

**STUDIES ON SUSTAINABLE APPROACH FOR
DEVELOPING FIRE RETARDANT
CELLULOSIC TEXTILES USING PLANT
BASED BIO-MACROMOLECULES**

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by

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Submitted

**in fulfillment of the requirements of the degree of Doctor of
Philosophy**

to the



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DEDICATED
TO
MY GUIDE & DAUGHTER

CERTIFICATE

This is to certify that the thesis entitled “**Studies on sustainable approach for developing fire retardant cellulosic textiles using plant based bio-macromolecules**” being submitted by **Mr. Santanu Basak**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile and Fibre Engineering, is a record of bonafide research work carried out by him. Mr. Basak has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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Abstract

Cellulosic material easily catches fire and generates toxic flammable gases and high temperature during combustion. Different synthetic chemicals are available in the market for making fire retardant cellulosic fabric. However, most of them have been reported as toxic and their requirement in large quantity for delivering flame retardancy make the approach unworthy. Moreover, treatment processes are also cumbersome. Therefore, getting an eco-friendly, cheap, widely available flame retardant material is a big challenge and unmet needs. In this connection, plant extracts have been popularly explored for making functional textiles to impart functionalities like protection against harmful UV rays, bacterial growth and to build aesthetic look by using them as a natural coloring material. In this study, an attempt has been made to explore different wastage plant extract as a novel and green flame retardant for making textile materials fire retardant.

In this research work, three different widely available wastage plant based bio-macromolecules named banana (*Musa*) peel sap (BPS), coconut (*Cocos nucifera*) shell extract (CSE) and pomegranate (*Punica granatum*) rind extract (PRE) have been chosen for the experiment. Primarily, extraction process of the aforementioned bio-macromolecules has been optimized in terms of time and temperature. Thermal stability of the extracted bio-molecules have been examined by different characterization techniques like TGA, EDX, AAS, FTIR, etc. In addition, thesis also elaborates the application of the water based extract and comparison of the potential of fire retardant efficacy of different bio-molecules, once these are applied on cotton textile material. Experimental results on fire retardant efficacy of the treated cotton fabric have been registered systematically in the context. As of summary of the experimental analysis, it has been revealed that the pomegranate rind extract (PRE) has more effectivity towards flame retardancy on cotton

fabric as compared to the other two extracts (BPP and CSE). Therefore, on later part of the thesis, PRE has been explored for further in depth study on its flame retardant action on cotton fabric.

PRE has been applied to the cellulosic cotton fabric by padding and exhaust method. Suitable concentration (400g/L) of application of PRE has been optimized on the basis of the Limiting Oxygen Index (LOI) value of the treated fabric (32). For application of PRE on cotton fabric, different treatment processes [padding (both cold and hot), exhaust with varying time, temperature and material to liquor ratio] have been explored. In each and every application process, add-on% of the treated fabric has been recorded. Moreover, fire retardancy of all the treated fabrics has been examined in terms of LOI value and the vertical flammability test. It has been noticed that the hot padding method is the best approach for the uniform application of PRE on the cotton fabric. Apart from the hot padding method, it has also been mentioned that the exhaust process is also suitable for the uniform application, if it is being carried out in a dyeing machine where both the fabric and the liquor are in circulation. Thermal stability of the treated fabric has also been evaluated by forced combustion test. Both the control and treated cotton fabric have been combusted in cone calorimeter machine with a heat flux level of 35kW/m^2 which is suitable for the upholstery, curtain like (home-furnishing) materials. It has been observed that the average peak heat release rate of the treated fabric (treated by 400g/L PRE) is almost half (45kW/m^2) compared to the peak heat release rate of the control cotton fabric (80kW/m^2).

Thermo-gravimetry test of the same treated fabric illustrates earlier dehydration and more amount of char mass formation at the end of the test. The resulting fire retardancy of the treated fabric is the combined reaction effect of the acid source (carbamic acid, ammonium salt, hexacontanoic acid, etc.), phenolic source (poly phenolic tannin, gallic acid, ellagic acid, betacyanin, coumarin, etc.) carbon source (carbonic dihydrazide, nona hexacontanoic acid, 1 hydroxy 2 pentanone, sugar

based material), blowing agent, Nitrogen containing bases like guanidine, asparagine (amino acid of protein), etc. present in the PRE extracts as observed from the Gas Chromatography Mass Spectroscopy (GC-MS) and Liquid Chromatography Mass Spectroscopy (LC-MS) analysis. FTIR analysis of the char mass (char of PRE treated fabric) shows structural stability and aromatized cellulosic structure. Surface morphological analysis of the char mass of the treated fabric displays structural integrity (weaves are present clearly like control cotton) with a presence of small bubbles on its surface. On the contrary, char mass of the control cotton fabric shows grey colour, net like fragile structure. Energy dispersive X-ray (EDX) analysis of the treated fabric char reveals the presence of Carbon element which is another positive indication of the aromatized structure. For further confirmation, connected with the flammable gas formation, volatile species coming out during burning of the treated fabric also have been analyzed by GC-MS. It has been observed that the peaks (mass/charge) assigned with the levoglucosan and its derivatives (77, 65, 91, 162) are very less intensive in the smoke of the treated fabric whereas smoke of the control cotton fabric shows levoglucosan based components and tar like products, terpenoids, etc. For understanding the char formation mechanism, solid NMR analysis of the char mass of the control and treated fabric also has been performed and discussed in detail in the concern chapter. It has been noticed that PRE helps in aromatization of the cellulosic based cotton fabric in increasing the Carbon content in char mass and restricts the flammable gas formation at higher temperature.

PRE treated fabric shows afterglow duration of more than 200s and the add-on% required for the self-extinguishment is also more than 35%. Therefore, for reducing the extent of afterglow and the add-on%, a mixed formulation of the pomegranate rind extract (PRE) and Sodium tri polyphosphate (STPP) has been integrated into cotton fabric to evaluate its efficacy of flame

retardancy. It has been found that the control, 3% (w/v) STPP and PRE treated cotton fabric register LOI value of 18, 21 and 26, respectively and completely burns within 80, 120 and 420s, respectively in the vertical flammability test. On the contrary, (PRE+ 3% STPP) treated cotton fabric exhibits the LOI value of 35 with a specific char length of 30mm. Extent of afterglow duration on the treated fabric has been found to be around 70-80s. Thermo-gravimetry (TG) analysis of the control, PRE and 3% STPP treated cotton fabric shows only 1-2 % remaining char mass at 550°C whereas the (PRE+ 3% STPP) treated fabric registers the char mass retention of more than 10% at the said temperature. Cone calorimetric data reveals that the peak heat release rate (PHRR) for the treated fabric is 25kW/m² (almost one third) compared to the heat release value of the control cotton fabric (79kW/m²).

At last part of the thesis, some experimental works have been investigated to improve the wash durability of the treatment on cotton fabric. Corroborated with the wash durability, different carboxylic acid based compounds Butane Tetra Carboxylic Acid (BTCA), Citric Acid (CA) have been explored. It has been found that 10% citric acid formulation based PRE treatment on the cotton fabric assists to achieve the LOI value of 26 after one single ISO2 washing in launder-o-meter machine, while BTCA treatment registers the similar LOI value of 26-27 after single washing by following same washing method

सार

सेल्यूलोसिक सामग्री आसानी से आग पकड़ लेती है और दहन के दौरान ज्वलनशील गैसों और उच्च तापमान उत्पन्न करती है। अग्निरधी सेल्यूलोसिक कपड़े बनाने के लिए विभिन्न सिंथेटिक रसायन बाजार में उपलब्ध हैं। हालांकि, उनमें से ज्यादातर को विषाक्त बताया गया है और लौ मंदता प्रदान करने के लिए बड़ी मात्रा में उनकी आवश्यकता दृष्टिकोण को अयोग्य बनाती है। इसके अलावा, उपचार प्रक्रियाएं भी बोझिल हैं। इसलिए, एक पर्यावरण के अनुकूल, सस्ते, व्यापक रूप से उपलब्ध लौ रिटार्डेंट सामग्री प्राप्त करना एक बड़ी चुनौती है। इस संबंध में, टेक्सटाइल पदार्थों को हानिकारक यूवी किरणों और बैक्टीरिया के विकास से बचाने के लिए पौधों के अर्क का पता लगाया गया है। इस अध्ययन में, अग्निरधी कपड़ा सामग्री बनाने के लिए विभिन्न अपशिष्ट पौधा के अर्क का पता लगाने का प्रयास किया गया है।

इस शोध कार्य में, केले (मूसा) के छिलके (बीपीएस), हरा नारियल (कोकस न्यूसीफेरा) के खोल (सी एस इ) और अनार (प्युनिका ग्राण्टम) के छिलके (पी आर इ) के नाम से तीन अलग-अलग व्यापक रूप से उपलब्ध अपशिष्ट पौधे आधारित जैव-मैक्रोमोलेक्यूल्स को चुना गया है। मुख्य रूप से, उपरोक्त जैव-मैक्रोमोलेक्यूल्स की निष्कर्षण प्रक्रिया को समय और तापमान के संदर्भ में अनुकूलित किया गया है। निकाले गए जैव-अणुओं की थर्मल स्थिरता की जांच टीजीए, ईडीएक्स, एएएस, एफटीआईआर, आदि जैसे विभिन्न लक्षण वर्णन तकनीकों द्वारा की गई है। इसके अलावा, थीसिस ने सूती वस्त्र सामग्री पर विभिन्न बायोमोलेक्यूल्स की अग्निरधी प्रभावकारिता की क्षमता के आधार पर पानी के अर्क और तुलना के आवेदन को विस्तृत किया। उपचारित सूती कपड़े की अग्निरधी प्रभावकारिता पर प्रायोगिक परिणाम संदर्भ में व्यवस्थित रूप से दर्ज किए गए हैं। प्रयोगात्मक विश्लेषण से यह पता चला है कि अनार के छिलके का अर्क अन्य दो अर्क की तुलना में सूती कपड़े पर अधिक प्रभावी है। इसलिए, थीसिस के बाद के हिस्से में, सूती कपड़े पर लौ रिटार्डेंट कार्बवाई के विस्तृत अध्ययन के लिए अनार के छिलके को चुना गया है।

PRE को पैडिंग और एग्जॉस्ट विधि द्वारा सेल्यूलोसिक सूती कपड़े पर लगाया गया है। पी आर इ की एक सांद्रता

(400g / L) को उपचारित कपड़े (32) के सीमित ऑक्सीजन सूचकांक (LOI) मूल्य के आधार पर अनुकूलित किया गया है। अलग अलग समय और तापमान के साथ पी आर इ को सूती बस्तो पर प्रयोग किया गया हैं। प्रत्येक आवेदन प्रक्रिया में, उपचारित कपड़े का ऐड-ऑन% दर्ज किया गया है। सभी उपचारित कपड़ों की अग्नि मंदता LOI मूल्य और ऊर्ध्वधर ज्वलनशीलता परीक्षण के संदर्भ में जांच की गई है। यह देखा गया है कि सूती कपड़े पर पीआरई के समान अनुप्रयोग के लिए गर्म पैडिंग विधि सबसे अच्छा तरीका है। हॉट पैडिंग प्रक्रिया के अलावा, एक्सहॉस्ट प्रक्रिया भी समरूप उपयोग के लिए एक अच्छा तरीका हैं। उपचारित कपड़े की थर्मल स्थिरता का मूल्यांकन भी फोर्स्ट कम्बशन परीक्षण द्वारा किया गया है। नियंत्रण और उपचारित सूती कपड़े को 35 किलोवाट / मी² के ऊष्मा प्रवाह स्तर के साथ कोण केलोरीमीटर मशीन में जलाया गया है जो उपहोल्स्टरी, पर्दे की तरह (घर की सजावट) सामग्री के लिए उपयुक्त है। यह देखा गया है कि नियंत्रण सूती कपड़े (80 किलोवाट / मी²) की पीक हीट रिलीज़ दर की तुलना में उपचारित कपड़े (400g / L PRE द्वारा इलाज) की औसत पीक हीट रिलीज़ दर लगभग आधी है (45kW / m²)।

उपचारित कपड़े का थर्मो-ग्रेविमेट्री परीक्षण पहले निर्जलीकरण और अधिक मात्रा में चार द्रव्यमान गठन को दिखाता है। उपचारित कपड़े की अग्नि मंदता PRE अर्क में मौजूद एसिड स्रोत, फेनोलिक स्रोत, कार्बन स्रोत, ब्लोइंग एजेंट, नाइट्रोजन युक्त क्षार आदि का संयुक्त प्रतिक्रिया का प्रभाव है। चार मास (पीआरई उपचारित कपड़े का चार) का एफटीआईआर विश्लेषण संरचनात्मक स्थिरता और अरोमाटैस्ड सेलुलोसिक संरचना को दर्शाता है। उपचारित कपड़े के चार द्रव्यमान का सतही रूपात्मक विश्लेषण संरचनात्मक अखंडता को प्रदर्शित करता है। इसके विपरीत, नियंत्रण सूती कपड़े का चार द्रव्यमान नाजुक संरचना को दर्शाता है। उपचारित फैब्रिक चार के एनर्जी डिस्पर्सिव एक्स-रे (EDX) विश्लेषण से कार्बन तत्व की उपस्थिति का पता चलता है। ज्वलनशील गैस निर्माण से जुड़ी आग की पुष्टि के लिए, उपचारित कपड़े से निकलने वाली अस्थिर स्पेसिस का विश्लेषण GC-MS द्वारा किया गया है। यह देखा गया है कि उपचारित कपड़े के धुएं में लेवोग्लुकोसन की पीक (द्रव्यमान / आवेश) कम सघन होती हैं जबकि नियंत्रण सूती कपड़े का धुआँ लेवोग्लुकोसन आधारित कॉम्पोनेन्ट को दर्शाता है। नियंत्रण और उपचारित कपड़े के

चार द्रव्यमान के सॉलिड एनएमआर विश्लेषण को भी चार गठन तंत्र को समझने के लिए किया गया है। यह देखा गया है कि PRE सेल्युलॉसिक आधारित सूती कपड़े के अरोमाटाइजेशन में मदद करता है।

PRE से उपचारित सूती कपड़ा 200 सेकंड से अधिक आफ्टरग्लो दर्शाता है और सेल्फ एक्सटींग्विशमेंट के लिए ऐड ऑन 35 प्रतिशत देखा गया है। इसके लिए आफ्टरग्लो की मात्रा और ऐड ऑन की कमी के लिए पी आर इ एवं सोडियम ट्राई पॉलीफोस्फेट (STPP) का मिश्रण का प्रयोग करके फ्लेम बिरोधी गुण का बिश्लेषण किया गया है। यह देखा गया है की तीन प्रतिशत एस टी पी पी और पी आर इ द्वारा उपचार किया गया सूती कपड़े का LOI 18, 21 और 26 हैं और संपूर्ण और से 80, 120 और 420 सेकंड में जल जाता है वर्टिकल फ्लम्माबिलिटी टेस्ट में। इसके विपरीत, (PRE + 3% STPP) उपचारित सूती कपड़े 30 मिलीमीटर की एक विशिष्ट चार लंबाई के साथ 35 का LOI मान प्रदर्शित करता है। उपचारित कपड़े पर आफ्टरग्लो की अवधि 70-80 सेकंड के आसपास पाई गई है। थर्मो-ग्रेविमेट्री (TG) अनालिसिस में कंट्रोल PRE और 3% एसटीपीपी उपचारित सूती कपड़े 550 ° C पर केवल 1-2% शेष चार द्रव्यमान दिखाते हैं जबकि (PRE + 3% STPP) उपचारित कपड़े में 10% अधिक चार रिटेंशन दिखा गया है। कोन कैलोरीमीटर डेटा से पता चलता है कि उपचारित कपड़े का हीट रिलीज़ रेट (25kW/m^2) एक तिहाई है कंट्रोल फैब्रिक के मुकाबले (75kW/m^2)।

थीसिस के अंतिम भाग में, सूती कपड़े पर वाश दूरबिलिटी के स्थायित्व को बेहतर बनाने के लिए कुछ प्रयोगात्मक कार्यों की जांच की गई है। वाॅश ड्यूरेबिलिटी से ग्रसित, विभिन्न कार्बोक्जिलिक एसिड आधारित यौगिकों ब्यूटेन टेट्रा कार्बोक्जिलिक एसिड (BTCA), साइट्रिक एसिड (CA) का पता लगाया गया है। वाॅश ड्यूरेबिलिटी से सम्बंधित विभिन्न कार्बोक्जिलिक एसिड आधारित यौगिकों ब्यूटेन टेट्रा कार्बोक्जिलिक एसिड (BTCA), साइट्रिक एसिड (CA) का पता लगाया गया है। यह पाया गया है कि सूती कपड़े पर 10% साइट्रिक एसिड निर्माण आधारित PRE उपचार धोने के बाद 26 के LOI मूल्य को प्राप्त करने में सहायता करता है, जबकि BTCA उपचार धुलाई के बाद 26-27 के समान LOI मूल्य को पंजीकृत करता है।

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List of Acronyms

LOI	Limiting Oxygen Index
DNA	Deoxyriboneuclic acid
PVC	Polyvinyl Chloride
ATO	Antimony Trioxide
BrFr	1,2-bis (pentabromophenyl)ethane
UV	Ultraviolet
THPC	Tetrakis Hydroxymethyl Phosphonium Chloride
g/L	Gram per Litre
BPS	Banana peel sap
CSE	Coconut shell extract
TG	Thermo-gravimetry
DTG	Differential thermos-gravimetry
EDX	Energy dispersive X-ray
AMU	Atomic mass unit
SJ	Spinach Juice
KDa	Kilodalton
MPP	Melamine pyrophosphate
DTA	Differential thermal analysis
XRF	X-ray fluorescence
BA	Boric acid
BX	Borax
CFP	Chicken feather protein
WP	Whey protein
DWP	Denatured whey protein
FTIR	Fourier transform infrared spectroscopy
PET	Polyethyleneterephthalate
ATR	Attenuated total reflectance
ASTMD	American Society for Testing and Materials
DMDHEU	Dimethyl Dihydroxyl ethylene urea
FMVSS	Federal Motor Vehicle Safety Standard
AAS	Atomic absorption spectroscopy
ANOVA	Analysis of Variance
GCMS	Gas chromatography mass spectroscopy
IS	Indian Standard
MJ	Millijoule
kW	Kilowatt
MLR	Material to liquor ratio
MARHE	Maximum average rate of heat emission
GPC	Gel permeation chromatography
LCMS	Liquid crystal mass spectroscopy
m/z ratio	Mass/ charge ratio
Mn	Number average molecular weight
Mp	Peak average molecular weight

Mw	Weight average molecular weight
Mz	Z-Average molecular weight
DSC	Differential Scanning Calorimetry
NMR	Nuclear magnetic resonance
CV	Coefficient of variation
ToF-SIMS	Time of flight secondary ion mass spectroscopy
ml	Mililitre
Kg	Kilogram
l	Litre
g	Gram