater to avoid charging of the specimen [23, 24]. The observations were made at an operating voltage of 15 KV using usual magnification of 6000, or using a higher or lower magnification wherever specifically required.

3. Results & Discussion

Jute is a highly combustible material and the ignition time is 10 sec, LOI value of untreated bleached jute fabric is found as shown in Table 2 to be 20.5, flame spread time to be 49 sec for the entire test length and the afterglow is 55 sec. This work related to find a suitable recipe for fire-retardant finish of jute fabric using SA/AS/Urea is reported and it is felt necessary to investigate the effect of individual fire-retardant compounds on jute fabric vis. a vis. application of different mixtures of such compounds with or without additive to evaluate their fire-retardant performance. A commercial fire-retardant finishing agent for cellulosic materials, Saraflam-CWF (THPC based fire-retardant agent) is also studied for the same jute fabric for comparison. The fire-retardant performance of the newer indigenous formulations applied on jute fabric are compared with the fire-retardant performance of commercial fire-retardant finishing agent applied on the same fabric. From earlier studies on fire-retardant treatment of cellulosic, using Sulfamate [11-18] it is known that Sulfamate based compounds are effective fire-retardants for cellulosic materials. So, Sulfamic Acid and Ammonium Sulfamate have been applied on jute fabric at different concentrations to achieve a certain level of fire retardancy. Bleached jute fabric was therefore treated with 5-20% Sulfamic Acid and Ammonium Sulfamate and subsequently the treated fabric have been tested for fire-retardant performance and the results are shown in Table 2.

It was observed from the data given in Table 2 that treated jute fabric achieved a good and effective fire retardancy for some level of concentrations of each of the said chemicals used. LOI value observed for application of 15% & 20% Sulfamic Acid treatment is around 30. However, for use of above 10% concentration level of Sulfamic Acid (SA), it causes noticeable loss in tensile strength in treated jute fabric. Ammonium Sulfamate (AS) treated jute fabric also showed good degree of flame retardancy. 20% AS treated jute showed LOI value of 32 and also reduces the char length to minimum. But, use of more than 15% AS causes higher loss in fabric tenacity.

Further, for application of fire-retardant compounds containing nitrogen and weak nitrogen bases e.g. Urea (5 - 20%), have been found to render some degree of fire-retardant property for some level of concentration individually. It was observed that urea at higher concentration (20%) imparts moderate level of fire-retardant property to jute (LOI value 25).

So, it is thought that use of suitable and judicious mixture of such fire-retardant compounds with or without additives may give better improvement in fire-retardant performance with least affecting the desirable textile related properties.

Table 2. *Physical And Flammability Properties of bleached jute fabric treated with individual chemicals.*

Treatments	Physical properties				Vertical flammability test			LOI %
	% Loss in Tenacity	Elongation (%)	Bending Length (cm)	Whiteness Index (Hunter)	Flame Spread Time (sec)	After Glow Time (sec)	Char Length (cm)	
Untreated jute	-	3.1	4. 0	62.03	49 (BEL*)	55.0	-	20.5
Sulfamic Acid 5%	21	3.4	4.2	59.26	30 SE *	40	8	21
Sulfamic Acid 10%	35	3.5	4.2	58.63	28 SE	33	7.5	27
Sulfamic Acid 15%	41	3.9	4.6	53.65	21 SE	28	5.5	30
Sulfamic Acid 20%	51	4.1	4.4	48.15	20 SE	25	5	30.5
Ammonium Sulfamate 5%	18	3.3	4.5	59.71	28 SE	38	6	23
Ammonium Sulfamate 10%	24	3.6	4.4	57.95	20 SE	30	5.5	28.5
Ammonium Sulfamate 15%	29	3.5	4.2	55.68	15 SE	24	4.5	30
Ammonium Sulfamate 20%	36	4.0	4.9	55.63	18 SE	20	4	32
Urea 5%	8	3.6	4.3	60.34	45 (BEL)	-	BEL	20
Urea 10%	13	3.7	4.6	59.21	50 (BEL)	-	BEL	21
Urea 15%	18	3.9	4.9	58.36	56 (BEL)	-	BEL	23.5
Urea 20%	20	4.2	4.8	57.69	59 (BEL)	-	BEL	25

*BEL: Burned entire length: S.E.; Self Extinguishing

3.1. Effect of Treatment with Combination of Urea and Ammonium Sulfamate (Formulation - 1; Code J - UAS)

The effect may be better understood if the possible reaction mechanism is discussed here before proceeding for the analysis of property parameters and fire-retardant performance on application of these chemicals. So, the following postulations were made for possible reaction mechanism

3.2. Reaction Mechanism - 1

The cellulose of jute may react with Ammonium Sulfamate at elevated temperature possibly in the following manner. AS at high temperature reacts with the hydroxyl groups of jute fibre. Based on reported literature [23] the following structure for treated jute is given. According to reports in earlier literature reported [24] there might be the following chemical reactions when urea and Ammonium Sulfamate applied together on a cellulosic textiles and cured at a temperature of 140°C for 5 minutes.

$$\text{Cell-CH}_2\text{OH} + \text{NH}_4\text{OSO}_2\text{NH}_2 \rightarrow \text{Cell-CH}_2\text{OSO}_2\text{NH}_2 + \text{H}_2\text{O} + \text{NH}_3\uparrow \qquad (1)$$

Ammonium Sulfamate

$$\text{NH}_2\ \text{CO}\ \text{NH}_2 + \text{NH}_4\text{OSO}_2\text{NH}_2 \rightarrow \text{NH}_2\ \text{CO}\ \text{NH}\ \text{SO}_3\text{NH}_4 + + \text{NH}_3\uparrow \qquad (2)$$

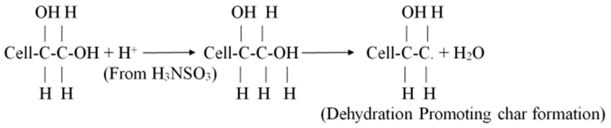
Ammonium Ureasulfonate

$$\text{Cell-CH}_2\text{OH} + \text{NH}_2\ \text{CO}\ \text{NH}\ \text{SO}_3\text{NH}_4 \rightarrow \text{Cell-CH}_2\ \text{OSO}_2\text{NH}\ \text{CO}\ \text{NH}_2 + \text{H}_2\text{O} + \text{NH}_3 \qquad (3)$$

Cellulose Ureasulfonate

$$\text{NH}_4\text{OSO}_2\text{NH}_2 \rightarrow \text{H}_2\text{O. H}_2\text{NOSO}_2\text{H} + \text{NH}_4\text{OH} \qquad (4)$$

$$\text{NH}_4\text{OSO}_2\text{NH}_2 \rightarrow \text{NH}_3\ \text{SO}_2 + \text{NH}_3\uparrow \qquad (5)$$



$$\text{Cell-}\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}\text{-}\underset{\text{H}}{\overset{\text{H}}{\text{C}}}\text{-OH} + \text{H}^+ \xrightarrow[\text{(From H}_3\text{NSO}_3\text{)}]{} \text{Cell-}\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}\text{-}\underset{\text{H}}{\overset{\text{H}}{\text{C}}}\text{-}\underset{\text{H}}{\text{OH}} \longrightarrow \text{Cell-}\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}\text{-}\underset{\text{H}}{\overset{\text{H}}{\text{C}}}. + \text{H}_2\text{O} \qquad (6)$$

(Dehydration Promoting char formation)

The changes in flammability and related textile properties of jute fabrics after being treated with combination of Urea (10%, 15%) and Ammonium Sulfamate in varying amount (viz. 10%, 15%.20%) under specific controlled conditions of treatment have been assessed and the results are shown in Table 3 & 4, for formulation 1.

The superiority of Sulfamate compounds for flame retardancy almost all over nitrogen compound is known [11 - 18]. Hence, AS is the main fire-retardant agent but function of Urea is manifold e.g. moderate flame retardancy, have some buffer action, facilitates formation of Sulfonate ester with cellulose, reduces acidity of the formulation, reduces loss in tenacity and swells cellulose to enhance penetration of the applied chemicals.

Relevant data in Table 3& 4 also indicate that for formulation (a-f) with the application of 10-20% Ammonium Sulfamate (AS) with 10% & 15% urea, LOI value is found to increase to 31-38 (from original LOI value 20.5 for untreated jute) with simultaneous loss (28-37%) in tenacity. 15% Urea and 15% AS combination (formulation 1e) showed optimum flame retardancy of jute fabric with LOI value of 38 and char length of 1 cm. It may also be noted that 10 % Urea and 15% combination (formulation 1b) AS treatment shows almost at per results with formulation 1e showing a bit lower LOI 35 and Char length 2.5 cm whereas application of 10 % Urea and 20% AS combination (formulation 1d) treatment causes 37% loss of tenacity of jute fabric with no further improvement in LOI Value. With increase in Ammonium Sulfamate (10-20%), the increase in LOI value upto a certain level (31 to 38) may be explained by increased blocking of C_6 position of Jute cellulose preventing Levoglucosan (the flammable gas produced by burning of cellulose) as per equation 3 (reaction mechanism 1) moreover higher AS produces higher amount of Sulfamic Acid (SA) (eq. 4) with H^+ ion (proton) of SA promotes char formation in jute cellulose (eq. 5) and improves fire-retardant performance and LOI value.

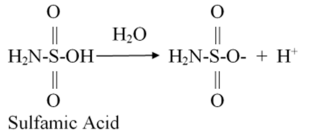
The bending length of these fire-retardant treated jute fabrics are found to be increased with the increase in concentration of AS causing the fabric handle to become slightly stiffer and hence this treatment may need to be combined with application of some chemical softener, if required. For the surface appearance properties, it is noticed that whiteness indices are found to be decreased with increase in concentration of AS, irrespective of concentration of urea used.

3.3. Effect of Treatment with Combination of Urea and Sulfamic Acid (Formulation - 2, Code J - USA)

It was thought to use of Sulfamic Acid instead of Sulfamates which may give rise to similar fire retardancy at lower cost. However it may be better understood, if possible reaction mechanism is given before proceeding to the discussion on the effect on FR performance and textile related properties. Hence, for application of these chemicals at different dosages, the following postulations were made for possible reaction mechanism between jute-cellulose and sulfamic acid in combination with urea applied by pad-dry-cure technique, cured at 140°C for 4 - 5 min.

3.4. Reaction Mechanism - 2

Also jute cellulose may react with Sulfamic Acid (H_3NSO_3) at elevated temperature possibly in the following manner as shown in eq. 8 at higher temperature react (more than 205°C, its decomposition temperature) with the C_6 position - primary hydroxyl groups of jute cellulose. So, actually as jute fabrics cannot be treated above 130 - 140°C that also for 4 - 5 mins eq. 8 does not happen. Following reaction as shown in eq. 9 and eq. 10 may occur when Urea and Sulfamic Acid are applied together in a combination at a temperature of 140°C. Sulfamic acid may be hydrolysed in presence of water as shown in eq. 7. H^+ liberated from sulfamic acid then may follow the eq. 6 in reaction mechanism 1 for promoting char formation in jute cellulose when burns and thus became fire - retardant.



$$H_2N\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}OH \xrightarrow{H_2O} H_2N\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}O^- + H^+ \qquad (7)$$

Sulfamic Acid

$$\text{Cell - }CH_2OH + H_3NSO_3 \rightarrow \text{Cell - }CH_2\,NH_2\,SO_2 + H_2O \qquad (8)$$

$$NH_2\,CO\,NH_2 + NH_3OSO_2 \rightarrow NH_2\,CO\,NH\,SO_3H + + NH_3\uparrow \qquad (9)$$

Urea Sulfamic Acid Sulfonated Urea

$$\text{Cell - }CH_2OH + NH_2\,CO\,NH_2SO_3 \rightarrow \text{Cell - }CH_2\,OSO_2\,CONH_2 + H_2O + NH_3 \qquad (10)$$

As the eq. 8 has limited possibility to occur eq. 9 & eq. 10 are the most possibilities. The changes in flammability and related textile properties of jute fabrics after being treated with combination Urea (10%, 15%) and Sulfamic Acid in varying amount (viz. 5%, 10%, 15%) under specific controlled conditions of treatment have been assessed and the results are shown in Table 3 & 4, formulation 2.

Relevant results shown in Table 3 & 4 for formulation 2 also indicate that with the application of 5 - 15% Sulfamic Acid along with 10% & 15% urea, LOI value is found to increase to 26-35 (from original LOI value 20.5) with some loss in tenacity (30-47%) in treated fabric. 15% Urea and 10% Sulfamic Acid combination (formulation 2e) showed optimum flame retardancy of jute fabric with LOI value of 35 and char length of 2cm. It may also be noted that 10 % Urea and 10% Sulfamic Acid combined treatment shows less LOI value 28.5 with loss of fabric tenacity (36 %) whereas application of 10 % Urea and 15% Sulfamic Acid treatment causes 47% loss of tenacity of jute fabric having LOI value of 33. Thus with increase in concentration of Urea from 10% to 15% keeping SA concentration same (10%) the LOI value increases from 28.5 to 35 is due to the specific characteristics of both Urea and SA that its amino group is linked to electron withdrawing centres that can participate easily in delocalized bonding with jute cellulose. However Urea is basic in nature and SA is acidic in nature and hence, SA in combination with Urea neutralizes some of the strong action of SA acids and reduces acidic degradation. However fire-retardant performance for formulation 2a-2f with direct Sulfamic Acid than Ammonium Sulfamate causes higher loss in tenacity and lower LOI value than formulations (1a-1f), due to more acidic degradation by Sulfamic Acid of cellulose/hemi - cellulose chain scission of jute rather than coupling with cellulose and consumption of more Urea neutralizing acidity of SA rather than forming a coordinate complex for attaching to cellulose of Jute.

The bending length of these fire-retardant treated jute fabrics are found to be however increased to some extent with the increase in concentration of Sulfamic Acid causing the fabric handle to become slightly stiffer, like Sulfamate and should post treated or simultaneously treated with some softener for combating this. For the surface appearance properties, it is noticed that whiteness indices are found to be decreased with increase in concentration of Sulfamic Acid, irrespective of concentration of Urea used.

3.5. Effect of Treatment with Combination of Urea and Ammonium Sulfamate with Binder (Formulation - 3, Code J-UAS - AC)

The wash stability (upto 1-5 wash cycle) of Urea - Ammonium Sulfamate is slightly better than Urea - Sulfamic Acid treated jute fabric as shown in Table 5. So to make the formulation wash stable to some extent a commercial binder treatment was tried along with Urea - Ammonium Sulfamate formulation under specific controlled conditions and the results are shown in Table 3 & 4.

Relevant results in Table 5 indicate that the changes in flammability and related textile properties along with the wash stability (upto 1-5 wash cycle) have been assessed for jute fabrics after being treated with combination Urea (15%) and Ammonium Sulfamate (15%) without any binder, after 1 -5 was cycle. The reduction of LOI value in this case (Urea (15%) and Ammonium Sulfamate (15%) combination) is almost 2 unit per wash cycle and after 5 wash the LOI is 29 (from before wash 38).

Relevant data in Table 3 & 4 also indicate that with the application of Urea (15%) and Ammonium Sulfamate (15%) along with Arkofix NEC Plus Lid (50gpl) & Ceralube HD .In Lid (30gpl) with Magnesium Chloride as catalyst (10gpl), LOI value is found to be almost same as without binder, i.e. 38 (from original LOI value 25) and char length of 1.5 cm with a little higher loss in tenacity (32%) with binder as said above. The reduction of LOI value in this case (Urea (15%) and Ammonium Sulfamate (15%) combination with binder) is almost 0.5 to 1 unit per wash cycle and after 5 wash the LOI is 36 (from before wash 38). Thus the effectiveness of this binder is proved to be important but still not highly satisfactory and need more research for obtaining more durability.

3.6. Effect of Treatment with Combination of Varying Concentration of Saraflam - CWF (Formulation 4, Code J - S - CWF)

Saraflam-CWF, a commercial grade fire-retardant agent based on THPC, (Tetrakis Hydroxy methyl phosphonium chloride) has been reported by the supplier to provide reasonable fire-retardant performance on cellulosic. To understand the rating of fire-retardant performances of newer combination of indigenous chemicals used in this present work as compared to the fire-retardant performance that obtained by Saraflam-CWF additional experiment were carried out by applying varying concentration of Saraflam-CWF on Jute Fabric. The changes in important textile related properties of jute fabrics after being treated with formulation-4 [Saraflam-CWF] in varying amount viz.10%, 20%, 30%, 40% have been assessed and relevant results shown in Table 3 & 4. Results for formulation 4 in Table 3 & 4 indicates that there is noticeable improvement in fire-retardant performance by almost all the treatments with Saraflam-CWF (Formulation 4) as indicated in terms of LOI values, flame spread time, after glow time and char length. The fire-retardant performance is also found to be increased with increase in concentration of Saraflam-CWF from 10% - 40% in Formulation 4. Highest value of LOI 33-35 is achieved with 30%-40% application of Saraflam-CWF as compared to LOI value 38 obtained in case of formulation 1e. The flame spread time, after glow time and char length are also found to be higher than the corresponding formulation 4 & formulation 1e it is found that strength loss is higher in case of formulation 4c than that of Formulation 1e. There is always some loss in tensile strength for all the fire-retardant, however comparing treatments using formulation 4.The loss of tensile strength is found to increase with the increase in the percentage application of Saraflam-CWF. For all the treatment with Saraflam-CWF formulation 4, the bending length values are found to be increased as usual with the increase in percentage application of Saraflam-CWF in Formulation 4. And also whiteness indices are to some extent deteriorated with Saraflam-CWF treatment in Formulation 4 for jute fabrics.

Thus it is evident from experimental data in Table 3&4 and Fig 1 that the fire-retardant performance of 15% Urea and 15 % AS treated jute fabric is found to be superior to even commercially available/non-ecofriendly fire-retardant formulations at the same dose level and even for higher % of application.

Table 3. *Physical properties of bleached jute fabric treated with FR - formulations 1 - 4.*

Treatments	**Physical properties**			
	% Loss in Tenacity	**Elongation (%)**	**Bending Length (cm)**	**Whiteness Index (Hunter)**
Untreated jute	-	3.10	4. 0	62.03
Formulation 1; Code J - UAS (Urea & Ammonium Sulfamate)				
Formulation 1a U 10%; AS 10%	28	4.12	4.1	59.61
Formulation 1b U 10%; AS 15%	30	4.31	4.2	58.38

Treatments	**Physical properties**			
	% Loss in Tenacity	**Elongation (%)**	**Bending Length (cm)**	**Whiteness Index (Hunter)**
Formulation 1c U 10%; AS 20%	37	4.53	4.5	57.46
Formulation 1d U 15%; AS 10%	25	4.41	4.6	55.73
Formulation 1e U 15%; AS 15%	28	4.62	4.8	56.42
Formulation 1f U 15%; AS 20%	35	4.73	5.0	58.31
Formulation 2; Code J - USA (Urea & Sulfamic Acid)				
Formulation 2a U 10%; SA 5%	31	4.81	4.0	58.24
Formulation 2b U 10%; SA 10%	36	4.31	4.1	56.87
Formulation 2c U 10%; SA 15%	47	4.81	4.2	54.12
Formulation 2d U 15%; SA 5%	30	4.50	4.3	57.56
Formulation 2e U 15%; SA 10%	34	4.90	4.1	55.34
Formulation 2f U 15%; SA 15%	42	4.87	4.2	54.91
Formulation 3; Code J - UAS - AC (Urea & Ammonium Sulfamate with commercial binder)				
Formulation 3 U 15%; AS 15%; Arko 50gpl; Celu 30gpl; MgCl2	32	4.1	5.3	54.53
Formulation 4; Code J - S - CWF (commercial Fire - retardant chemical SARAFLAM - CWF)				
Formulation 4a S - CWF 10%	23	4.1	4.5	59.01
Formulation 4b S - CWF 20%	28	4.4	4.7	57.52
Formulation 4c S - CWF 30%	33	4.3	5.0	56.46
Formulation 4d S - CWF 40%	35	4.5	5.2	55.84

Table 4. *Flammability properties of bleached jute fabric treated with FR - formulations 1 - 4.*

Treatments	**Vertical flammability test**			**LOI %**
	Flame Spread Time (sec)	**After Glow Time (sec)**	**Char Length (cm)**	
Untreated jute	49.0 BEL*	55.0	-	20.5
Formulation 1; Code J - UAS (Urea & Ammonium Sulfamate)				
Formulation 1a U 10%; AS 10%	25 SE	30	3.5	31.0
Formulation 1b U 10%; AS 15%	15 SE	23	2.5	35.0
Formulation 1c U 10%; AS 20%	8 SE	11	2	36.0
Formulation 1d U 15%; AS 10%	10 SE	7	2.5	32.0
Formulation 1e U 15%; AS 15%	5 SE	3	1	38.0
Formulation 1f U 15%; AS 20%	5 SE	3	1	38.5
Formulation 2; Code J - USA (Urea & Sulfamic Acid)				
Formulation 2a U 10%; SA 5%	24 SE	30	4.0	26.0
Formulation 2b U 10%; SA 10%	14 SE	25	3.5	28.5
Formulation 2c U 10%; SA 15%	9 SE	11	2.5	33
Formulation 2d U 15%; SA 5%	13SE	9	3.0	26.5
Formulation 2e U 15%; SA 10%	7 SE	5	2.0	35
Formulation 2f U 15%; SA 15%	6 SE	5	2.0	34.5
Formulation 3; Code J - UAS - AC (Urea & Ammonium Sulfamate with commercial binder)				
Formulation 3 U 15%; AS 15%; Arko 50gpl; Celu 30gpl; MgCl2	4SE	2	1.5	38.0
Formulation 4; Code J - S - CWF (commercial Fire - retardant chemical SARAFLAM - CWF)				
Formulation 4a S - CWF 10%	16 SE	10	5.0	29.5
Formulation 4b S - CWF 20%	11 SE	8	4.5	30.0
Formulation 4c S - CWF 30%	8 SE	5	3.8	33.5
Formulation 4d S - CWF 40%	8 SE	5	3.2	35.0

*BEL: Burned entire length: S.E.; Self Extinguishing

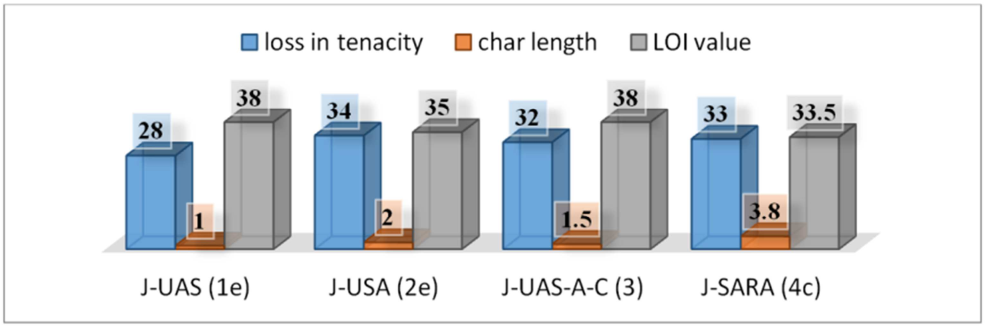


Fig. 1. *Comparison between commercially available FR Chemical (SARAFLAM) and newer formulation Developed.*

3.7. Wash Stability of Different Fire-retardant Treated Jute Fabrics

After normal washing of this fire-retardant treated jute fabrics with 0.1% non-ionic detergent solution for 30 minutes at room temperature, the fire-retardant performance is found to be decreased to some extent after 1-5 cycles of washing and observed results are shown in Table 4. It is observed that formulation 1e (J-UAS) the reduction in LOI value per cycle is almost 2 unit, for formulation 2e (J-USA) the value is almost same, while formulation 3 i.e. modified formulation 1e with admixture of a binder (Arkofix NEC Plus) show much higher wash stability of the formulation upto 5 wash cycles and the reduction in LOI value per cycle is 1 unit in this case. The higher loss of LOI value in all the cases except formulation 3 is due to the unfixed fire-retardant chemicals applied on and also for hydrolysis of some already fixed fire-retardant chemicals etc., however which is not so rapid after 3rd or 5th wash because such unfixed chemicals are washed out in 1st and 2nd washes. However, the changes of LOI value observed in 3rd & 5th wash is due to the hydrolysis of the already fixed chemicals.

Table 5. Flammability property of the different Formulation treated fabric at the optimized level after soap washing.

Formulation Code	Treatment	LOI - value Before Soap Washing	LOI –value after Soap Washing		
			1st wash	3rd wash	5th wash
J - UAS (1e)	Urea –15%, Ammonium Sulfamate – 15%	38	34	30	29
J - USA (2e)	Urea –15%, Sulfamic Acid – 15%	35	29	28	27
J - UAS - AC (3)	Urea (15%) and Ammonium Sulfamate (15%), Arkofix NEC Plus Lid (50gpl) & Ceralube HD. In Lid (30gpl) & Magnesium Chloride as catalyst (10gpl)	38	37	36.5	36
J - S - CWF (4c)	Saraflam CWF - 30%	33.5	31	29	28

3.8. Analysis of the Thermal Decomposition of Treated and Untreated Jute Fabric

The thermal degradation behaviour is extremely important for flame retardant materials [25]. Thermo-Gravimetric Analysis (TGA) in air and Differential Scanning Calorimetric (DSC) study in air of jute and chemically treated jute samples are shown in Fig 2 & Fig 3 respectively. The effectiveness of Fire-retardant chemicals on cellulosic material may be indicated by substantial lowering of the decomposition temperature as well as higher char formation (leaving higher residue at max. temp.) by treated fabrics as compare to the untreated fabric.

TGA analysis of jute fabric treated with Sulfamate/Sulfamic Acid based fire-retardant chemicals with or without additives (formulations 1 to 3) show that residue left at 500°C is more in these cases than that of untreated jute as shown in Table 6. Amongst the different fire-retardant treated jute fabric, it is observed that the treatment with formulation 3 leaves highest residue (25.5% at 500°C) or min. weight loss whereas residue of untreated jute is almost nil at 500°C. Therefore, the formulation 3 is expected to give best fire-retardant property. The LOI value and vertical flammability test and other flammability performance also confirm this observation as shown in Table 4 earlier. Treatment with formulation 1e also leaves a residue of 20.5% (2nd highest) at 500°C which is also matched with the observed higher flame retardant properties amongst other treatments and is 2nd best after formulation 3. Residue left for formulation - 4c (with 30% Saraflam CWF) treatment is 18% at 500°C which signify high level of fire retardancy for this commercial fire-retardant agent. However, jute fabric treated with Formulation 2e showed residue of 15% at 500°C which is somewhat lesser than other treatments. This can be explained by lesser extent of Sulfonation to jute cellulose as compared to other treatments on jute cellulose.

Table 6. Weight loss % of treated and untreated jute fabrics subjected to heating in varied temperature, indicating nature of thermal decomposition.

Temperatures	Approximate Residue Left (in %) at respective temperatures (°C)						
Formulations	80	200	250	350	400	450	500
Untreated Jute	92	88	86	38	29	13	Nil
J - UAS (1e)	94	90	63	45	37	28	20.5
J - USA (2e)	92	87	59	40	31	22	15
J - UAS - AC (3)	97	89	74	43	36	28	25.5
J - S - CWF (4c)	96	89	64	25	22	19	18

From the Thermo-gravimetric curve, the Initial Weight loss Temperature (T_{onset}) of untreated jute and treated jute can be found. Formulation-1 to 4 shows the T_{onset} as 245°C, 270°C respectively which are 35 - 10°C lower than that of untreated jute (280°C). This indicates that sulfamate based formulations facilitates the degradation of jute forming lesser amount of volatile product with increasing char formation giving rise to higher LOI values.

All the DSC thermograms for 4 types of fire-retardant treated Jute Fabrics and also untreated jute fabric is shown in Fig 3. DSC thermograms for bleached jute shows broad endothermic peak at 50°C (for evaporation of moisture present in jute), a broad exotherm with a hump at 325°C (for degradation of hemicellulose part of jute), a sharp endotherm i.e. peak at 36°C (for degradation of cellulose component of jute) and a broad exotherm with two small hump at 450°C &

460°C (for degradation of lignin part of jute) which corroborates earlier findings of thermal behaviour study of control jute by DSC [26]. The thermal decomposition temperatures in treated jute fabrics is found to be gradually decreases for all four formulations. In DSC Thermograms for all these four treatments the thermal decomposition rate is found to be highest increased in case of formulation 3 followed by formulation 2e followed by the next increase in formulation 1e.

All these DSC thermograms in Fig 3 for fire-retardant treated jute fabrics the changes in pattern of thermal degradation showing only one broad hump instead of two different exotherm & one endotherm at specific temperature as shown in bleached jute fabrics for degradation of major 3 constituents of jute (hemicellulose degradation at 325°C, cellulose degradation at 364 - 365°C and lignin degradation at 450 - 460°C) indicate that all these fire-retardant chemicals perhaps chemically attached with both cellulose, hemicellulose and lignin changes the thermal degradation behavior with early degradation of all these components within 250°C - 400°C /425°C by showing a bigger combined exothermic hump.

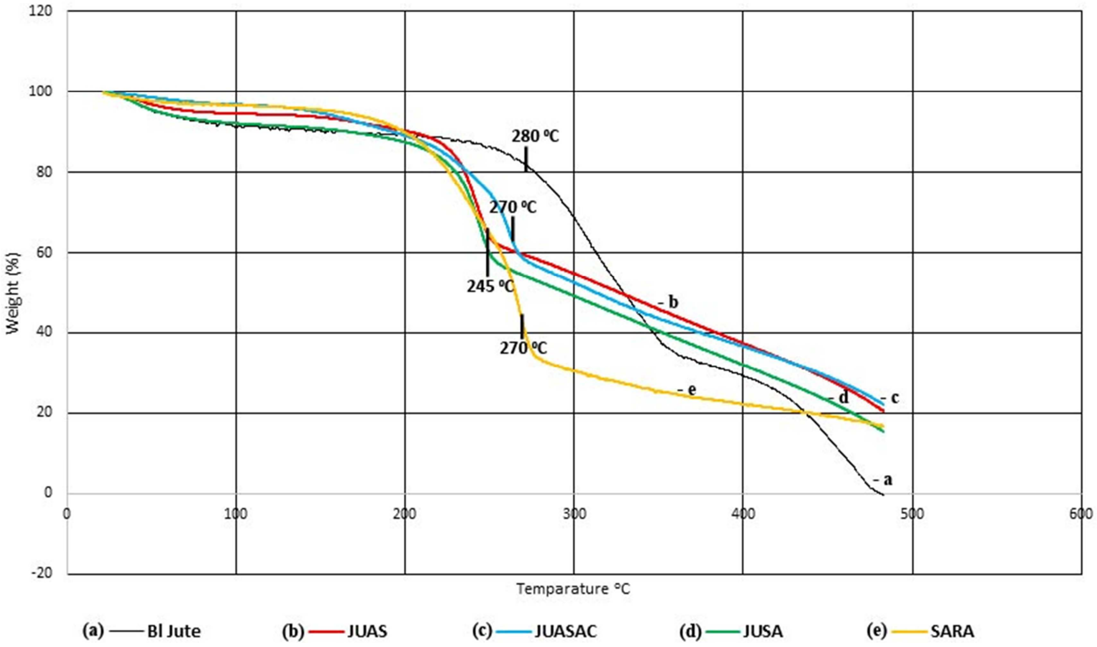


Fig. 2. *TGA Thermograms of Treated & untreated jute fabric.*

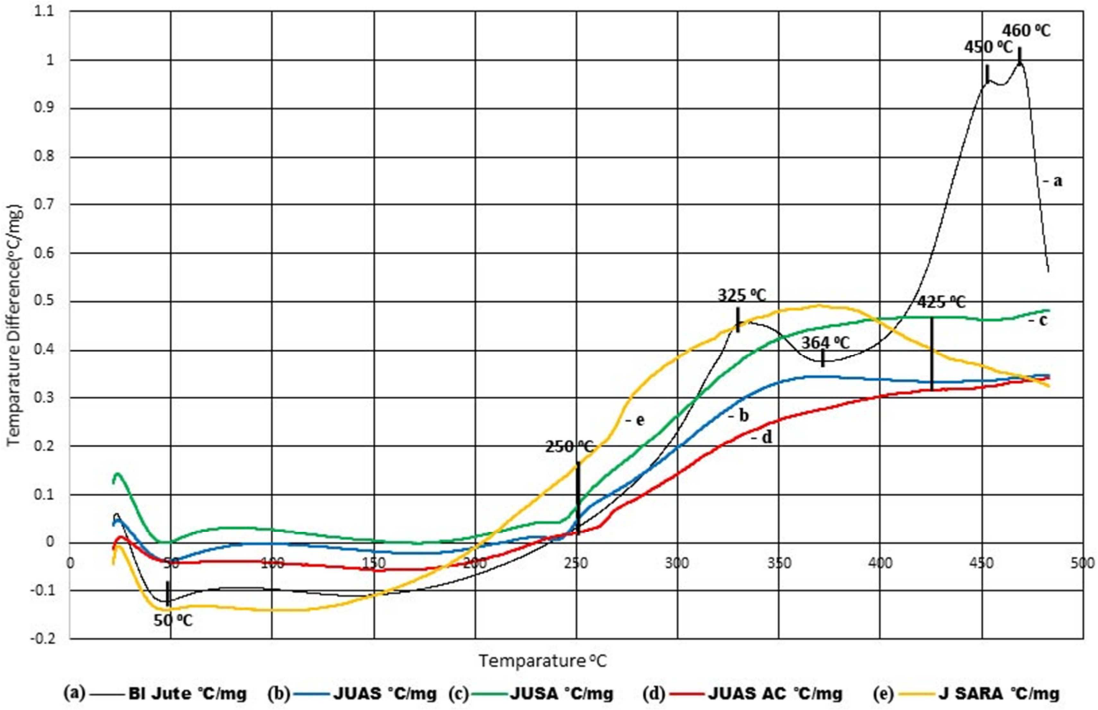


Fig. 3. *DSC Thermograms of Treated & untreated jute fabric.*

3.9. FTIR Studies of Untreated & Fire-retardant Jute Fibres

FTIR spectra of (a) Untreated Jute; (b) J - UAS - Formulation 1e; (c) J - USA - Formulation 2e; (d) J - UAS - AC - Formulation 3; (e) J - Sara - Formulation 4c are shown in *Spectra* (a) to (e) in *Fig*. 4 from wave no. 4000 cm $^{-1}$ - 500 cm $^{-1}$. For all the five FTIR spectra there are some common characteristic features due to its three major constituents alpha-cellulose, hemi-cellulose and lignin is stated in tabular form in the following Table 7 [27, 28]:

Table 7. *Common Transmittance peaks with their significance of untreated and treated jute fabric.*

Sl. No.	Transmittance Peaks in FTIR Spectra	Significance
1	550 cm^{-1}	for −OH out of plane bending
2	890 cm^{-1}	for β - glycosidic linkage
3	1030 cm^{-1}	assigned to aromatic C - H in plane deformation & C - o deformation for primary alcohol in lignin
4	1245 cm^{-1}	for −C−O−C and −C=O stretching in xylan side substituent and lignin aromatic C=O stretching
5	1335 cm^{-1}	for −OH in plane bending
6	1370 cm^{-1}	for C - H deforming (symmetric) may be attributed to cellulose, hemicellulose and lignin
7	1446 cm^{-1}	for C - H deforming (asymmetric) may be attributed to lignin
8	1508 cm^{-1}	for lignin aromatic ring vibration and stretching
9	1596 cm^{-1}	for C=C stretching in lignin olefinic units
10	1735 cm^{-1}	for C=O stretching of ester group
11	2355 cm^{-1}	for C−H stretching in polysaccharide chains
12	2905-2920 cm^{-1}	for C−H stretching vibrations of aliphatic methylene groups
13	3350 cm^{-1}	for H bonded H - O Stretching

J-UAS- Formulation 1e treated jute [Spectrum (b), Fig. 4], by and large retain similar characteristics in their FTIR spectra as that obtained for the bleached jute, thereby showing some change in functional group pattern by the said treatment, though show some minor decrease / increase or weakening / and some additional peaks observed. In Spectrum (b), Fig. 4, for J-UAS - Formulation 1e treated jute, there is introduction of a new peak at 810 cm^{-1} (indicating the presence of $–HSO_4$) and there is a minor increase in band intensity at 1030 cm^{-1} (due to $–OSO_3$ -) and appearance of $–SO_4^{2-}$ stretching vibration of sulfamate salt at 1109 cm^{-1} due to sulfamation of ester groups during the treatment. Additional appearance of Transmittance peaks between 1300 cm^{-1} to 1400 cm^{-1} is attributed to C-N stretching vibration in primary and secondary amines due to incorporation of urea in the formulation, increase in the band intensity of the peak at 1446 cm^{-1} is ascribed the presence of $N\text{-}CH_2$ component [29] in the treated jute. Transmittance peaks corresponding to 1681 cm^{-1} is attributed to C=O stretching vibration in intra - molecular H bonded acids. Another huge peak at 1681 cm^{-1} is attributed to NH^+ stretching vibration in $C=NH^{+.}$ The treatment results in some modification of both hemicellulose and cellulose is evident from FTIR Spectrum (b), Fig. 4, which shows some decrease in band size at 2920 cm^{-1} and 4000 cm^{-1} as compared to the corresponding bands in FTIR Spectrum (a), Fig. 4 for bleached jute. Also the new sharp peak in this Spectrum (b), Fig. 4 at 2370 cm^{-1} is observed for N-H vibration of urea present in the formulation.

J-USA - Formulation 2e treated jute [Spectrum (c), Fig. 4], is showing some minor changes in functional group pattern by the said treatment compare to the Spectrum (b), Fig. 4, discussed earlier though some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed. In Spectrum (c), Fig. 4, for J-USA - Formulation 2e treated jute, there is difference in the band intensity at 810 cm^{-1} (indicating the presence of $–HSO_4$) and a duplet arrived at 989 cm $^{-1}$ near 1030 cm $^{-1}$ (due to $–OSO_3$ -) The increase in band intensity of the transmittance peaks between 1700 cm^{-1} to 1400 cm^{-1} is attributed to more reaction (in more acidic condition partial loss of hemicellulose and cellulose) as compare to Ammonium sulfamate in the treated jute. Also the new sharp peak in this Spectrum (b), Fig. 4 at 2370 cm^{-1} is observed for N-H vibration of urea present in the formulation. Transmittance peaks corresponding 3800 cm^{-1} to 3500 cm^{-1} is attributed to O-H stretching free OH and increased H bonded OH for incorporation of these chemicals.

J-UAS-AC Formulation 3 treated jute [Spectrum (d), Fig. 4], is modified formulation of J-UAS- Formulation 1e treated with a commercial binder for improving the durability of the treatment it largely retain similar characteristics in their FTIR spectra as that obtained for the J-UAS Formulation 1e treated jute Spectrum (b), Fig. 4, thereby showing some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed. Only the major change is appearance of a duplet at 3000 cm^{-1} -2750 cm^{-1} spectral region denotes the presence of polyolefin attributed to - CH_2 -asymmetric and symmetric stretching vibration (as additional polyolefin Characteristics for incorporation of PE - emulsion softener along with the fixing binder to improve the stability of this fire-retardant formulation).

For comparison purpose the jute is treated with a THPC based chemical commercially available chemical SARAFLAM. J-SARA Formulation 4c treated jute FTIR spectra [Spectrum (e), Fig. 4] compare to the FTIR spectra as that obtained for the bleached jute, thereby showing some change in functional group pattern by the said treatment, though show some minor decrease / increase or weakening / strengthening of some FTIR peaks / bands as observed. In Spectrum (e), Fig. 4, there is introduction of a new peak at 1646 cm^{-1} (indicating C-O stretching vibration) and there is a increase in band intensity at 2355 cm^{-1} (due to N-H stretching vibration for associated amines) and appearance of a duplet in the region 2839 cm^{-1} with 2920 cm^{-1} signifies C-H stretching and deformation vibration of CHO due to the oxidation of hemicellulose and cellulose during the phosphorylation treatment. The treatment results in blocking of some -OH group due to Phosphorylation which is evident from FTIR Spectrum (b), Fig. 4, which shows some decrease in band size at 3350 cm^{-1} as compared to the corresponding bands in FTIR Spectrum (a), Fig. 4 for bleached jute.

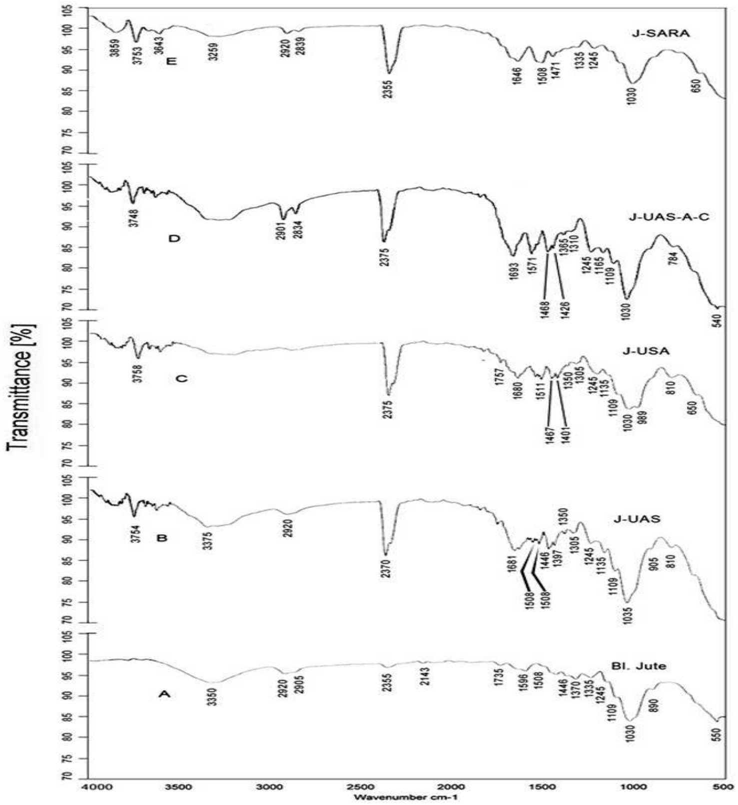


Fig. 4. *FTIR Spectra of treated and untreated jute.*

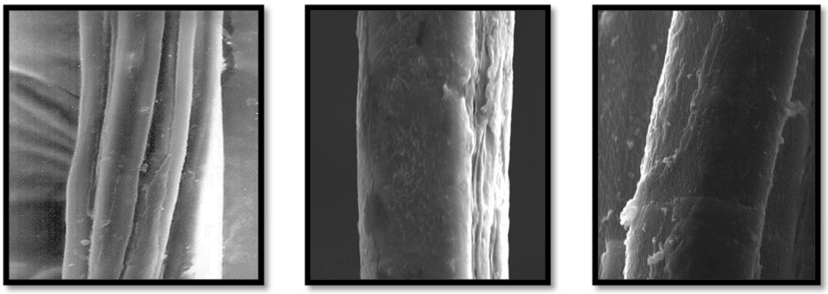


Fig5a: Bleached Jute

Fig5b: J - UAS

Fig5c: J - USA

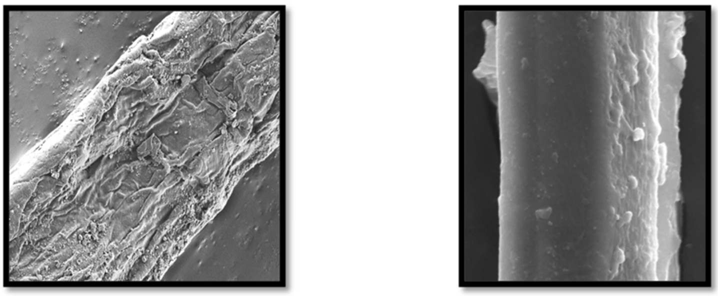


Fig5d: J - UAS - AC

Fig5e: J - SARA

Fig. 5. *Scanning Electron Micrographs of Untreated and Treated Jute Fibres.*

3.10. Study of Surface Morphology of Untreated & Fire-retardant Jute Fibres

The scanning electron micrographs showing the surface appearance of bleached and different fire-retardant chemical treated jute fabrics (after thorough washing water and alcohol) are shown in Fig. 5 (a - e). SEM – micrograph 5a of bleached jute fabric show the smoother surfaces with small serrations, smooth whereas all the fire-retardant treated jute fibres (for formulation 1-4) show that there are some distinct surface deposition having varying degree of uniformity and non-uniformity with extraneous deposition of anchored fire-retardant compounds on the fibre surface. Amongst all the fire-retardant treated jute fibres SEM micrograph 5d shows a coated surface appearance having almost an irregular but continuous coating of specific fire-retardant chemical in presence of a binder resin applied on it, making the serrations of multi cellular jute while SEM micrograph 5e also shows a similar look of continuous coating, on surface of jute fibre making the serrations of multi cellular jute. But SEM micrograph 5b also shows lesser deposition of fire-retardant chemicals on the fibre surface, partly keeping serrations of multi cellular jute visible. Thus the SEM–micrographs clearly indicate the surface deposition of fire-retardant chemicals with or without additional binder applied, even after washing the samples in water followed by alcohol & acetone, indicating the firm anchorage of the deposited chemicals on jute.

4. Conclusions

Application of sulfamic Acid, Ammonium Sulfamate and urea on jute fabric individually renders treated jute fabric some degree of fire-retardancy achieving LOI value from 30 - 32 with some loss of tenacity in all the cases, finally showing the better result by the treatment with 20% Ammonium sulfamate. Combination of 15% Urea and 15% Ammonium sulfamate shows a synergistic effect achieving a LOI value up to 38 with char length of 1 cm at the cost of 28% loss in tenacity. This particular combination is found to be better than an equivalent dose of application of 15% Urea and 15% Sulfamic Acid achieving LOI up to 34.5, char length 2 cm and 42% loss of tenacity. Test of wash stability indicates that though the above combination stated in 5.2.2 (i.e. 15% Urea and 15% Ammonium sulfamate) gives LOI value up to 38, but the effect is gradually reduces with the no. of wash cycle and become 29 from 38 after 5 wash cycle. Hence the use of 5% Arkofix commercial binder (Polycarboxylic Acid based) along with 3% Ceralube (Polyethylene based softener) shows much better wash fastness and LOI value become 36 from 38 after 5 wash cycle for application of 15% Urea and 15% Ammonium sulfamate + 5% Arkofix commercial binder + 3% Ceralube.

A comparison with commercially available fire-retardant agent for cellulose at the equivalent doses i.e 30% of SARAFLAM-CWF (THPC based) as compared to application of 30% Fire - retardant chemical as stated earlier (i.e. 15% Urea and 15% Ammonium sulfamate), reveals that the LOI value is 4.5% higher and tenacity loss is 5% lower for Urea and Ammonium Sulfamate combination than those for SARAFLAM-CWF. Analysis of DSC & TGA also show earlier degradation of hemicellulose and cellulose component of Urea and Ammonium Sulfamate combined treated jute substrate with or without binder, with higher residue for heating up to 500^{O}C than untreated jute and SARAFLAM (a commercial fire-retardant agent) treated jute. The maximum thermal stability is obtained with 15% Urea and 15% Ammonium Sulfamate with binder confirming better fire-retardant performance with this treatment. FTIR spectra for differently treated jute for the above said treatment (Urea, Ammonium Sulfamate, Sulfamic Acid with binder in different combination) confirms in corporation of O - SO_3 group by a duplet at 810 cm^{-1} and 905 cm^{-1} as well as 1681 cm^{-1} is attributed to NH^+ stretching vibration in $C=NH^+$ and 1300 cm^{-1} to 1400 cm^{-1} is attributed to C-N stretching vibration in primary and secondary amines due to incorporation of Urea proving the chemical anchoring of both urea and ammonium sulfamate to jute for the observed fire-retardant effect, moreover appearance of a duplet at 3000 - 2750 cm^{-1} spectral region denotes the presence of polyolefin attributed to -CH_2 asymmetric and symmetric stretching vibration for incorporation of PE - emulsion softener another peak at 1681 $cm^{-1}$is attributed to C=O stretching vibration for the polycarboxyl based binder Arkofix which is incorporated to improve the wash stability of the formulation. Scanning Electron Micrographs of untreated and treated jute fabric before and after treatment with Urea, Ammonium Sulfamate, Sulfamic Acid and the commercial binder in different combination show that all the treatments show some masking effect by deposition of the fire-retardant chemicals to a large extent amongst all the said treatment the deposition of fire-retardant chemical appears to be maximum in the case of jute treated with 15% Urea and 15% Ammonium sulfamate with binder showing better physical coverage and perhaps better anchoring of the said fire-retardant chemicals.

Finally it is concluded that jute treated with 15% Urea and 15% Ammonium sulfamate + 5% Arkofix commercial binder + 3% Ceralube gives very good fire - retardant performance with lower loss of tenacity and other textile related properties achieving LOI value up to 38 with 1 cm char length and well stable to 5 normal wash cycle.

Acknowledgements

The authors express their sincere thanks to the Head of the Department, Department of Jute & Fibre Technology, Institute of Jute Technology, University of Calcutta for all sorts of administrative support to carry out this work. The authors are also thankful to National Jute Board (earlier JMDC), Ministry of Textiles, Govt. of India for sponsoring JTM - R&D - project to this Institute under Jute Technology Mission –MM - IV - scheme 7.1 as project no. 10 on 'Development of fire-retardant jute fabric' during 2009 - 2012.

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Fire retardant finish of jute fabric with nano zinc oxide

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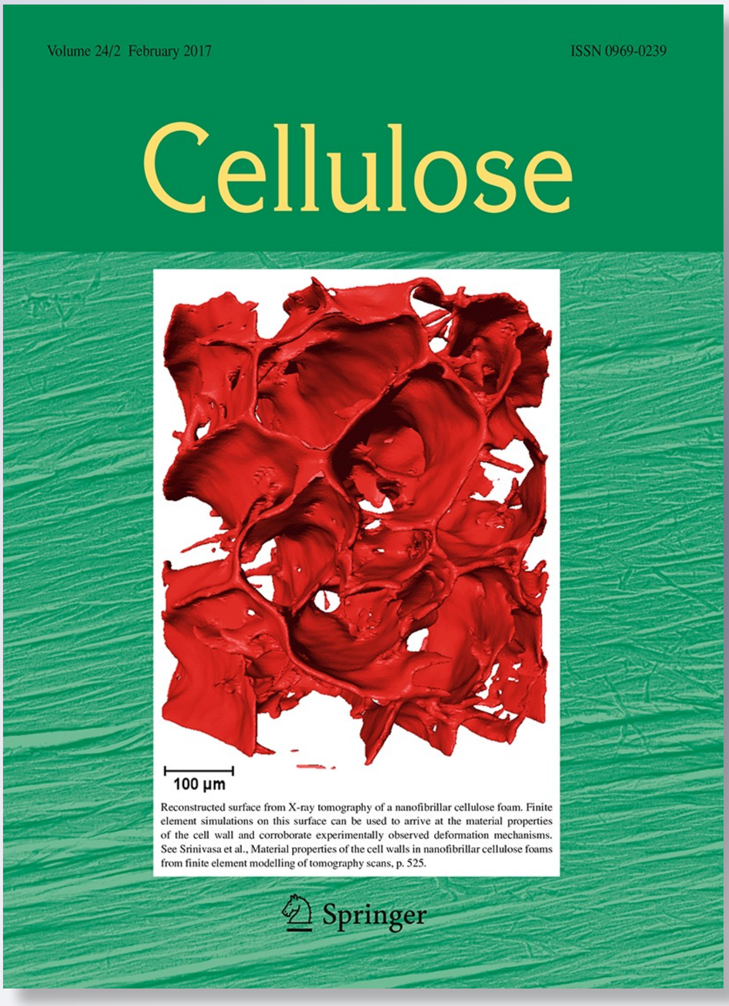
Cellulose

ISSN 0969-0239
Volume 24
Number 2

Cellulose (2017) 24:1143-1157
DOI 10.1007/s10570-016-1171-z



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Cellulose (2017) 24:1143–1157
DOI 10.1007/s10570-016-1171-z

ORIGINAL PAPER

Fire retardant finish of jute fabric with nano zinc oxide

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Received: 12 November 2015 / Accepted: 19 December 2016

Abstract Nano zinc oxide (ZnO) was applied on bleached jute fabric to impart fire retardant finish. Nano zinc oxide was prepared from aqueous Zinc acetate by co-precipitation method in the presence of NaOH followed by calcination at 600 °C. It was then applied on the jute fabric using an aqueous solution of Potassium Methyl Siliconate as dispersing media by pad-dry method. Among different dosages of nano ZnO treatment, application of a 0.01% nano ZnO on jute fabric showed reasonably good fire retardant performance. Nano ZnO powder so produced was characterized by confirming particle size and its distribution along with XRD. Nano zinc oxide particles coating on treated jute fabric was evidenced by FTIR, EDX, AAS and SEM analysis. Analysis of physical properties of the coated jute fabric has shown some extent of reduction in fabric tenacity, whiteness index and increase in stiffness as compared to untreated bleached jute fabric. The coating had reasonably good LOI values for as many as five wash cycles.

Keywords Char length · Fire retardant finish · Jute · Limiting oxygen index · Potassium methyl siliconate (PMS) · Nano zinc oxide

Introduction

With the advent of nanotechnology, nano Zinc oxide (ZnO) has been used for applications in making nano semi-conductors, solar energy conservers, electrostatic dissipate coatings, UV-protective coatings, chemical sensors (Chen et al. 2006), etc. Use of nano ZnO for fire retardant finish of textiles is rather a new conception. Fire retardant finishing of jute using different organophosphates and other chemicals are available from earlier reports (Matei et al. 2008; Reddy et al. 2007; Klingshirn 2007). Some decorative furnishing and other fabrics require a fire-retardant finish. The major problems associated with fire retardant formulations for jute are high chemical add-on, noticeable strength loss, yellowing of the treated fabric, stiffness, and high cost. Moreover, most of the fire retardant method developed for jute is non-durable type. So it is highly essential to find a solution to obtain an eco-friendly and somewhat durable fire-

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retardant formulation of jute. Moreover, no reports are known so far for imparting a fire retardant finish on jute fabrics with nano ZnO. Hence, this method may have an importance to find really a newer recipe/formulation based on nano ZnO application for good fire retardant performance with minimum sacrifice of fabric tenacity. Some conventional fire retardant finishes lose its effectiveness during washing with soap/alkaline detergent or hard water. An ideal fire retardant fabric for textile applications must be reasonable fast to washing, eco-friendly and cost effective too, as fire retardant jute fabrics are seldom washed (not more than once in a year), the fire retardant finish should be fast to five wash cycles.

Particles having 30–100 nm are special group of nano sized materials with many unique features are used extensive applications in diverse field (Matei et al. 2008). However, nano textiles finishes have a particle size around 30–500 nm, which is considered as nano particle textile finish. The formation of nano particles changes the properties of many conventional materials (Reddy et al. 2007). Recent advances in the field of nanotechnology, leads to the preparation of highly ordered nano particulates of any size and shape. Among metal oxide nano particles, nano ZnO as one of the multifunctional inorganic nano particles which has many significant features such as chemical and physical stability, high catalytic activity, effective antibacterial activity as well as intensive ultraviolet and infrared adsorption with a broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, etc. (Ghule et al. 2006). The antimicrobial (Azam et al. 2012; Rajendra et al. 2010), self cleaning (Çakır et al. 2012) as well as UV protection (Kathirvelu et al. 2009; Becheri et al. 2008; Shateri-Khalilabad and Yazdanshenas 2013) properties of nano ZnO on textiles have been studied by several researchers. One report from El-Hady et al. (2013) described the action of sodium hypophosphite as a main flame retardant in the presence of nano ZnO, for cotton and cotton/polyester blend fabrics and presence of nano ZnO was reported as an effective compound in increasing the char formation. As it is known that, nano particles formed is having a tendency of agglomeration; it is applied in a dispersing medium, i.e., potassium methyl siliconate (PMS) to reduce the agglomeration. In this study nano Zinc oxide was applied along with PMS emulsion on jute fabric for obtaining a desired level of durable or semi durable flame retardancy on bleached jute fabric.

Experimental

Materials used

Hydrogen peroxide bleached plain weave jute fabric having 63 end/dm (linear density-256 tex), 55 pick/dm (linear density-256 tex) with 275 g/m^2 area density was used.

Chemicals

Zinc acetate dihydrate (assay, 98% pure, Loba chemicals, India), NaOH (assay, 97% pure, E Merk, India), Aqueous solution of potassium methyl siliconate (PMS), obtained from Wacker Chemicals, Germany were used without any further purification.

Preparation of nano zinc oxide

The ZnO nano powder was prepared by co-precipitation method. Fifty grams of Zinc acetate dihydrate was added into 1000 ml of water under vigorous stirring. After 10 min, 2 M NaOH aqueous solution was introduced into the above solution drop by drop, resulting in a slurry like white solution, which was then placed on a magnetic stirrer for stirring for 2 h. The precipitate was then taken out and washed repeatedly with water followed by ethanol to remove the impurities for the final products. White powder obtained after drying at 100 °C in vacuum oven for 6 h was then calcinated at 600 °C for 4 h in Muffle furnace in order to get purified ZnO nano powder (Thilagavathi and Geetha 2013).

Application of nano ZnO on jute fabric

ZnO nano powder (0.005, 0.01 and 0.02 g) was weighed and made dispersion with 10 ml PMS. Required amount of water was added to that and the solution was finally made up to 100 ml. It was then poured into a tray and the bleached jute fabric was immersed and kept for 30 min. This chemically soaked jute fabric was then padded through the padding mangle with the pressure of 20 kg/cm^2 for maintaining 100% expression. The padded fabric was finally dried at 90 °C for 5 min.

Method of testing

The nano ZnO powder and also nano ZnO coated jute fabrics were subjected to evaluation for its important textile related physical and mechanical properties and also for understanding thermal degradation behaviour (DSC and TGA), fire retardant performance (LOI and char length) and characterization of nano ZnO and nature of the nano ZnO coating by EDX, SEM, FTIR, AAS (for zinc content analysis) and particle size distribution analysis as detailed below.

Tenacity

Breaking tenacity (cN/tex) of selected jute fabric samples were measured by the raveled strip method following IS-1969-1985 (Majumdar et al. 1993) specification using Instron (Model-1445) CRT-Universal tensile tester with a traverse speed of 100 mm/min maintaining a pretension of 0.5 N. The sample size of the fabric was 50 mm × 20 mm between the jaws.

Fabric stiffness

The bending length of selected jute fabric samples was measured according to IS-6490-1971 method using Cantilever principle.

Whiteness indices

Whiteness index of selected jute fabric samples was directly evaluated as per Hunter Lab-Scale formula using a computer aided Macbeth 2020 plus reflectance spectrophotometer (with D65 standard illuminant and 10 deg standard observer setting) and associated color lab plus colour measurement software.

Vertical flammability test

Untreated and treated jute fabric samples (15 cm long and 5 cm wide) were mounted vertically in a specimen holder and was then exposed to a standard flame (Propane/butane flame) of one inch at 90° angle with the specimen for 12 s and left for burning. The flame spread time, afterglow time, and char length (in cm) after the burning were recorded as per the ASTM D6413/D6413M-13b method.

Limiting oxygen index

Limiting Oxygen Index (LOI) value is the percentage critical oxygen value required to maintain the flame, indicating a relative measure of flame retardancy of any materials or textiles. LOI values of untreated and nano ZnO treated jute fabric samples were determined by a standard LOI tester (Make: S C Dey& Co., Kolkata) as per ASTM-D-2863-77 method by using the following expression

$$\text{Limiting Oxygen Index } (n) = \frac{100 \times \text{Volume concentration of } O_2}{\text{Volume concentration of } N_2 + \text{Volume concentration of } O_2}$$

Fourier transform infrared spectroscopy (FTIR) analysis

Finely crushed selected jute fibre samples (3 mg) taken out from selected jute fabrics were examined in a double beam FTIR spectrophotometer by ATR (Attenuated Total Reflectance) attachment.

Scanning electron microscopy (SEM)

The surface morphology of untreated, nano ZnO treated jute and nano ZnO powder samples were examined using Scanning Electron Microscope at different magnifications. The fibre samples for the SEM study were prepared with Gold–Palladium alloy coating following a standard procedure (Samanta et al. 2007a).

Energy dispersive X ray (EDX) spectroscopy

In order to quantify the amount of Zinc content from ZnO and silicon content from PMS present on jute fabric surface, Energy Dispersive X-ray (EDX) spectroscopy analysis was performed with the SEM instrument (Tescan SEM VEGA 3 XM) with a separate EDS detector connected to that instrument.

Particle size analysis

The size of the nano particles were analysed by using Malvern Mastersizer 2000 model particle size analyzer by making dispersion of nano ZnO powder with water.

Atomic absorption spectroscopy (AAS)

In order to quantify the amount of Zinc present (from nano ZnO) in bulk of the treated jute fibre, AAS was performed on the nano ZnO treated jute fibre using GBC-Avanta AAS spectrophotometer with specific detector(s).

DSC and TGA

TGA and DSC thermograms of untreated and nano ZnO treated jute fibre samples (finely crushed) taken out from selected jute fabric were obtained from the Q600 provides simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample at a heating rate of 10 °C/min, using a pre-fixed sample weight over a temperature range from 30 °C (ambient) to 500 °C, following the usual procedure (Samanta et al. 2007b) from ambient to 500 °C. It features a field-proven horizontal dual beam design with automatic beam growth compensation, and the ability to analyze two TGA samples simultaneously. DSC heat flow data is dynamically normalized using the instantaneous sample weight at any given temperature.

Result and discussion

Before discussing the fire retardant performance and changes in important physical properties of jute fabric after nano ZnO treatment, it is appropriate to study the possible reaction mechanism for preparation of nano ZnO powder is discussed as below.

Reaction mechanism showing the preparation of ZnO nano particles

Nano ZnO, for the application to jute fabric was generated by co-precipitation method. Zinc acetate dihydrate and NaOH were used as a precursor for generating nano ZnO by co-precipitation method followed by calcination at higher temperature (600 °C). The growth of ZnO by this method undergoes the following steps of reactions (Ghule et al. 2006).

1. $Zn(CH_3COO)_2 + NaOH \rightarrow Zn(CH_3COO)(OH) + Na(CH_3COO)$
2. $Zn(CH_3COO)OH + NaOH \rightarrow Zn(OH)_2 + Na(CH_3COO)$
3. $Zn(CH_3COO)OH + NaOH \rightarrow ZnO + Na(CH_3COO) + H_2O$
4. $Zn(OH)_2 \rightarrow Zn^{2+} + OH^- \rightarrow ZnO$

The conversion of normal ZnO to powdered nano ZnO was made by calcination at 600 °C. However, any nano particles, including nano ZnO suffer agglomeration (Luo et al. 2003) and hence use of dispersing medium is preferred. That is why; PMS dispersion is used in the present work as a dispersive medium to apply nano ZnO on jute fabric.

XRD analysis

Figure 1 shows the XRD spectrum of synthesized nano ZnO produced from Zinc acetate by co-precipitation method. All the diffracted peaks are well assigned as hexagonal (Wurtzite) ultra nano crystalline phases of ZnO. Phase peaks corresponding to the JCPDS card number 01-089-0511 with lattice constants of a = 3.245 Å and c = 5.205 Å. From XRD spectrum, the characteristic peaks with high intensities corresponding to (100), (002), (101) planes and lower intensities corresponding to (102), (110), (103), (200), (112) and (201) planes indicate that this nano ZnO product produced as above is of high-purity hexagonal ZnO quartzite structure. The sharpness of the peaks point out that ZnO is well crystalline in nature (Luo et al. 2003). The broadness of these peaks

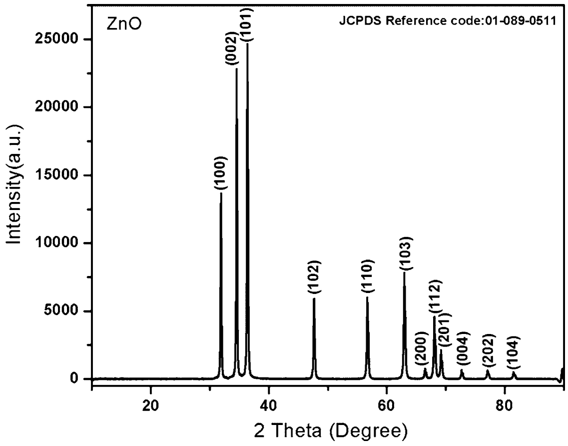


Fig. 1 XRD of nano ZnO powder

Table 1 Physical properties of PMS and nano ZnO coated jute fabrics

S. no.	Treatments	Physical properties		
		% Loss in breaking tenacity	Bending length (cm)	Whiteness index (hunter)
1	Untreated (control)	–	3.8	75.20
2	1% PMS	5	3.9	70.06
3	5% PMS	8	4.0	62.16
4	10% PMS	10	4.2	59.24
5	15% PMS	20	4.7	58.32
6	1% PMS + 0.01% nano ZnO	5.5	4.0	70.68
7	5% PMS + 0.01% nano ZnO	8	3.9	63.52
8	10% PMS + 0.01% nano ZnO	10	4.5	60.25
9	15% PMS + 0.01% nano ZnO	21	4.8	58.96
10	10% PMS + 0.005% nano ZnO	10	4.4	60.32
11	10% PMS + 0.02% nano ZnO	10	4.7	61.64
12	10% PMS + 0.01% nano ZnO (After 5 cycle of washing)	10	4.0	67.35
13	20% SARA Flame CFW	28	4.7	67.52

shows the low crystallite size for the synthesised ZnO. The crystallite diameter was calculated using well known Scherrer equation: $D = (k\lambda)/(\beta \cos \theta)$. The average size of one such crystallite particle of nano ZnO obtained for its prominent peak in (101) plane is ~36.4 nm, confirmed the presence of nano sized crystalline ZnO particle, which is obviously much lower than the particle size of commercially available bulk ZnO (Tran 2016).

Effect of application of nano ZnO particles on the changes in the textile related properties of jute fabric

To understand the effects of application of nano ZnO (in presence of PMS as a dispersing medium as well as a binder) coating on the changes of important textile related properties of the jute fabric viz., tensile strength, stiffness, and whiteness index of treated and untreated jute fabric were evaluated. Table 1 shows the effects of nano ZnO particle coating treatment on important physical properties of jute fabric, in comparison with that of untreated jute fabric.

Tensile strength of jute fabric was found to be reduced to an extent of 10–20% after different dosages of treatment of nano particles in presence of required amount of PMS. This reduction in fabric tenacity may be considered due to the alkaline degradation of major jute constituents by alkaline PMS dispersion, particularly during pad-dry process. Due to the alkalinity of PMS, partial removal of hemicellulose and a small part of removal of the lignin takes place, which ultimately results some reduction in the tensile strength of treated jute fabric. The initial bending length of untreated jute fabric was 3.8 cm, which was found to be increased up to 4.8 cm, showing increased stiffness after different dosages of treatment with nano ZnO. This may be due to the effect of coating of the binder polymer (PMS) over the fabric. It is also observed that the bending length reduces after five cycles of washing of the treated fabric, which indicates the partial removal of PMS binder coating from the treated jute fabric. It is there for clear that the nano ZnO does not contribute towards the loss in tenacity and an increase in bending length. The initial Hunter whiteness index of untreated bleached jute fabric was measured as 75.20, after nano ZnO coating formulation of 10% PMS + 0.01% ZnO, it decreased to 60.25 and it shows increase up to 67.35, after five cycles of washing. The reduction of whiteness index may be caused due to the drying of treated fabric at a higher temperature at alkaline pH (in presence of PMS, which has alkaline pH). Thus, treated jute fabric shows slight yellow shade after treatment with 10% PMS + 0.01% nano ZnO powder applied by pad dry method. Thus, the formulation having Sl. No. 8 (0.01% nano

Table 2 Flammability properties of ZnO coated fabric

S. no.	Treatments	Vertical flammability test			Limiting oxygen index (%)
		Flame spread time (s)	After glow time (s)	Char length (cm)	
1	Untreated	49.0 (BEL)	55.0	12.5 (BEL)	20.5
2	1% PMS	28	20	BEL	21
3	5% PMS	26	22	BEL	22
4	10% PMS	25	23	BEL	22
5	15% PMS	26	23	BEL	24
6	1% PMS + 0.01% ZnO	5, SE	35	2.2	30
7	5% PMS + 0.01% ZnO	7, SE	35	1.3	32
8	10% PMS + 0.01% ZnO	Nil, SE, NFS	37	1	35
9	15% PMS + 0.01% ZnO	Nil, NFS	37	1	35
10	10% PMS + 0.005% ZnO	10, SE	40	2	29
11	10% PMS + 0.02% ZnO	Nil, NFS	45	1	35
12	10% PMS + 0.01% ZnO (after washing)	5, SE	30	2	30
13	20% SARA Flame CSW	11, SE	8	4.5	30

BEL Burnt entire length, *SE* self extinguished, *NFS* no flame spread

ZnO + 10% PMS) applied on jute fabric appeared to be better option if it passes fire retardant performance criteria, as discussed below.

Effect of application of nano ZnO on fire retardant performance for jute fabrics

Results of fire retardant performances for experiment SI. No. 2–11 are shown in Table 2. Corresponding data in Table 2 for SI. No. 8 formulation (10% PMS + 0.01% ZnO) show that in this case the char length was found to be 1.0 cm and flame does not spread at all and afterglow remained for 37 s. The presence of silica metal (from PMS) as a metallic residue on the fabric surface is causing this afterglow on the treated jute fabric. The measurement of char length is an important factor too in order to study the influence of any flame retardancy (Chen et al. 2005).The maximum LOI value was found to be 35, among all the formulations used, where LOI value for experiment in SI. No. 8 (10% PMS + 0.01% ZnO) were also 35. Data of LOI values for experiment SI. No. 8, 9 and 11 show that an increase in the concentration of nano ZnO from 0.01 to 0.02% does not increase the LOI value any more, but experiment SI No. 10 with a reduction of nano zinc oxide to 0.005% shows a reduction in LOI value to 29. After 5 cycles of washing, there is a marginal decrease in fire retardant performances, showing an adverse decrease in LOI value (30–35), decrease in afterglow time (30–37 s), adverse increase in char length (2–1 cm) and adverse effect showing flame spread time to be 5 s instead of nil/no flame spread though the flame still remains self-extinguishing in nature. This may be due to the partial removal of the PMS binder along with nano ZnO from jute fabric by 5 wash cycles. Generally, a fabric is said to be flame retardant, if its LOI value is above 27. This result was comparable with commercial fire retarding chemicals (result of application of 20% SARA Flame—CFW as commercial fire retardant, as shown in SI. No. 13 in Table 2. For a commercial fire retardant formulation, for getting LOI value of 30–35, around 200–300 gpl (i.e. 20–30%) concentration may be needed, while for application of this nano zinc oxide, much lower concentration is sufficient. For 0.01% nano ZnO along with 10% PMS (silicone emulsion) treated jute fabric, the LOI value was found to be maximum (35), which indicates that the treated jute fabric has very good fire retardant property even with much lower % of application of zinc oxide in nano form. Since PMS forms a binder coating over the fabric, the fabric

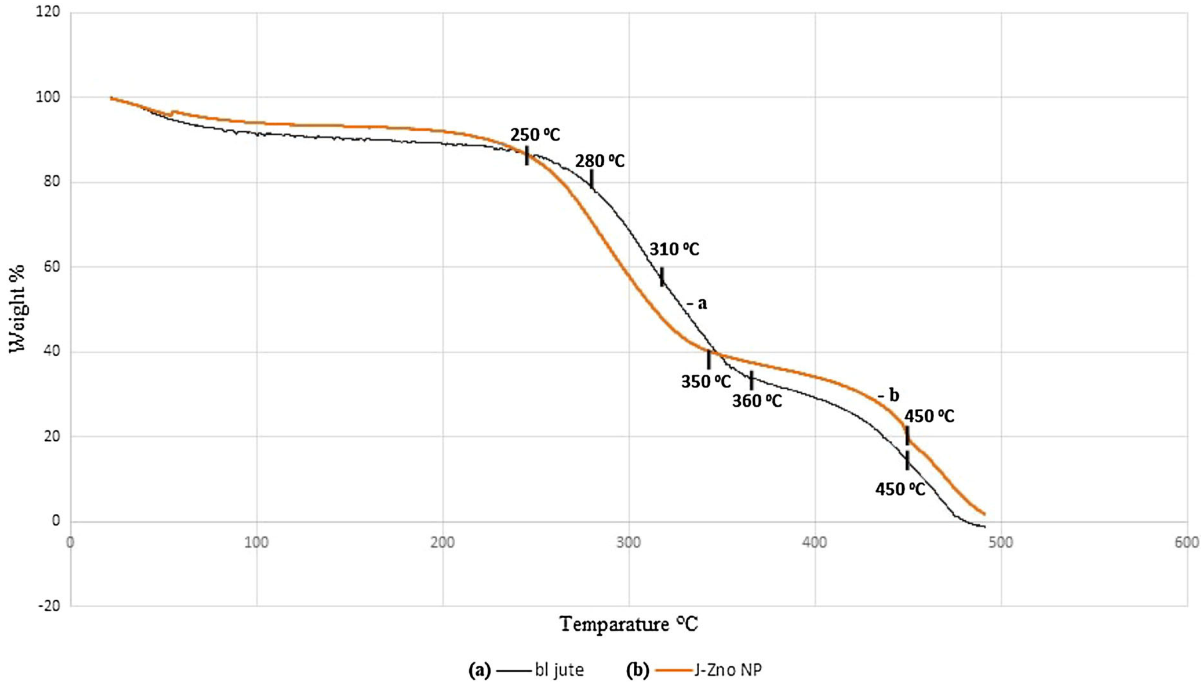


Fig. 2 TGA thermograms of nano ZnO treated and untreated jute

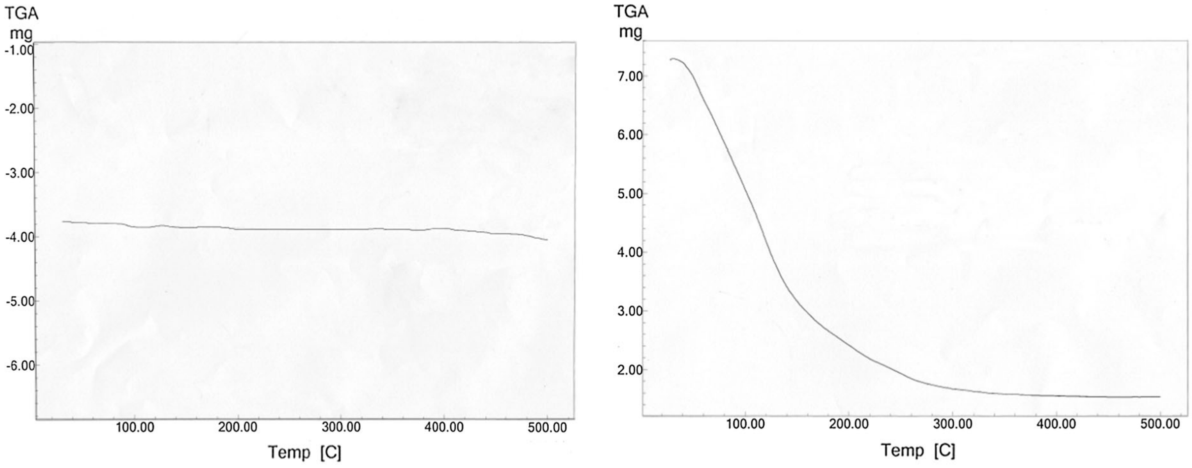
coated with PMS even without nano ZnO (only 10% PMS treated jute fabric), shows LOI value of 22 (LOI value of untreated jute is 20.5). In the case of formulation 0.01% nano ZnO along with 10% PMS, even after 5 cycles of washing, LOI value is still around 30, which can also be considered good flame retardant in terms of LOI value for moderate to good flame retardancy for jute fabric, as jute fabric or flame retardant treated jute fabric are seldom washable. These shows the nano ZnO along with the silicone binder emulsion are fairly adhered on the jute fabric surface. However, on repeated 5 cycles of washing, some loosely held nano ZnO with the silicone emulsion are washed out from the surface of the treated jute fabric. A treatment with a commercial flame retardant agent like, SARA Flame—CFW, applied in 20% concentration on jute fabric shows LOI value of 30. Thus, experiment SI. No. 8 can be considered as the best option to be optimum for imparting semi-permanent and reasonably wash stable flame retardant jute fabric using 0.01% nano zing oxide dispersed in 10% PMS applied by pad dry method. However, for the scientific understanding of the changes on thermal behaviour and surface character as well as structural changes in chemical functionality, etc. the treated jute fabric was subjected to analysis with DSC, TGA, EDX, AAS, SEM and FTIR Spectroscopic analysis as discussed below.

Study of analysis of the thermal decomposition of nano ZnO treated jute fabric using DSC & TGA thermograms

The thermal degradation behaviour is extremely important for flame retardant materials. Thermo-Gravimetric Analysis (TGA) in air and Differential Scanning Calorimetry (DSC) study in air for untreated jute and nano ZnO coated with PMS binder jute samples are shown in Figs. 2 and 4 respectively. The effectiveness of fire retardant chemicals in lignocellulosic material is generally indicated by somewhat lowering of the thermal decomposition temperature of individual major jute constituents. It was found in both Figs. 2 and 4 that there is an early thermal decomposition of hemicellulose part of jute along with indicating higher char formation (leaving higher residue at 500 °C max. temp studied) by nano ZnO treated jute substrate as compared to the untreated jute substrate. Untreated jute fabric in Fig. 2 shows its 1st thermal degradation at 280–310 °C for hemicellulose

Table 3 Weight loss % of nano ZnO treated and untreated jute fabrics subjected to heating in varied temperature, indicating the nature of thermal decomposition

Sample	Approximate residue left (%) at respective temperatures (°C)						
	80	200	250	350	400	450	500
Untreated jute	92	88	86	38	29	14	Nil
10% PMS + 0.01% nano ZnO treated jute fabric	94	91	85	39	34	19	5



(a) **(b)**

Fig. 3 **a** TGA thermograms of nano ZnO, **b** TGA thermograms of PMS

and 2nd thermal degradation at 360–380 °C for cellulose and 3rd thermal degradation at about 430–450 °C for lignin, indicating a change in slope at those temperatures (Singhee 2007), as shown in Fig. 2 (TGA). While, TGA thermogram of nano ZnO (0.01%) along with 10% PMS treated jute sample also shown in Fig. 2 shows its 1st thermal degradation at about 250–280 °C for hemicellulose and 2nd thermal degradation at about 330–350 °C and 3rd thermal degradation occur at about 430–450 °C showing marginally more residue (5% difference) left at 400–500 °C. This indicates a marginally early thermal degradation of hemicellulose and cellulose part, but not in the lignin part. Moreover, it is revealed by the observation that the said treated jute sample render more residue left at 400–500 °C causing more char formation (showing 5% higher amount of residue left at 400–500 °C. This may be due to early dehydration of cellulose and hemicellulose part showing early degradation with more char formation probably resulting less formation of flammable (levo-glucosan) gases.

The weight loss at different temperature zones during TGA analysis is shown in Table 3. It is observed from both the thermograms and the data given in Table 3 that the nano ZnO treated jute fabric leaves 5% higher residue than the untreated one at the temperature zone of 400–500 °C. The results of LOI value, vertical flammability test and other flame retardancy performance for treated jute also supports this observation.

Nano ZnO coated jute fabric shows marginal early degradation of hemicellulose and cellulose part of jute forming lesser amount of volatile product leading to less levo-glucosan formation and higher LOI values (Table 2) with higher residue left after heating up to 500 °C (Table 3).

Figure 3a, b shows the TGA thermogram of nano ZnO and Potassium methyl siliconate. In the case of nano ZnO, the graph is almost linear which indicate that the weight loss is minimal during heat treatment. The higher thermal stability may be because of prior calcination given to the nano ZnO. In the case of PMS, there is a gradual trend in the weight loss along with

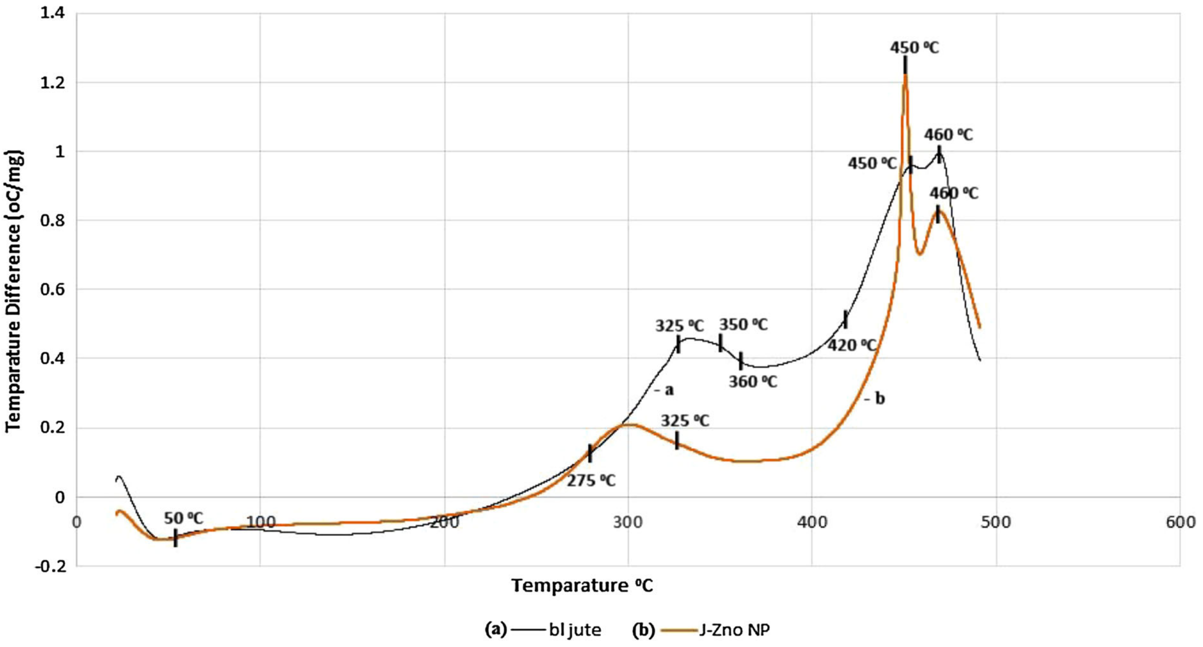
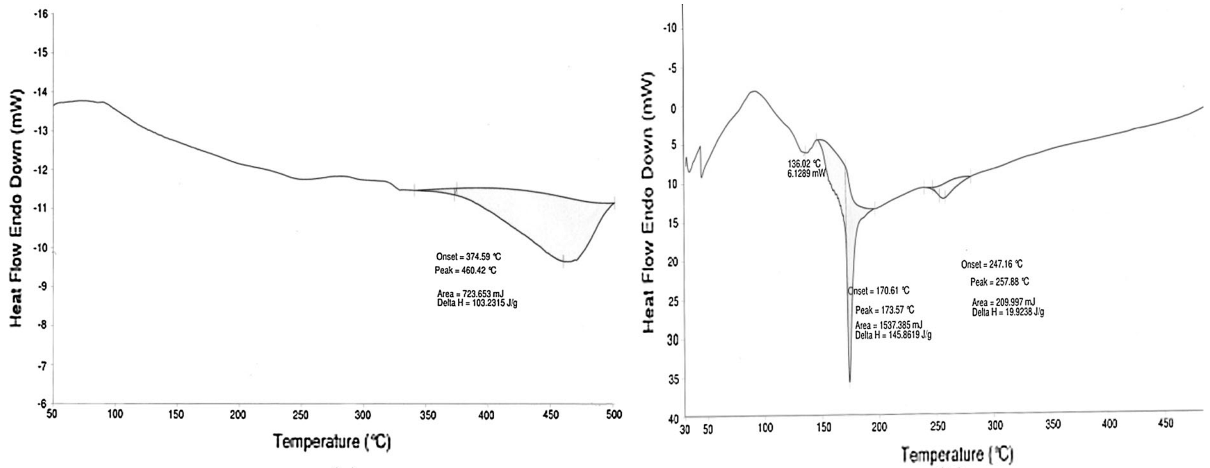


Fig. 4 DSC thermograms of nano ZnO treated and untreated jute

temperature up to 300 °C and the product is found to be stable upon further increase in temperature.

DSC thermograms of untreated jute and treated jute (with 0.01% nano ZnO along with 10% PMS) are shown in Fig. 4. DSC thermogram (a) of untreated jute as shown in Fig. 4 shows moisture evaporation at 50–60 °C, thermal decomposition of hemicellulose part at around 335 °C (with an exothermic hump at 325–350 °C). It can also be seen that the thermal decomposition of cellulose part occurs at around 390 °C (with an endothermic crest at 360–420 °C) and thermal decomposition of lignin part occur at with two exothermic duplet at 450 and 460 °C. While in Fig. 4, the DSC thermograms (b) for 0.01% nano ZnO along with 10% PMS treated jute substrate shows moisture evaporation at 50–60 °C (showing no change); but thermal degradation of hemicellulose part of the said treated jute occur at around 300 °C (showing exothermic hump at 250–325 °C, i.e. much earlier than 325–340 °C, as observed in untreated jute). This indicates an observed lowering of thermal decomposition temperature of hemicellulose part of treated jute. The said DSC thermogram (b) in Fig. 4 also shows a broad trough for the thermal degradation at 325–420 °C for cellulose part i.e. cellulose part also starts thermal degradation early at 325 °C but otherwise thermal behaviour of the cellulose part of the nano ZnO treated jute remains almost same with said minimum changes requiring much less ΔH, showing less heat consumption. But the thermal degradation of lignin part of the nano ZnO treated jute occurs at same temperature showing a much sharper duplet peaks at the same temperature zone as shown for untreated jute lignin part at 450–460 °C. This DSC study thus reveals that the treated jute fabric, due to the presence of nano ZnO powder and PMS lowers the thermal degradation temperature of mainly for hemicellulose part and partially for cellulose part, while lignin part remains unaffected. Presence of nano ZnO with PMS over the treated jute is also thus evidenced by changes of DSC and TGA thermograms. Moreover, comparing the two DSC thermograms of treated and untreated jute in Fig. 4, it may be concluded that the effect of the nano ZnO with PMS treatment is much more localized and probably restricted to the hemicellulose part predominantly than the cellulose part (which is less affected) and have almost no effect on lignin, so far their thermal degradation temperatures for nano ZnO particle with PMS treated jute fabrics.

The DSC thermogram of nano ZnO as well as PMS is as shown in Fig. 5a, b. The thermal decomposition of nano ZnO occurs within 350–460 °C, showing a broad endothermic peak at 460 °C. Similarly, the thermal decomposition of PME occurs within



(a) (b)

Fig. 5 **a** DSC thermograms of nano ZnO, **b** DSC thermograms of PMS

136–173 °C, having a strong endothermic peak at 173 °C.

FTIR analysis of untreated and nano ZnO treated jute fabric

To investigate the molecular interaction of nano ZnO with jute, FTIR spectroscopic analysis of PMS, nano ZnO powder, untreated jute (bleached control sample), PMS + nano ZnO treated jute fabric was performed(after washing the samples in water and alcohol followed by drying) and the said four (4) FTIR Spectra are shown in Fig. 6. FTIR spectrum of nano ZnO (Fig. 6) shows significant peaks at 3800, 2325, 1600 and below 500 cm^{-1}. The peak below 500 cm^{-1} show the distinct lattice vibrations of ZnO and the band at 760 cm^{-1} attributed to the asymmetric stretching vibration of Zn–O–Zn bridging evidencing some agglomeration of nano ZnO. The broad peak at 3800 cm^{-1} of the OH stretching and a peak at 1600 cm^{-1} for OH bending suggests also the presence of moisture absorbed by $Zn(OH)_2$ produced by a combination of aerial moisture and nano ZnO.

The common FTIR transmittance peaks corresponding to 550 cm^{-1} (for −OH out of plane bending), 890 cm^{-1} (for β-glycosidic linkage), 1030 cm^{-1} (assigned to aromatic C–H in plane deformation and C–O deformation for primary alcohol in lignin), 1245 cm^{-1} (for –C–O–C and –C=O stretching in Xylan side substituent and lignin aromatic C=O stretching), 1335 cm^{-1} (for –OH in plane bending), 1370 cm^{-1} (for C–H deforming (symmetric) may be attributed to cellulose, hemicellulose and lignin), 1446 cm^{-1} (for C–H deforming (asymmetric) may be attributed to lignin), 1508 cm^{-1} (for lignin aromatic ring vibration and stretching), 1596 cm^{-1} (for C=C stretching in lignin olefinic units), 1735 cm^{-1} (for C=O stretching of ester group), 2355 cm^{-1} (for C–H stretching in polysaccharide chains), 2905–2920 cm^{-1} (for C–H stretching vibrations of aliphatic methylene groups), and 3350 cm^{-1} (for H bonded H–O Stretching) were observed in both the FTIR-spectra of untreated and nano ZnO treated jute fibres (Sinha and Rout 2009).

The FTIR spectrum of the jute fabric treated with nano ZnO with PMS (silicone binder dispersion) shows broadening of some of the FTIR peak present jute like peaks at 1335–2355, 2905 cm^{-1} and also at 3350 cm^{-1} while peak at 1735 cm^{-1} is reduced in the treated jute. Also, presence of PMS is indicated by few additional small peaks at 1290–1300 cm^{-1} corresponding to Si–C in the silicone compound (original FTIR curve for PMS show the peaks at 1260 cm^{-1}, which on jute after application shifted to 1290–1300 cm^{-1} showing small peaks which was absent in bleached jute). Si–O stretching vibration of silicone which usually occur at 960 cm^{-1} at FTIR peak of PMS (spectrum b) is when applied on jute merge with the peak already present in the jute at 1030 cm^{-1} and shows a sharper peak at 1050 cm^{-1} (spectrum b). The additional very small peak observed at 550 cm^{-1} indicates the presence of ZnO in the

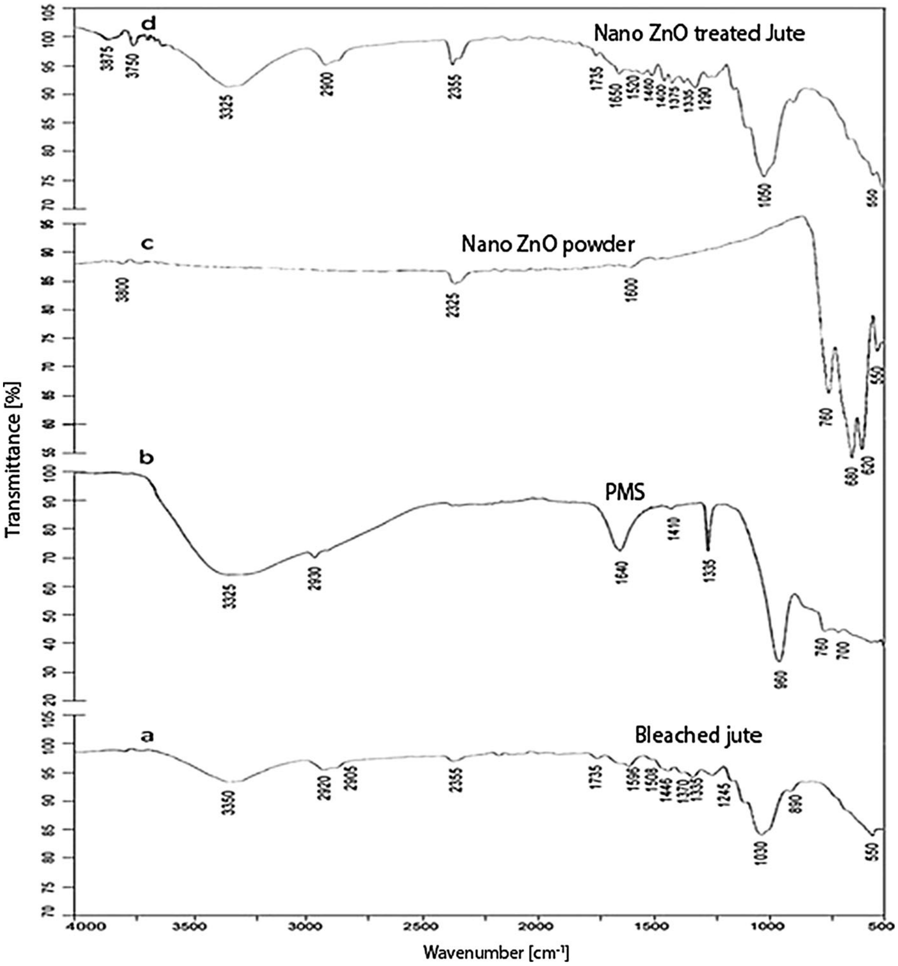


Fig. 6 FTIR spectra of PMS, nano ZnO powder, untreated jute and nano ZnO along with PMS treated jute samples

coated jute fibre (which is also shown in FTIR spectrum c for nano ZnO powder).

Elemental analysis of Zn and Si of the treated jute fabric by EDX and AAS study

EDX analysis was performed on the optimized formulation (10% PMS + 0.01% ZnO) treated jute fabric for the quantitative estimation of Zn from nano ZnO and Si from PMS present on the treated jute fibre surface and is shown in Fig. 7. The EDX analysis shows distinct peaks for O, C, Si, K and Zn. The elemental content of bleached jute (control fabric) as well as nano ZnO treated jute as per EDX result is as tabulated in the Table 4. It is apparent from the table that, the carbon content of the jute has been reduced drastically. This may be due to the partial removal of hemi cellulose and lignin from jute fabric during the treatment. On the other hand, the increase oxygen content may be because of the deposition of nano ZnO as well as Potassium methyl siliconate (K_4SiO_4) both compounds contains oxygen in their chemical structure.

The presence of Zinc along with its qualitative content on treated fabric was confirmed from EDX analysis and as per EDX analysis the atomic wt% of Zn was found to be 1.05 (atomic wt%) for 0.01% nano ZnO + 10% PMS treated fabric, which may be converted to 0.0093% by molecular weight percentage. Since EDX analysis gives quantitative estimation of Zn content in the jute fabric surface only, the total quantity of zinc in nano coated fabric was further estimated by AAS spectrophotometry and is found to be 588.4 mg/kg, which is equivalent to 0.0588 in wt% of fabric weight (against the application of 0.01% nano ZnO particle along with 10% PMS). The

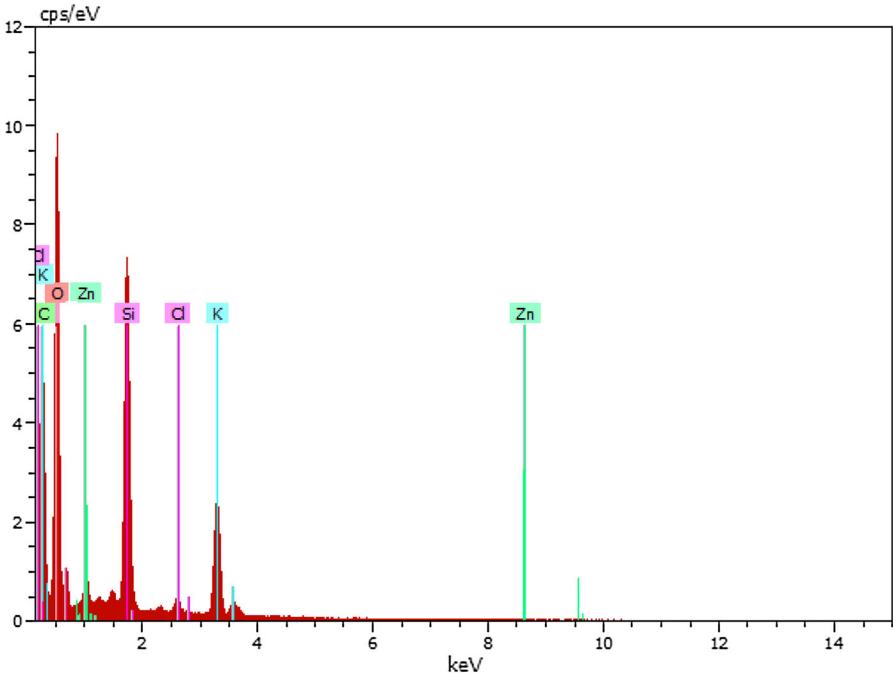


Fig. 7 EDX spectrum of nano ZnO + PMS treated jute fabric

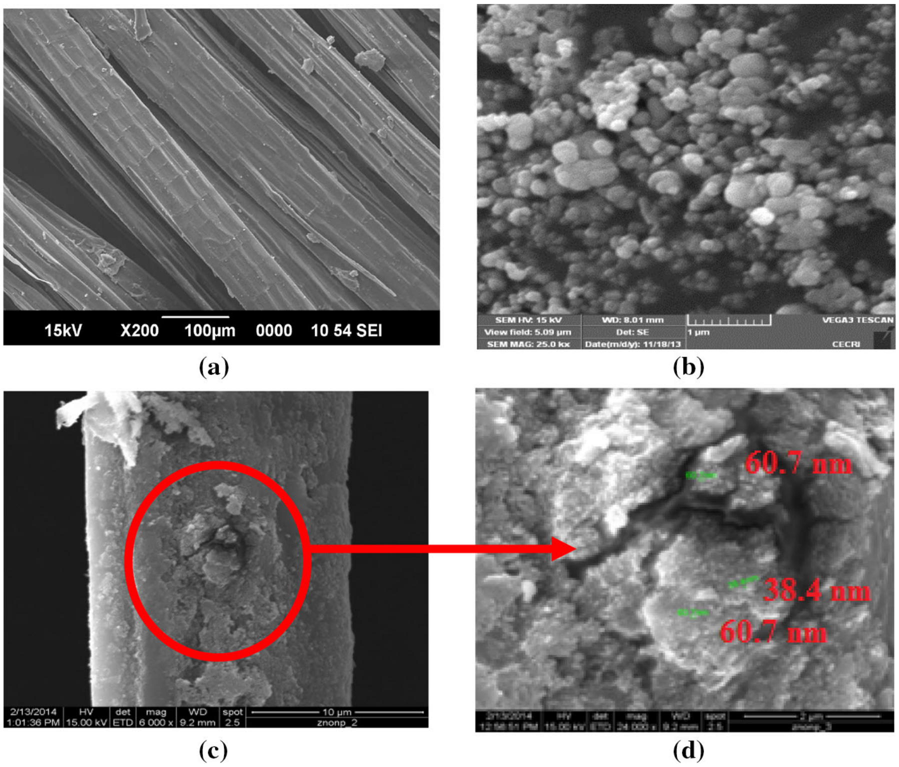
Table 4 Element content (atomic wt%) as per EDX analysis of nano ZnO and PMS coated jute fabric

Substrate	O	C	Si	K	Zn	Cl	N	Ca	Mg	Total
Bleached jute	33.19	65.55	Nil	Nil	Nil	Nil	1.06	0.10	0.10	100
Nano ZnO and PMS coated jute	55.46	20.79	13.32	8.47	1.05	0.91	Nil	Nil	Nil	100

variation/difference in the data of Zn content (as element not as ZnO) as observed by EDX analysis and by AAS analysis, may be because of the reason that EDX measures Zn content on the surface of the treated jute fabric, whereas AAS data show Zn content in the bulk of treated fabric on fabric wt%. EDX data also show Si content (from 10% PMS application) to be 13.32 as atomic wt%, which is equivalent to 6.66 by molecular wt% of Si present on the fabric surface and rest may be in the bulk.

Study of surface morphology of untreated &nano ZnO treated jute fabric

SEM investigates the changes in the topography of the nano ZnO treated jute fabrics in comparison with untreated jute fabric. The corresponding SEM micrographs are shown in Fig. 8. The scanning electron micrographs (8a) and (8c) shows the surface appearance of bleached jute and nano ZnO treated jute fibre surface. SEM micrograph (8b) shows the microscopic view of the calcinated nano ZnO deposited on the surface of the jute fibres. SEM micrograph (8a) of bleached jute fibre (from fabric) shows the smoother surfaces with small serrations of untreated jute fibre, while the nano ZnO treated jute fibre shows that there are some distinct surface deposition having varying degrees of uniformity with extraneous deposition of anchored nano ZnO embedded in the PMS dispersion on the surface of treated jute fibre. The agglomeration of nano ZnO particles over the fibre surface is also partly understood from the SEM micrographs of treated jute fibre. The surface deposition on jute fabric in a higher magnification is shown in SEM micrograph (8d). The size of the nano ZnO particles analysed from SEM picture on the treated jute fibre surface was found to be in between 38 and 60 nm by the measurement of average dimension



(a) (b)

(c) (d)

Fig. 8 SEM micrographs of untreated and nano ZnO + PMS treated jute samples. **a** Bleached jute, **b** nano ZnO, **c** bleached jute fibre with nano ZnO coating, **d** magnification of Fig. 8c indicating the nano size

of the few such nano ZnO particles chosen from magnified images of SEM picture. However, to understand the actual average size and distribution of size of nano ZnO, the particle size analysis of nano ZnO powder produced in the present work is felt essential, as some agglomeration of nano ZnO are also visible in the magnified SEM micrograph of treated jute fabric (SEM micrograph 8d in Fig. 8).

Hence, analysis of size profile of nano ZnO powder produced and the distribution of size of nano ZnO in water was analyzed by using particle size analyzer and the size distribution is shown in Fig. 9, which indicates a majority (60%) of the particles are below 0.5 μm (i.e. within 500 nm) and the rest are bigger or agglomerated producing micro particle by agglomeration in nano ZnO powder. This shows somewhat poor dispersibility of nano ZnO powder dispersed in water. The size and quality of the nano particles have effect on particle's settling velocity in dispersion medium. The larger the particle, higher is its settling velocity. Nano particles owe to the properties of small dimension, large specific surface area and high surface activity, which may lead also to agglomeration. The results indicate that, for better nano coating, one must use some better dispersing media for breaking/preventing the agglomeration of nano ZnO. This is the one of the reasons for the selection of PMS dispersion as application media in which nano ZnO are dispersible and help to restrict the agglomeration of nano ZnO, resulting in the formation of uniform dispersion of nano ZnO crystallites having the size 38–60 nm. However, considering this as a textile finish application, as 60% of the nano ZnO are within the desired range of common nano textile finish application, i.e. within 30–500 nm average size of the nano finish application usually used for textile finishing, this experiment is considered acceptable as the nano fire retardant finish.

Sample Name:
2341 - Average

SOP Name:

Measured:
Monday, March 14, 2016 4:34:05 PM

Sample Source & type:

Measured by:
sd

Analysed:
Monday, March 14, 2016 4:34:07 PM

Sample bulk lot ref:

Result Source:
Averaged

Particle Name:
Nano ZnO

Accessory Name:
Hydro 2000MU (A)

Analysis model:
General purpose

Sensitivity:
Normal

Particle RI:
2.000

Absorption:
0.01

Size range:
0.020 to 2000.000 um

Obscuration:
11.21 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.333 %

Result Emulation:
Off

Concentration:
0.0045 %Vol

Span :
3.632

Uniformity:
1.1

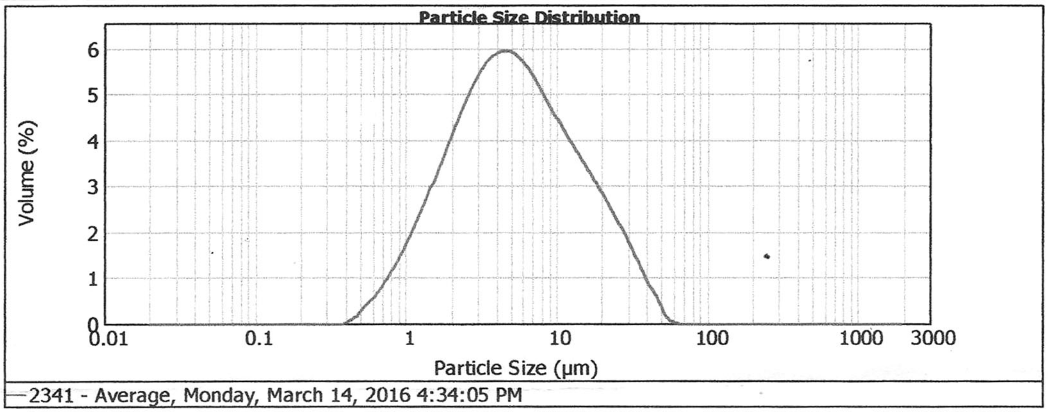
Result units:
Volume

Specific Surface Area:
1.8 m²/g

Surface Weighted Mean D[3,2]:
3.339 um

Vol. Weighted Mean D[4,3]:
8.305 um

d(0.1): 1.461 um   d(0.5): 5.107 um   d(0.9): 20.007 um



Size (μm)	Volume In %
0.010	0.00
0.011	0.00
0.013	0.00
0.014	0.00
0.016	0.00
0.018	0.00
0.021	0.00
0.024	0.00
0.027	0.00
0.030	0.00
0.034	0.00
0.038	0.00
0.043	0.00
0.049	0.00
0.055	0.00
0.062	0.00
0.070	0.00
0.080	

Size (μm)	Volume In %
0.080	0.00
0.090	0.00
0.102	0.00
0.115	0.00
0.130	0.00
0.147	0.00
0.166	0.00
0.187	0.00
0.211	0.00
0.239	0.00
0.270	0.00
0.305	0.00
0.345	0.00
0.389	0.03
0.440	0.11
0.497	0.28
0.561	0.43
0.634	

Size (μm)	Volume In %
0.634	0.62
0.717	0.82
0.810	1.05
0.915	1.31
1.034	1.59
1.168	1.90
1.320	2.23
1.491	2.57
1.684	2.93
1.903	3.28
2.150	3.63
2.429	3.95
2.745	4.24
3.101	4.47
3.503	4.64
3.958	4.73
4.472	4.75
5.053	

Size (μm)	Volume In %
5.053	4.69
5.709	4.55
6.450	4.36
7.287	4.13
8.233	3.87
9.302	3.62
10.510	3.37
11.874	3.13
13.416	2.91
15.157	2.69
17.125	2.47
19.348	2.25
21.860	2.00
24.698	1.74
27.904	1.46
31.527	1.17
35.620	0.88
40.244	

Size (μm)	Volume In %
40.244	0.62
45.469	0.40
51.371	0.10
58.041	0.02
65.575	0.00
74.089	0.00
83.707	0.00
94.574	0.00
106.852	0.00
120.724	0.00
136.397	0.00
154.104	0.00
174.110	0.00
196.714	0.00
222.251	0.00
251.105	0.00
283.704	0.00
320.535	

Size (μm)	Volume In %
320.535	0.00
362.148	0.00
409.163	0.00
462.281	0.00
522.296	0.00
590.102	0.00
666.711	0.00
753.265	0.00
851.056	0.00
961.542	0.00
1086.372	0.00
1227.408	0.00
1386.753	0.00
1566.785	0.00
1770.189	0.00
2000.000	

Operator notes: *Nano ZnO2*

Fig. 9 Particle size distribution of nano ZnO particle in water

Conclusion

In the present study, nano ZnO was generated by co-precipitation method followed by its application on bleached jute fabric using 0.01% nano ZnO particles in a dispersion of 10% Potassium Methyl Siliconate (PMS), which shows a good level of fire retardancy comparable with a commercial flame retardant formulation SARA Flame CFW (THPC based) applied on the same jute fabric to achieve the same level of LOI value.The nano ZnO treated fabric shows LOI value 35 and minimum char length of 1 cm with satisfied level of washing fastness for five cycles of wash. TGA and DSC analysis reveals that the nano

ZnO treated jute fabric produced more char than untreated jute fabric, with 5% higher residue (char) at 400–500 °C. The presence of nano ZnO in jute fabric was also confirmed by EDX, AAS and FTIR analysis. The particle size of nano ZnO was confirmed by particle size analysis showing 60% of the particles are within 30–500 nm, with some agglomeration of the rest of the nano ZnO as micro particles. FTIR studies indicate that the nano ZnO has not reacted with jute, while SEM studies indicate that it has adhered/deposited on the jute fibre surface with the help of PMS as a binder, which also act as a dispersive medium for the application of nano ZnO on jute fabric. Thus 0.01% nano ZnO + 10% PMS formulation can be a better economic alternative for commercial fire retardant formulations for jute fabric since other commercial fire retardant formulations like SARA Flame CFW need very high pick up (at least 20% i.e. 200 gpl) for obtaining the same level of fire retardancy performance (i.e. LOI value and char length etc.). Thus, with very low concentration of 0.01% nano ZnO in combination with 10% Potassium methyl silicate application for jute fabric renders acceptable level of fire retardant performance, which could be considered as a better option for commercial applications for producing various domestic and industrial jute based fire protective technical textiles.

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