FLAME RETARDANT FINISHING OF COTTON FLEECE

by

XIALING WU

(Under the Direction of Charles Q. Yang)

ABSTRACT

In this research, an inorganic phosphorus-containing flame retardant system was developed for cotton fleece. The aluminum hydroxyphosphate (AHP) formed *in situ* on cotton by the reaction of aluminum sulfate and sodium phosphates was effective in reducing the flammability of cotton fleece from Class III to Class I. The treated cotton fleece retained Class I flammability after one home laundering or the combination of dry-cleaning and hand washing procedure.

Non-phosphorus polycarboxylic acid and phosphorus-containing polycarboxylic acid flame retardant finishing systems were developed for cotton fleece and they were the major part of this research. Polycarboxylic acids themselves without esterification were not effective in reducing the flammability of cotton fleece. The esterification of bi-functional carboxylic acids, succinic acid and malic acid, with cotton cellulose, reduced the flammability of cotton fleece from Class III to Class I. The treatment of cotton fleece with bi-functional carboxylic acids was also durable to multiple home laundering cycles. The esterification of multi-functional carboxylic acids, BTCA and citric acid, with cotton cellulose, was more effective than that of bi-functional carboxylic acids in reducing the flammability of cotton fleece, since multi-functional carboxylic acids had higher esterification efficiency with cotton cellulose. The treatment of multi-functional carboxylic acids with cotton cellulose also increased the dimensional stability of cotton fleece, yet, decreased the bursting strength. The treated cotton fleece passed the 45 ° flammability after 20 home launderings.

In the phosphorus-containing polycarboxylic acid system, unsaturated bi-functional carboxylic acid, maleic acid (MA), and sodium hypophosphite were used to flame retardant finish cotton fleece. MA esterified cotton cellulose at relatively low temperatures in the presence of NaH_2PO_2 as catalyst, and that MA esterified to cotton was able to further react with NaH_2PO_2 at higher temperatures (≥150ºC), which bonded phosphorus to the cotton cellulose. The reactions between MA and NaH_2PO_2 on cotton also lead to the crosslinking of cotton cellulose. The treatment of MA and NaH_2PO_2 was effective in reducing the flammability of cotton fleece from Class III to Class I and durable to multiple home laundering cycles.

The possible mechanism of polycarboxylic acids flame retardant finishing of cotton fleece was that the esterification of cotton cellulose with polycarboxylic acids reduced the depolymerization reaction, yet, increased the dehydration reaction during the thermal decomposition process.

INDEX WORDS: Cotton fleece, 45 ° Flammability, Inorganic-phosphorus containing system, Polycarboxylic acids, Phosphorus-containing polycarboxylic acid system, Succinic acid, Malic acid, 1,2,3,4-butanetetracarboxylic acid (BTCA), Citric acid, Maleic acid, Thermal analysis, TG, DSC, Depolymerization, Dehydration.

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DEDICATION

This dissertation is dedicated to my husband, Fenghai Guo, my new born baby girl, Maggie Yichen Guo, my parents, Lishu Wu and Longhua Xu, my sister and brother, and my parents-in-law, for their support and patience.

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CHAPTER 1

INTRODUCTION

Flame resistance is a critical property for textile products to ensure the safety of consumers. The U.S. Consumer Product Safety Commission (CPSC) promulgates and enforces the flammability regulations of general wearing apparel, children's sleepwear, carpets, and mattresses, etc. The flammability of general wearing apparel, including raised surface fabrics, is regulated under Standard 16 CFR 1610 (Standard for the Flammability of Clothing Textiles). Fabrics having Class III flammability are not allowed to be sold in the U.S. market [1].

Cotton is a highly combustible fiber compared with wool and synthetic fibers. Whenever untreated cotton is exposed to oxygen and the temperature is high enough to initiate combustion (360-420 ℃), it will either burn (flaming combustion) or smolder (smolder combustion) [2]. The flammability of a cotton fabric largely depends on the construction and density of the fabric. Cotton fleece is a knitted fabric with a highly napped surface. It usually has low density and contains a considerable amount of air in its fuzzy surface. Thus, cotton fleece usually has higher flammability than most woven and knitted cotton fabrics. In the most cases, 100% cotton fleece cannot meet the Standard 16 CFR 1610 without chemical treatment [3-5].

There are three ways to reduce the flammability of cotton fleece, i.e., blending cotton fiber with a synthetic fiber such as polyester, treating the fabric with a flame retardant, or changing the construction of the fleece fabric. However, blending cotton with synthetic fibers is not always a guarantee for the fleece to meet the standard. Sometimes 90/10 and 80/20 cotton/polyester blend fleeces still fail the 16 CFR 1610 test [3-4]. Blending cotton with polyester also changes the desired property of 100% cotton fleece. Changing the construction alters the desirable characteristics of cotton fleece. Thus, treating cotton fleece with a flame retardant becomes the most practical procedure to produce a 100% cotton fleece fabric.

The durable phosphorus-based flame retardants commonly used in the textile industry are tetrakis(hydroxymethyl)phosphonium chloride, known as "THPC", and N-methylol dimethylphosphonopropionamide [6-8] under the trade name of "Pyrovatex CP". The Proban process of THPC requires a special ammoniation chamber and requires multiple alkaline after-washes. This treatment adds a high cost to the final product. Pyrovatex CP finishing always involves the usage of melamine resin; thus the treated cotton fleece has high levels of formaldehyde and a very stiff hand. Therefore, the conventional phosphorus-based flame retardants are not suitable for the flame retardant finishing of cotton fleece.

Recently, polycarboxylic acids have been used to reduce the flammability of cotton/polyester blend carpet and cotton/polyester blend fleece [9-10]. Cotton Inc. has done some preliminary work on the application of polycarboxylic acids to reduce the flammability of cotton fleece [3]. The treated cotton fleece passed the 45 ° flammability test. The polycarboxylic acid-based flame retardant finishing system is very promising since this finishing tends to improve the dimensional stability of treated cotton fleece and imparts a soft hand in addition to achieving flame retardancy. In addition, the polycarboxylic acid system is non-formaldehyde-based, cost-effective, and environmentally friendly. However, the polycarboxylic acid-based system has not been fully studied yet. The mechanism by which polycarboxylic acids reduce the flammability of cotton fleece is not clear. Improvement of the flame retardant performance of the polycarboxylic acid-based system needs to be investigated.

Recently, fleece fabric has become more and more popular in the U.S. and the world. Because of its high flammability, 100% cotton fleece is excluded from this market. It is very important to develop a commercially feasible, cost-effective, and environmentally friendly polycarboxylic acid flame retardant finishing system for 100% cotton fleece. If a 100% cotton fleece can be made to meet the federal mandatory textile flammability standards, then 100% cotton fleece products will be available to customers and the market share of 100% cotton fleece can be increased in the future.

The objectives of this research are as follows:

(1) To develop a phosphorus-containing inorganic flame retardant system for cotton fleece by forming insoluble aluminum hydroxyphosphate (AHP) *in situ* on the fabric; To develop non-formaldehyde polycarboxylic acid-based flame retardant finishing systems for cotton fleece, which includes unsubstituted and hydroxyl-substituted bi-functional carboxylic acids, polycarboxylic acids with different functionality, and phosphorus-containing polycarboxylic acid systems. The flame retardant systems should have the following features: high performance, environmentally friendly, low add-on levels and cost effectiveness.

(2) To study the reactions of these systems, the flammability performance, and the physical performance.

(3) To study the mechanism of the flame retardancy of polycarboxylic acid treated cotton fleece. The effectiveness of polycarboxylic acids themselves and the effect of different amounts of ester formed on cotton fleece on the flammability will be studied. Thermal analysis will be conducted on the treated cotton fleece. A mechanism will be proposed.

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CHAPTER 2

REVIEW OF LITERATURE

THERMAL DEGRADATION OF CELLULOSE

Cotton is a highly flammable fiber. When cotton is heated until the temperature reaches its pyrolysis temperature, initially it will pyrolyze to produce char, volatiles and gases (Figure 2.1). Flammable volatiles comprise primarily alcohols, aldehydes and alkanes. Flammable gases are carbon monoxide, ethylene and methane. The pyrolysis of cellulose occurs through two competing reactions, i.e., dehydration, which produces char, and depolymerization, which produces high flammable levoglucosan [1]. Combustion occurs when the flammable pyrolysis product, levoglucosan, is oxidized by oxygen. The dehydration reaction occurs below 300 ℃, as shown in Figure 2.2. The depolymerization reaction happens between 300-600 ℃, as shown in Figure 2.3 [2].

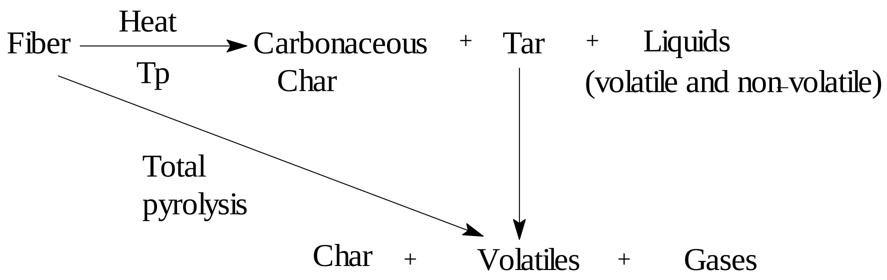


Figure 2.1. Pyrolysis of cotton cellulose [1]

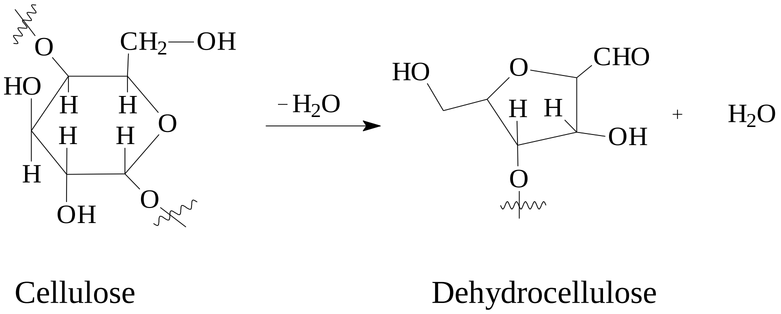


Figure 2.2. The dehydration of unmodified cellulose [3]

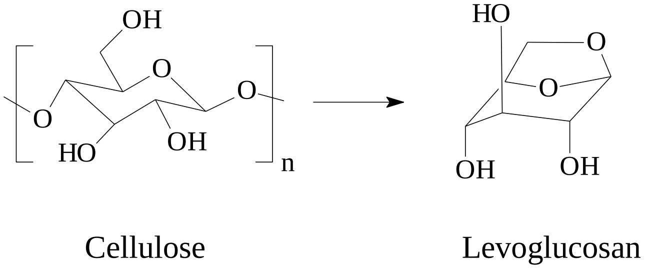


Figure 2.3. The depolymerization of unmodified cellulose [3]

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are the most commonly used methods to study the thermal degradation behavior of cellulosic materials. TGA can also be used to determine the kinetic parameters for thermal decomposition of cotton cellulose, such as activation energy and enthalpy. Many studies have been done on the thermal degradation of cotton cellulose, flame retardant finished cotton cellulose and fully esterified cellulose esters [4-8]. Faroq and his co-workers' study shows that the activation energy of cotton fabric treated with Proban CC® is higher than that treated with Pyrovatex CP® and that they are both higher than that of the untreated cotton [6]. Therefore, the organophosphorus treated cotton fabric is more thermally stable than the untreated cotton fabric. The rate of weight loss, i.e. volatile evolution, is evaluated too. The lower the activation energy, the faster is the volatile evolution. For the organophosphorus treated cotton fabric, the evolution of volatile species and consequently diffusion of these species into and out of the char is slower than that for untreated cotton fabric. Therefore, the treated cotton fabric has a higher char residue than the untreated cotton fabric. It was found that the thermal stability of the esters of the cellulose acetates prepared in homogeneous esterification reaction is proportional to their molecular weights and increases with the degree of substitution [4]. The thermal degradation behavior of cellulose partially esterified with some long chain organic acids was investigated and the results showed that the thermal stability of the modified cellulose is inferior to that of unmodified cellulose [9].

FLAME RETARDANT MAECHANISMS

There are three mechanisms related to flame retardancy, i.e., physical effects, condensed phase, and gas-phase [10-12].

The first mechanism is physical effects, in which a flame retardant may take effect in the condensed phase as well as in the gaseous phase by providing a heat sink or by forming an insulating layer around the fiber at temperature below the fiber pyrolysis temperature. Most of the flame retardants that are applied for the physical effects are inorganic compounds. One of the main effects of these materials is to dilute the organic part of the structure by filling the inorganic with the polymer. Pyrolyzing the structure becomes more difficult since the organic part is insulated by the inorganic and less heat is available for the organic part to reach the pyrolysis temperature. One method to provide a heat sink is to use a material that thermally decomposes through strongly endothermic reactions. When enough heat is absorbed by these reactions, the pyrolysis temperature of the fiber will not be reached and combustion will not take place [10, 11].

The second mechanism is condensed-phase, in which the effect of the flame retardant is concentrated on decreasing the amount of fuel produced in the pyrolysis and increasing the formation of char. The mechanism of phosphorus-containing flame retardants are often considered to function in the condensed-phase. The hydroxyl group on the polymer can be phosphorylized by the phosphoric acid produced during the thermal decomposition, thus altering the pyrolysis to yield less flammable by-products. The other function of phosphorus-containing flame retardants for cellulosic material is to catalyze the dehydration reaction and prevent the formation of levoglucosan as shown in Figure 2.4 [11, 12].

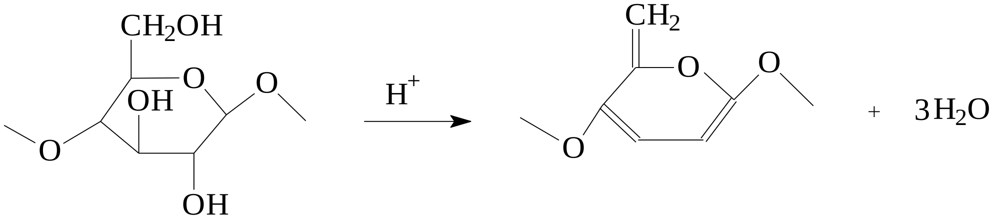


Figure 2.4. Strong acid catalyzed dehydration of cellulose [11]

In the gas phase mechanism, the flame retardant produces free radicals to interfere with the free radical reactions that provide the heat needed for the process to continue. Flame retardants that act in the gas phase include halogen-containing compounds. They decompose to relatively long lived, less reactive free radicals, effectively reducing the heat available for supporting the combusting cycle [11]. The gas-phase mechanism is illustrated in Figure 2.5.

$MX \rightleftharpoons M\cdot + X\cdot$ (Flame retardant releasing a halogen atom)

$RH + X\cdot \rightleftharpoons R\cdot + HX$ (Halogen atom reacting with the fuel)

$H\cdot + HX \rightleftharpoons H_2 + X\cdot$ (HX behaves as flame inhibitor by

$OH\cdot + HX \rightleftharpoons H_2O + X\cdot$ inhibiting the fuel chain propagation)

Figure 2.5. Free radical reactions during combustion of halogen containing flame retardants [10]

FLAME RETARDANTS USED FOR COTTON FABRIC

Inorganic Flame Retardants

Inorganic oxide and hydroxide are the two major additive inorganic flame retardants. Aluminium trihydroxide, $Al(OH)_3$, magnesium hydroxide, $Mg(OH)_2$, and antimony trioxide, Sb_2O_3, are the major inorganic hydroxide and oxide flame retardants used today. Metal hydroxides are normally smoke suppressants and work predominantly in the condensed phase of combustion by decomposing endothermically to release water. Metal oxides are smoke suppressants working only in the gas phase of the combustion and are used together with halogen-containing compounds to achieve a synergistic effect [13-15].

$Al(OH)_3$ is usually obtained from bauxite ore by the Bayer process, which is a low cost procedure used to extract caustic soluble aluminum compounds from bauxite. It was developed by Dr. Karl Joseph Bayer [14]. $Al(OH)_3$ decomposes to aluminium oxide and water at 190-230 °C, which absorbs around 1500 J/g of heat [14]:

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

$Mg(OH)_2$ is the second largest selling mineral hydroxide flame retardant after $Al(OH)_3$. It is more thermally stable than $Al(OH)_3$. $Mg(OH)_2$ decomposes at temperatures above 300 °C to produce magnesium oxide and water absorbing about 1600 J/g, heat as shown in the following equation.

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

$Al(OH)_3$ and $Mg(OH)_2$ decompose to release water into vapor phase when heated. The elimination of water is endothermic and allows the substrate to remain below its ignition temperature. The water released into the vapor phase along with the decomposition gases dilutes the amount of fuel available [13]. The decomposition reaction occurs in the condensed phase and interferes with heat feedback from the burning gases to the decomposing cellulose. The aluminium oxide or magnesium oxide produced during the decomposition process forms one layer of inert char, which further protects and insulates unburned material. $Al(OH)_3$ is commonly used in elastomers, thermosets and thermoplastics processed below its decomposing temperature. $Mg(OH)_2$ is commonly used in engineering resins. The mineral hydroxides are usually used at above 50% of the weight of the substrate to achieve good flame retardant effect [14].

Unlike elastomers, plastics, and engineering resins, mineral hydroxides cannot be used as additives for cotton fiber. It is possible to apply mineral hydroxides on cotton fiber by *in situ* deposition or by back coating.

Diammonium phosphate ($(NH_4)_2HPO_4$) and antimony/halogen (Sb_2O_3) are some other inorganic flame retardants used for cotton cellulose. They are usually applied on cotton fabric by direct deposit or back coating to achieve nondurable or semi-durable flame retardancy [14].

Organo-Phosphorus Containing Flame Retardants

Many flame retardants have been developed for cotton cellulose. Among those, reactive organophosphorus flame retardants are the most important, such as alkyphosphonamide derivatives (Pyrovatex CP® and CP New®, Ciba), tetrakis (hydroxyl methyl) phosphonium (THP) salt condensates (Proban CC®, Rhodia), and hydroxyl-functional organophosphorus oligomers (HFPO) (Fyrotex HP®, Akzo Nobel) [16-22]. It is generally agreed that a phosphorus-containing flame retardant functions in the condensed-phase by enhancing char formation and producing more carbon dioxide and water instead of flammable gases and tar.

Most of the organophosphorus-based durable flame retardant treatments have been well-established during the last thirty years and few changes have been made to the basic chemistry. The application of tetrakis-(hydroxymethyl)phosphonium chloride (THPC) on cotton fabric is probably the most important development in flame retardancy field. The Proban® process of THPC involves pre-condensation, ammonia cure and oxidation, and requires a well-sealed ammoniation chamber. The chemistry of Proban® process is shown in Figure 2.6 [12]. Although the Proban® process is highly effective, it has a number of limitations such as high cost, and release of free formaldehyde.

Dimethyl (N-hydroxymethylcarbamoylethyl) phosphonate (Pyrovatex CP®) is another effective reactive organophosphorus flame retardant for cotton fabric. Pyrovatex CP® contains a N-methylol functional group and it is applied together with trimethlolmelamine (TMM) by a pad-dry-cure procedure. TMM is added to increase the nitrogen content to enhance the P-N synergism. The chemistry of Pyrovatex CP® is presented in Figure 2.7 [12]. Pyrovatex CP® finishing is highly effective and durable to multiple launderings. Yet, Pyrovatex CP has its own problems too. Both Pyrovatex CP® and TMM have the potential to release formaldehyde, a suspected carcinogen, during the processing as well as the consumer wearing process. The treated fabric has a high add-on, stiff hand, and high strength loss [18, 23]. Pryrovatex CP "New"®, a modified Pyrovatex CP®, has replaced the original formulation by removing TMM from the formulation and adding a more ecologically friendly cross-linking agent. It achieves similar effect to that with Pryrovatex CP except it is more easily to hydrolyze over an extended period of time [24]

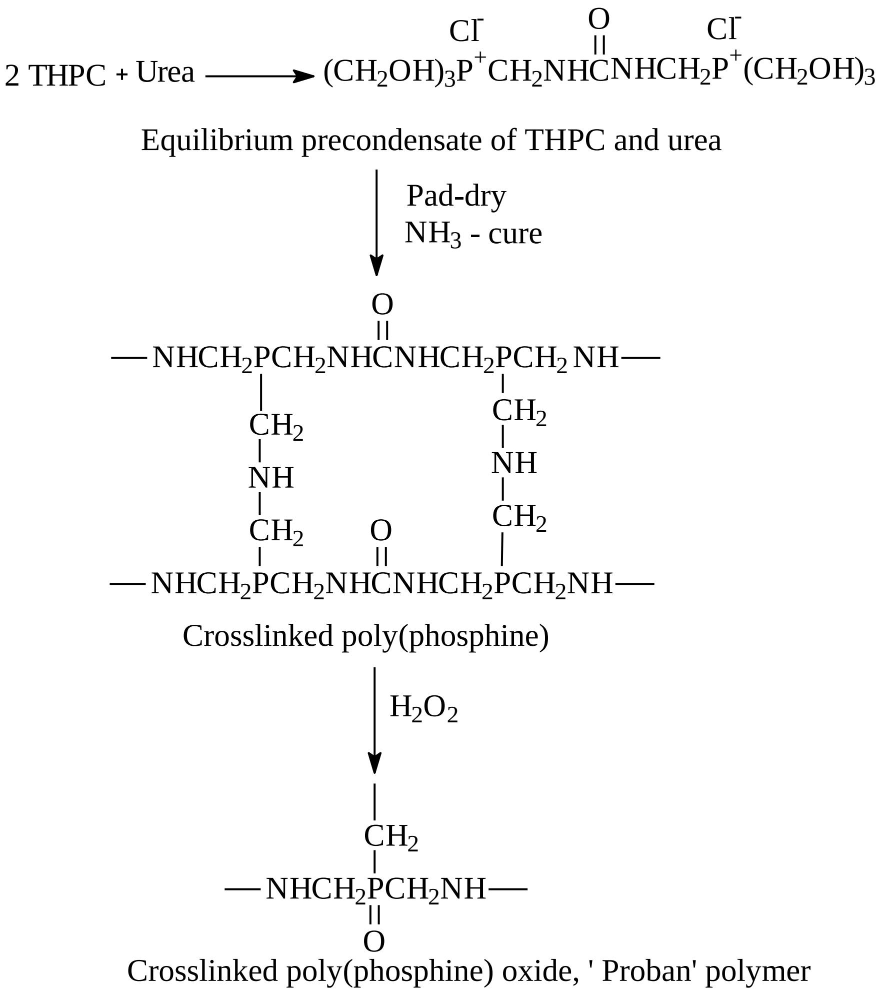


Figure 2.6. Chemistry of the THPC-urea-NH_3 (Proban) process [12]

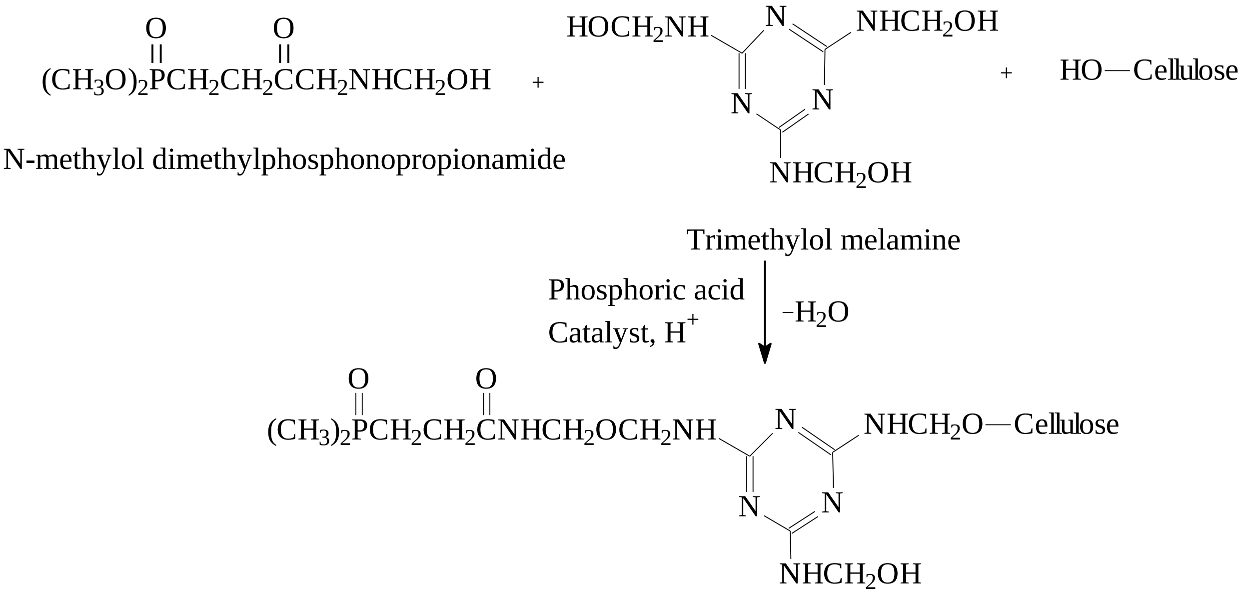


Figure 2.7. Chemistry of the Pyrovatex CP system [12]

Recently, some research has been done on the application of a hydroxyl-functional organophosphorus oligomer (HFPO) (Fyrotex HP®, Akzo Nobel) on cotton fabric [20-22, 25]. Both DMDHEU and trimethylolmelamine (TMM) have been used as bonding agents to bond HFPO to cellulose and have achieved very good flame retardant performance and durability to multiple home laundering cycles. The chemistry of Fyroltex HP® with bonding agents DMDHEU and TMM is shown in Figure 2.8 and 2.9, respectively. Compared with TMM, DMDHEU is more effective in forming cross-links with cellulose and with HFPO. Yet, TMM is more effective in providing a P-N synergism. When TMM is used as binding agent for the HFPO finishing system, it forms a crosslinked polymeric network in addition to react with cotton cellulose [21]. However, the flame retardant system with HFPO and bonding agents DMDHEU and TMM has the potential to release formaldehyde. Polycarboxylic acid, BTCA, can also serve as bonding agent between cellulose and HFPO, which is a non-formaldehyde finishing system. However, the flammability of cotton fleece treated with HFPO and BTCA deteriorates quickly after several home laundering cycles due to the adsorption of calcium ion in the laundering process [25].

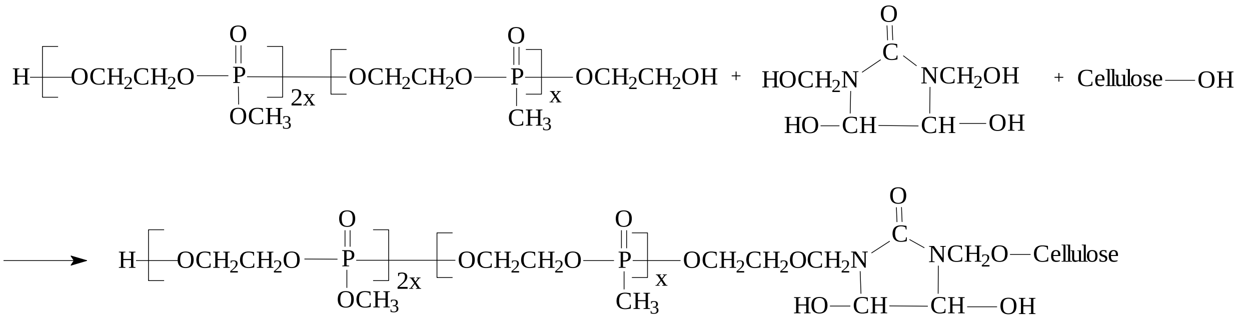


Figure 2.8. The chemistry of Fyrotex HP® with bonding agent DMDHEU [20]

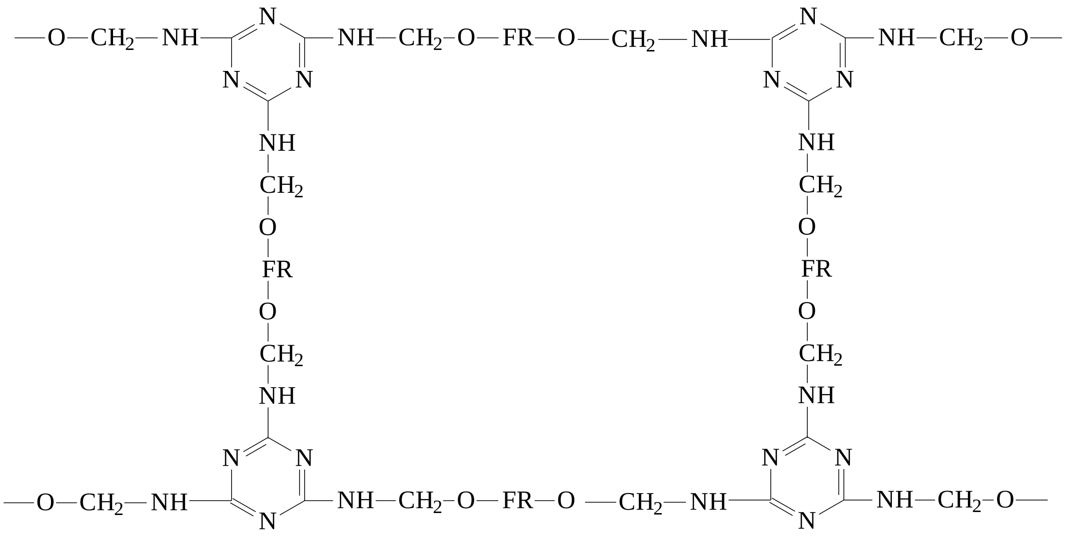


Figure 2.9. Fyrotex HP® (FR)/trimethylolmelamine crosslinked polymeric network [21]

POLYCARBOXYLIC ACIDS

Application as Durable Press Agents

Polycarboxylic acids have been widely studied as durable press agents for cotton fabric [26-34]. Rowland and coworkers first found that polycarboxylic acids could impart high levels of wrinkle recovery to cotton fabric and maintain higher than normal strength retention [35, 36].

Compounds having two or more carboxyl groups on each molecule are sometimes referred as polycarboxylic acids. Those containing three or more carboxyl groups on each molecule are able to form cross-links in cotton by esterifying the hydroxyl groups of adjacent cellulose chains. A series of weak bases can serve as esterification catalyst for polycarboxylic acids. They are mostly alkali metal salts of phosphoric, polyphosphoric, phosphorous, and hypophosphorous acids. Among these catalysts, sodium hypophosphite (NaH_2PO_2) is the most effective and affords the most satisfactory whiteness in the treated fabric [37-40]. The ability of these catalysts to catalyze the esterification of BTCA finishing of cotton is ranked as follows:

$$NaH_2PO_2 > NaHPO_3 = NaH_2PO_3 > NaH_2PO_4 > NaH_2P_2O_7 > Na_4P_2O_7$$
$$Na_5P_3O_{10} = (NaPO_3)_6 > Na_2HPO_4 = Na_3PO_4 > Na_2CO_3$$ [37]

The Mechanism of the Cross-linking of Cellulose by Polycarboxylic Acids

Welch and Andrews [39] proposed the mechanism of base-catalyzed cross-linking by polycarboxylic acids where polycarboxylic acids having carboxyl groups on adjacent carbon atoms cross-link cotton via formation of cyclic anhydrides as the cellulose esterifying agents, as shown in Figure 2.10. According to the mechanism, acids having only two carboxyls per molecule cannot cross-link cotton cellulose, since two carboxyls are needed to form an anhydride ring. Maleic acid and itaconic acid are exceptions. They can be polymerized or copolymerized *in situ* or in solution to higher molecule polycarboxylic acids [41, 42]. Many researchers have tried to prove this mechanism by various methods. Thermogravimetric studies show that the loss of weight of BTCA is equal to the water loss as anhydrides are formed when BTCA is heated. Mass spectroscopy was used to characterize the molecular fragments corresponding to cyclic anhydride formation [43, 44]. Yang et al. [45, 46] confirmed the esterification mechanism by Fourier transform infrared spectroscopy (FT-IR) measurement to identify the cyclic anhydride intermediates formed by various polycarboxylic acids on the cotton fabric under curing conditions. Two distinct bands at 1850 and 1781 cm^{-1} corresponding the asymmetric and symmetric stretching modes of acid anhydride carbonyls were found in the infrared spectrum of the treated cotton fabric. FTIR was also widely used to determine the degree of esterification in polycarboxylic acid cross-link finishing of cotton [47-49].

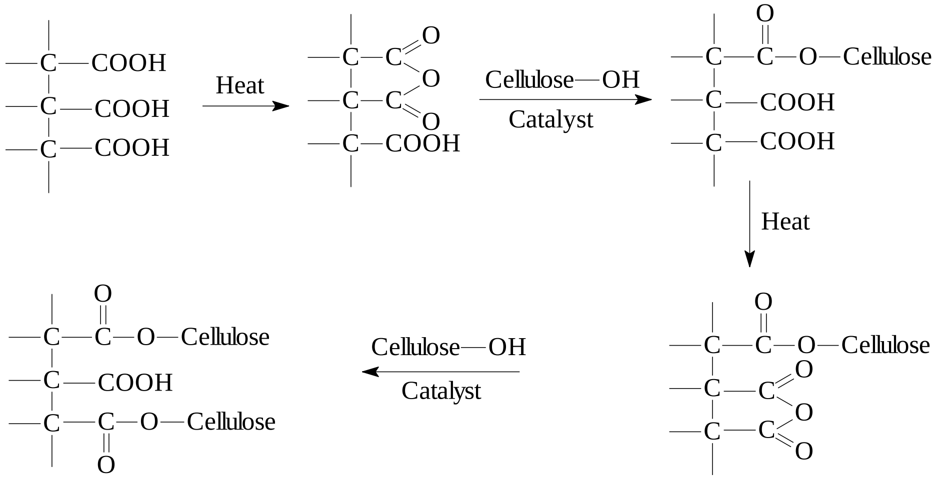
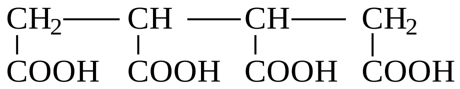


Figure 2.10. Proposed mechanism for esterification of cellulose by polycarboxylic acids [47]

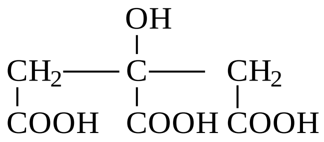
BTCA, 1,2,3,4-butanetetracarboxylic acid, is the most effective durable press agent of the polycarboxylic acids that have been studied so far. The structure of BTCA is shown in Figure 2.11. Brodman [50] compared the properties of cotton fabrics treated with BTCA and DMDHEU with respect to durable press appearance rating, tensile and tearing strengths, shrinkage resistance, and flex abrasion resistance. The durable press performance of BTCA with sodium hypophosphite as catalyst is equal to that of DMDHEU catalyzed by magnesium chloride. Also, cotton fabric treated with BTCA has a higher retention of tensile strength, tearing strength, and flex abrasion resistance. The breaking strength retention of polycarboxylic acid treated cotton printcloth is 54-57% and the tearing strength retention is 60-68%. That treated with DMDHEU catalyzed with magnesium chloride has 44% breaking strength retention and 54% tearing strength retention [39].



$$\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH_2}}}-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH_2}}}$$

Figure 2.11. Structure of BTCA

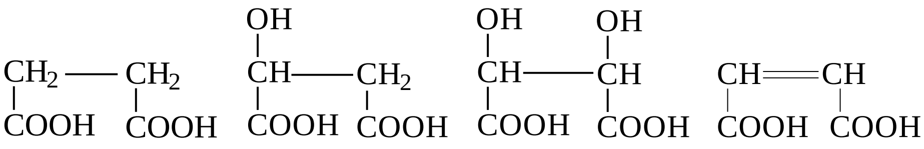
Citric acid is another polycarboxylic acid which is widely studied as a DP agent for cotton fabric due to its low cost, easy availability, and safety. The structure of citric acid is shown in Figure 2.12. However, citric acid is considerably less effective and less durable than BTCA as a DP finishing agent [39, 50]. The α-hydroxyl group of citric acid interferes with the desired esterification and cross-linking of cellulose with citric acid. Yang et al. [51] demonstrated the α-hydroxyl adverse effect through FTIR spectroscopy. Their results showed that 1,2,3-propanetetracarboxylic acid-treated cotton shows a higher ester carbonyl band absorbance than does citric acid-treated cotton. The yellowness of citric acid-treated fabric has also been a problem. Some curing additives, such as triethanolamine and its salts, triisopropanolamine, N-methyldiethanolamine, and polyethylene glycols, can improve the fabric whiteness of citric acid finished cotton [52, 53].



$$\underset{\mathrm{COOH}}{\mathrm{CH_2}}-\overset{\mathrm{OH}}{\underset{\mathrm{COOH}}{\mathrm{C}}}-\underset{\mathrm{COOH}}{\mathrm{CH_2}}$$

Figure 2.12. Citric acid

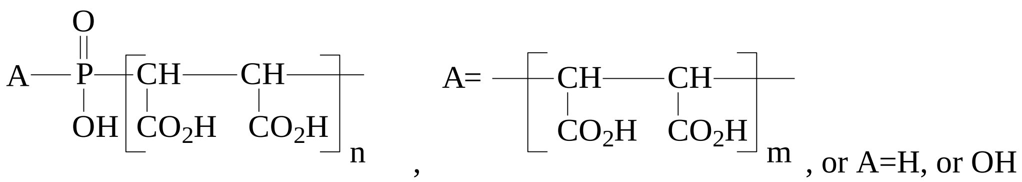
Polycarboxylic acids containing only two carboxyl groups in their structure, such as succinic acid, malic acid, tartaric acid, and maleic acid, are not able to form cross-linking with cellulose. Their structures are shown in Figure 2.13. Contrary to other bi-functional polycarboxylic acids, maleic acid and itaconic acid are unsaturated carboxylic acids. It is possible to use their polymerization products to cross-link cotton fabric. It is very difficult to polymerize maleic acid since it does not polymerize under conditions commonly used for vinyl monomers. Many U.S. Patents [54-59] disclose the polymerization of maleic acid in the presence of sodium hypophosphite and initiator potassium persulfate. The product thus produced is a ploymaleic acid oligomer containing phosphinate composition. This structure is shown in Figure 2.14. U.S Patents 6,277,152 B1, 5,385,680, 5,300,240 and 5,447,537 [60-64] reported the application of the polymaleic acid oligomer to cotton fabrics. The thus treated fabric achieves good durable press, wrinkle recovery, and other mechanical properties.



$$\underset{\mathrm{COOH}}{\mathrm{CH_2}}-\underset{\mathrm{COOH}}{\mathrm{CH_2}} \qquad \overset{\mathrm{OH}}{\underset{\mathrm{COOH}}{\mathrm{CH}}}-\underset{\mathrm{COOH}}{\mathrm{CH_2}} \qquad \overset{\mathrm{OH}}{\underset{\mathrm{COOH}}{\mathrm{CH}}}-\overset{\mathrm{OH}}{\underset{\mathrm{COOH}}{\mathrm{CH}}} \qquad \underset{\mathrm{COOH}}{\mathrm{CH}}=\underset{\mathrm{COOH}}{\mathrm{CH}}$$

Succinic acid Malic Acid Tartaric acid Maleic acid

Figure 2.13. Structures of bi-functional polycarboxylic acids



$$\mathrm{A{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}\left[\underset{\underset{\displaystyle CO_2H}{|}}{CH}{-}\underset{\underset{\displaystyle CO_2H}{|}}{CH}\right]_n{-}}\;,\quad \mathrm{A= {-}\left[\underset{\underset{\displaystyle CO_2H}{|}}{CH}{-}\underset{\underset{\displaystyle CO_2H}{|}}{CH}\right]_m{-}}\;,\text{ or A=H, or OH}$$

Figure 2.14. The structure of polymaleic acid oligomer

Yang et al. studied the *in situ* polymerization of maleic acid and itaconic acid on cotton fabric [65]. They found that *in situ* polymerization occurs only when both potassium persulfate and sodium hypophosphite are present on the cotton fabric. Both itaconic acid and maleic acid polymerized *in situ* on cotton fabric in the presence of a $K_2S_2O_8/NaH_2PO_2$ are able to crosslink cotton cellulose, thus imparting wrinkle resistance to cotton woven fabric.

Application as Flame Retardant for Raised-Surface Fabric

Table 2.1. Estimated volumes of raised-surface fabrics potentially affected by existing or proposed flammability regulations [66].

Fabric	Total Fiber (Bales)	Cotton Fiber (Bales)
Fleece	1,057,000	403,700
Corduroy	165,000	47,100
Flannel	364,000	285,400
Velour	200,000	48,200

Raised-surface and lightweight apparel are regulated under the Standard of General Wearing Apparel Standard, 16 CFR 1610 [66]. Table 2.1 lists the estimated volumes of raised-surface fabrics potentially affected by existing or proposed flammability regulations. Raised-surface apparel affected by the regulation accounts for about 1,700,000 bale equivalents of fiber (a bale equals to 480 lb). Nowadays, fleece fabric is becoming more and more popular. The amount of affected raised-surface apparel is still increasing. Normally, 100% cotton fleece without chemical treatment fails the 16 CFR 1610 standard and is not allowed for sale in the U.S. [66-69]. According to the requirement of 16 CFR 1610, raised-surface fabric will be classified as Class 1, normal flammability, under two situations. The first situation is when the flame spread time is more than 7 seconds. The second situation is when the fabrics burn with a rapid surface flash (from 0 to 7 seconds) without base burn [70].

The application of polycarboxylic acids to depress the flammability of raised-surface fabric is a recent issue. Some preliminary work has been done on flame retardant finishing of cotton fleece using polycarboxylic acid by Rearick, Wallace and etc. [66]. Blanchard and Graves investigated the application of polycarboxylic acids on cotton and cotton/polyester carpets [71]. Their results showed that the treated carpet has reduced flammability and durable flame retardancy. The application of phosphorus-containing polymaleic acid oligomer on cotton/polyester fleece as flame retardants has been studied [72]. The thus-treated cotton/polyester fleece has lower flammability and increased char formation upon combustion. Previous studies showed that the treatment of woven fabric with phosphorus-containing polymaleic acid oligomer imparts wrinkle resistance to the treated woven fabric [61-63]. Yang and Qiu studied the application of HFPO/DMDHEU to cotton fleece [73]. They found that cotton fleece treated with HFPO/DMDHEU passes the federal flammability standard, shows high strength retention and is durable to multiple home launderings.

Cross-linking is recognized as enhancing char formation in cellulose by creating a carbon-carbon network [74]. A study by H. Rodrig et al. [75] indicated that cross-linking helps to stabilize the polymeric structure by providing additional covalent bonds that are stronger than hydrogen bonds that have to be broken during the pyrolysis process. The increased thermal stability is reflected in the decreased pyrolysis rates, increased endotherm peak temperature and energy of activation in DSC. However, a low degree of cross-linking or substitution decreases thermal stability by weakening or breaking of interchain hydrogen bonds by physical separation of the polymer chain [75].

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CHAPTER 3

FLAME RETARDANT FINISHING OF COTTON FLEECE: I. INORGANIC PHOSPHORUS-CONTAINING COMPOUNDS[*]

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ABSTRACT

Cotton fleece is not able to meet the federal flammability standard for general apparels (CFR 1610) without flame retardant treatment. Consequently, cotton fleece is not available in the market in spite of high demands. In our previous research, we studied the application of a hydroxyl-functional organophophorus oligomer as a flame retardant finishing agent for cotton fleece. In this research, we investigated the use of aluminum hydroxyphosphate (AHP) formed *in-situ* on cotton by the reaction of aluminum sulfate and sodium phosphates to reduce the flammability of cotton fleece. We found that the AHP formed on cotton was effective in reducing the cotton fleece's flammability from "Class 3" to "Class 1". Elemental analysis of aluminum and phosphorus in the AHP showed that the mole ratio of Al/P changeed as the pH value of the sodium phosphates solution changes. The pH of the sodium phosphates solutions also affected the quantity of AHP formed on the cotton fleece. The treated cotton fleece retained "Class 1" flammability after one home laundering or the combination of dry-cleaning and hand washing procedures. The treatment increased the whiteness of the cotton fleece whereas it reduced its bursting strength. The cotton fleece thus treated was also investigated using differential scanning calorimetry and scanning electron microscopy.

INDEX WORDS: Aluminum hydroxyphospate; Cotton fleece; Flammability, Flame retardant finishing; Textile flammability.

INTRODUCTION

Raised surface and lightweight apparel fabrics, including fleece fabrics, are regulated by the federal government in the U.S. under “General Wearing Apparel Standard” (16 CFR 1610) [1]. Compared with other fabrics, raised surface fabrics have lower density and contain more air in their fuzzy surfaces, and therefore have higher flammability. Fleece, a knitted fabric with a napped surface, is particularly more flammable than other raised surface fabrics. Generally, 100% cotton fleece fabrics are not able to meet the 16 CFR 1610 standard without chemical treatment [2-4].

There are three ways to reduce the flammability of cotton fleece: blending cotton fiber with a synthetic fiber such as polyester, treating cotton fleece with a flame retardant and changing the construction of fleece fabric. However, blending cotton with a synthetic fiber is not always a guarantee for success. Many 90/10 and 80/20 cotton/polyester fleece fabrics still fail the 16 CFR 1610 standard. Blending cotton with polyester also changes the properties of 100% cotton fleece. Changing the construction alters the desirable characteristics of cotton fleeces. Thus, treating cotton fleece with a flame retardant using a traditional finishing procedure is probably the most practical method to reduce the flammability of cotton fleece fabrics.

The durable flame retardant chemicals most commonly used in the industry, including tetrakis(hydroxymethyl)phosphonium chloride, known as “Proban” and N-methylol dimethylphosphonopropionamide under the commerical name of “Pyrovatex CP” [5-7] are not practical or suitable for uses on cotton fleece. Polycarboxylic acids have been investigated as flame retardants for cotton/polyester fleece [8]. In our previous research, we successfully applied a hydroxyl-functional organophosphorus compound in combination with dimethyloldihydroxyethyleneurea to treat cotton fleece [9]. However, these technologies have not been commercialized.

Alumina trihydrate and magnesium hydroxide are commonly used as flame retardants for plastics, including elastomers, thermoset and thermoplastic polymers [10-11]. Both compounds cannot be applied to cotton textiles as durable flame retardants except as back coatings because they are not water-soluble and are not able to form covalent bonding with cellulose. The back coating method is not applicable to cotton fleece.

In the absence of phosphate anions, an aluminum ion (Al^{3+}) precipitates in an aqueous solution to form amorphous aluminum hydroxide at pH 4.5 to 8.0 [12, 13]. In the presence of phosphate anions, Al^{3+} forms aluminum hydroxyphosphate (AHP) as a precipitate [13, 14]. In this research, the AHP was formed *in situ* on cotton fleece when the fleece was first impregnated in an $Al_2(SO_4)_3$ solution, dried and then treated in a 2nd solution containing NaH_2PO_4 at different pHs. We studied the effectiveness of the AHP thus formed *in situ* on the cotton fleece in reducing the flammability of cotton fleece and its durability to home laundering, hand washing and dry-cleaning procedures. We also evaluated the physical properties of the treated cotton fleece.

EXPERIMENTAL

Materials

The cotton fleece fabric (233 g/m^2) was produced by Cotton Inc., Cary, NC. $Al_2(SO_4)_3 \cdot xH_2O$ (x=14-18) and "Tergitol", a non-ionic wetting agent, were supplied by Sigma-Aldrich, Milwaukee, WI. $Na_3PO_4 \cdot 12H_2O$ and $NaH_2PO_4 \cdot H_2O$ were supplied by Fisher Scientific, Fair Lawn, NJ. NaOH was supplied by Mallinckrodt Baker, Phillipsburg, NJ.

Fabric Treatment, Home Laundering (HL), Dry-Clean (DC) and Hand-Wash (HW) Procedures

The cotton fleece fabric was treated using a two-step procedure. In the first step, the fleece was impregnated in an $Al_2(SO_4)_3$ solution, which also contained 0.02% wetting agent, Tergitol, for 5 min. The fabric sample was padded through a two-roll laboratory padder with two dips and two nips. The wet pick-up was 140 ±2%. The sample was then dried at 100 ℃ for 7 min in a laboratory oven manufactured by Werner Mathis, Oberhasli, Switzerland. In the second step, the fabric sample was again impregnated in a solution consisting of the mixture of NaH_2PO_4 and NaOH at different pHs for 5 minutes, then padded as described above, and finally dried at 100 ℃ for 7 min. The HL procedure was performed according to "AATCC Method 124" using a standard reference detergent ("AATCC Detergent 1993"). The DC procedure was carried out by a commercial dry-cleaner. The HW was performed following the 16CFR1610 procedure except that we used a standard reference detergent ("AATCC Detergent 1993") instead of a neutral detergent. The fleece was naturally dried following the HW procedure.

Fabric 45 ° Flammability Test

The flammability of the cotton fleece was measured according to ASTM Method D1230-94 ("Standard Test Method for Flammability of Apparel Textiles" re-approved in 2001). According to ASTM D1230, a fabric specimen mounted in a specimen holder was first brushed, dried at 105 ℃ in an oven for 30 min, cooled down in a desiccator for 50 min, and then moved to a special 45 ° flammability tester (Model TC-45 manufactured by Govmark, Bellmore, NY). The specimen was then exposed to a standard butane flame for 1 sec to cause ignition, and the burning time and burning characteristics were recorded. The arithmetic mean burning time of 5 specimens and the burning characteristics were used as the basis to determine the flammability classifications. The flammability classifications for the fabrics with a raised surface are divided into the following three categories: (1) "Class 1" (normal flammability): fabric having burning time more than 7 sec or having surface flash (SF) without base burn (BB) regardless of burning time; (2) "Class 2" (intermediate flammability): fabric having burning time 4–7 sec with BB; (3) "Class 3" (high flammability with rapid and intense burning): fabric having burning time less than 4 sec and BB. A fabric can be classified as "Class 1" only when the fabric before and after a refurbishing procedure consisting of a DC procedure followed by HW procedure using a neutral detergent are determined to be "Class 1".

Quantitative Analysis of Aluminum and Phosphorus of AHP

In order to determine the composition of the AHP precipitated on cotton fleece, we analyzed the aluminum (Al) and phosphorus (P) contents of the AHP precipitated by mixing a NaH_2PO_4 solution with a $Al_2(SO_4)_3$ solution. The 0.300 M (200 g/l, see the concentration conversions in Table 3.1) $Al_2(SO_4)_3$ solutions (different volumes) were added to five 0.600 M NaH_2PO_4 solutions (40 ml each) to achieve the final pHs ranging from 4.8 to 8.5. The pHs of the mixtures thus prepared are presented in Table 3.2. The pHs after mixing the solutions presented in Table 3.2 were the same as the pHs of the solutions used in the second treatment step after impregnation of the fleece when the pH effect was studied. The precipitates were separated and dried to a constant weight, and 0.10 g precipitate of each sample was weighed and completely dissolved in a 10% HCl solution. The homogeneous solution thus prepared was transferred to a 50 ml volumetric flask, and then diluted with distilled water to the mark. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP-AES) to determine the P and Al concentrations.

Table 3.1. The concentrations of $Al_2(SO_4)_3$ and NaH_2PO_4 solutions used for the treatment of cotton fleece.

$Al_2(SO_4)_3 \bullet 18H_2O$		NaH_2PO_4	
Mole Concentration (M)	W/V (g/l)	Mole Concentration (M)	W/V (g/l)
0.150	100	0.320	38.4
0.225	150	0.480	57.6
0.300	200	0.640	76.8
0.375	250	0.800	96.0

Note: The X of $Al_2(SO_4)_3 \bullet XH_2O$ is calculated as 18.

Table 3.2. The pH of the 40 ml 0.600 M NaH_2PO_4 solution before and after addition of 0.300 M $Al_2(SO_4)_3$ solution of different volumes.

$Al_2(SO_4)_3$ Added (ml)	pH	
	Before Addition	After Addition
1.9	8.5	7.8
2.2	7.5	7.2
2.8	6.5	6.2
3.4	5.5	4.9

Thermal Analysis

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 821 calorimeter at the heating rate of 10°C/min in nitrogen. The sample size was 4-8 mg.

Scanning Electron Microscopy

Cotton fleece fabric was studied using Zeiss1450 EP environmental scanning electron microscope (ESEM). The ESEM was operated at 20 KV to observe the cotton fiber of the fleece.

Fabric Bursting Strength and Whiteness Index

The bursting strength of the cotton fleece was measured according to ASTM Method D 3786-01 (“Standard Test Method for Hydraulic Bursting Strength of Textile Fabrics-Diaphragm Bursting Strength Tester Method”) using a “Truburst” tester made by James H. Heal &

Company, Halifax, UK. The fabric CIE whiteness index was measured according to AATCC Method 110 ("Whiteness of Textiles") using a "Macbeth Color-Eye" 7000A spectrocolorimeter made by Hunter Associates Laboratory, Reston, VA.

RESULTS AND DISCUSSION

Formation of AHP

A variety of analytical techniques have been used in the past to study the structures of AHP. Researchers find that the structures of AHPs are difficult to determine because they are amorphous and possibly heterogeneous. The situation becomes even more complicated when several different structures co-exist in one AHP sample [13, 14].

In order to investigate the composition of the AHP formed on the cotton fleece, we studied the AHP precipitated in an aqueous solution by adding a $Al_2(SO_4)_3$ solution to a NaH_2PO_4 solution as described in Table 3.2. The contents of Al and P and the P/Al mole ratio of the AHP precipitated from the solutions with different pHs are shown in Figure 3.1 and 3.2, respectively. One observes that both the Al and P contents of AHP depend on the pH of the solution at which it is precipitated. The Al content increases whereas P content decreases as the pH increases from 6.5 to 8.5 (Figure 3.1). Consequently, the P/Al mole ratio decreases from 1.71 to 1.23, respectively (Figure 3.2). The data presented here indicate that the composition of the AHP formed by the reaction of Al^{3+} and the phosphate anions in an aqueous solution is pH-dependent and that the AHP formed at pH 8.5 has the lowest P/Al mole ratio.

The reaction to form AHP in an aqueous solution is shown in Scheme 3.1. Phosphoric acid (H_3PO_4) ionizes to form three different anions ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in an aqueous solution. The percent mole composition of those anionic species at different pH values are presented in Table 3.3. Since the solution pH affects the concentrations of those anionic species in the solution, it affects the composition of the AHP precipitated from the solution. As the solution pH is increased from 5.0 to 8.5, the percent mole concentration of $H_2PO_4^-$ decreases from 99.36 to 4.60, whereas that of HPO_4^{2-} increases from 0.20 to 95.40. This explains why P/Al ratio decreases as the pH increased, as shown in Figure 3.2.

$$aAl^{3+} + b\,OH^{-} + c\,HPO_4^{2-} + d\,H_2PO_4^{-} + x\,H_2O \longrightarrow Al_a(OH)_b(HPO_4)_c(H_2PO_4)_d\,.xH_2O$$

$$3a=b+2c+d$$

Scheme 3.1. Formation of AHP

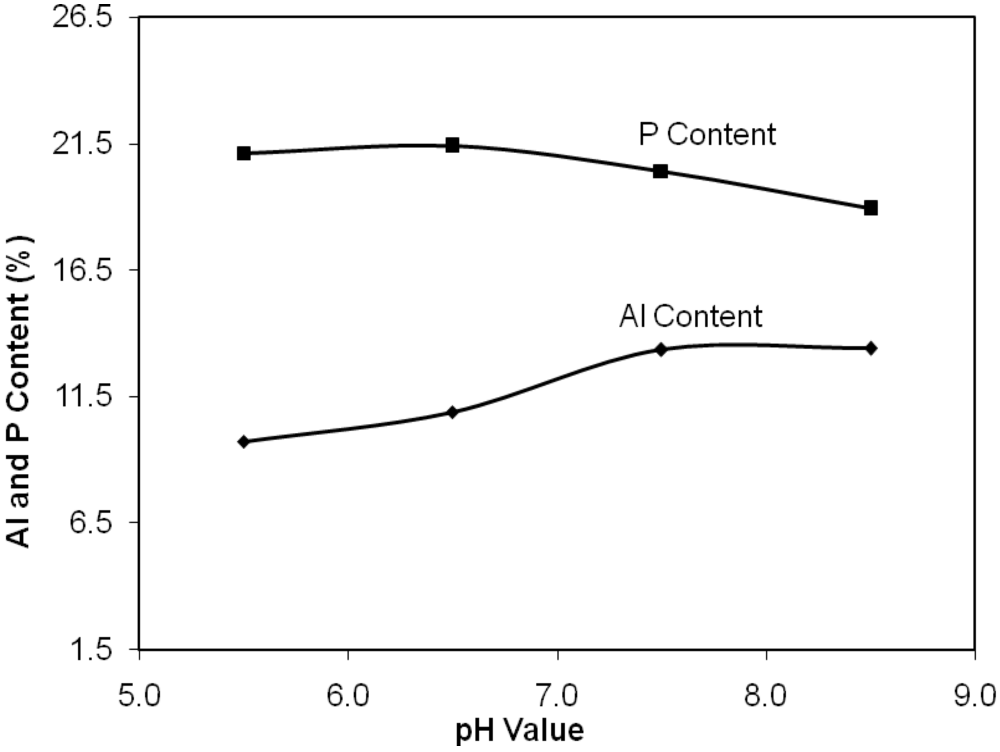


Figure 3.1. The aluminum and phosphorus content of the AHP precipitated at different pH

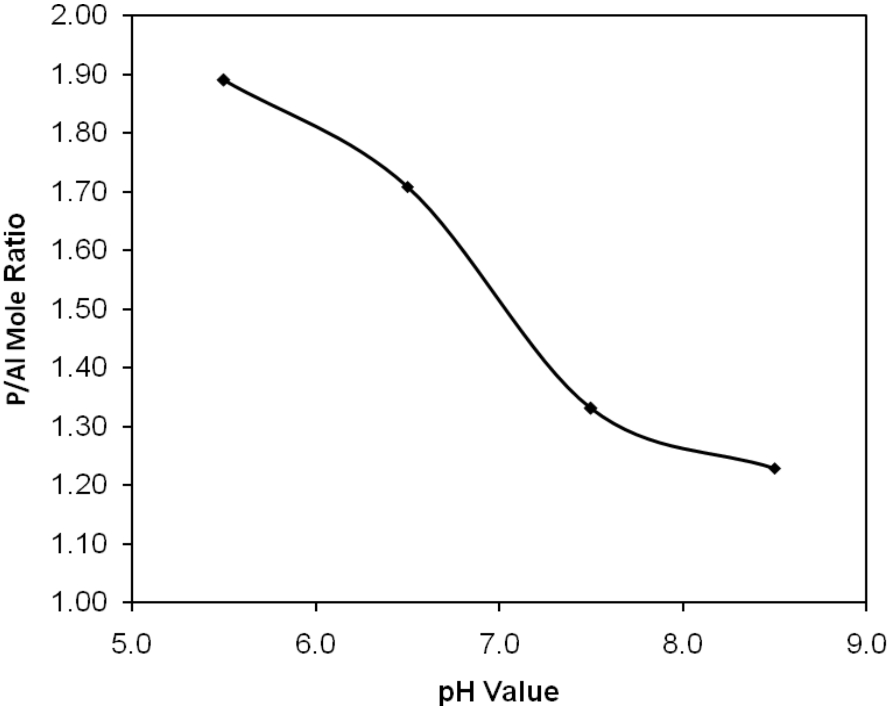


Figure 3.2. The phosphorus/ aluminum mole ratio of the AHP precipitated at different pH

Table 3.3. The percent mole compositions of phosphate solutions at different pHs.

Solution pH	H_3PO_4 (%)	$H_2PO_4^-$ (%)	HPO_4^{2-} (%)	PO_4^{3-} (%)
5.0	0.44	99.36	0.20	0
5.5	0.04	98.00	1.96	0
6.5	0	83.33	16.67	0
7.5	0	33.35	66.65	0
8.5	0	4.60	95.40	0

The Effectiveness of AHP as a Flame Retardant for the Cotton Fleece

Cotton fleece fabric is treated with a 0.300 M $Al_2(SO_4)_3$ solution, dried, then treated with a 0.600 M NaH_2PO_4 solution with pH ranging from 5.5 to 8.5, and finally dried. The 45 ° flammability of the cotton fleece thus treated is shown in Table 3.4. After the 2nd step treatment, the pH of the NaH_2PO_4 solution decreases because of the acidic nature of $Al_2(SO_4)_3$ on the fleece. The flammability data include the number of specimens having surface flash only, the average burning time and the number of specimens having base burn. The flammability ranking of the fleece is based on those data as discussed previously. The untreated cotton fleece fails the test ("Class III" flammability). All the treated fleece fabrics pass the test with "Class I" flammability ranking. Therefore, the data demonstrate that the AHP formed on the cotton fleece by the two-step procedure is indeed effective in reducing the flammability of cotton fleece.

Table 3.4. The pH of the solutions used for the 2nd step treatment before and after the impregnation of the cotton fleece and the 45 ° flammability of treated cotton fleece.

pH of the NaH_2PO_4 solutions		45 ° flammability			
Before treatment	After treatment	No. of specimen SF*	Ave. burning time (s)	No. of specimen BB*	Class
Control	-	5	1.1	5	III
5.5	4.9	5	1.1	0	I
6.5	6.2	5	1.1	0	I
7.5	7.2	5	1.1	0	I
8.5	7.8	5	1.1	0	I

*SF: surface flash only; BB: base burn.

Shown in Figure 3.3 is the weight increase of the cotton fleece treated first with a 0.300 M $Al_2(SO_4)_3$ solution then treated in the 2nd step with a 0.600 M NaH_2PO_4 solution as a function of the pH of the NaH_2PO_4 solutions. The weight increase of the cotton fleece thus treated increases sharply as the pH increases from 5.5 to 7.5 (Figure 3.3). We observed that a significant amount of AHP is precipitated in the solution when pH is below 6.5, indicating some of the $Al_2(SO_4)_3$ dissolves in the solution and consequently reacts with NaH_2PO_4 to form AHP. When pH is increased above 7.5, little AHP precipitate is seen in the solution after impregnation of the fleece. Therefore, the data show that the quantity of AHP formed on the cotton fleece is pH-dependent. In all the experiments discussed in the rest of this paper, we adjusted the pH of NaH_2PO_4 solutions to 8.5 in the 2nd step experiment.

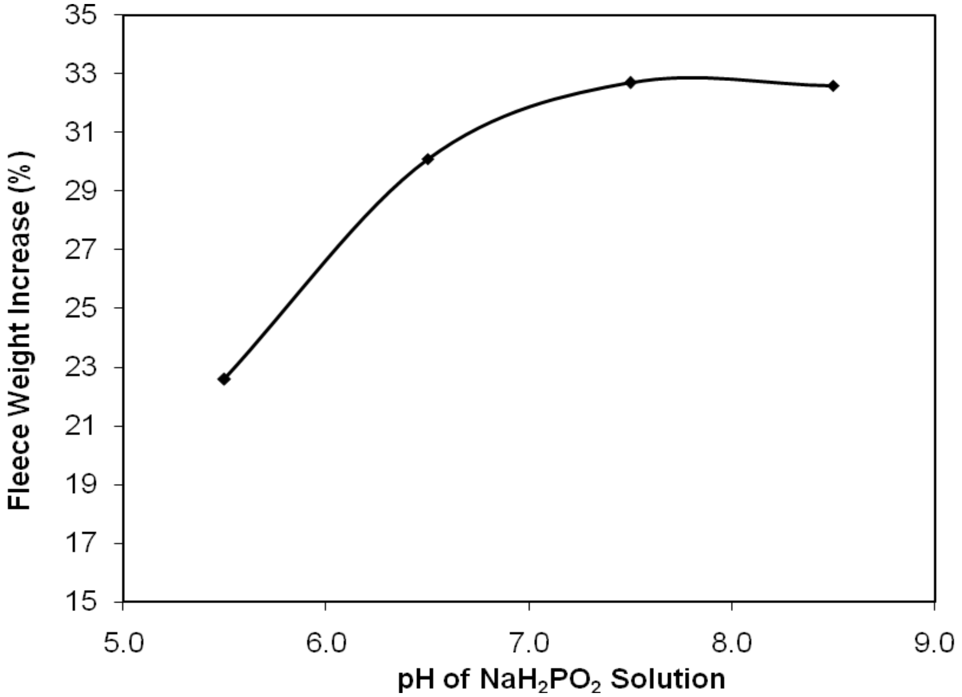


Figure 3.3. The weight increase of the cotton fleece treated first with 0.300 M $Al_2(SO_4)_3$ and then with 0.600 M NaH_2PO_4 at different pHs.

Table 3.5. The pHs of the NaH_2PO_4 solution before and after impregnation and 45 ° flammability of the cotton fleece treated using different concentrations of NaH_2PO_4.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	pH of the NaH_2PO_4 solution		Weight increase (%)	45 ° flammability			
		Before treatment	After treatment		No. of spe. SF	Ave. burning time (s)	No. of spe. BB	Class
Control		-	-	-	5	1.1	5	III
0.375	0.400	8.5	6.8	26.1	5	1.1	0	I
0.375	0.600	8.5	7.1	35.9	5	1.1	0	I
0.375	0.800	8.5	7.2	43.8	5	1.1	0	I

We studied the effect of NaH_2PO_4 concentration in the 2nd step treatment on the weight increase and the flammability of the treated fleece (Table 3.5). The concentration of $Al_2(SO_4)_3$ in the first treatment solution is 0.375 M. The pH of all the NaH_2PO_4 solutions decreases after the 2nd treatment. The weight increase of the treated fleece becomes higher as the NaH_2PO_4

concentration increases, indicating that more AHP is formed on cotton fleece at higher NaH_2PO_4 concentrations (Table 3.5). The data show that all the treated fleece samples pass the flammability test and achieve the flammability of "Class I". We also observe that Na_2SO_4, which is formed by the reaction during the 2^{nd} step treatment, becomes saturated and starts to precipitate on the fabric surface when the NaH_2PO_4 concentration is increased above 0.800 M. Therefore, we used the $Al_2(SO_4)_3/NaH_2PO_4$ mole ratio of 0.47 in all the experiments discussed in the rest of this paper.

Table 3.6. The 45 ° flammability of the cotton fleece treated at different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ before laundering.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)*	45 ° flammability			
		No. of specimen SF	Ave. burning time (s)	No. of specimen BB	Class
Control		5	1.1	5	III
0.150	0.320	5	1.1	0	I
0.225	0.480	5	1.1	0	I
0.300	0.640	5	1.1	0	I
0.375	0.800	5	1.1	0	I

*****The pH of the NaH_2PO_4 solutions used in 2^{nd} step treatment was adjusted with NaOH solution to 8.5, and it became 7.3 after the treatment.

The cotton fleece was treated using $Al_2(SO_4)_3/NaH_2PO_4$ with a constant mole ratio of 0.47 but different concentrations. The 45 ° flammability of the treated cotton fleece is shown in Table 3.6. The data show that the fleece treated using $Al_2(SO_4)_3/NaH_2PO_4$ at the lowest concentration still passes the flammability test and achieves "Class I" flammability ranking. All the data presented here clearly demonstrate the effectiveness of the AHP formed *in situ* on the cotton fleece in reducing the flammability of the fleece.

The Durability of AHP to Different Refurbishing Procedures

The cotton fleece is treated with $Al_2(SO_4)_3/NaH_2PO_4$ (mole ratio 0.47) at different concentrations, and the treated fleece was subjected to one HL cycle. The weight increase of the cotton fleece before and after the laundering procedure is shown in Figure 3.4. Before HL, the percent weight increase of the treated cotton fleece increases from 15.9 to 43.4 % as the concentration of $Al_2(SO_4)_3$ is increased from 0.150 to 0.375 M, respectively. After 1 HL, the percent weight increase of the cotton fleece decreases significantly due to the removal of the AHP from the cotton fleece during the laundering procedure. When the fleece is treated with 0.150 M $Al_2(SO_4)_3$, the percent weight increase is 3.6% after 1 HL, representing 23% retention of the AHP formed on the fleece after the 2nd treatment. When the $Al_2(SO_4)_3$ concentration is increased to 0.375 M, the percent weight increase of the fleece becomes 13.0%, representing 30% retention of the AHP. The data indicate that significant amount of AHP remains on the fleece after one HL cycle whereas the laundering procedure removes more than 2/3 of the AHP from the fleece. Therefore, the AHP formed *in situ* on the cotton fleece is considered to be a semi-durable flame retardant.

We also used DSC to study the thermal degradation of the untreated cotton fleece and the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and 0.800 M NaH_2PO_4 after one HL cycle (Figure 3.5). The untreated cotton fleece shows a strong endothermic peak at 355 °C due to the depolymerization of cellulose with the formation of levoglucosan and its decomposition products [15-16]. For the cotton fleece treated with $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to one laundering cycle, the endothermic peak shifts to 360°C and the peak is much weaker than that of untreated cotton fleece. Thus, the data indicate that the AHP on cotton fleece retards the cellulose depolymerization process. This may explain why AHP reduces the flammability of the cotton fleece.

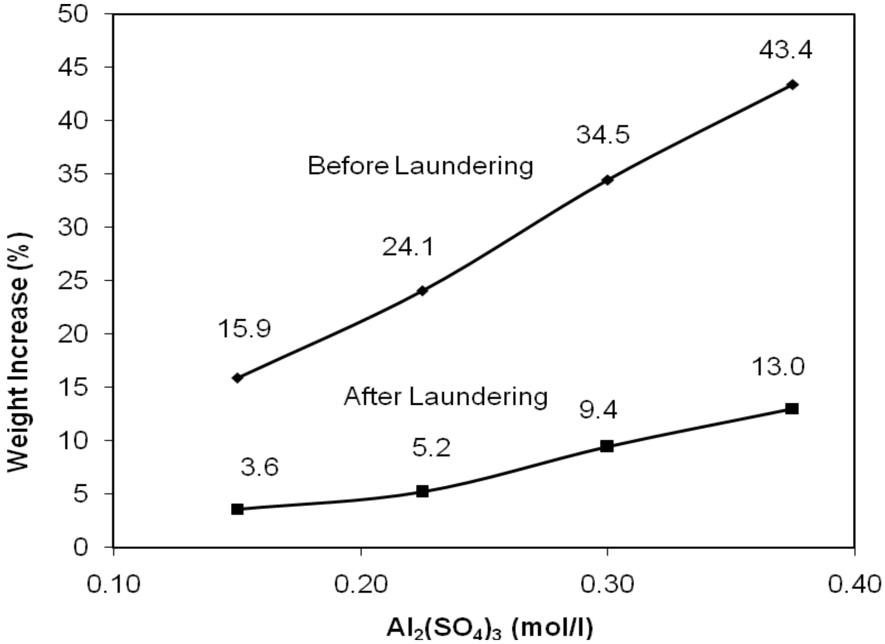


Figure 3.4. The weight increase of the cotton fleece treated with $Al_2(SO_4)_3/NaH_2PO_4$ before and after one HL cycle.

Presented in Figures 3.6A and 3.6B are the SEM images of the untreated cotton fleece fiber and the cotton fleece fiber treated with 0.375 M $Al_2(SO_4)_3$ and 0.800 M NaH_2PO_4 and subjected to one HL cycle, respectively. Figure 3.6A shows the bean-shaped cross-section of the untreated cotton fiber with a collapsed lumen (marked). The image of the cross-section of the treated cotton fiber shown in Figure 3.6B, however, is different. The fiber appears to be swollen and has a round-shaped cross-section. The lumen (marked) almost disappears in Figure 3.6B due to the presence of AHP inside. Therefore, the SEM images shown in Figure 3.6 confirm that the AHP formed inside the lumen and it is retained after the laundering procedure. The data presented in Figure 3.4 show that the particular treated fleece still has 13.0% weight increase after 1 HL cycle.

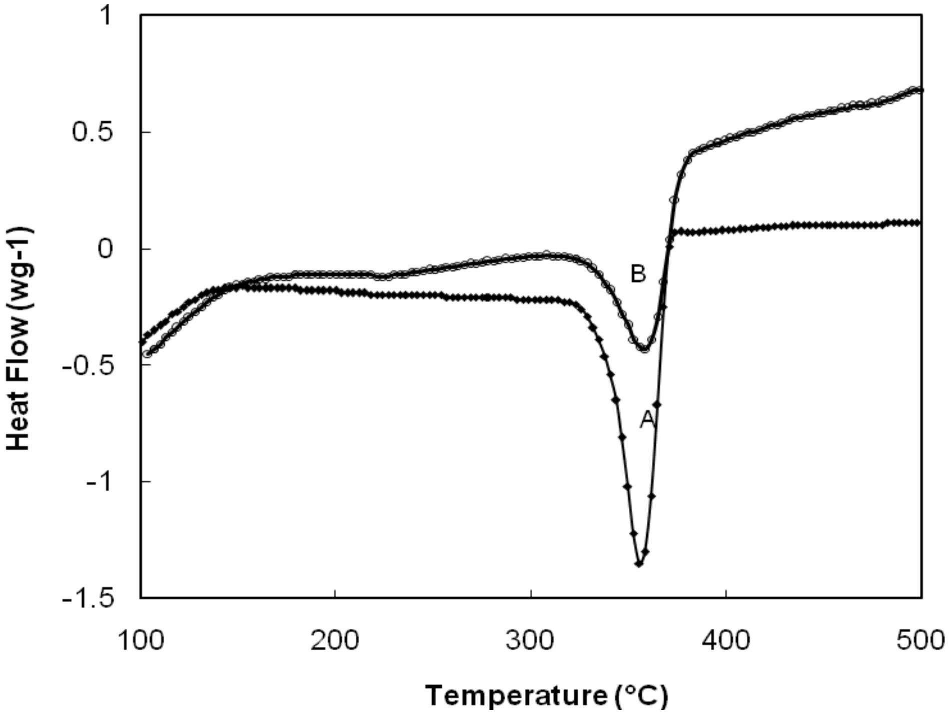
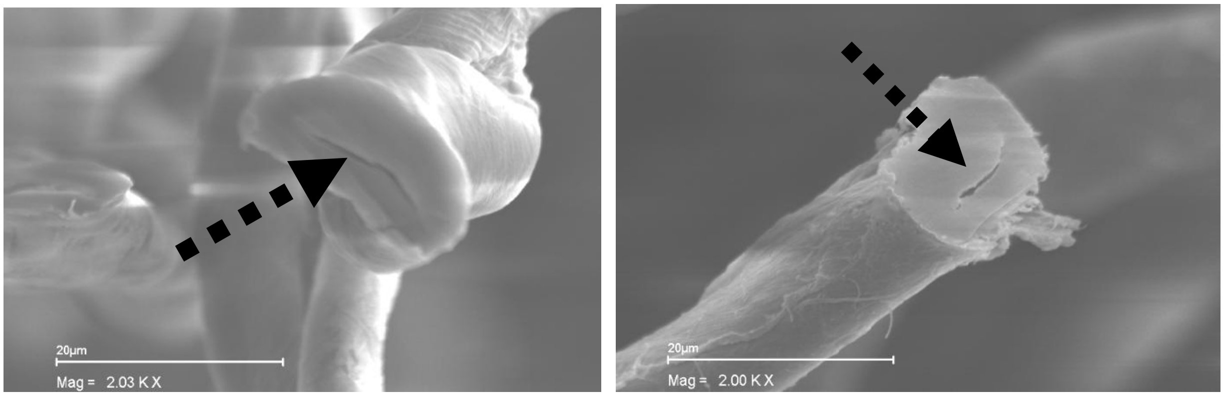


Figure 3.5. The DSC curve of (A) the cotton fleece without treatment and (B) the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and 0.800 M NaH_2PO_4 and subjected to one HL procedure.



A B

Figure 3.6. The SEM images of (A) a cotton fiber taken from the untreated fleece and (B) a cotton fiber taken from the fleece treated with 0.375 M $Al_2(SO_4)_3$ and 0.800 M NaH_2PO_4 and subjected to one HL cycle.

The 45 ° flammability of the cotton fleece treated with $Al_2(SO_4)_3/NaH_2PO_4$ at different concentrations after 1 HL cycle is presented in Table 3.7. The untreated cotton fleece fails the 45 ° flammability test before and after laundering. All the four treated fleece samples pass the 45 ° flammability test before HL as shown in Table 3.6. However, the two fleece samples treated with 0.150 and 0.225 M $Al_2(SO_4)_3$ with weight increase of 3.6 and 5.2%, respectively, after one HL cycle fail the 45 ° flammability test. Only when the concentration of $Al_2(SO_4)_3$ is increased to 0.300 and 0.375 M with weight increase of 9.4% and 13.0%, respectively, the cotton fleece samples thus treated pass the 45 ° flammability test after 1 HL (Table 3.7). It is evident that removal of the AHP by the laundering procedure increases the flammability of the fleece and makes it necessary to use higher $Al_2(SO_4)_3/NaH_2PO_4$ concentrations to maintain "Class I" flammability ranking.

Table 3.7. The 45 ° flammability of the cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to one HL.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)*	45 ° flammability			
		No. of specimen SF	Ave. burning time (s)	No. of specimen BB	Class
Control		5	1.1	5	III
0.150	0.320	5	1.1	5	III
0.225	0.480	5	1.1	5	III
0.300	0.640	5	1.1	0	I
0.375	0.800	5	1.1	0	I

Table 3.8. The weight increase of the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and NaH_2PO_4* of different concentrations and subjected to HL, DC and DC/HW.

NaH_2PO_4 concentration (M)	Weight increase before refurbishing (%)	Weight increase after refurbishing (%)		
		1 HL cycle	DC	DC/HW
0.400	26.5	9.5	24.1	11.4
0.600	35.5	12.3	27.3	12.6
0.800	43.4	13.0	36.4	13.6

*The pH of the NaH_2PO_4 solution was adjusted with NaOH to 8.5.

Table 3.9. The percent retention of the AHP on the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and NaH_2PO_4 of different concentrations and subjected to HL, DC and DC/HW.

NaH_2PO_4 concentration (M)	Weight increase before refurbishing (%)	AHP retention after refurbishing (%)		
		1 HL cycle	DC	DC/HW
0.400	26.5	36	90	43
0.600	35.5	35	77	35
0.800	43.4	30	80	31

We also measured the weight increase of the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and NaH_2PO_4 at different concentrations and subjected to different refurbishment procedures (Tables 3.8 and 3.9). The weight increase of the fleece after the 2nd treatment increases from 26.5 to 43.4% as the NaH_2PO_4 concentration is increased from 0.400 to 0.800 M, respectively (Table 3.8). After one HL cycle, the weight increase decreases to 9.5-13.0%, representing 30-36% retention of the AHP formed on the fleece (Tables 3.8 and 3.9). When the treated fleece is subjected to DC, the weight increase becomes 24.1-36.4%, representing 77-90% retention of the AHP. The weight increase of the fleece subjected to a DC procedure is much higher than that subjected to a HL procedure. Therefore, a DC procedure is a much milder process and it removes far less AHP than a HL procedure. The weight increase after the combination of DC and HW procedures is in the range of 11.4-13.6% representing 31-43% retention, which is similar to that after the laundering procedure. The weight increase of the treated cotton fleece increases as the NaH_2PO_4 concentration increases after the refurbishing procedures.

The 45 ° flammability of cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and NaH_2PO_4 of different concentrations after HL, DC and DC/HW is shown in Table 3.10. All the treated cotton fleece samples pass the 45 ° flammability test to achieve "Class I" after the three different refurbishing procedures, but we also observe more severe surface flash due to the partial removal of AHP from the fleece after the refurbishing procedure.

Table 3.10. The 45 ° flammability of the cotton fleece treated with 0.375 M $Al_2(SO_4)_3$ and NaH_2PO_4 of different concentrations and subjected to HL, DC and DC/HW.

NaH_2PO_4 concentration (M)	45 ° flammability ranking		
	1 HL cycle	DC	DC/HW
Control	III	III	III
0.400	I	I	I
0.600	I	I	I
0.800	I	I	I

Table 3.11. The weight increase of cotton fleece treated with different concentration of $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to one HL, DC and DC/HW.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	Weight increase before refurbishing (%)	Weight increase after refurbishing (%)		
			1HL cycle	DC	DC/HW
0.150	0.320	15.9	3.6	11.8	5.6
0.225	0.480	24.1	5.2	23.6	8.2
0.300	0.640	34.5	9.4	29.4	11.2
0.375	0.800	43.4	13.0	35.4	13.8

Table 3.12. The percent retention of the AHP on the cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to HL, DC and DC/HW.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	Weight increase before refurbishing (%)	AHP retention after refurbishing (%)		
			1 HL cycle	DC	DC/HW
0.150	0.320	15.9	23	74	35
0.225	0.480	24.1	22	98	34
0.300	0.640	34.5	27	85	32
0.375	0.800	43.4	30	82	32

The durability of cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ is evaluated and the weight increase of the treated fleece after different refurbish process is presented in Table 3.11 and 3.12. The weight increase of treated cotton fleece increases with the concentration of $Al_2(SO_4)_3/NaH_2PO_4$ from 15.9 to 43.4% when the concentration of $Al_2(SO_4)_3$ is 0.150 and 0.375 mol/l, respectively (Table 3.11). The weight increase decreases to 3.6-13.0% after 1 HL, representing 22-30% of the AHP retention (Table 3.11 and 3.12). DC procedure removes a part of the AHP from the treated fleece. After DC, the AHP retention is 75-98% (Table 3.12). DC/HW process further removes AHP from the treated cotton fleece. The weight increase of treated cotton fleece decreases to 5.6-13.8% after DC/HW, representing 32-35% of the AHP retention.

Table 3.13. The 45 ° flammability of the cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to HL, DC and DC/HW.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	45 ° flammability ranking		
		1 HL cycle	DC	DC/HW
Control		III	III	III
0.150	0.320	III	I	I
0.225	0.480	III	I	I
0.300	0.640	I	I	I
0.375	0.800	I	I	I

The 45 ° flammability of cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ after different refurbishing procedure is presented in Table 3.13. After DC and DC/HW, all the treated fabrics still have Class I flammability and pass the 45 ° flammability test. In order to pass the 45 ° flammability test after 1 HL, the weight increase of cotton fleece should be higher than 9.0%. But here when the weight increase of the treated cotton fleece after DC/HW is only 5.6%, it still passes the 45 ° flammability test. This is because cotton fleece becomes less fluffy after DC/HW, which decreases the flammability of cotton fleece. On the contrary, cotton fleece becomes fluffier after 1 HL cycle, which requires a higher weight increase of AHP in order to pass the 45 ° flammability test.

Table 3.14. Bursting strength retention and CIE whiteness index of cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ before washing.

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	Bursting Strength (Kg/cm^2)	Bursting Strength Retention (%)	CIE Whiteness Index
0.150	0.320	1.37	55	138
0.225	0.480	1.35	54	137
0.300	0.640	1.39	55	130
0.375	0.800	1.34	53	135
0.000	0.000	2.51	-	130

Table 3.15. Bursting strength retention and CIE whiteness index of cotton fleece treated with 0.375 mol/l $Al_2(SO_4)_3$ at different concentrations of NaH_2PO_4 before washing.

NaH_2PO_4 (M)	Bursting Strength (Kg/cm^2)	Bursting Strength Retention (%)	CIE Whiteness Index
0.400	1.41	56	139
0.600	1.45	58	139
0.800	1.34	53	137

The Physical Properties of the Treated Cotton Fleece

The bursting strength retention and CIE whiteness index of the cotton fleece treated with different concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ and that with NaH_2PO_4 are shown in Table 3.14 and 3.15, respectively. The treated fabric retains 53-58% of the original bursting strength. The fabric strength loss as a result of the treatment can be attributed to two factors. First, the AHP imbedded inside and between the yarns may reduce the flexibility of yarns, and thus, reduces the bursting strength. Secondly, cotton fleece is subjected to Lewis acid degradation when it is impregnated in $Al_2(SO_4)_3$ solution and dried. $Al_2(SO_4)_3$ has high acidity and is a strong Lewis acid. Both acid and Lewis acid cause cellulose depolymerization, thus reduces the fabric strength [17]. One also observes that the CIE whiteness index of the treated cotton fleece increases after the treatment. This is obviously caused by the additional light scattering of the AHP particles on the fabric surface.

CONCLUSIONS

(1) The composition of the AHP formed by the reaction of Al^{3+} and the phosphate anions in an aqueous solution is pH-dependent and the AHP formed at pH 8.5 has the lowest P/Al mole ratio. The quantity of AHP formed on the cotton fleece treated with $Al_2(SO_4)_3$ and NaH_2PO_4 is also pH-dependent.

(2) The AHP formed *in situ* on the cotton fleece by the two-step procedure is effective in reducing the flammability of cotton fleece. AHP on cotton fleece retards cellulose depolymerization process at elevated temperatures.

(3) The AHP formed *in situ* on the cotton fleece is a semi-durable flame retardant. The lumen of a cotton fiber is filled with AHP solid upon the 2nd step treatment of the cotton fleece. A significant portion of AHP remains on the fleece after the treated fleece is subjected to one HL procedure or the combination of DC and HW procedure. Consequently, the treated cotton fleece fabric passes the 45° flammability test both before and after one HL procedure or the combination of DC and HW procedure. A HL procedure using a detergent removes significantly more AHP from the treated fleece than a DC procedure.

(4) The treatment of the cotton fleece increases the whiteness and decreases the bursting strength of the treated cotton fleece by 42-47%.

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CHAPTER 4

FLAME RETARDANT FINISHING OF COTTON FLEECE: II. UNSUBSTITUTED AND HYDROXYL-SUBSTITUTED BI-FUNCTIONAL CARBOXYLIC ACIDS*

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* Wu, X., Yang, C.Q. To be submitted to Journal of Fire Sciences.

ABSTRACT

Polycarboxylic acids containing three or more than three carboxyl groups on their structure can not only crosslink cotton cellulose, but also the esterification of cotton cellulose with polycarboxylic acids is effective in reducing the flammability of cotton fleece. In this paper, we evaluated the effectiveness of non-substituted and hydroxyl-substituted bi-functional carboxylic acids in reducing the flammability of cotton fleece. The 45 ° flammability of treated cotton fleece after one or multiple home launderings was evaluated. Fourier transform infrared (FTIR) spectroscopy was used to analyze the amount of ester formed on the fabric after curing. The data indicated that unsubstituted polycarboxylic acid, succinic acid, had the highest reactivity with cotton cellulose. The esterification of cotton cellulose with hydroxyl-substituted polycarboxylic acids was more effective in reducing the flammability of cotton fleece based on the same amount of ester. Succinic acid treated cotton fleece had the highest bursting strength retention and whiteness and the treatment was the most durable to multiple home launderings. Overall, succinic acid was the most promising flame retardant for cotton fleece due to its high reactivity, durability to multiple home launderings, bursting strength retention, and high whiteness.

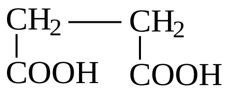
INDEX WORDS: cotton fleece, succinic acid, malic acid, tartaric acid, 45 ° flammability, ester band intensity, FTIR, durability to multiple home launderings, bursting strength retention, CIE whiteness index

INTRODUCTION

The flammability of a cotton fabric largely depends on the construction and density of the fabric. Cotton fleece usually has very high flammability because it has lower density and contains considerable amount of air in its fuzzy surface. It is extremely difficult for 100% cotton fleece to meet the mandatory federal flammability standard for general wearing apparel (16 CFR Part 1610) without chemical treatment [1-4].

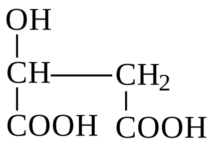
Polycarboxylic acids that contain three or more than three carboxyl groups on its structure, such as 1, 2, 3, 4-butanetetracarboxylic acid (BTCA) and citric acid (CA), can form crosslinking with cotton cellulose; thus, they can be applied on cotton as non-formaldehyde durable press finishing agent [5-8]. Yang and etc. used Fourier transform infrared (FTIR) spectroscopy to analyze the amount of ester formed on the fabric quantitatively. They also used acid-base titration to determine the amount of polycarboxylic acid applied to cotton fabric before curing and the amount of ester on the fabric quantitatively after a curing process [9-14]. Blanchard and Graves applied polycarboxylic acids, such as BTCA and CA, and bi-functional carboxylic acid, such as maleic acid, on cotton/polyester blend carpets and reduced the flammability of the cotton/polyester blend carpet effectively [15]. They also studied a phosphorus-based polycarboxylic acid for reducing the flammability of cotton/polyester fleece [16]. However, the effectiveness of other bi-functional carboxylic acids in reducing the flammability of cotton fabric has not been studied.

In this paper, we studied the effectiveness of three bi-functional carboxylic acids in reducing the flammability of cotton fleece and their reactivity with cotton, i.e., nonsubstituted carboxylic acid, succinic acid (SUA), one hydroxyl-substituted carboxylic acid, malic acid (MLA), and two hydroxyl-substituted carboxylic acid, tartaric acid (TTA). The structures of these three acids are shown in Scheme 4.1, Scheme 4.2 and Scheme 4.3, respectively. The physical properties of SUA, MLA, and TTA are presented in Table 4.1. The solubilities of TTA and MLA are very high at room temperature, 139.0 and 55.8 g/100 g H_2O, respectively. However, the solubility of SUA is only 7.7 g/100g H_2O at room temperature. We used FTIR spectroscopy to study the amount of ester formed on cotton fleece. We also evaluated the durability of the treatment to multiple home launderings, bursting strength, and the CIE whiteness index of treated cotton fleece.



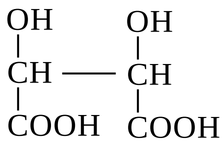
$HOOC-CH_2-CH_2-COOH$

Scheme 4.1. Succinic acid (SUA)



$HOOC-CH(OH)-CH_2-COOH$

Scheme 4.2. Malic acid (MLA)



$HOOC-CH(OH)-CH(OH)-COOH$

Scheme 4.3. Tartaric acid (TTA)

Table 4.1. Physical properties of SUA, MLA, and TTA.

Physical Properties	SUA	MLA	TTA
Molecular Weight	118	134	150
Solubility at RT (g/100 g water)	7.7	55.8	139.0
Melting Point (℃)	185-187	131-133	168-170

EXPERIMENTAL

Materials

The cotton fleece was supplied by Esquel Group (Gaoming, China) with a density of 370 g/m^2. The polycarboxylic acids, succinic acid (SUA), malic acid (MLA) and tartaric aicd (TTA), sodium hypophosphite, and sodium hydroxide were reagent grade chemicals supplied by Aldrich, Milwaukee, WI.

Fabric Treatment and Home Laundering Procedures

The cotton fleece was first immersed in a solution containing polycarboxylic acid and catalyst NaH_2PO_2 with a molar ratio of 2:1, then passed through a laboratory padder with two dips and two nips, dried at 90 ℃ for 3 min 45 sec, and finally cured in a Mathis oven at 170 ℃ for 4 min. All the concentrations presented here are mole concentration of treatment solution. The molar concentration and weight/volume concentration are presented in Table 4.2. The wet pick-up of the cotton fleece fabric was approximately 105 ±2%. The treated fleece fabric was also subjected to different numbers of home laundering (washing) cycles with the use of a standard detergent (“AATCC Detergent 1993”). The home laundering procedure was done according to AATCC Method 124. The water temperature for laundering was approximately 46-47 ℃.

Table 4.2. The mole concentration and weight/volume concentration of the chemicals used in this paper.

Acids				NaH_2PO_2	
Mole Concentration (M)	W/V (g/l)			Mole Concentration (M)	W/V (g/l)
	SUA	MLA	TTA		
0.09	10.62	12.06	13.5	0.045	3.96
0.18	21.24	24.12	27.0	0.090	7.92
0.36	42.48	48.24	54.0	0.180	15.84
0.54	63.72	72.36	81.0	0.270	23.76
0.72	84.96	96.48	108.0	0.360	31.68

Fabric Performance Evaluation

Fabric 45˚ Flammability

The 45˚ flammability of the cotton fleece was measured according to ASTM Method D1230-94 (Standard Test Method for Flammability of Apparel Textiles, reapproved in 2001). The fabric specimen mounted in a specimen holder was first brushed, dried at 105 ℃ in a oven for 30 min, cooled down in a desiccator for 90 min, then tested in a 45 ° flammability tester (Model TC-45 manufactured by Govmark, Bellmore, NY). After the specimen was exposed to a standard butane flame for 1 second to cause ignition, the burning time and burning characteristics were recorded. The average burning time of 5 specimens and the burning characteristics were used to determine the flammability classification.

The details about the classification of the flammability of raised-surface fabric are in Reference 17 [17]. According to ASTM 1230, the flammability of a textile fabric can be characterized as "Class I" only when both the fabric as received and that after a refurbishing procedure are tested and both are ranked as "Class I". The refurbishing procedure includes first dry-clean, followed by a home laundering cycle using a reference standard detergent ("AATCC Detergent 1993").

Fabric Bursting Strength

The bursting strength of the cotton fleece fabric was measured after one home laundering according to ASTM Method D3786 (Standard Test Method for Hydraulic Bursting Strength of Textile Fabrics – Diaphragm Bursting Strength Tester Method) using a "Truburst" bursting strength tester manufactured by James H. Heal & Company, Halifax, England.

Fabric CIE Whiteness Index

The fabric CIE whiteness index was measured according to AATCC Method 110 (“Whiteness of Textiles”) using a “Macbeth Color-Eye” 7000A spectrometer manufactured by Hunter Associates Laboratory, Reston, VA.

FTIR Measurement

A Nicolet 760 FTIR spectrometer was used to collect all the infrared spectra with a Specac diffuse reflectance accessory, presented at absorbance mode ($-\log R/R_0$). The resolution for all the infrared spectra was 4 cm^{-1}, and there were 120 scans for each spectrum. Potassium bromide powder was the reference material for producing a background diffuse reflectance spectrum. A smoothing function was not used. The cured cotton fleece was washed in deionized water to remove the unreacted acid, and treated with 0.1 M NaOH solution at room temperature for 3 minutes to convert the free carboxyl groups to carboxylate. The fabric sample thus treated was finally dried at 90 ℃ for 10 minutes, and ground in a Wiley mill before it was analyzed by FTIR spectroscopy to determine the amount of ester and carboxylate groups. The carbonyl band absorbance in the infrared spectra was normalized against the 1318 cm^{-1} band associated with the C-H bending mode of cellulose.

Determination of the Phosphorus Concentration of the Treated Cotton Fabric

Approximately 2 g of a treated cotton fabric sample taken from four different parts of a specimen was ground in a Wiley mill to powder to improve sample uniformity. Two milliliters of concentrated H_2SO_4 was gradually added to 0.1 g of cotton powder. Ten milliliters of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated to approximately 250 ℃ to digest the powder and to evaporate the water until a dense SO_3 vapor was produced. The completely digested cotton sample was transferred to a 50 ml volumetric flask, then diluted with distilled/deionized water to the mark. The sample thus prepared was analyzed with a "Thermo-Farrell-Ash" Model 965 inductively coupled plasma atomic emission spectrometer to determine the phosphorus concentration. This experimental procedure was developed by the laboratory of Akzo Nobel Functional Chemicals, Dobbs Ferry, New York.

RESULTS AND DISCUSSION

Reactivity of the Polycarboxylic Acids with Cotton Cellulose

The polycarboxylic acid treated cotton fleece was analyzed with an FTIR spectrometer. The treated and cured cotton fleece was home laundered once to remove the polycarboxylic acids not bound to cotton, and then rinsed in a 0.1M NaOH solution for 3 minutes to convert carboxyl groups bound to the fabric to carboxylate anions, so that the ester carbonyl band was not overlapped by the carboxyl carbonyls [18]. The infrared spectrum of the cotton fabric thus treated showed two intense carbonyl bands around 1730 and 1590 cm^{-1} due to the carbonyls of ester and carboxylate anion, respectively.

The ester carbonyl band intensity of cotton fleeces treated with polycarboxylic acids as a function of polycarboxylic acid concentration is shown in Figure 4.1. The ester carbonyl band intensity indicates the amount of ester formed on cotton fleece. From the figure we can see that the amount of ester on SUA treated cotton fleece is much higher than that on MLA and TTA treated cotton fleece, which means SUA has much higher reactivity with cotton cellulose than MLA and TTA do. The ester carbonyl band intensity of SUA treated cotton fleece increases sharply with a slope of 0.75. The ester carbonyl band intensity of MLA treated cotton fleece also increases with a slope of 0.44. The ester carbonyl band intensity of TTA treated cotton fleece increases only slightly with a slope of 0.12. Both SUA and TTA contain two carboxyl groups on their structures. SUA has the highest reactivity with cotton cellulose and TTA has the lowest reactivity. The difference in the reactivity is due to the structure difference. The steric hindrance of the α-hydroxyl group inhibits the esterification reaction of MLA with cotton cellulose. The steric hindrance of the two α-hydroxyl groups inhibits the esterification reaction of TTA with cotton cellulose even further. Therefore, SUA has the highest reactivity with cotton cellulose and TTA has the lowest reactivity with cotton cellulose.

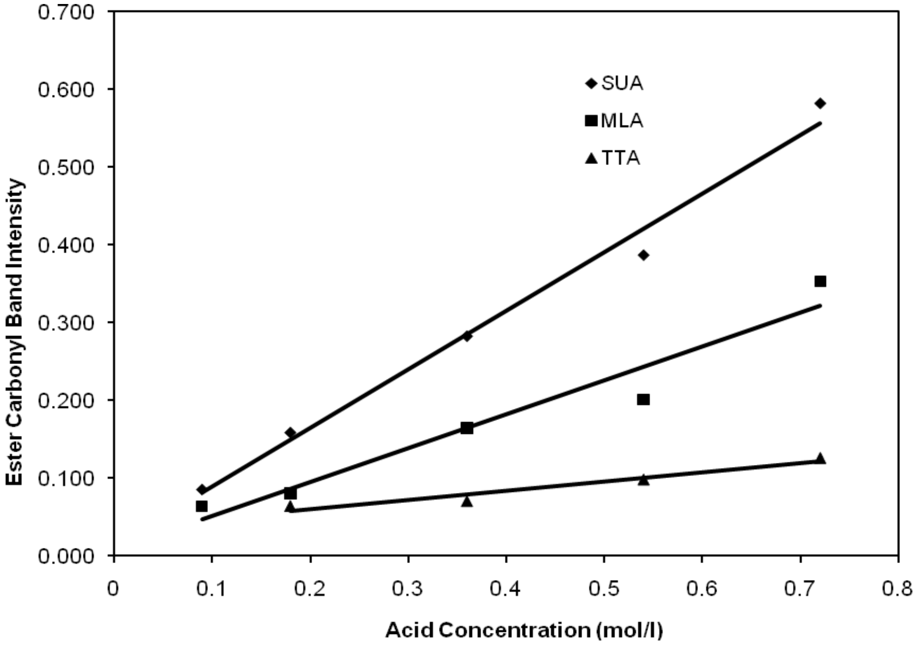


Figure 4.1. The ester carbonyl band intensity of cotton fleece treated with SUA, MLA and TTA with NaH_2PO_2 as catalyst as a function of polycarboxylic acid concentration.

The carboxylate carbonyl band intensity of cotton fleece treated with polycarboxylic acids as a function of polycarboxylic acid concentration is shown in Figure 4.2. The carboxylate carbonyl band intensity indicates the amount of free carboxyl group bound on cotton cellulose. Polycarboxylic acids form ester bond with cotton cellulose through the formation of a 5-member cyclic anhydride intermediate. Since SUA, MLA and TTA are all bi-functional carboxylic acids, the 5-member cyclic anhydride intermediate can only form once. Therefore, only one carboxyl group on bi-functional carboxylic acid can esterify with the hydroxyl group on cellulose, leaving one free carboxyl group. Similar to the intensity of the ester carbonyl band, the SUA treated cotton fleece has the highest carboxylate carbonyl intensity and TTA treated cotton fleece shows the lowest carboxylate carbonyl intensity. Thus, the amount of free carboxyl group on cotton fleece treated with SUA is the highest and that treated with TTA is the lowest, which further proves that SUA has the highest reactivity with cotton cellulose and TTA has the lowest reactivity.

Figure 4.3 shows the FTIR spectra of cotton fleece treated with 0.54 mol/l polycarboxylic acids. Though the cotton fleece was treated with the same mole concentration of polycarboxylic acids, the ester carbonyl and the carboxylate carbonyl band intensity shows big differences. The cotton fleece treated with SUA shows the most intense ester carbonyl band at 1727 cm^{-1}. The cotton fleece treated with TTA shows the weakest ester carbonyl band at 1731 cm^{-1}. The carboxylate carbonyl band intensity of cotton fleece treated with SUA is also the strongest and that of cotton fleece treated with TTA is the least intensive. Figure 4.3 further proves that SUA has the highest reactivity and TTA has the lowest reactivity with cellulose.

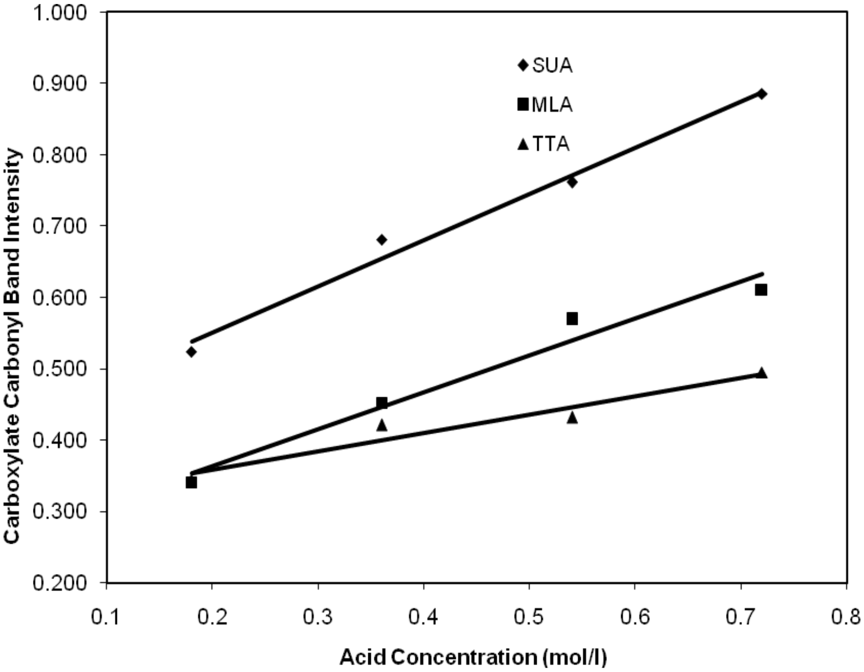


Figure 4.2. The carboxylate carbonyl band intensity of cotton fleece treated with SUA, MLA, and TTA with NaH_2PO_2 as catalyst as a function of polycarboxylic acid concentration

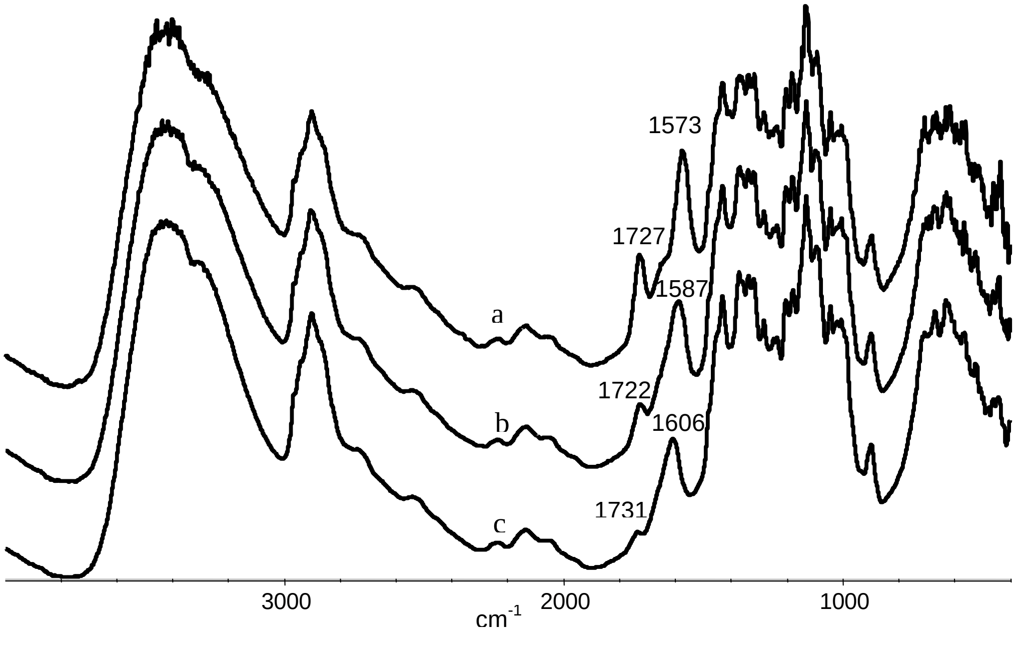


Figure 4.3. FTIR spectra of cotton fleece treated with 0.54/0.27 mol/l polycarboxylic acids/NaH_2PO_2. a: SUA; b: MLA; c: TTA

3.2. Effectiveness of the Treatment with SUA, MLA and TTA

We evaluated the effectiveness of SUA, MLA, and TTA themselves in reducing the flammability of cotton fleece. Table 4.3 shows the 45° flammability of cotton fleece treated with 0.54 mol/l SUA, MLA, and TTA dried at 90 ℃ for 6 min without washing. The flammability data includes the number of specimens having surface flash, average burning time, and number of specimens having base burn, and the flammability classification of the fabric sample. The untreated cotton fleece has Class III flammability with 5 specimens having base burn. All the treated cotton fleeces fail in the 45° flammability test with both base burn and surface flash (Class III). Therefore, polycarboxylic acids themselves are not able to reduce the flammability of cotton fleece.

The effectiveness of SUA, MLA, and TTA in reducing the flammability of cotton fleece after esterification was also evaluated. The cotton fleece was treated with polycarboxylic acids with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min. The 45° flammability of cotton fleece treated with SUA after one home laundering is presented in Table 4.4. When the concentration of SUA is 0.09 mol/l (10.62 g/l), the treated cotton fleece has 1 base burn, and thus fails in the 45° flammability test (Class III). When the concentration of SUA increases to 0.18 mol/l (21.24 g/l), the treated cotton fleece only has surface flash without base burn, and thus has Class I flammability. When the concentration of SUA is further increased, the treated cotton fleeces pass the 45° flammability test. The 45° flammability of cotton fleeces treated with SUA after dry-clean/home laundering procedure (refurbish process) is shown in Table 4.5. Cotton fleeces treated with SUA that pass the 45° flammability test after one home laundering also pass the 45° flammability test after dry-clean/home laundering procedure.

Therefore, we can conclude that the esterification of cotton cellulose with SUA is very effective in reducing the flammability of cotton fleece.

Table 4.3. The 45° flammability of cotton fleece treated with 0.54 mol/l SUA, MLA and TTA dried at 90 ℃ for 6 min without washing.

Acid	45° flammability			
	No. of Specimen SF*	Average Burning Time (s)	No. of Specimen BB*	Classification
Control	5	1.1	5	III
SUA	5	1.1	5	III
MLA	5	1.1	5	III
TTA	5	1.1	5	III

Note: *SF: surface flash.
*BB: base burn.

Table 4.4. The 45° flammability of cotton fleece treated with SUA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

SUA (mol/l)	NaH_2PO_2 (mol/l)	45° flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.09	0.045	5	1.1	1	III
0.18	0.09	5	1.1	0	I
0.36	0.18	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.1	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

Table 4.5. The 45° flammability of cotton fleece treated with SUA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

SUA (mol/l)	NaH_2PO_2 (mol/l)	45° flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.18	0.09	5	1.1	0	I
0.36	0.18	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.1	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

The 45 ° flammability of cotton fleece treated with MLA followed by one home laundering is presented in Table 4.6. When the concentration of MLA is 0.09 mol/l (12.06 g/l), the treated cotton fleece has 4 base burns. The amount of base burns is higher than the 1 base burn of SUA treated cotton fleece at the same mole concentration due to the lower reactivity of MLA with cotton cellulose. When MLA concentration increases to 0.18 mol/l (24.12 g/l) and above, the treated cotton fleeces pass the 45 ° flammability test. The ester carbonyl band intensity of the cotton fleece treated with MLA at 0.18 mol/l is similar with that treated with SUA at 0.09 mol/l (Figure 4.1). However, the cotton fleece treated with SUA at 0.09 mol/l fails in the 45 ° flammability test. Therefore, the esterification of cotton cellulose with MLA is more effective in reducing the flammability of cotton fleece than that with SUA based on the same amount of ester, possibly because the esterified product of MLA with cellulose can release one molecule of water and absorbs heat during the burning process. The 45 ° flammability of cotton fleece treated with MLA followed by dry-clean/home laundering procedure is shown in Table 4.7. Similar to the SUA treated cotton fleece, the treated cotton fleece passes the 45 ° flammability test followed by one home laundering and also passes the flammability test followed by dry-clean/home laundering procedure. Thus, the esterification of cotton cellulose with MLA is also effective in reducing the flammability of cotton fleece.

Table 4.6. The 45 ° flammability of cotton fleece treated with MLA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

MLA (mol/l)	NaH_2PO_2 (mol/l)	45 ° flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.09	0.045	5	1.1	4	III
0.18	0.09	5	1.1	0	I
0.36	0.18	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.1	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

Table 4.7. The 45 ° flammability of cotton fleece treated with MLA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

MLA (mol/l)	NaH_2PO_2 (mol/l)	45 ° flammability			
		No. of Spec. SF	Average Burning Time (s)	No. of Spec. BB	Class
Control	-	5	1.1	5	III
0.18	0.09	5	1.1	0	I
0.36	0.18	5	1.2	0	I
0.54	0.27	5	1.6	0	I
0.72	0.36	5	2.8	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

The effectiveness of the esterification of cotton cellulose with TTA in reducing the flammability of cotton fleece is also investigated. The cotton fleece treated with 0.09 mol/l (13.5 g/l) TTA fails in the 45 ° flammability test with 5 base burns (Table 4.8). Compared with the cotton fleece treated with 0.09 mol/l SUA and MLA, the cotton fleece treated with TTA at 0.09 mol/l has higher flammability since the treated fabric has more base burns. That is because TTA has the lowest reactivity with cotton cellulose. The treated cotton fleece passes the 45 ° flammability test when the concentration of TTA increases to 0.18 mol/l (27.0 g/l). The ester carbonyl band intensity of cotton fleece treated with 0.18 mol/l TTA is lower than that of cotton fleece treated with 0.09 mol/l SUA. However, the cotton fleece treated with 0.09 mol/l SUA fails in the flammability test. Therefore, the esterification of cotton cellulose with TTA is more effective in reducing the flammability of cotton fleece than the esterification with SUA based on the same amount of ester. The treated cotton fleece that passes the 45 ° flammability test followed by one home laundering also pass the 45 ° flammability test followed by dry-clean/home laundering procedure (Table 4.9). At this point, we can conclude that the esterification of cotton cellulose with TTA is effective in reducing the flammability of cotton fleece.

Table 4.8. The 45° flammability of cotton fleece treated with TTA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

TTA(mol/l)	NaH_2PO_2 (mol/l)	45° flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.09	0.045	5	1.1	5	III
0.18	0.09	5	1.2	0	I
0.36	0.18	5	1.9	0	I
0.54	0.27	5	1.2	0	I
0.72	0.36	5	2.0	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

Table 4.9. The 45° flammability of cotton fleece treated with TTA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

TTA(mol/l)	NaH_2PO_2 (mol/l)	45° flammability			
		No. of Spec. SF	Average Burning Time (s)	No. of Spec. BB	Class
Control	-	5	1.1	5	III
0.18	0.09	5	2.2	0	I
0.36	0.18	5	1.4	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.4	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

The phosphorus contents on the cotton fleeces treated with 0.54/0.27 mol/l SUA/NaH_2PO_2, MLA/NaH_2PO_2, and TTA/NaH_2PO_2 followed by one home laundering are shown in Table 4.10. The phosphorus contents of the treated cotton fleece are very low. They are 0.03, 0.09, and 0.08% for cotton fleeces treated with SUA, MLA, and TTA, respectively, which indicates that the effect of phosphorus in the flammability of cotton fleece is very small. The esterification of cotton cellulose with polycarboxylic acids plays a major role in reducing the flammability of cotton fleece.

Table 4.10. Phosphorus content on the cotton fleeces treated with 0.54 mol/l SUA, MLA, and TTA with 0.27 mol/l NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

Acid	Phosphorus Content (%)
SUA	0.03
MLA	0.09
TTA	0.08

Though SUA, MLA and TTA have different reactivities with cotton cellulose, the esterification of cotton cellulose with these three polycarboxylic acids is effective in reducing the flammability of cotton fleece. From the study above, we know that cotton fleece treated with 0.54 mol/l SUA, MLA, and TTA pass the 45 ° flammability test after one home laundering. But can all the treatments be durable to multiple home launderings? Table 4.11 shows the 45 ° flammability and ester carbonyl band intensity of cotton fleece treated with 0.54 mol/l polycarboxylic acids followed by multiple home launderings. From the table we can see that cotton fleece treated with 0.54 mol/l SUA passes the 45 ° flammability test after 20 home launderings. The ester band intensity decreases from 0.387 after 1 home laundering to 0.249 after 20 home launderings, representing 64.3% retention of the ester carbonyl band intensity. Cotton fleece treated with 0.54 mol/l MLA passes the 45 ° flammability test after 10 home launderings and it fails the flammability test after 15 home launderings. The ester carbonyl band intensity drops from 0.201 after one home laundering to 0.107 after 10 home launderings, representing 53.2% retention of the ester carbonyl band intensity. The decrease of ester carbonyl band intensity is due to the ester hydrolysis during the home laundering process. Cotton fleece treated with 0.54 mol/l TTA barely passes the 45 ° flammability test after 5 home launderings and the ester carbonyl band is only 0.064 after 5 home launderings. It fails the 45 ° flammability test after 10 home launderings. The low durability of the cotton fleece treated with TTA is due to its low reactivity and the ester hydrolysis during the laundering process. It is very clear that cotton fleece treated with SUA is much more durable to multiple home launderings than that treated with MLA and TTA. And cotton fleece treated with TTA is the least durable to multiple home launderings.

Table 4.11. The 45° flammability and ester carbonyl band intensity of cotton fleeces treated with 0.54mol/l polycarboxylic acid with 0.27 mol/l NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by multiple home launderings.

No. of HL		Ester carbonyl band intensity	45° flammability			
			No. of Spec. SF	Average Burning Time (s)	No. of Spec. BB	Class
SUA	1	0.387	5	1.1	0	I
	5	0.269	5	1.1	0	I
	10	0.270	5	1.1	0	I
	15	0.249	5	1.1	0	I
	20	0.249	5	1.1	0	I
MLA	1	0.201	5	1.1	0	I
	5	0.115	5	1.1	0	I
	10	0.107	5	1.2	0	I
	15	-	5	1.2	4	III
TTA	1	0.098	5	1.2	0	I
	5	0.064	5	1.1	0	I
	10	-	5	1.2	5	III

Physical Properties of Cotton Fleece Treated with Polycarboxylic Acids

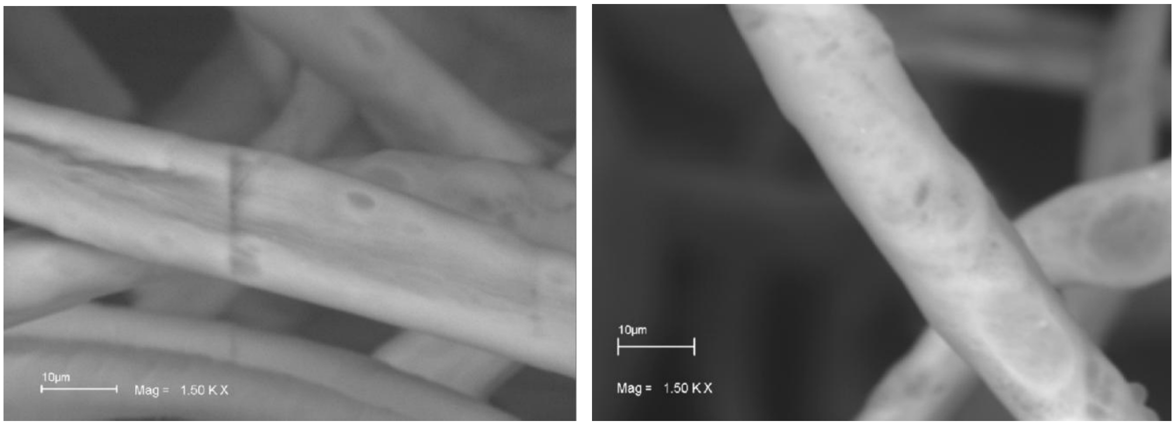
Table 4.12 shows the CIE whiteness index of cotton fleeces treated with polycarboxylic acids with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min. The CIE whiteness indexes were measured after one home laundering. After treated with SUA, the CIE whiteness index of cotton fleece is around 121, slightly lower than 127, the whiteness index of untreated cotton fleece. The effect of SUA concentration on whiteness is not obvious. The treatment of MLA has higher effect on the whiteness index of cotton fleece. Cotton fleece shows lower whiteness after being treated with MLA and the whiteness index decreases as MLA concentration increases probably due to the decomposition of MLA to unsaturated compounds during curing process. The effect of treatment with TTA on the whiteness index of cotton fleece is not significant. After treated with TTA, the whiteness index is around 120, slightly lower than the whiteness index of untreated cotton fleece. And the effect of TTA concentration on whiteness is not obvious, either.

Table 4.12. CIE Whiteness index of cotton fleeces treated with polycarboxylic acids with NaH_2PO_2 as catalyst after one home laundering.

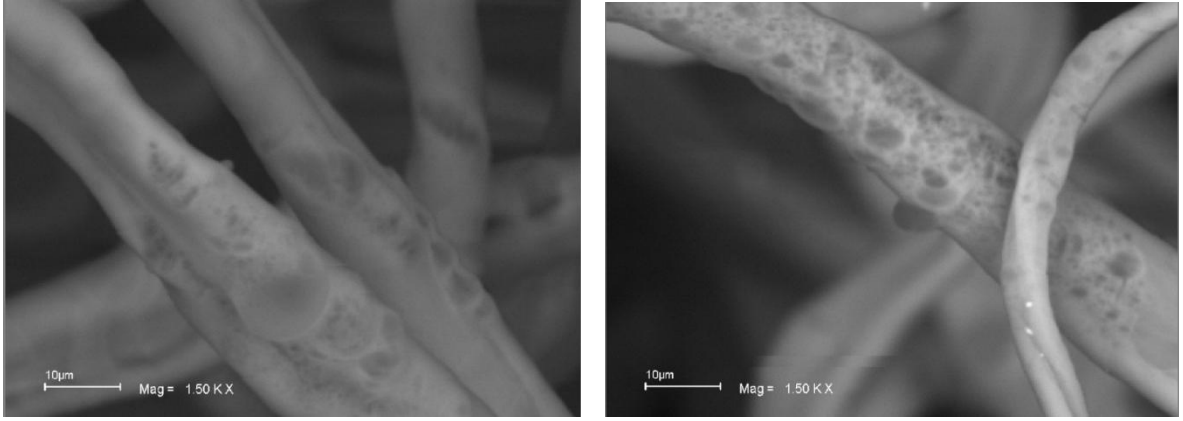
Acid/NaH_2PO_2	Concentration (mol/l)	CIE Whiteness Index
Control	-	127
SUA/NaH_2PO_2	0.18/0.09	120
	0.36/0.18	121
	0.54/0.27	122
	0.72/0.36	120
MLA/NaH_2PO_2	0.18/0.09	120
	0.36/0.18	118
	0.54/0.27	116
	0.72/0.36	114
TTA/NaH_2PO_2	0.18/0.09	122
	0.36/0.18	120
	0.54/0.27	120
	0.72/0.36	120

Table 4.13. Bursting strength of cotton fleeces treated with 0.54 mol/l polycarboxylic acid with 0.27 mol/l NaH_2PO_2 as catalyst followed by one home laundering.

	Control	SUA	MLA	TTA
Bursting Strength (psi)	54	41.7	36.1	33.3
Bursting Strength Retention (%)	-	77	67	62



(a) Control (b) SUA



(c) MLA (d) TTA

Figure 4.4. SEM photos of the cotton fleece treated with 0.54/0.27 mol/l polycarboxylic acid/NaH_2PO_2 dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

The bursting strength of cotton fleeces treated with 0.54 mol/l polycarboxylic acids with NaH_2PO_2 as catalyst followed by one home laundering is shown in Table 4.13. The bursting strength of cotton fleece treated with 0.54 mol/l SUA is 41.7 psi, representing 77% retention of the original strength. The bursting strength of cotton fleece treated with MLA and TTA is 36.1 and 33.3 psi, respectively, representing 67, and 62% retention of the original strength. Cotton fleece is subjected to acid-catalyzed depolymerization when it is treated with polycarboxylic acids. The acid-catalyzed depolymerization plays an important role in the strength loss [18]. The acid-catalyzed depolymerization can be seen from the SEM photos shown in Figure 4.4. The untreated cotton fibers show a quite smooth surface. The cotton fibers treated with SUA show many small and large corrosion areas on the fiber surface due to the acid-catalyzed depolymerization. The surface of the cotton fiber treated with MLA shows more large corrosion areas than that treated with SUA. The surface of the cotton fibers treated with TTA has many more corrosion areas than that treated with SUA and MLA. From the previous discussion we know that SUA has the highest reactivity with cotton cellulose and TTA has the lowest reactivity. Therefore, cotton fleece is subjected to less amount of free carboxylic acid-catalyzed depolymerization when it is treated with SUA and it is subjected to the most amount of free carboxylic acid-catalyzed depolymerization when it is treated with TTA. That is why cotton fleece treated with SUA has the highest bursting strength retention and cotton fleece treated with the same molar concentration of TTA has the lowest bursting strength retention.

CONCLUSIONS

The esterification of cotton cellulose with unsubstituted and hydroxyl-substituted bi-functional carboxylic acids studied in this paper, i.e., SUA, MLA and TTA, is effective in reducing the flammability of cotton fleece. The esterification of cellulose with MLA and TTA is more effective in reducing the flammability of cotton fleece than that with SUA based on the same amount of ester. Overall, unsubstituted bi-functional carboxylic acid, SUA, is the most promising flame retardant for cotton fleece. First of all, the reactivity of SUA is much higher than hydroxyl-substituted polycarboxylic acids, MLA and TTA. The steric hindrance of the α-hydroxyl reduces the reactivity of hydroxyl-substituted polycarboxylic acids. The more the hydroxyl groups on the structure, the lower the polycarboxylic acid reactivity is. Secondly, the durability of SUA treated cotton fleece to multiple home launderings is the highest. Thirdly, cotton fleece treated with SUA has the highest bursting strength retention since it has the highest reactivity and the fiber is subjected to less free acid-catalyzed depolymerization. Cotton fleece treated with TTA has the lowest bursting strength retention. Fourthly, the treatment of SUA does not have much effect on the fabric whiteness. The treatment of MLA reduces the whiteness of treated cotton fleece and the whiteness index decreases with the increase of MLA concentration. The limitation for the application of SUA on reducing the flammability of cotton fleece is its low solubility at room temperature, which restricts its application on some high flammable cotton fleece. In order to reduce the flammability of high flammable cotton fleece, we can consider treating cotton fleece with the combination of SUA and MLA.

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CHAPTER 5

FLAME RETARDANT FINISHING OF COTTON FLEECE: III. POLYCARBOXYLIC ACIDS WITH DIFFERENT FUNCTIONALITY*

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* Wu, X., Yang, C.Q. To be submitted to Journal of Fire Sciences.

ABSTRACT

In previous research, polycarboxylic acids were studied as the flame retardant agents to reduce the flammability of cotton fleece. In this research, the cotton fleece fabric was treated with polycarboxylic acids of different functionality, i.e., unsubstituted polycarboxylic acids, including succinic acid (SUA) and 1,2,3,4-butanetetracarboxylic acid (BTCA), and hydroxyl-substituted acids, including malic acid (MLA) and citric acid (CA). We studied the reactivity of these polycarboxylic acids to esterify cotton cellulose and their effectiveness in reducing the flammability of the cotton fleece. The data indicated that unsubstituted polycarboxylic acid (BTCA and SUA) had higher reactivity with cellulose than hydroxyl-substituted polycarboxylic acid (CA and MLA). All the polycarboxylic acids studied here were effective in reducing the flammability of the cotton fleece from Class III to Class I at low add-on. Cotton fleece treated with multi-functional carboxylic acids had higher dimensional stability than bi-functional carboxylic acid. The cotton fleece treated with BTCA, CA and SUA were durable to multiple home laundering cycles. The cotton fleece treated with unsubstituted polycarboxylic acids had very high whiteness. Cotton fleece treated with SUA had the highest bursting strength retention and BTCA treated cotton fleece had the lowest bursting strength retention.

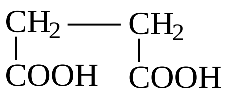
INDEX WORDS**:** Cotton fleece, unsubstituted polycarboxylic acid, BTCA, succinic acid, hydroxyl-substituted polycarboxylic acid, citric acid, malic acid, 45 ° flammability, ester band intensity, bursting strength, CIE whiteness index, durability, home laundering

INTRODUCTION

Cotton fleece usually has very high flammability because it has lower density and contains considerable amount of air in its fuzzy surface. Cotton-containing fleece fabric must be tested and those not reaching the General Wearing Apparel Standard (16 CFR part 1610) are not salable in the U.S. market. Usually, 100% cotton fleece is not able to meet the standard without chemical treatment [1-4].

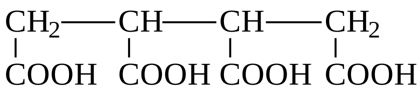
Polycarboxylic acids that contain three or more carboxyl groups, such as 1, 2, 3, 4-butanetetracarboxylic acid (BTCA) and citric acid (CA), have been applied on cotton woven fabrics as non-formaldehyde durable press finishing agents, since they form crosslinkings with hydroxyl groups on adjacent cotton cellulose molecules [5-8]. Yang and etc. used Fourier transform infrared (FTIR) spectrometer to study the cyclic anhydrides intermediate formed in the esterification process of polycarboxylic acids with cotton cellulose. FTIR was also used to quantitatively determine the amount of ester and free carboxyl groups bound on the fabric after a curing process [9-14]. Blanchard and Graves treated cotton/polyester blend carpet with polycarboxylic acids, such as BTCA, CA and maleic acid, and reduced the flammability of the cotton/polyester carpet effectively [15]. They also treated the cotton/polyester fleece with phosphorus-based polymaleic acid oligomer and reduced the flammability of the treated cotton/polyester fleece [16]. However, not much research has been done on flame retardant finishing of cotton fleece using polycarboxylic acids.

In this paper, we studied the effectiveness of bi-functional carboxylic acids and high-functional carboxylic acids. The polycarboxylic acids studied in this paper were succinic acid (SUA), BTCA, malic acid (MLA) and citric acid (CA). Their structures were shown in Scheme 5.1, 5.2, 5.3, and 5.4. We used FTIR spectroscopy to study the amount of ester carbonyl and carboxylate carbonyl formed on cotton fleece. We also evaluated the durability of treated cotton fleece to multiple home laundering cycles, bursting strength, and the CIE whiteness index of treated cotton fleece.



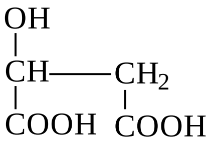
$$\underset{\text{COOH}}{\text{CH}_2} - \underset{\text{COOH}}{\text{CH}_2}$$

Scheme 5.1. Succinic acid (SUA)



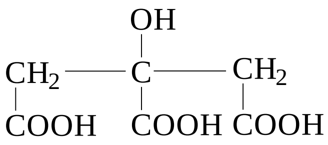
$$\underset{\text{COOH}}{\text{CH}_2} - \underset{\text{COOH}}{\text{CH}} - \underset{\text{COOH}}{\text{CH}} - \underset{\text{COOH}}{\text{CH}_2}$$

Scheme 5.2. BTCA



$$\underset{\text{COOH}}{\overset{\text{OH}}{\text{CH}}} - \underset{\text{COOH}}{\text{CH}_2}$$

Scheme 5.3. Malic Acid (MLA)



$$\underset{\text{COOH}}{\text{CH}_2} - \underset{\text{COOH}}{\overset{\text{OH}}{\text{C}}} - \underset{\text{COOH}}{\text{CH}_2}$$

Scheme 5.4. Citric acid (CA)

EXPERIMENTAL

Materials

The cotton fleece with a density of 370 g/m^2 was supplied by Esquel Group (Gaoming, China). The carboxylic acids, SUA, BTCA, MLA and CA, sodium hypophosphite, and sodium hydroxide were reagent grade chemicals supplied by Sigma-Aldrich, Milwaukee, WI.

Fabric Treatment and Home Laundering Procedures

The cotton fleece was first immersed in a solution containing polycarboxylic acid and catalyst NaH_2PO_2 with mole ratio of carboxyl group to NaH_2PO_2 of 4:1, then passed through a laboratory padder with two dips and two nips, dried at 90 ℃ for 3 min 45 sec, and finally cured in a Mathis oven at 170 ℃ for 4 min. All the concentrations presented here are mole concentrations of the treatment solution. The wet pick-up of the cotton fleece fabric was approximately 105±2%. The treated fleece fabric was also subjected to different numbers of home laundering cycles with the use of a standard detergent ("AATCC Detergent 1993"). The home laundering procedure was done according to AATCC Method 124. The water temperature for laundering was approximately 46-47 ℃.

Fabric Performance Evaluation

Fabric 45˚ Flammability

The 45˚ flammability of the cotton fleece fabric was measured according to ASTM Method D1230-94 ("Standard Test Method for Flammability of Apparel Textiles", reapproved in 2001). A fabric specimen mounted in a specimen holder was brushed. Then the specimen was dried at 105 ℃ in an oven for 30 min. After that, it was moved to a desiccator to cool down for 90 min before it was tested in the 45˚ flammability tester (Model TC-45, manufactured by Govmark, Bellmore, NY). The specimen was ignited with a standard butane flame for 1 sec. The burning time and burning characteristics were recorded. The average burning time of 5 specimens, the number of specimens with surface flash (SF) and the number of specimens with base burn (BB) were used to determine the flammability classifications. The flammability of a textile fabric can be characterized as "Class I" only when both the fabric as received and that after a refurbishing procedure are tested and ranked as "Class I". The refurbishing procedure included a dry-clean procedure done by a commercial dry-cleaner and a home laundering procedure (AATCC method 124).

Fabric Bursting Strength

The bursting strength of the cotton fleece fabric was measured after one home laundering cycle according to ASTM Method D3786 (Standard Test Method for Hydraulic Bursting Strength of Textile Fabrics – Diaphragm Bursting Strength Tester Method) using a "Truburst" bursting strength tester manufactured by James H. Heal & Company, Halifax, England.

Fabric CIE Whiteness Index

The fabric CIE whiteness index was measured according to AATCC Method 110 ("Whiteness of Textiles") using a "Macbeth Color-Eye" 7000A spectrometer manufactured by Hunter Associates Laboratory, Reston, VA.

FTIR Measurement

A Nicolet 760 FTIR spectrometer was used to collect all the infrared spectra with a Specac diffuse reflectance accessory, presented at absorbance mode ($-\log R/R_0$). Resolution for all the infrared spectra was 4 cm^{-1}, and there were 120 scans for each spectrum. Potassium bromide powder was the reference material for producing a background diffuse reflectance spectrum. The smoothing function was not used. The cured cotton fleece was home laundered once to remove the unreacted acid, and treated with 0.1 M NaOH solution at room temperature for 3 minutes to convert the free carboxyl to carboxylate. The fabric sample thus treated was finally dried at 90 ℃ for 10 minutes, and ground in a Wiley mill before it was analyzed by FTIR spectroscopy to determine the amount of ester and carboxylate groups. The carbonyl band intensity in the infrared spectra was normalized against the 1318 cm^{-1} band associated with the C-H bending mode of cellulose.

RESULTS AND DISCUSSION

Reactivity of Unsubstituted and Hydroxyl-Substituted Polycarboxylic Acids with Cotton Fleece

The cotton fleece treated with polycarboxylic acids was analyzed by FTIR spectrometer. The treated and cured cotton fleece was home laundered to remove the polycarboxylic acids not bound to cotton, and then rinsed in 0.1 M NaOH solution for 3 minutes to convert free carboxyl groups bound to the fabric to carboxylate anions so that the ester carbonyl band was not overlapped by the carboxyl carbonyls [18]. The infrared spectrum of the cotton fabric thus treated showed two intense carbonyl bands around 1730 and 1590 cm^{-1} due to the carbonyls of ester and carboxylate anion, respectively.

In order to study the reactivity of SUA, BTCA, MLA, and CA with cotton fleece, we treated cotton fleece with different mole concentrations of SUA, BTCA, MLA and CA with catalyst NaH_2PO_2. We compared the reactivity of polycarboxylic acids with cotton based on the same mole concentration of carboxyl group.

Both SUA and BTCA are unsubstituted polycarboxylic acids. SUA contains two carboxyl groups on its structure and BTCA contains four. The difference in the amount of carboxyl groups results in their difference in reactivity with cotton fleece. The ester carbonyl bond intensity around 1730 cm^{-1} of the cotton fleece treated with SUA and BTCA after one home laundering as a function of carboxyl group concentration is shown in Figure 5.1. The ester carbonyl band intensity indicates the amount of ester formed on cotton fleece. The data show that the amount of ester formed on the cotton fleece treated with BTCA is significantly higher than that on the cotton fleece treated with SUA at the same carboxyl group concentration. The data indicate that BTCA has higher reactivity with cotton cellulose than SUA does. Polycarboxylic acid esterifies cotton cellulose through the formation of a five-member cyclic anhydride intermediate [9]. Since

BTCA has four carboxyl groups, it can form cyclic anhydride intermediate more than twice and form ester crosslinks with cotton cellulose. However, with only two carboxyl groups SUA can form cyclic anhydride intermediate at most once. Therefore, the carboxyl groups on BTCA molecule have much more chance to react with cotton cellulose than the carboxyl groups on SUA molecule do, which explains the higher ester carbonyl band intensity of BTCA treated cotton fleece.

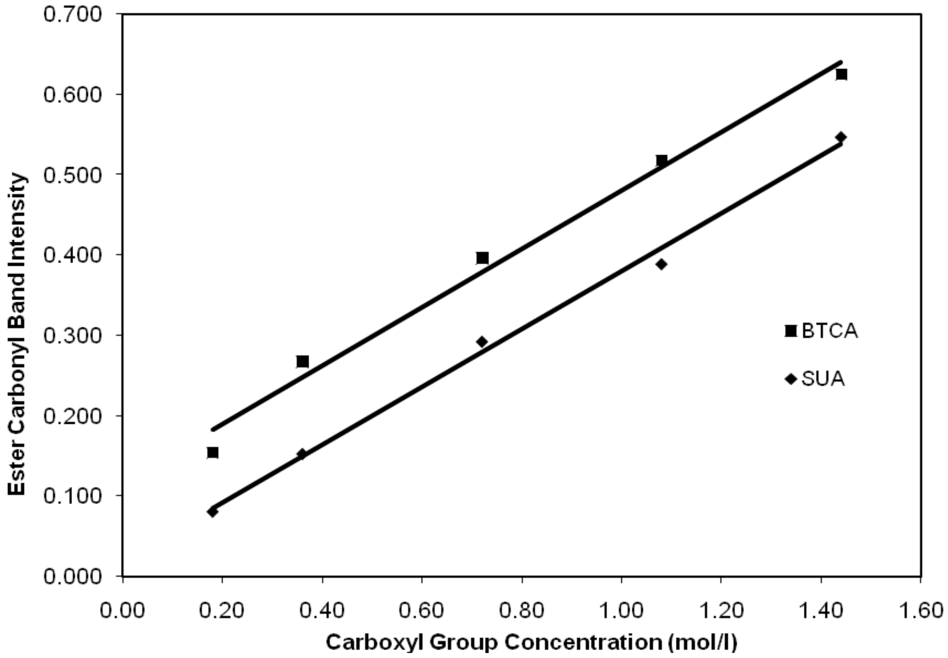


Figure 5.1. The ester carbonyl band intensity of cotton fleece treated with SUA and BTCA as a function of carboxyl group concentration.

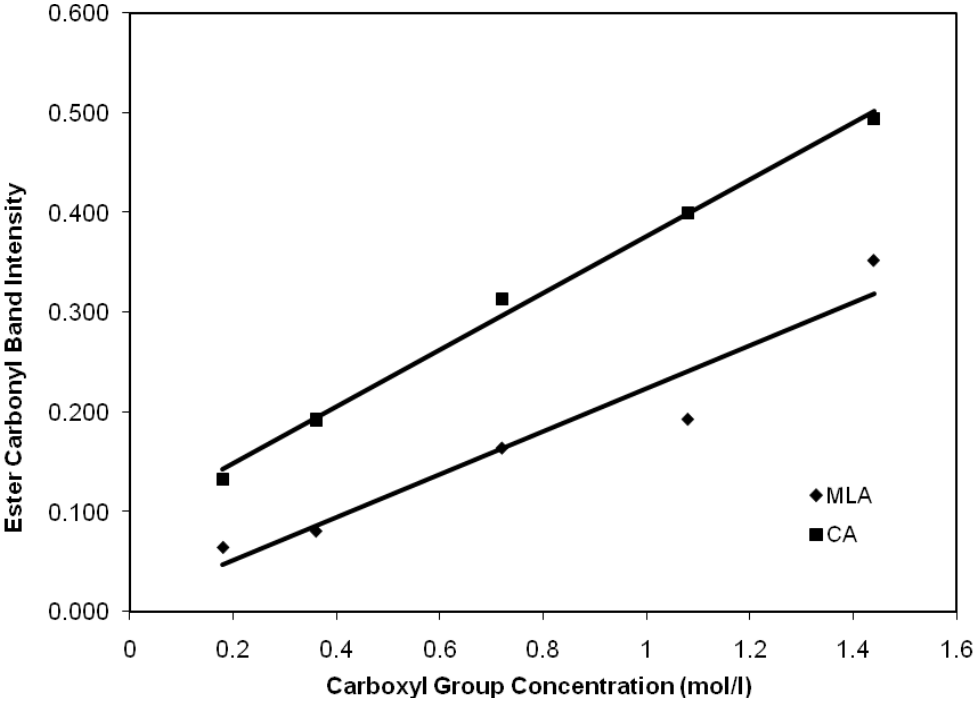


Figure 5.2. The ester carbonyl band intensity of cotton fleece treated with MLA and CA as a function of carboxyl group concentration.

MLA is bi-functional carboxylic acid and CA is tri-functional carboxylic acid and they both contain one hydroxyl group on their molecules. The ester carbonyl band intensity around 1730 cm^{-1} of cotton fleece treated with MLA and with CA after one home laundering is shown in Figure 5.2. From Figure 5.2 we can see that the amount of ester formed on the cotton fleece treated with CA is significantly higher than that treated with MLA at the same mole concentration of carboxyl group, especially at high carboxyl group concentration. The data indicate that CA has much higher reactivity with cotton cellulose than MLA does. The difference in reactivity is due to difference in the structure. With three carboxyl groups on its structure, CA can form crosslinking with cotton cellulose. With only two carboxyl groups on its structure, MLA can only form ester once with cotton cellulose. Therefore, CA has even higher reactivity with cotton cellulose than MLA does.

Presented in Figure 5.3 is the carboxylate carbonyl band intensity around 1590 cm^{-1} of cotton fleeces treated with SUA and BTCA after one home laundering as a function of carboxyl group concentration. The carboxylate carbonyl band intensity indicates the amount of free carboxyl group bound on the treated cotton fleece. For both BTCA and SUA treated cotton fleece, the amount of free carboxyl groups on the treated cotton fleece increases with the carboxyl concentration. The amount of carboxyl groups on the cotton fleece treated with BTCA is higher than that treated with SUA. Since the amount of ester on cotton fleece treated with BTCA is higher than that treated with SUA, the reactivity of BTCA with cotton cellulose is much higher than the reactivity of SUA.

Figure 5.4 shows the carboxylate carbonyl band intensity of the cotton fleeces treated with CA and MLA as a function of carboxyl group concentration. Evidently, the amount of free carboxyl groups bound on the cotton fleece treated with CA is higher than that treated with MLA over the concentration range. Since there is more ester on the cotton fleece treated with CA, CA has higher esterification efficiency with cotton fleece than MLA does.

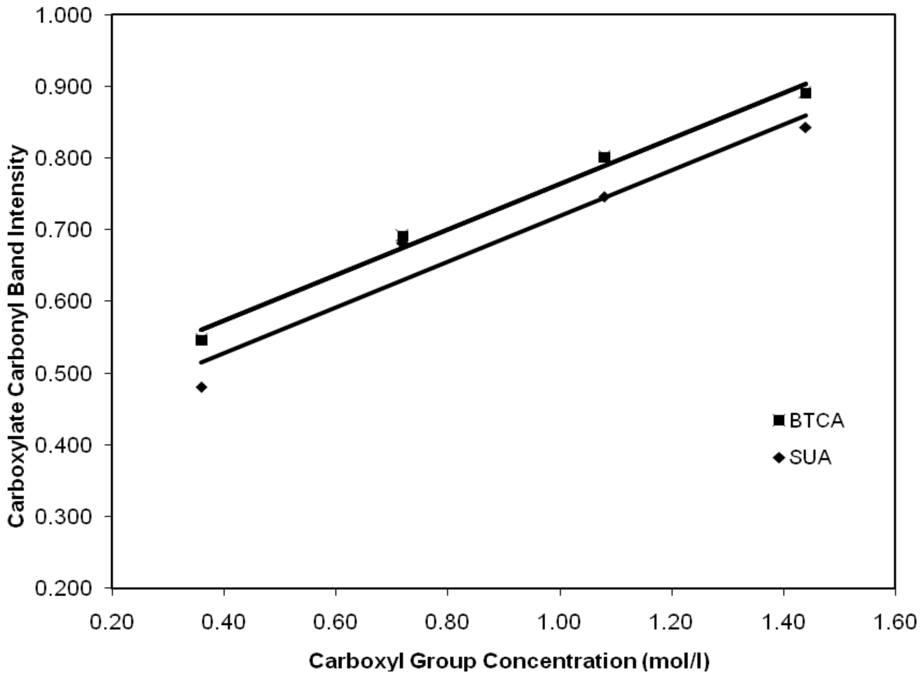


Figure 5.3. The carboxylate carbonyl band intensity of cotton fleece treated with SUA and BTCA as a function of carboxyl group concentration.

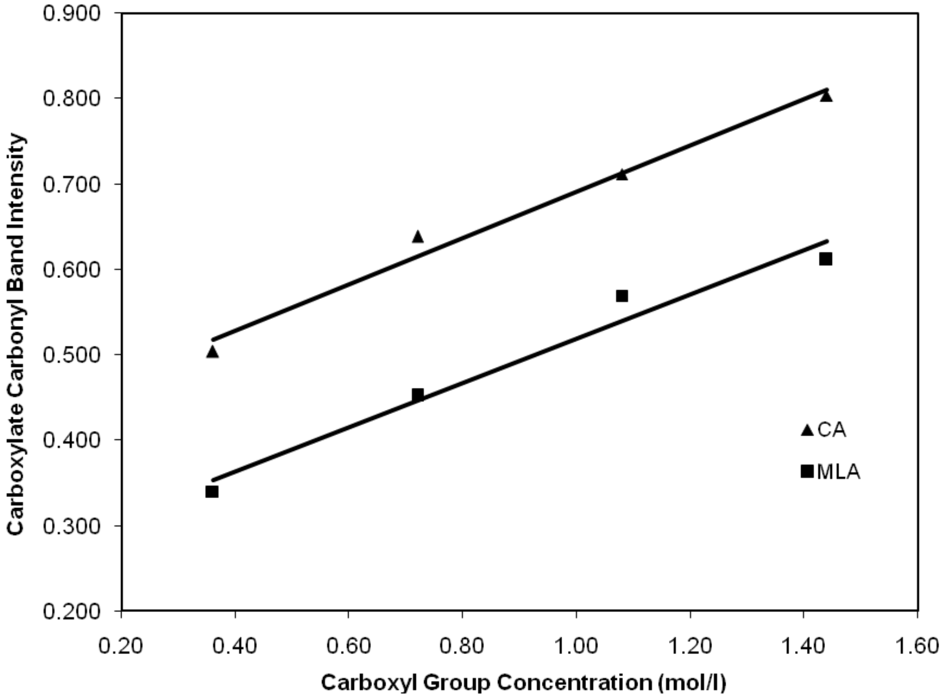


Figure 5.4. The carboxylate carbonyl band intensity of cotton fleece treated with MLA and CA as a function of carboxyl group concentration.

Figure 5.5 shows the FTIR diffusion reflectance spectra of cotton fleeces treated with 0.54 mol/l SUA and with 0.27 mol/l BTCA. It is very clear that ester carbonyl band at around 1730 cm^{-1} and the carboxylate carbonyl band at around 1590 cm^{-1} in the spectrum of cotton fleece treated with 0.27 mol/l BTCA is much stronger than that treated with 0.54 mol/l SUA. Figure 5.5 further proves that BTCA has a higher esterification efficiency with cotton cellulose than SUA does.

Figure 5.6 shows the FTIR spectra of cotton fleeces treated with 0.54 mol/l MLA and 0.36 mol/l CA. The ester carbonyl band at around 1730 cm^{-1} and the carboxylate carbonyl band at around 1590 cm^{-1} in the spectrum of cotton fleece treated with CA are much stronger than that in the spectrum of cotton fleece treated with MLA. This figure further proves that CA has higher esterification efficiency with cotton cellulose than MLA does.

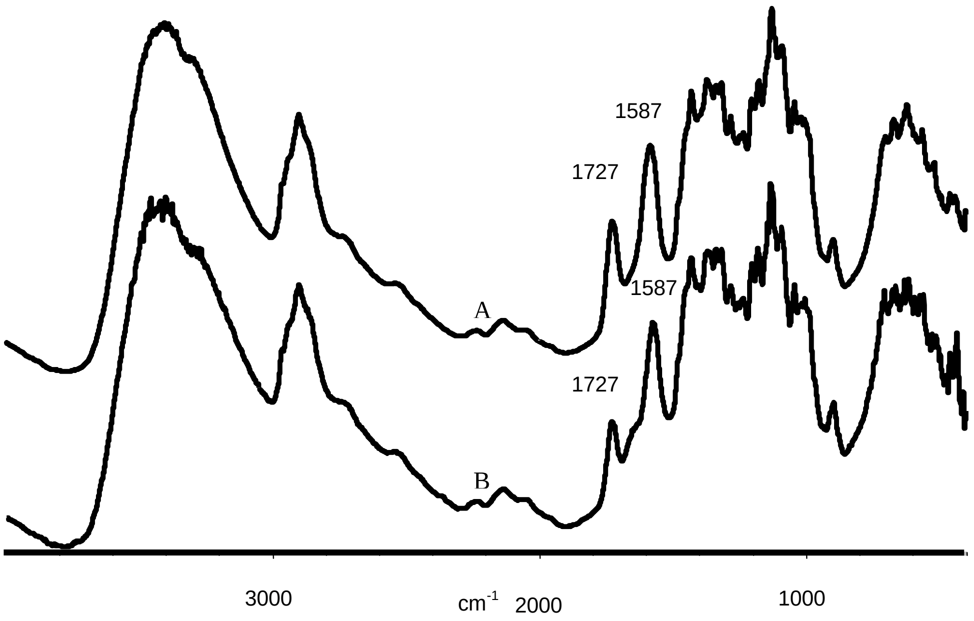


Figure 5.5. FTIR diffusion reflectance spectra of cotton fleece treated with 0.54 mol/l SUA and 0.27 mol/l BTCA with NaH_2PO_2 as catalyst. A: BTCA; B: SUA.

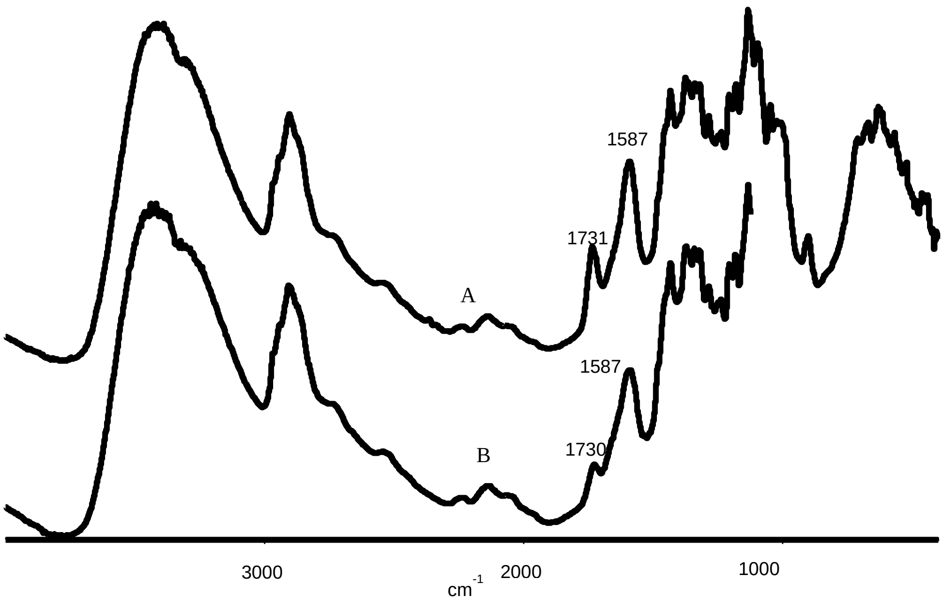


Figure 5.6. FTIR diffusion spectra of cotton fleece treated with 0.54 mol/l MLA and 0.36 mol/l CA with NaH_2PO_2 as catalyst. A: CA; B: MLA.

The Effectiveness of Polycarboxylic Acids in Reducing the Flammability of Cotton Fleece

Table 5.1 shows the 45 ° flammability of cotton fleece treated with 0.54 mol/l SUA, 0.27 mol/l BTCA, 0.54 mol/l MLA, and 0.36 mol/l CA dried at 90 °C for 6 min without washing. The flammability data includes the number of specimens having surface flash, average burning time, the number of specimens having base burn, and the flammability classification of the fabric samples. The untreated cotton fleece has Class III flammability with 5 specimens having base burn. All the treated cotton fleece fails in the 45 ° flammability test with both base burn and surface flash (Class III). Therefore, polycarboxylic acids without esterification are not able to reduce the flammability of cotton fleece.

Table 5.1. The 45 ° flammability of cotton fleeces treated with 0.54 mol/l SUA, 0.27 mol/l BTCA, 0.54 mol/l MLA and 0.36 mol/l CA dried at 90 ℃ for 6 min without washing.

Acid	Concentration (mol/l/g/l)	45 °Flammability			
		No. of Specimen SF*	Average Burning Time (s)	No. of Specimen BB*	Class
Control	-	5	1.1	5	III
SUA	0.54/63.72	5	1.1	5	III
BTCA	0.27/63.18	5	1.1	5	III
MLA	0.54/72.36	5	1.1	5	III
CA	0.36/69.12	5	1.1	5	III

Note: *SF: surface flash.
*BB: base burn.

Table 5.2. The 45 ° flammability of cotton fleece treated with SUA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

SUA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45 °Flammability			
		No. of Specimen SF*	Average Burning Time (s)	No. of Specimen BB*	Class
Control	-	5	1.1	5	III
0.09/10.62	0.045	5	1.1	1	III
0.18/21.24	0.09	5	1.1	0	I
0.36/42.48	0.18	5	1.1	0	I
0.54/63.72	0.27	5	1.1	0	I
0.72/84.96	0.36	5	1.1	0	I

Note: The pH of treatment solution is adjusted to 2.5 using NaOH solution.

Table 5.3. The 45 ° flammability of cotton fleece treated with SUA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure (refurbishing procedure).

SUA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45 °Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.18/21.24	0.09	5	1.1	0	I
0.36/42.48	0.18	5	1.1	0	I
0.54/63.72	0.27	5	1.1	0	I
0.72/84.96	0.36	5	1.1	0	I

Table 5.4. The 45 ° flammability of cotton fleece treated with BTCA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

BTCA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.045/10.53	0.045	5	1.1	1	III
0.09/21.06	0.09	5	1.2	0	I
0.18/42.12	0.18	5	1.6	0	I
0.27/63.18	0.27	5	1.1	0	I
0.36/84.24	0.36	5	1.1	0	I

The 45 ° flammability of cotton fleece treated with SUA with NaH_2PO_2 as catalyst followed by one home laundering is presented in Table 5.2. When the concentration of SUA is 0.09 mol/l (10.62 g/l), the treated cotton fleece has 1 base burn, and thus fails in the 45 ° flammability test (Class III). When the concentration of SUA increases to 0.18 mol/l (21.24 g/l) and further, the treated cotton fleece only has surface flash without base burn, thus, has Class I flammability. Cotton fleece treated with SUA that passes the 45 ° flammability test after one home laundering also passes the 45 ° flammability test followed by dry-clean/home laundering procedure (refurbishing process) (Table 5.3). When the concentration of SUA is very low, the amount of ester formed on cotton cellulose is not enough to reduce the flammability of cotton cellulose. When cotton fleece is esterified at higher SUA concentration, cotton fleece shows reduced flammability. Therefore, the esterification of cotton cellulose with SUA is effective in reducing the flammability of cotton fleece.

Presented in Table 5.4 is the 45 ° flammability of cotton fleece treated with BTCA with NaH_2PO_2 as catalyst followed by one home laundering. When the concentration of BTCA is 0.045 mol/l (10.53 g/l), the treated cotton fleece has 1 base burn, and thus it fails in the 45 ° flammability test. Similarly with SUA, when the concentration of BTCA is very low, the ester formed on cotton cellulose is not enough to reduce the flammability of cotton cellulose. When cotton fleeces are treated with BTCA at higher concentrations, the treated cotton fleeces after one home laundering all pass the 45° flammability test with surface flash only. The cotton fleeces treated with BTCA that passes the 45° flammability test followed by one home laundering also pass the test followed by one refurbishing procedure (Table 5.5). From the above data, we can also conclude that the esterification of cotton cellulose with BTCA is very effective in reducing the flammability of cotton fleece.

Table 5.5. The 45° flammability of cotton fleece treated with BTCA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

BTCA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45° Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.09/21.06	0.09	5	1.6	0	I
0.18/42.12	0.18	5	1.5	0	I
0.27/63.18	0.27	5	2.0	0	I
0.36/84.24	0.36	5	1.2	0	I

Table 5.6. The 45° flammability of cotton fleece treated with MLA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

MLA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45° Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.09/12.06	0.045	5	1.1	4	III
0.18/24.12	0.09	5	1.1	0	I
0.36/48.24	0.18	5	1.1	0	I
0.54/72.36	0.27	5	1.1	0	I
0.72/96.48	0.36	5	1.1	0	I

The 45 ° flammability of cotton fleece treated with MLA followed by one home laundering is shown in Table 5.6. When the concentration of MLA is 0.09 mol/l (12.06 g/l), the treated cotton fleece fails in the 45 ° flammability test with 4 specimens having base burn. The treated cotton fleece that passes the 45 ° flammability test after one home laundering also passes the 45 ° flammability test followed by the refurbishing procedure (Table 5.7). Thus, we can conclude that the esterification of cotton cellulose with MLA is effective in reducing the flammability of cotton fleece.

Table 5.8 presents the 45 ° flammability of cotton fleece treated with CA followed by one home laundering. From the table we can see when CA concentration is as low as 0.06 mol/l (11.52 g/l), the same carboxyl group mole concentration with 0.09 mol/l MLA, the treated cotton fleece passes the 45 ° flammability test with surface flash only. However, the cotton fleece treated with 0.09 mol/l MLA fails in the 45 ° flammability test due to the low reactivity of MLA with cotton cellulose. When the concentration of CA is further increased, the treated cotton fleece still passes the 45 ° flammability test. The 45 ° flammability of cotton fleece treated with CA after refurbishing procedure is presented in Table 5.9. All the treated cotton fleece still passes the 45 ° flammability test after refurbishing. The data illustrate that the esterification of cellulose with CA is effective in reducing the flammability of cotton fleece.

Table 5.7. The 45 ° flammability of cotton fleece treated with MLA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

MLA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Spec. SF	Average Burning Time (s)	No. of Spec. BB	Class
Control	-	5	1.1	5	III
0.18/24.12	0.09	5	1.1	0	I
0.36/48.24	0.18	5	1.2	0	I
0.54/72.36	0.27	5	1.6	0	I
0.72/96.48	0.36	5	2.8	0	I

Table 5.8. The 45° flammability of cotton fleece treated with CA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

CA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45° Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.06/11.52	0.045	5	1.1	0	I
0.12/23.04	0.09	5	1.9	0	I
0.24/46.08	0.18	5	1.1	0	I
0.36/69.12	0.27	5	1.1	0	I
0.48/92.16	0.36	5	2.0	0	I

Table 5.9. The 45° flammability of cotton fleece treated with CA with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one dry-clean/home laundering procedure.

CA (mol/l/g/l)	NaH_2PO_2 (mol/l)	45° Flammability			
		No. of Specimen SF	Average Burning Time (s)	No. of Specimen BB	Class
Control	-	5	1.1	5	III
0.06/11.52	0.045	5	1.3	0	I
0.12/23.04	0.09	5	1.1	0	I
0.24/46.08	0.18	5	1.7	0	I
0.36/69.12	0.27	5	2.3	0	I
0.48/92.16	0.36	5	1.3	0	I

Durability to Multiple Home Launderings

From the above study we know that the esterification of cellulose with polycarboxylic acids is very effective in reducing the flammability of cotton fleece. Is this treatment durable to multiple home launderings? Table 5.10 shows the 45° flammability and the ester carbonyl band intensity on the cotton fleece after multiple home launderings. The durability of the treatment with 0.54 mol/l SUA to multiple home launderings is very good. The treated cotton fleece passes the 45° flammability test after 20 home launderings. The ester carbonyl band intensity decreases from 0.387 after 1 home laundering to 0.249 after 20 home launderings, representing 64.3%

retention of ester band intensity. The durability of the treatment with 0.27 mol/l BTCA to cotton fleece is even better. The cotton fleece treated with BTCA passes the 45 ° flammability test after 20 launderings. The ester carbonyl band intensity decreases slightly from 0.517 after 1 home laundering to 0.468 after 20 launderings, representing 90.5% retention of the ester band intensity. The data indicate that cotton fleece treated with BTCA has very good resistance to ester hydrolysis during the multiple home launderings. The cotton fleece treated with 0.54 mol/l MLA passes the 45 ° flammability test after 10 home launderings and fails the test after 15 home launderings. The ester carbonyl band intensity on the cotton fleece treated with MLA is only 0.201 after 1 home laundering and it drops to 0.107 after 10 home launderings. The low durability of cotton fleece treated with MLA is due to the low esterification and the hydrolysis of ester during the laundering process. The cotton fleece treated with 0.36 mol/l CA passes the 45 ° flammability test after 20 home launderings. The ester carbonyl band intensity on the cotton fleece treated with CA decreases from 0.400 after 1 home laundering to 0.314 after 20 home launderings, representing 78.5% retention of the ester carbonyl band intensity. Thus, the cotton fleece treated with CA also has very good durability to multiple launderings. The durability of cotton fleece treated with multi-functional carboxylic acids (BTCA and CA) is better than that treated with bi-functional carboxylic acids (SUA and MLA). And the durability of cotton fleece treated with unsubstituted polycarboxylic acids (SUA and BTCA) is better than that treated with hydroxyl-substituted polycarboxylic acids (MLA and CA). Among these four acids, BTCA treated cotton fleece has the best durability to multiple launderings and CA treated cotton fleece comes next.

Table 5.10. The 45 ° flammability and ester carbonyl band intensity of cotton fleece treated with 0.54 mol/l SUA, 0.27 mol/l BTCA, 0.54 mol/l MLA, and 0.36 mol/l CA with 0.27 mol/l NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by a different number of home launderings (HL).

No. of HL		Ester carbonyl band intensity	45 ° flammability			
			No. of Spec. SF	Average Burning Time (s)	No. of Spec. BB	Class
SUA	1	0.387	5	1.1	0	I
	5	0.269	5	1.1	0	I
	10	0.270	5	1.1	0	I
	15	0.249	5	1.1	0	I
	20	0.249	5	1.1	0	I
BTCA	1	0.517	5	1.1	0	I
	5	0.483	5	3.2	0	I
	10	0.466	5	1.1	0	I
	15	0.460	5	2.6	0	I
	20	0.468	5	3.0	0	I
MLA	1	0.201	5	1.1	0	I
	5	0.115	5	1.1	0	I
	10	0.107	5	1.2	0	I
	15	-	5	1.2	4	III
CA	1	0.400	5	1.1	0	I
	5	0.339	5	1.1	0	I
	10	0.330	5	1.5	0	I
	15	0.317	5	1.4	0	I
	20	0.314	5	2.8	0	I

Physical Properties of Cotton Fleece Treated with Polycarboxylic Acids

The CIE whiteness index of cotton fleece treated with different acids is shown in Table 5.11. From the table we can see that the treatment of cotton fleece with unsubstituted acids, SUA and BTCA, has very little effect of the fabric whiteness. The whiteness index of untreated cotton fleece is 127, and the whiteness index of cotton fleece treated with SUA and BTCA is around 121 and 123, respectively. The concentration effect of SUA and BTCA in whiteness is not obvious, either. Yet, the treatment of cotton fleece with hydroxyl-substituted polycarboxylic acid, MLA and CA, has an obvious impact on the whiteness, especially the treatment with CA. The whiteness index of cotton fleece treated with MLA decreases from 120 at 0.18 mol/l to 114 at 0.72 mol/l. And the whiteness index of cotton fleece treated with CA drops from 119 at 0.12 mol/l to 101 at 0.48 mol/l. CA tends to decompose and produce some unsaturated double bond compounds, aconitic acid and itaconic acid, which causes the decrease of the whiteness index.

Table 5.11. CIE whiteness index of cotton fleece treated with polycarboxylic acids with NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

Acid/NaH_2PO_2	Concentration (mol/l)	CIE Whiteness Index
Control	-	127
SUA/NaH_2PO_2	0.18/0.09	120
	0.36/0.18	121
	0.54/0.27	122
	0.72/0.36	120
BTCA/NaH_2PO_2	0.09/0.09	122
	0.18/0.18	124
	0.27/0.27	123
	0.36/0.36	123
MLA/NaH_2PO_2	0.18/0.09	120
	0.36/0.18	118
	0.54/0.27	116
	0.72/0.36	114
CA/NaH_2PO_2	0.12/0.09	119
	0.24/0.18	115
	0.36/0.27	103
	0.48/0.36	101

Table 5.12. Dimensional stability of cotton fleece treated with polycarboxylic acids with 0.27 mol/l NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

Acid	Concentration (mol/l)	Tumble dried dimensional stability (%)	
		Length	Width
Control	-	-8.3	0.0
SUA	0.54	-11.0	3.9
BTCA	0.27	-1.2	-0.4
MLA	0.54	-5.5	0.0
CA	0.36	-3.1	-0.8

Table 5.13. Bursting Strength of cotton fleece treated with polycarboxylic acids with 0.27 mol/l NaH_2PO_2 as catalyst dried at 90 ℃ for 3 min 45 sec and cured at 170 ℃ for 4 min followed by one home laundering.

Acid	Control	SUA	BTCA	MLA	CA
Concentration (mol/l)	-	0.54	0.27	0.54	0.36
Bursting Strength (psi)	54	41.7	25.7	36.1	30.2
Bursting Strength Retention (%)	-	77.2	47.6	66.9	55.9

The dimensional stability of cotton fleece treated with polycarboxylic acids to home laundering is also evaluated and shown in Table 5.12. The untreated cotton fleece shrinks 8.3% in length direction and there is no change in width direction when it is tumble dried. Basically, this cotton fleece does not have good dimensional stability to home laundering. Cotton fleece treated with BTCA has the best dimensional stability with 1.2% shrinkage in length direction and 0.4% shrinkage in width direction. The cotton fleece treated CA has the second best dimensional stability with 3.1% shrinkage in length direction and 0.8% shrinkage in width direction. Cotton fleece treated with SUA has the worst dimensional stability with 11.0% shrinkage in length direction and 3.9% elongation in the width direction. MLA treated cotton fleece has better dimensional stability than SUA treated cotton fleece with 5.5% shrinkage in length direction. The probably reason is that MLA decomposes during the curing process and produce unsaturated maleic acid, which can form crosslinks with cellulose chain and increase the fabric dimensional stability [19]. With multiple carboxyl groups on the structure, CA and BTCA form crosslinking with cellulose, which increases the dimensional stability of treated cotton fleece.

The bursting strength of cotton fleece treated with the polycarboxylic acids is shown in Table 5.13. The bursting strength of cotton fleece treated with 0.54 mol/l SUA is 41.7 psi, representing 77% retention of the original strength. The bursting strength of cotton fleece treated with 0.54 mol/l MLA is 36.1 psi, representing 67% retention of the original strength. When cotton fleece is treated with bi-functional polycarboxylic acid, it is subjected to acid-catalyzed depolymerization and the acid-catalyzed depolymerization plays a major role in the strength loss. The more acidic the system is the more acid degradation the cotton fleece will suffer. From the reactivity study, we know that SUA has higher esterification efficiency with cotton cellulose than MLA does. Therefore, cotton fleece is subjected to less free carboxylic acid-catalyzed depolymerization when it is treated with SUA. Cotton fleece treated with CA and BTCA has a lower bursting strength retention than bi-functional polycarboxylic acids. Besides the acid-catalyzed depolymerization, crosslinking plays a very important role in the bursting strength loss of CA and BTCA treated cotton fleece. BTCA is more effective in crosslinking cotton fabric; thus, BTCA treated cotton fleece has the lowest bursting strength retention [19].

CONCLUSIONS

The esterification of cotton fleece with polycarboxylic acids (SUA, BTCA, MLA and CA) is effective in reducing the flammability of cotton fleece. Before esterification, polycarboxylic acids are not able to reduce the flammability of cotton fleece. High functional carboxylic acids (BTCA and CA) have higher reactivity with cotton cellulose than bi-functional carboxylic acids (SUA and MLA). BTCA has the highest reactivity with cotton fleece. The cotton fleece treated with BTCA, CA and SUA is durable to multiple home launderings and they passes the 45 °flammability test after 20 home launderings. The cotton fleece treated with MLA has lower durability to multiple home launderings due to the low esterification and the ester hydrolysis in the laundering process. Overall, the cotton fleece treated with high-functional carboxylic acids is more durable to multiple launderings than that treated with bi-functional carboxylic acids. The cotton fleece treated with BTCA is the most durable to multiple home launderings. The cotton fleece treated with SUA has the highest bursting strength retention and that treated with BTCA has the lowest bursting strength retention. The treatment of cotton fleece with unsubstituted polycarboxylic acids, BTCA and SUA, has very little effect on the fabric whiteness. The treatment of cotton fleece with hydroxyl-substituted polycarboxylic acids, especially CA, affects the whiteness of treated cotton fleece.

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CHAPTER 6

FLAME RETARDANT FINISHING OF COTTON FLEECE: IV. THE COMBINATION OF MALEIC ACID AND SODIUM HYPOPHOSPHITE*

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ABSTRACT

Cotton fleece is not able to meet the federal flammability standard (16 CFR Part 1610: “Standard for the Flammability of Clothing Textiles”) without chemical treatment. In this research, we investigated the chemical reactions of maleic acid (MA) on cotton in the presence of sodium hypophosphite (NaH_2PO_2) and the use of the combination of MA and NaH_2PO_2 as a flame retardant finishing system for cotton fleece. We found that MA esterifies cotton cellulose at relatively low temperatures in the presence of NaH_2PO_2 as catalyst, and that MA esterified to cotton is able to further react with NaH_2PO_2 at higher temperatures (≥150ºC), which bonds phosphorus to the cotton cellulose. The reactions between MA and NaH_2PO_2 on cotton also lead to the crosslinking of cotton cellulose. The treatment using the combination of MA and NaH_2PO_2 is effective in reducing the flammability of cotton fleece from “Class III” to “Class I” (16CFR1610). This is a nonformaldehyde and low cost flame retardant finishing system for cotton fleece. The treated cotton fleece still maintains “Class I” flammability after 20 home laundering cycles.

INDEX WORDS: Cotton; flame retardant finishing; fleece; maleic acid; sodium hypophosphite.

INTRODUCTION

Cotton is one of the most flammable fibers. Most of the cotton fleece fabrics are not able to meet the federal “Standard for the Flammability of Clothing Textiles” (16 CFR 1610) [1]. Fleece has a highly napped surface and low density, thus becoming more flammable than other raised surface fabrics. Most cotton fleece is not able to meet 16 CFR 1610 “Class I” standard without chemical treatment [2, 3].

Durable flame retardants commonly used for cotton include those based on tetrakis(hydroxymethyl)phosphonium (THPX), typically under the commercial name of Proban® (Rhodia), and N-methylol dimethylphosphonopropionamide, exemplified by the commercial product Pyrovatex® CP or Pyrovatex® CP New (Ciba) [4, 5]. However, those traditional flame retardants are not suitable for applications to cotton fleece. The Proban® process is exceedingly expensive whereas Pyrovatex® CP requires multiple after-washing procedures, thus making them impractical for applications on cotton fleece. Multifunctional carboxylic acids have been used as non-formaldehyde durable press finishing agents for cotton since the late 1980s [6]. Blanchard and Graves investigated the application of polycarboxylic acids to reduce the flammability of cotton and cotton/polyester carpets [7]. Phosphorus-containing maleic acid (MA) oligomer was also used to reduce the flammability of cotton/polyester fleece as reported recently [8]. The treated cotton/polyester fleece had lower flammability and increased char formation upon combustion.

In our previous study, we developed a flame retardant finishing system based on the combination of a hydroxyl-functional organophosphorus oligomer (HFPO) and a bonding agent, such as dimethyloldihydroxylethyleneurea (DMDHEU) or trimethylolmelamine, for cotton and cotton blends [9-13]. We successfully applied the combination of HFPO and DMDHEU as a durable flame retardant finishing system for cotton fleece [14]. The cotton fleece treated with HFPO/DMDHEU achieved “Class I” flammability and showed high strength retention with little change in fabric whiteness and hand. The flame retardant finishing system is durable to multiple home launderings [14]. In this research, we investigated the use of the combination of an unsaturated bifunctional acid (MA) and a phosphorus-containing inorganic compound (NaH_2PO_2) to reduce the flammability of cotton fleece and the chemical reactions of MA and NaH_2PO_2 on cotton.

EXPERIMENTAL

Materials

Two cotton fabrics were used in this research: (1) a desized, scoured, and bleached plain weave fabric with density of 109 g/m^2 (Testfabrics style 400); and (2) a cotton fleece with density of 370 g/m^2 produced by Esquel Group (Gaomin, Guandong Province, China). MA, NaH_2PO_2, and sodium hydroxide (NaOH) were reagent grade chemicals supplied by Sigma-Aldrich, Milwaukee, WI.

Fabric Treatment and Home Laundering Procedures

The cotton woven fabric and cotton fleece were first immersed in a solution containing MA and NaH_2PO_2, then passed through a laboratory padder with two dips and two nips. The cotton woven fabric was dried at 80 ℃ for 2 min and cured in a Mathis oven at specified temperatures for 2 min. The cotton fleece was dried at 90 ℃ for 3 min 45 sec, then cured at 170 ℃ for 4 min if it is not specified otherwise. The concentrations of MA and NaH_2PO_2 presented as mole concentrations (mol/l) in this paper are converted to % (w/v) in Table 6.1. The wet pick-ups of the cotton woven fabric and cotton fleece fabric were approximately 98±2% and 105±2%, respectively. The treated fabrics were also subjected to different numbers of home laundering cycles with the use of a standard detergent ("AATCC Detergent 1993"). The home laundering procedure was done according to AATCC Method 124. The water temperature for laundering was approximately 46-47 ℃.

Table 6.1. The concentrations of NaH_2PO_2 and MA used for the treatment of the cotton fabrics.

NaH_2PO_2		MA	
Mole Concentration (mol/l)	W/V (g/l)	Mole Concentration (mol/l)	W/V (g/l)
0.067	5.9	0.18	21
0.090	7.9	0.36	42
0.14	12	0.54	63
0.18	16	0.72	84
0.27	24	-	-
0.32	29	-	-
0.36	32	-	-

Fabric 45˚ Flammability Measurement

The 45˚ flammability of the cotton fleece fabric was measured according to ASTM Method D1230-94 ("*Standard Test Method for Flammability of Apparel Textiles*", reapproved in 2001). A fabric specimen mounted in a specimen holder was first brushed. Immediately after the specimen was dried at 105 ℃ in an oven for 30 min, it was moved to a desiccator to cool down for 90 min. It was then tested in the 45˚ flammability tester (Model TC-45 manufactured by Govmark, Bellmore, NY). The specimen was exposed to a standard butane flame for 1 sec for ignition, and the burning time and burning characteristics were recorded. The arithmetic mean burning time of 5 specimens and the number of specimens with surface flash (SF) and the number of specimens with base burn (BB) were used as the basis for flammability classification determination. The flammability classifications of the cotton fleece were described in our previous paper [14]. According to ASTM 1230, the flammability of a textile fabric can be characterized as “Class I” only when both the fabric as received and that after a refurbishing procedure are tested and ranked as “Class I”. The refurbishing procedure includes dry-cleaning undertaken by a commercial dry-cleaner followed by a home laundering cycle using a reference standard detergent (“AATCC Detergent 1993”).

Wrinkle Recovery Angle (WRA) Measurement

The WRA of the cotton woven fabric was measured according to AATCC Standard Method 66-1990 after the fabric was subjected to 1 home laundering.

FT-IR Spectroscopy Measurement

The diffuse reflectance infrared spectra were collected using a Nicolet Magna 760 spectrometer with a Specac diffuse reflectance accessory and were presented in absorbance mode (-log R/R0). Resolution for all the infrared spectra was 4 cm^{-1}, and there were 120 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. To measure the ester carbonyl band intensity, the cured cotton fleece was laundered once to remove the unreacted MA and NaH_2PO_2, dried and then treated with a 0.1 M NaOH solution at room temperature for 3 min to convert the free carboxyl groups on the fabric to carboxylate anions. The fabric sample thus treated was first dried using paper towel to absorb excess solution, then dried at 90 ℃ for 10 min, and finally ground in a Wiley mill before it was analyzed by the FT-IR spectrometer to determine the intensities of the ester and carboxylate carbonyl bands. The carbonyl band in the infrared spectra was normalized against the 1318 cm^{-1} band associated with the C-H bending mode of cellulose. This analytical method was discussed in detail previously [15-16].

Analysis of Phosphorus Concentration of the Treated Fabric

The treated cotton fleece fabric specimens were conditioned to constant weight before the analysis. Approximately 2 g of the treated fabric taken from 3 different parts in a fabric specimen was ground in a Wiley mill into a powder, and the powder was thoroughly mixed to improve sample uniformity. Two milliliters of concentrated H_2SO_4 was added to 0.10 g of cotton powder in a beaker. Ten mililiters of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250 ℃ to digest the powder and to evaporate the water until a dense SO_3 vapor was produced. The completely digested cotton sample as a clear solution was transferred to a 50 ml volumetric flask, and then diluted with distilled water to the mark. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer to determine the phosphorus concentration. The percent phosphorus fixation = [(the phosphorus concentration of the fabric after 1 home laundering) ÷ (the phosphorus concentration of the fabric before laundering)] x 100%.

RESULTS AND DISCUSSION

The Reactions of MA and NaH_2PO_2 on Cotton

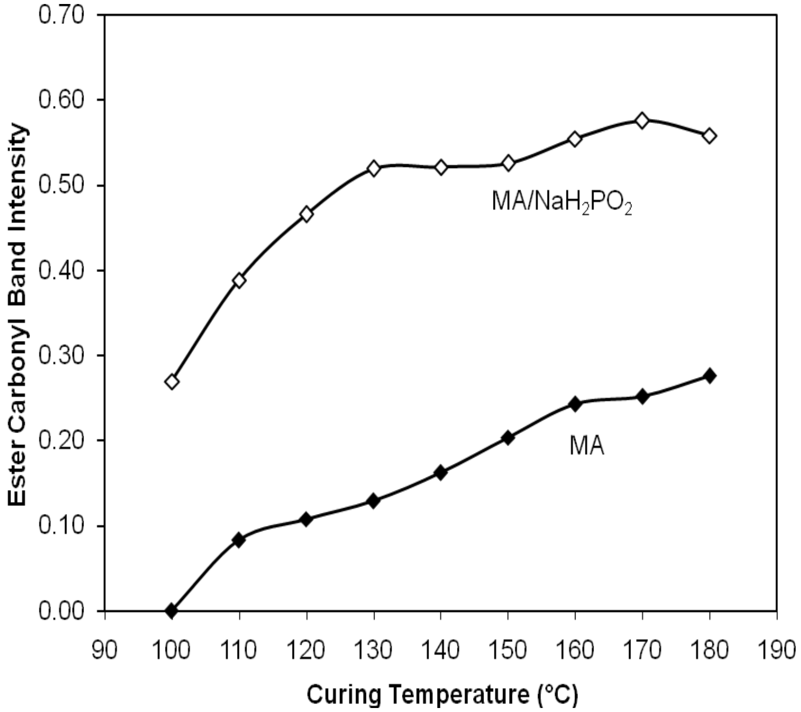


Figure 6.1. The ester carbonyl band intensity of the cotton woven fabric treated with (1) 0.54 mol/l MA alone and (2) the combination of 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and cured at different temperatures (after 1 home laundering).

The cotton woven fabric is treated with a solution containing 0.54 mol/l MA only and also with a solution containing the combination of 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2, dried at 80 ℃ for 2 min, and then cured at different temperatures for 2 min. The ester carbonyl band intensity of the cotton woven fabric thus treated is shown in Figure 6.1. The ester carbonyl band intensity is a quantitative measurement of the amount of ester formed on cotton as discussed in our previous papers [15-16]. The ester carbonyl band intensity is 0.27 at a curing temperature of 100 ℃, when it is treated with MA and NaH_2PO_2. It increases drastically to 0.52 when the curing temperature is increased to 130 ℃, and then increases modestly to 0.56 as the curing temperature is increased to 180 ℃ (Figure 6.1). The data presented in Figure 6.1 also show that the amount of ester formed on cotton is significantly reduced when NaH_2PO_2 is not present. Therefore, the data clearly indicate that NaH_2PO_2 functions as a catalyst for the esterification of MA on cotton as reported in our previous research [17].

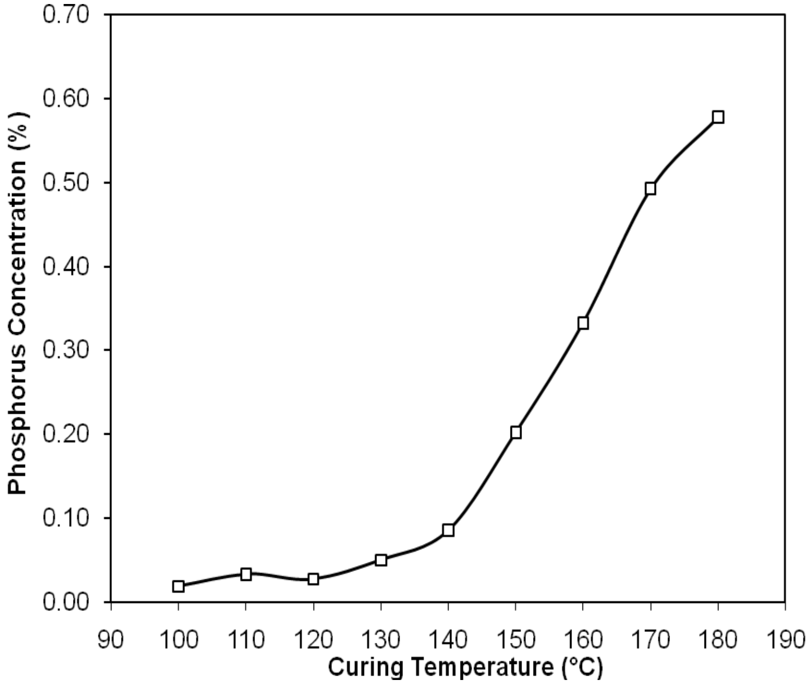


Figure 6.2. The phosphorus concentration of the cotton woven fabric treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and cured at different temperatures (after 1 home laundering).

The phosphorus concentrations of the cotton woven fabric treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and cured at different temperatures are shown in Figure 6.2. The phosphorus concentration is in the range from 0.02 to 0.09% when the curing temperature is in the range from 100 to 140 ℃. It increases rapidly to 0.20% when the curing temperature is increased to 150 ℃, and it reaches 0.58% at 180 ℃. The quantity of phosphorus bound to the cotton fabric increases with the curing temperature. Significant amounts of phosphorus are bound to cotton only when the curing temperature is increased to 150 ℃ and beyond (Figure 6.2). The slope of the phosphorus concentration vs. curing temperature curve drastically increases when the curing temperature is increased above 140 ℃. Thus, the data indicate that the bonding of phosphorus to cotton takes place at a temperature significantly higher than that of esterification of cotton by MA shown in Figure 6.1.

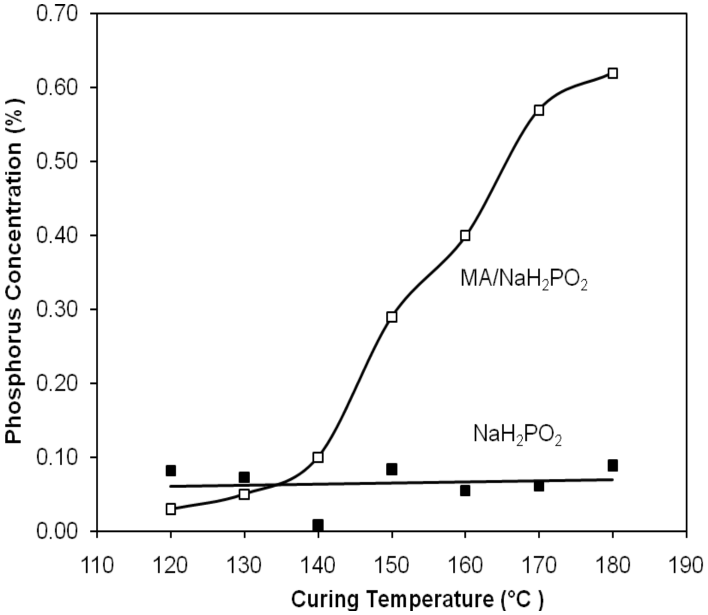


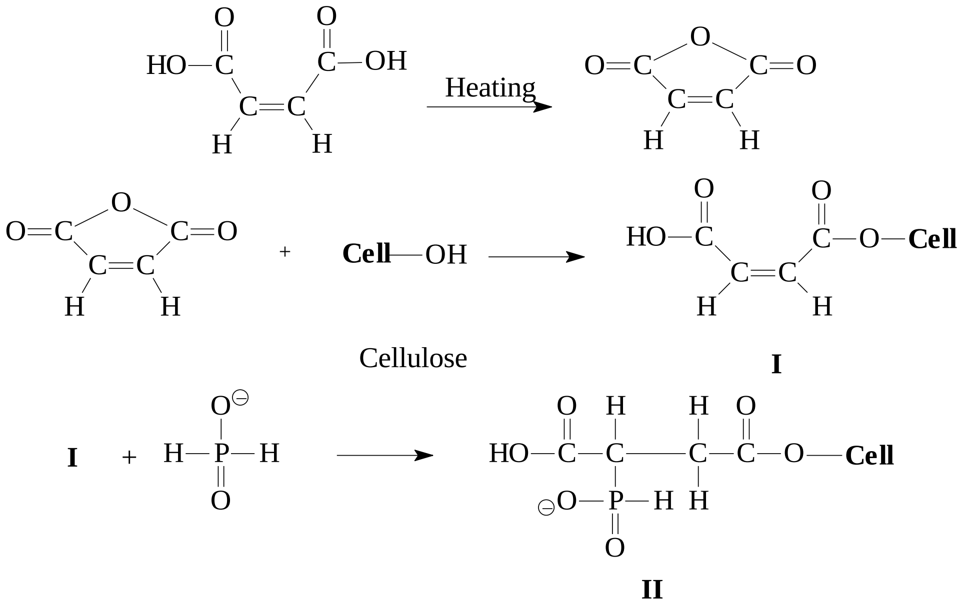
Figure 6.3. The phosphorus concentration of the cotton fleece treated with (1) 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and (2) 0.27 mol/l NaH_2PO_2 alone and cured at different temperatures (after 1 home laundering).

The fleece fabric treated with 0.27 mol/l NaH_2PO_2 alone and with the combination of 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 are cured at temperatures from 120 to 180 ℃. The phosphorus concentrations on treated fabrics after one home laundering are shown in Figure 6.3. When NaH_2PO_2 is applied by itself, phosphorus retention appears to be low and independent of curing temperature. When the cotton fleece is treated with NaH_2PO_2, the pH of the solutions is adjusted to 1.36 by HCl. The phosphorus concentration of the treated cotton fleece is ~0.04% regardless of the curing temperature. The small quantity of phosphorus bound to the cotton treated with NaH_2PO_2 only is possibly due to the phosphorylation of cellulose by H_3PO_2 under the acidic condition. The results for the cotton fleece treated with both MA and

NaH_2PO_2 (Figure 6.3) are similar to those of the treated cotton woven fabric presented above (Figure 6.2) in that the phosphorus concentration on the treated fabric increases with the curing temperature and significant amounts of phosphorus are bound to cotton only when the curing temperature is increased above 140 ℃ (Figure 6.3).

The data shown in Figures 6.2 and 6.3 demonstrate that in the presence of MA, significant amount of phosphorus is bound to both the woven cotton fabric and the cotton fleece when the temperature is increased to 150 ℃. Therefore, a possible mechanism for the majority of phosphorus being bound to the cotton fabric when it is treated with the combination of MA and NaH_2PO_2 is an addition reaction of $H_2PO_2^-$ to the MA on cotton as shown in Scheme 6.1. MA first esterifies cotton cellulose to form **I** through the formation of a cyclic anhydride intermediate. **I** further reacts with $H_2PO_2^-$ to form **II**, thus bonding phosphorus to cotton cellulose.

The cotton woven fabric treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and that treated with 0.54 mol/l MA alone were cured over the range of 100-180 ℃. The WRA of the cotton fabric thus treated and subjected to 1 home laundering cycle is presented in Table 6.2. The WRA of the fabric is 181 ° before treatment. It increases to 201 ° when the cotton woven fabric treated with MA/NaH_2PO_2 is cured at 140 ℃ and it reaches 247 ° when the curing temperature is increased to 180 ℃. The WRA of the fabric treated with MA only slightly increases from 181 ° at curing temperature of 100 ℃ to 200 ° at the curing temperature of 180 ℃. The significantly increased WRA of the cotton fabric treated with MA/NaH_2PO_2 at increasing curing temperatures indicates that crosslinking takes place on the treated cotton fabric.

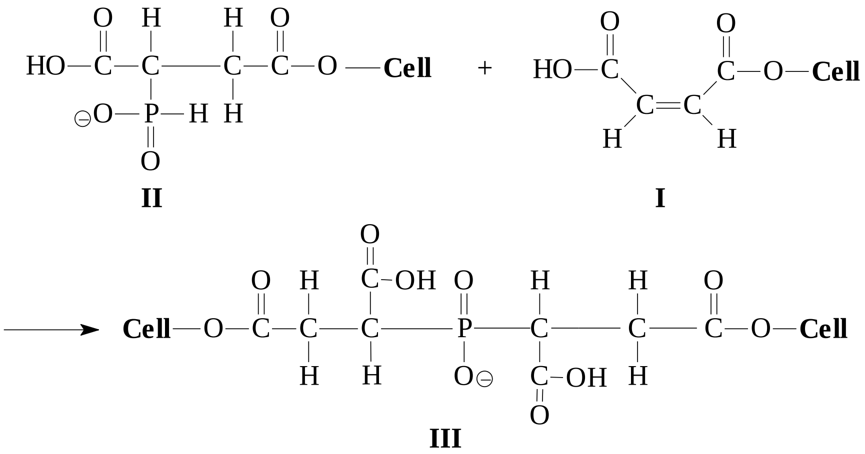


Scheme 6.1 The bonding of hypophosphite to cotton by MA

Table 6.2. The WRA of the cotton woven fabric treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 and that treated with 0.54 mol/l MA, cured at different curing temperatures (after 1 home laundering).

Curing Temperature (℃)	WRA (W+F, °)	
	0.54 mol/l MA	0.54 mol/l MA and 0.27 mol/l NaH_2PO_2
100	181	185
110	181	190
120	183	199
130	184	198
140	191	201
150	191	200
160	195	230
170	199	231
180	200	247
Control	181	

In our previous research, we proved that a polycarboxylic acid esterifies cotton cellulose by first forming a 5-membered cyclic anhydride as a reactive intermediate [18, 19]. Therefore, only one of the two carboxyl groups of MA is able to esterify cotton cellulose. Consequently, MA is not able to crosslink cellulose and imparts wrinkle resistance to cotton fabric by itself as shown in Table 6.2. The probable mechanism for MA to crosslink cotton cellulose in the presence of NaH_2PO_2 on cotton is shown in Scheme 6.2, in which the esterification product of MA with cotton cellulose (**I** in Scheme 6.1) reacts with the addition product of NaH_2PO_2 with the esterification product of MA on cotton (**II** in Scheme 6.1) to form a phosphorus-containing crosslinkage between two cotton cellulose molecules.



Scheme 6.2. The formation of crosslinking on cotton cellulose treated with MA and NaH_2PO_2

The Flammability of Cotton Fleece Treated with MA and NaH_2PO_2

The cotton fleece is treated with 0.54 mol/l MA and NaH_2PO_2 at different concentrations, and cured at 170 ℃ for 4 min. The 45 °flammability of the treated cotton fleece after one home laundering cycle is presented in Table 6.3. The cotton fleece without any treatment has both base burn and surface flash for all 5 specimens; therefore it fails the 45° flammability test with “Class III” flammability ranking. The cotton fleece treated with MA without NaH_2PO_2 also shows both base burn and surface flash and it maintains “Class III” flammability. When 0.067 mol/l NaH_2PO_2 is used together with 0.54 mol/l MA, the treated cotton fleece has 3 specimens with base burn, thus failing the 45 ° flammability test. When the NaH_2PO_2 concentration is increased to 0.14 mol/l and higher, the flammability of the treated cotton fleece is significantly reduced so that it only has surface flash without base burn for all 5 specimens, thus passing the test and achieving “Class I” flammability. The cotton fleece samples treated with the combination of 0.54 mol/l MA and NaH_2PO_2 with concentrations ranging from 0.14 to 0.32 mol/l also pass the 45 ° flammability test after each is subjected to the combination of dry-cleaning and home laundering procedures and so achieves “Class I” flammability (Table 6.4).

Table 6.3. The 45 ° flammability of the cotton fleece treated with 0.54 mol/l MA and NaH_2PO_2 at different concentrations, and cured at 170 ℃ for 4 min (after one home laundering cycle).

MA (mol/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Specimens SF	Ave. Burning Time (s)	No. of Specimens BB	Class
Control		5	1.1	5	III
0.54*	0	5	2.7	5	III
0.54	0.067	5	1.1	3	III
0.54	0.14	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.54	0.32	5	1.1	0	I

* The cotton fleece was treated with 0.54 mol/l MA, but it was not cured and laundered.

Table 6.4. The 45 ° flammability of the cotton fleece treated with 0.54 mol/l MA and NaH_2PO_2 at different concentrations, and cured at 170 ℃ for 4 min (after dry-clean followed by home laundering).

MA (mol/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Specimens SF	Ave. Burning Time (s)	No. of Specimens BB	Class
0.54	0.14	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.54	0.32	5	1.1	0	I

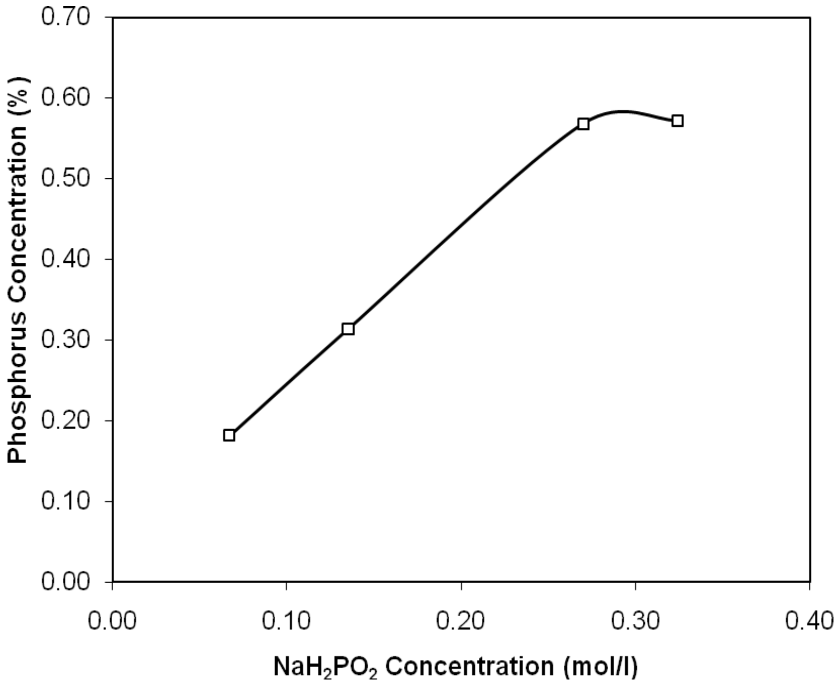


Figure 6.4. The phosphorus concentration of the cotton fleece treated with 0.54 mol/l MA and NaH_2PO_2 at different concentrations and cured at 170 ℃ (after 1 home laundering) versus NaH_2PO_2 concentration.

Table 6.5. The 45 ° flammability of the cotton fleece treated with the combination of MA and NaH_2PO_2 at different concentrations and constant 2:1 mole ratio, cured at 170 ℃ and followed by one home laundering cycle.

MA (mol/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Specimens SF	Ave. Burning Time (s)	No. of Specimens BB	Class
Control		5	1.1	5	III
0.18	0.09	5	1.1	3	III
0.36	0.18	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.1	0	I

The phosphorus concentrations of the fleece samples treated with 0.54 mol/l MA and NaH_2PO_2 at different concentrations and followed by 1 home laundering are shown in Figure 6.4. The phosphorus concentration of the fabric increases as the concentration of NaH_2PO_2 is increased, and it reaches the maximum (P=0.57%) when the NaH_2PO_2 concentration is increased to 0.27 mol/l with MA to NaH_2PO_2 mole ratio of 2:1. Thus, the data supports the crosslinking reaction mechanism of MA and NaH_2PO_2 with cotton cellulose shown in Scheme II, in which two molecules of MA react with one molecule of $H_2PO_2^-$.

Table 6.6. The 45 ° flammability of the cotton fleece treated with the combination of MA and NaH_2PO_2 at different concentrations and constant 2:1 mole ratio, cured at 170 ℃ and subjected to a dry-clean procedure followed by one home laundering cycle.

MA (mol/l)	NaH_2PO_2 (mol/l)	45 ° Flammability			
		No. of Specimens SF	Ave. Burning Time (s)	No. of Specimens BB	Class
Control		5	1.1	5	III
0.36	0.18	5	1.1	0	I
0.54	0.27	5	1.1	0	I
0.72	0.36	5	1.1	0	I

The 45 ° flammability of the cotton fleece treated with MA/NaH_2PO_2 (2:1 mole ratio) at different concentrations, cured at 170 ℃ and subjected to one home laundering cycle is shown in Table 6.5. When the concentration of MA and NaH_2PO_2 is 0.18 and 0.09 mol/l, respectively, the treated cotton fleece fails the 45 ° flammability test. However, it passes the 45 ° flammability test when the MA concentration is increased to 0.36 mol/l and higher.

The cotton fleece treated with MA and NaH_2PO_2 at different concentrations is subjected to a dry-cleaning procedure followed by one home laundering cycle. The 45 ° flammability of the fleece thus treated is shown in Table 6.6. The cotton fleece sample treated with 0.36 mol/l MA and 0.18 mol/l NaH_2PO_2 and those samples treated with higher MA/NaH_2PO_2 concentrations all pass the 45 ° flammability test after a dry-cleaning procedure followed by one home laundering cycle. Therefore, the treated cotton fleece can be classified as “Class I” flammability according to 16 CFR 1610.

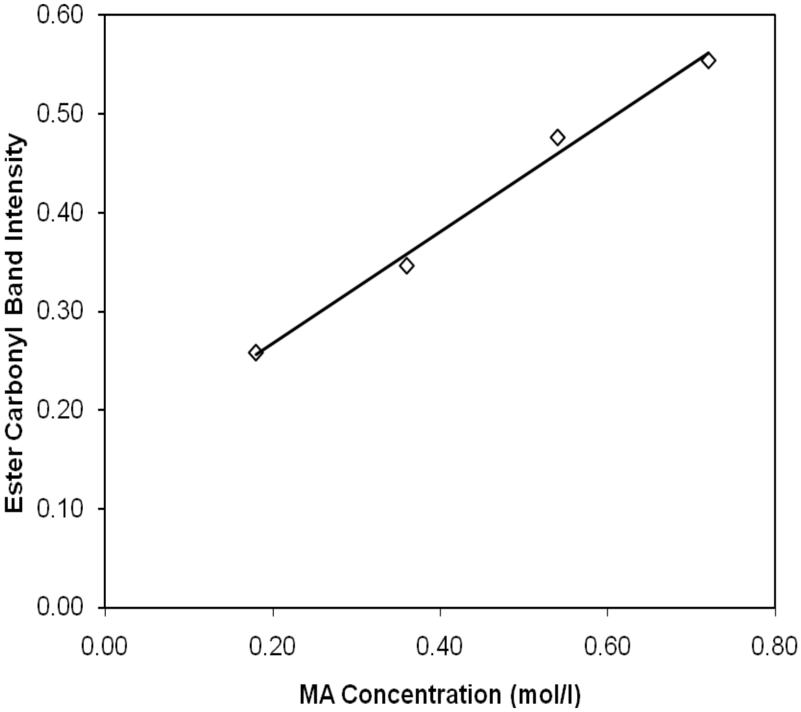


Figure 6.5. The ester carbonyl band intensity of the cotton fleece treated with MA/NaH_2PO_2 (mole ratio 2:1) of different concentrations and cured at 170 ℃ (after 1 home laundering) versus MA concentration.

The ester carbonyl band intensities of cotton fleeces treated with MA and NaH_2PO_2 (2:1 mole ratio) at different concentrations, cured at 170 ℃ and subjected to 1 home laundering cycle are shown in Figure 6.5. It is seen that the ester carbonyl band intensity increases linearly with the MA concentration and that this trend is parallel to the rise in phosphorus concentration on cotton as a consequence of the increasing NaH_2PO_2 concentration (see Figure 6.6). Thus, the data presented here again confirm that $H_2PO_2^-$ is bound to the cotton fabric by its reaction with the MA esterified to cotton, as demonstrated in Scheme 6.2.

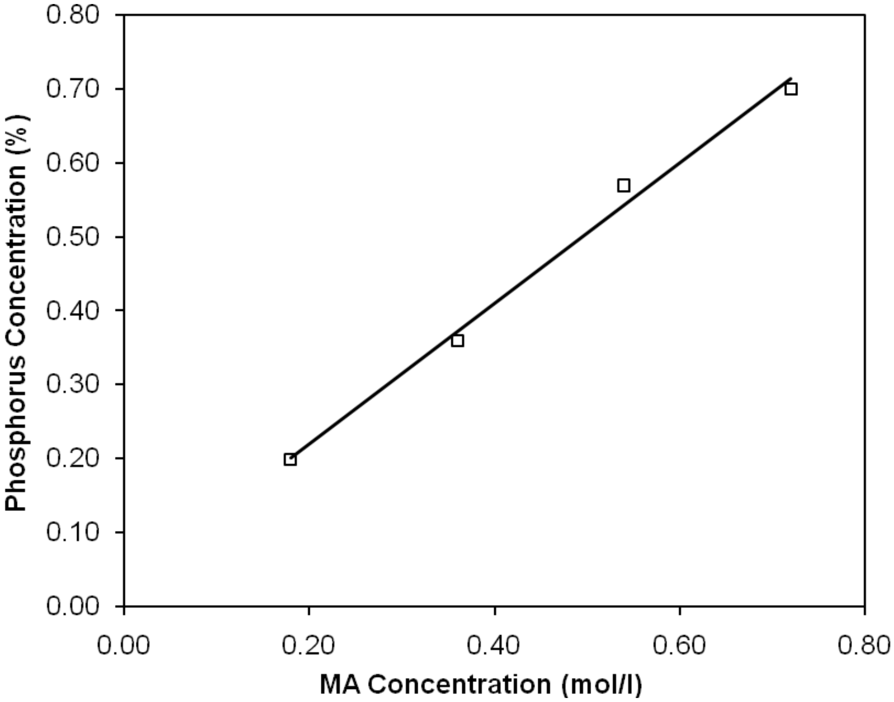


Figure 6.6. The phosphorus concentration of the cotton fleece fabrics with MA/NaH_2PO_2 (mole ratio 2:1) of different concentrations and cured at 170 ℃ (after 1 home laundering) versus MA concentration.

Table 6.7. The 45 ° flammability of the cotton fleece treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2, cured at 170 ℃ and subjected to different numbers of home launderings cycles.

Sample Treatment	No. of Home Laundering Cycle	45 ° Flammability			
		No. of Specimens SF	Ave. Burning Time (s)	No. of Specimens BB	Class
Control	5	5	1.3	5	III
	10	5	1.7	5	III
	15	5	2.0	5	III
	20	5	1.1	5	III
0.54 mol/l MA 0.27 mol/l NaH_2PO_2	5	5	1.1	0	I
	10	5	1.1	0	I
	15	5	1.1	0	I
	20	5	1.1	0	I

The durability of the cotton fleece treated with MA/NaH_2PO_2 to multiple home launderings was also studied. The 45 ° flammability of the cotton fleece treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2, cured at 170 ℃ for 4 min and subjected to different numbers of home laundering cycles is presented in Table 6.7. As expected, the untreated cotton fleece (control) fails the 45 ° flammability test after all home laundering cycles. In contrast, the cotton fleece treated with 0.54 mol/l MA and 0.27 mol/l NaH_2PO_2 passes the 45 ° flammability test after 20 home laundering cycles. Some of the surface fibers are likely broken and removed from the fleece due to friction during the multiple home launderings process, which may reduce the flammability of the cotton fleece. But the data presented in Table 6.7 show that the control cotton fleece maintains Class III flammability during the entire 20 home launderings. Therefore, we can conclude that the flammability of the cotton fleece treated with MA/NaH_2PO_2 is not reduced significantly after multiple home launderings.

The water used for the home laundering procedure has low hardness. It should be pointed out that calcium and magnesium cations in hard water form insoluble salts with the free carboxylic anions on the fleece during the home laundering process, thus diminishing the flame retardancy of any cotton fabric treated with organophosphorus flame retardants. Since the flame retardancy of the treated cotton fleece is contributed by both the hypophosphite bound to cotton and the esterification of cotton by MA, the formation of calcium salts on the fleece may increase the fleece's flammability if water with high hardness is being used. The topic will be reported in a future paper.

CONCLUSIONS

(1) When the combination of MA and NaH_2PO_2 is applied to the cotton fleece, NaH_2PO_2 functions as a catalyst for the esterification of MA on cotton. The esterification of MA with cotton cellulose takes place in the presence of NaH_2PO_2 at relatively low temperatures (≤130 °C). NaH_2PO_2 is also able to react with MA on cotton by adding to the C=C bond of MA, which takes place at relatively high temperatures (≥150ºC). Thus, the application of the combination of MA and NaH_2PO_2 to cotton is able to bond phosphorus to the cotton fiber and consequently to reduce the flammability of cotton fleece.

(2) The treatment of the cotton fleece using the combination of MA and NaH_2PO_2 is effective in reducing the 45º flammability from "Class III" (high flammability) to "Class I" (normal flammability), thus making it possible to produce 100% cotton fleece legally salable in the U.S. The MA/NaH_2PO_2 system bound to cotton fleece using pad-dry-cure process is durable to multiple home launderings. The combination of MA and NaH_2PO_2 is a non-formaldehyde and cost-effective flame retardant system for cotton fleece.

ACKNOWLEDGEMENTS

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CHAPTER 7

FLAME RETARDANT FINISHING OF COTTON FLEECE WITH POLYCARBOXYLIC ACIDS: V. MECHANISM STUDY *

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ABSTRACT

Cotton fleece was treated with 1,2,3,4 butanetetracarboxlic acid, and succinic acid (SUA), with NaH_2PO_2 as catalyst and cured at different temperatures. Polycarboxylic acids themselves are not effective in reducing the flammability of cotton fabric. The cotton fleece treated with polycarboxylic acids with NaH_2PO_2 as catalyst followed by 1 home laundering achieves Class I flammability at elevated curing temperature due to the increasing amount of ester formed on cellulose. The LOI of the treated cotton fleece also increases. Thermal analysis shows that cotton fleece esterified with polycarboxylic acids has increased thermal stability, lower initial decomposition temperature, maximum decomposition rate temperature, and higher char ratio. The depolymerization of the esterified cotton cellulose to produce small highly flammable molecules decreases while the dehydration of cellulose to produce char increases. The possible mechanism of the flame retardancy of cotton fleece esterified with polycarboxylic acids is that the esterification of C-6 hydroxyl on cellulose retards the depolymerization to produce highly flammable levoglucosan and facilitates the dehydration.

INDEX WORDS**:** Polycarboxylic acids; 1,2,3,4 butanetetracarboxlic acid; Succinic acid; Esterification; Flammability; Thermal analysis; TG; DSC

INTRODUCTION

Cotton is highly combustible fiber compared to wool and synthetic fibers. When cotton is subjected to heat or fire until it reaches the pyrolysis temperature, initially it will pyrolyze to produce char, volatiles and gases. The pyrolysis of cellulose occurs through two competing reactions, i.e., dehydration, which takes place below 300 ℃ and results in a decomposition of the glycosyl units of cellulose to produce water, carbon monoxide, carbon dioxide and char, and depolymerization, which occurs between 300 and 600 ℃ and produces high flammable levoglucosan by cleavage of glycosyl units [1].

Polycarboxylic acids containing three or more than three carboxyl groups esterify cellulose at elevated temperature and produce durable press cotton fabrics [2-4]. Other than imparting durable press properties to cotton fabrics, esterification of cellulose with polycarboxylic acids is effective in reducing the flammability of cotton fabrics. Previous studies showed that the cotton/polyester carpet and fleece treated with polycarboxylic acids had reduced flammability [5-6]. However, it is not clear how the esterification of cellulose reduces the flammability. Many studies have been done on the thermal degradation of cotton cellulose, flame retardant finished cotton cellulose and fully esterified cellulose ester [7-11]. It was found that the thermal stability of the esters of the cellulose acetates prepared in homogeneous esterification reaction is proportional to their molecular weights and increases with the degree of substitution [7]. The thermal degradation behavior of cellulose partially esterified with some long chain organic acids was also investigated and the results showed that the thermal stability of the modified cellulose is inferior to that of unmodified cellulose [12].

In this paper, cotton fleeces were treated with 1,2,3,4 butanetetracarboxlic acid (BTCA), and succinic acid and cured at different temperatures. The effect of different amount of ester formed on cotton cellulose in the flammability of cotton fleece was studied. The 45° flammability and the LOI of the treated cotton fleece and cotton woven fabric were also tested. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the thermal degradation behavior of the treated cotton fleece in nitrogen from ambient temperature to 500 ℃. Kinetic and thermodynamic parameters such as enthalpy and free energy of activation have been determined. A possible mechanism of the flame retardancy of cotton fleece treated with polycarboxylic acids was speculated.

EXPERIMENTAL

Materials

Two cotton fleeces were used in this research: white cotton fleece with a density of 370 g/m^2 and black cotton fleece of higher flammability, with a density of 379 g/m^2. Both the white fleece and the black fleece were supplied by Esquel Group, Gaomin, Guandong Province, China. The cotton woven fabric used in this research was a desized, scoured, and bleached plain weave fabric with density of 109 g/m^2 (Testfabrics style 400); BTCA, succinic acid, sodium hypophosphite (NaH_2PO_2), and sodium hydroxide (NaOH) were reagent grade chemicals supplied by Sigma-Aldrich, Milwaukee, WI.

Fabric Treatment and Home Laundering Procedures

The cotton woven fabric and cotton fleeces were first immersed in a solution containing polycarboxylic acid and 3.0% NaH_2PO_2, and 0.02% nonionic wetting agent Tergitol (a non-ionic wetting agent, were supplied by Sigma-Aldrich, Milwaukee, WI), then passed through a laboratory padder with two dips and two nips. The polycarboxylic acids concentrations used in this paper were BTCA 6.0%, and succinic acid (SUA) 6.05%. If it was not specified, NaH_2PO_2 was used as catalyst and the concentration was 3.0%. The cotton woven fabric was dried at 80 ℃ for 2 min and cured in a Mathis oven at different temperatures for 2 min. The cotton fleece were dried at 90 ℃ for 4 min, then cured at different temperatures for 4 min. The wet pick-up of the cotton woven fabric and cotton fleece fabrics were approximately 98±2% and 109±2%, respectively. The treated fabrics were also subjected to one home laundering cycle with the use of a standard detergent ("AATCC Detergent 1993"). The home laundering procedure was done according to AATCC Method 124. The water temperature for laundering was approximately 46-47 ℃.

Fabric 45˚ Flammability Measurement

The 45˚ flammability of the cotton fleece fabric was measured according to ASTM Method D1230-94 ("Standard Test Method for Flammability of Apparel Textiles", reapproved in 2001). A fabric specimen mounted in a specimen holder was brushed. Then the specimen was dried at 105 ℃ in an oven for 30 min. After that, it was moved to a desiccator to cool down for 90 min before it was tested in the 45˚ flammability tester (Model TC-45, manufactured by Govmark, Bellmore, NY). The specimen was ignited with a standard butane flame for 1 sec. The burning time and burning characteristics were recorded. The average burning time of 5 specimens, the number of specimens with surface flash (SF) and the number of specimens with base burn (BB) were used to determine the flammability classifications. The 45˚ flammability test method and classifications were described in our previous paper [13].

FT-IR Spectroscopy Measurement

The ester and carboxylate carbonyl bands intensity was measured by a Nicolet Magna 760 spectrometer with a Specac diffuse reflectance accessory. The cured cotton fleece was laundered once to remove the unreacted polycarboxylic acid and NaH_2PO_2. To eliminate the overlap of ester carbonyl and carboxyl carbonyl band, the home laundered cotton fleece sample was treated with a 0.1 M NaOH solution at room temperature for 3 minutes to convert the free carboxyl groups to carboxylate anions. The fabric sample thus treated was extracted in a washer to remove excessive solution, then dried at 90 ℃ for 10 minutes, and ground in a Wiley mill before it was analyzed by the FT-IR spectrometer. The diffuse reflectance infrared spectra were collected and presented in absorbance mode (-log R/R0). There were 120 scans for each spectrum and resolution for all the infrared spectra was 4 cm^{-1}. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. The carbonyl band reflectance in the infrared spectra was normalized against the 1318 cm^{-1} band, which was associated with the C-H bending mode of cellulose. This analytical method was previously discussed in detail [13-14].

Limiting Oxygen Index (LOI)

The LOI of the cotton woven fabric and cotton fleece was measured according to ASTM Standard Method D2863-97.

Thermal Analysis

The untreated and treated white fleece cured at 170 ℃ for 4 min after 1 home laundering were ground to powder in a Wiley mill. Differential scanning calorimetry (DSC) analysis was performed in a Mettler Toledo DSC 821 calorimeter at the heating rate of 10°C/min in nitrogen atmosphere. The sample size was 4-6 mg.

Thermogravimetric (TG) analysis was conducted in a Mettler Toledo TGA 851. Four heating rates (β) were used, 5, 10, 20, and 40°C/min in nitrogen atmosphere. The sample size was 10 ±1 mg. The Kissinger method was used to determine the activation energy (E). In order to determine the activation energy, the maximum decomposition rate temperatures (T_{max}) at different heating rate need to be estimated from the first derivative of the TG curves. The following equation will be used:

$$\ln\left(\frac{\beta}{T^2 max}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}}$$

Where α_{max} is conversion rate at T_{max}, and n is the reaction order. Kissinger’s approximation states that $f'(\alpha_{max}) = n(1-\alpha_{max}) \approx$ const. Therefore, the activation energy E can be determined from a plot of $\ln(\beta/T^2_{max})$ against $1/T_{max}$. The activation energy E=S*R (S is the slope of the line and R is the gas constant) [15-16].

RESULTS AND DISCUSSION

The Flammability of Treated Cotton Fleece with Different Amount of Ester

Figure 7.1 shows the ester carbonyl band intensity of the white fleece treated with 6.0% BTCA and 6.05% SUA cured at different temperatures. The ester carbonyl band intensity on the treated cotton fleece increases with the curing temperature for both polycarboxylic acids. The ester carbonyl band intensity on cotton fleece treated with BTCA is higher than that treated with SUA. Therefore, BTCA has higher reactivity with cotton cellulose than SUA. When the curing temperature is 100 ℃, the ester carbonyl band intensity is almost zero on the cotton fleece treated with BTCA, indicating that no BTCA is bound on cotton cellulose at 100 ℃. When the curing temperature is 100 and 120 ℃, the ester carbonyl band intensity on the cotton fleece treated with SUA is almost zero. No SUA is bound on the cotton fleece at temperature lower than 120 ℃. Presented in Figure 7.2 is the carboxylate carbonyl band intensity of the white fleece treated with 6.0% BTCA and 6.05% SUA cured at different temperatures. Similar to the ester carbonyl band intensity, the amount of free carboxyl group bound on cotton fleece increases with the curing temperature for both polycarboxylic acids.

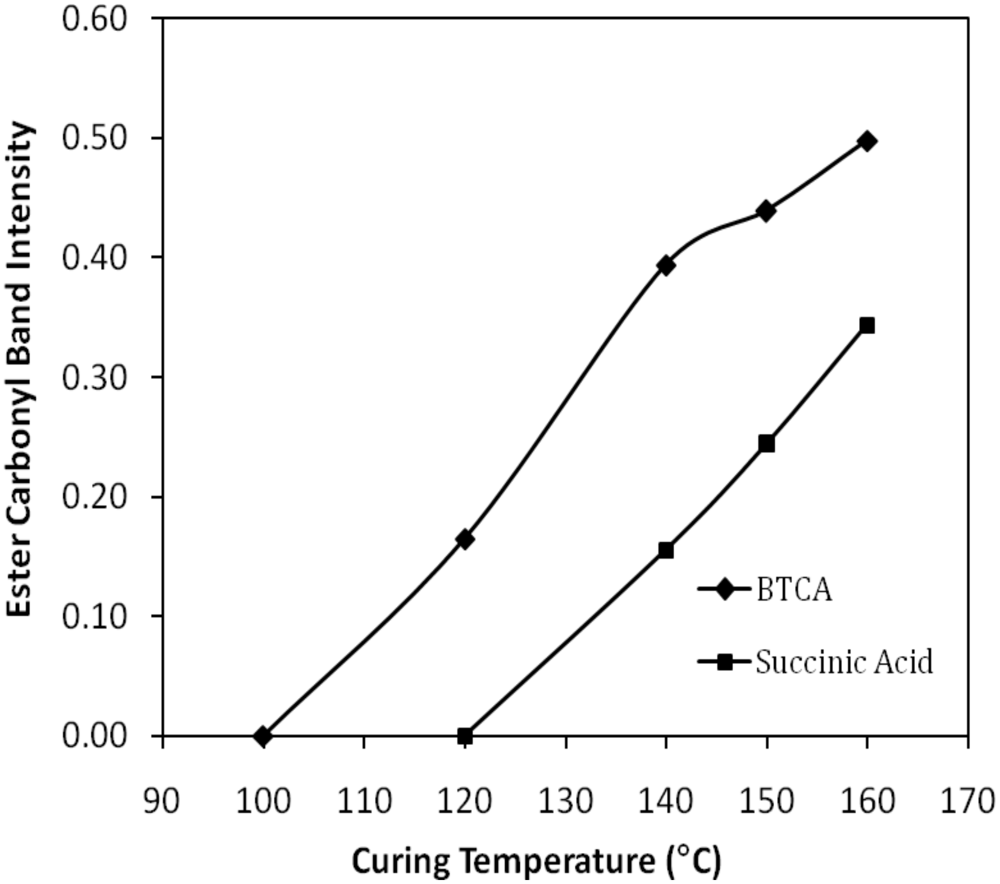


Figure 7.1. The ester carbonyl band intensity of the white fleece treated with 6.0% BTCA and 6.05% SUA cured at different temperatures (catalyst NaH_2PO_2 is 3.0%).

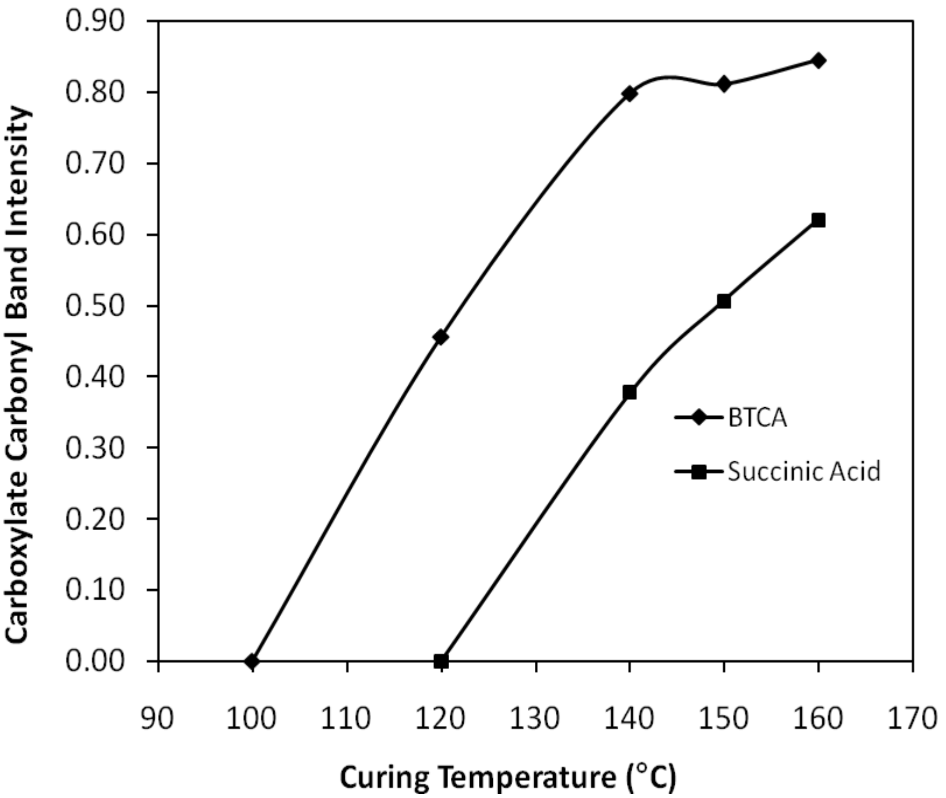


Figure 7.2. The carboxylate carbonyl band intensity of the white cotton fleece treated with 6.0% BTCA and 6.05% SUA cured at different temperatures (catalyst NaH_2PO_2 is 3.0%)

Table 7.1. The 45 °flammability of white cotton fleece treated with polycarboxylic acid solution, dried at 90°C with and without pH adjustment.

Acid	Concentration (g/l)	45 °flammability			
		No. of Spec. SF*	Ave. Burning Time (s)	No. of Spec. BB*	Class
Control	-	5	1.1	5	III
BTCA	63.18	5	1.1	5	III
SUA	63.72	5	1.1	5	III

Note: * The pH of the polycarboxylic acid solution was adjusted to 2.5.
SF*: Surface flash.
BB*: Base burn.

Presented in Table 7.1 is the 45 ° flammability of the white fleece treated with polycarboxylic acid solution only, dried at 90°C without pH adjustment. The untreated cotton fleece shows both surface flash and base burn; thus, fails in the 45 °flammability test. The cotton fleece treated with BTCA and SUA also shows both surface flash and base burn, and thus fails in the 45° flammability test. Therefore, polycarboxylic acids themselves are not effective in reducing the flammability of cotton fleece.

Table 7.2. The 45° flammability classification of the white cotton fleece treated with 6.0% BTCA, 6.05% SUA, with 3.0% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering.

Curing Temperature (℃)	45° Flammability Classification	
	BTCA	SUA
100	III	III
120	I	III
140	I	I
150	I	I
160	I	I
170	I	I
180	I	I

Note: The pH of the treatment solution was adjusted to 2.5.

Presented in Table 7.2 is the 45° flammability of the white cotton fleece treated with polycarboxylic acids with 3.0% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering. The cotton fleece shows Class III flammability at lower curing temperature and Class I flammability at higher curing temperature. The cotton fleece has Class III flammability at 100 ℃ when it is treated with BTCA and it shows Class I flammability at curing temperature of 120 ℃ and above. The cotton fleece has Class III flammability at curing temperature lower than 140 ℃ when it is treated with SUA. It has Class I flammability when the curing temperature is 140 ℃ and above. When cotton fleece is treated with BTCA, the ester carbonyl band intensity is almost zero at curing temperature of 100 ℃, indicating no BTCA is bound on cotton fleece, which explains the Class III flammability at curing temperature of 100 ℃ (Table 7.2). When the curing temperature is higher than 100 ℃, the ester carbonyl band intensity on the cotton fleece treated with BTCA increases drastically, indicating that the amount of ester formed on cotton cellulose increases with the curing temperature. Therefore, the flammability of cotton fleece is reduced by the increasing amount of ester formed on cotton cellulose. When cotton fleece is treated with SUA, the ester carbonyl band intensity is almost zero at curing temperature of 120 ℃, indicating that almost no SUA is bound to cotton fleece, which also justifies the Class III flammability at curing temperature of 120 ℃. The cotton fleece treated with SUA has Class I flammability at curing temperature 140 ℃ and above. From the above discussion, we can conclude that the esterification of cotton fleece with polycarboxylic acids reduces flammability of cotton fleece.

Table 7.3. The LOI of cotton woven fabric (Test Fabric 400) treated with 6.0% BTCA and 3.0% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering.

Curing Temperature (℃)	Untreated	6.0% BTCA, Dry only*	100	120	140	150
LOI	17.3	17.3	17.7	19.5	19.9	20.3

Note: * Cotton woven fabric treated with 6.0% BTCA was not home laundered.

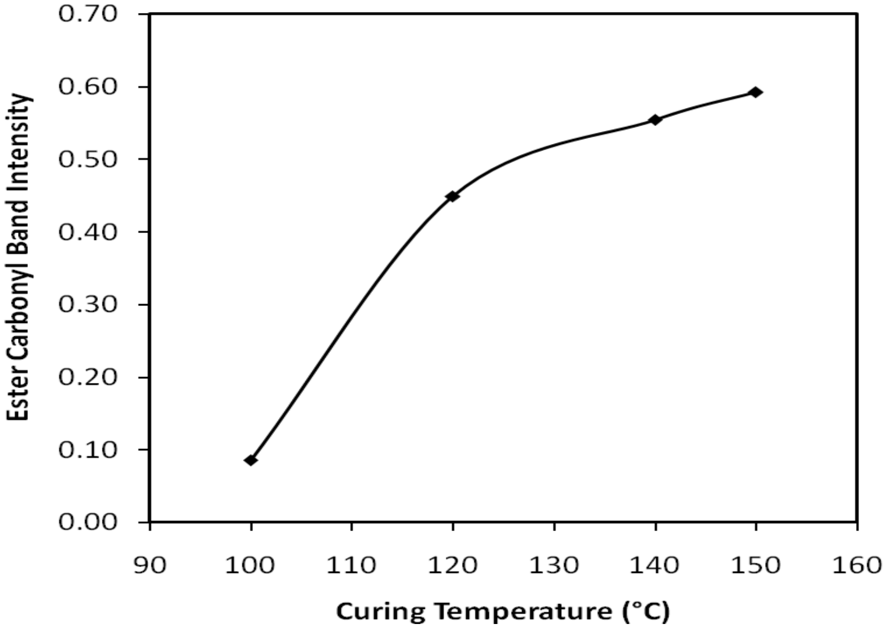
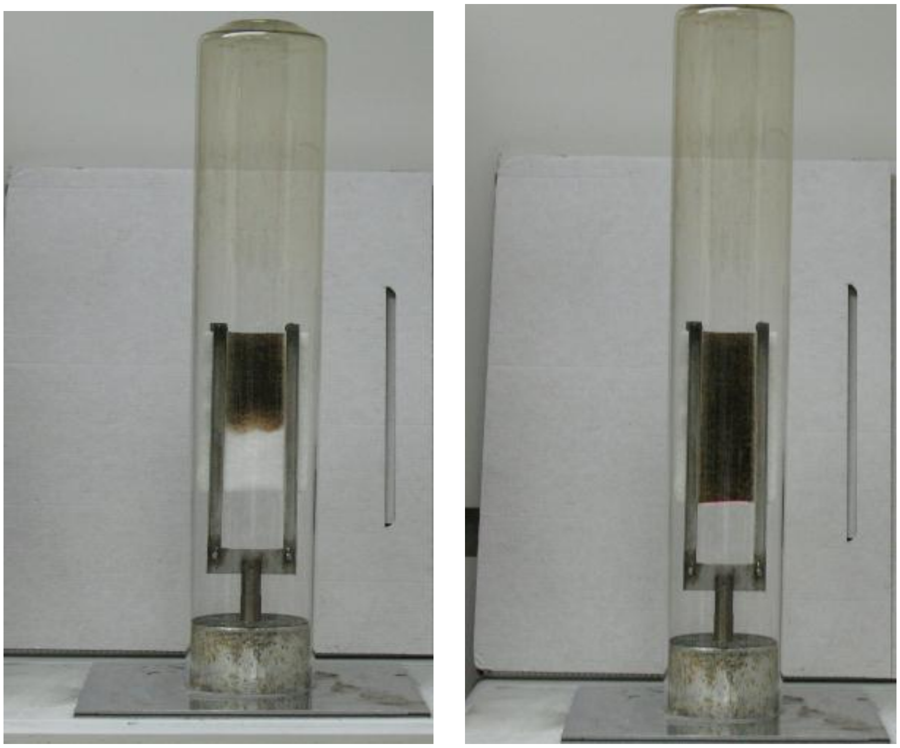


Figure 7.3. The ester carbonyl band intensity of cotton woven fabric treated with 6.0% BTCA and 3.0% NaH_2PO_2 cured at different temperatures (The treated fabric was home laundered).

The LOI of cotton woven fabric treated with 6.0% BTCA and 3.0% NaH_2PO_2 cured at different temperatures is studied and presented in Table 7.3. The LOI of untreated cotton woven fabric is 17.3. The LOI of that treated with 6.0% BTCA only without pH adjustment is 17.3, which further indicates that BTCA itself is not effective in reducing the flammability of cotton fabric. When the cotton woven fabric is treated with 6.0% BTCA with 3.0% NaH_2PO_2 as catalyst, the LOI of the treated fabric after 1 home laundering increases from 17.7 at 100 ℃ to 20.3 at 150 ℃. From Figure 7.3, we can see that the ester carbonyl band intensity increases with the curing temperature. Therefore, the LOI of the cotton woven fabric treated with BTCA increases with the amount of ester formed on the fabric.



(a) Surface flash (b) Base burn

Figure 7.4. The LOI test of cotton fleece.

Table 7.4. LOI of cotton fleece treated with 6.0% BTCA and 3.0% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering.

Curing Temperature (℃)	Untreated	100	120	140	150
LOI	18.5	18.9	19.8	21.5	21.5

Table 7.5. The LOI of cotton fleece treated with 6.05% SUA and 3% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering.

Curing Temperature (℃)	Trial 1	Trial 2	Trial 3	Average	STDEV
100	19.6	19.4	19.4	19.5	0.12
120	19.6	19.6	19.4	19.5	0.12
140	20.4	20.6	20.6	20.5	0.12
150	22.5	22.7	22.3	22.5	0.20

Figure 7.4 shows the LOI test of cotton fleece. As opponent to the behavior of cotton woven fabric, the burning of cotton fleece includes surface flash (Figure 7.4 (a)) and base burn (Figure 7.4 (b)). Since the surface of cotton fleece is very fluffy and contains a lot of air, it always burns before the base does. During the LOI measurement, the surface of cotton fleece is ignited first. The surface flash spreads from the top to the bottom. If the oxygen content is not high enough, the surface flash will extinguish and won't cause base burn. The oxygen content will be further increased until the surface flash spreads to the bottom and finally causes base burn. The oxygen content at which the surface flash causes the base burn will be the LOI value of the cotton fleece.

The LOI of the white fleece treated with BTCA is presented in Table 7.4. The LOI of the untreated cotton fleece is 18.5. When it is treated with BTCA, the LOI of the treated cotton fleece increases from 18.9 at curing temperature of 100 ℃ to 21.5 at curing temperature of 150 ℃. The LOI of the white fleece treated with SUA is shown in Table 7.5. Each specimen is measured 3 times and the standard deviation is calculated. When it is treated with SUA, the LOI of the treated cotton fleece increases from 19.5 at curing temperature of 100 ℃ to 22.5 at curing temperature of 150 ℃. The standard deviation is around 0.1 to 0.2. From the LOI data of cotton fleece treated with BTCA and SUA cured at different temperatures, we can see the esterification of cotton cellulose increases the LOI of treated cotton fleece. The LOI measurement of cotton fleece is reproducible as well.

Table 7.6. The 45 ° flammability classification of the black cotton fleece treated with 6.0% BTCA, 6.05% SUA with 3.0% NaH_2PO_2 as catalyst cured at different temperatures followed by 1 home laundering.

Curing Temperature (℃)	45 °Flammability Classification	
	BTCA	SUA
Control	III	-
100	III	III
120	III	III
140	I	III
150	I	I
160	I	I
170	I	I
180	I	I

One higher flammable black cotton fleece was also treated with BTCA and SUA. The 45 °flammability classification of the treated fleece is presented in Table 7.6. The untreated black cotton fleece has Class III flammability. In order to achieve Class I flammability, the black cotton fleece needs to be cured at higher temperature than the white cotton fleece. Still, the esterification of cotton fleece with polycarboxylic acids is effective in reducing the flammability of the black cotton fleece.

Thermal Analysis

DSC Analysis

Figure 7.5 shows the DSC curves of the untreated white cotton fleece, and white fleece treated with BTCA and SUA, and cured at 170 ℃ for 4 min in a nitrogen atmosphere. The treated cotton fleece was home laundered once before the thermal analysis. The peak temperature, enthalpy, and nature of peak are shown in Table 7.7. As we can see, all the curves show an endothermic peak below 100 ℃ due to the evaporation of the extra-cellulosic water. Dehydration and depolymerization are the two competing reactions involved in the thermal degradation process of cotton cellulose. In the dehydration reaction, cellulose loses water to produce "dehydrocellulose". In the depolymerization reaction, the previously unreacted cellulose decomposes to produce tar via an endothermic process. The untreated cotton fleece shows a sharp endothermic peak at around 355 ℃ due to the depolymerization of the cellulose molecule to form tar (the major component is levoglucosan) [18]. The enthalpy of the endothermic reaction is 246.2 J/g (Table 7.7). Afterwards, the exotherm corresponds to a char-forming reaction with the evolution of water and small carbon containing compounds [18]. Evidently, the depolymerization is the dominating reaction for the control cotton fleece during the thermal degradation process. As for the cotton fleece treated with BTCA, the endothermic peak totally disappears. It indicates that the depolymerization of the cellulose molecule to form levoglucosan is greatly reduced and the dehydration is the dominating reaction. An exothermic peak appears around 370 ℃ with an enthalpy of 8.4 J/g, which is associated with the decomposition of the dehydrocellulose into various gaseous products and residual char. The cotton fleece treated with SUA shows a much smaller endothermic peak at 355 ℃ with an enthalpy of 45.9 J/g than the control cotton fleece. It indicates that only a very small portion of the cellulose depolymerizes to produce levoglucosan. From the above discussion, we know that the depolymerization reaction of the cotton fleece treated with polycarboxylic acids to produce levoglucucosan is greatly reduced and the dehydration reaction increases. Therefore, the esterified cotton fleece shows reduced flammability.

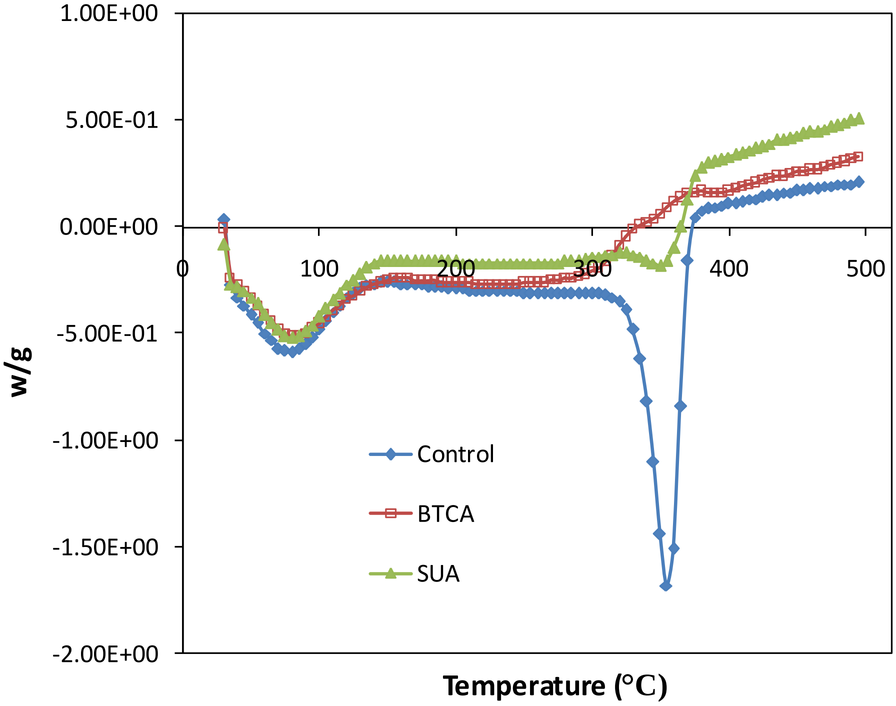


Figure 7.5. DSC curves of untreated white cotton fleece, cotton fleece treated with 6% BTCA, and 6.05% SUA cured at 170 ℃ for 4 min after 1 home laundering in a nitrogen atmosphere (3% NaH_2PO_2 was used as catalyst).

Table 7.7. Peak temperature, enthalpy, and nature of peak of the DSC curves of cotton fleece treated with BTCA, SUA, in a nitrogen atmosphere.

Treatment	Peak Temperature (℃)	Enthalpy (J/g)	Nature of Peak
Control	355	246.2	Endo
BTCA	370	8.4	Exo
SUA	355	45.9	Endo

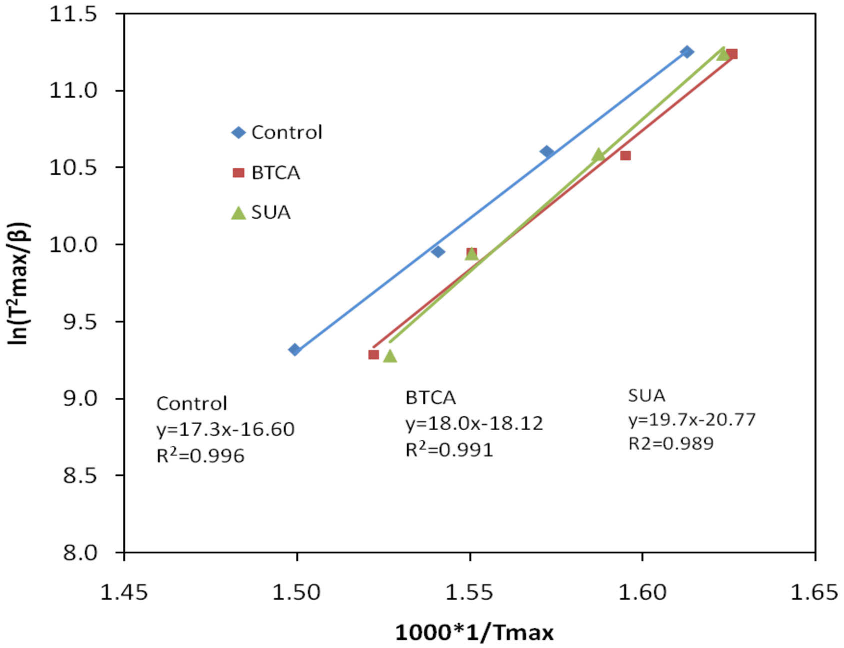


Figure 7.6. Kissinger's plot of the thermal degradation of cotton fleece treated with 6% BTCA, 6.05% SUA, with 3% NaH_2PO_2 as catalyst, cured at 170 ℃ for 4 min, and followed by 1 home laundering.

TG Analysis

TG analysis of cotton fleece treated with BTCA and SUA was conducted in a nitrogen atmosphere. The maximum decomposition rate temperatures at different heating rates are shown in Table 7.8. The cotton fleece treated with BTCA and SUA both shows lower maximum decomposition rate temperature than the control cotton fleece. The Kissinger's plot of the thermal degradation of cotton fleece treated with BTCA and SUA is shown in Figure 7.6. The activation energy of the treated cotton fleece is presented in Table 7.9. The untreated cotton fleece has an activation energy of 140.8 kJ/mol. The activation energies of the cotton fleece treated with BTCA and SUA are 146.8 and 160.7 kJ/mol, respectively, and are higher than that of the control cotton fleece. Higher values of activation energy are associated with more thermally stable polymers [11]. Therefore, cotton fleece treated with polycarboxylic acids is thermally more stable than untreated cotton fleece. This is another eveidence that cotton fleece treated with polycarboxylic acids has lower flammability.

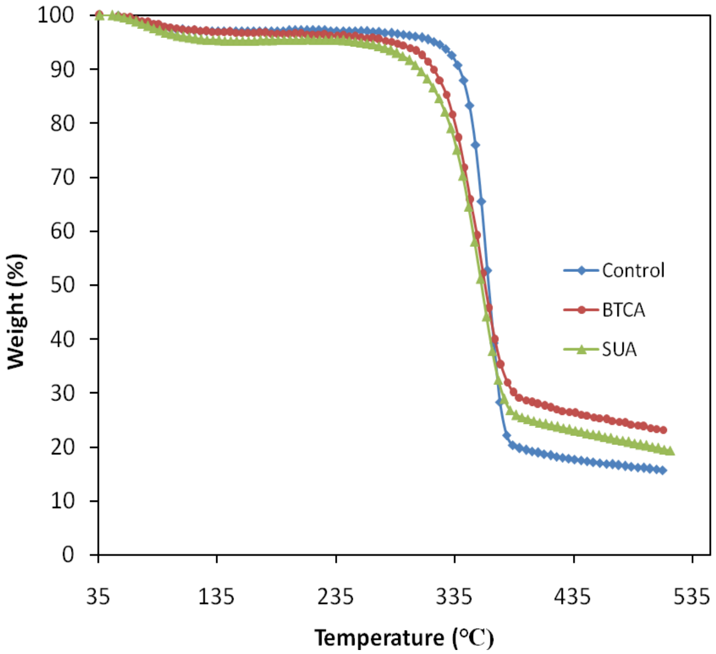


Figure 7.7. TG curves of control white cotton fleece, cotton fleece treated with 6% BTCA, 6.05% SUA, cured at 170 ℃ for 4 min, and followed by 1 home laundering.

Table 7.8. The maximum decomposition rate temperature of the TG curves of white cotton fleece treated with 6.0% BTCA and 6.05% SUA cured at 170 ℃ for 4 min at different heating rates in a nitrogen atmosphere (the treated cotton fleece was home laundered once before TG analysis).

Heating Rate (β) (℃/min)	Control	BTCA	SUA
5	347	342	343
10	363	354	357
20	376	372	372
40	394	384	382

The TG curves of control cotton fleece, cotton fleece treated with BTCA and SUA are shown in Figure 7.7. Clearly, the control cotton fleece has a higher maximum decomposition rate and initial decomposition temperature than the cotton fleece treated with polycarboxylic acids.

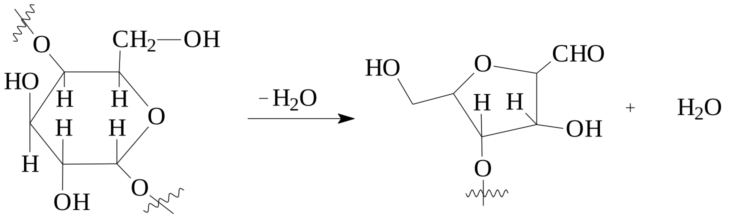
The treated cotton fleece has higher residue than the control cotton fleece. The maximum decomposition rate temperature, initial decomposition temperature, and residue at a heating rate of 10 °C/min are presented in Table 7.9. The initial decomposition temperature of control cotton fleece is 317 °C and that of cotton fleece treated with BTCA and SUA is 282, 252 °C, respectively. The major reaction at the initial decomposition temperature is the dehydration of cotton cellulose. Clearly, the dehydration of cotton fleece treated with polycarboxylic acid takes place at lower temperature due to the acids catalysis.

Table 7.9. The activation energy, T_{di}, T_{max}, and residue of cotton fleece control, cotton fleece treated with BTCA and SUA at a heating rate of 10 °C/min.

Treatment	Activation Energy (kJ/mol)	T_{di} (°C)	T_{max} (°C)	Residue (%)
Control	140.8	317	363	16.0
BTCA	146.8	282	354	23.5
SUA	160.7	252	357	20.0

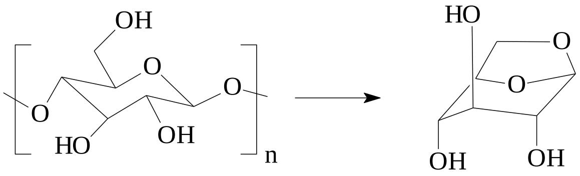
Note: T_{di}: Initial decomposition temperature at 5% weight loss.
T_{max}: Maximum decomposition rate temperature.

3.3. Speculated Mechanism of Thermal Degradation



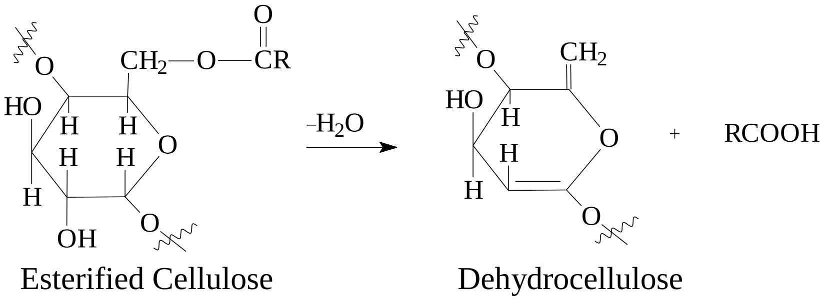
Cellulose Dehydrocellulose

Scheme 7.1. The dehydration of unmodified cellulose [18]

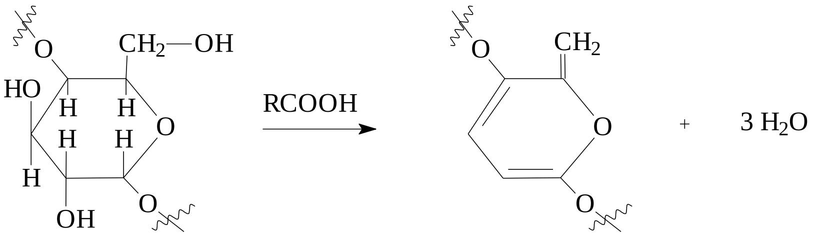


Cellulose 1.6-Anhydro-β-D-Glucopyranose (Levoglucosan)

Scheme 7.2. The depolymerization of unmodified cellulose [18]



Scheme 7.3. The dehydration of esterified cellulose



Scheme 7.4. Acid catalyzed dehydration of cellulose [19]

Dehydration and depolymerization are two competing reactions during cellulose thermal pyrolysis. Unmodified cellulose dehydrates at temperature below 300 ℃ (Scheme 7.1) to produce dehydrocellulose and depolymerizes at above 300 ℃ (Scheme 7.2) to produce levoglucosan, the precursor of flammable volatiles. The major mechanism of the esterified cellulose is to reduce the production of levoglucosan. As shown in Scheme 7.3, the dehydration of the esterified cellulose is the major reaction and the depolymerization of cellulose to produce levoglucosan is prevented after the C-6 hydroxyl on cellulose is esterified. The acid released during the dehydration of the esterified cellulose further catalyses the dehydration of cellulose as shown in Scheme 7.4.

CONCLUSIONS

The cotton fleece was treated with BTCA, SUA with NaH_2PO_2 as catalyst. The results show that the treated cotton fleece has reduced flammability at elevated curing temperature due to the increasing amount of ester formed on cotton fleece. Both the cotton woven fabric and cotton fleece treated with BTCA shows increased LOI. The cotton fleece treated with SUA shows increased LOI value as well. DSC analysis indicates that the depolymerization of the cotton fleece esterified with polycarboxylic acids reduces and the dehydration increases. TG analysis shows that the cotton fleece treated with polycarboxylic acids has increased activation energy, i.e., higher thermal stability, lower maximum decomposition rate and initial decomposition temperature, and higher char content. The mechanism of the flame retardancy is probably due to that the esterification of the cotton fleece reduces the depolymerization of cellulose, thus, the production of levoglucosan, and increases the dehydration of cellulose.

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CHAPTER 8

CONCLUSIONS

New feasible non-formaldehyde flame retardant systems have been developed for cotton fleece, i.e., inorganic phosphorus-containing, non-phosphorus containing polycarboxylic acid, and phosphorus-containing polycarboxylic acid system. These treatments can be successfully applied on cotton fleece to reduce the flammability from Class III to Class I with a low add-on.

In the inorganic phosphorus-containing flame retardant system, the cotton fleece was treated by $Al_2(SO_4)_3$ and sodium phosphates in a two-step procedure. The aluminum hydroxyphosphate (AHP) formed *in situ* on the cotton fleece is effective in reducing the flammability of cotton fleece. AHP on cotton fleece retards the cellulose depolymerization process at elevated temperatures. The composition of the AHP formed by the reaction of Al^{3+} and the phosphate anions in an aqueous solution is pH-dependent and the AHP formed at pH 8.5 has the lowest P/Al mole ratio. The quantity of AHP formed on the cotton fleece treated with $Al_2(SO_4)_3$ and NaH_2PO_4 is also pH-dependent. The AHP formed *in situ* on the cotton fleece is a semi-durable flame retardant. The lumen of a cotton fiber is filled with AHP solid upon the 2nd step treatment of the cotton fleece. A significant portion of AHP remains on the fleece after the treated fleece is subjected to one HL procedure or the combination of DC and HW procedure. Consequently, the treated cotton fleece fabric passes the 45° flammability test both before and after one HL procedure or the combination of DC and HW procedure. The treatment of the cotton fleece increases the whiteness and decreases the bursting strength of the treated cotton fleece by 42-47%.

Polycarboxylic acid flame retardant systems are the major part of this research. Unsubstituted and hydroxyl-substituted bi-functional carboxylic acids, succinic acid, malic acid and tartaric acid, were applied to flame retardant finish cotton fleece. The esterification of cotton cellulose with succinic acid, malic acid, and tartaric acid is effective in reducing the flammability of cotton fleece. The esterification of cellulose with malic acid and tartaric acid is more effective in reducing the flammability than that with succinic acid based on the same amount of ester. Overall, unsubstituted bi-functional carboxylic acid, succinic acid, is the most promising flame retardant for cotton fleece. First of all, the reactivity of succinic acid is much higher than hydroxyl-substituted polycarboxylic acids, malic acid and tartaric acid. The steric hindrance of the α-hydroxyl reduces the reactivity of hydroxyl-substituted polycarboxylic acids. Secondly, succinic acid treated cotton fleece has the highest durability to multiple home launderings. Thirdly, cotton fleece treated with succinic acid has the highest bursting strength retention since it has the highest reactivity and the fiber is subjected to less free acid-catalyzed depolymerization. Fourthly, the treatment of succinic acid does not have much effect in the fabric whiteness. The treatment of malic acid reduces the whiteness of treated cotton fleece and the whiteness index decreases as the increase of malic acid concentration. The limitation for the application of succinic acid on reducing the flammability of cotton fleece is its low solubility at room temperature, which restricts its application on some high flammable cotton fleece.

The effectiveness of bi-functional carboxylic acids and high-functional carboxylic acids in reducing the flammability of cotton fleece was studied. Before esterification, polycarboxylic acids are not able to reduce the flammability of cotton fleece. The esterification of cotton fleece with polycarboxylic acids is effective in reducing the flammability of cotton fleece. High-functional carboxylic acids (BTCA and citric acid) have higher reactivity with cotton cellulose than bi-functional carboxylic acids (succnic acid and malic acid). BTCA has the highest reactivity with cotton fleece. The cotton fleece treated with BTCA, citric acid and succinic acid is durable to multiple home launderings and it passes 45 ° flammability test after 20 home launderings. The cotton fleece treated with malic acid has lower durability to multiple home launderings due to the low esterification and the ester hydrolysis in the laundering process. Overall, the cotton fleece treated with high-functional carboxylic acids is more durable to multiple launderings than that treated with bi-functional carboxylic acids. The cotton fleece treated with BTCA is the most durable to multiple home launderings. The cotton fleece treated with succinic acid has the highest bursting strength retention and that treated with BTCA has the lowest bursting strength retention. The treatment of cotton fleece with unsubstituted polycarboxylic acids, BTCA and succinic acid, has very little effect on the fabric whiteness. The treatment of cotton fleece with hydroxyl-substituted polycarboxylic acids, especially citric acid, affects the whiteness of treated cotton fleece.

The treatment with the combination of maleic acid and NaH_2PO_2 introduces phosphorus into the flame retardant system. Therefore, the maleic acid/ NaH_2PO_2 is a phosphorus-containing polycarboxylic acid system. NaH_2PO_2 functions as a catalyst for the esterification of maleic acid on cotton and also a reactant in the reaction of cellulose and maleic acid. Three reactions involves in the reaction of maleic acid, NaH_2PO_2 and cellulose. The esterification of maleic acid with cotton cellulose takes place in the presence of NaH_2PO_2 at relatively low temperatures (≤130 ºC). The addition of NaH_2PO_2 to C=C bond of the esterification product of maleic acid with cotton cellulose takes place at relatively high temperatures (≥150ºC). Thus, the application of the combination of maleic acid and NaH_2PO_2 to cotton is able to bond phosphorus to the cotton fiber and consequently to reduce the flammability of cotton fleece. The treatment of maleic acid/ NaH_2PO_2 also forms cross-linking structure with cotton cellulose and increases the wrinkle recovery angle of woven fabric. The treatment of the cotton fleece with maleic acid/ NaH_2PO_2 is effective in reducing the 45º flammability from “Class III” (high flammability) to “Class I” (normal flammability), thus making it possible to produce 100% cotton fleece legally salable in the U.S. The maleic acid/NaH_2PO_2 system bound to cotton fleece using pad-dry-cure process is durable to multiple home launderings.

The mechanism of how the esterification of polycarboxylic acids with cotton cellulose reduced the flammability of cotton fleece was studied. The results show that the treated cotton fleece has reduced flammability at elevated curing temperature due to the increasing amount of ester formed on cotton fleece. Both the cotton woven fabric and cotton fleece treated with BTCA show increased LOI. Cotton fleece treated with succinic acid shows increased LOI value as well. DSC analysis indicates that the depolymerization reaction of cotton fleece esterified with polycarboxylic acids reduces and the dehydration reaction increases. TG analysis shows that the cotton fleece treated with polycarboxylic acids has increased activation energy, i.e., higher thermal stability, lower maximum decomposition rate and initial decomposition temperature, and higher char content. The mechanism of the flame retardancy is probably due to that the esterification of cotton fleece reduces the depolymerization of cellulose, and thus the production of levoglucosan, and increases the dehydration of cellulose.

In general, the esterification of cotton cellulose with polycarboxylic acids is a durable, non-formaldehyde flame retardant finishing for cotton fleece at a low add-on level. This treatment is economic, environmentally friendly, easy to apply, and is a promising process.

APPENDIX

EFFECT OF SILICONE FINISHES ON THE BURNING BEHAVIOR OF PET*

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[*] Wu, X., Yang, C.Q. To be submitted to Polymer Degradation and Stability.

ABSTRACT

A modified 45° flammability test method was established for polyester materials. Combined with the Student t-test, the modified 45° flammability test can be used to semi-quantitatively determine the flammability of polyester materials. The flammabilities of polyester nonwoven and mat materials were evaluated. The treatment with silicone Softener 2 increased the flammability of polyester nonwoven and mat materials significantly. Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis showed that inorganic silicon dioxide and silicon fibers were produced during the burning process. The decomposition of silicone softener to inorganic silicon dioxide and silica reduced the surface energy of the polyester and provided an inert supporting layer for melting polyester, and thus increased the flammability of the polyester significantly. Thermogravimetric analysis showed that the polyester mat treated with silicone Softener 2 had increased thermal stability before the maximum decomposing rate temperature in air and had higher residue.

INDEX WORDS**:** silicone softener, modified 45° flammability test, polyester, flammability, Student t-test, energy dispersive x-ray (EDX), scanning electron microscopy (SEM)

INTRODUCTION

"Silicones are a class of polymers having the formula $[R_mSi(O)_{4-m/2}]_{n,}$ m=1-3 and n≥2" [1]. Silicone products have been widely applied on textiles for various end uses. The primary applications of silicones in textile are fabric softeners, fiber and thread lubricants, antifoaming agents, and antistatic agents. The treatment of silicone products also achieves some additional benefits such as antimicrobial effect, water repellency, and elasticity [2]. The most commonly used silicone softener is polydimethylsiloxane (PDMS). Reactive polydimethylsiloxanes, such as hydrogen siloxanes, terminal silanols, epoxy reactive polydimethylsiloxanes, and aminofunctional siloxanes, can achieve more durable effects than PDMS [3]. However, silicones have an antagonistic effect on the flame retardant properties of polyester. Polyester normally melts and flows at above 260°C. Without silicone finishing, polyester material shrinks away from the ignition flame, melts and self extinguishes when subjected to a flammability test. Weil [4] discussed the antagonistic effect of silicone oil on the flame retardant properties of polyester. Silicone oil provides "wicks" for burning and increases the flammability significantly. There are several possible mechanisms for the increased flammability caused by silicones: the scaffold effect attributed to thermal degradation of silicones to form a three dimensional, crosslinked, inorganic Si-O-Si or silica itself, and the reduced tendency to shrink away from an ignition source caused by the lowered surface energy [5, 6, 7].

Swihart and Campbell [7] studied the flammability of polyester treated by polydimethylsiloxanes by vertical flame test and oxygen index. Their result showed that silicones interacted with polyester both chemically and physically. The increased flammability of silicone treated-polyester was primarily attributed to the alteration in the melt characteristics of the polyester. However, the effect of silicone softener on the flammability of polyester materials has not been clearly defined yet. No testing method has been developed to test the flammability of polyester materials. The mechanisms of the increased flammability of silicone softener treated polyester are not clear as well. In this paper, we established a modified 45° flammability test for polyester material to measure the flammability of silicone softener treated polyester material. The mechanism of the increased flammability of silicone softener treated polyester was investigated. The thermogravimetric analysis of the polyester mat was conducted as well.

EXPERIMENTAL

Materials

The polyester nonwoven with a density of 136.5 g/m^2 and polyester mat material with a density of 144.1 g/m^2 were supplied by Clemson University, Clemson, SC. Silicone softener Wetsoft CTA (an aminofunctional hydrophilic self-dispersible softener) named as Softener 1 and reactive silicone softener CT205E named as Softener 2 were supplied by Kelmar Industries, Duncan, SC.

Fabric Treatment

The polyester nonwoven used for the establishment of a test method was soaked in Softener 1, then padded through a two-roll laboratory padder with two dips and two nips and dried at 140 ℃ for 4 min in a laboratory oven manufactured by Werner Mathis, Concord, NC. The fabric wet pick-up was 150±10%. For the rest of the experiments, the polyester nonwoven and polyester mat material were sprayed with a nebulizer containing Softener 2 solution, and then dried in an oven at 160°C for 10 min. The fabric wet pick-up was 120±10%.

Thermogravimetric (TG) Analysis

TG analysis was used to investigate the thermal degradation behavior of the untreated and silicone softener treated polyester materials. Thermogravimetric (TG) analysis was conducted using a Mettler Toledo TGA/SDTA 851 Thermogravimeter from 50 to 550 ℃ at a heating rate of 10°C/min in air. The sample size was 1.5-2.5 mg.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)

Polyester fiber and the char samples from the burning test were analyzed by Zeiss1450 EP environmental scanning electron microscopy (ESEM) and EDX using back scattering detector. The ESEM operated at 20 Kv was used to observe the morphologies of polyester fiber and char samples. The EDX was used to analyze the composition of elements on the fiber and on some of the char areas.

RESULTS AND DISCUSSION

The Establishment of the Flammability Test Method for Polyester Material

There is no standard flammability test method for polyester materials. In this research, in order to measure the flammability of polyester materials, we modified the 45 ° flammability test, the ASTM Method D1230-94 (Standard Test Method for Flammability of Apparel Textiles, reapproved in 2001). The fabric specimens were mounted in a specimen holder, and then moved to a standard 45° flammability tester (Model TC-45 manufactured by Govmark, Bellmore, NY) with the specimen at an angle of 45 °. The ignition time was changed to 5 sec instead of 1 sec, since the ignition time of 1 sec was not enough to cause ignition. After the specimen was exposed to a standard butane flame for 5 sec to cause ignition, the burning time and burning characteristics were recorded. Nine or ten specimens were tested for each sample. The weight loss after the burning test was recorded and the percentage weight loss was calculated based on the weight in the tested area. The arithmetic mean percentage weight loss and the Student t-test of 9 or 10 specimens were used to determine the flammability of the polyester materials.

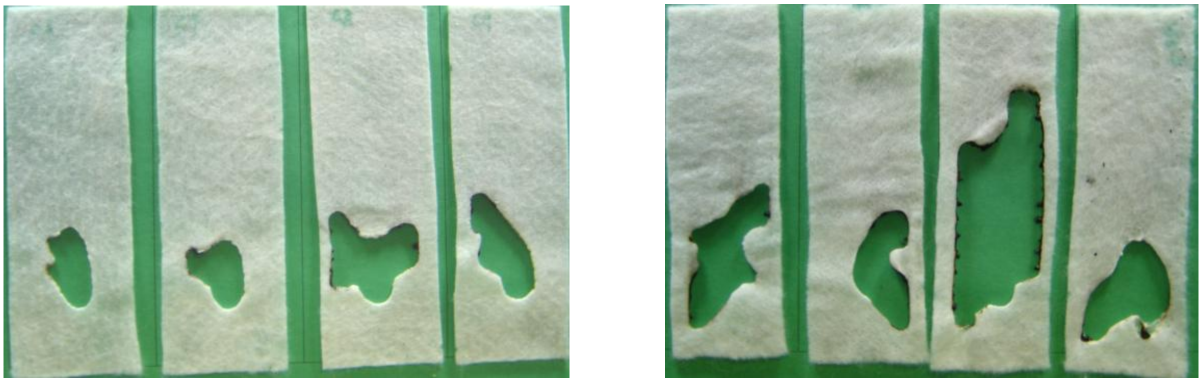
Table A1. The average percent weight loss of polyester nonwoven finished by Softener 1 after the flammability test, standard deviation of the percent weight loss, t-value and critical t-value.

Softener 1 (%)	Average Percent Weight Loss (%)	Standard Deviation of Percent Weight Loss	t-value (Paired with Control)	Critical t-Value (α=0.05)
Control	0.9	1.3	-	-
0.1	13.4	9.3	4.0	2.12
0.5	20.0	9.4	6.0	2.12
1.0	24.9	12.7	5.6	2.12

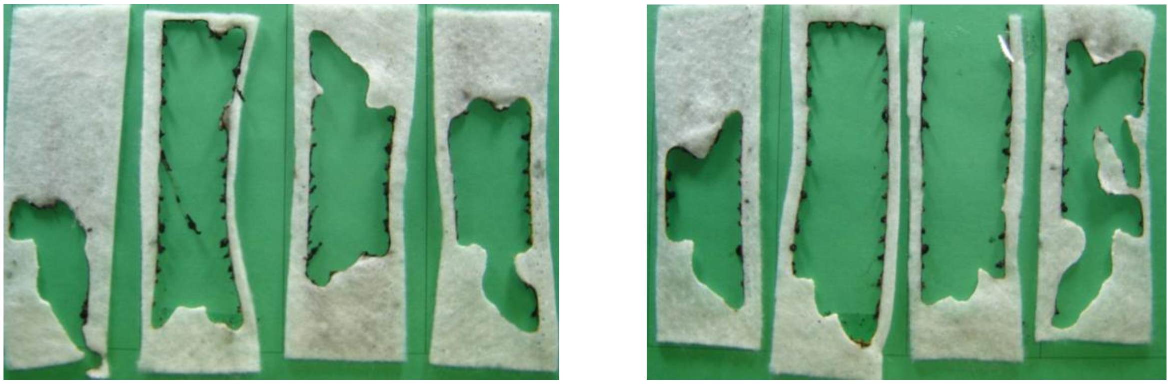
Note: a) The fabric was padded and dried in a laboratory oven at 140 ℃ for 3 minutes. The wet pick-up was about 150 ±10%.
b) The specimens were tested in the cross direction and 9 specimens were measured.

Presented in Table A1 is the average percent weight loss of polyester nonwoven finished with Softener 1 after the flammability test, standard deviation of the percent weight loss, t-value and critical t-value. The average percent weight loss of untreated polyester nonwoven is only 0.9%. The percent weight loss of polyester nonwoven treated with silicone softener is much larger than that of the untreated and it increases with the concentration of silicone softener. The standard deviation of the percent weight loss increases with the silicone softener concentration. The t-values of the percent weight loss paired with the control are all larger than the critical t-value at 95% confidence level. Therefore, there is significant difference in the percent weight loss between control and the treated polyester nonwoven and the treatment of silicone softener increases the flammability of polyester nonwoven. From the average percent weight loss and the

Student t-test, we can determine whether the treatment of silicone softener increases the flammability of polyester materials or not.



a) Control b) Softener 1, 0.1%



c) Softener 1, 0.5% d) Softener 1, 1.0%

Figure A1. The pictures of polyester nonwoven treated with silicone Softener 1 tested in the cross direction

Figure A1 shows the pictures of polyester nonwoven after the flammability test. The untreated polyester nonwoven shows a small empty area after the flammability test primarily due to melt and shrinkage of polyester fiber. The treated polyester nonwoven shows much larger empty area and chars on the edge of the specimen holder due to fiber combustion, melt, and shrinkage. The nonwoven specimens show larger burned area at higher concentrations.

From the above discussion, we know that the modified 45 ° flammability test combined with Student t-test can be used to determine the flammability of polyester materials. The average percent weight loss after the flammability test indicates the flammability of polyester materials. The higher the average percent weight loss, the more flammable the polyester materials are.

The Flammability of Polyester Nonwoven and Mat Material Finished by Softener 2

The flammability of polyester nonwoven material was measured in machine direction. The average percent weight loss, standard deviation of percent weight loss, t-values paired with the control, t-values paired with two concentrations are shown in Table A2. The treatment with Softener 2 has an obvious impact on the flammability of polyester nonwoven. When the concentration of Softener 2 is 0.1%, the percent weight loss is 38.0% after the flammability test. When the concentration increases, the percent weight loss does not increase. The t-values of the percent weight loss paired with control are all larger than the critical t-value at 95% confidence level. Therefore, there is significant difference in the percent weight loss between the finished and the untreated polyester nonwoven. The treatment of Softener 2 increases the flammability of polyester nonwoven. The t-values of percent weight loss of treated polyester nonwoven paired with two concentrations are all smaller than the critical t-values at 95% confidence level. Thus, there is no significant difference in the weight loss of polyester nonwoven treated at different concentrations of silicone softener. The flammability of polyester nonwoven is increased significantly by a small amount of silicone softener. The increase of silicone softener concentration does not increase the flammability of the treated polyester nonwoven.

Table A2. The average percent weight loss of polyester nonwoven materials treated with Softener 2 after flammability test, standard deviation of percent weight loss, t-values paired with the control, and t-values paired with two concentrations.

Softener 2 (%)	Ave. Percent Weight Loss (%)	Standard Deviation	t-Value (Paired with Control)	t-Value (Paired with 2 Concentrations)	Critical t-Value (α=0.05)
Control	1.4	1.8	-	-	-
0.1	38.0	12.8	9.0	1.3 (0.1% &0.5%)	2.10
0.5	28.9	17.5	4.9	1.3 (0.1% &1.0%)	2.10
1.0	29.1	17.2	5.1	0.03 (0.5% &1.0%)	2.10

Note: a) The fabric was sprayed with a nebulizer with Softener 2 solution and dried in an oven at 160 ℃ for 10 min. The wet pick-up was about 110 ±10%.

b) The specimens were tested in the machine direction and 10 specimens were measured.

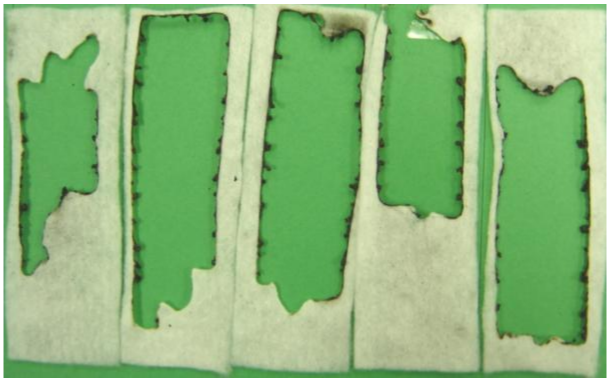


Figure A2. The picture of polyester nonwoven treated with 0.1% Softener 2 tested in the machine direction

The pictures of polyester nonwoven tested in the machine direction are shown in Figure A2. The specimens after the burning test show large burned area, which further proves that the treatment of Softener 2 increases the flammability of polyester nonwoven.

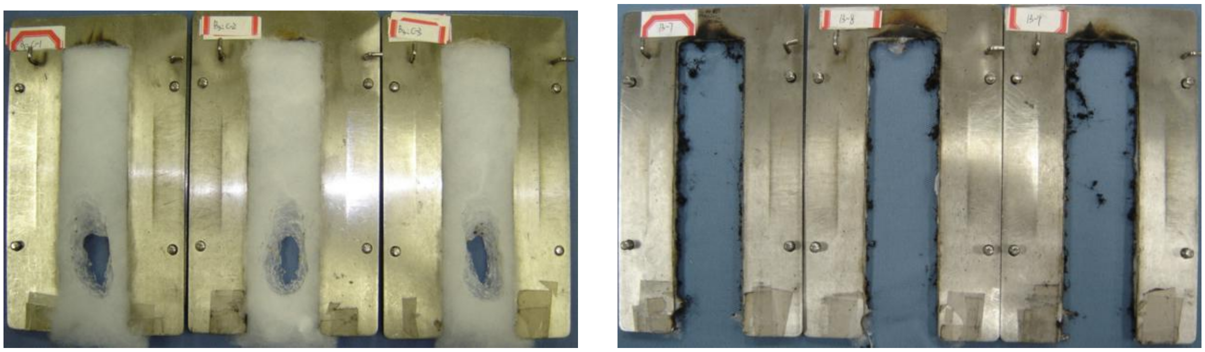
The effect of Softener 2 on the flammability of polyester mat material was also studied. Different with nonwoven, mat material is very fluffy and contains a considerable amount of air. The flammability problem of polyester mat material is more serious than that of polyester nonwoven. The average percent weight loss of polyester mat material treated with Softener 2, standard deviation of percent weight loss, t-values paired with the control, t-values paired with two concentrations are shown in Table A3. When the concentration of Softener 2 is 0.1%, the average percent weight loss is 26.6% and is much higher than the percent weight loss of the control. When the concentration of Softener 2 is 0.5%, the weight loss increases to 55.8%. The whole tested area is burned. Char and some fine black fibers formed at the edge and across the sample holder (Figure A3). However, the untreated polyester mat does not burn and has almost no weight loss after the flammability test. The small empty area of the untreated polyester mat is due to the melt and shrinkage of polyester fibers (Figure A3). All the t-values of percent weight loss paired with the control are larger than the critical t-value at 95% confidence level. Thus, the flammability of the polyester mat treated with silicone softener even at very low concentrations is significantly higher than the untreated polyester mat. The flammability of polyester mat treated with 0.5% and 1.0% Softener 2 is significantly higher than that treated with 0.1% Softener 2 since the t-values paired with 2 concentrations are larger than the critical t-value (Table A3). The treatment of Softener 2 significantly increases the flammability of polyester mat.

Table A3. The average percent weight loss of polyester mat material treated with Softener 2 after flammability test, standard deviation of percent weight loss, t-values paired with the control, and t-values paired with two concentrations.

Softener 2 (%)	Ave. Percent Weight Loss (%)	Standard Deviation	t-Value (Paired with Control)	t-Value (Paired with 2 Concentrations)	Critical t-Value
Control	0.8	0.8	-	-	-
0.1	26.6	16.6	4.9	5.0 (0.1%&0.5%)	2.1
0.5	55.8	7.8	22.2	3.0 (0.1%&1.0%)	2.1
1.0	47.3	13.9	10.6	1.7 (0.5% &1.0%)	2.1

Note: a) The fabric was sprayed with a nebulizer with Softener 2 solution and dried in an oven at 160 ℃ for 10 min. The wet pick-up was about 110 ±10%.

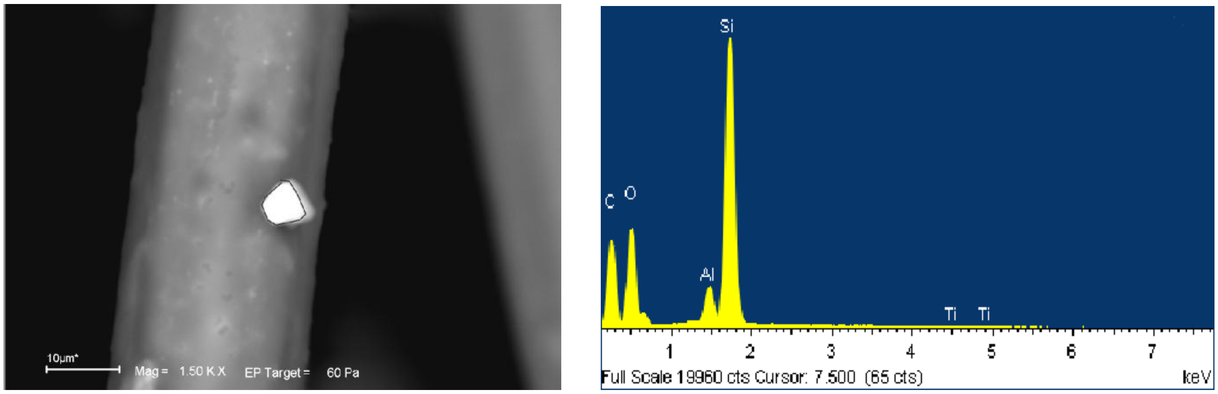
b) The specimens were tested in the machine direction and 10 specimens were measured.



(a) Polyester mat, Control (b) Polyester mat, Softener 2, 0.5%

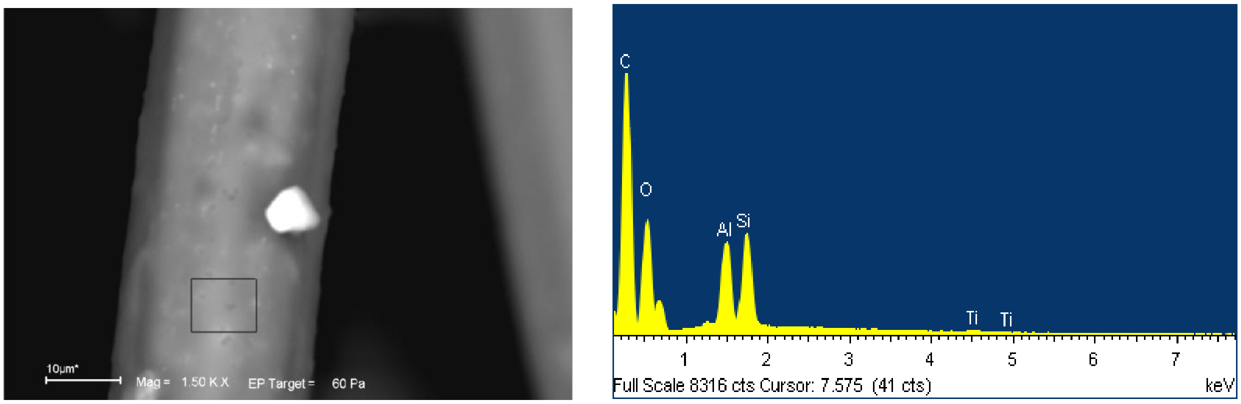
Figure A3. The pictures of polyester mat treated with Softener 2 tested in the machine direction

SEM and Energy Dispersive X-ray (EDX) Analysis



(a) SEM picture of polyester mat (b) EDX of spectrum of the silicone particle

Figure A4. The SEM picture and the EDX spectrum of the silicone particle on polyester mat fiber treated with 0.5% Softener 2



(a) SEM picture of polyester mat (b) EDX spectrum of the selected area

Figure A5. The SEM picture and EDX spectrum of the selected area on polyester mat fiber treated with 0.5% Softener 2

EDX analysis is a semi-quantitative method providing relative element compositions in the scanned area. The quantity of the elements depends largely on the penetration ability of the X-ray. The SEM picture and EDX spectrum of the polyester mat treated with 0.5% Softener 2 are shown in Figure A4 and A5, respectively. Some big particles are observed on the fiber surface in Figure 4 (a). The EDX spectrum shows that the major components in the scanned area are carbon, oxygen, silicon, aluminum, and titanium (Figure A4 (b)). The aluminum comes from the SEM aluminum sample stub. The titanium comes from the delustrant TiO_2 added during the polyester spinning process. The atomic compositions of carbon, oxygen, and silicon are 55.02, 35.18 and 8.65%, respectively (Table A4), which indicates that the particle is a silicone softener particle. Hydrogen cannot be measured by the EDX. The EDX analysis of the area other than the particle is shown in Figure A5 (b). Other than carbon and oxygen, the major components of polyester, silicon is also observed on the fiber surface. Again, the aluminum comes from the aluminum sample stub. The element compositions of the scanned area other than the silicone particle are shown in Table A5. The atomic composition of silicon is 2.05%, much lower than that in the particle area. From the above discussion, we can conclude that silicone softener accumulates on the polyester fiber surface as big particles and spreads out on the fiber surface as invisible small particles.

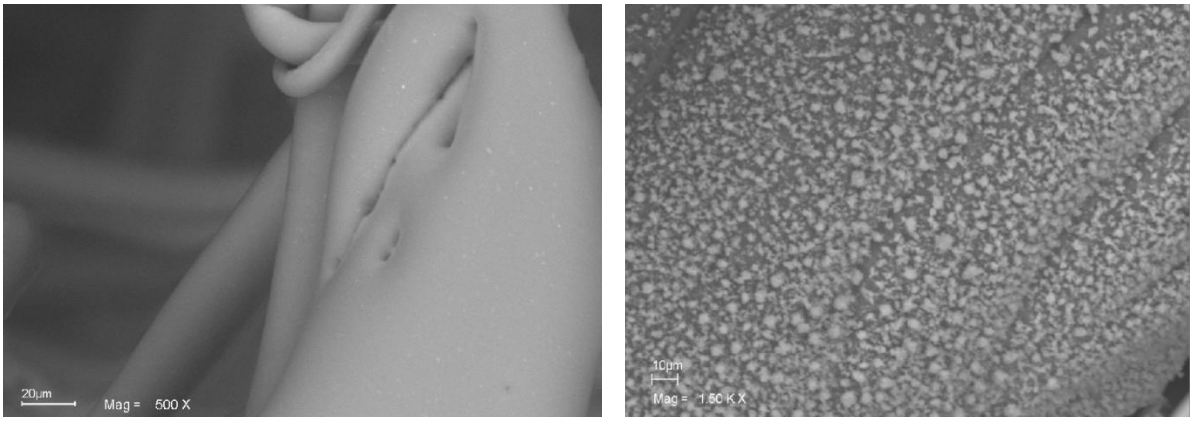
Table A4. Element composition of the particle on polyester mat treated with 0.5% Softener 2.

Element	*Weight%*	*Atomic%*
C K	44.12	55.02
O K	37.58	35.18
Al K	2.02	1.12
Si K	16.22	8.65
Ti K	0.07	0.02
Totals	100.00	

Table A5. Element composition of the selected area on polyester fiber of the mat treated with 0.5% Softener 2.

Element	*Weight%*	*Atomic%*
C K	59.22	67.92
O K	32.55	28.02
Al K	3.79	1.93
Si K	4.18	2.05
Ti K	0.26	0.08
Totals	100.00	

The SEM pictures of the melt surface of untreated polyester mat after flammability test are shown in Figure A6. Untreated polyester has very high surface energy and intends to shrink away from the igniting source. Thus, the untreated polyester mat melts away from igniting flame and shows a very smooth melting surface (Figure A6 (a)). The melted surface of polyester mat treated with 1.0% Softener 2 shows a rough surface with a large amount of particles (Figure A6 (b)). After treatment with silicone softener, the surface energy of polyester is lowered and polyester mat burns vigorously dropping flaming droplets instead of melting and shrinking away from the flame.



(a)Untreated polyester mat (b) Polyester mat treated with 1.0% Softener 2

Figure A6. The SEM pictures of the melt surface of the untreated polyester mat and polyester mat treated with 1.0% Softener 2 after the flammability test

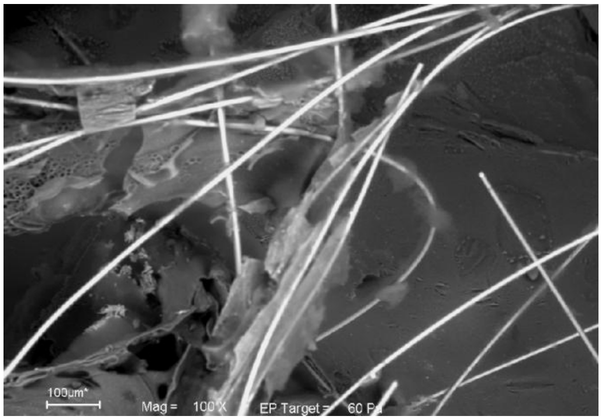
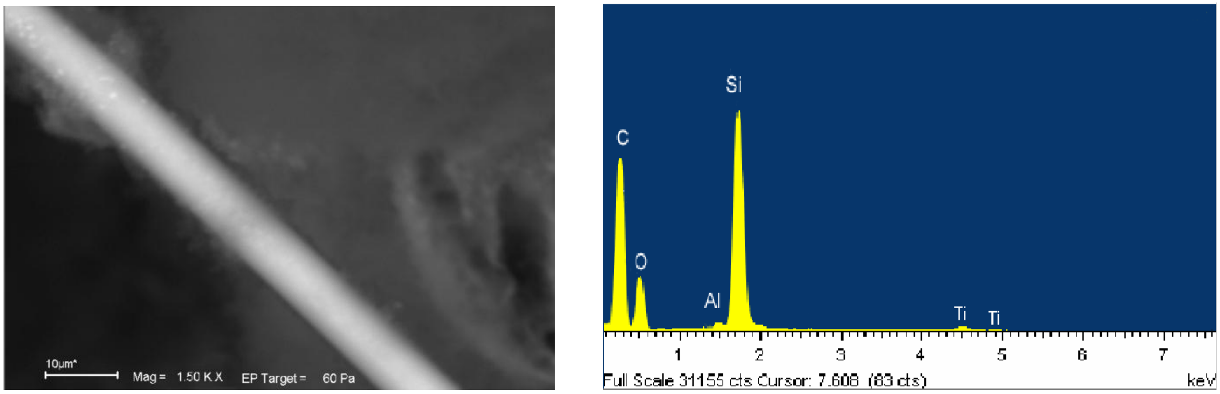


Figure A7. The SEM picture of the char of polyester mat treated with 0.5% Softener 2 after the flammability test



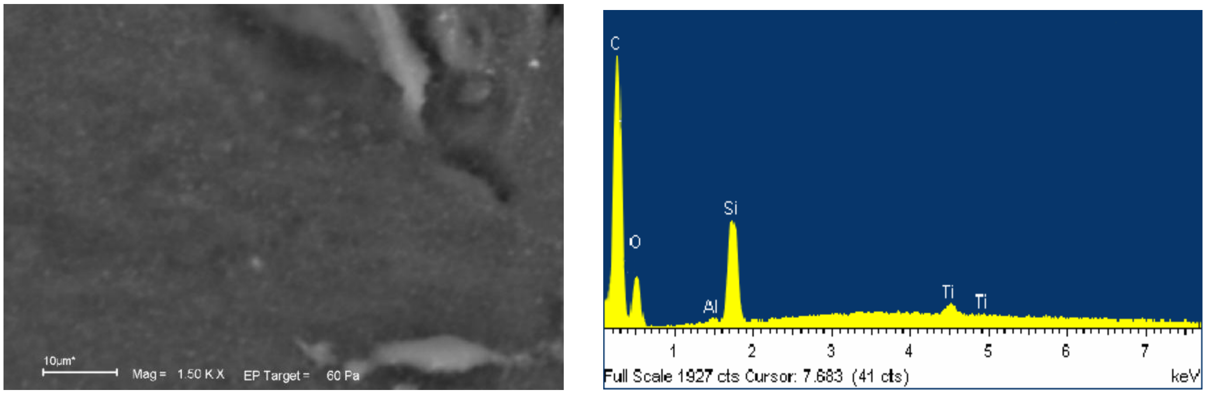
(a) SEM picture of the charred fiber (b) The EDX spectrum of the charred fiber

Figure A8. The EDX spectrum of the charred fiber obtained from polyester mat treated with 0.5% Softener 2

A lot of small fibers form on the edge of the specimen holder and on the char after the flammability test for polyester mat treated with Softener 2. The polyester char is observed under SEM and the picture is shown in Figure A7. A lot of bright charred fibers distinguished from polyester char are found in the SEM picture. The bright charred fibers contain higher atomic weight elements since higher atomic weight elements have higher signal under back scattering detector. The EDX spectrum of the charred fiber obtained from polyester mat treated with 0.5% Softener 2 after flammability test is shown in Figure A8. Silicon shows a very intensive band in the EDX spectrum. The element composition of the charred fibers is shown in Table A6. The major components of the charred fiber are oxygen and silicon and the mole ratio of oxygen to silicon is around 1.67. Therefore, the most possible compositions of the charred fiber are silicon dioxide and silica. The small amount of aluminum comes from the SEM aluminum sample stub. Silicone softener decomposes to produce silicon dioxide and silica during the burning and they crystallize to form silicon dioxide and silica fibers as the burning continues. The fibers serve as supporting layer for polyester and inhibit the melting shrinkage of polyester and the melted polyester served as fuel for continuing burning.

Table A6. Element composition of the selected area on the charred fiber obtained from polyester mat treated with 0.5% Softener 2 after the flammability test.

Element	*Weight%*	*Atomic%*
O K	46.04	60.77
Al K	1.05	0.82
Si K	49.43	37.17
Ti K	2.62	1.15
Totals	100.00	



(a) SEM picture of the char area (b) EDX spectrum of the selected char area

Figure A9. The EDX spectrum of the char area of polyester mat treated with 0.5% Softener 2

The EDX spectrum of the char of polyester mat treated with 0.5% Softener 2 is shown in Figure A9. The surface of the char is sand like. The element composition of the char area is shown in Table A7. The atomic percentage of carbon, oxygen, and silicon in the char area is

74.98, 21.86, and 2.70%, respectively. Compared with the element compositions of treated polyester mat before the flammability test, the char area contains higher carbon, lower oxygen, and slightly higher silicon (Table A5). Most of the silicone softener decomposes to produce silicon dioxide and silicon fiber. Therefore, the composition of silicon in the char does not have much difference with that on the polyester fiber before the flammability test.

Table A7. Element composition of the selected area on charred area of polyester mat treated with 0.5% Softener 2.

Element	*Weight%*	*Atomic%*
C K	66.91	74.98
O K	25.98	21.86
Al K	0.21	0.11
Si K	5.63	2.70
Ti K	1.27	0.36
Totals	100.00	

Table A8. T_{di} and T_{max} of untreated polyester mat and polyester mat treated with 0.1% and 0.5% Softener 2.

Softener 2 Concentration (%)	T_{di} (℃)	T_{max} (℃)
Control	170	440
0.1	260	435
0.5	385	440

Note: T_{di}: the initial decomposing temperature; T_{max}: the maximum decomposing rate temperature.

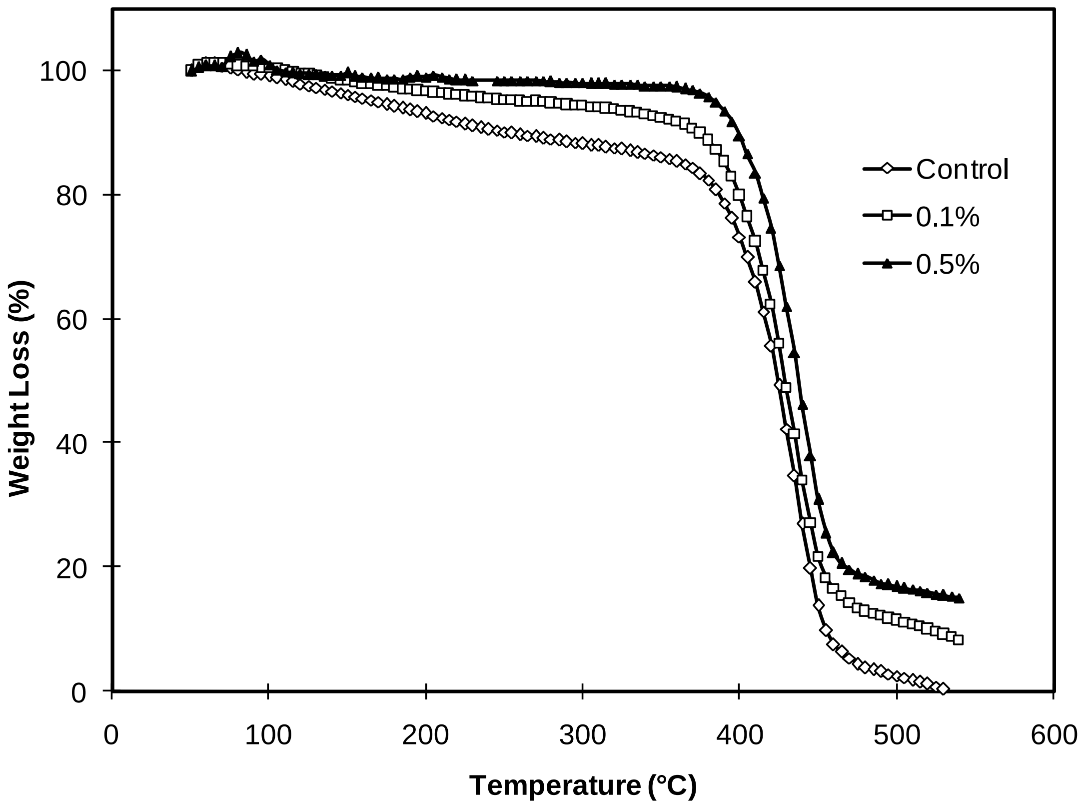


Figure A10. The TG curves of polyester mat treated with 0.1% and Softener 2 at a heating rate of 10°C/min in air

Thermogravimetric (TG) Analysis

Figure A10 shows the TG curves of untreated polyester mat, and polyester mat treated with 0.1 and 0.5% Softener 2 at a heating rate of 10 ℃/min in air. The characteristic decomposition temperatures derived from Figure A10 are presented in Table A8. The initial decomposition temperature (T_{di}) is the temperature at which the weight loss of the samples reaches 5 wt %. The T_{di} of untreated polyester mat is 170 ℃. The T_{di} of polyester mat treated with 0.1% and 0.5% Softener 2 is 260 and 385 ℃, respectively, much higher than the untreated polyester mat. Therefore, the treatment of polyester mat with silicone softener increases the stability of polyester. The treated polyester mats decompose slower and show a smaller weight loss before the maximum decomposition rate temperature (T_{max}) than untreated polyester mat (Figure A10). Before T_{max}, the reactive silicone softener self-condenses on the surface of polyester and inhibits the evaporation of polyester oligomer. Therefore, treated polyester mats have higher stability before T_{max}. The T_{max} of untreated and treated polyester mat does not show much difference and is about 435 ℃. Therefore, the treatment of silicone softener does not increase the thermal oxidative stability. However, the residues of thermal oxidative degradation of untreated polyester mat and polyester mats treated with 0.1% and 0.5% Softener 2 are quite different (Figure A10). The treatment of silicone softener increases the residue of treated polyester significantly. The residue of untreated polyester mat is 0.45% at 530 ℃. The residues of polyester mat treated with 0.1% and 0.5% Softener 2 are 8.2 and 15.1% at 540 ℃, respectively, much higher than that of the untreated polyester mat. The low concentration of Softener 2 would not contribute to the 7.8% and 14.7% increase in the char residue for polyester mat treated with 0.1% and 0.5% Softener 2, respectively. The result can be explained by the charring effect of silicone softener on polyester in air at high temperature. Silicone softener decomposes to produce inorganic silicon dioxide and silica as shown in SEM pictures of the char. The inert silicon dioxide protects the polyester underneath and facilitates the charring of polyester. Thus, the polyester mat treated with silicone softener has higher residue.

CONCLUSIONS

The modified 45 ° flammability test established in this paper combined with the Student t-test can be used as a semi-quantitative method to determine the flammability of polyester materials. The treatment of Softener 2 significantly increases the flammability of polyester nonwoven and polyester mat materials. The treated polyester materials show much higher weight loss and larger burning area than the untreated polyester materials. The major mechanism of the increased flammability of polyester material treated with silicone softener is that silicone softener decomposes to produce inert inorganic silicon dioxide and silica fiber during the burning process, which serves as an inert support for the melted polyester. The melt polyester is the fuel supply for continuing burning. Silicone softener also lowers the surface energy of treated polyester and inhibits the melt shrinkage of polyester fiber when subjected to an ignition source. Thermogravimetric analysis shows that the treatment of silicone softener increases the thermal stability of polyester in air before the maximum decomposition rate temperature and increases the residue of polyester.

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