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Development of eco-friendly flame retardant fabric using phosphorus based intumescence chemistry

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Development of Eco-friendly Flame Retardant Fabric Using Phosphorous based Intumescence Chemistry

By

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Abstract

The research aims at developing Eco-friendly flame retardant textile fabric using phosphorous based intumescence chemistry. Phosphorous in the structure of Spirocyclic pentaerythriol diphosphoryl chloride (SPDPC) acts as the main group to impart flame retardancy. Intermediate compounds were synthesized in the laboratory and finally converted into sol. The silane sol was applied to the textile material using pad-dry-cure method. The intermediate compounds and the coated material were tested using Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimeter (DSC), and Thermogravemetric analysis (TGA) testing instruments. Vertical flammability testing was performed as per ASTM D-6413 standards to test the fabric for its flame retardancy. Tensile testing of the coated fabric was performed as per ASTM D5035 standards. Change in thickness of the coated fabric was measured as per ASTM B499 test method. The research concludes that phosphorous based intumescence chemistry is effective in imparting flame retardancy to the cotton textile substrate. The change in tensile strength and thickness of coated textile substrate was found to be statistically significant.

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Chapter 1: Introduction

Textile fabrics, like any other solid substrates, experience a rise in temperature when exposed to the heat source. Textile substrate catches fire when the substrate reaches the ignition temperature and initiates the pyrolytic decomposition of the fiber material in textile substrate. The possible products of this pyrolytic reaction are combustible gases, non-combustible gases, and carbonaceous char. These combustible gases mix with the oxygen in air and produce flame.

Flame retardants were developed to minimize financial and life losses that occurred due to fire. These flame retardants have following major actions in case of fire:

1. The flammability of textile material is reduced and hence the product ignites less easily under the influence of heat source (Hofer, 1999).
2. The flame spread is reduced in case there is ignition of textile substrate. This gives higher escape times from buildings and fire premises in case of fire (Hofer, 1999).

There are several requirements for safety of apparel and furnishing textiles. Some of them are discussed below:

1. Safety: In daily life situations, personal and organizational losses occur due to fire where furniture, wall coverings, curtains, and industrial fabrics act as fuel. These losses due to fire can be minimized by using textiles coated with fire retardant finish.
2. Federal law: It is federally mandatory that certain home furnishings and children clothing have certain degree of flame retardancy in them. Hence these classes of textiles must be treated with suitable flame retardant finishes (Beard and Marzi, n.d).

Flame retardancy has been an area of keen interest among researchers and industrialists, and considerable work has been undertaken since early 1990 to investigate the behavior of intumescent in textile structures. The current established intumescent chemistry has few drawbacks and has few issues which need to be addressed.

The current flame retardant chemistry is mainly dominated with the use of brominated diphenyl oxide flame retardants and other halogen-based flame retardants (De wit, 2002). The European community (EC) and the US government have expressed concerns about formation of potentially carcinogenic and highly toxic substances during combustion of these halogen based flame retardants (De wit, 2002). Dermal exposure of halogen-based flame retardants may cause local irritation to skin, acute to long-term toxicity, genotoxicity, and mutagenicity.

In an effort to address the above concerns, the current studies is aimed at developing new nonhalogen-based eco-friendly intumescent flame retardant chemistry and apply it on textile substrates to make a flame retardant textile substrate.

This research is an effort to develop a phosphorous-based flame retardant that would minimize the health hazards caused by the presence of halogen compounds, especially bromine-based compounds. In this research a new technique to attach the phosphorous-based flame retardant to the textile substrate specifically, cotton with silane-based system to make the finish durable to normal laundering of textiles, will be investigated.

Owing to the possible health hazards because of the use of halogen-based fire retardants, research scientists, industry, and military are diligently working towards finding a new, less hazardous, more environmentally responsible and durable flame retardant.

Problem statement

This research intends to develop an environmental friendly and durable fire- retardant fabric thus addressing the current problem associated with available fire retardant fabrics of producing toxic gases during ignition.

Purpose and objective

Purpose:

This research aims at developing an eco-friendly flame retardant finish by synthesizing nonhalogen-based flame retardants and applying them to textile substrates, specifically cotton fabric.

Based on this purpose, the following four objectives emerged:

1. Synthesize Spirocyclic pentaerythriol diphosphoryl phosphorous (SPDPC) in the laboratory.
2. The synthesized SPDPC will be converted into Bis-diglycol Spirocyclic pentaerythriol bisphosphorate (BSPB).
3. Further, the BSPB will be attached to the fabric using sol gel chemistry to make ecofriendly flame retardant finish, which is durable to laundering.
4. Finally, essential tests would be conducted on the treated fabric to investigate the flame retardancy of fabric and other essential fabric properties such as tensile strength and change in stiffness of the coated cotton sample.

Theoretical framework

SPDPC as flame retardant

Spirocyclic pentaerythriol diphosphoryl chloride is a cyclic structure with phosphorous atom attached to its structure (Horrocks, 2005).

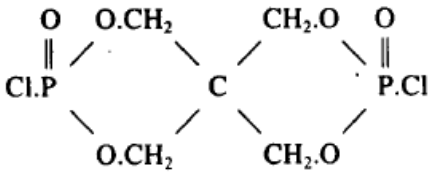


Figure 1 .SPDPC structure

Phosphorus present in the cyclic structure of SPDPC plays a vital role in imparting flame retardant property to the compound. It is proposed, therefore, that polyol phosphonyl chlorides like SPDPC will substitute active hydrogens present in fiber-forming molecules and thereby introduce substituent that is both a char promoter and a char former. In turn, this will decompose via a liquid intermediate phase following release of phosphoric acid as the monomeric or polymeric or polymeric form (Horrocks, 2001).

Fiber-forming polymers such as cellulose, polyamides, and polyester have –OH, -NH_2, and –NH as the common active groups present in them. Cellulose, which is the main fiber-forming material in cotton, contains both primary hydroxyl (C [6] and C [4] positions) and secondary hydroxyl (C [3], [C4] positions) groups are possible phosphorylation sites.

Chapter 2: Literature review

Over the years a considerable amount of work has been done to explore the potential of intumescent flame retardant fiber combinations to produce flame retardant effects in textile materials (Horrocks, 2000). With regard to the use of the established intumescent based on ammonium polyphosphate, melamine phosphate, and pentaerythriol derivatives, two major drawbacks are evident within the fiber and textile areas. First, they can only be applied as a fibrous surface treatment in a bonding resin that affects desirable textiles properties such as appearance and handle (Horrocks, 2000). Second, and perhaps of greater importance even for applications whose aesthetics are less important, are their relatively high solubility in water, hence poor fastness to laundering (Horrocks, 2000). Ideally, the intumescent should be integrated within the fiber structure at the molecular level. As a consequence, attempts to develop substantive intumescent treatments for cellulose, flame retardant cellulose, polyamide 6, polyamide 6, 6, and wool have been intensely researched since 1999 (Horrocks, 2001).

Few reviews concluded that fiber-substantive intumescence require following properties (Horrocks, 2005):

(i) The intumescent moiety within the fiber structure is a single molecular species; or
(ii) The fiber functions as one of the intumescent components.

Nifant'ev et al. have demonstrated that by reacting SPDPC with melamine, a single intumescent molecule may be synthesized (Nifant'ev, 1965). More recently, SPDPC has been incorporated as a comonomer in polyesters and demonstrated its char-forming activity in these polyester thermoplastic polymer matrices (Wang L, 2010).

These ideas have been extended by reacting polyol phosphoryl chlorides with fiber-forming polymers, expecting the polyol to substitute active hydrogen in polymer substance to confer inherent intumescence (Wang L, 2010). SPDPC has been shown to transfer its intumescent properties onto cellulosic fibers following their phosphorylation (Horrocks, 2004). A feature of SPDPC is the six-membered cyclic phosphate structure, which contributes to its high yield during synthesis, and its general stability apart from its tendency to form char when heated (Horrocks, 2004).

The use of polyol phosphonyl chlorides as phosphorylating agents for cellulose is taken as means of introducing a char-forming center in association with an acid-generating moiety into a functional polymer like cellulose, which itself is potentially char-forming (Nifant'ev, 1965). Flame retardancy has been successfully introduced with polyol phosphonyl chloride specifically, Spirocyclic pentaerythriol di (phosphoryl chloride) (SPDPC) (Horrocks, 2005).

Proban treated flame retardant cotton fabric

PROBAN® is a process developed by Rhodia industries for imparting flame retardancy property to cellulosic and cellulosic blend textile substrates. Flame retardancy of proban process is based on phosphorous containing compound tetrakis (hydroxymethyl) phosphonium chloride (THPC). THPC is further reacted with urea, and the final product is applied on the cotton substrate using pad-dry-cure method. The fabric is further reacted with ammonia and oxidized with hydrogen peroxide. Proban forms an insoluble polymer in the interstices of fibers and yarns of the cotton fabric. Thus, there is no chemical bonding between cotton and proban, but proban is held mechanically to the cotton fibers (Horrocks, S.Anand, p.165). This is one of the reasons for the harsh feel of proban-treated cotton textiles.

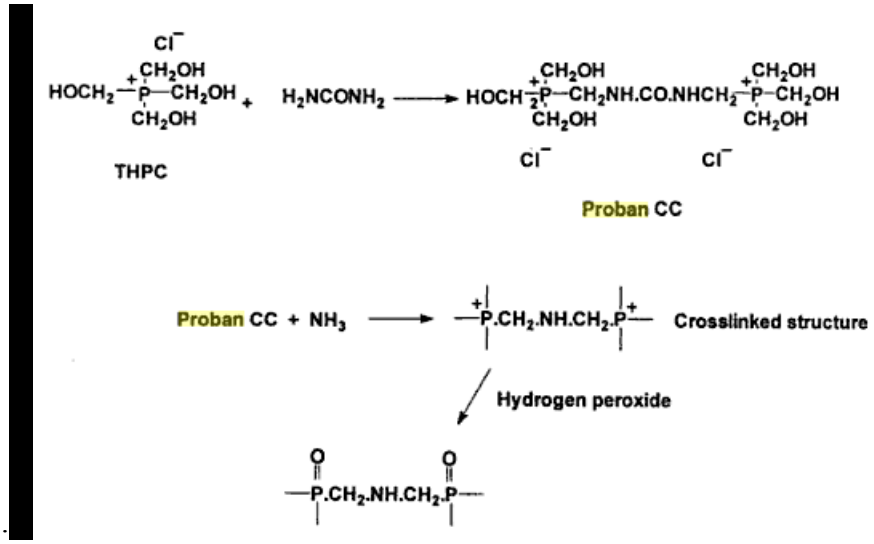


Figure2. Proban chemistry.

Horrocks and Kandola et al, in their study for application of SPDPC on cotton substrate, studied flame retardant properties of proban-treated fabric with application of various phosphorous base flame retardants. His study concluded that a proban-treated cotton sample can be more easily phosphorylated than a pure cotton sample at 160 ^{o}C at various SPDPC: fiber ratios. The greatest phosphorous value occurs for proban-treated cotton: SPDPC ratio of 3:1 at 160 degree Celsius for 2h (Horrocks, 2005).

Sol-gel chemistry

Sol-gel is defined as follows: Sol is made up of dispersed colloidal particles (size 1-1000 nm) and a liquid phase together. Gels are interconnected, rigid networks with pores of sub-micrometer dimensions and polymeric chains whose average length is greater than a micrometer (Hench, 1990). C.J. Brinker (1991) noted that the sol-gel process uses inorganic or metal compounds as raw ingredients. These compounds are hydrolyzed and condensed in aqueous or organic solutions to form inorganic polymers with M-O-M bonds. Metal

alkoxides M $(OR)_z$, where R is the alkyl group, are the most commonly used organic compounds. The alkoxides are dissolved in alcohol hydrolyzed by dissolving under acidic, neutral, or basic conditions. A typical condensation reaction for hydroxyl ligand M-O-M for silicates is shown below:

$$Si(OR)_3OH + Si(OR)_4 \rightarrow (RO)_3Si{-}O{-}Si(OR)_3 + ROH$$
$$2Si(OR)_3OH \rightarrow (RO)_3Si{-}O{-}Si(OR)_3 + H_2O$$

Figure3. Condensation reaction for hydroxyl ligand for silicates

Metals and metalloids surrounded by various ligands is a good example of sol-gel precursor. The precursors undergo polymerization to form a giant molecule and reach a stage where "gel" is formed. This point is called "gel point." Hench defined a gel as a "two component semi-solid system which is rich in liquid" (Hench, 1990). Sol gel-system is used for application of various finishes like soil repellent, flame retardant, perfume release, and antimicrobial finish on textile substrates. The application proceeds with drying and curing. Drying by evaporation results into shrinkage of the gel. This dried gel is known as "Xerogel." Xerogels have labile chemical sites that can be exploited for further modification of properties of coated surface.

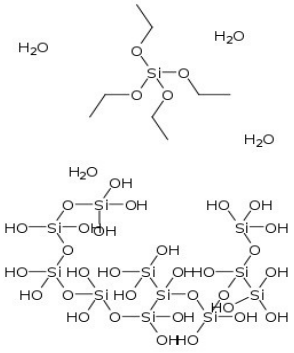
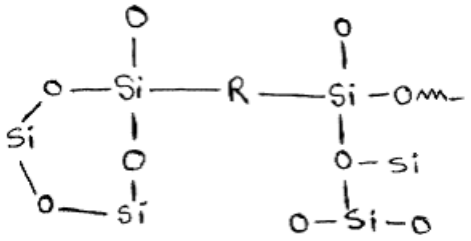


Figure 4. Schematic of sol-gel formation from silane precursor

In current research Bis-silane is converted into sol and applied to cotton fabric using pad-dry-cure method. The following reaction occurs:



R (Bis-silane) = 

Figure 5. Sol formations with Bis- silane

Sol-gel treatment of cotton substrates

Cotton fabrics have been treated by a sol-gel process in order to create a silica compact coating on the fibers to enhance their thermal stability and flame retardancy. The effect of process parameters such as silica precursor: water molar ratio and drying conditions (temperature and time) has been thoroughly investigated and optimization has been done.

Jenny Alongi et al. applied sol-gel prepared using Tetramethoxy silane (TMOS) as a precursor for sol-gel preparation. Combustion behavior of cotton before and after the sol-gel treatments was studied, and it was concluded that improvement in flame retardancy of sol-gel coated cotton fabric can be related to the formation of silica coating on cotton fibers that acts as physical barrier to heat and oxygen diffusion. As a consequence it hinders cotton combustion, favoring cellulose carbonization and thus imparting the flame retardancy to the cotton fabric. The Silica coating was found resistant to washing treatment.

The current research uses intumescent chemistry by using SPDPC as flame retardant and using sol-gel process to adhere the flame retardant onto cotton fabric using pad-dry-cure to impart flame retardancy onto cotton fabric.

Study design

This study includes synthesis of basic flame-retardant SPDPC and further conversion of SPDPC to BSPB. A sol system will be prepared out of BSPB, and this sol-gel would be applied on cotton fabric using Pad-Dry-Cure process.

Study type

The best optimum process for making eco-friendly flame retardant finish using the process described in study design would be the one that produces a fabric sample that gives maximum flame retardancy quotient on vertical flammability tester.

Data gathering

Data were collected from the vertical flammability tester, which indicated the flame retardant properties of the cotton fabric. To test the flame retardant properties of the treated fabric, vertical flammability test was done according to ASTM D-6413 standards. Tensile test of the treated fabric will be tested on MTS tensile tester.

Chemical and physical properties of synthesized flame retardants would be tested on TA Q 200 Differential scanning calorimeter (DSC) and Bruker Tensor 27 FTIR instruments. Thermal decomposition study of treated and untreated fabric would be done using TA Q 50 Thermogravemetric analysis instrument.

Measures to insure safety and confidentiality for human or animal subjects

No human subject will be involved in this study. The researcher will insure safety by carrying out the synthesis under a closed hood with an exhaust, and wearing protective goggles, a lab coat, and protective gloves during the time of experimentation.

Data analysis

Data were studied on the basis of the readings obtained from the vertical flammability tester showing time required for flame to cover specific distance on the treated fabric. Analysis of variance was used to test any significant change in properties after coating of cotton sample.

Chapter 3: Research design and Methodology

Materials and chemicals

The substrate used for this experiment was 100% cotton desized and scoured fabric and was used as received from the manufacturer. Pentaerythriol, 98% pure, MP 253-258 degree Celsius and Phosphorous Oxychloride, 99% pure (BP. 105 degree Celsius) were obtained from Sigma Aldrich Inc. and used as received. Dibutyltin dilaurate reagent, Ethylene glycol, 99.8 % pure (B.P 195-198 degree Celsius), Diethyl ether anhydrous, 99.7% pure (B.P 34.6 degree Celsius), Acetone, 99.9% pure, and ethanol were obtained from sigma Aldrich and were used as received. Silquest A-Link 25 γ-Isocyanatopropyltriethoxysilane (B.P 238) was obtained from Momentive and used as received.

Experimental methods

Synthesis of Spirocyclic pentaerythriol diphosphoryl chloride

Reaction between pentaerythriol and Phosphorous (V) Oxychloride:

1. Weighing of chemicals: Pentaerythriol and phosphoryl chloride were reacted in molar ratio of 0.5:3.5.

2. These two chemicals were added in a three-neck glass reactor. Nitrogen gas, temperature controller, and condenser were connected to the reactor. A magnetic stirrer was used to stir the mixture with gradual drop-by-drop addition of phosphoryl chloride to pentaerythriol.

3. Temperature was gradually increased to 80 degrees Celsius using an oil heated heating system. Reaction was continued at 80 degree Celsius for 2 hours. Further temperature was raised to 115 degree Celsius gradually and held for 20 hours.

4. Semi-viscous white mass was collected at end the end of reaction. The product was washed four times with Diethyl ether and acetone.

5. The reaction product was air dried.

Synthesis of Bis diglycol Spirocyclic pentaerythriol bisphosphorate (BSPB).

Reaction between SPDPC and ethylene glycol:

1. Weighing of chemicals: The synthesized SPDPC and ethylene glycol were reacted in molar ratio 0.1:0.25.

2. This solution was taken in a three-neck glass reactor. Nitrogen gas, temperature controller, and condenser were connected to the reactor. A magnetic stirrer was used for stirring, and the mixture was heated gradually to 80 degree Celsius and the held there for 6 hours. Further temperature was raised to 130 degrees Celsius, and the reaction mixture was held there for 4 hours.

3. The reaction system was cooled and the product was washed with diethyl ether and acetone to obtain white powder. The product was further dried under vacuum at 40 degree Celsius for 1 hour.

Synthesis of Bis-Silane

1. Weighing of chemicals: BSPB synthesized in step 2 was reacted with isocyanato trimethoxysilane in in molar ratio 1:2.

2. 0.1 gram Dibutyltin dilaurate was used as catalyst for the reaction. The reaction mixture was put in a three-neck glass reactor with arrangements for nitrogen and temperature controller. The reaction mixture was gradually heated to 60 degree Celsius for 4 hours.

3. Reaction mixture was cooled down to room temperature and tested for formation of Bis silane using Fourier transformation infrared spectroscopy

Synthesis of Sol-gel

1. Weighing: 2 gm. of Bis silane was mixed with 18 ml water and 58 ml of ethanol.

2. The reaction mixture was stirred at 450 rpm using magnetic stirrer for 15 minutes.

Application of sol-gel on cotton fabric:

1. Sol- gel was applied on cotton fabric using pad-dry-cure technique.

2. Mangle pressure was adjusted to 25 psi, and fabric was treated after 4 dip and 4 nips

3. After dip and nip, fabric was dried in oven at 60 degree Celsius for 10 minutes.

4. Finally, dried fabric was cured at 115 degree Celsius for 6 minutes.

Characterization of cotton fabric treated with flame retardant finish:

FTIR technique to determine the presence of necessary chemical groups and bonds in product

FTIR stands for Fourier Transform Infrared Spectroscopy. According to quantum mechanics, every substance is made of molecules. These molecules are capable of attaining a vibrational excited state by taking energy from a basic unit of light, which is quanta. Specific vibrations correspond to specific chemical bonds and chemical groups, and this correlation is described in terms of wavenumbers (Schmitt & Flemming, 1998).

FTIR spectrum of synthesized SPDPC was taken to ensure the presence of P-Cl peak stretching (550 cm^{-1}), P-O (1307 cm^{-1}), and P-O-C (1027 cm^{-1}). Presence of these peaks ensures formation of SPDPC (Horrocks, 2005).

FTIR spectrum of synthesized BSPB was taken to ensure the absence of P-Cl peak (550 cm^{-1}) and presence of P=O (1257 cm^{-1}) and P-O-C (1027 cm^{-1}). Absence of P-Cl peak ensures formation of BSPB (Wilkie, 2006). The silane synthesized from BSPB and IPTMS was tested for presence of bonds N- C (1530 cm^{-1}), and C=O (1700 cm^{1}).

One drop of the sample was placed on the conical sample plate of a BRUKER FTIR Tensor 27 model testing machine. Before the actual sample was tested, it was necessary to run a background signal on the FTIR instrument.

Differential scanning calorimeter (DSC) to test melting behavior of SPDPC

DSC instrument measures the heat changes occurring in a material during increase or decrease in temperature. By studying the behavior of materials under exposure of heat, it becomes possible to study materials in their native state.

DSC is defined as “measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program” (Powell, 1998).

A sample of synthesized SPDPC was tested on DSC to determine its melting point. The melting point of SPDPC should range between 235-240 degree Celsius (Horrocks, 2001).

Flame retardant testing

The cotton fabric treated with flame retardant was tested for its flame retardancy according to ASTM D6413-99 vertical flame resistance testing.

A cotton specimen was cut 12 inch x 3 inch, length being parallel to the warp side of the fabric specimen. The sample was positioned vertically above a controlled flame and exposed for a specified period of time. The flame was then removed and afterflame time and afterglow time were measured. Char length and any evidence of melting or dripping were noted.

The specimen was adjusted 0.75 inch above the flame and is exposed to the flame for 12 seconds. After flame time, char length and any melting or dripping were reported (Lewin, 1973).

Durability testing of coated cotton fabric

Cotton fabric coated with flame retardant was tested for its durability using standard textile testing procedures. The specimen was tested for its tensile strength using the ASTM D 5035-95 method and bending resistance using ASTM D5342-97. Thickness testing was done using Electro Physik precision Elektro Physik precision standard 526 μm ± 1% on the Minitest 600B coating thickness gauge.

Tensile testing of the flame retardant coated fabric

The flame retardant coated fabric sample was tested for tensile strength properties using ASTM D5035-95 standard. The specimen under test is clamped to the MTS tensile testing instrument and a force is applied gradually until it breaks. The sample was prepared of size 8 inch x 1inch and clamped to jaws which were 6 inches apart as their start position. The sample was subjected to constant extension as the jaws moved apart at 2 inches per minute.

Five coated samples and five uncoated cotton samples were tested for breaking strength. Change in breaking strength after coating and standard deviation were reported.

Bending resistance of flame retardant coated fabric

This test determines the stiffness of the coated specimen by bending the specimen of defined dimension through a specified angle using a specific testing instrument. In this case it is Teledyne Taber stiffness tester (model 150- B). The sample is bent on both the left and right sides through 15 degrees.

ASTM D5342 method was followed as guide for testing

Five test specimens of 1.50 ± 0.01" x 2.75 ± 0.01" dimension were tested for bending resistance after coating of flame retardant coating. The value obtained after the average of the deflections to right and left, which is taber unit, was multiplied by 0.098066 to express the stiffness is millinewton meters.

Thickness of coating

The thickness of the coated fabric was determined using Elektro Physik precision standard 526 μm ± 1% on the Minitest 600B coating thickness gauge. Thickness of the coated fabric sample was subtracted from thickness of uncoated cotton sample to determine the thickness of the coat after a specific number of dips and nips of coating. Operating instruction from Elektro Physik Minitest 600 manual was followed to conduct the testing.

Chapter 4: Results and Discussion:

The primary focus of the thesis was to develop eco-friendly flame retardant fabric having the necessary durable properties. Thus an experiment consisting of synthesis plans and textile testing was designed to achieve this objective.

This chapter discusses various testings like FTIR and DSC that were carried out to ensure correct product after each stage of synthesis of the flame retardant finish. Along with that, the chapter covers reporting and analysis of test data gathered from textile testing of coated fabric for its flame retardancy and durable properties.

Synthesis of SPDPC: Reaction of Phosphorous Oxychloride and pentaerythriol.

In the synthesis of SPDPC, pentaerythriol and phosphorous Oxychloride were reacted in ratio 0.5:3.5 for 2 hours at 80 degrees Celsius and then for 20 hours at 115 degrees Celsius. The reaction was carried out in a three-neck glass reactor under inert atmosphere created with a supply of nitrogen. Detailed scheme of synthesis is explained in the methodology section.

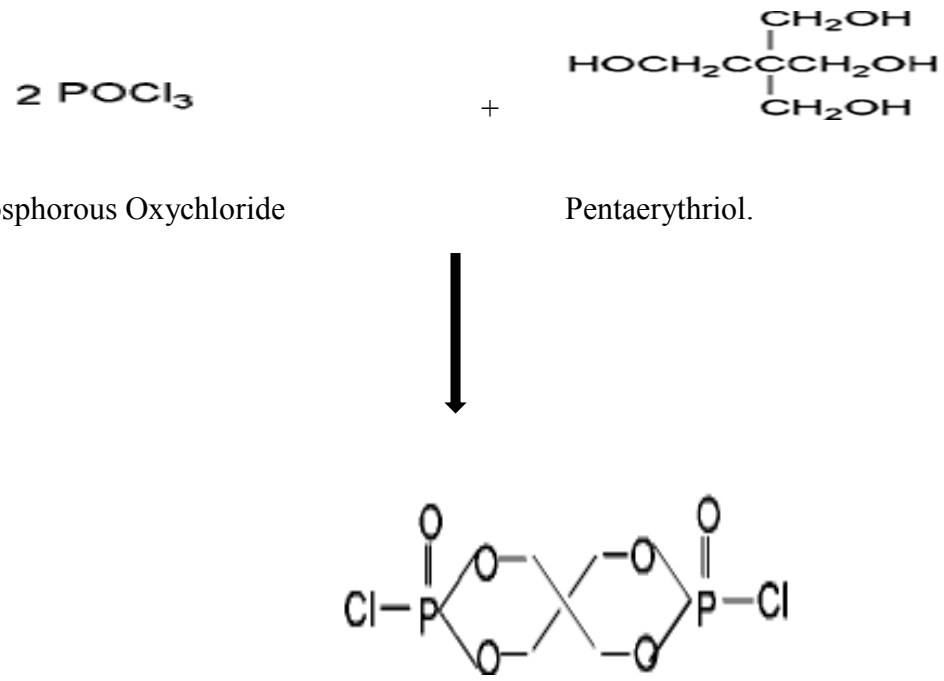


Figure 6. Spirocyclic pentaerythriol diphosphoryl chloride

Figure 6 shows the reaction between pentaerythriol and phosphorous Oxychloride leading to formation of P-Cl linkage, which is the key reacting link for further synthesis of BSPB from SPDPC.

SPDPC FTIR Analysis

Fourier transform infrared spectroscopy can be used to identify the presence of particular chemical groups in a compound. In this study, the Bruker tensor 27 FTIR instrument was used to

identify the presence of P-Cl at (550 cm^{-1}), P-O vibration stretching at (1307 cm^{-1}), and P-O-C vibration stretching at (1027 cm^{-1}) in the synthesized product after reaction between pentaerythriol and phosphorous Oxychloride. Presence of these bonds indicates the synthesis of SPDPC.

The FTIR spectra of the product formed after reaction of pentaerythriol and phosphorous Oxychloride was tested on Bruker Tensor 27 instrument. Following FTIR spectra was obtained. The presence of following peaks in IR spectrum of the product indicates formation of SPDPC.

Table 1

SPDPC FTIR data

Serial number	Bond	Wavenumber
1	P-Cl	550 cm^{-1}
2	P-O	1307 cm^{-1}
3	-P-O-C	1027 cm^{-1}

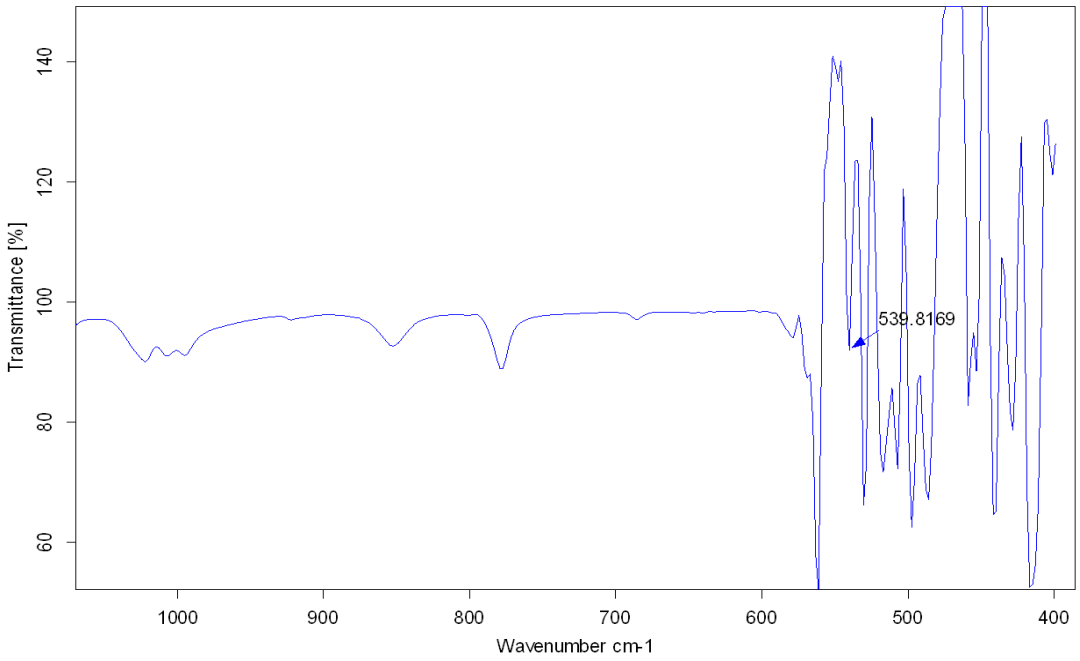


Figure 7. FTIR curve for SPDPC

Figure 7 shows the presence of peak 540 cm^{-1} stretching is related to P-Cl stretching.

Differential scanning calorimeter to test melting point of SPDPC

SPDPC was synthesized in lab as discussed earlier in methodology section. The synthesized sample was tested on differential scanning calorimeter to determine its melting point. This melting of the synthesized sample was compared to the previously reported melting behavior of SPDPC to confirm the success of synthesis. It has been reported that SPDPC melts in range of 235-240 degree Celsius (Horrocks, 2001).

The instrument used for testing was DSC Q200 V24.4 Build 116. A 10 mg sample of SPDPC was tested by heating the specimen from ambient temperature to 270 degree Celsius at 10 degree Celsius /min .Melting point of SPDPC was found out to be 245.57 degree Celsius by analyzing the peak in DSC curve obtained from the testing.

Differential scanning calorimeter can be used to study the behavior of material under the influence of heat.

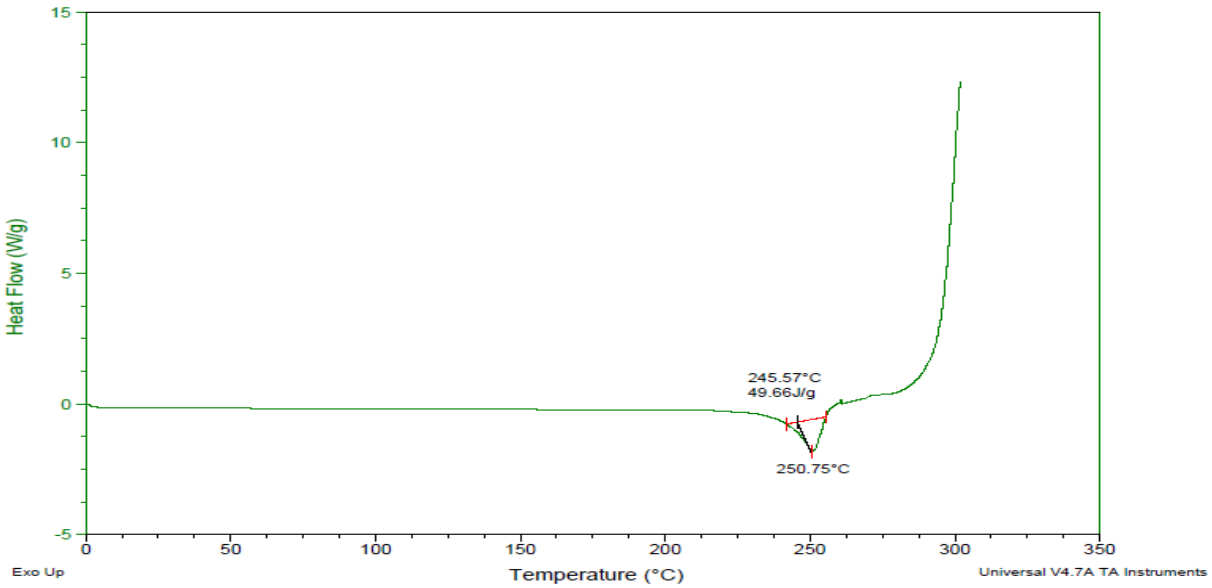


Figure 8. DSC curve for SPDPC melting behavior

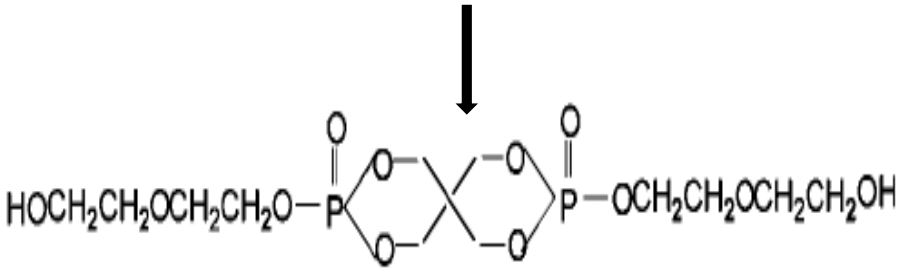
Since the obtained melting temperature and the FTIR data of the synthesized SPDPC was found to match the reported melting temperature and FTIR data of SPDPC in the literature, it is concluded that SPDPC was successfully synthesized in the lab for this experiment.

Figure 8 shows the melting point of the synthesized SPDPC was 245 .57 degree Celsius, which compares to the reported melting point value of SPDPC, 240 degree Celsius.

Synthesis of Bis - diglycol Spirocyclic pentaerythriol bisphosphorate (BSPB)

In the synthesis of BSPB, synthesized SPDPC and ethylene glycol were reacted in molar ratio 0.1:0.25 at 80 degree Celsius and held there for 6 hours. After that, temperature was raised to 130 degree Celsius and reaction mixture was held there for 4 hours (Wilkie, 2006). Reaction was carried under inert atmosphere in a three-neck glass reactor in the presence of nitrogen gas. A detailed synthesis and purification scheme is reported in the methodology section.

Spirocyclic Pentaerythriol diphosphoryl chloride Ethylene glycol



Bis-diglycol Spirocyclic pentaerythriol bisphosphorate (BSPB)

Figure 9. Synthesis of BSPB

Figure 9 shows the reaction scheme for synthesis of BSPB by reacting previously synthesized SPDPC with ethylene glycol under conditions described in synthesis section.

FTIR analysis of BSPB

FTIR analysis of synthesized BSPB was carried out on a Bruker Tensor 27 testing instrument. The curve obtained was compared to the reported literature for peaks present in BSPB to confirm the correct synthesis of BSPB. Reaction between SPDPC and ethylene glycol indicates the disappearance of P-Cl bond in process of formation of BSPB; thus the disappearance of P-Cl bond in the final product indicates formation of BSPB. Other groups whose presence confirms the correct synthesis of BSPB are shown in table 2.

Table 2

BSPB FTIR peaks

Serial number	Bond	Wavenumber
1	-OH	3362 cm^{-1}
2	-P=O	1257 cm^{-1}
3	-P-O-C	1027 cm^{-1}
4	-C-O-C	1130 cm^{-1}

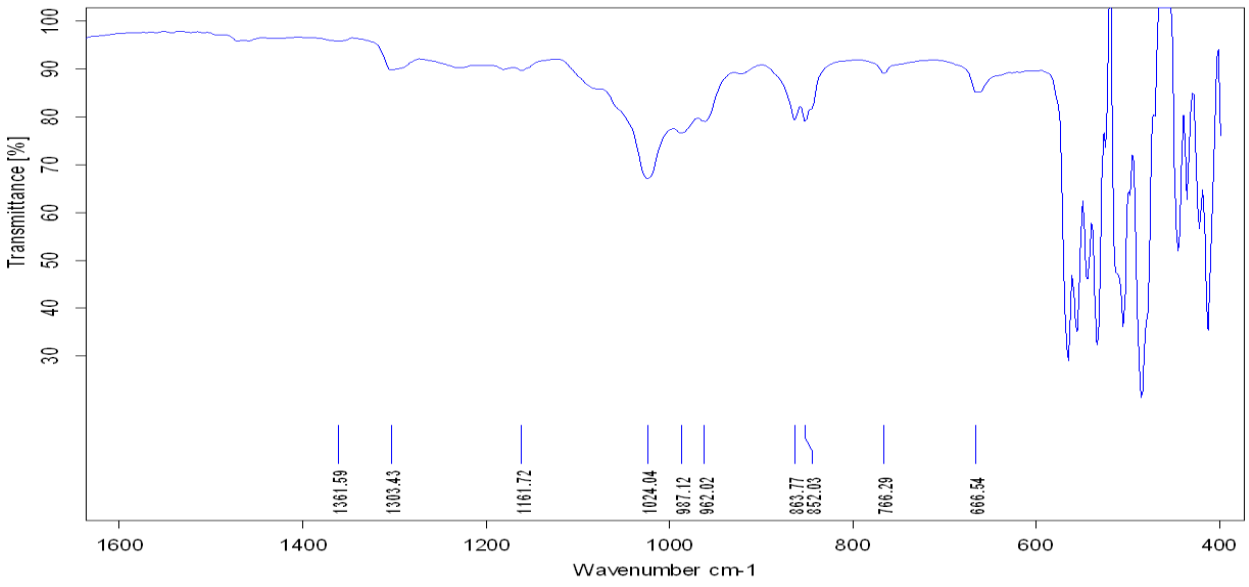


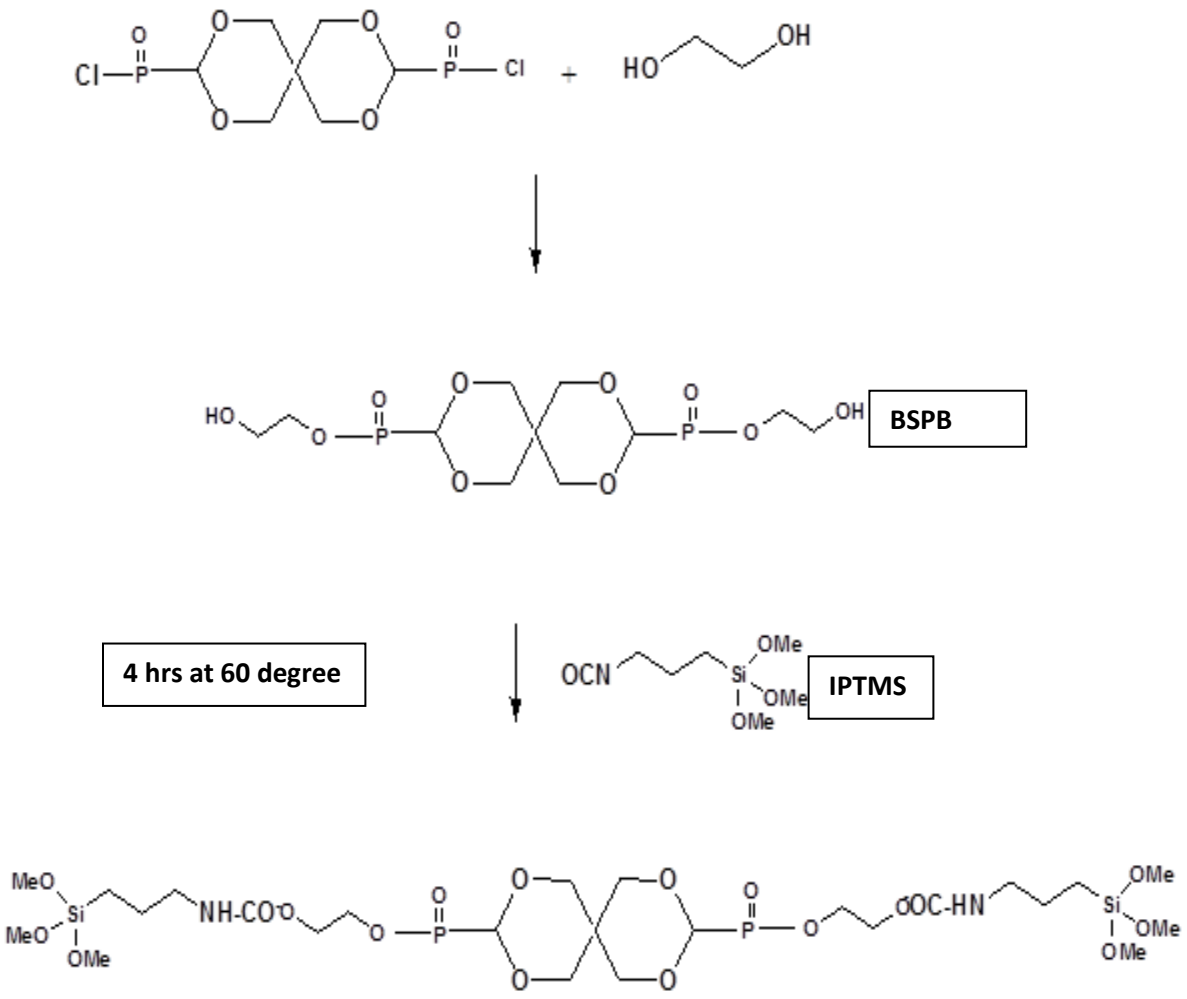
Figure 10. FTIR Curve for BSPB

FTIR curve for sample taken out of synthesized BSPB confirms the correct synthesis of BSPB as the P- Cl curve has disappeared at 550 cm^{-1}.

Synthesis of Bis-Silane

BSPB synthesized in earlier reaction was reacted with Isocyanatopropyl trimethoxysilane in in molar ratio 1:2. Reaction was carried out for 4 hours at 60 degrees Celsius with Dibutyl tin dilaurate as catalyst. A detailed scheme of the synthesis is explained in the methodology section.

Reaction scheme of Bis-Silane synthesis by reacting



Bis-Silane

Figure 11. Reaction scheme for Bis-Silane

The above scheme of reaction shows the synthesis of Bis silane from the reaction between BSPB and Isocyanatopropyl trimethoxysilane.

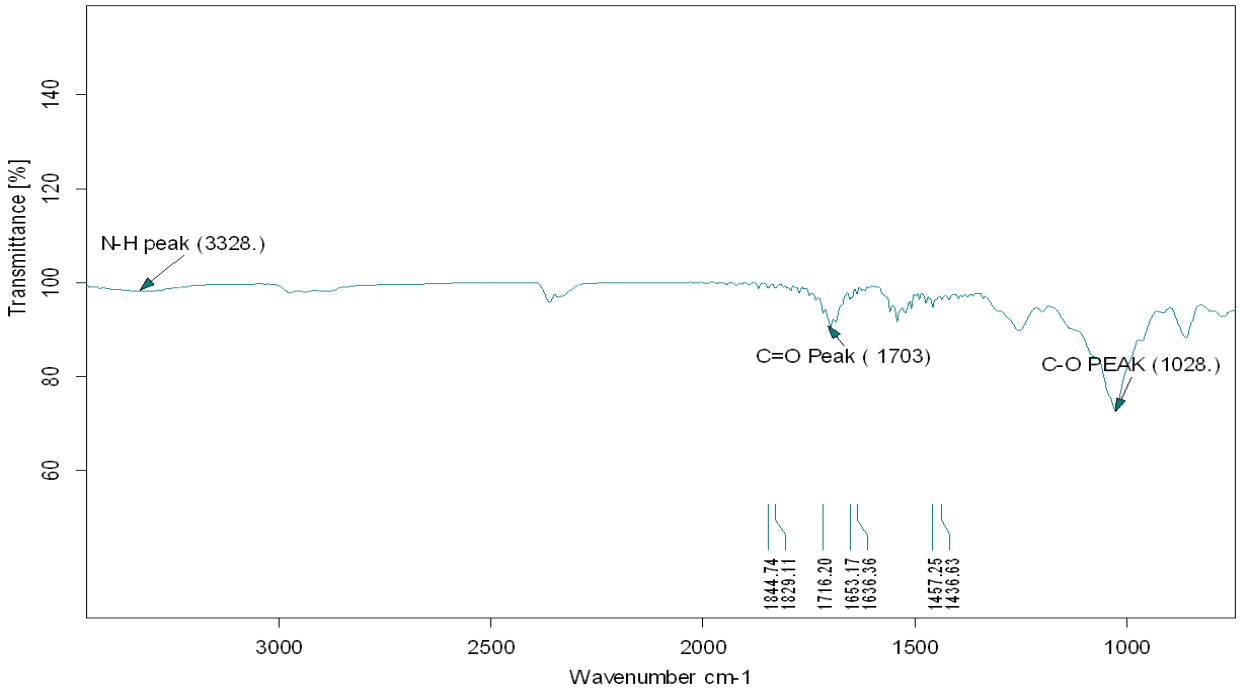


Figure 12. FTIR analysis of Bis Silane

The reaction scheme for Bis silane shows Bis silane has urea linkage, which consists of C=O linkage and N-H bond. Formation of Bis silane is confirmed with presence of following peaks in the FTIR curve taken of the Bis silane synthesized.

Table 3

FTIR peaks for Bis- Silane

Serial number	Bond	Wavenumber
1	N-H	3328 cm^{-1}
2	C=O	1703 cm^{-1}
3	C-O	1028 cm^{-1}

Synthesis of Sol-gel and its application on textile substrate:

Sol-gel is made by dispersing the Bis -silane synthesized in water and methanol and stirring it in high speed magnetic stirrer at 450 rpm. The ratios of various ingredients mixed together in the sol-gel recipe are discussed in the methodology section.

pH of the sol gel solution was found to be acidic, pH 3. Electronic pH meter was used to take the pH readings.

Application of the finish:

The synthesized flame retardant finish was applied on a 100% cotton sample using a padding mangle and Pad-Dry-Cure method. Detailed application scheme is mentioned in methodology section. The Hydroxyl group of the Sol-gel flame retardant finish reacts chemically with the cellulose in cotton to form strong covalent bonds, thus attaching the flame retardant finish to cotton substrate (Alongi, 2011).

Bis - Silane has $-OCH_3$ group as reacting groups which gets converted into –OH after reacting with water and ethanol, thus forming the Sol-gel. Further, when cotton cellulose

which has primary and secondary hydroxyl (-OH) groups react with the –OH groups in Sol-gel and forms a strong covalent bond (Alongi, 2011).

Thermo gravimetric analysis (TGA) testing of thermal behavior of flame-retardant coated sample:

A 100% cotton sample was treated with the synthesized flame retardant following the procedure described in methodology section. A sample was prepared from this treated cotton sample for thermal testing on TGA using the procedure guide for TGA. Thermal behavior of treated and untreated cotton samples in terms of rate of "%weight loss" was studied to draw conclusions about effectiveness of the flame retardant finish. Temperature ramp rate was set at 20 deg.celsius/minute.

TGA curve of thermal behavior of cotton sample treated with flame retardant and untreated cotton sample.

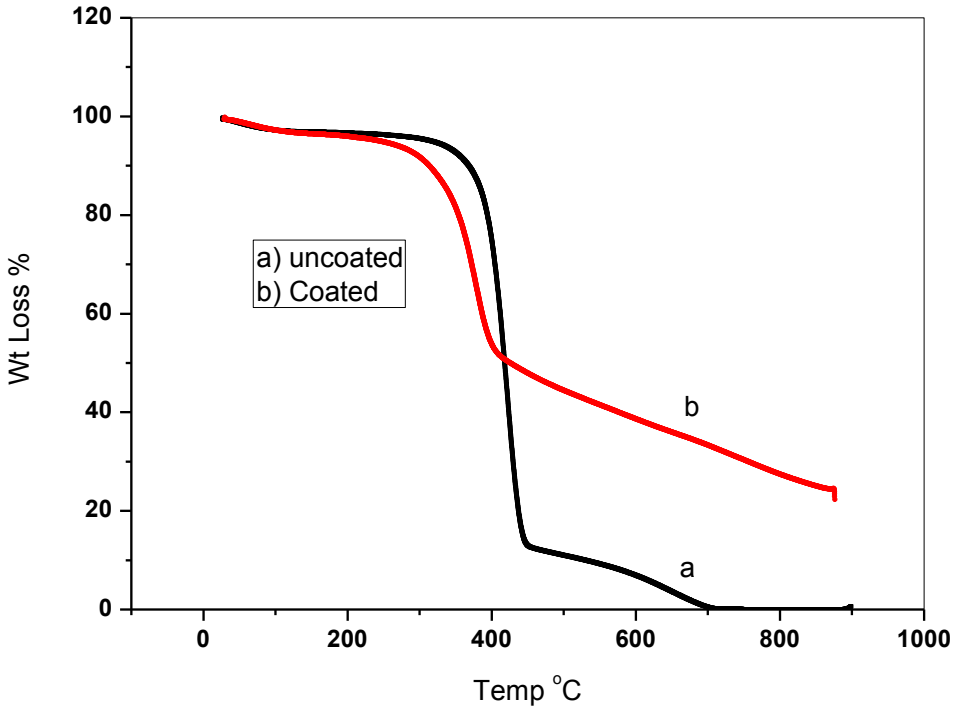


Figure 13. TGA analysis of treated cotton

The TGA thermal degradation curve for coated and uncoated cotton samples indicate that the thermal degradation curve for a coated sample of cotton has a lower slope than the thermal degradation curve of an uncoated sample. This indicated that the coated sample lost weight at a slower rate as than the uncoated sample due to thermal degradation. The uncoated sample lost no weight till 380 degree celsius and then abruptly went thermal degradation at about 420 degree celsius, which is degradation temperature of cotton. The uncoated sample was completely degraded at about 700 degree celsius. The coated sample started weight loss at 360 degree celsius and followed a steady weight loss unlike abruptly degradating like uncoated cotton sample. The coated sample did not degrade completely until 900 degrees celsius. This analysis clearly indicates that a coated flame retardant sample is thermally more stable than the uncoated cotton sample.

Textile testing to test physical properties of Flame retardant coated textile substrate: Tensile strength testing of treated textile substrate:

Textile substrated coated with synthesized flame retardant was tested for any significant change in its tensile strength after coating. Test data for peak load, strain at break in %, and modulus of uncoated and coated sample in warp and weft directions were recorded using MTS tensile testing instrument (Appendix A). The ASTM D5035 test method was followed for testing.

ANOVA test for comparison of means was run to test if there was significant change in tensile change of fabric after coating.

Analysis of change in peak load (lbf) of fabric sample: T testing for test of Tensile test data is shown in Table 4.

Table 4

ANOVA for peak load

Value	Uncoated sample (Warp) (lbf)	Coated sample (Warp) (lbf)
Mean	42.405	36.615
Standard Deviation	3.1538	4.534
Stand.error in mean	1.41	2.02
N = Sample size	6	6

So calculated t –value = 2.3196, Df =8.

At 95% confidence interval the two tailed p –value = 0.0496.

Thus, we conclude that the change in peak load of uncoated and coated fabric was significant. This could be attributed to a loss in strength of cotton due to reaction of the acid with the cotton, resulting in formation of hydrocellulose. Hydrocellulose are formed due to breaking of 1-4 linkage in cotton, thus reducing the strength of cotton fiber.

Further, the difference in mean values of peak load for uncoated and coated fabric shows that there is 13.65% reduction in the strength of coated fabric. As per data received from the US military, the acceptable standards for strength reduction post-flame retardant treatment in army uniform is 54% . Hence, the strength reduction of 13.65% is acceptable

although it can be reduced by working on maintaining the pH of the finish in slightly acidic pH (pH 5-6).

Thickness measurement for coated and uncoated fabric:

Flame retardant finish was applied on the cotton substrate using pad-dry-cure method. Thickness testing was performed on the coated and uncoated fabric to see if there was a significant change in thickness of fabric after coating.

The thickness of the fabric was determined using the Elektro Physik precision standard 526 μm± 1% on the Minitest 600B coating thickness gauge. Thickness of coated and uncoated fabric was measured at 10 different areas on the sample (Appendix B). Testing was done as per guidelines in the ASTM B499 test method.

ANOVA test for comparison of means was run to determine if there was significant change in thickness of fabric after coating.

Table 5

ANOVA for thickness

Value	Thickness of Uncoated sample(μm)	Thickness of Coated sample(μm)
Mean	744.00	781.00
Standard Deviation	10.75	21.83
Stand.error in mean	3.4	6.9
N = Sample size	10	10

So calculated t-value = 4.8079, Df = 18.

At 95% confidence interval, the two tailed p –value = 0.0001.

Thus since the P value is significantly lower than 0.05, there was a statistically significant change in thickness of fabric after coating. Mean values of thickness of coated and uncoated show that there was a 5% increase in thickness of coated fabric. Padding mangle nip pressure is the determining factor in pad-dry-cure process to decide the thickness of coat. The thickness of final coat can be adjusted by adjusting the nip pressure of padding mangle.

Flame retardancy testing of treated fabric sample:

The flame retardant coated samples were tested for flame retardancy in a vertical flame retardancy testing instrument. The cotton sample treated with the synthesized flame retardant finish was tested for flame retardancy with the ASTM D6413-99 method. The objective of the test was to test the treated sample for flame retardancy based on its flame time, burn length, and any dripping behavior on exposure to flame. According to ASTM D6413-99, burn length is defined as distance from the original edge to the farthest evidence of damage to the test specimen due to flame impingement, including areas of partial or complete consumption, charring, or embrittlement, but not including areas sooted, stained, warped, or discolored, nor areas where material has shrunk or melted away from the heat source.

ASTM- D 6413 vertical flammability test was followed for testing.

Table 6

Test results for vertical flame retardant testing of coated fabric:

Test result	Coated	Uncoated
Flame extinguishes time:	10.5 seconds	Burnt to char
Char length:	113 mm	Burnt to char
Afterglow.	No	NO
Dripping	No, as it was a natural fiber (cotton).	NO

Test pictures

Coated sample

Uncoated sample: Burnt to char

Figure 14. Comparative illustration of the burn sample in the Vertical flammability test.

The images for vertical flammability test for the coated and uncoated fabric sample indicates that the coated sample had significant flame retardancy and resisted propagation of flame. The uncoated fabric sample turned to char.

Thus we conclude that the fabric coated with flame retardant finish resisted the propagation of flame and exhibited flame retardancy.

Chapter 5: Conclusion

This research was set up to achieve the basic objective of developing a new ecofriendly flame retardant finish and applying it on the cotton fabric to test for its flame retardancy behavior. After the analysis of results obtained from experiments in this study, following conclusions were reached for the set objectives:

Objective 1: Synthesize Spirocyclic pentaerythriol diphosphoryl phosphorous (SPDPC) in laboratory.

Conclusion: From FTIR data and DSC curve analysis, it was confirmed that SPDPC was successfully synthesized in this experiment.

Objective 2: Convert the synthesized SPDPC into Bis diglycol Spirocyclic pentaerythriol bisphosphorate (BSPB).

Conclusion: FTIR analysis of the synthesized BSPB confirmed that BSPB was successfully synthesized.

Objective 3: Attach the BSPB to the fabric using sol gel chemistry to make ecofriendly flame retardant finish.

Conclusion: Sol-gel was prepared using BSPB and applied on cotton fabric using pad-dry cure. Vertical flammability results showed that the coated fabric retarded the propagation of flame.

Objective 4: Conduct essential tests on the treated fabric to investigate the flame retardancy of fabric and other essential fabric properties such as tensile strength and change in stiffness of the coated cotton sample.

Conclusion: Flame retardant testing results and Thermo gravimetric analysis showed positive results for flame retardancy of coated textile substrate. Coated fabric showed 13.5 % reduction in tensile strength. There was a 5% increase in thickness of the coated textile material.

Further, analysis of physical properties of coated substrate showed a statistically significant decrease in tensile strength after coating and curing of the sample. The increase in thickness of the coated textile substrate was found to be statistically significant.

Future research recommendations:

Further research can be in done in areas of improving the synthesis and purification process of SPDPC and BSPB by working on reducing of pH of products close to neutral. Advances in this research could be made by working on interaction of sol-gel with cotton fabric to test the efficiency of bonding between sol gel and hydroxyl groups of cotton. Another interesting feature can be added by the grafting of the hydrophobic group along with the flame retardancy imparting groups to make the final product multi-functional.

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Appendix A:

Tensile strength testing of fabric :

Instrument : MTS tensile tester

Sample size: 1”x 8” sample.

Table for tensile testing:

Sr no.	Uncoated sample		Coated samples	
	Warp (lbf)	Weft (lbf)	Warp (lbf)	Weft (lbf)
1	39.97	35.62	36.56	33.11
2	42.22	34.89	38.90	37.60
3	41.56	38.11	34.71	31.89
4	43.52	33.33	36.00	34.25
5	42.60	36.59	35.63	37.50
6	44.56	38.23	37.89	36.21
Mean load (lbf)	42.405	36.12	36.615	35.09

Appendix B:

Thickness testing for coated and uncoated fabric:

Fabric Thickness Measurement		
Sr. No.	Coated (µm)	Uncoated (µm)
1	801	737
2	797	743
3	780	760
4	760	749
5	785	765
6	768	749
7	815	745
8	769	726
9	780	726
10	756	729
Mean	781	744.00