

FLAME RETARDANT FINISHING OF COTTON BLEND FABRICS USING AN  
ORGANOPHOSPHORUS-BASED SYSTEM

by

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(Under the Direction of Charles Q. Yang)

ABSTRACT

In this research, I discovered that both dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) are able to covalently bond hydroxy-functional organophosphorus oligomer (HFPO) to nylon by the formation of a crosslinked polymeric network. Nylon treated with HFPO/DMDHEU shows higher phosphorus retention and significantly lower stiffness than that treated with HFPO/TMM. The bonding of HFPO to cotton using DMDHEU as a bonding agent was also studied. The laundering durability of HFPO bound to cotton through DMDHEU is attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/cotton cellulose, which also increases the fabric stiffness.

Even though both TMM and DMDHEU are able to covalently bond HFPO to nylon/cotton blend fabric, DMDHEU is more effective for bonding HFPO to the nylon/cotton blend fabric than TMM. The nylon/cotton fabric treated with HFPO/DMDHEU shows higher flame retardant performance and lower stiffness than that treated with HFPO/TMM after multiple launderings. The nylon/cotton blend fabric treated with HFPO/DMDHEU shows high levels of flame retardant performance and passes the vertical flammability test even after 50 laundering cycles. HFPO may function through the condensed phase mechanism in the both individual fibers and their blend.

In addition, I also discovered that DMDHEU can covalently bond HFPO to polyester and acetate, which creates a new way to durable flame retardant finishing of other cotton blends including cotton/polyester and cotton/acetate blends.

The advantages of the above finishing system include: single flame retardant effective for both individual fibers in the blends; high level of flame retardant performance and good laundering durability; easy application; limited effects on the physical properties of the treated fabric; and low cost.

I also developed a non-formaldehyde flame retardant finishing system based on HFPO for the Nomex/cotton blend fabric using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a bonding agent and triethanolamine (TEA) as a co-reactant. The main functions of TEA are to improve the hydrolysis-resistance of the HFPO bound to the Nomex/cotton blend and also enhance the flame retardant performance of HFPO through the phosphorus-nitrogen synergism. The Nomex/cotton blend fabric treated with the HFPO/BTCA/TEA system shows high levels of flame retardant performance at relatively low add-on levels.

**INDEX WORDS:** Reactive organophosphorus chemicals, Cotton, Nylon-6.6, Nylon 6, Nomex, Nylon/cotton blend, Nomex/cotton blend, Durable flame retardant finishes, Dimethyloldihydroxyethyleneurea, Trimethylolmelamine, Phosphorus-nitrogen synergism, Thermal analysis.

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## DEDICATION

This dissertation is dedicated to my wife, Ran Hu, for her forever love, patience, and support.

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# CHAPTER 1

## INTRODUCTION

In spite of the existence of stringent fire safety and regulations, fire is still a serious threat to life and property in the U.S [1-2]. In 2005 in the U.S., there were 1.6 million fires reported. 3,675 civilians and 115 firefighters lost their life due to fire. Fire also resulted in 17,925 civilian injuries and \$10.7 billion of direct property loss. Further analysis of the 2005 U.S. statistics for fires showed that 83 percent of all civilian fire deaths occurred in homes [3]. Despite the more stringent fire safety standards, the escape time from an average home reduced from 17 minutes in 1975 to 3 minutes in 2004, mainly due to the existence of more and more flammable items such as textiles and related products in homes [4]. The UK Fire Statistics up to 2000 demonstrated that textile materials were identified as the first item to be ignited in around 20% of home fires, which caused over 50% of the deaths [5-6]. Textile materials, especially in home fires, also function as sources of fuel to maintain combustion [6].

The desire to reduce the flammability of textiles can be traced back to man's recorded history and has been further driven mainly by several factors including regulations and environmental concerns [5-6]. The importance of regulations to reduce the death rate in fires has been further realized by policy-makers and consumers since the Furniture and Furnishings Regulations took effect in the UK in 1989 [5]. In the U.S., Congress passed the Flammable Fabrics Act (FFA) in 1953, and it was amended to extend its coverage in 1967 [9]. With the continuous concerns for fire safety, the development of new regional and national regulations has continued [9]. The most recent mandatory regional regulation on textiles in the U.S. is the California's Technical

Bulletin 603 (TB603), which became effective on January 1, 2005. A similar federal standard, 16 Code of Federal Regulations 1633, is expected to become effective on July 1, 2007 [7]. The development of regulations not only provides more protection for people from the fire hazards but also drives the need for new products and technology to reduce the flammability of textile materials.

In response to stricter fire safety regulations, the flame retardant market continues to grow at the rate of 4-5% annually in the U.S. [10-11]. Due to their effectiveness and relative low cost, halogenated compounds still hold 43% market share in 1998 while the organophosphorus compounds account for 25%. The environmental effect and health safety of halogenated flame retardants are still under investigation. In the long term, the movement to non-halogenated compounds such as phosphorus is expected to continue and might be speeded up by ongoing regulations [11-14].

### **The significance of this research**

Even though cotton still dominated the fiber market [15-16], cotton blends continued to grow and increased in market share of clothing from 20.4% in 2001 to 25% in 2005 [17]. In recent years, flame retardant finishing of nylon/cotton blend fabrics has become increasingly important because these blend fabrics are widely used in the protective clothing, including battle dress uniform (BDU) in the U.S. Army [18-19]. In spite of urgent need and high market demand, there is no practical technology available for flame retardant finishing of nylon/cotton blends, and research related to this topic is very limited [5-7]. Therefore, it is necessary to develop a new durable flame retardant finishing system for nylon/cotton blend fabric.

The Nomex/cotton blend fabric, which is a potential material for protective clothing, has attracted attention since the 1970s [20]. In previous research, Pyrovatex CP was used to impart durable flame retardancy to Nomex/cotton blend fabric. However, one of its major limitations is a high level of free-formaldehyde released in the production process and end-uses [21]. Increasing concerns about the hazard of formaldehyde continue to drive the demand for non-formaldehyde flame retardant finishing for Nomex/cotton blend fabrics [22-23].

### **The objectives of this research**

The purpose of this research is to develop new flame retardant finishing systems for cotton blend fabrics, especially nylon/cotton blend fabrics and Nomex/cotton blend fabrics.

The objectives of this research are shown below:

- (1) To develop a durable flame retardant finishing system for nylon/cotton blend fabrics based on a hydroxy-functional organophosphorus oligomer (HFPO). This flame retardant finishing system should at least have the following features: high levels of flame retardant performance, excellent laundering durability, reasonable cost and environmental friendliness.
- (2) To investigate the bonding of HFPO to nylon fabric using dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) as bonding agents and compare DMDHEU and TMM as bonding agents for HFPO to nylon fabrics.

- (3) To investigate the bonding of HFPO to cotton fabric using DMDHEU as a bonding agent.
- (4). To compare DMDHEU and TMM as bonding agents for HFPO to nylon/cotton blend fabric. The following features will be compared: flame retardant performance, laundering durability, phosphorus-nitrogen synergism, and physical properties.
- (5). To examine the effects of flame retardant finishing systems containing HFPO on the thermal degradation of cotton/nylon blend fabric and nylon fabric by thermal analysis using TGA and DSC.
- (6). To develop a durable non-formaldehyde flame retardant finishing system for Nomex/cotton blend fabric based on HFPO. This flame retardant finishing system should at least have the following features: no formaldehyde release, excellent flame retardant performance, a high level of laundering durability, reasonable cost and environmental friendliness.

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## CHAPTER 2

### REVIEW OF LITERATURE

#### 2.1 Flame retardant mechanisms of textiles

Before understanding the flame retardant mechanisms of textile, the basic knowledge of combustion should be introduced. In general, combustion is a very complicated process. A diagrams of the combustion model of textiles is shown in Fig.2.1 [1]. At the beginning stage, fiber pyrolysis is initiated by the supplied heat. Then, flammable gases are produced during pyrolysis procedures. When flammable gases combine with oxygen in air and the combustion temperature is reached, a series of gas phase free radical reactions occur, and combustion takes place. As a result, a large amount of heat is generated, and part of the heat returns back to the surface of fiber to initiate a new cycle of fiber pyrolysis, thus maintaining combustion. Based on the model in Fig.2.1, combustion requires three necessary components: fuel, heat and oxygen. In order to inhibit or stop combustion, one or more of those three necessary components should be reduced or removed during the process of combustion [1-4].

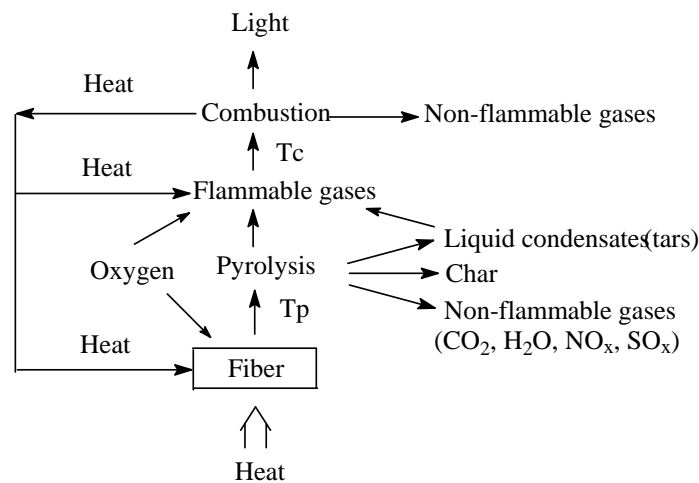
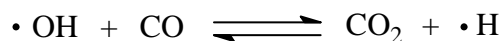


Fig.2.1 Combustion model of fiber [1]

There are several reviews [1, 4-9] on the flame retardant mechanisms of textiles. It is generally accepted that there are three flame retardant mechanisms for textiles. The first one is the physical mechanism. The flame retardants acting via the physical mechanism may function in both the condensed phase and the gas phase through two different modes: coating and heat sink. The typical examples of coating mode are boric acid and its hydrated salts [4, 8], and the alumina trihydrate mainly function through the heat sink mode [4].

The second mechanism is the gas/vapor phase mechanism [1, 4, 8-9]. Gas-phase active flame retardants function only in the gas phase by interfering with the free radical reactions in the flame, and they do not alter the pyrolysis path of the substrate during combustion. It is generally agreed that a series of free radical reactions occurs in the flame in the combustion process. Equation 1 shows the main exothermic reaction, which generates the most heat to maintain combustion. It has been found that reducing the OH radical and H radical concentration in the flame is an effective way to inhibit the main exothermic reactions, thus stopping the combustion.



Equation 1 The main exothermic reaction in the flame [4]

A gas-phase active flame retardant is able to capture the OH radical before it undergoes the main exothermic reaction. The typical gas-phase flame retardants are halogenated compounds, including chlorinated and brominated compounds. When heated, the halogenated compounds decompose to release hydrogen halides, which deplete the OH radical and H radical. As a result, the exothermic reactions are inhibited, and combustion is stopped [1, 4, 8-9].

The third mechanism is the condensed phase mechanism. Unlike the gas-phase active flame retardants, the condensed-phase active flame retardants mainly act by altering the pyrolysis pathway of the substrate [1, 4-10]. The typical example is the phosphorus-containing flame retardants for cotton cellulose [4]. Detailed information is shown in the next section.

## **2.2 Mechanism of phosphorus-compounds**

The phosphorus-containing flame retardants have been widely used to impart flame retardant properties to textiles. There are several reviews on the mechanism of phosphorus-containing flame retardants on textiles [4-6, 10]. In this section, the flame retardant mechanisms of phosphorus-containing compounds on cellulose and nylons are focused on.

It is generally agreed that most phosphorus-containing compounds mainly act through the condensed phase mechanism in cellulose [[4-6, 10]. It is generally accepted that the pyrolysis of cellulose can take at least two competitive pathways: depolymerization and dehydration [9-10]. In the process of depolymerization, cellulose mainly produces levoglucosan, which further decomposes into flammable gases [9-13]. Dehydration, however, tends to produce char and non-flammable gases with less heat release in comparison to depolymerization [14]. Without phosphorus-containing flame retardants, depolymerization is the main reaction in cellulose pyrolysis, while dehydration only occurs at the very slow rate in the whole pyrolytic process [9-10]. With phosphorus-containing compounds, dehydration becomes dominant. The phosphorus-containing compound favors the formation of char and inflammable gases such as carbon

dioxide and water vapor through the two following ways. One is the esterification of C-6 hydroxyls of cellulose before pyrolysis to form phosphate esters, which decomposes into 5,6-cellulose structure and phosphoric acids. The 5,6-cellulose structure further decomposes into char with the phosphoric acid as a catalyst. The phosphoric acid also catalyzes a new cycle of esterification of cellulose. The other function of phosphorus-containing flame retardants is to inhibit the depolymerization of cellulose by enhancing acid hydrolysis of cellulose [4, 10].

Even though both pyrolysis and flame retardancy of nylons have been investigated extensively, the mechanism of phosphorus-containing flame retardants in nylons are less certain [15-23]. Based on previous research [4, 15-17], the phosphorus-containing compounds for nylons may have the following three functions. First, phosphorus-containing compounds decompose to release phosphoric and related acids, which may enhance the dehydration of nylons during pyrolysis and the formation of char. Second, the phosphoric and related acids function as a heat sink by slowing down the oxidation of carbon monoxide to carbon dioxide. Third, the phosphoric and related acids also act through the physical effect mechanism by forming a protective coating on the nylon fibers.

Generally, most phosphorus-containing compounds lower the pyrolysis temperature of nylons because nylons are sensitive to acids produced by the decomposition of phosphorus-containing compounds when heated [4, 15-17]. Levchik [24] studied the effects of ammonia polyphosphate on nylons and proposed the flame retardant mechanisms. The decomposition temperature decreases in the presence of

ammonia polyphosphate. In the case of nylon-6.6, ammonia polyphosphate also enhances the formation of char [25].

### **2.3 Flame retardants for cellulose**

Due to high flammability and commercial demand, the importance of the flame retardancy of cellulose has been realized for a long time and significant efforts have been made in this field [1-9, 20, 26-27]. It is generally agreed that most flame retardants for cellulose function through the condensed phase mechanism. Based on their laundering durability on the treated textiles, flame retardants can be divided into three categories: non-durable, semi-durable and durable [4, 26].

In the case of durable flame retardant finishing of cotton cellulose, there are at least two ways to covalently bond flame retardants to cotton cellulose. The first one is to form a water insoluble crosslinked polymeric network inside cellulose fiber. The representative one is THP-based compounds such as tetrakis (hydroxymethyl) phosphonium chloride (THPC) [2-4]. THPC, initially documented by Hoffman in 1921 [28], is a water-soluble crystalline solid. THPC is prepared from phosphine, formaldehyde, and hydrochloric acid at room temperature [29-30]. Even though THPC reacts with cellulose slowly [31], THPC is able to react with other compounds such as N-methylol compounds including urea and trimethylolmelamine (TMM) [32-33]. Because TMM has three identical methylol groups in each molecule, it reacts with THPC to form a tri-dimensional water insoluble polymeric network on cellulose [4], thus creating durable flame retardancy. The main limitations include fabric tendering, high stiffness, and the loss of the mechanical properties. In order to overcome these limitations, a process called "Proban" was developed by Albright and Wilson Ltd and achieved

commercial success due to excellent laundering durability and limited effect on fabric properties.

In the Proban process (as shown in Fig.2.2, [1-3, 20]), a finishing solution containing precondensate is prepared by the reaction of THPC with urea in a 2:1 molar ratio with a P:N ratio of 1:1. Then, this finishing solution is applied to cellulose fabric through pad-dry-ammonia cure to form a crosslinked polymeric structure. Finally, the fabric thus treated is oxidized by hydrogen peroxide to improve laundering durability and light fastness of dyes.

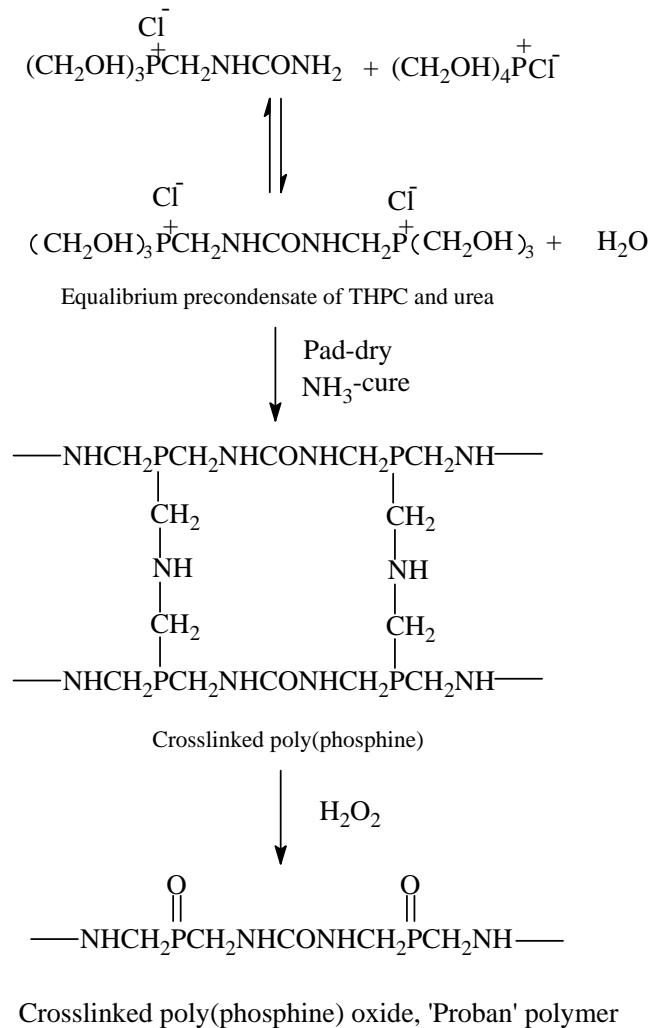


Fig.2.2 Outline chemistry of the Proban Process [2]

However, the use of the ammonia gas curing reactor makes it incompatible with traditional textile mills and results in high costs. In addition, moisture must be controlled carefully to achieve better performance [1-4, 20].

Reacting flame retardants with hydroxyl groups of cellulose is the second way to covalently bond flame retardants to cellulose. The representative flame retardant is N-methylol dimethylphosphonopropionamide (MDPA), also known as Pyrovatex CP, or Pyrovatex CP New, supplied by Ciba [1-6]. It is usually applied together with TMM using phosphoric acid as a catalyst [2-4]. The debate on the role of TMM is still ongoing. Some researchers believe that MDPA mainly reacts directly with hydroxyl groups of cotton cellulose by forming an ether linkage (Fig.2.3). TMM tends to self-condense to form a water insoluble polymeric network on the fabric, and it enhances flame retardancy by the phosphorus-nitrogen synergistic effect [1, 4, 34]. This conclusion was further supported by recent studies [35-36]. Others agree that MDPA may be bound to cellulose through TMM (as shown in Fig.2.4) [2].

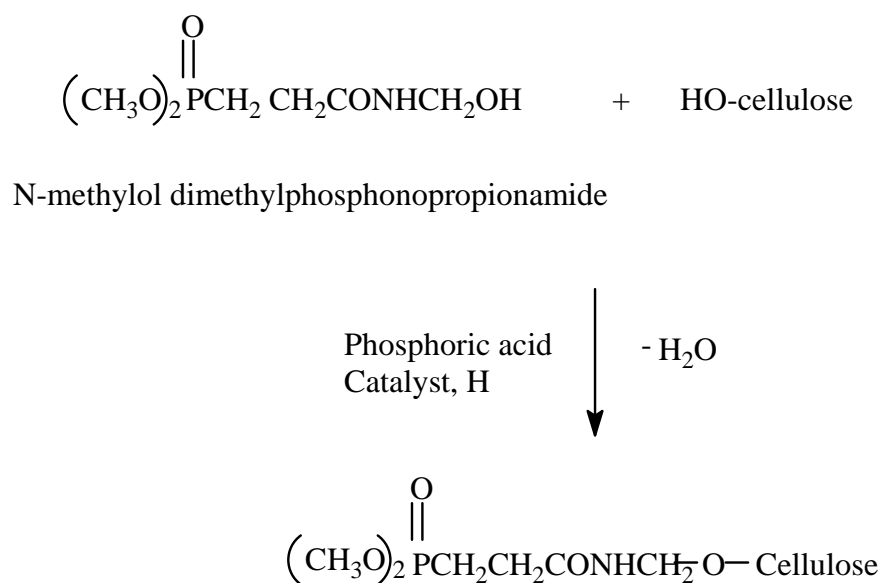


Fig.2.3 Reaction of MDPA with cellulose [1]

Cotton fabric treated by MDPA has a soft handle, excellent laundering durability and high levels of flame retardant performance. However, there are three main disadvantages: First, a strong unpleasant odor is created in the curing process. Second, multiple washing is required to remove acid residue on the treated fabric after curing, thus resulting in additional cost. Third, MDPA also releases a high level of free-formaldehyde, which is a suspected carcinogen.

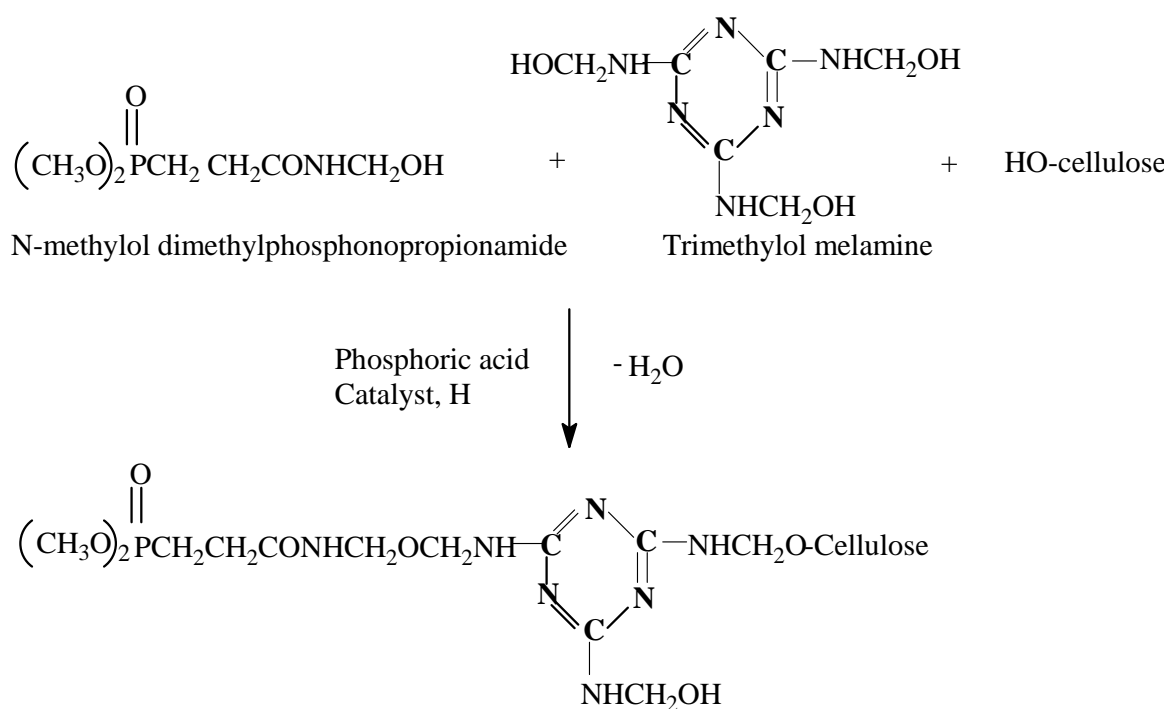


Fig.2.4 Chemistry of Pyrovatex CP system

In recent years, a reactive phosphorus-containing flame retardant has been reintroduced into the market by Akzo Nobel under the trade name of Fyroltex HP (former Fyrol 51) [37]. Fyroltex HP is a hydroxy-functional organophosphorus oligomer (HFPO) which is water soluble and has a high phosphorus content (~20%). The chemical structure of this compound is shown in Fig.2.5 [38].



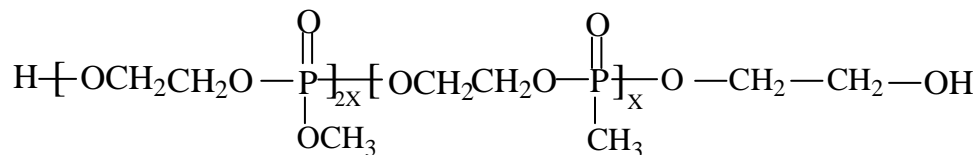


Fig.2.5 Structure of HFPO

Wu and Yang [39-43] found that HFPO cannot react with cotton cellulose directly. A bonding agent is required to create covalent bonding between HFPO and cotton cellulose. It was found that both TMM and dimethyloldihydroxyethyleneurea (DMDHEU) can be used as bonding agents to covalently bond HFPO to cotton cellulose. DMDHEU is more effective as a bonding agent for cotton than TMM, and the bonding formed by DMDHEU between HFPO and cotton is more durable to laundering than that formed by TMM [39]. However, TMM is more effective at enhancing the flame retardant performance because TMM has a significantly stronger phosphorus-nitrogen synergism with HFPO than DMDHEU on the treated cotton fabric. As a result, the cotton fabric treated with HFPO/TMM showed higher flame retardant performance than that treated with HFPO/DMDHEU. In addition, TMM caused less fabric strength loss than DMDHEU [39].

The bonding of HFPO to cotton using TMM as a bonding agent was studied [40]. It was found that HFPO may react with TMM to form a crosslinked polymeric network of HFPO/TMM on the treated cotton. The formation of the crosslinked network not only improves the laundering durability of HFPO bound to cotton but also increases the fabric stiffness. The effects of finish bath pH were also investigated, and the optimum pH of this finish was found to be around 4. The bonding of HFPO to cotton and the performance of the cotton fabric treated with HFPO/TMM were compared with that treated with MDPA/TMM.

DMDHEU was assumed to form a linear polymer (Fig.2.6) by linking HFPO to cotton [41]. However, there is no strong evidence to support this assumption. Therefore, further research is needed to elucidate the bonding of HFPO to cotton using DMDHEU as a bonding agent.

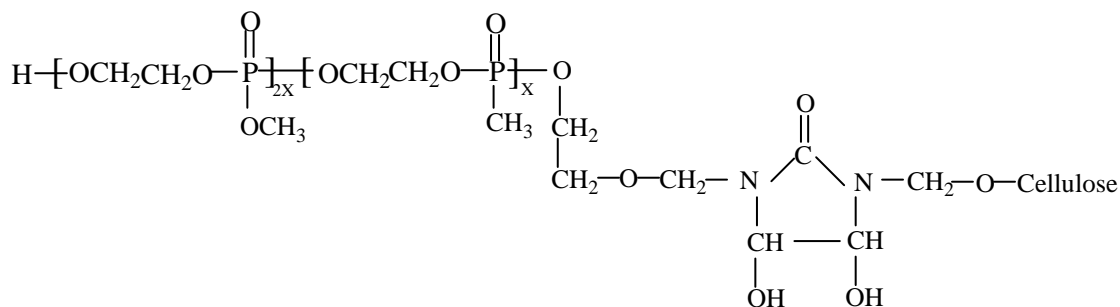


Fig.2.6

A non-formaldehyde flame retardant finish has been investigated for cotton cellulose based on HFPO using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a bonding agent [42-43]. BTCA is able to covalently bond HFPO to cotton, and the cotton treated with HFPO/BTCA can maintain approximately 70% phosphorus retention after 1 laundering cycle [42]. The treated cotton fabric had high initial flame retardant performance, but lost its flame retardant property quickly after several launderings, mainly due to the formation of insoluble calcium salts [43]. Triethanolamine (TEA) was added to the finishing system containing HFPO and BTCA to reduce the formation of water insoluble calcium salt [43].

## 2.4 Flame retardants for nylons

In comparison to cotton, nylons such as nylon 6 and nylon-6.6 have relatively low flammability due to melting and dripping when heated [2-4]. Generally, there are three ways to enhance the flame retardancy of nylons: (1). incorporation of a flame retardant

additive during fiber extrusion; (2). grafting or otherwise bonding fire-retardant groups onto the surface of the polymer; (3). copolymerization of flame-retarding monomers into the polymer chain. The first approach is often used commercially in plastics, whereas the second approach is applied in durable finishing of nylon fibers. In spite of significant efforts, the third approach has never resulted in commercial success, mostly because of the loss of physical properties by fire-retardant nylon copolymers and unfavorable cost-effectiveness. [1-4].

The second way, grafting or otherwise bonding fire-retardant groups onto the surface of the polymer, has been considered as a practical way to impart flame retardancy to nylon fabrics [1-4]. Currently, coating is the most successful way to achieve satisfactory flame retardant performance together with excellent laundering durability [1-2]. However, the serious damage of aesthetic properties limits its application in textiles such as carpets.

Durable flame retardant finishing is considered as an effective way to impart flame retardant property to nylon fabrics. Because of low reactivity of nylons and poor penetration of finishing solutions inside nylons, it is very difficult for flame retardants to achieve laundering durability and a high level of flame retardant performance on nylons [2-4]. In the case of durable flame retardant finishing of nylon fabrics, the flame retardants can be covalently bound to nylon fibers through two ways. One is grafting flame retardants onto polymer chains of nylons. Nylon 6 was first modified by a formaldehyde aqueous solution to produce more reactive groups, and then reacted with MDPA (also known as Pyrovatex CP, or Pyrovatex CP New) to create durable flame retardancy [44]. The other way of bonding flame retardants to nylons is to form a

crosslinked polymeric network that is water insoluble and durable to multiple laundering cycles. One of the typical examples is THPC. THPC is applied to the fabric by a traditional pad-dry-cure procedure together with TMM to form a crosslinked polymeric network, thus enhancing nylons flame retardancy [45].

Among durable flame-retardant finishing agents for nylons, thiourea-based flame retardants are the most effective, and it is applied to nylons through pad-dry-cure procedures [1-4, 15-18]. The main function of flame retardants effective for nylons is to lower the melting point of nylons and enhance dripping of molten nylons [46]. As a result, the dripping of molten nylons takes away heat as well as flame so that the combustion of nylons is inhibited. From this point of view, phosphorus-based compounds were not recommended as an effective flame retardants for nylons because their main function is to enhance the char formation instead of enhancing dripping of the molten nylon [2-4]. In the case of coating, however, phosphorus-containing compounds showed higher efficiency than halogenated compounds [47].

## **2.5 Flame retardants for cotton blend fabric**

Durable flame retardant finishing for cotton blend fabrics including nylon/cotton blend and Nomex/cotton blend fabrics is reviewed in this section. In theory, there are at least two ways to create flame retardant cotton/nylon blend fabrics. One is blending flame retardant cotton fiber with inherent flame-resistant nylon fiber. The other is the flame-retardant finishing of the cotton/nylon blend fabrics [3, 9]. The former approach has never led to a commercial success due to the unavailability of inherent flame-resistant

nylon fiber [17]. Therefore, durable flame retardant finishing of nylon and nylon/cotton blend fabrics seems more practical and feasible.

The major challenge of flame retardant finishing of cotton/nylon blend fabric is due to large difference in properties between cotton and nylon in the cotton/nylon blend fabrics [2-4, 9]. One difference is in chemical/physical properties. Cotton is hydrophilic and chemically active. It is easy for finishing solutions to penetrate inside the cotton and create covalently bond flame retardants to cotton [2-3]. However, nylons can be considered as chemically inert because they only have a small amount of chemical-active end-groups, and most of them may not be available for reaction. Moreover, the finishing solution has poor penetration inside nylon fibers [4, 48]. Therefore, covalent bonding HFPO to nylon is a very challenging problem to be solved for durable flame retardant finishing of nylon and nylon/cotton blend fabrics.

The other difference is thermal property. When heated, nylons often melt and drip away while cotton tends to be char and maintain its texture structure. When blends are heated, the molten nylon sticks to the cotton char instead of flowing-away, thus enhancing the combustion. This phenomenon was defined as “scaffolding effect” [3].

In addition, the flame retardants designed for nylons or cotton may not be effective for cotton/nylon blend fabrics. Most flame retardants for nylons function by decreasing the melting temperature of nylons and thus enhancing dripping of molten nylons [46-47]. In the cotton/nylon blend fabric, however, the molten nylon will wick on the cotton char instead of flowing away, thus enhancing the combustion of cotton/nylon blend fabrics [2-4, 9]. On the other hand, most flame retardants for cotton such as phosphorus-containing compounds are not effective for nylons [4].

Currently, coating is the most effective way to impart durable flame retardant property to cotton blend fabrics. However, serious damage to the fabric handle limits their uses [2]. Generally, durable flame retardant finishing for the cotton/nylon blend fabrics can be divided into two categories based on the numbers of components in the finishing system: single component flame retardant systems and bi-component flame retardant systems.

A single component flame retardant finishing system, which contains only one active flame retardant chemical, is usually used for cotton-rich blend fabrics. THP-based systems such as Proban have been studied as a single component flame retardant finishing system [2]. Even though MDPA (Pyrovatex CP) has a higher flame retardant efficiency on the treated cotton/polyester blend fabric before laundering, it was rejected as a durable flame retardant for the cotton/polyester blend fabric because of poor bonding of MDPA on polyester [48-50].

The use of bi-component flame-retardant finishes was proposed to make flame retardant nylon/cotton blend fabrics [51-54] because it is necessary to render both component fibers flame retardant in blends to achieve satisfactory flame retardancy for the blend [55-56]. The bi-component finishing system contains two flame retardants. One flame retardant is effective for the cotton component, and the other is effective for the nylon component. The preferred flame retardants for the cotton component fiber in blends are THP-based salts such as THPC and THPS. The flame retardants specific for the nylon component include cyclic phosphonate esters. Two flame retardants might be applied in a single-step method [51] or two-step method [52-53]. It has been claimed that satisfactory flame retardance can be achieved initially when the nylon/cotton blend fabric

was treated with a combination of Proban and cyclic phosphonate ester. However, the treated blends lost most flame retardant property after about 15 launderings [51-52].

Johnson et al. applied cyclic phosphonate ester to nylon fiber in the cotton/nylon blend fabric during a continuous dyeing procedure. Then, another flame retardant, typically THPC or THPS, was applied to the fabric [54]. So far, no durable flame retardant finishing for nylon/cotton blend fabrics has been successfully commercialized.

## **2.6 Phosphorus-nitrogen synergism**

Synergism is defined as the phenomenon that the net effect of combination (two flame retardants or one flame retardant and one additive compound) is greater than the additive effect of individual compounds [4, 57]. The phosphorus-nitrogen synergism in textiles, especially cotton cellulose, has been studied intensively and reviewed by several authors [2-4, 9, 57]. In the case of cotton cellulose, certain forms of nitrogen compounds, but not all of them, show the synergistic effect with phosphorus compounds [3-4]. The flame retardant efficiency closely depends on the chemical structures of the nitrogen compounds. Even though urea and melamine have synergistic effects with phosphorus compounds, melamine derivatives have higher efficiency than urea derivatives. However, nitrile compounds have antagonistic effects with phosphorus compounds [58-61]. It is generally agreed that some nitrogen compounds may enhance flame retardancy of phosphorus compounds in the following ways [2-4, 9, 57]. First, nitrogen compounds may increase electrophilicity of the phosphorus atom by formation of P-N bonds instead of P-C bonds, thus improving the phosphorylation of cellulose hydroxyls [62-64]. In addition, the more electron deficient phosphorus has a higher Lewis acidity, which

accelerates the acid-catalyzed degradation of the cellulose. Second, the formation of P-N bonds enhances the char formation and also fixes the phosphorus in the condensed phase by preventing the volatilization of phosphorus.

In the case of nylons, no phosphorus-nitrogen synergism was observed between phospham and nitrogen compounds even though phospham acts like red phosphorus in nylon-4,6 [64-65].

## **2.7 Summary of literature review**

Most studies in the literature are concentrated on the durable flame retardant finishing of individual component fabrics. Since there is a major difference between cotton and synthetic fibers such as nylons in the cotton blends, durable flame retardant finishing of the cotton blend fabrics is still a very challenging topic that textile chemists are facing. In order to achieve satisfactory durable flame retardant performance in the whole blend, it is necessary to covalently bond flame retardants to synthetic fibers in the cotton blends which contain more than 50% synthetic fibers. Therefore, it is important to study the covalent bonding of flame retardants to synthetic fibers in their cotton blends, which will pave a new way to develop new flame retardant finish systems for cotton blend fabrics.

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### CHAPTER 3

## THE BONDING OF A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS OLIGOMER TO NYLON USING DMDHEU/TMM AS A BONDING AGENT

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<sup>1</sup> Yang, H. and Yang, C.Q. Submitted to *Polymer Degradation and Stability*, 06/25/2007

### Abstract

Previously, dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylol-melamine (TMM) were used as crosslinking agents to produce wrinkle-resistant cotton. They were also used as bonding agents in a flame retardant system to covalently bond hydroxy-functional organophosphorus oligomer (HFPO) to cotton. In previous research, the nylon/cotton blend fabric treated with HFPO using a mixture of DMDHEU and melamine-formaldehyde as a bonding system achieved high levels of flame retardant performance and good laundering durability. In this research, the bonding of HFPO to nylon using either DMDHEU or TMM as a bonding agent was investigated. It was found that both DMDHEU and TMM are able to covalently bond HFPO to nylon. The laundering durability of the HFPO bound to nylon is attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU on nylon. It was also found that DMDHEU is more effective as a bonding agent for HFPO to nylon than TMM. Nylon fabric treated with HFPO/DMDHEU shows a higher percent phosphorus retention after multiple launderings than that treated with HFPO/TMM. The nylon fabric treated with HFPO/DMDHEU also shows a limited increase in fabric stiffness in comparison to that treated with HFPO/TMM, which demonstrates significantly higher fabric stiffness due to the self-condensation of TMM.

**Key Words:** DMDHEU, flame retardant finishing, nylon-6.6, organophosphorus chemicals, TMM.

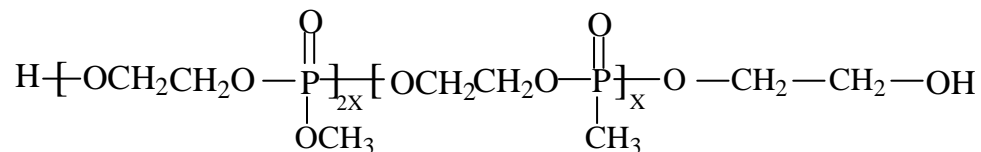
## Introduction

In spite of significant efforts made in the past [1-2], it is still difficult to produce flame-resistant nylon fabrics. Generally speaking, there are three technical approaches to create flame-resistant nylons [1-4]. First, flame-resistant nylon fibers can be produced by copolymerization with flame retardant monomers, but none has been commercialized successfully [1]. Second, incorporation of the flame retardant additives into nylons during the spinning stage is another way to make flame-resistant nylons. However, its major problems include polymer degradation during fiber spinning and the need for a high addition level of additives [1-2]. Third, the flame-retardant finishes have been commonly considered as a practical way to impart flame retardancy to nylon fabrics [1-4]. There are two reviews on the flame retardant finishing for nylon fabrics [1-2]. The most successful durable flame retardant finishes for nylon fabrics are based on thiourea-formaldehyde, and the limitation of this finish includes high stiffness [6].

In comparison to the individual component fabric, it is more difficult to achieve satisfactory flame retardant performance on the nylon/cotton blend fabric due to the 'scaffolding effect' [7]. Currently, coating is the most successful approach to impart durable flame retardancy to the cotton/synthetic fiber blend fabric. However, this technical approach severely alters the aesthetic property of those treated textile fabrics [6]. In the literature [8-11], two flame retardant chemicals or two flame retardant finishes are usually needed to impart durable flame retardant property to the nylon/cotton blend fabric: one is specific for the cotton component and the other is designed for the nylon component. The typical flame retardants for the nylon component are the cyclic phosphonate esters, which can be fixed inside nylons through a pad-dry-thermosol

process [6] or exhausted in a dye bath [11]. However, most cyclic phosphonate esters fixed in nylons are only durable to 15 laundering cycles [9]. In addition, the cyclic phosphonate esters are not sustainable on the cotton component in the blend fabrics [6]. Hence, another flame retardant which is specific for the cotton component is required [8-11]. So far, no technical approach has been commercially successfully to make flame retardant nylon/cotton blend fabrics.

In previous research, a durable flame retardant finish based on hydroxy-functional organophosphorus oligomer (HFPO, also known with the trade name FYROL 51 or FYROLTEX HP, both names for the same product and both trademarks of Akzo-Nobel or, later, Supresta, as shown in Scheme 3.1) was developed for cotton [12-19]. DMDHEU, TMM, and 1,2,3,4-butanetetracarboxylic acid (BTCA) were used to form covalent bonding between cotton cellulose and HFPO [12-19]. TMM/HFPO is able to form a crosslinked polymeric network on cotton at appropriate TMM/HFPO molar ratio [19]. The bonding of HFPO to cotton by TMM and the performance of the cotton fabric treated with HFPO/TMM were compared with that of MDPA by TMM [16-17]. A non-formaldehyde flame retardant finish for the Nomex/cotton blend fabric using BTCA as a bonding agent and triethanolamine (TEA) as a co-reactant was developed [20]. In addition, HFPO was applied to nylon/cotton blend fabric using a mixture of DMDHEU and melamine-formaldehyde as a bonding system. The mixture of melamine-formaldehyde and DMDHEU was able to covalently bond HFPO to nylon fabrics [21], and the nylon/cotton blend fabric treated with HFPO using a mixture of DMDHEU and TMM as a bonding system showed high levels of flame retardant performance and good laundering durability [21].



Scheme 3.1 Structure of HFPO

In this research, the bonding of HFPO to nylon using either DMDHEU or TMM as a bonding agent was studied. DMDHEU was compared with TMM as a bonding agent for HFPO to nylon.

## Experimental

### Materials

Two kinds of fabrics were used in this study: (1) 100% nylon-6.6 woven fabric (Testfabrics Style 306A) weighing 59 g/m<sup>2</sup>; (2) the 50%/50% nylon/cotton Battle Dress Uniform (BDU) pure finish ripstop fabric printed with three-color Day Desert camouflage weighing 220 g/m<sup>2</sup> (Military specification: MIL-C-44031 CL1) was supplied by Bradford Dyeing Association, Inc. Bradford, RI. HFPO, under the commercial name of “Fyroltex HP” (also known as “Fyrol 51”, CA Registry No. 70715-06-9), was supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. N-methylol dimethylphosphonopropionamide (MDPA), marked under the commercial name of “Pyrovatex CP New” (CA Registry No. 20120-33-6), was supplied by Ciba Specialty Chemicals, High Point, North Carolina. DMDHEU was a commercial product (44% solid content) with the trade name of “Freerez 900” supplied by Noveon, Cleveland, Ohio. TMM was a commercial product (80% solid content) with the trade name of “Aerotex M-3”, supplied by Noveon, Cleveland, Ohio. The catalyst was an NH<sub>4</sub>Cl-based commercial product under the trade name of “Catalyst RD”, supplied by Eastern Color & Chemical, Greenville, South Carolina.

### **Fabric Treatment and Laundering Procedures**

The fabric was treated in the following procedures. First, the fabric was immersed in a finishing solution and passed through a laboratory padder with two dips and two nips. Then, the nylon fabric thus treated was dried at 90°C for 1.5 min, and the nylon/cotton blend fabric thus treated was dried at 90°C for 3 min. Finally, all treated fabric samples were cured in a Mathis curing oven at 165°C for 2 min. All concentrations used in this study are based on weight of bath (w/w, %), and concentrations of HFPO, DMDHEU and TMM in all solutions were based on the solid content of the chemicals in those chemical products. The wet pick-up of the nylon-6.6 fabric was 52±2%, and the wet pick-up of the nylon/cotton blend fabric was 76±2%. After curing, the treated fabric was subjected to a specified number of laundering cycles using “AATCC Standard Detergent 1993.” The laundering process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics after Repeated Home Laundering”), and the water temperature of laundering was approximately 46°C.

### **Evaluation of the Flame Retarding Performance of the Fabrics**

The vertical flammability of the fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the fabric was measured according to ASTM Standard Method D2863-97.

### **Evaluation of the Fabric Stiffness**

The fabric stiffness was measured according to ASTM Standard Method D6828-02 using the Handle-O-Meter tester (Model 211-300), manufactured by Thwing-Albert instrument company, Philadelphia, U.S.A. The slot width used in this study was 5 mm, and the beam size used in this study was 1000 g. The fabric stiffness reported in this

study was the mean of total stiffness obtained from 5 specimens.

### **Determination of Phosphorus Concentration on the Treated Fabric**

Approximately 2 g of the treated fabric sample taken from three different parts of a “10×12” fabric specimen were ground into powder in a Wiley mill to improve sample uniformity. Then, 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were added to 0.1 g of the powder in a beaker. Finally, 10 ml of 30% H<sub>2</sub>O<sub>2</sub> were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until a dense SO<sub>3</sub> vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration. The percent phosphorus retention was calculated by dividing the phosphorus concentration of the fabric after laundering by that of the fabric before laundering.

## **Results and Discussion**

### **The bonding of HFPO to nylon by DMDHEU**

The nylon 6.6 fabric was first treated with the combination of 32% HFPO and DMDHEU at different concentrations, cured at 165 °C for 2min, and finally subjected to 1 and 10 laundering cycles. The phosphorus concentration and the percent phosphorus retention of the nylon fabric thus treated are shown in Figure 3.1 and Table 3.1, respectively. When the DMDHEU concentration increases from 1% to 8%, the phosphorus concentration of the treated nylon fabric after 1 laundering cycle increases

from 0.21% to 1.75%. The corresponding phosphorus retention also increases from 9% to 75%, respectively. After 10 laundering cycles, 1.04% phosphorus (45% retention) remains on the fabric treated with 8% DMDHEU.

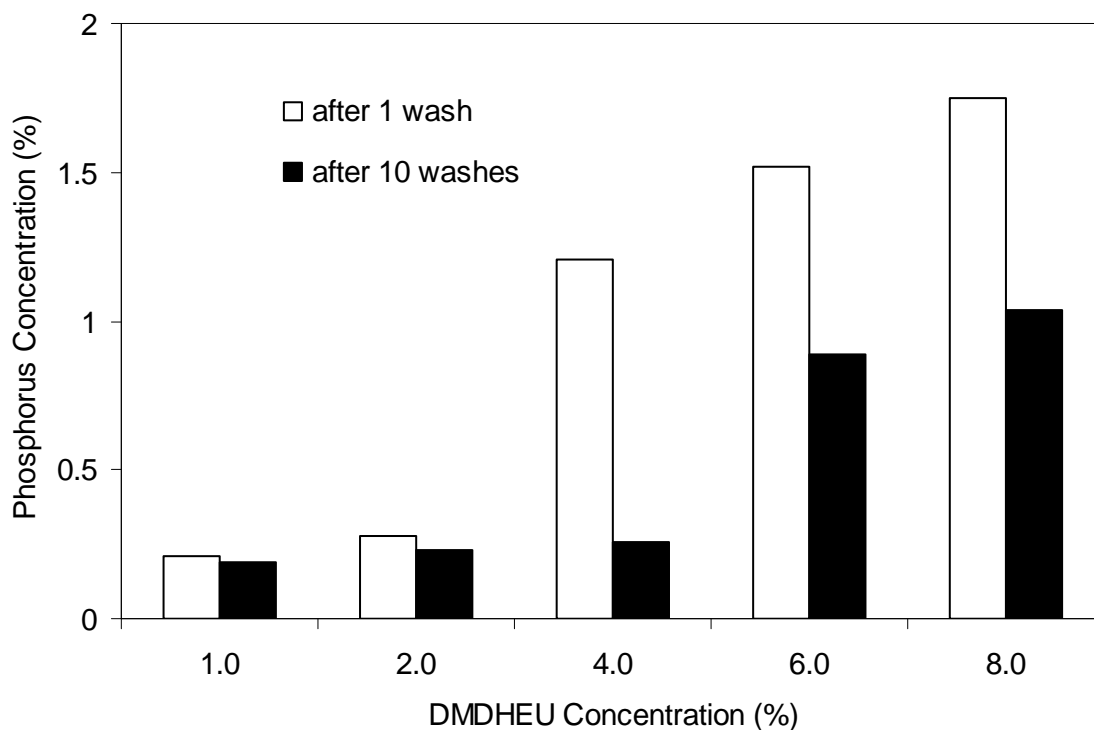


Figure 3.1 The phosphorus concentration of the nylon-6.6 fabric treated with 32% HFPO and DMDHEU cured at 165°C for 2 min and finally subjected to 1 and 10 laundering cycles versus TMM concentration.



Table 3.1 The percent phosphorus retention of the nylon 6.6 fabric treated with 32% HFPO and DMDHEU at different concentrations, cured at 165°C for 2min and finally subjected to 1 and 10 laundering cycles.

HFPO (%)	DMDHEU (%)	Molar Ratio (hydroxyl/hemi-acetal)*	Phosphorus Retention (%)	
			after 1 laundering cycle	after 10 laundering cycles
32	1	6.19	9	8
32	2	3.10	12	10
32	4	1.55	52	11
32	6	1.03	65	38
32	8	0.77	75	45

\* The molar ratio of the hydroxyl group of HFPO to the hemi-acetal group of DMDHEU.

The concentration of the terminal amine groups of nylon 6.6 was reported as 40  $\mu\text{mole/g}$  in the literature [22]. Assuming that (1) all terminal amine groups of the nylon fabric react with HFPO and (2)  $x=1$  in Scheme 1 through DMDHEU as a ‘bridge’, the maximum phosphorus concentration on the nylon 6.6 fabric is 0.37% (w/w). Due to the poor penetration of the finishing solution into the fiber interior and the low reactivity of the terminal amine groups as a result of a high degree of crystallinity and H-bonding in nylon 6.6, the concentration of phosphorus bound to the fabric by nylon’s terminal groups should be significantly less than the theoretical maximum value (0.37%). The phosphorus concentration of nylon fabric treated with 32% HFPO after 1 and 10 laundering cycles is 0.20% and 0.17%, respectively. The data presented here show that the phosphorus concentration on the nylon fabric after 1 laundering cycle reaches 1.21, 1.52 and 1.75 when 4, 6 and 8% DMDHEU, respectively, is used for the treatment. The

HFPO bound to the fabric is also durable to multiple launderings as shown in Figure 3.1 and Table 3.1. Therefore, the majority of HFPO on the fabric must be bound to nylon by the reactions of DMDHEU, not the reactions of nylon's terminal groups.

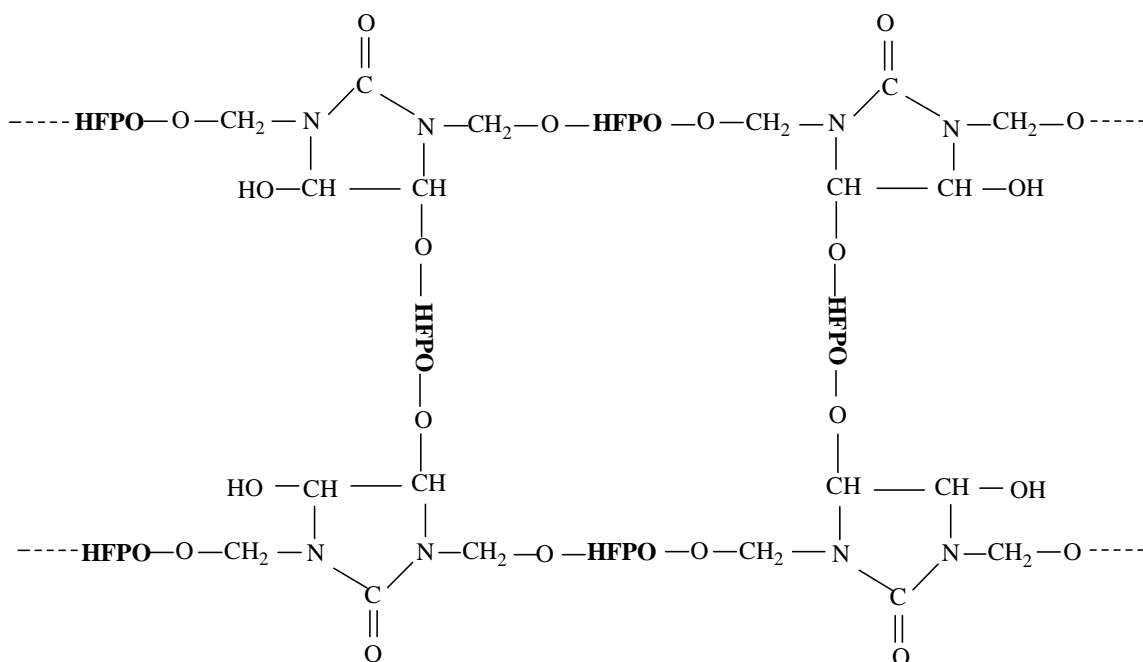
In order to elucidate the bonding mechanism of HFPO to nylon, we measured the stiffness of the fabric treated with DMDHEU and that treated with HFPO and DMDHEU (Table 3.2). The fabric is first treated with a solution containing DMDHEU alone at different concentrations or the combination of 32% HFPO and DMDHEU at different concentrations, cured at 165 °C for 2min and finally subjected to 1 laundering cycle. The stiffness of the untreated fabric is 50 grams. When the nylon fabric is treated with DMDHEU alone, the stiffness of treated nylon fabric appears to change very little (52-54 grams) as DMDHEU concentration increases (Table 3.2). In the presence of both HFPO and DMDHEU, however, the stiffness of the nylon fabric shows a significant increase (52-61 grams) as the DMDHEU concentration increases from 1 to 8% (Table 3.2). The phosphorus concentration on the treated fabric increases from 0.21 to 1.75% at the same DMDHEU concentration range (Table 3.1).

DMDHEU has four chemically active hemi-acetal groups, and each HFPO molecule has two hydroxyl groups. The simultaneous increase in both the phosphorus retention after launderings and the increase in the fabric stiffness as the DMDHEU concentration is increased shown here suggests that a crosslinked polymeric network probably forms on the fabric as shown in Scheme 3.2, and the bonding of HFPO to the nylon fabric and the retention of HFPO on the fabric after multiple launderings is probably attributed to the formation of the polymeric network on the fabric. The formation of the crosslinked network also causes modest increase in fabric stiffness as

shown in Table 3.2. The data presented in Table 3.2 also show that the fabric treated with DMDHEU alone does not show a significant increase in its stiffness. Thus, the data suggest that DMDHEU probably does not form a crosslinked network by self-condensation.

Table 3.2 The stiffness of the nylon-6.6 fabric treated with a finishing solution containing DMDHEU at different concentrations or a finishing solution containing 32% HFPO and DMDHEU at different concentrations, then cured at 165°C for 2min, and finally subjected to 1 laundering cycle.

DMDHEU Concentration (%)	Stiffness (grams)	
	DMDHEU	32% HFPO+DMDHEU
1	52	52
2	53	56
4	54	59
6	52	60
8	52	61
Control	50	



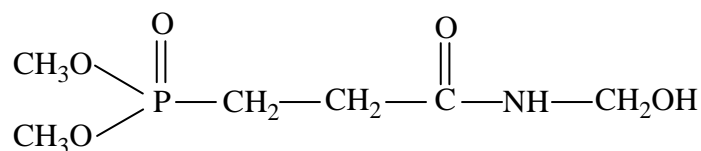
Scheme 3.2 Crosslinked polymeric network of HFPO/DMDHEU

For the purpose of further elucidating the bonding mechanism of HFPO to nylon by DMDHEU, we applied MDPA, as shown in Scheme 3.3, to the nylon fabric. The MDPA molecule has only one methylol group which may react with the terminal amine groups on nylon. The nylon 6.6 fabric was treated with 32% MDPA and DMDHEU at different concentrations, cured at 165 °C for 2min and finally subjected to 1 laundering cycle. The phosphorus concentration and stiffness of the nylon-6.6 fabric thus treated is presented in Table 3.3. The phosphorus concentration on the nylon fabric treated with MDPA without DMDHEU is 2.53% before laundering, and it becomes 0.23% after 1 laundering cycle, representing 9% retention (Table 3.3). In the presence of DMDHEU, the phosphorus concentration on the fabric thus treated appears to be unchanged at 0.23-0.26% (Table 3.3). The small amount of MDPA bound onto the nylon fabric is probably due to (1) the reaction between MDPA and the terminal amine group on the fiber and (2) physical

adsorption. The phosphorus concentration on the fabric increases little as the DMDHEU concentration increases (Table 3.3). The stiffness of the treated nylon fabric also remains unchanged at 52-53 grams (Table 3.3).

Table 3.3 The phosphorus concentration and stiffness of the nylon-6.6 fabric treated with 32% MDPA and DMDHEU at different concentrations, then cured at 165°C for 2 min, and finally subjected to 1 laundering cycle.

MDPA (%)	DMDHEU (%)	PHOSPHORUS CONCENTRATION (%)	STIFFNESS (GRAMS)
32	0	0.23	52
32	2	0.26	52
32	4	0.25	53
32	6	0.24	53
32	8	0.23	52
32	0	2.52% (before laundering)	-



Scheme 3.3 MDPA

HFPO is a bifunctional compound and it is able to form a crosslinked polymeric network by its reaction with DMDHEU. Unlike HFPO, MDPA is a monofunctional agent

and has only one methylol group in its molecule. Therefore, MDPA is not able to form a crosslinked polymeric network in the presence of DMDHEU. The data presented here shows (1) the amount MDPA bound to nylon is small and is independent of the amount of DMDHEU used, and (2) the fabric stiffness does not increase as the DMDHEU concentration increases. Those facts are consistent with the hypothesis that HFPO reacts with DMDHEU on the nylon fabric to form a crosslinked polymeric network as shown in Scheme 3.2.

### **The bonding of HFPO to nylon by TMM**

The nylon 6.6 fabric was treated with 32% HFPO and TMM at different concentrations, cured at 165 °C for 2min, and finally subjected to 1 and 10 laundering cycles. The phosphorus concentration and the percent phosphorus retention of the nylon fabric thus treated are presented in Figure 3.2 and Table 3.4, respectively. The phosphorus concentration on the treated nylon fabric after 1 laundering cycle increases from 0.24% to 1.76% (Figure 3.2) and the percent phosphorus retention increases from 9% to 67% (Table 3.4) as the TMM concentration is increased from 1% to 8%, respectively. One observes a similar trend when the treated fabric was subjected to 10 laundering cycles (Figure 3.2 and Table 3.4). The data presented here indicate that TMM is able to covalently bond HFPO to the nylon fabric. The data also show that the relative amount of HFPO bound to cotton depends on the molar ratio of the hydroxyl of HFPO to the methylol groups of TMM. The phosphorus retention on the fabric after one laundering increases very little (from 9 to 10%) as the TMM concentration increases from 1 to 2% and accordingly the molar ratio (hydroxyl of HFPO to methylol groups of

TMM) decreases from 10.0 to 5.01 (Table 3.4). When the TMM concentration increases from 2 to 4% and the molar ratio of hydroxyl to methylol groups decreases from 5.01 to 2.51, however, the phosphorus retention increases drastically from 10 to 36% (Table 3.4). The phosphorus retention increases further to 67% as the molar ratio of hydroxyl to methylol groups decreases further to 1.25 (Table 3.4).

Table 3.4 The percent phosphorus retention of the nylon 6.6 fabric treated with 32% HFPO and TMM at different concentrations, cured at 165°C for 2 min and finally subjected to 1 and 10 laundering cycles.

HFPO (%)	TMM (%)	Molar Ratio (hydroxyl/methylol)*	Percent Phosphorus Retention (%)	
			after 1 laundering cycle	after 10 laundering cycles
32	1	10.02	9	6
32	2	5.01	10	8
32	4	2.51	36	17
32	6	1.67	50	28
32	8	1.25	67	35

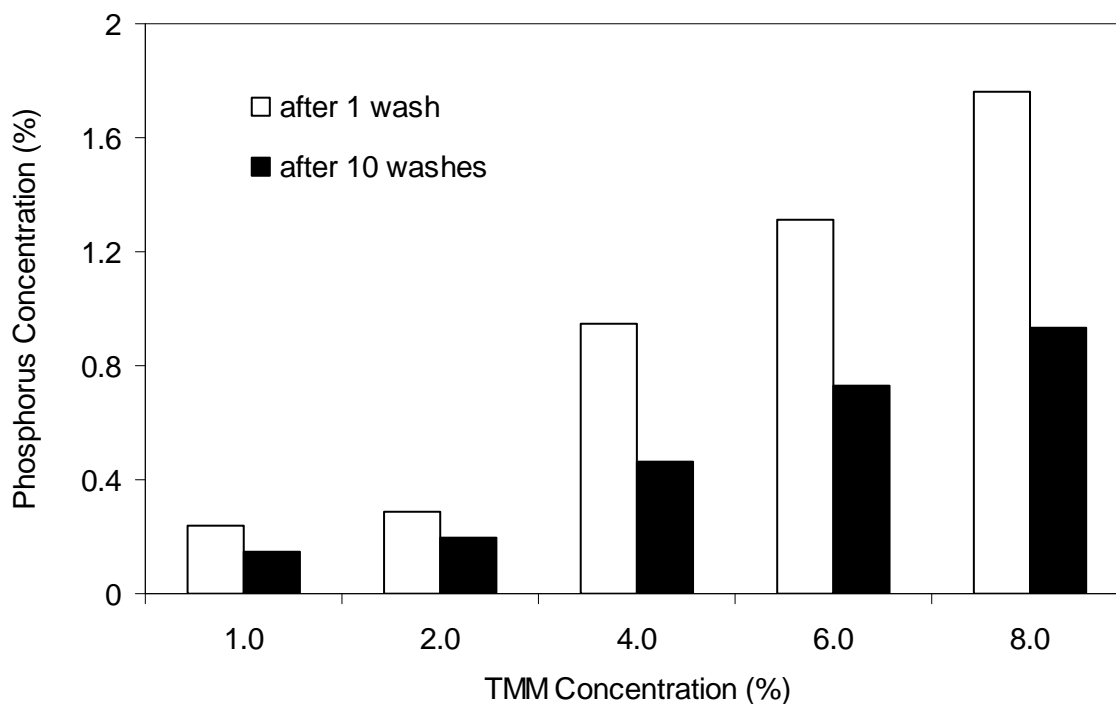


Figure 3.2 The phosphorus concentration of the nylon-6.6 fabric treated with 32% HFPO and TMM, cured at 165°C for 2 min and finally subjected to 1 and 10 laundering cycles versus TMM concentration.

We also investigated the change in the stiffness of the nylon fabric treated with TMM alone and with HFPO/TMM. The nylon fabric was treated with TMM at different concentrations, cured at 165 °C for 2 min and finally subjected to 1 laundering cycle. The stiffness of nylon fabric thus treated increases from 51 to 110 grams as the TMM concentration is increased from 1% to 8%, respectively (Figure 3.3). TMM, a tri-functional reagent, apparently undergoes self-condensation to form a three-dimensionally crosslinked network. TMM forms crosslinking by forming methylene (Scheme 3.4) under neutral and acidic conditions [23-25]. When pH is above 9, TMM crosslinks by forming dimethylene ether bond, as shown in Scheme 3.5 [23-25]. The increase in the stiffness of



the nylon fabric treated with TMM shown in Figure 3.3 is evidently attributed to the self-condensation of TMM and to the self-crosslinked polymeric network on the fabric. One also observes that the slope of the curve (stiffness vs. TMM concentration) increases as the TMM is increased more significantly to 6% and beyond, indicating the formation of self-condensed network dependent on the amount of TMM.

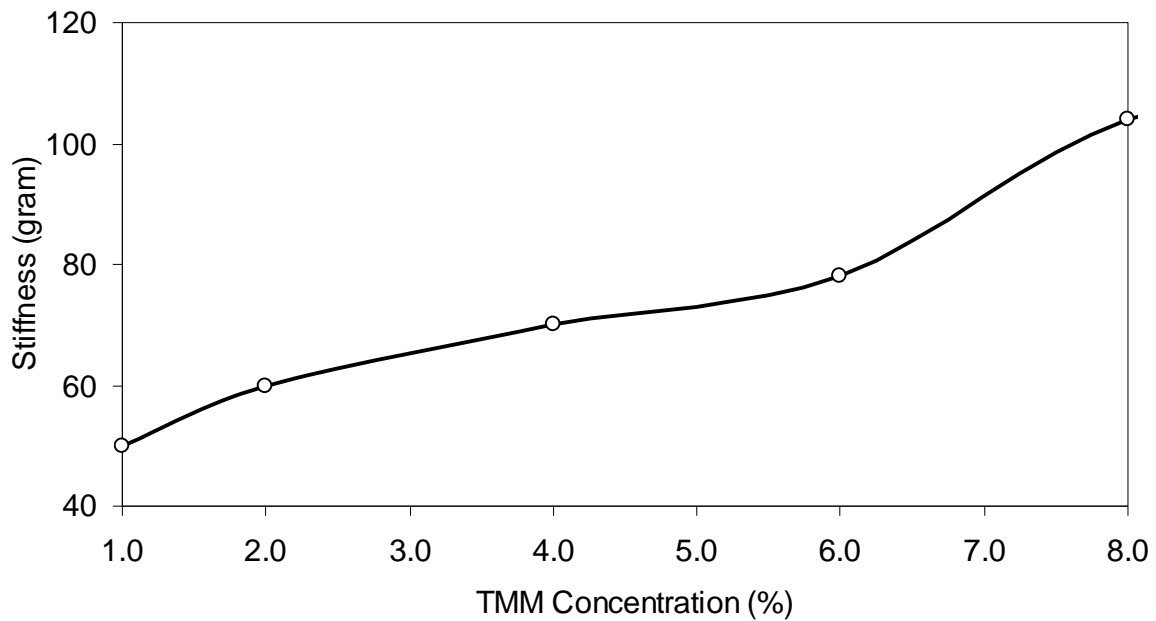
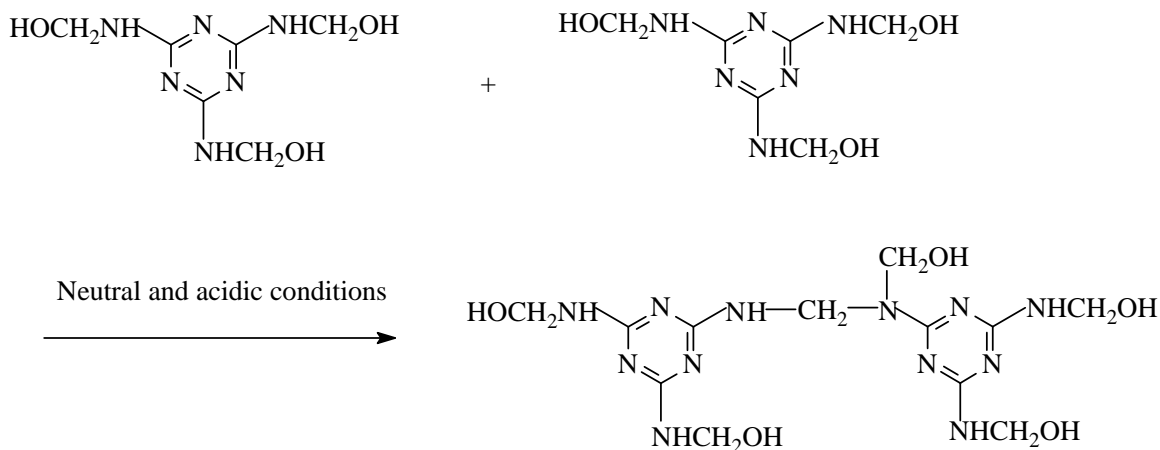
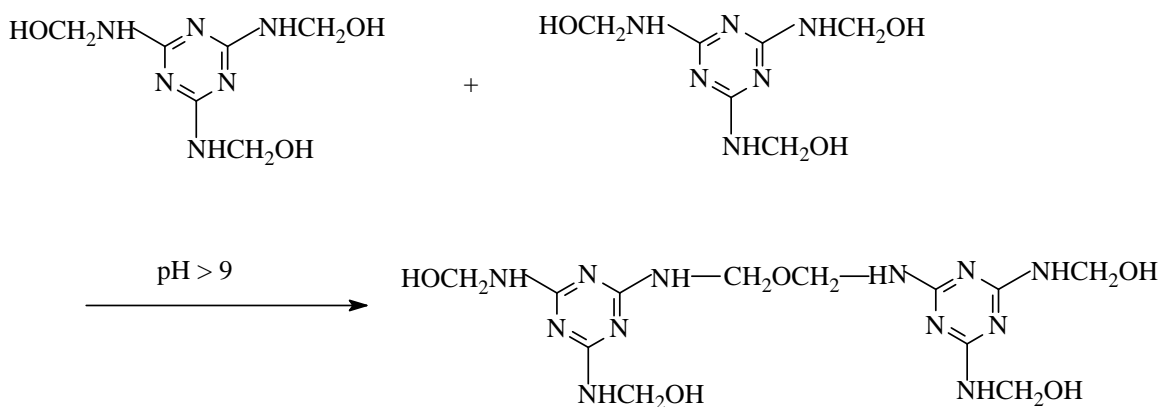


Figure 3.3 The stiffness of the nylon fabric treated with TMM and cured at 165°C for 2 min and finally subjected to 1 laundering cycle versus the TMM concentration.



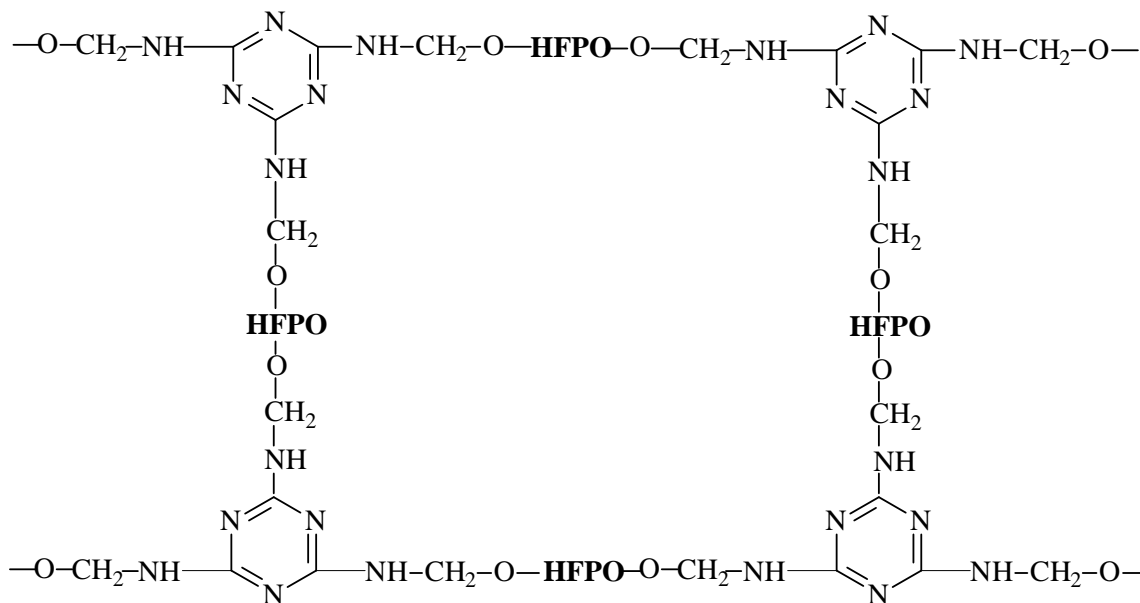
Scheme 3.4



Scheme 3.5

The nylon 6.6 fabric was treated with 6% TMM and HFPO at different concentrations, cured at 165 °C for 2 min and finally subjected to 1 laundering cycle. The phosphorus concentration of the nylon fabric thus treated is presented in Table 3.5. The stiffness and percent phosphorus retention after 1 laundering of the treated fabric are plotted against the HFPO concentration in Figure 3.4. The stiffness of nylon fabric treated with the combination of 6% TMM and 8% HFPO at the hydroxyl-to-methylol molar ratio of 1.67 is 150 grams, which is approximately twice of that for the nylon fabric treated with 6% TMM alone (76 grams shown in Figure 3.1). The increased stiffness of

the nylon fabric treated with the combination of HFPO and TMM is probably attributed to the formation of polymeric HFPO/TMM crosslinked network. The reaction between TMM and HFPO to form a crosslinked polymeric network and the crosslinking of TMM by self- condensation takes place simultaneously. Shown in Scheme 3.6 is an “ideal” crosslinked polymeric network of HFPO/TMM.



Scheme 3.6 Crosslinked Polymeric Network of TMM/HFPO

The data presented in Figure 3.4 show that as the concentration of HFPO is increased from 8% to 40% at a constant 6% TMM and the hydroxyl-to-hemiacetal molar ratio (HFPO/TMM) increases from 0.6 to 3.1 accordingly, the stiffness of treated nylon fabric decreases from 150 to 69 grams and the percent phosphorus retention after one laundering decreases from 85% to 40%, respectively. One also observes that as the HFPO concentration increases, the percent phosphorus retention decreases whereas the phosphorus concentration on the fabric increases (Figure 3.4 and Table 3.5). Thus the data suggest that TMM reacts with the hydroxyl groups of HFPO and TMM also self-

condenses to form crosslinking. Consequently HFPO is covalently bound to TMM by forming two linkages in the HFPO/TMM crosslinked network and by forming one single linkage with TMM, as shown in Scheme 3.7. The reaction of HFPO with TMM reduces the self- crosslinking among the TMM molecules, thus causing the fabric stiffness to decrease as shown in Figure 3.4. As the HFPO concentration increases, the percent phosphorus retention after laundering also decreases along with the fabric stiffness. Thus the data also indicate that the HFPO bound to the fabric by the HFPO/TMM crosslinked network has higher laundering durability than that by HFPO-TMM single linkage.

Table 3.5 The phosphorus concentration of the nylon fabric treated with 6% TMM and HFPO at different concentrations, cured at 165°C for 2 min and finally subjected to 1 laundering cycle versus the TMM concentration.

HFPO (%)	TMM (%)	Molar ratio (hydroxyl/methylol)*	Phosphorus concentration (%)	
			Before laundering	After 1 laundering
8	6	0.6	0.77	0.65
16	6	1.3	1.50	0.96
24	6	1.9	2.55	1.18
28	6	2.2	2.75	1.27
32	6	2.5	2.99	1.31
36	6	2.8	3.32	1.33
40	6	3.1	3.45	1.37

\* The molar ratio of the hydroxyl group of HFPO to the methylol group of TMM.

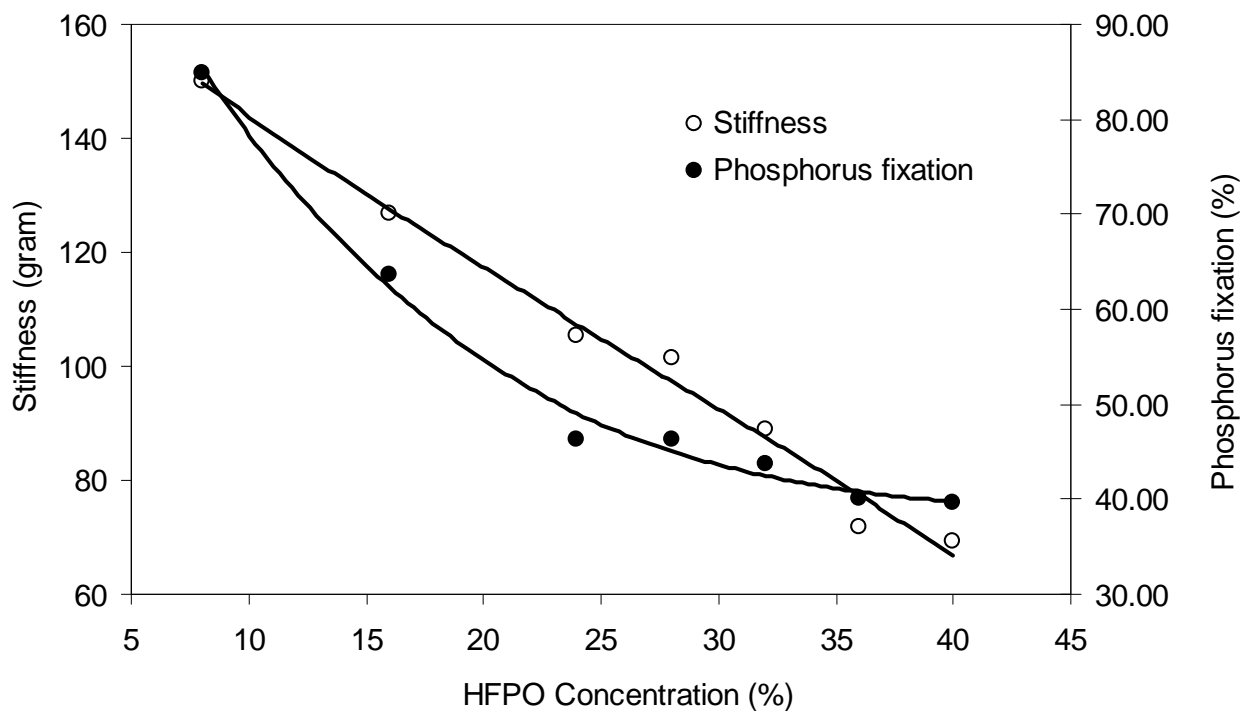
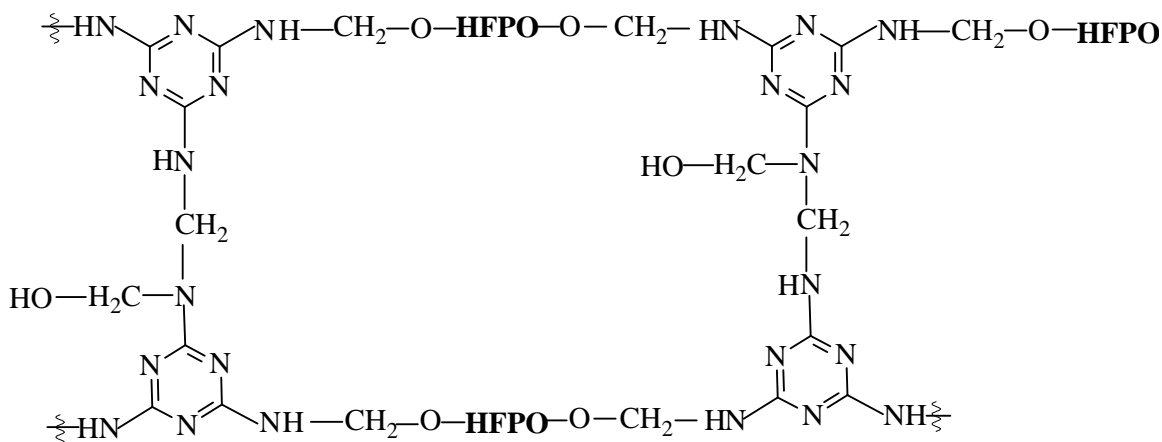
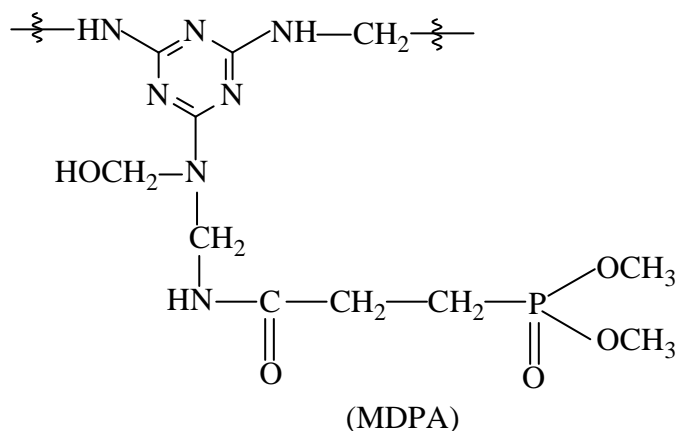


Figure 3.4 The stiffness and phosphorus fixation of the nylon fabric treated with 6% TMM and HFPO at different concentrations, cured at 165°C for 2 min and finally subjected to 1 laundering cycle versus the TMM concentration.



Scheme 3.7. The TMM self-crosslinked network and the reaction of HFPO/TMM

The nylon fabric is treated with 32% MDPA and TMM at different concentrations, cured at 165 °C for 2 min and finally subjected to 1 laundering cycle. The stiffness, phosphorus concentration and percent phosphorus retention of nylon fabric thus treated after 1 laundering cycle is shown in Table 3.6. The stiffness of nylon fabric treated with 32% MDPA without TMM is the same as that of the untreated nylon fabric (50 grams). As the TMM concentration is increased from 1% to 6%, the stiffness of the treated nylon fabric increases from 51 to 82 grams. Since MDPA is a monofunctional compound, it is impossible for MDPA to form a crosslinked polymeric network on the nylon fabric by reacting with TMM. The increase in the stiffness of the treated fabric is obviously due to the crosslinking of TMM by self-condensation. One also observes that the phosphorus concentration of nylon fabric increases from 0.23% to 0.84%, representing an increase in phosphorus retention from 10% to 38%, respectively (Table 3.6). As shown in Scheme 3.8, the increase in the phosphorus retention on the nylon fabric as a result of increasing TMM concentration is attributed to the reaction between MDPA and methylol groups of TMM's self-crosslinked polymeric network.



Scheme 3.8. TMM self-crosslinked network and the reaction of MDPA/TMM

Table 3.6 The stiffness, phosphorus concentration and percent phosphorus fixation of the nylon-6.6 fabric treated with 32% MDPA and TMM at different concentrations, cured at 165°C for 2 min, and subjected to 1 laundering cycle.

MDPA (%)	TMM (%)	Stiffness (grams)	Phosphorus Concentration (%)	Phosphorus Retention (%)
32	0	50	0.23	10
32	2	51	0.35	16
32	4	52	0.43	19
32	6	82	0.84	38

#### **Performance of the treated nylon and nylon/cotton blend fabrics**

We applied three different formulas (HFPO/DMDHEU, HFPO/TMM and MDPA/TMM) to the 50/50 nylon/cotton fabric. The nylon/cotton fabric samples treated with the three formulas have approximately the same phosphorus concentration (~3.80%) before laundering. The fabric was cured at 165°C for 2 min and finally subjected to 10 laundering cycles. The LOI, char length, phosphorus concentration and percent phosphorus retention of the fabric thus treated are presented in Table 3.7. The nylon/cotton fabric treated with MDPA has 1.20% phosphorus retained and has a low LOI (23.9%) and it failed the vertical flammability test. The fabric samples treated with HFPO/DMDHEU and HFPO/TMM has LOI of 27.3 and 27.1%, respectively, and passes the vertical flammability test.

The fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM retains 58% and 55%, respectively, of the original HFPO after 10 launderings (Table 3.7). For the fabric treated with MDPA, only 32% of the flame retardant remains after 10

laundering. Our previous research shows that MDPA has excellent flame retardant performance and high laundering durability on cotton [16], but is not effective on the nylon/cotton blend fabric. The monofunctional MDPA is incapable of forming a crosslinked polymeric network as discussed above. The MDPA/TMM system is not suitable for the flame retardant finishing of the cotton/nylon blend fabric.

Table 3.7 The LOI, char length, phosphorus concentration and percent phosphorus retention of 50/50 nylon/cotton blend fabric treated with different flame retardants and different binders and subjected to 10 laundering cycles.

Flame Retardant	Bonding Agent	Catalyst	LOI (%)	Char length (mm)	Phosphorus Concentration (%)	Phosphorus Retention (%)
HFPO 32%	DMDHEU 6%	NH <sub>4</sub> Cl 0.12%	27.3	75	2.20	58
HFPO 32%	TMM 6%	NH <sub>4</sub> Cl 0.12%	27.1	77	2.10	55
MDPA 45%	TMM 6%	H <sub>3</sub> PO <sub>4</sub> 2.0%	23.9	>300	1.20	32



## Conclusions

Both DMDHEU and TMM are able to covalently bond HFPO to nylon 6.6 fabric probably by the formation of a crosslinked HFPO/DMDHEU and HFPO/TMM polymeric network. DMDHEU is more effective as a bonding agent for HFPO to nylon than TMM, and the nylon fabric treated with HFPO/DMDHEU shows higher percent retention of HFPO after multiple launderings than that treated with HFPO/TMM. In addition, the nylon fabric treated with HFPO/DMDHEU demonstrates less an increase in fabric stiffness than that treated with HFPO/TMM. Both HFPO/DMDHEU and HFPO/TMM are effective as durable flame retardants for the nylon/cotton blend, and the details will be discussed in our next paper.

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**CHAPTER 4**

**THE BONDING OF A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS**

**OLIGOMER TO COTTON USING DMDHEU AS A BONDING AGENT**

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<sup>1</sup> Yang, H. and Yang, C.Q. To be submitted to *Polymer Degradation and Stability*.

### Abstract

In previous research, it was found that dimethyloldihydroxyethyleneurea (DMDHEU) is an effective bonding agent to covalently bond hydroxy-functional organophosphorus oligomer (HFPO) to nylon through the formation of a crosslinked polymeric network. Previously, DMDHEU was also used as a bonding agent to create covalent bonding between HFPO and cotton. In this study, the bonding of HFPO to cotton using DMDHEU as a bonding agent was investigated. It was found that the stiffness of the cotton fabric treated with DMDHEU appears to be unchanged. In the presence of HFPO, however, DMDHEU not only improves the laundering durability of HFPO bound to the treated cotton fabric but also increases the fabric stiffness. This is attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/cotton cellulose on the treated cotton fabric at an appropriate molar ratio. Increasing the DMDHEU concentration leads to a higher number of crosslinks and the involvement of more hydroxyl groups of cotton cellulose in the whole crosslinked polymeric network, thus improving laundering durability of HFPO bound onto the cotton fabric and also increasing the fabric stiffness. In order to lower the stiffness of treated fabric, a high ratio of HFPO/DMDHEU is recommended in the formulas. In comparison to magnesium chloride, ammonium chloride is a preferred catalyst for HFPO/DMDHEU in cotton because it causes less strength loss.

**Key Words:** Cotton, Crosslinking, Durable flame retardant finishing, DMDHEU, Organophosphorus chemicals, Phosphorus-nitrogen synergism.

## Introduction

Cotton is one of the most important textile fibers but is highly flammable.

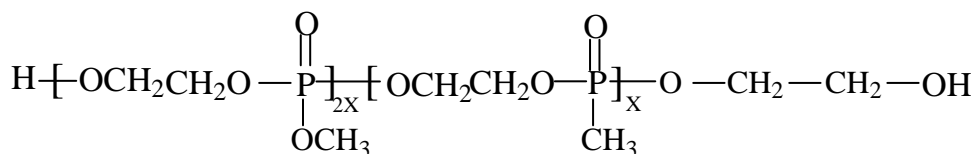
Therefore, flame retardant finishing of cotton and cotton blend fabrics is sometimes necessary, and related research is still ongoing to meet regulations [1-5].

Previously, two successful durable flame retardant finishing systems have been developed for cotton [1-2]. One is reactive organophosphorus chemicals such as N-methylol dimethylphosphonopropionamide (MDPA) with the commercial name of “Pyrovatex CP” and “Pyrovatex CP New” (trademarks of Ciba Corp). Even though it is often applied to cotton with trimethylolmelamine (TMM), MDPA is believed primarily to react directly with hydroxyl groups of cotton cellulose by forming an ether linkage, thus creating durable flame retardancy in the treated cotton fabrics [6-7]. Its limitations include the need for multiple after-washes and a strong unpleasant odor [8]. The other is tetrakis (hydroxymethyl) phosphonium chloride (“THPC”, also known as “Proban”, a trademark originally of Albright & Wilson, Ltd.). THPC is covalently fixed into cotton cellulose through the formation of a water-insoluble crosslinked polymeric network [1-2]. The requirement of special equipment, which is incompatible with the conventional finishing equipment in textile mills, results in high cost [8].

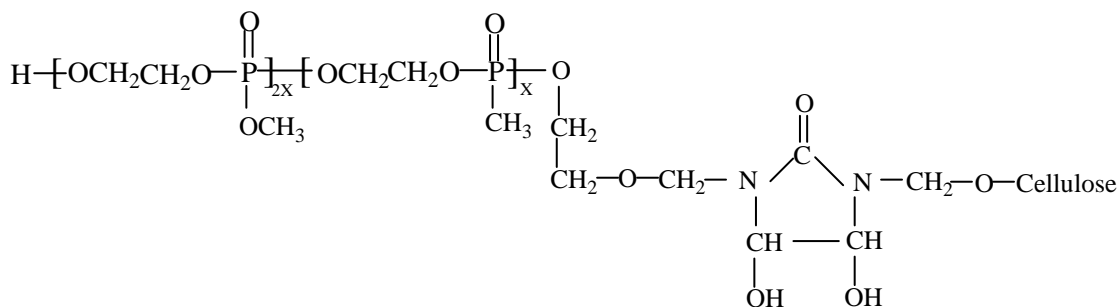
In previous research, a new durable flame retardant finishing system was developed for cotton based on hydroxy-functional organophosphorus oligomer (HFPO) (also known under the trade name FYROL 51 or FYROLTEX HP, both names for the same product and both trademarks of Akzo-Nobel or, later, Supresta), as shown in Scheme 4.1 [7, 9-16]. It was found that HFPO can be covalently bound to cotton through bonding agents such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and N-methylol compounds including

dimethyloldihydroxyethyleneurea (DMDHEU) and TMM [9-16]. The bonding of HFPO to cotton by TMM has been studied, and it was found that HFPO is covalently bound to cotton by the formation of a crosslinked polymeric network of HFPO/TMM [16].

DMDHEU was assumed to covalently bond HFPO to cotton by the formation of HFPO-DMDHEU-Cotton cellulose (as shown in Scheme 4.2), but no strong evidence was provided to support this assumption [11]. Therefore, more research is needed to elucidate the bonding of HFPO to cotton through DMDHEU.



Scheme 4.1 Structure of HFPO



Scheme 4.2 Previous model of HFPO/DMDHEU/Cotton cellulose [11]

In chapter 3, It was shown that both DMDHEU and TMM are able to covalently bond HFPO to nylon by the formation of a crosslinked polymeric network. DMDHEU is a more efficient agent for bonding HFPO to nylon than TMM. It was also found that the nylon/cotton blend fabric treated with HFPO using the mixture of DMDHEU and TMM as a bonding system showed high levels of flame retardant performance and good



laundering durability [17].

In this study, the bonding of HFPO to cotton using DMDHEU as a bonding agent was investigated. The flame retarding performance of the cotton fabric treated with HFPO/DMDHEU was evaluated. In addition, the effects of catalysts were studied.

## Experimental

### Materials

Four kinds of fabrics were used in this study: (1) 100% cotton twill fabric (242 g/m<sup>2</sup>) dyed with vat dyes (S/5570 C/4551) without softener treatment supplied by Milliken, Blacksburg, South Carolina; (2) a scoured, bleached and desized plain weave 40×40 cotton print cloth (Testfabrics Style 400) weighing 102 g/m<sup>2</sup>; (3) 100% filament polyester oxford weave fabric (Testfabrics Style 749) weighing 168 g/m<sup>2</sup>; and (4) 100% acetate sand crepe (Testfabrics Style 101S) weighing 85 g/m<sup>2</sup>. HFPO under the commercial name of “Fyroltex HP” (also known as “Fyrol 51”, CA Registry No. 70715-06-9) was supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. MDPA under the commercial name of “Pyrovatex CP New” (CA Registry No. 20120-33-6) was supplied by Ciba Specialty Chemicals, High Point, North Carolina. DMDHEU was a commercial product (44% solid content) with the trade name of “Freerez 900” supplied by Noveon, Cleveland, Ohio. The catalyst was an NH<sub>4</sub>Cl-based commercial product with the trade name of “Catalyst RD” supplied by Eastern Color & Chemical, Greenville, South Carolina. Magnesium Chloride 6-hydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O) was purchased from J. T. Baker, Phillipsburg, NJ.

### Fabric Treatment and Laundering Procedures

The fabric was immersed in a finish solution and passed through a laboratory padder with two dips and two nips, then dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2 min. All concentrations presented in this study were based on weight of bath (w/w, %), and concentrations of HFPO and DMDHEU in all solutions were based on the solid content of the chemicals in those chemical products. The wet pick-up of the cotton twill fabric was 87±3%. The wet pick-up of the cotton plain weave fabric was 110±4%. The wet pick-up of the polyester woven fabric was 40±2%. The wet pick-up of the acetate fabric was 181±4%. After curing, the treated fabric was subjected to a specified number of laundering cycles using “AATCC Standard Detergent 1993”. The laundering process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics after Repeated Home Laundering”). The water temperature of laundering was approximately 46°C.

### **Evaluation of the Flame Retarding Performance of the Fabrics**

The limiting oxygen index (LOI) of the fabric was measured according to ASTM Standard Method D2863-97. The vertical flammability of the fabric was measured according to ASTM Standard Method D6413-99.

### **Evaluation of the Stiffness of the Fabric**

The fabric stiffness was measured according to ASTM Standard Method D6828-02 using the Handle-O-Meter tester (Model 211-300), manufactured by Thwing-Albert instrument company, Philadelphia, U.S.A. The slot width used in this paper was 5 mm, and the beam size used in this study was 1000 g.

### **Determination of Phosphorus Concentration on the Treated Fabric**

Approximately 2 g of the treated fabric sample taken from three different parts of

a “10×12” fabric specimen were ground in a Wiley mill into powder to improve sample uniformity. 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were added to 0.1 g of the powder in a beaker. 10 ml of 30% H<sub>2</sub>O<sub>2</sub> were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until a dense SO<sub>3</sub> vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the percent concentration of phosphorus. The percent phosphorus retention was calculated by dividing the phosphorus concentration of the fabric after laundering by that of the fabric before laundering.

## Results and Discussion

The plain weave cotton fabric was treated with finishing solutions containing DMDHEU at different concentrations, then cured at 165 °C for 2.5 min, and finally subjected to 1 laundering cycle. The stiffness, wrinkle recovery angle (WRA), tensile strength, LOI, and char length of the cotton fabric thus treated are presented in Table 4.1. When DMDHEU concentration is increased from 1% to 8%, the stiffness (around 101 grams) of the treated cotton fabric appears to be unchanged. It clearly shows that DMDHEU has no significant effect on the stiffness of the treated cotton fabric.

The WRA of the untreated plain weave cotton fabric is 205°. When DMDHEU concentration is increased from 1% to 8%, the WRA of the treated plain weave cotton fabric increases from 206° to 246°, whereas the tensile strength in the warp direction

decreases from 276N to 230N. WRA is a measure of the amount of crosslinking between DMDHEU and cotton cellulose [18], and the crosslinking of cotton cellulose leads to the tensile strength loss of the treated cotton fabric [19]. Therefore, both increasing of WRA and decreasing of tensile strength strongly indicate the crosslinking of cotton cellulose by DMDHEU. The data presented here clearly indicate that the crosslinking of cotton by DMDHEU does not change the fabric stiffness. The LOI of the treated cotton fabric is around 18.3%, and the treated samples fail to pass the vertical flammability test (>300 mm). The above data clearly demonstrate that DMDHEU has no significant effect on the flammability of cotton fabric.

Table 4.1 The stiffness, WRA, tensile strength, LOI, and char length of the cotton fabric (plain weave) treated with DMDHEU at different concentrations and subjected to 1 laundering cycle.

DMDHEU (%)	Stiffness (grams)	WRA (degree)	Tensile Strength(N)	LOI (%)	Char length (mm)
1	100	206	276	18.2	BEL
2	101	209	260	18.2	BEL
4	101	223	249	18.2	BEL
6	102	234	237	18.4	BEL
8	99	246	230	18.3	BEL

Note: Tensile strength\* means tensile strength in the warp direction

The twill cotton fabric was treated with finishing solutions containing DMDHEU at different concentrations or 32%HFPO and DMDHEU at different concentrations, then cured at 165 °C for 2.5 min, and finally subjected to 1 and 10 laundering cycles. The phosphorus concentration of cotton twill fabric treated with 32%HFPO and DMDHEU at

different concentrations after 1 and 10 laundering cycles is presented in Table 4.2. The percent phosphorus retention of the cotton fabric thus treated is plotted against the DMDHEU concentration in Fig.4.1. When DMDHEU concentration is increased from 1% to 8%, the phosphorus concentration of the treated nylon fabric after 1 laundering cycle increases from 1.27% (33% retention) to 3.04% (78% retention). After 10 laundering cycles, the phosphorus concentration increases from 0.82% to 2.62% and the corresponding percent phosphorus retention also increases from 21% to 67%. The data presented above clearly demonstrate that DMDHEU is necessary to create a covalent bonding between HFPO and cotton cellulose, and HFPO bound onto cotton is durable to multiple launderings.

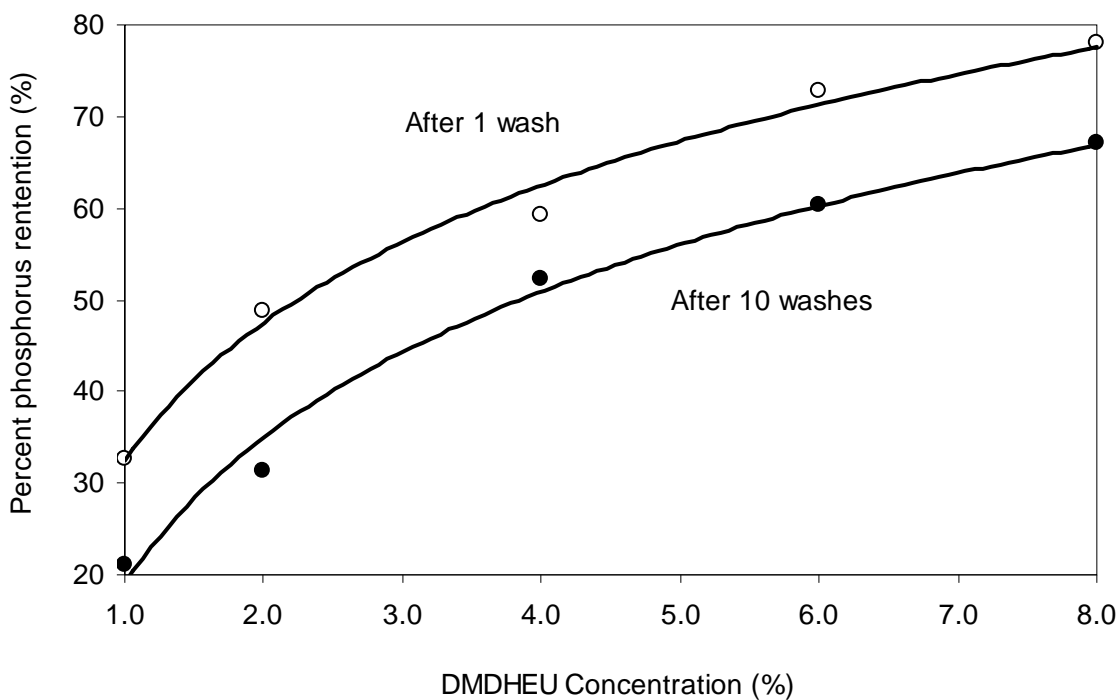


Fig.4.1 The phosphorus retention of the cotton twill fabric treated with 32% HFPO and DMDHEU at different concentrations, then cured at 165°C for 2.5 min, and finally subjected to 1 and 10 laundering cycles versus the DMDHEU concentration.

Table 4.2 The phosphorus concentration of the cotton twill fabric treated with 32%HFPO and DMDHEU at different concentrations and subjected to 1 and 10 laundering cycles.

DMDHEU (%)	Phosphorus concentration (%)	
	after 1 laundering cycle	after 10 laundering cycles
1	1.27	0.82
2	1.90	1.22
4	2.31	2.04
6	2.84	2.35
8	3.04	2.62

The LOI and char length of cotton fabric thus treated is shown in Table 4.3 and Table 4.4, respectively. When the DMDHEU concentration is increased from 1% to 8%, the LOI of treated cotton fabric before laundering increases from 31.0% (char length 83 mm) to 31.6% (char length 54 mm). This is caused by the phosphorus-nitrogen synergism between HFPO and DMDHEU. After 1 laundering cycle, the LOI of cotton fabric thus treated increases from 25.4% (char length 122 mm) to 30.7% (char length 86 mm) as DMDHEU concentration is increased from 1% to 8%. A similar situation is observed in the treated cotton fabric after 10 laundering cycles. The data presented here clearly show that increasing DMDHEU concentration in the formulas results in higher flame retardant performance, which mainly results from the increasing phosphorus fixation and phosphorus retention of HFPO on the treated cotton fabric after laundering.

Table 4.3 The LOI of the cotton twill fabric treated with 32% HFPO and DMDHEU at different concentrations and subjected to 1 and 10 laundering cycles.

HFPO (%)	DMDHEU (%)	LOI (%)		
		before wash	after 1 wash	after 10 washes
32	1	31.0	25.4	23.0
32	2	31.1	27.6	25.5
32	4	31.2	28.9	28.5
32	6	31.3	29.9	29.6
32	8	31.6	30.7	29.8

Table 4.4 The char length of the cotton twill fabric treated with 32% HFPO and DMDHEU at different concentrations and subjected to 1 and 10 laundering cycles.

HFPO (%)	DMDHEU (%)	Char length (mm)		
		before wash	after 1 wash	after 10 washes
32	1	83	122	BEL
32	2	90	90	85
32	4	78	88	71
32	6	68	94	68
32	8	54	86	83

When DMDHEU concentration is increased from 1% to 8%, the stiffness of cotton fabric thus treated after 1 laundering cycle increases only slightly from 626 grams to 642 grams (Fig.4.2). In the presence of 32% HFPO, however, the stiffness of twill cotton fabric thus treated drastically increases from 575 grams to 1985 grams as DMDHEU concentration is increased from 1% to 8%. Without HFPO, DMDHEU reacts only with cotton cellulose to form a crosslinking, which significantly improves the

wrinkle recovery angle of the treated cotton fabric, but only slightly increases the stiffness of the treated cotton fabric. In the presence of HFPO, DMDHEU reacts with HFPO as well as cotton cellulose to form a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose, which leads to a drastic increase in the fabric stiffness.

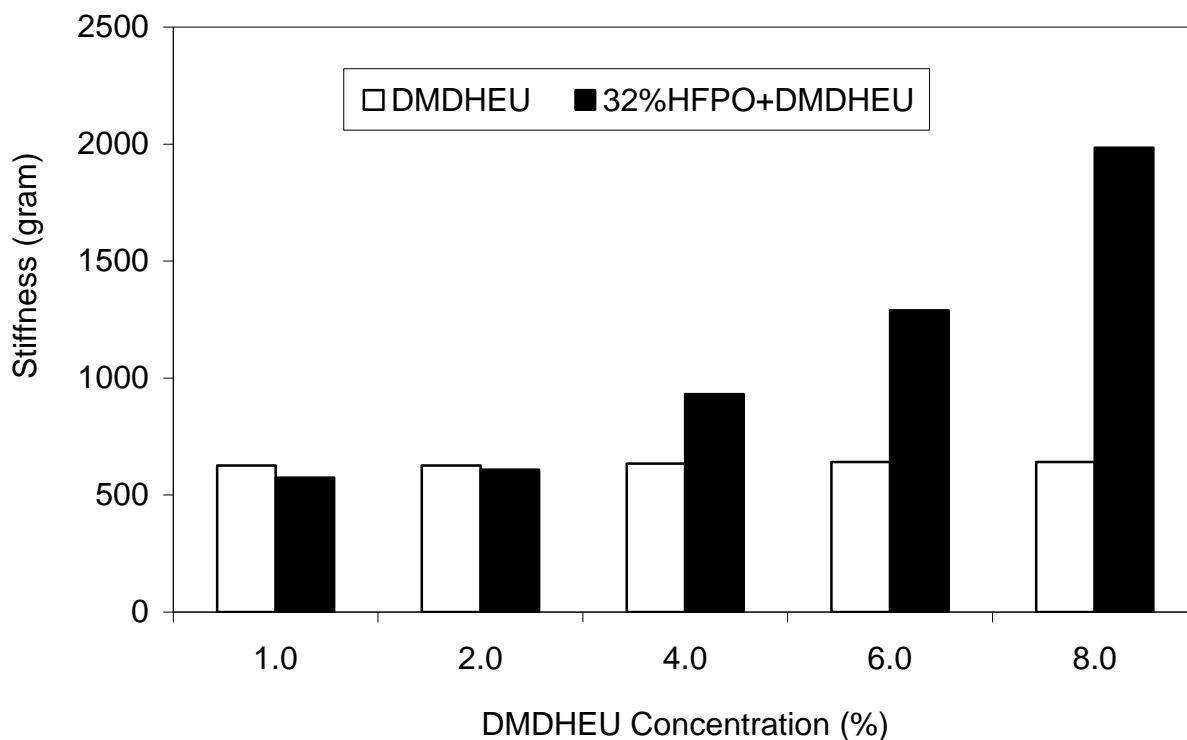


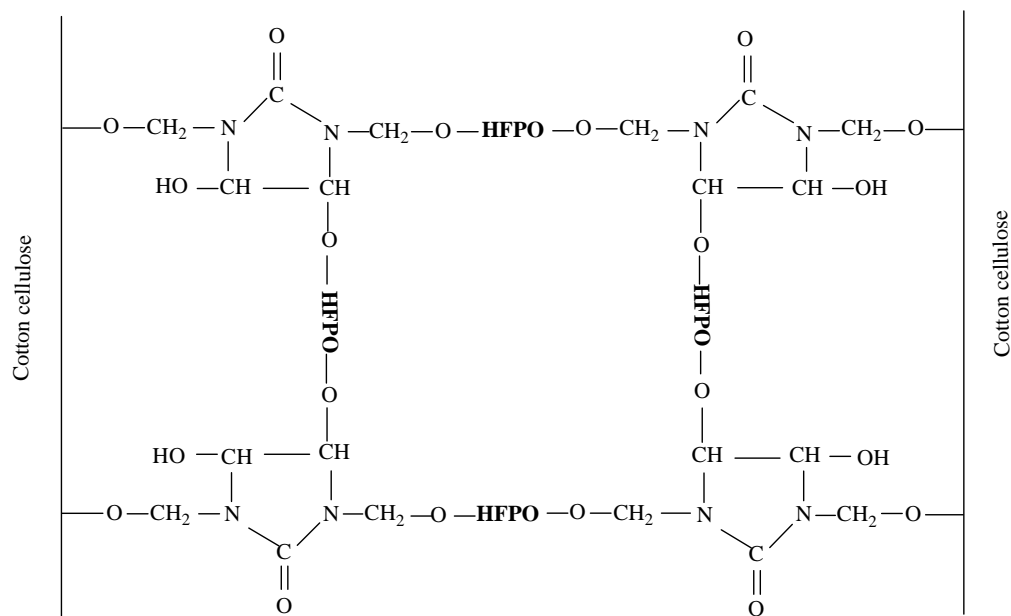
Fig.4.2 The stiffness of the cotton twill fabric treated with DMDHEU at different concentrations, then cured at 165°C for 2.5 min, and finally subjected to 1 laundering cycle versus the DMDHEU concentration.

The twill cotton fabric was treated with 6% DMDHEU and HFPO at different concentrations, and then cured at 165 °C for 2.5 min. The stiffness of cotton fabric thus treated after 1 laundering cycle is plotted against the HFPO concentration in Fig.4.3.

Assuming  $x=1$  in Scheme 4.1, the mole ratio of HFPO/DMDHEU increases from 0.26 to



1.81, and the stiffness of the treated cotton fabric notably increases from 590 grams and achieves the maximum at around 28% HFPO when the HFPO concentration is increased from 4% to 28%. The data presented in Fig.4.3 strongly indicate that a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose (as shown in Scheme 4.3) is formed on the treated cotton fabric. However, further addition of HFPO in the finishing solution decreases the fabric stiffness from 1398 grams to 737 grams when the HFPO concentration is further increased from 28% to 44%. It is possible that there are two competitive reactions: the reaction between DMDHEU and HFPO and the reaction between DMDHEU and cotton cellulose. When DMDHEU concentration is fixed at 6% and HFPO concentration is increased in the formulas, the reaction between HFPO and DMDHEU becomes dominant, whereas less DMDHEU reacts with the hydroxyl groups of the cotton cellulose. As a result, less cotton cellulose are involved in the whole crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose on the treated cotton, thus probably reducing the fabric stiffness.



Scheme 4.3 Crosslinked polymeric network of HFPO/DMDHEU/cotton cellulose

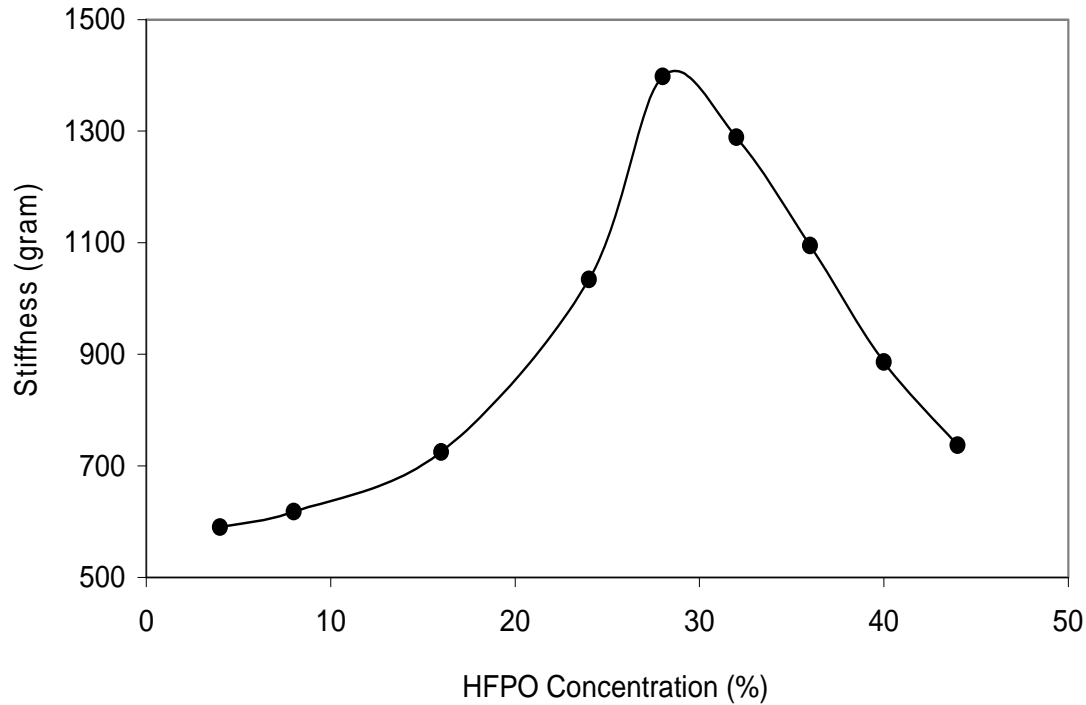


Fig.4.3 The stiffness of the cotton twill fabric treated with 6% DMDHEU and HFPO at different concentrations, then cured at 165°C for 2.5 min, and finally subjected to 1 laundering cycle versus the HFPO concentration.

The following research provides more evidence to support the hypothesis in Scheme 4.3. The finishing solutions containing 32% MDPA and DMDHEU at different concentrations were applied to the twill cotton fabric. The cotton fabric thus treated was cured at 165 °C for 2.5min and then subjected to 1 laundering cycle. The stiffness of cotton fabric thus treated is plotted against the DMDHEU concentration and compared with that of the cotton fabric treated with 32% HFPO and DMDHEU at different concentrations in Fig.4.4. In comparison to the stiffness of cotton fabric treated with HFPO/DMDHEU increasing from 575 grams to 1985 grams when the DMDHEU concentration is increased from 1% to 8%, the stiffness of cotton fabric treated with MDPA/DMDHEU is around 710 grams and appears to be unchanged. This is due to the

fact that MDPA (as shown in Scheme 4.4) has only one methylol group on its molecule. Hence, it is unlikely for MDPA to react with DMDHEU to form a crosslinked polymeric network.

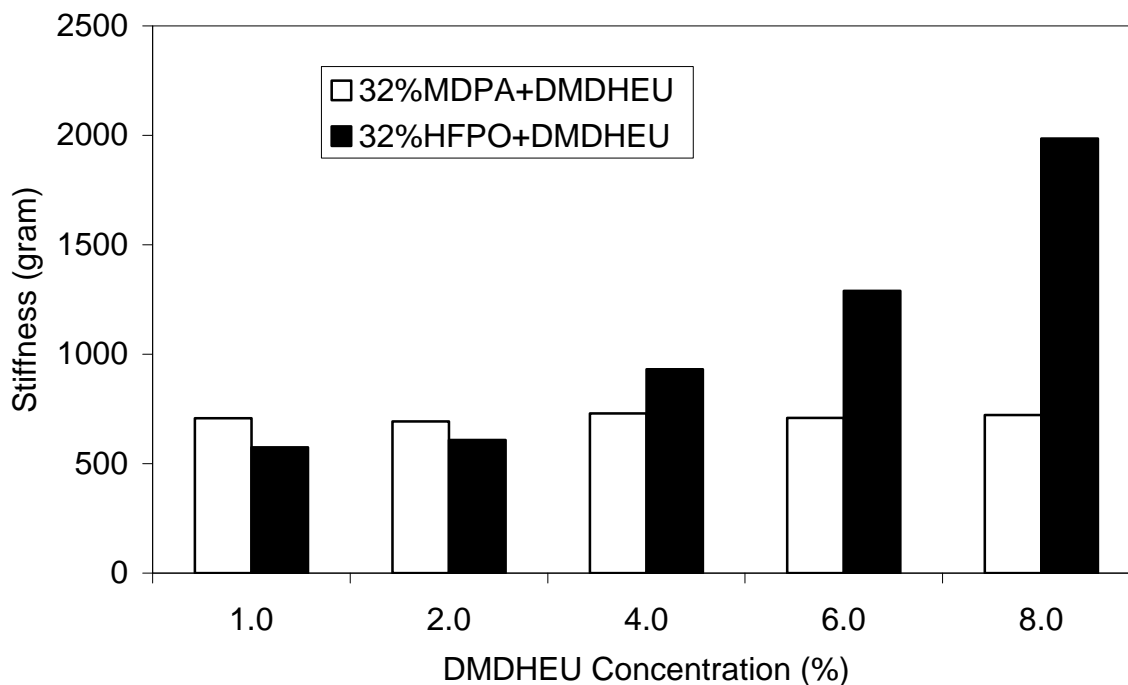
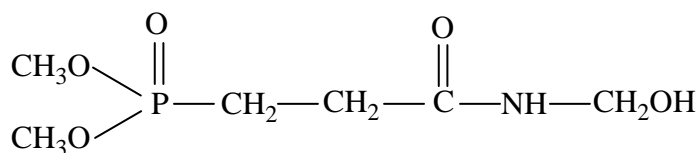


Fig.4.4 The stiffness of the cotton twill fabric treated with DMDHEU at different concentrations, then cured at 165°C for 2.5 min, and finally subjected to 1 laundering cycle versus the DMDHEU concentration.



Scheme 4.4 Structure of MDPA

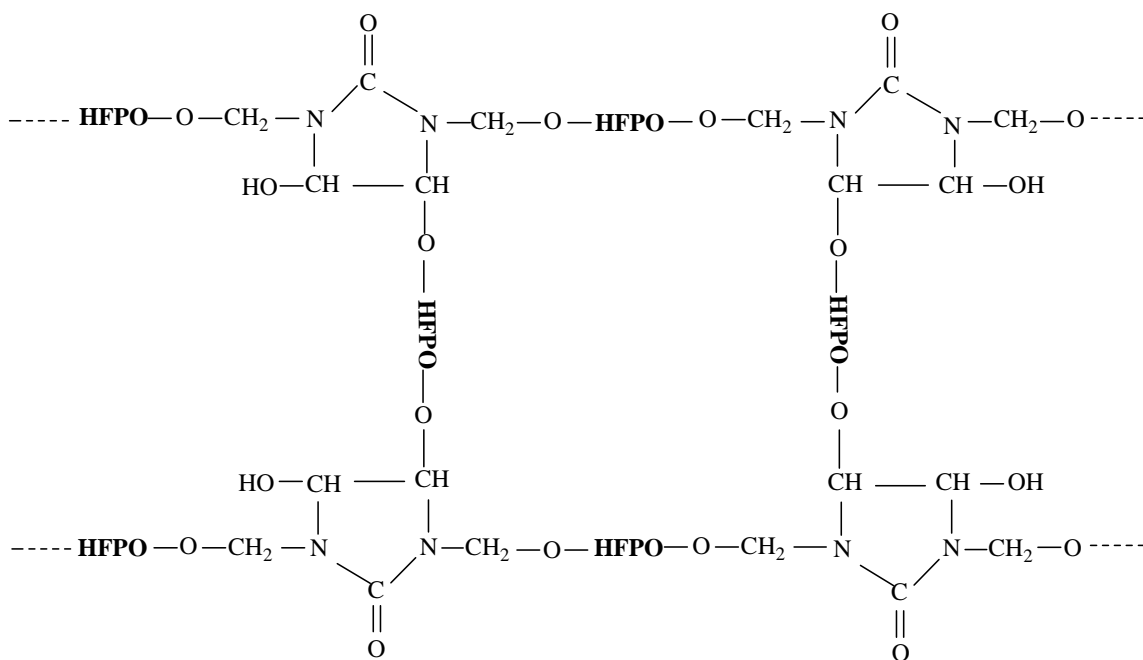
In chapter 3, nylon-6.6 woven fabric was treated with 32% HFPO and DMDHEU at different concentrations, and cured at 165 °C for 2 min, and finally subjected to 1 laundering cycle. When the DMDHEU concentration is increased from 1% to 8%, the

phosphorus concentration of the treated nylon fabric after 1 laundering cycle increases from 0.22% to 1.75%, but the stiffness of nylon fabric thus treated only increases from 51 grams to 61 grams by around 20%. This strongly indicates the formation of a crosslinked polymeric network of HFPO/DMDHEU. The formation of crosslinked polymeric network of HFPO/DMDHEU can dramatically improve the laundering durability of HFPO bound to nylon, but causes only a slight increase of the fabric stiffness. The drastic increase of the stiffness of the cotton fabric treated with HFPO/DMDHEU (Fig.4.2) is probably caused by the involvement of the cotton cellulose in the whole crosslinked polymeric network.

The polyester was treated with 6% DMDHEU and HFPO at different concentrations, then cured at 165 °C for 2 min, and finally subjected to 1 laundering cycle. The phosphorus concentration of the polyester fabric thus treated is shown in Table 4.5. When the HFPO concentration is increased from 24% to 40%, the phosphorus concentration on the polyester fabric thus treated increases from 1.06% to 1.84%. The data presented here show that HFPO can be covalently bound to polyester using DMDHEU as a bonding agent. Like nylons, polyester fiber can be considered as chemically inert [20]. Therefore, the bonding of HFPO to polyester is attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU (Scheme 4.5).

Table 4.5 The phosphorus concentration of the polyester fabric treated with 6% DMDHEU and HFPO at different concentrations and subjected to different laundering cycles.

HFPO (%)	Phosphorus concentration (grams)	
	before laundering	after 1 laundering cycle
24	1.65	1.06
28	1.97	1.25
32	2.62	1.41
36	3.03	1.58
40	3.34	1.70
44	3.92	1.84



Scheme 4.5 Crosslinked polymeric network of HFPO/DMDHEU [17]

The acetate fabric was treated with 6% DMDHEU and HFPO at different concentrations, then cured at 165 °C for 2 min, and finally subjected to 1 laundering cycle. The phosphorus concentration of the acetate fabric thus treated is shown in Table 4.6. When the HFPO concentration is increased from 24% to 40%, the phosphorus concentration on the acetate fabric thus treated increases from 3.58% to 4.96%. The data presented here demonstrate that HFPO can be covalently bound to the acetate fabric using DMDHEU as a bonding agent.

Table 4.6 The phosphorus concentration of the acetate fabric treated with 6% DMDHEU and HFPO at different concentrations and subjected to different laundering cycles.

HFPO (%)	Phosphorus concentration (grams)	
	before laundering	after 1 laundering cycle
24	5.73	3.58
28	5.97	4.13
32	6.30	4.51
36	6.59	4.81
40	7.17	5.13
44	7.39	4.96

### Effects of catalysts

The twill cotton fabric was treated by two finishing formulas which contain 32% HFPO/6% DMDHEU but different catalysts. One catalyst is  $\text{NH}_4\text{Cl}$  (2% of DMDHEU weight) as a catalyst. The other is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (20% of DMDHEU weight). The fabric thus treated was dried at 90°C, then cured at 165°C for 2.5min, and finally subjected to 1 laundering cycle. The phosphorus concentration and flame retardant performance of fabrics thus treated are shown in Table 4.7. The LOI (31.3%) of the

cotton fabric treated with a finishing solution using  $\text{NH}_4\text{Cl}$  as a catalyst does not seem significantly different from that (31.4%) using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . After 1 laundering cycle, the same situation is observed. The LOI of cotton fabric treated with a finishing solution using  $\text{NH}_4\text{Cl}$  is 29.9, which is almost the same as that (29.8) using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The phosphorus concentration of cotton fabric treated with a finishing solution using  $\text{NH}_4\text{Cl}$  (after 1 laundering cycle) is 2.2%, which is almost equal to that (2.1%) using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . As shown in Table 8, the tensile strength in the warp direction of cotton fabric treated with a finishing solution using  $\text{NH}_4\text{Cl}$  is 543 N, which is notably higher than that (503 N) treated with a finishing solution using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The tensile strength in the filling direction of cotton fabric using  $\text{NH}_4\text{Cl}$  is 328 N, which is significantly higher than that (314 N) treated with a finishing solution using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The data presented above demonstrate that the cotton fabric treated with a finishing solution using  $\text{NH}_4\text{Cl}$  has almost identical phosphorus concentration and flame retardant performance but less tensile strength loss than that using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

Table 4.7 The LOI and phosphorus concentration of the cotton twill fabric treated with 32% HFPO and 6% DMDHEU using different catalysts and cured at 165°C for 2 min

Catalyst	LOI (%)		Phosphorus concentration (%)	
	before wash	after 3 washes	before wash	after 3 washes
$\text{NH}_4\text{Cl}$	31.3	29.9	3.3	2.2
$\text{MgCl}_2$	31.4	29.8	3.3	2.1

## Conclusions

When DMDHEU is applied to cotton fabric, it improves wrinkle-resistance by forming crosslinks between cotton cellulose. The crosslinking of cotton cellulose by DMDHEU has no effect on the fabric stiffness. In the presence of HFPO, however, DMDHEU reacts with HFPO as well as cotton cellulose, thus forming a crosslinked polymeric network of HFPO/DMDHEU/cotton cellulose on the treated cotton fabric. The formation of a water-insoluble crosslinked polymeric network of HFPO/DMDHEU/cotton cellulose not only improves the laundering durability of HFPO bound to the treated cotton fabric but also increases the fabric stiffness. DMDHEU is necessary to covalently bond HFPO to cotton. Increasing DMDHEU concentration leads to higher laundering durability of HFPO to cotton, and also causes an increase of the fabric stiffness. In order to lower the fabric stiffness, a high ratio of HFPO/DMDHEU in the formulas is recommended. In addition, the cotton treated with HFPO/DMDHEU using ammonium chloride as a catalyst shows less loss of tensile strength than that using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , although both treated samples show no significant difference in the flame retardant performance and phosphorus retention after multiple launderings.



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**CHAPTER 5**

**COMPARISON OF DMDHEU AND TRIMETHYLOLMELAMINE AS THE**

**BONDING AGENTS FOR A HYDROXY-FUNCTIONAL**

**ORGANOPHOSPHORUS OLIGOMER FLAME RETARDING AGENT ON THE**

**NYLON/COTTON BLEND FABRIC**

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<sup>1</sup> Yang, H. and Yang, C.Q. To be submitted to *Polymer Degradation and Stability*.

### **Abstract**

In previous research, I found that the nylon/cotton blend fabric treated with hydroxy-functional organophosphorus oligomer (HFPO) using the mixture of melamine-formaldehyde and dimethyloldihydroxyethyleneurea (DMDHEU) as a bonding system showed high levels of flame retardant performance and good laundering durability. In this study, both DMDHEU and trimethylolmelamine (TMM) were applied as the bonding agents to nylon/cotton blend fabric in combination with HFPO. I found that both TMM and DMDHEU are able to covalently bond HFPO to nylon/cotton blend fabric. The nylon/cotton blend fabric treated with HFPO/DMDHEU has higher phosphorus fixation and phosphorus retention with notably lower stiffness than that treated with HFPO/TMM. Even though the phosphorus-nitrogen synergistic effect between TMM and HFPO becomes weaker in the nylon/cotton blend fabric than that in the cotton fabric, however, TMM shows more notable phosphorus-nitrogen synergism with HFPO than DMDHEU on the nylon/cotton blend. After 10 laundering cycles, the nylon/cotton blend fabric treated with HFPO/DMDHEU shows higher flame retardant performance than that treated with HFPO/TMM. Therefore, DMDHEU appears to be more effective as a bonding agent for HFPO to the nylon/cotton blend fabric than TMM.

**Key Words:** Cotton, DMDHEU, Durable flame retardant finishing, Nylon-6.6, Nylon/cotton blend, Organophosphorus chemicals, Trimethylolmelamine.

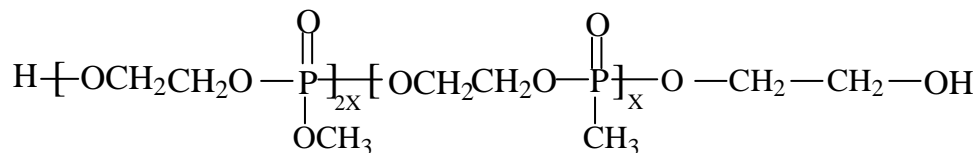
### **Introduction**

Flame resistance is a very desirable property for the nylon/cotton blend fabric, especially when it is used as a material for protective clothing [1-2]. In spite of urgent need, it is difficult to create durable flame retardancy in the nylon/cotton blend fabric, and research on this topic is very limited [3-4]. Therefore, study on the durable flame retardant finishing of the nylon/cotton blend fabrics has both academic and commercial significance.

Currently, coating is the most effective way to impart durable flame retardant property to the cotton blend fabrics. However, its major limitation is the serious damage to aesthetic properties of the treated fabric [3]. Durable flame retardant finishing of nylon/cotton blend fabric was disclosed in several patents [5-8]. Usually, two flame retardants or flame retardant finish systems are used for durable flame retardant finishing of the nylon/cotton blend fabrics. One is effective for the cotton component. The other is effective for the nylon component in the blends. The typical flame retardant for the cotton component is tetrakis (hydroxymethyl) phosphonium chloride (THPC). Cyclic phosphonate esters are the representative flame retardants for the nylon component. However, none of them has been commercialized successfully.

In previous research, a durable flame retardant finishing system based on hydroxy-functional organophosphorus oligomer (HFPO) [9], as shown in Scheme 5.1, has been developed for cotton [10-17]. Dimethyloldihydroxyethyleneurea (DMDHEU) was compared with trimethylolmelamine (TMM) as a bonding agent for HFPO on cotton [17]. Even though both DMDHEU and TMM can create a covalent bonding between

HFPO and cotton cellulose, the cotton treated with HFPO/TMM has a higher flame retardant performance than that treated with HFPO/DMDHEU [17].



Scheme 5.1 Structure of HFPO

In my previous research [18], I discovered that both DMDHEU and TMM are also able to covalently bond HFPO to nylon, and DMDHEU is more effective as a bonding agent for HFPO to nylon than TMM. I also found that the nylon/cotton blend fabric treated with HFPO using the mixture of DMDHEU and melamine-formaldehyde as a bonding system showed high levels of flame retardant performance and good laundering durability [19].

In this paper, DMDHEU was compared with TMM as a bonding agent for HFPO on the nylon/cotton blend fabric. I also studied and compared the phosphorus-nitrogen synergism, the flame retardant performance, and other physical properties of the nylon/cotton blend fabric treated with HFPO using DMDHEU/TMM as a bonding agent.

## Experimental

### Materials

Three fabrics were used in this study: (1) the 50%/50% nylon/cotton BDU pure finish twill fabric with three-color woodland camouflage weighing 216g/m<sup>2</sup> (Military specification: MIL-C-44436 CL3) was supplied by Bradford dyeing association, Inc. Bradford, RI; (2) 100% nylon-6.6 woven fabric (Testfabrics Style 306A) weighing 59 g/m<sup>2</sup>; (3) 100% cotton fabric (242 g/m<sup>2</sup>) dyed with vat dyes (S/5570 C/4551) and without

softener treatment supplied by Milliken, Blacksburg, South Carolina. HFPO under the trade name of “Fyroltex HP” (also known as Fyrol 51) was supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. DMDHEU was a commercial product (44% solid content) with the trade name of “Freerez 900” supplied by Noveon, Cleveland, Ohio. TMM was a commercial product (80% solid content) with the trade names of “Aerotex M-3” supplied by Noveon, Cleveland, Ohio. The catalyst was an  $\text{NH}_4\text{Cl}$ -based commercial product with the trade name of “Catalyst RD” supplied by Eastern Color & Chemical, Greenville, South Carolina.

### **Fabric Treatment and Laundering Procedures**

The fabric was first immersed in a finish solution and passed through a laboratory padder with two dips and two nips. Then, all cotton and nylon/cotton blend fabrics were dried at  $90^\circ\text{C}$  for 3 min and cured in a Mathis curing oven at  $165^\circ\text{C}$  for 2.5 min. Nylon-6.6 fabric was dried at  $90^\circ\text{C}$  for 1.5min, and then cured in a Mathis curing oven at  $165^\circ\text{C}$  for 2min. All concentrations presented in this study were based on weight of bath (w/w, %), and concentrations of HFPO, DMDHEU and TMM in all solutions were based on the solid of the chemicals in those chemical products. The wet pick-up of the 100% cotton fabric was  $87\pm 3\%$ . The wet pick-up of the nylon/cotton fabric was  $78\pm 3\%$ . The wet pick-up of the nylon-6.6 woven fabric was  $52\pm 2\%$ . After curing, the treated fabric was subjected to a specified number of laundering cycles with the use of “AATCC Standard Detergent 1993.” The laundering process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics after Repeated Home Laundering”). The water temperature of laundering was approximately  $46^\circ\text{C}$ .

### **Evaluation of the Flame Retarding Performance of the Fabrics**



The vertical flammability of the fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the fabric was measured according to ASTM Standard Method D2863-97.

#### **Evaluation of the Stiffness of the Fabric**

The stiffness of the fabric was measured according to ASTM Standard Method D6828-02 using Handle-O-Meter tester (Model 211-300), manufactured by Thwing-Albert instrument company, Philadelphia, U.S.A. The slot width used in this paper was 5 mm, and the beam size used in this paper was 1000 grams. The stiffness of fabric represented the mean of total stiffness obtained from 5 specimens.

#### **Determination of Phosphorus Concentration on the Treated Fabric**

Approximately 2 g of the treated fabric sample taken from three different parts of a “10×12” fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of concentrated  $\text{H}_2\text{SO}_4$  were added to 0.1 g of the powder in a beaker. Ten milliliters of 30%  $\text{H}_2\text{O}_2$  were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250 °C to digest the powder and to evaporate the water until dense  $\text{SO}_3$  vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the % concentration of phosphorus. The percent phosphorus retention was calculated by dividing the phosphorus content of the fabric after laundering by that of the fabric before laundering.

## Results and Discussion

### Laundering Durability of HFPO Bound to the Nylon/Cotton Blend Fabric

The nylon/cotton blend fabric was treated with 40% HFPO and DMDHEU at different concentrations, then dried at 90°C for 3 min, and finally cured at 165°C for 2.5 min. The nylon/cotton fabric thus treated was subjected to 1 and 10 laundering cycles. The phosphorus concentration and percent phosphorus retention on the nylon/cotton blend fabric thus are presented in Table 5.1.

Table 5.1 Phosphorus content (%), phosphorus retention (%) and stiffness of the 50%/50% nylon/cotton fabric treated with 40%HFPO and DMDHEU at different concentrations, and cured at 165°C for 2.5 min, finally subjected to different number of laundering cycles.

DMDHEU (%)	After 1 laundering cycle		After 10 laundering cycles	
	Phosphorus concentration (%)	Phosphorus fixation (%)	Phosphorus concentration (%)	Phosphorus retention (%)
1	0.60	15.1	0.37	8.5
2	1.03	21.4	0.82	14.8
4	2.67	55.1	2.35	48.5
6	2.84	61.4	2.84	61.3
8	3.13	72.1	3.07	70.8

The phosphorus concentration of the nylon/cotton blend fabric treated with HFPO/DMDHEU after 1 laundering cycle increases from 0.60% to 3.13% and the percent phosphorus fixation increases from 15% to 75% as the DMDHEU concentration is increased from 1% to 8%. After 10 laundering cycles, the phosphorus concentration in the nylon/cotton blend fabric treated with 40%HFPO/8%DMDHEU still has 3.07%

phosphorus (72% phosphorus retention). The data presented here clearly indicate that DMDHEU is able to covalently bond HFPO to the nylon/cotton blend fabric, and HFPO bound to the nylon/cotton blend fabric is durable to multiple launderings.

The nylon/cotton blend fabric was treated with 40% HFPO and TMM at different concentrations, then dried at 90°C for 3 min, and finally cured at 165°C for 2.5 min. The nylon/cotton fabric thus treated was subjected to 1 and 10 laundering cycles. The phosphorus concentration and percent phosphorus retention of the nylon/cotton blend fabric thus treated are shown in Table 5.2.

Table 5.2 Phosphorus content (%), phosphorus retention (%) and stiffness of the 50%/50% nylon/cotton treated with 40% HFPO and TMM at different concentrations, and cured at 165°C for 2.5 min, finally subjected to different number of laundering cycles.

TMM (%)	After 1 laundering cycle		After 10 laundering cycles	
	Phosphorus concentration (%)	Phosphorus retention (%)	Phosphorus concentration (%)	Phosphorus retention (%)
1.6	0.46	10.9	0.27	6.4
3.2	0.70	16.1	1.03	23.9
4.8	1.81	40.2	1.20	33.4
6.4	2.08	43.3	2.04	42.5
8.0	2.45	48.8	2.27	45.2

After 1 laundering cycle, the phosphorus concentration in the nylon/cotton blend fabric treated increases from 0.46% to 2.45%, and the percent phosphorus fixation increases from 11% to 49% when the TMM concentration is increased from 1.6% to 8.0%. After 10 laundering cycles, a similar phenomenon is observed. The phosphorus concentration in the nylon/cotton blend fabric increases from 0.27% to 2.27%, and the

percent phosphorus retention increases from 6% to 45% as the TMM concentration is increased from 1.6% to 8.0%. The data presented here clearly indicate that TMM is also able to covalently bond HFPO to the nylon/cotton blend fabric, and HFPO bound to the nylon/cotton blend fabric is durable to multiple launderings.

The phosphorus concentration and the percent phosphorus retention of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU/TMM) after 1 laundering cycle are presented in Fig.5.1 and Fig.5.2, respectively. One can observe that the nylon/cotton blend fabric treated with HFPO/DMDHEU after 1 laundering cycle has higher phosphorus concentration and percent phosphorus fixation than that treated with HFPO/TMM. The phosphorus concentration and the percent phosphorus retention of the nylon/cotton blend treated with 40% HFPO and DMDHEU/TMM at different concentrations after 10 laundering cycles are shown in Fig.5.3 and Fig.5.4, respectively. They clearly show that the nylon/cotton blend fabric treated with HFPO/DMDHEU after 10 laundering cycles has higher phosphorus concentration and phosphorus retention than that treated with HFPO/TMM. Therefore, we can conclude that HFPO bound to the nylon/cotton blend fabric using DMDHEU as a bonding agent has higher laundering durability than that using TMM.

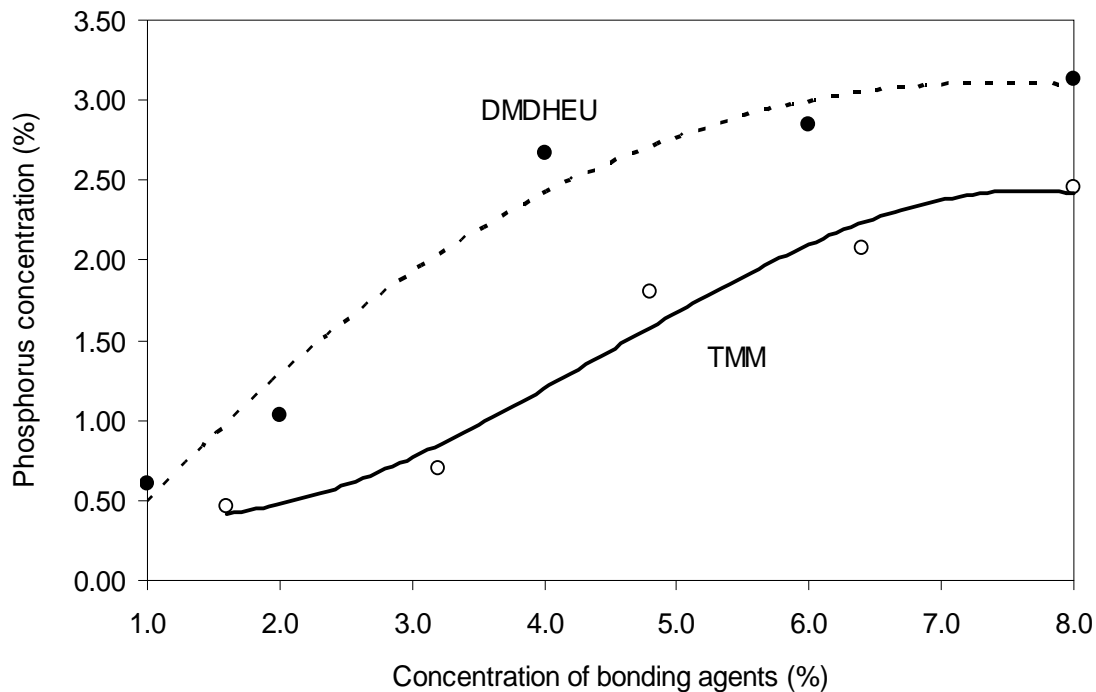


Fig.5.1 The phosphorus concentration of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, then cured at 165 for 2.5 min, and finally subjected to 1 laundering cycle.

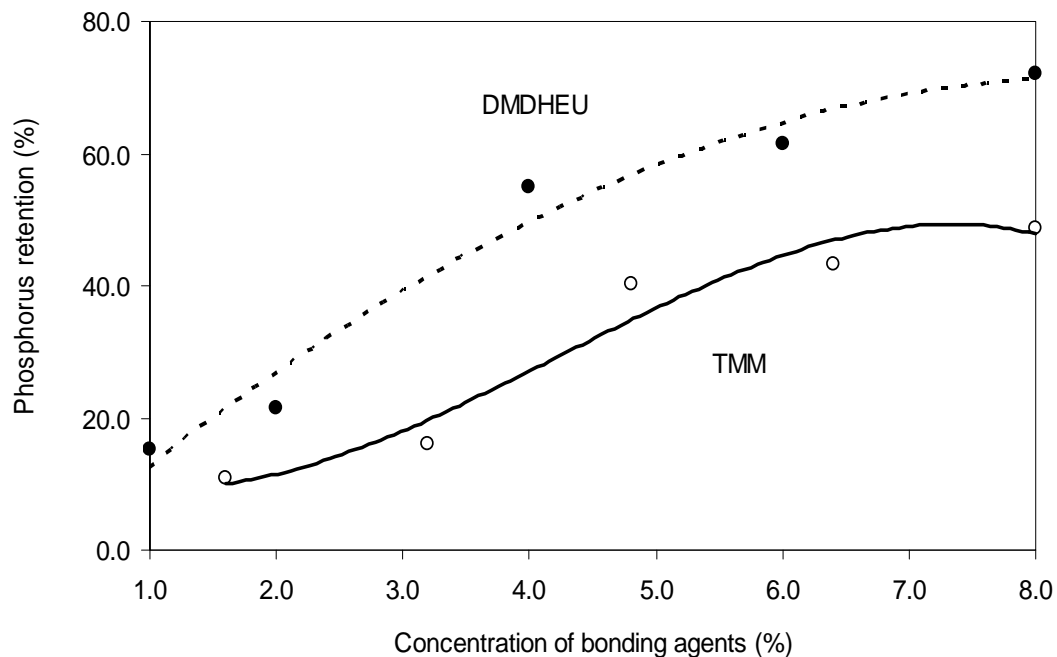


Fig.5.2 The percent phosphorus fixation of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, then cured at 165 for 2.5 min, and finally subjected to 1 laundering cycle.

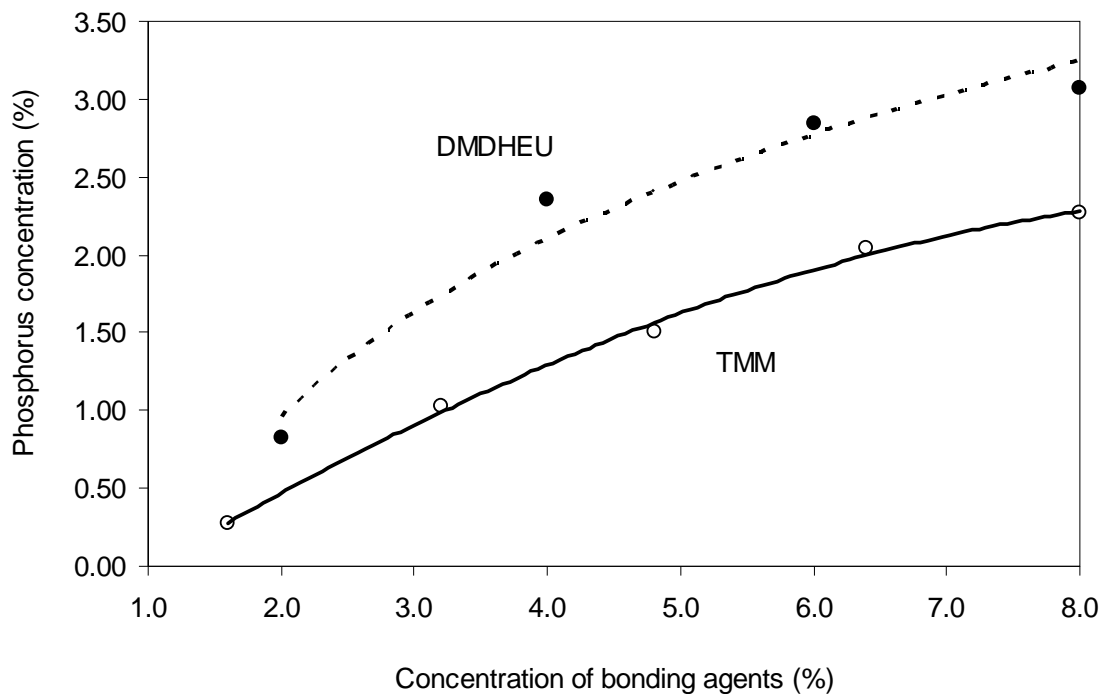


Fig.5.3 The phosphorus concentration of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, then cured at 165 for 2.5 min, and finally subjected to 10 laundering cycles.

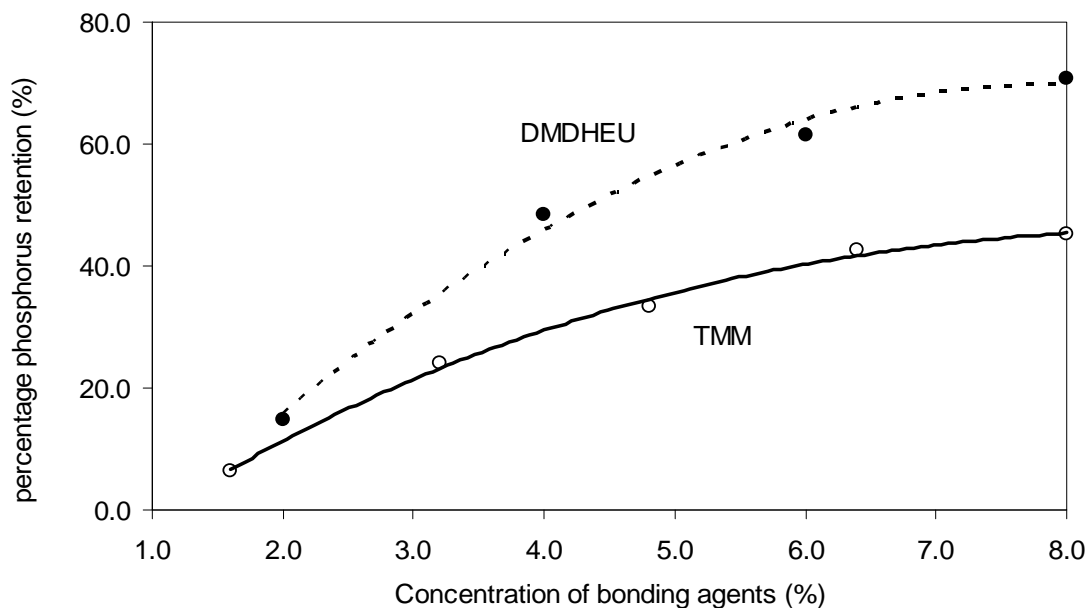


Fig.5.4 The percent phosphorus retention of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, then cured at 165 for 2.5 min, and finally subjected to 10 laundering cycles.

The nylon-6.6, cotton, and nylon/cotton blend fabrics were treated with 40% HFPO and TMM at different concentrations, then dried at 90°C for 3 min, and finally cured at 165°C for 2.5 min. The fabrics thus treated were subjected to 10 laundering cycles. The phosphorus fixation of the fabrics thus treated is plotted against the TMM concentration in Fig.5.5. One can observe that the percent phosphorus retention of the nylon/cotton blend fabric lies between the phosphorus retention of cotton and that of nylon fabric, but the phosphorus fixation of the nylon/cotton blend is much closer to that of cotton fabric than that of nylon fabric. The data shown in Fig.5.5 strongly indicate that most finish is absorbed and fixed into cotton component whereas a portion of finish is bound to the nylon component in the blend fabric.

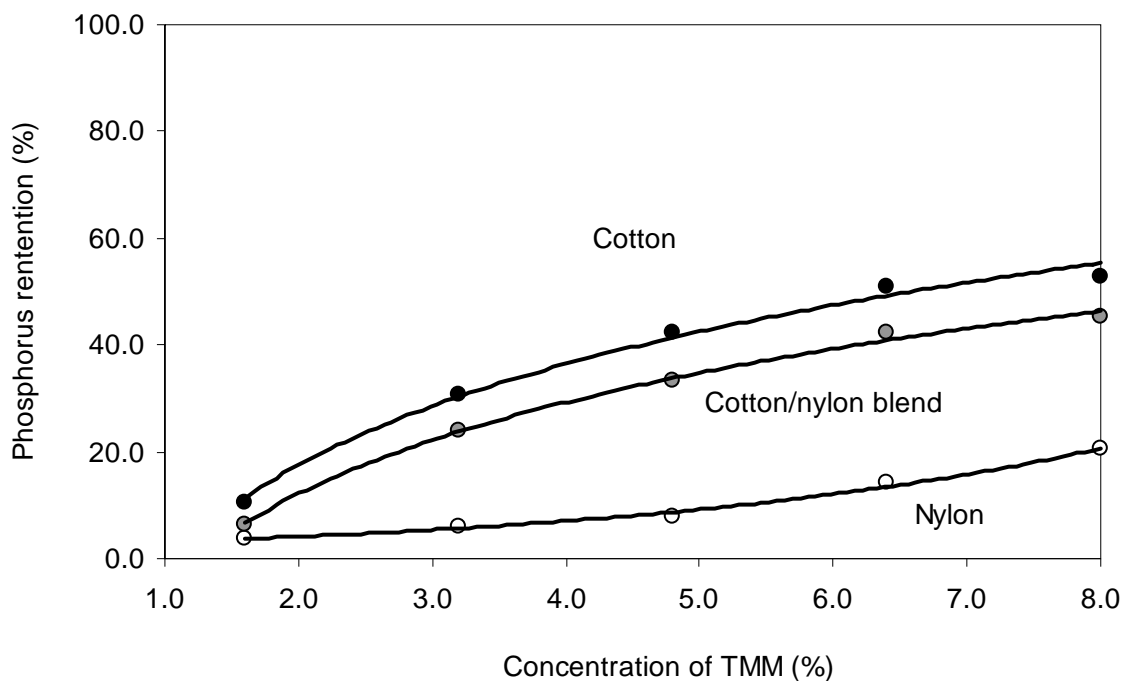


Fig.5.5 The phosphorus fixation of the nylon-6.6, cotton, and nylon/cotton blend treated with 40% HFPO and TMM at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles)

The nylon-6.6, cotton and nylon/cotton blend fabrics were treated with 40% HFPO and DMDHEU at different concentrations, then dried at 90°C for 3 min, and cured at 165°C for 2.5 min. The fabrics thus treated were subjected to 10 laundering cycles. The percent phosphorus retention of the fabrics thus treated is plotted against the DMDHEU concentration in Fig.5.6. We also can conclude that the phosphorus fixation of the nylon/cotton blend fabric is much higher than that of nylon-6.6 fabric but lower than that of the cotton fabric. This is due to the fact that most finish is absorbed into the cotton component whereas a portion of finish is bound to the nylon component in the nylon/cotton blend fabric.

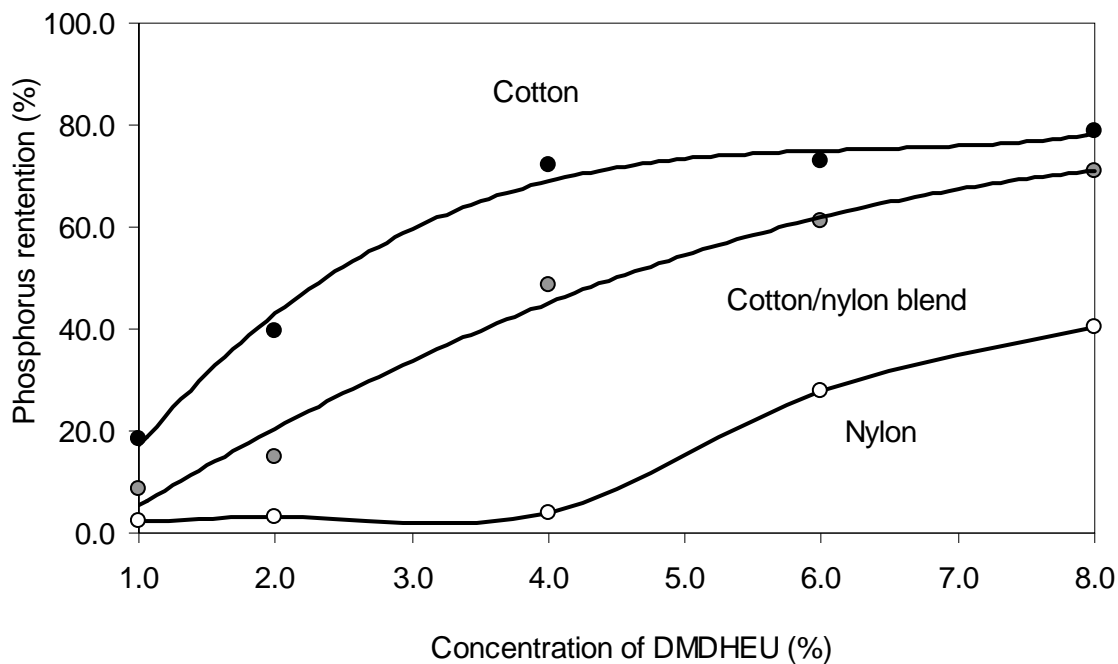


Fig.5.6 The phosphorus fixation of the nylon-6.6, cotton, and nylon/cotton blend treated with 40% HFPO and DMDHEU at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles)



### **Phosphorus-Nitrogen Synergism of DMDHEU and TMM with HFPO**

The nylon/cotton blend and cotton fabric was treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, and then cured at 165°C for 2.5 min. The LOI of the fabric thus treated (before laundering) is plotted against the concentration of bonding agents in Fig.5.7. The LOI of the nylon/cotton blend fabric treated with HFPO /TMM before laundering increases from 28.1% to 28.9% when the TMM concentration is increased from 1.6% to 8.0%. The increasing LOI of treated nylon/ cotton blend fabric is attributed to the phosphorus-nitrogen synergism between HFPO and TMM. When the DMDHEU concentration is increased from 1.0% to 8.0%, the LOI of the nylon/cotton blend fabric treated with HFPO/DMDHEU (before laundering) increases from 27.8% to 28.0%, which also results from the phosphorus-nitrogen synergism between HFPO and DMDHEU. It is very clear that TMM is more effective as a nitrogen provider than DMDHEU when they are applied to the nylon/cotton blend fabric together with HFPO.

The LOI of the cotton fabric treated with HFPO/TMM before laundering increases from 31.3% to 35.5% when the TMM concentration is increased from 1.6% to 8.0%, while the LOI of the cotton fabric treated with HFPO/DMDHEU and before laundering only insignificantly increased from 30.9% to 31.9% when the DMDHEU concentration is increased from 1% to 8%. The LOI of the nylon/cotton blend fabric treated with HFPO and a bonding agent (DMDHEU or TMM) at different concentrations is significantly lower than that of the cotton fabric, which could be attributed to the presence of nylon in the nylon/cotton blend fabric. When the concentration of bonding agents is 8.0%, the difference of LOI values between the cotton fabric treated with

HFPO/DMDHEU and that treated with HFPO/TMM is 3.6%. However, the difference of LOI between the nylon/cotton blend fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM is only 0.9%. The phosphorus concentration of the cotton fabric thus treated before laundering is around 4.2%, which is less than 4.6% on the nylon/cotton blend fabric thus treated before laundering. Therefore, the data presented here strongly indicate that the difference of LOI due to phosphorus-nitrogen synergism becomes notably weaker on nylon/cotton blend fabric than that on cotton due to the presence of nylon in the nylon/cotton blend fabric.

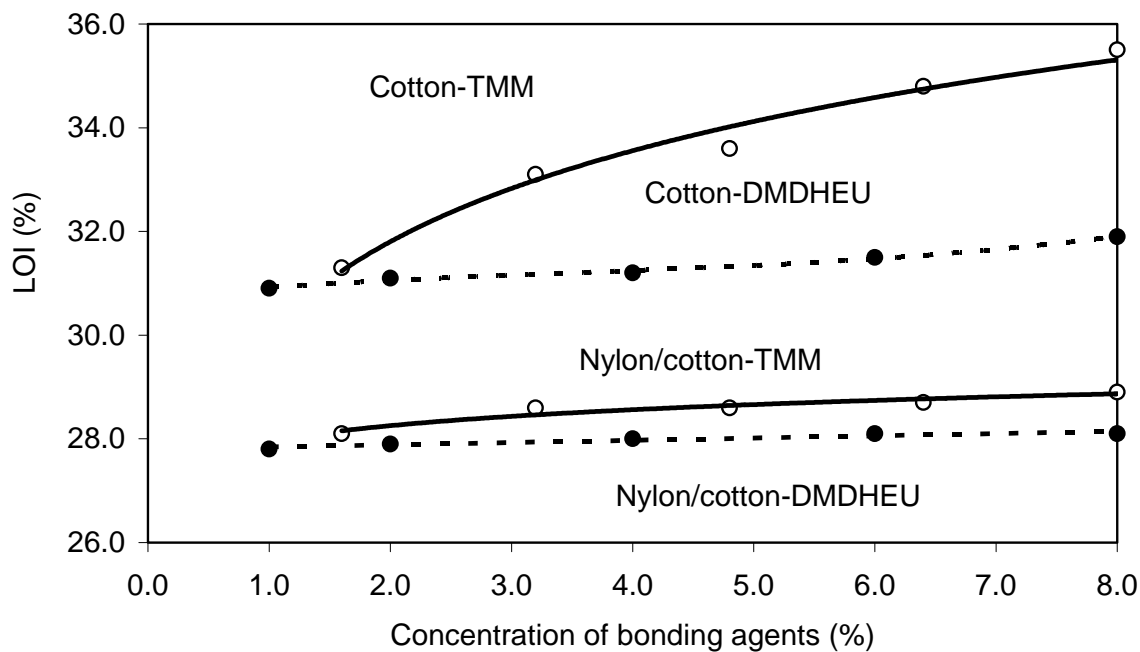


Fig.5.7 The LOI of the cotton and the nylon/cotton blend fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (before laundering).

#### Flame Retardant Performance of the Treated Nylon/Cotton Blend Fabric

The nylon/cotton blend fabric was treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations, then cured at 165°C for 2.5 min, and

finally subjected to 1 laundering cycle. The LOI of the nylon/cotton blend fabric thus treated is plotted against the concentration of bonding agents (TMM or DMDHEU) in Fig.5.8. When DMDHEU concentration is increased from 1.0% to 8.0, the LOI of nylon/cotton blend fabric thus treated increases from 22.9% to 28.1%. The increasing LOI value mainly results from the increasing phosphorus concentration on the treated nylon/cotton blend fabric. The LOI of the treated nylon/cotton blend fabric after 1 laundering cycle increases from 22.6% to 28.5% as TMM concentration is increased from 1.6% to 8.0% in the finishing solutions. The increased LOI value is attributed to the combined effect of increasing phosphorus concentration on the treated nylon/cotton blend fabric and phosphorus-nitrogen synergism between HFPO and TMM.

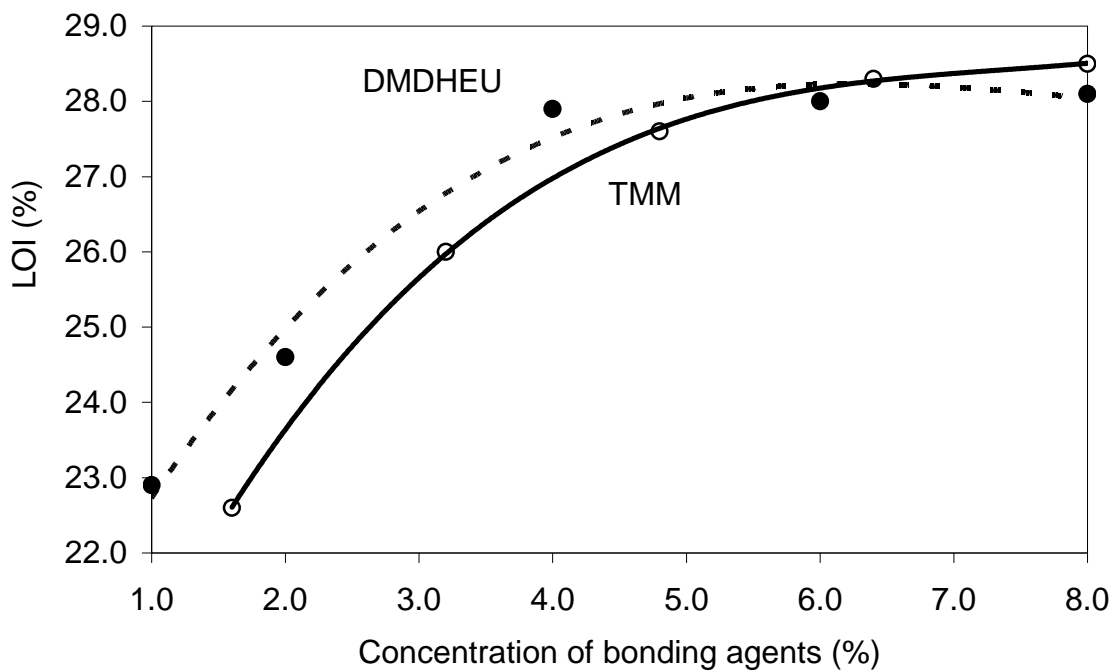


Fig.5.8 The LOI of the cotton and nylon/cotton blend fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 1 laundering cycle).

The LOI of nylon/cotton blend fabric treated with HFPO/TMM after 1 laundering cycle is higher than that treated with HFPO/DMDHEU when the concentration of bonding agents is lower than around 6%. When the concentration of bonding agent increases from 1.6% to 8.0%, the LOI of the nylon/cotton blend fabric treated with HFPO/DMDHEU gradually approaches and then becomes higher than that treated with HFPO/TMM. A similar trend is observed in the case of cotton thus treated even though the larger LOI difference exists between the cotton treated with HFPO/TMM and that treated with HFPO/DMDHEU.

The LOI of the fabric thus treated after 10 laundering cycles is plotted against the concentration of bonding agents (TMM or DMDHEU) in Fig.5.9. In the case of cotton, the LOI of cotton treated with HFPO/DMDHEU first is higher and then lower than that treated with HFPO/TMM when the concentration of bonding agents is increased in the formula. However, all nylon/cotton blend fabrics treated with HFPO/DMDHEU have notably higher LOI value than those treated with HFPO/TMM.

In the case of cotton, TMM appears significantly stronger phosphorus-nitrogen synergism with HFPO than DMDHEU (Fig.5.8). As a result, the cotton fabric treated with HFPO/TMM has much higher LOI value than that treated with HFPO/DMDHEU in spite of the fact that the cotton treated with HFPO/TMM has notably lower phosphorus concentration and percent phosphorus retention than that treated with HFPO/DMDHEU.

As we mentioned in Fig.5.8, both TMM and DMDHEU have the phosphorus-nitrogen synergism with HFPO on the nylon/cotton blend fabric as well as the cotton fabric, but the phosphorus-nitrogen synergism in the nylon/cotton blend fabric becomes weaker than that in the cotton fabric due to the presence of nylon in the nylon/cotton

blend. Moreover, the cotton and nylon fabric treated with HFPO/DMDHEU has higher percent phosphorus retention and is more durable to laundering than that treated with HFPO/TMM. The LOI of treated nylon/cotton blend fabric thus treated should be attributed to the combinational flame retardant effect of HFPO bound onto fabric and phosphorus-nitrogen synergism. After 10 laundering cycles, the nylon/cotton fabric treated with HFPO/DMDHEU has higher flame retardant performance than that treated with HFPO/TMM because the phosphorus-nitrogen synergistic effect between TMM and HFPO on the nylon/cotton blend treated with HFPO/TMM is overwhelmed by the flame retardant effect of more HFPO on the nylon/cotton fabric treated with HFPO/DMDHEU.

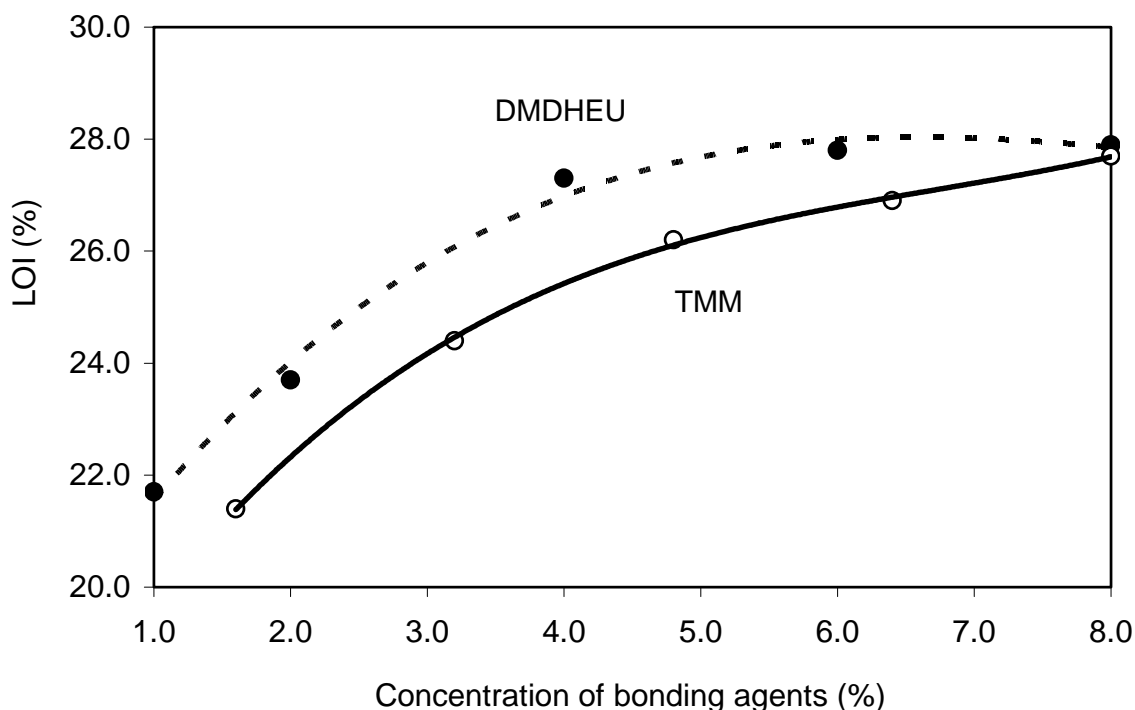


Fig.5.9 The LOI of the cotton and nylon/cotton blend fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles).

### **Effects of finish on physical properties**

The stiffness of the nylon/cotton blend fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations (after 1 laundering cycle) is plotted as a function of the phosphorus concentration of the fabric thus treated in Fig.5.10. When the phosphorus concentration on the nylon/cotton blend treated with HFPO/TMM increases from 0.46% to 1.81%, the corresponding stiffness gradually increases from 680 grams to 951grams. The fabric stiffness drastically increases from 951grams to 1831 grams as the phosphorus concentration further increases from 1.81% to 2.08%. This is probably caused by the self-condensation of TMM. For the nylon/cotton blend fabric treated with HFPO/DMDHEU, the stiffness only increases from 512 grams to 1089 grams as the DMDHEU concentration increases from 1% to 8%. The increased stiffness is mainly attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose. One can observe similar trends in the nylon/cotton blend fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations (after 10 laundering cycles), as shown in Fig.5.11. It can be concluded that the nylon/cotton blend fabric treated with HFPO/DMDHEU has a notably lower stiffness than that treated with HFPO/TMM to achieve the same phosphorus concentration on the treated fabric.

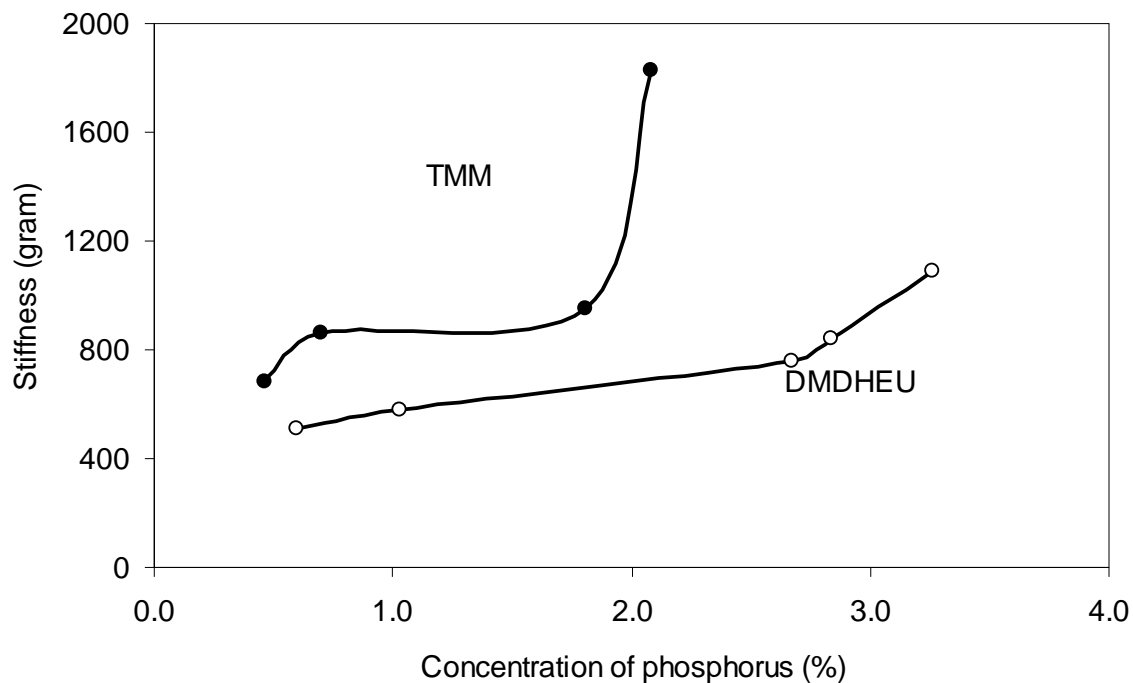


Fig.5.10 The stiffness of the nylon/cotton blend treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 1 laundering cycle).

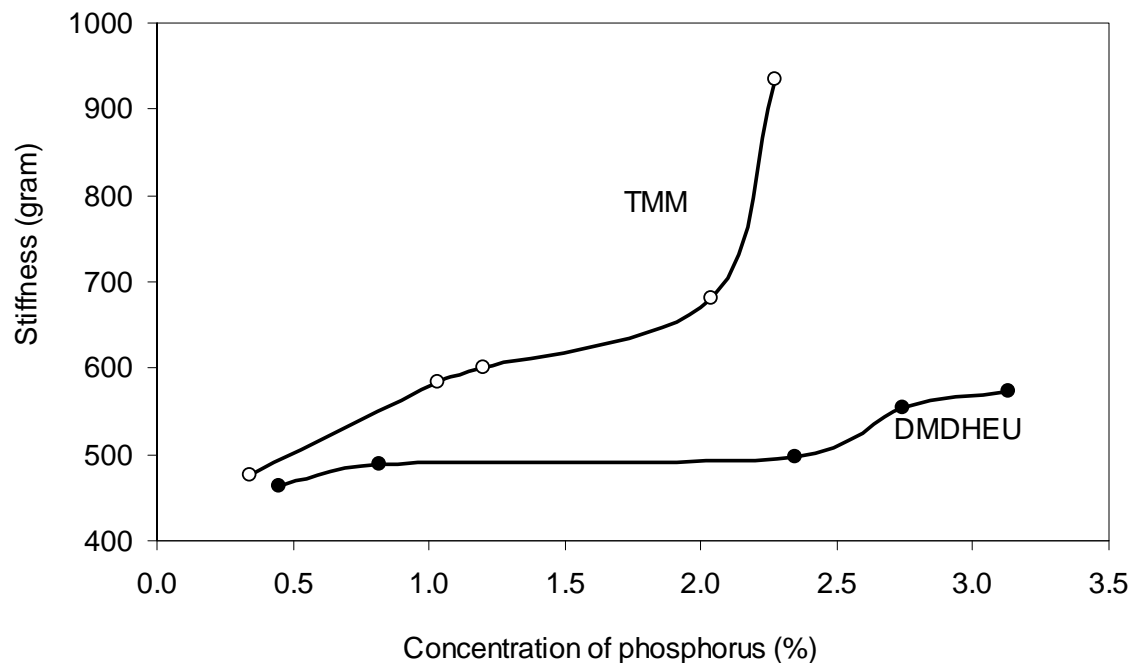


Fig.5.11 The stiffness of the cotton fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles).

The stiffness of the cotton fabric treated with 40% HFPO and bonding agent (DMDHEU or TMM) at different concentrations (after 1 laundering cycle) is plotted as a function of phosphorus concentration of the fabric thus treated in Fig.5.12. When the phosphorus concentration on the treated cotton fabric is increased from 0.66% to 1.55%, the stiffness of cotton fabric treated with HFPO/TMM only slightly increases from 684 grams to 779 grams. When the phosphorus concentration is increased from 1.55% to 2.60%, TMM causes a sharp increase of stiffness from 779 grams to 2201 grams, and then becomes overloaded (>5000 grams). But the stiffness of cotton fabric treated with HFPO/DMDHEU only increases from 577 grams to 1083 grams when the phosphorus concentration is lower than 2.92% on the treated cotton fabric. However, further addition of phosphorus concentration on the cotton fabric treated with HFPO/DMDHEU results in a sharp increase of the fabric stiffness. The stiffness of the cotton fabric treated with 40% HFPO and bonding agent (DMDHEU or TMM) at different concentrations and subjected to 10 laundering cycles is plotted as a function of phosphorus concentration of the treated cotton fabric in Fig.5.13. A similar situation is observed. Therefore, the cotton fabric treated with HFPO/DMDHEU has a notably lower stiffness than that treated with HFPO/TMM to achieve the same phosphorus concentration on the treated cotton fabric.



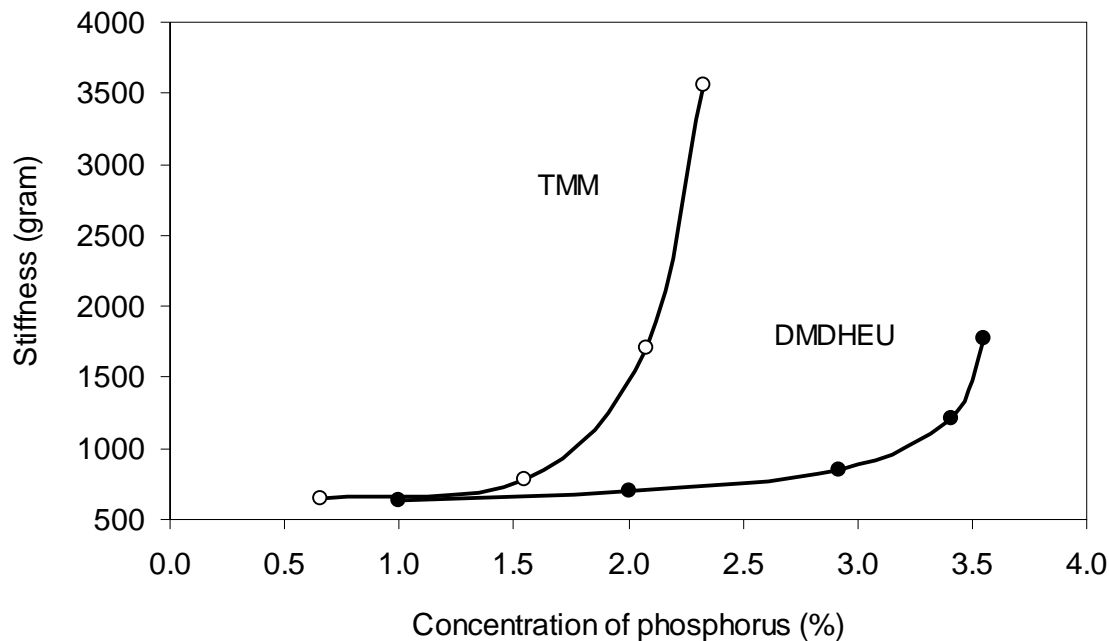


Fig.5.12 The stiffness of the cotton fabric treated with 40%HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 1 laundering cycle).

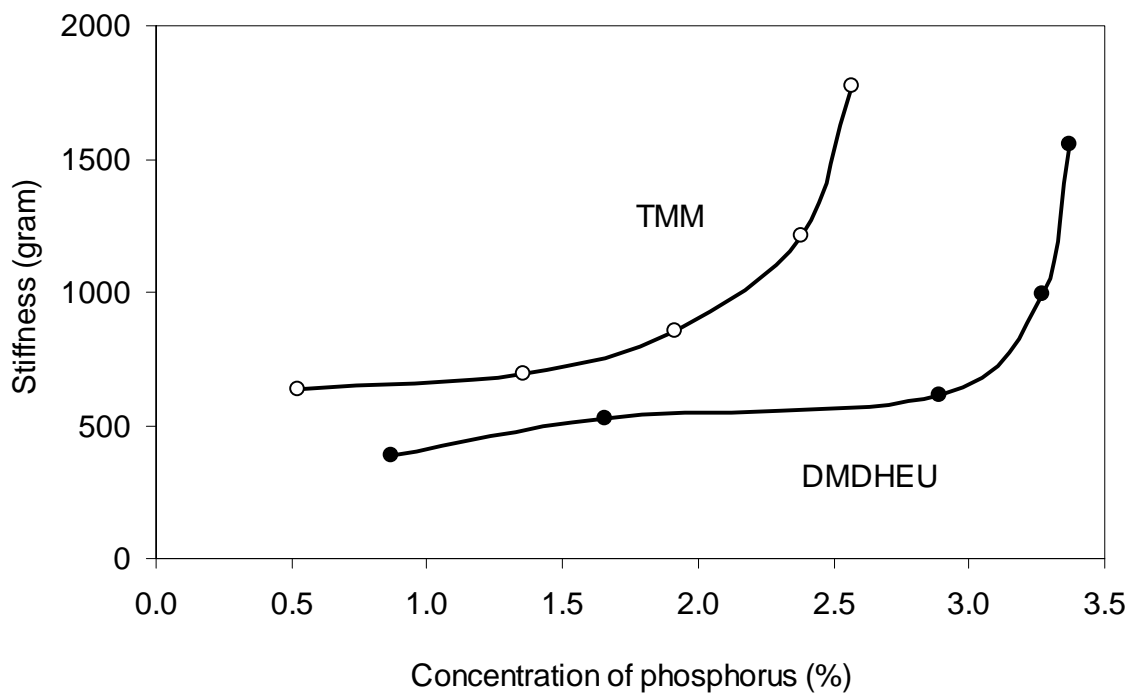


Fig.5.13 The stiffness of the cotton fabric treated with 40%HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles).

The following hypothesis is proposed to explain above results. When HFPO is applied to cotton using DMDHEU as a bonding agent, DMDHEU reacts with hydroxyl groups of both cotton and HFPO. HFPO is bound to cotton fabric by a formation of linear structure of HFPO-DMDHEU-Cotton cellulose at the high molar ratio of HFPO/DMDHEU in the finishing solution. When HFPO is exhausted, however, the crosslinking between DMDHEU and cotton hydroxyl groups to form a crosslinked polymeric network became dominant, thus resulting in a significant increase of fabric stiffness.

In the case of cotton fabric treated with HFPO/TMM, two competitive reactions occurred: one is polymerization of TMM with hydroxyl groups of HFPO; the other is the self-condensation of TMM. The self-condensation of TMM becomes dominant at the lower molar ratio of HFPO to TMM. The self-condensation of TMM probably is mainly responsible for the increased fabric stiffness.

The stiffness of the nylon fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations (after 10 laundering cycles) is plotted as a function of the phosphorus concentration of the fabric thus treated in Fig.5.14. When the phosphorus concentration on the treated nylon fabric treated with HFPO/TMM increases from 0.12% to 0.64%, the fabric stiffness thus treated also increases from 65 grams to 91 grams. However, the stiffness of nylon fabric treated with HFPO/DMDHEU (after 10 laundering cycles) appears to be unchanged when the phosphorus concentration on the nylon fabric thus treated increases from 0.14% to 1.30%. The data presented here strongly indicate that high stiffness of the nylon fabric treated with HFPO/TMM is mainly caused by the self-condensation of TMM. However, DMDHEU may not self-

condense when it is applied to nylon with HFPO. As a result, the nylon treated with HFPO/DMDHEU has only a slight increase of fabric stiffness.

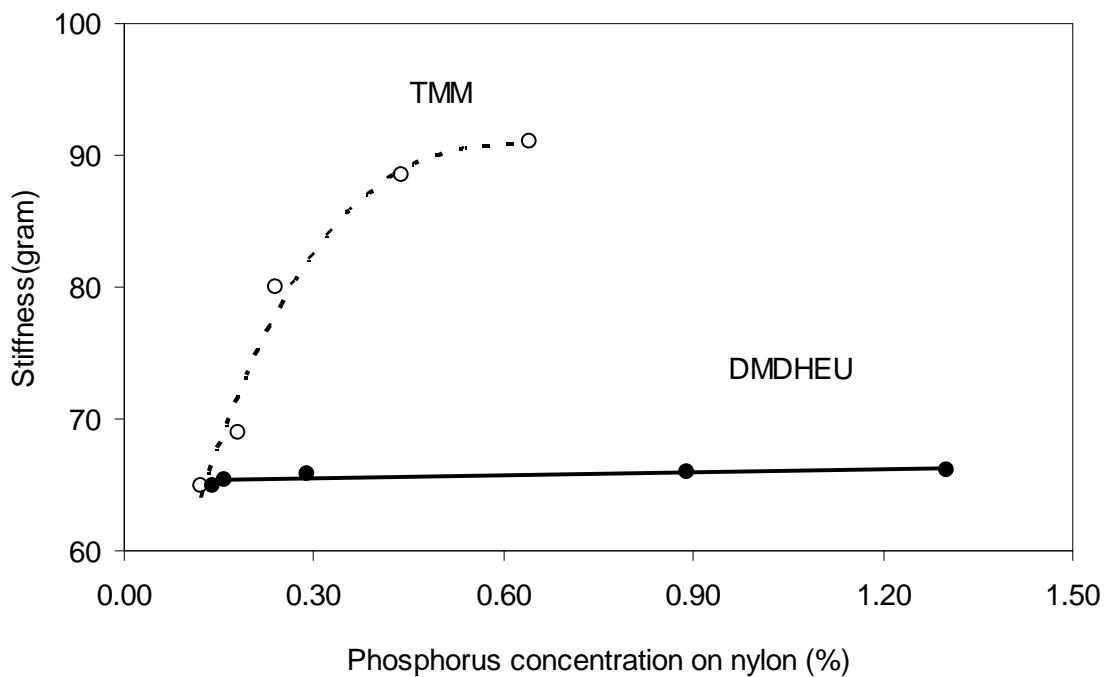


Fig.5.14 The stiffness of the nylon fabric treated with 40% HFPO and a bonding agent (DMDHEU or TMM) at different concentrations and cured at 165°C for 2.5 min (after 10 laundering cycles).

## Conclusions

Both TMM and DMDHEU are able to covalently bond HFPO to the nylon/cotton blend fabric. The nylon/cotton blend fabric treated with HFPO/DMDHEU has higher phosphorus concentration and percent phosphorus retention than that treated with HFPO/TMM. However, TMM has more notable phosphorus-nitrogen synergism with HFPO on the nylon/cotton blend fabric than DMDHEU. The phosphorus-nitrogen synergism between HFPO and DMDHEU/TMM in the nylon/cotton blend fabric becomes much weaker than that in the cotton fabric due to the presence of nylon in the nylon/cotton blend fabric. As a result, the nylon/cotton fabric treated with HFPO/DMDHEU after 10 laundering cycles has higher flame retardant performance than that treated with HFPO/TMM. The percent phosphorus retention of the nylon/cotton blend fabric is much closer to the percent phosphorus retention of cotton fabric than that of nylon, which strongly indicates that most finish fixes into the cotton component whereas a portion of finish is bound to the nylon component. In addition, both TMM and DMDHEU cause an increase of fabric stiffness when they are applied to the nylon/cotton blend fabric and cotton fabric with HFPO. In order to achieve the same amount of phosphorus concentration on cotton fabric, TMM causes significantly higher fabric stiffness than DMDHEU, which might be mainly attributed to the self-condensation of TMM.

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**CHAPTER 6**

**FLAME RETARDANT PERFORMANCE OF THE NYLON/COTTON BLEND  
FABRIC TREATED BY A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS  
OLIGOMER**

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<sup>1</sup> Yang, H. and Yang, C.Q. To be submitted to *Polymer Degradation and Stability*.



### Abstract

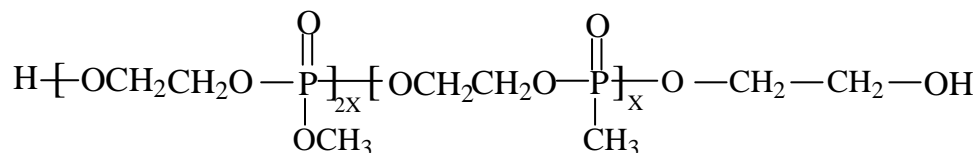
In my previous research, nylon/cotton blend fabric treated with hydroxy-functional organophosphorus oligomer (HFPO) using a mixture of dimethyloldihydroxyethyleneurea (DMDHEU) and melamine-formaldehyde as a bonding system achieved high levels of flame retardant performance and good laundering durability. I also discovered that DMDHEU is able to covalently bond HFPO to nylon as well as cotton. In this research, I applied HFPO to nylon/cotton blend fabric using DMDHEU as a bonding agent. The treated fabric shows high levels of flame retardant performance and good laundering durability. The treated fabric passes the vertical flammability test even after 50 laundering cycles. The DMDHEU concentration plays an important role in the flame retardant performance of the treated fabric. At a certain DMDHEU concentration level, increasing HFPO concentration in the formulas not only increases the phosphorus fixation but also lowers the fabric stiffness. However, the laundering resistance of HFPO bound to the nylon/cotton blend fabric decreases with an increase of the molar ratio of HFPO/DMDHEU. The fabric treated with HFPO/DMDHEU has very limited loss of the tensile strength. The pH of the finish bath has no significant effect on the flame retardant performance, phosphorus retention and tensile strength of the nylon/cotton blend fabric treated with HFPO/DMDHEU.

**Key Words:** Dimethyloldihydroxyethyleneurea, Durable flame retardant finishing, Organophosphorus chemicals, Nylon/cotton blend.

## Introduction

Durable flame retardant finishing is important for nylon/cotton blend fabric, especially when it is used as a material for protective clothing [1-3]. However, durable flame retardant finishing is a very challenging topic up to today, and related research is very limited [4-7]. Currently, no practical technique has been commercialized successfully for the flame retardant finishing of nylon/cotton blend fabric.

In my previous research [8], I found that nylon/cotton blend fabric treated with hydroxy-functional organophosphorus oligomer (HFPO, as shown in Scheme 6.1) using a mixture of dimethyldihydroxyethyleneurea (DMDHEU) and trimethylol-melamine (TMM) as a bonding system showed high levels of flame retardant performance and good laundering durability. However, fabric stiffness was a major limitation for practical use.



Scheme 6.1 Structure of HFPO

In chapter 3, I report that DMDHEU is able to covalently bond HFPO to nylon through the formation of a crosslinked polymeric network of HFPO/DMDHEU. In chapter 4, I describe how DMDHEU can covalently bond HFPO to cotton by the formation of a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose. In chapter 5, I demonstrate that DMDHEU is a more effective agent for bonding HFPO to the nylon/cotton blend fabric than TMM. The nylon/cotton blend fabric treated with HFPO/DMDHEU after 10 laundering cycles shows higher flame retardant performance with notably lower stiffness than that treated with HFPO/TMM.

In this research, I applied HFPO to the nylon/cotton blend fabric using DMDHEU

as a bonding agent. The flame retardant performance and physical properties were evaluated. The effects of pH value of the finishing bath on the flame retardant performance were also studied.

## **Experimental**

### **Materials**

Two kinds of fabrics were used in this study: (1) the 50%/50% nylon/cotton Battle Dress Uniform (BDU) pure finish ripstop fabric printed with three-color Day Desert camouflage weighing  $220 \text{ g/m}^2$  (Military specification: MIL-C-44031 CL1) was supplied by Bradford dyeing association, Inc. Bradford, RI; (2) the 50%/50% nylon/cotton BDU pure finish twill fabric with three-color woodland camouflage weighing  $216 \text{ g/m}^2$  (Military specification: MIL-C-44436 CL3) was supplied by Bradford dyeing association, Inc. Bradford, RI. HFPO, under the commercial name of “Fyroltex HP” (also known as “Fyrol 51”, CA Registry No. 70715-06-9), was supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. DMDHEU was a commercial product (44% solid content) with the trade name of “Freerez 900” supplied by Noveon, Cleveland, Ohio. The catalyst was an  $\text{NH}_4\text{Cl}$ -based commercial product under the trade name of “Catalyst RD” supplied by Eastern Color & Chemical, Greenville, South Carolina.

### **Fabric Treatment and Laundering Procedures**

The fabric was treated in the following procedures. First, the fabric was immersed in a finish solution and passed through a laboratory padder with two dips and two nips. Then, the nylon/cotton blend fabric thus treated was dried at  $90^\circ\text{C}$  for 3 min and cured in

a Mathis curing oven at 165°C for 2 min. All concentrations presented in this study are based on weight of bath (w/w, %), and concentrations of HFPO and DMDHEU in all solutions are based on the solid of the chemicals in those chemical products. The wet pick-up of the nylon/cotton blend fabric is  $77\pm 2\%$ . After curing, the treated fabric was subjected to a specified number of laundering cycles using “AATCC Standard Detergent 1993”. The laundering process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics after Repeated Home Laundering”), and the water temperature of laundering is approximately 46°C.

### **Evaluation of the Flame Retarding Performance of the Fabrics**

The vertical flammability of the fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the fabric was measured according to ASTM Standard Method D2863-97.

### **Evaluation of the Fabric Properties**

The fabric stiffness was measured according to ASTM Standard Method D6828-02 using Handle-O-Meter tester (Model 211-300), manufactured by Thwing-Albert instrument company, Philadelphia, U.S.A. The slot width used in this study was 5mm, and the beam size used in this study was 1000g. The fabric stiffness presented in this study was the mean of total stiffness obtained of 5 specimens.

The tensile strength of the fabric was measured according to ASTM Standard Method D5035-95.

### **Determination of Phosphorus Concentration on the Treated Fabric**

Approximately 2 g of the treated fabric sample taken from three different parts of a “10×12” fabric specimen were ground in a Wiley mill into powder to improve sample

uniformity. 2 ml of concentrated  $\text{H}_2\text{SO}_4$  were added to 0.1 g of the powder in a beaker. 10 ml of 30%  $\text{H}_2\text{O}_2$  were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately  $250^\circ\text{C}$  to digest the powder and to evaporate the water until dense  $\text{SO}_3$  vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration. The percent phosphorus retention is calculated by dividing the phosphorus concentration of the fabric after laundering by that of the fabric before laundering.

## **Results and Discussion**

### **Flame retardant performance and laundering durability**

The nylon/cotton fabric (woodland) was treated with 32% HFPO and DMDHEU at different concentrations and cured at  $165^\circ\text{C}$  for 2 min. The phosphorus concentration of the fabric thus treated and subjected to different numbers of laundering cycles is shown in Table 6.1. The phosphorus retention of the treated fabric is plotted against the DMDHEU concentration in Fig.6.1. When DMDHEU increases from 1% to 10%, the phosphorus concentration of the treated fabric after one laundering cycle also increases from 0.56% (16% phosphorus fixation) to 2.69% (78% phosphorus fixation). A same situations is observed in the treated fabric after 20 and 40 laundering cycles. At a certain DMDHEU concentration level, the phosphorus concentration and phosphorus retention decreases with the number of laundering cycles, which is due to the hydrolysis of the HFPO bound to the

treated fabric during laundering. The fabric treated with 32%HFPO/10%DMDHEU after 40 laundering cycles still retains 1.84% phosphorus (54% phosphorus retention).

Table 6.1 The phosphorus concentration of the nylon/cotton fabric (woodland) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	Phosphorus concentration (%)		
	after 1 wash	after 20 washes	after 40 washes
1	0.56	0.30	0.25
2	1.34	0.52	0.42
4	1.81	0.72	0.64
6	2.47	1.79	1.01
8	2.59	2.00	1.13
10	2.69	2.18	1.84

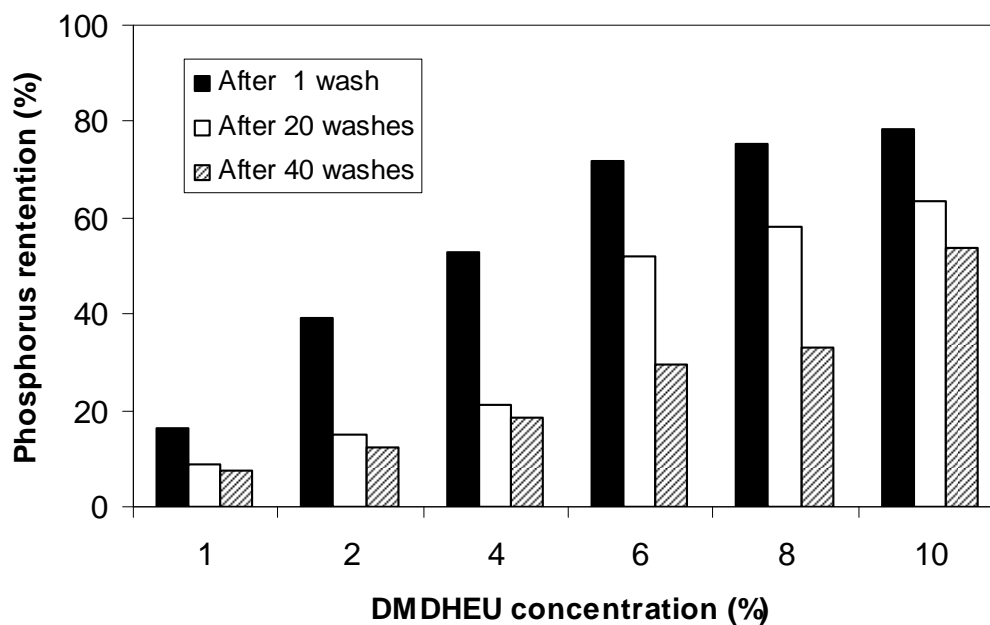


Fig.6.1 The percent phosphorus retention of the nylon/cotton fabric (woodland) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min.

The LOI and char length of the fabric thus treated and subjected to different numbers of laundering cycles is shown in Table 6.2 and Table 6.3, respectively. When the DMDHEU concentration is increased from 1% to 10%, the LOI of the treated fabric (after 1 laundering cycle) increases from 22.9% to 28.0%. Even though the LOI of the treated fabric decreases with the number of laundering cycles, a similar situation is observed in the treated fabric after 10, 20 and 40 laundering cycles. After 40 laundering cycles, the fabric treated with 32% HFPO and less than 4% DMDHEU fails to pass the vertical flammability test (char length >300mm) whereas fabric treated with 32% HFPO and over 6% DMDHEU passes the vertical flammability test. The LOI of the fabric treated with 32% HFPO/10% DMDHEU (after 40 laundering cycles) is 27.0% with char length of 81 mm. The data presented above clearly show that DMDHEU concentration plays an important role in the flame retardant performance of the nylon/cotton blend fabric treated with HFPO/DMDHEU. This is because DMDHEU increases the amount of HFPO bound to the treated fabric and also improves the laundering resistance of HFPO bound onto the treated fabric.

Table 6.2 The LOI of the nylon/cotton fabric (woodland) treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	LOI (%)			
	after 1 wash	after 10 washes	after 20 washes	after 40 washes
1	22.9	22.2	21.6	21.2
2	25.0	23.2	22.5	22.2
4	26.5	25.1	23.0	22.7
6	27.7	27.1	26.8	24.8
8	27.9	27.5	27.2	25.8
10	28.0	28.0	27.4	27.0

Table 6.3 The vertical flammability test of the nylon/cotton fabric (woodland) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	Char length (mm)			
	after 1 wash	after 10 washes	after 20 washes	after 40 washes
1	>300	>300	>300	>300
2	77	>300	>300	>300
4	80	94	>300	>300
6	77	99	88	114
8	79	66	83	105
10	49	62	68	81

The nylon/cotton fabric (desert) was treated with 32% HFPO and DMDHEU at different concentrations, then cured at 165°C for 2 min, and finally subjected to different numbers of laundering cycles. The phosphorus concentration of the nylon/cotton fabric thus treated is shown in Table 6.4. The percent phosphorus retention of the nylon/cotton fabric (Desert) thus treated is plotted against the DMDHEU concentration in Fig.6.2. When the DMDHEU concentration is increased from 6% to 10%, the phosphorus concentration of the treated fabric after one laundering cycle increases from 2.11% (61% fixation) to 2.69% (78% fixation). Even though laundering causes the loss of phosphorus, after 50 laundering cycles the fabric treated with 32%HFPO/10%DMDHEU still has 0.96% (28% retention), which is almost two times that (0.50%) of the fabric treated with 32%HFPO/6%DMDHEU. The data presented here clearly demonstrate that DMDHEU notably increases the phosphorus retention and also improves the laundering resistance of the HFPO bound to the nylon/cotton blend fabric.



Table 6.4 The phosphorus concentration of the nylon/cotton fabric (Desert) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	Phosphorus concentration (%)		
	after 1 wash	after 25 washes	after 50 washes
6	2.11	0.71	0.50
8	2.50	1.28	0.66
10	2.69	1.68	0.96

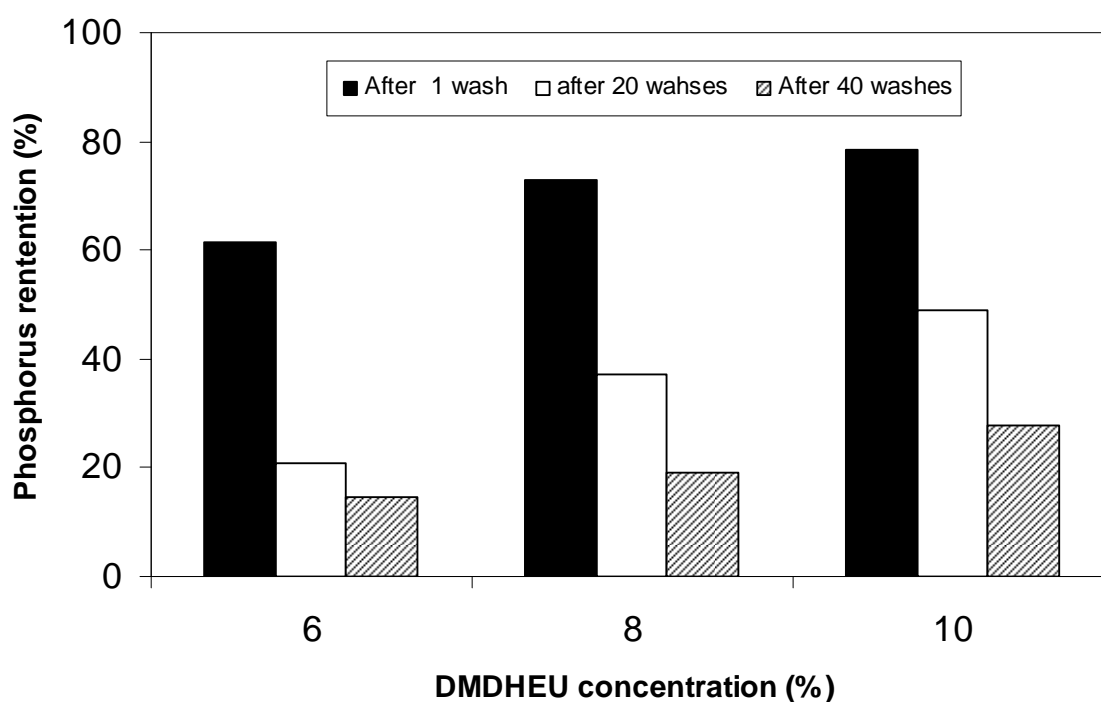


Fig.6.2 The percent phosphorus retention of the nylon/cotton fabric (Desert) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min.

The LOI of the treated fabric (desert) after 1 laundering cycle increases from 28.0% to 28.5% (Table 6.5) as HFPO is fixed at 32% and DMDHEU concentration increases from 6% to 10%. The fabric treated with 32%HFPO/6%DMDHEU has a LOI of 23.8% and fails to pass the vertical flammability test after 25 laundering cycles, whereas the fabric treated

with 32% HFPO/10% DMDHEU has a LOI of 24.8% and passes the vertical flammability test after 50 laundering cycles (Table 6.5 and Table 6.6). The data presented here strongly demonstrate that DMDHEU plays a critical role in enhancing the flame retardant performance of the nylon/cotton blend fabric treated with HFPO/DMDHEU.

Table 6.5 The LOI of the nylon/cotton fabric (desert) treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min.

DMDHEU (%)	LOI (%)			
	after 1 wash	after 25 washes	after 40 washes	after 50 washes
6	28.0	23.8	23.1	22.5
8	28.4	26.1	23.6	23.2
10	28.5	27.1	25.5	24.8

Table 6.6 The vertical flammability test of the nylon/cotton fabric (desert) treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	Char Length (mm)			
	after 1 wash	after 25 washes	after 40 washes	after 50 washes
6	68	>300	>300	>300
8	74	94	103	>300
10	53	81	92	92

The nylon/cotton blend fabric (woodland) was treated with either 32% HFPO or 40% HFPO in combination with DMDHEU at different concentrations and cured at 165°C for 2 min. The LOI of the fabric thus treated after 1 and 10 laundering cycles are shown in Fig.6.3 and Fig.6.4, respectively. At the same DMDHEU concentration levels, increasing HFPO concentration from 32% to 40% results in a slight increase of LOI value of the treated fabric after 1 and 10 laundering cycles.

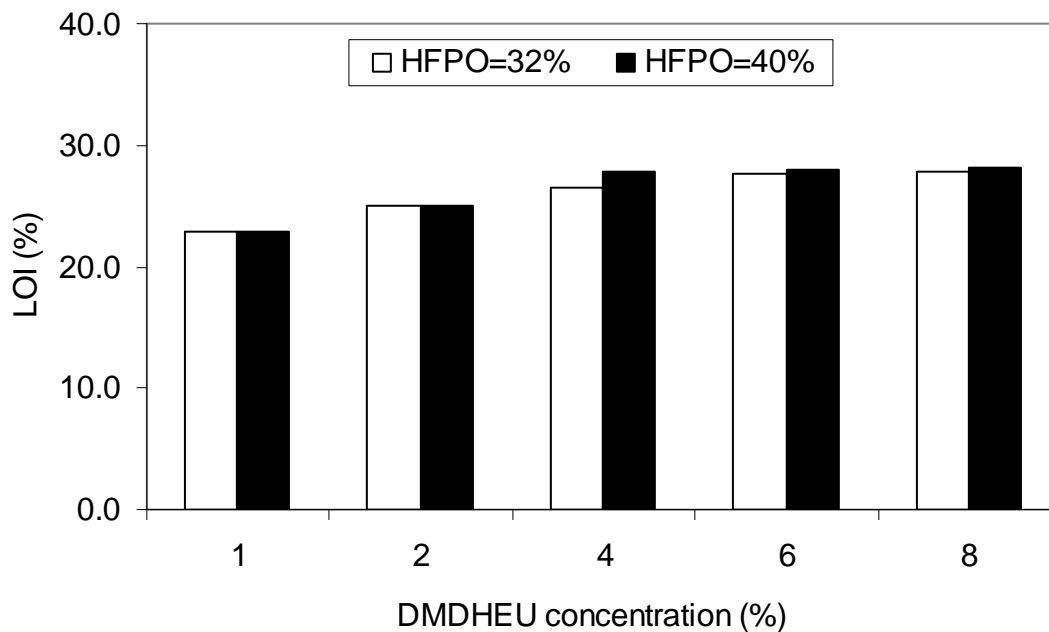


Fig.6.3 the LOI of the fabric (woodland) treated with 32%HFPO or 40%HFPO in combination with DMDHEU at different concentrations (after 1 laundering cycle)

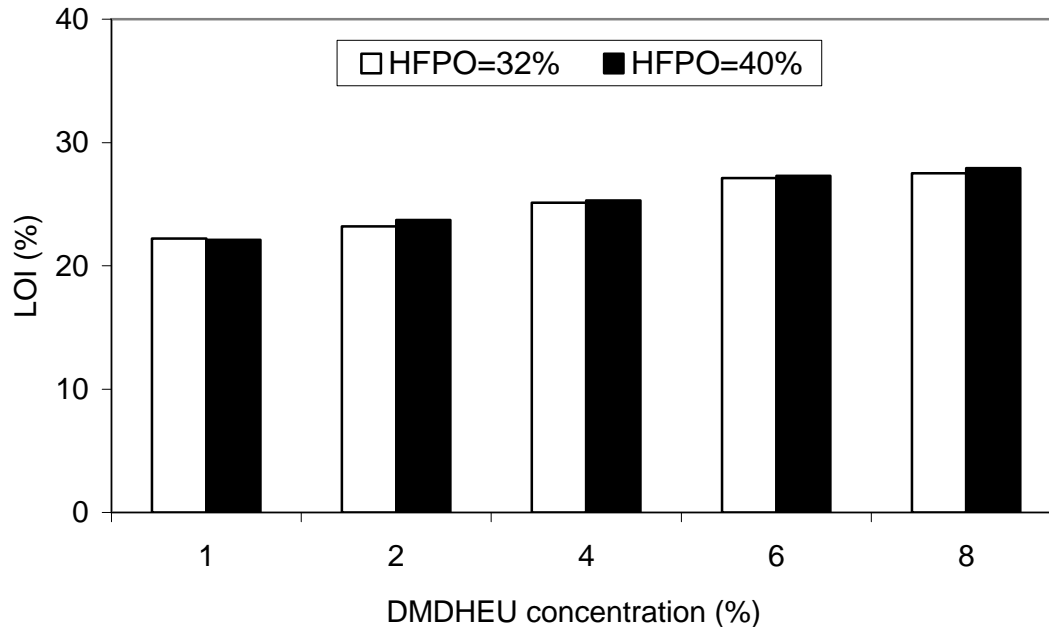


Fig.6.4 the LOI of the fabric (woodland) treated with 32%HFPO or 40%HFPO in combination with DMDHEU at different concentrations (after 10 laundering cycles)

The nylon/cotton fabric (desert) was treated with 8% DMDHEU and HFPO at different concentrations, then cured at 165°C for 2 min, and finally subjected to different numbers of laundering cycles. The phosphorus concentration and percent phosphorus retention are shown in Table 6.9 and Fig.6.5. When the HFPO concentration is increased from 24% to 40%, the phosphorus concentration of the treated fabric after one laundering cycle also increases from 1.90% to 3.14%, but all phosphorus fixations are around 75%, appearing to be unchanged. After 25 laundering cycles, however, the phosphorus concentration decreases from 1.34% (58% retention) to 0.81% (19% retention) as the HFPO concentration increases from 24% to 40%. After 50 laundering cycles, the same situation is observed. The fabric treated with 24% HFPO/8% DMDHEU still retains 0.87% phosphorus (33% retention), which is significantly higher than that (0.54% phosphorus and 13% retention) of the fabric treated with 40% HFPO/8% DMDHEU. The data presented here clearly demonstrate that at a certain DMDHEU concentration level, increasing HFPO concentration results in higher initial phosphorus fixation, but lowers the laundering resistance of HFPO bound to the nylon/cotton blend fabric. This is probably because a crosslinked polymeric network is formed only at an appropriate molar ratio. When the DMDHEU concentration is fixed at 8%, increasing HFPO concentration results in a decrease of the molar ratio of HFPO/DMDHEU, and more HFPO tends to react with DMDHEU through a linear structure instead of a crosslinked polymeric network. As a result, the number of crosslinks decreases, which results in a decrease of laundering resistance of HFPO bound to the fabric and which also lowers the fabric stiffness (Table 6.15).

Table 6.9 The phosphorus concentration of the nylon/cotton blend fabric (desert) treated with 8%DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min

HFPO (%)	Phosphorus concentration (%)		
	after 1 wash	after 25 washes	after 50 washes
24	1.90	1.34	0.87
32	2.50	1.28	0.66
40	3.14	0.81	0.54

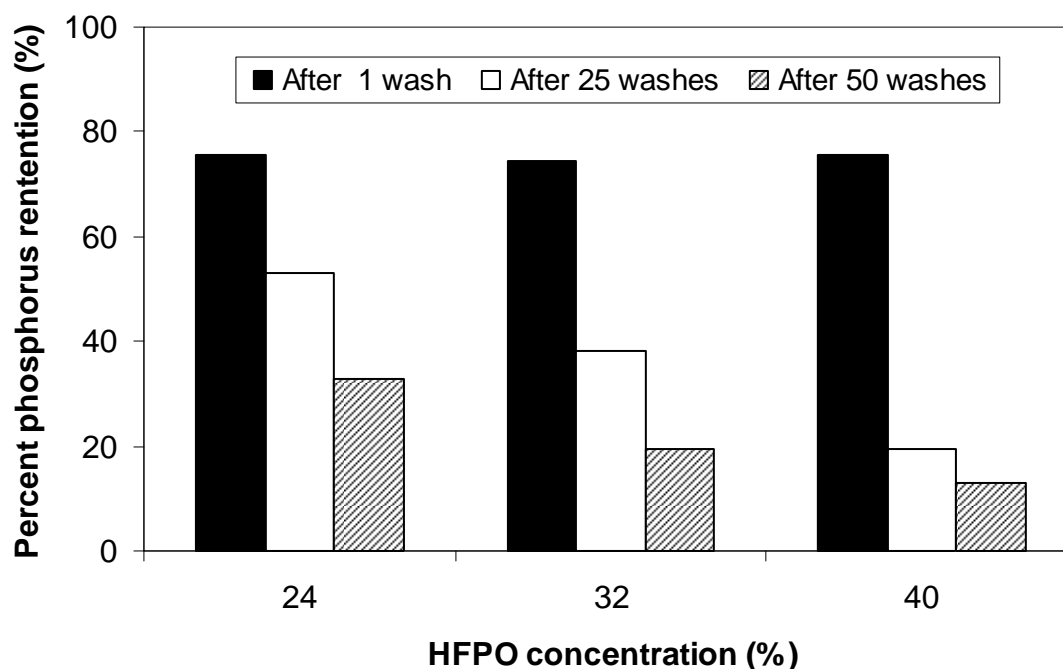


Fig.6.5 The percent phosphorus retention of the nylon/cotton blend fabric (Desert) treated with 8%DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min.

The LOI and char length of the fabric thus treated are shown in Table 6.10 and Table 6.11, respectively. When DMDHEU concentration is fixed at 8% and HFPO concentration is increased from 24% to 40%, the LOI of the treated fabric after 1 laundering cycle slightly increases from 27.8% to 28.4%. The LOI of the treated fabric

(after 50 laundering cycles) increases from 22.8% to 23.6% by 0.8%. The fabric treated with 24% HFPO/8% DMDHEU has a LOI of 24.7% and passes the vertical flammability test with a char length of 98 mm after 40 laundering cycles (Table 6.10 and Table 6.11), but the fabric treated with 40% HFPO/8% DMDHEU fails to pass the vertical flammability test with LOI of 24.3% after 40 laundering cycles (Table 6.10 and Table 6.11).

Table 6.10 The LOI of the nylon/cotton blend fabric (desert) treated with 8% HFPO and HFPO at different concentrations and cured at 165°C for 2 min.

HFPO (%)	LOI (%)			
	after 1 wash	after 25 washes	after 40 washes	after 50 washes
24	27.8	26.3	24.7	24.1
32	28.4	26.1	24.4	23.2
40	28.4	26.0	24.1	22.8

Table 6.11 The vertical flammability test of the nylon/cotton blend fabric (desert) treated with 8% DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min

HFPO (%)	Char Length (mm)			
	after 1 wash	after 25 washes	after 40 washes	after 50 washes
24	75	96	98	>300
32	74	94	103	>300
40	48	203	>300	>300

### Physical properties of the treated fabric

The nylon/cotton fabric (woodland) was treated with 32% HFPO and DMDHEU at different concentrations, then cured at 165°C for 2 min, and finally subjected to 1 and 10

laundering cycles. The tensile strength of the fabric thus treated after 1 laundering cycle is shown in Table 6.12. At 32% HFPO level, increasing DMDHEU concentration from 2% to 6% decreases the tensile strength in the warp direction from 703N (98% retention) to 685N (95% retention). The tensile strength in the filling direction is in the range from 445N (97 retention) to 454N (99% retention). The data presented here demonstrate that the fabric treated with HFPO/DMDHEU shows only very limited tensile strength loss.

Table 6.12 The tensile strength of the nylon/cotton fabric (woodland) treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min (after 1 laundering cycle)

DMDHEU (%)	Tensile strength (N)			
	Warp (N)	Strength Retention (%)	Filling (N)	Strength Retention (%)
2	703	98	454	99
4	694	96	449	98
6	685	95	445	97
Control	721	--	458	--

The stiffness of the fabric thus treated after 1 and 10 laundering cycles is shown in Table 6.13. At 32% HFPO level, increasing DMDHEU concentration from 1% to 10% causes an increase of the fabric stiffness after 1 laundering cycle from 483 grams to 1208 grams. After 10 laundering cycles, the fabric stiffness also increases from 479 grams to 685 grams. Therefore, it is very clear that DMDHEU concentration plays an important role in determining the fabric stiffness. The stiffness of the treated fabric increases with the DMDHEU concentration, which is attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose in the cotton component and a crosslinked

polymeric network of HFPO/DMDHEU on the nylon component in the blend fabric. When the number of laundering cycle increases from 1 to 10, the stiffness of the fabric treated with 32% HFPO/10% DMDHEU decreases from 1208 grams to 685 grams, which strongly indicates that laundering notably reduces the fabric stiffness.

Table 6.13 The stiffness of the nylon/cotton fabric (woodland) treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min

DMDHEU (%)	Stiffness (grams)	
	after 1 wash	after 10 washes
1	483	479
2	521	483
4	555	523
6	971	615
8	1118	638
10	1208	685

The nylon/cotton blend fabric (woodland) was treated with 6% DMDHEU and HFPO at different concentrations, then cured at 165 °C for 2.5 min, and finally subjected to 1 laundering cycle. The stiffness of the fabric thus treated is shown in Table 6.14.

When HFPO concentration is increased from 4% to 40%, the fabric stiffness notably increases from 782 grams, then achieves the maximum 1280 grams, and finally decreases to 833 grams. The change of fabric stiffness is mainly caused by the cotton component treated by HFPO/DMDHEU. Table 6.15 shows the stiffness of the nylon/cotton blend fabric (desert) was treated with 6% DMDHEU and HFPO at the different concentrations. A similar situation is observed. When HFPO concentration is increased from 4% to 40%,



the fabric stiffness notably increases from 445 grams, to the maximum 729 grams, and finally decreases to 488 grams.

Table 6.14 The stiffness of the nylon/cotton fabric (woodland) treated with 6% DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min.

HFPO (%)	Stiffness (grams)
4	782
8	1024
16	1280
24	1126
32	971
40	833

Table 6.15 The stiffness of the nylon/cotton fabric (desert) treated with 6% DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min.

HFPO (%)	Stiffness (grams)
4	445
8	512
16	729
24	510
32	504
40	488

The nylon/cotton fabric (Desert) was treated with 32% HFPO and DMDHEU at different concentrations, then cured at 165°C for 2 min, and finally subjected to 1 laundering cycle. Table 6.16 shows the stiffness, tensile strength, and tensile strength retention of the fabric thus treated after 1 laundering cycle. The fabric stiffness increases

from 504 grams to 830 grams as DMDHEU concentration is increased from 6% to 10%. This is mainly attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose in the cotton component and a crosslinked polymeric network of HFPO/DMDHEU on the nylon component in the nylon/cotton blend fabric.

When DMDHEU concentration is increased from 6% to 8% in the finishing solutions, the tensile strength in the warp direction is in the range of 599N (94% retention) to 604N (95% retention), and the tensile strength in the filling direction is in the range of 408N (98% retention) to 416N (100% retention). The data presented here strongly indicate that increasing DMDHEU concentration results in an increase of the fabric stiffness, but causes very limited loss of tensile strength (Table 6.16).

Table 6.16 The tensile strength of the nylon/cotton fabric (desert) treated with 32%HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min (after 1 laundering cycle)

DMDHEU (%)	Stiffness (grams)	Warp		Filling	
		Tensile Strength (N)	Strength Retention (%)	Tensile Strength (N)	Strength Retention (%)
6	504	604	95	416	100
8	542	599	94	415	99
10	830	599	94	408	98
Control	224	635	--	416	--

The nylon/cotton fabric (desert) was treated with 8% DMDHEU and HFPO at different concentrations, then cured at 165°C for 2 min, and finally subjected to 1 laundering cycle. Table 6.17 shows the stiffness, tensile strength, and tensile strength retention of the fabric thus treated after 1 laundering cycle. The fabric stiffness decreases

from 732 grams to 412 grams as HFPO concentration is increased from 24% to 40%. This is mainly attributed to the formation of a crosslinked polymeric network of HFPO/DMDHEU/Cotton cellulose in the cotton component and a crosslinked polymeric network of HFPO/DMDHEU on the nylon in the nylon/cotton blend fabric.

When HFPO concentration is increased from 24% to 40% in the finishing solutions, the tensile strength in the warp direction slightly increases from 589N (93% retention) to 605N (95% retention), and the tensile strength in the filling direction increases from 380N (91% retention) to 416N (100% retention). The data presented here strongly indicate that increasing HFPO concentration results in a decrease of the fabric stiffness, but only slightly increases the tensile strength of the treated fabric (Table 6.17).

Table 6.17 The tensile strength of the nylon/cotton fabric (Desert) treated with 8% DMDHEU and HFPO at different concentrations and cured at 165°C for 2 min (after 1 laundering cycle)

HFPO (%)	Stiffness (grams)	Warp		Filling	
		Tensile Strength (N)	Retention (%)	Tensile Strength (N)	Retention (%)
24	732	589	93	380	91
32	542	599	94	415	99
40	412	605	95	416	100
Control	224	635	--	416	--

### pH effects

The nylon/cotton blend fabric was treated with 32% HFPO/8% DMDHEU with their pH adjusted from 2.0 to 6.0 using either a 1M NaOH or 1M HCl solution, then

cured at 165°C for 2 min, and finally subjected to 1 laundering cycle. The LOI of fabric thus treated is presented in Table 6.18. The LOI of the treated fabric after 1 laundering cycle is around 28.4%, appearing to change very little in the pH range of 3.0-6.0. The phosphorus concentration and phosphorus fixation of the treated fabric is shown in Table 6.19. The phosphorus concentration is in the range of 2.24%-2.50%, and percent phosphorus fixation changes little (67%-73%).

The tensile strength and tensile strength retention of the fabric thus treated are shown in Table 6.20. When pH is increased from 3.0 to 6.0 in the finishing solutions, the tensile strength in the warp direction is in the range of 592N (92% retention) to 617N (97% retention). In the filling direction, the tensile strength is in the range of 405N (97% retention) to 416N (100% retention). The data presented here strongly indicate that pH has no significant effect on the flame retardant performance or the tensile strength.

Table 6.18 The LOI of the nylon/cotton blend fabric (Desert) treated with 32% HFPO/8% DMDHEU at different pH levels and cured at 165°C for 2 min (after 1 laundering cycle)

pH	LOI
3.0	28.2
4.0	28.7
4.2	28.4
5.0	28.4
6.0	28.3

Table 6.19 The phosphorus concentration of the nylon/cotton blend fabric (desert) treated with 32%HFPO/8%DMDHEU at different pH levels and cured at 165°C for 2 min (after 1 laundering cycle)

pH	Phosphorus concentration (%)	Percent phosphorus retention (%)
3.0	2.40	71
4.0	2.50	74
4.2	2.46	73
5.0	2.34	70
6.0	2.24	67

Table 6.20 The tensile strength of the nylon/cotton blend fabric (desert) treated with 32%HFPO/8%DMDHEU at different pH levels and cured at 165°C for 2 min (after 1 laundering cycle)

pH	Warp		Filling	
	Tensile strength (N)	Retention (%)	Tensile strength (N)	Retention (%)
3.0	592	92	409	98
4.0	597	94	405	97
4.2	599	93	416	100
5.0	590	93	405	97
6.0	617	97	414	99
Control	635	--	416	--

## Conclusions

The nylon/cotton blend fabric treated with HFPO using DMDHEU as a bonding agent shows high levels of flame retardant performance and good laundering durability. The treated fabric can pass the vertical flammability test after 50 laundering cycles. DMDHEU increases the phosphorus fixation and also improves the laundering resistance of HFPO bound to the nylon/cotton blend fabric. However, DMDHEU also causes an increase of the fabric stiffness. At a certain DMDHEU concentration level, increasing HFPO concentration in the formulas results in an increase of phosphorus fixation and also lowers the fabric stiffness. However, the laundering resistance of HFPO bound to the treated fabric also decreases with the increase of the molar ratio of HFPO/DMDHEU. The fabric treated with HFPO/DMDHEU shows very limited loss of the tensile strength. The pH of the finish bath is found to have no effect on the flame retardant performance, the phosphorus retention or the tensile strength of the nylon/cotton blend fabric treated with HFPO/DMDHEU in the pH range 2-6.

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**CHAPTER 7****EFFECTS OF THE FLAME RETARDANT FINISHING ON THE THERMAL  
DECOMPOSITION OF THE NYLON/COTTON BLEND FABRIC**

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<sup>1</sup> Yang, H. and Yang, C.Q. To be submitted to *Polymer Degradation and Stability*.



### Abstract

In my previous research, I found that the nylon/cotton blend fabric treated with hydroxy-functional organophosphorus oligomer (HFPO) using a mixture of DMDHEU and TMM as a bonding system showed high levels of flame retardant performance and good laundering durability. In this study, I investigated the effect of flame retardant finishing based on HFPO on the thermal decomposition of the nylon-6.6, cotton and nylon/cotton blend fabrics using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In the case of the nylon-6.6, the flame retardant finishing not only decreases the decomposition temperature but also enhances the char formation. In cotton, the flame retardant finish acts through the condensed-phase mechanism by altering the thermal degradation pathway of cotton. The nylon/cotton blend fabric after flame retardant treatment shows three degradation steps, whereas the untreated blend breaks into two stages. Increasing phosphorus concentration on the nylon/cotton blend fabric causes a decrease of decomposition temperature and an increase of char residue. In addition, the interaction between nylon component and cotton component is detected in the nylon/cotton blend fabric in the absence of HFPO. In comparison to the untreated nylon/cotton blend fabric, the interaction between nylon component and cotton component in the blend fabric after flame retardant treatment has been changed due to flame retardant finishing.

**Key words:** DSC; durable flame-retardant finishing, nylon/cotton blend; organophosphorus chemicals; thermal degradation; TG.

## Introduction

Due to the commercial importance, the thermal degradation of the cotton fabrics has been studied intensively, and the effects of phosphorus-containing flame retardant finishing on the thermal degradation of the cotton also have been investigated extensively [1-5]. Significant efforts have been made on the thermal degradation and flame retardancy of the nylons [5-10]. However, limited research focuses on the effects of flame retardant finishing on the thermal degradation of the nylon/cotton blend fabric.

It is important to confer durable flame retardant property to the nylon/cotton blend fabric, especially when it is used as the material for the protective clothing [11-13]. In spite of significant efforts, no durable flame retardant finishing has achieved commercial success for the nylon/cotton blend fabric [14-17]. In my previous research [18], I developed a flame retardant finishing system for the nylon/cotton blend. The treated blend showed high levels of flame retardant performance and good laundering durability. Further research is necessary to understand the flame retardant mechanism of flame retardant finishing on the nylon/cotton blend fabric.

Conventional thermal analysis including thermogravimetry (TG) and differential scanning calorimetry (DSC) is a useful tool to study the thermal degradation behavior of the fabrics [19-23]. By using thermal analysis, the effects of durable flame retardant finish on the thermal degradation of cotton were examined [19]. Fukatsu investigated the interaction between cotton and aramide fiber in their blends [23]. Wu also studied the phosphorus-nitrogen synergism between hydroxy-functional organophosphorus oligomer (HFPO) and N-methylol compounds including dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) using TG and DSC [5].

In this study, conventional thermal analysis including TG and DSC was undertaken to characterize the thermal degradation behavior of the nylon/cotton blend and individual fibers after flame-retardant treatment. The effects of flame retardant finishing on the thermal degradation of the nylon/cotton blend fabric were analyzed based on the characteristics of thermal degradation. In addition, the interaction between components in the blend with and without HFPO treatment was compared.

## **Experimental**

### **Materials**

Three kinds of fabrics were used in this study: (1) 50%/50% nylon/cotton Battle Dress Uniform (BDU) fabric printed with three-color woodland camouflage weighing  $216\text{g/m}^2$ ; (2) 100% nylon-6,6 woven fabric (Testfabrics Style 306A) weighing  $59\text{g/m}^2$ ; and (3) 100% bleached cotton woven fabric (Testfabric Style #400) weighing  $108\text{g/m}^2$ . HFPO (“Fyroltex HP”) was a commercial product with near 100% solid supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. TMM was a commercial product (80% solid content) with the trade names of “Aerotex M-3”, and XMM was commercial product of melamine-formaldehyde having the functionality of 4-5 (85% solid content) with the trade name of “Aerotex 3730”, both supplied by Noveon, Cleveland, Ohio. The catalyst was an  $\text{NH}_4\text{Cl}$ -based commercial product with the trade name of “Catalyst RD” supplied by Eastern Color & Chemical, Greenville, South Carolina.

### **Fabric Treatment and Laundering Procedures**

The fabric was first immersed in a finish solution, then passed through a laboratory padder with two dips and two nips, dried at  $90^\circ\text{C}$  for 3 min, and finally cured

in a Mathis curing oven at 165°C temperature. All concentrations presented in this study were based on weight of bath (w/w, %) and concentrations of HFPO, TMM and XMM are based on 100% solid content. The wet pick-up of the cotton/nylon fabric is 76±2%. The wet pick-up of the nylon-6.6 woven fabric is 60±2% and the wet pick-up of the cotton woven fabric is 122±4%. After curing, the treated fabric was subjected to a number of laundering cycles with the use of “AATCC standard detergent 1993.” The laundering process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics After Repeated Home Laundering”). The water temperature of laundering was approximately 46°C.

#### **Determination of Phosphorus Concentration on the Treated Fabric**

Approximately 2g of the treated fabric taken from three different parts of a “10×12” fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was added to 0.1 g of sample powder in a beaker. 10 ml of 30% H<sub>2</sub>O<sub>2</sub> was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO<sub>3</sub> vapor is produced. The completely digested sample as a clear solution was transferred to a 50-ml volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the % concentration of phosphorus. The percent phosphorus retention is calculated by dividing the phosphorus content of the fabric after laundering by that of the fabric before laundering.

## Thermal Analysis

Thermogravimetry (TG) and differential thermogravimetry (DTG) experiments were carried out on a Mettler Toledo TGA 851 thermogravimetric analyzer. Samples weight is in the range of 6-8 mg, respectively. All samples of TGA were measured from 50°C to 800°C at the heating rate 10°C/min. Differential scanning calorimetry (DSC) was measured using Mettler Toledo DSC 821 analyzer. All samples of DSC were measured from 50°C to 650°C at the heating rate of 10°C/min with a continuous air or nitrogen flow.

## Results and Discussion

The nylon-6.6 fabric was immersed into the finishing solution containing 40% HFPO and the mixture of 4.8% TMM and 3.4% XMM as a bonding system, then dried at 90°C for 3 min, finally cured at 165°C for 2 min. The fabric thus treated was subjected to different numbers of laundering cycles. Fig.7.1 and Fig.7.2 show the TGA and DTG curves of the untreated nylon fabric and nylon fabrics thus treated measured at a heating rate of 10°C/min in the air atmosphere, respectively. Table 7.1 presents characteristic DTG data analyzed in air and nitrogen. The thermal degradation of nylon-6.6 is relatively complex. When heated in air atmosphere, the untreated nylon-6.6 loses 87% weight in the temperature range 350-490°C with the 8% char residue (Fig.7.1, curve 1). It is generally accepted that nylon-6.6 undergoes crosslinking more easily than other aliphatic nylons during pyrolysis. However, no successful flame retardant agent has been developed to exploit this property [16]. Flame retardant finishing significantly enhances the char formation of nylon.6.6 and increases the char residue at 800 °C from 8% of untreated

nylon-6.6 to 14% of the treated nylon-6.6 after 10 laundering cycles by 75% (Fig.7.1, curve 2-4).

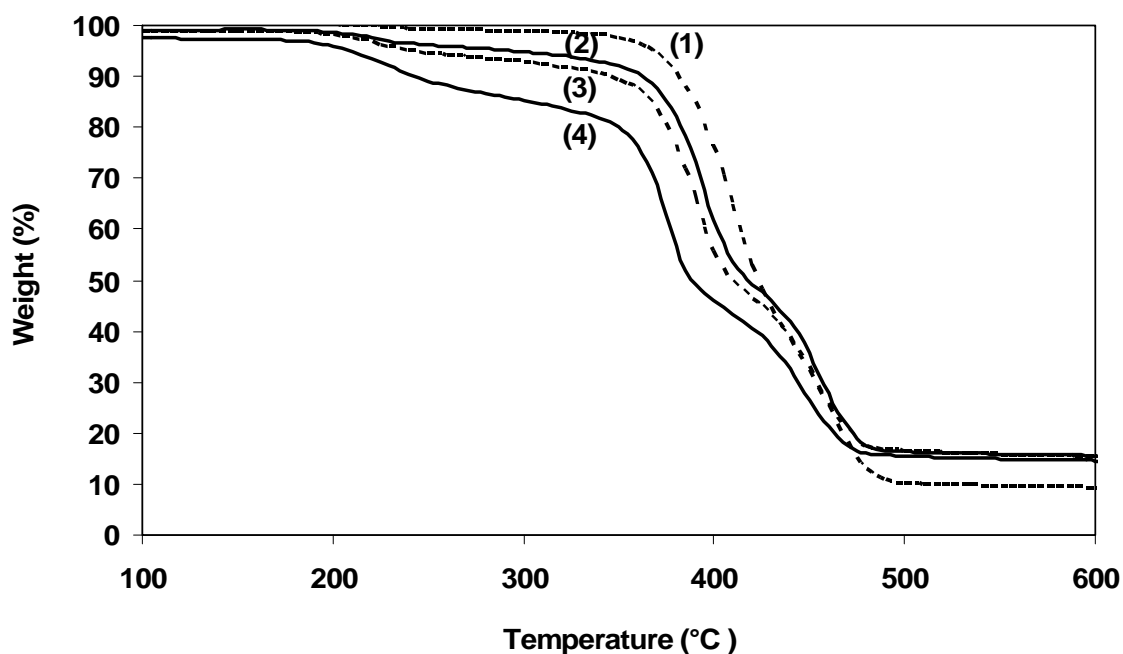


Fig.7.1 TG curves of the untreated and treated nylon-6.6 determined at a heating rate of  $10^{\circ}\text{C}/\text{min}$  in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

Table 7.1 DTG characteristic data for untreated and treated nylon-6.6 determined at a heating rate of  $10^{\circ}\text{C min}^{-1}$  analyzed in air and nitrogen.

Sample No.	In air		In nitrogen	
	Peak I ( $^{\circ}\text{C}$ )	Peak II ( $^{\circ}\text{C}$ )	Peak I ( $^{\circ}\text{C}$ )	Peak II ( $^{\circ}\text{C}$ )
Before wash	379	448	374	446
After 1 wash	391	450	393	455
After 10 wash	394	453	398	456
Untreated	411	461	412	460

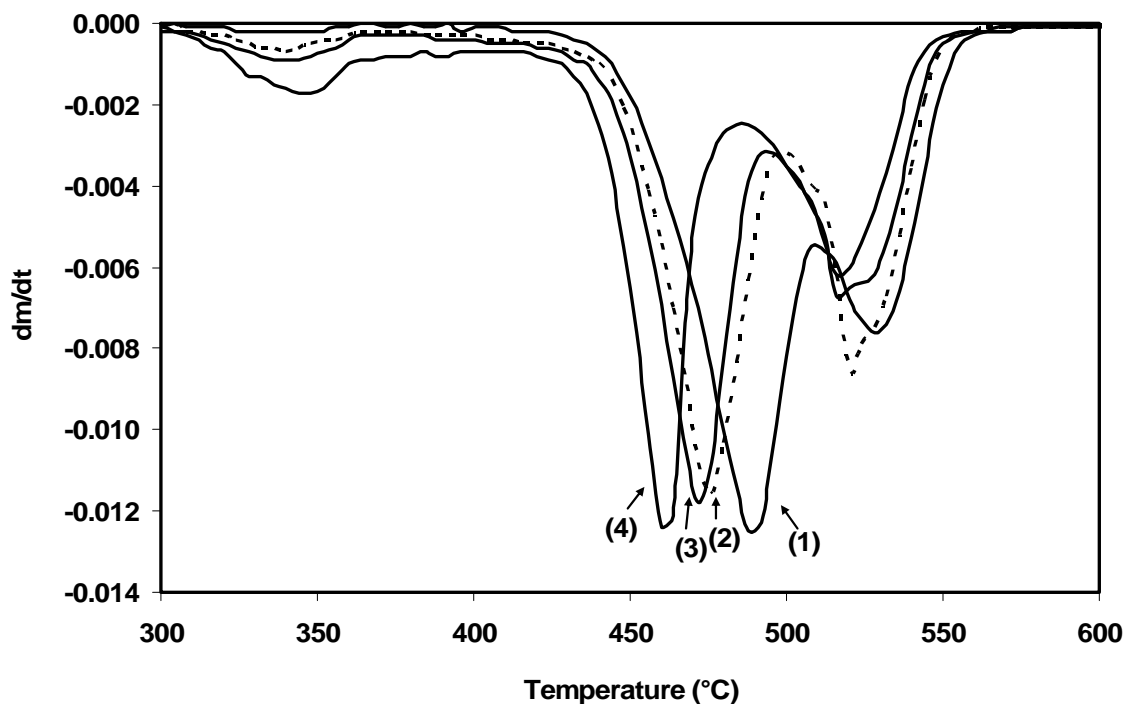


Fig.7.2 DTG curves of the untreated and treated nylon-6.6 determined at a heating rate of 10°C/min in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

Flame retardant finishing lowers the decomposition temperature of nylon-6.6. In air atmosphere, the peak of maximum rate of weight loss decreases from 411°C of the untreated sample to 379°C of the treated sample before laundering by 31°C. In nitrogen atmosphere, similar situation is observed. The peak of maximum rate of weight loss shifts from 412°C of the untreated nylon-6.6 to 374°C of the treated sample before laundering by 38°C (Fig.7.2). In addition, three separate decomposition peaks are observed in the nylon-6.6 after flame retardant finishing whereas untreated nylon-6.6 breaks down in a two-step process. The weight loss in the temperature range of 330-360°C increases with an increase of the flame retardants on the treated nylon-6.6. The corresponding decomposition peak is attributed to the decomposition of flame retardants.

Corresponding DSC curves (Fig.7.3) show two endothermic peaks. The first peak around 250°C is due to the melting of nylon-6.6 fabric. It shifts to the lower temperature with increasing amount of HFPO, which strongly indicates that the presence of HFPO lowers the melting point of nylon-6.6. The second peak, which is assigned to the thermal degradation of nylon-6.6, decreases from 411°C of untreated nylon-6.6 to 377°C of the treated sample before laundering. It is very clear that flame retardant finishing lowers the degradation temperature of nylon-6.6.

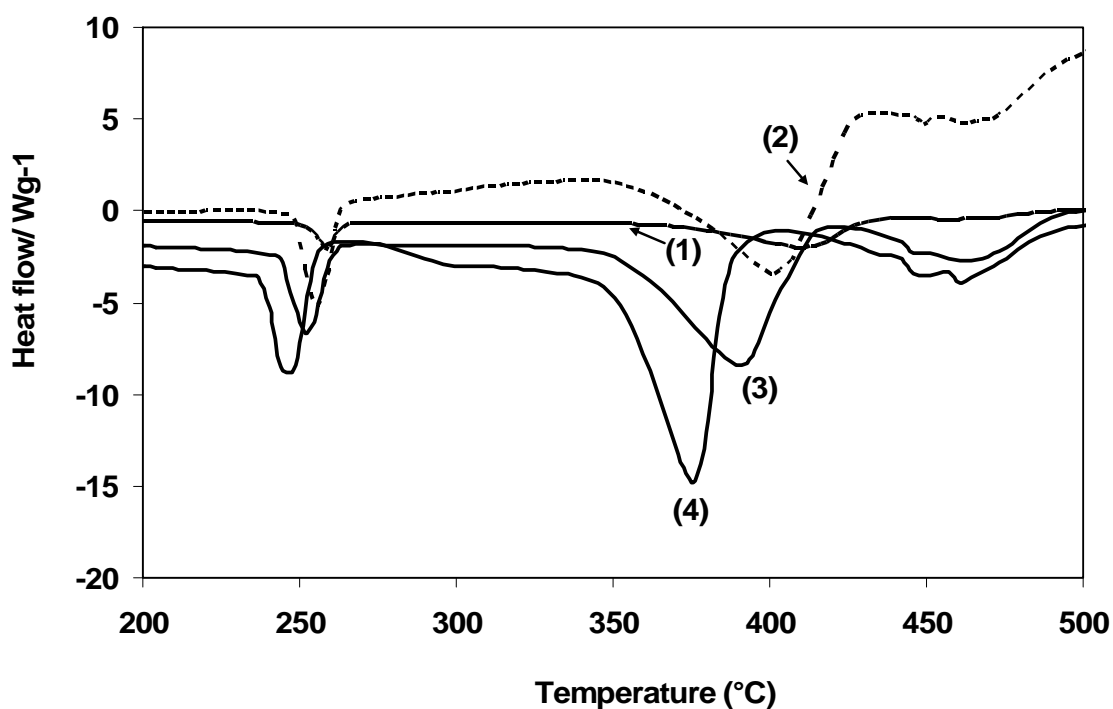


Fig.7.3 DSC curves of the untreated and treated nylon-6.6 determined at a heating rate of 10°C/min in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

In sum, flame retardant finishing not only enhances the char formation but also lowers the degradation temperature of nylon-6.6, which is caused by the presence of HFPO. When heated, HFPO may decompose to form condensed phosphoric acid, which



attacks the amide bonds of nylon-6.6 to form a phosphoric ester [7-10]. The phosphoric acid released by HFPO may act as a dehydrating agent and promote char formation [levchik combustion nylon]. The condensed phosphoric acids can also abstract hydrogens from nylon, thus forming the double bonds- a precursor of the polymer charring [6]. Hence, we can conclude that HFPO may mainly act through the condense phase mechanism in nylon-6.6. In addition, the bonding agents including TMM and XMM may decrease the degradation temperature of nylon and increase char residue. Nitrogen compounds may react with carboxylic chain-ends to enhance the crosslinking [6].

The cotton fabric was immersed into the finishing solution containing 40% HFPO along with 4.8% TMM and 3.4% XMM as a bonding system, then dried at 90°C for 3 min, finally cured at 165°C for 2 min. The fabric thus treated was subjected to different numbers of laundering cycles. Fig.7.4 and Fig.7.5 show TGA and DTG curves of untreated and the treated cotton fabric after different laundering cycles analyzed in air atmosphere. Corresponding characteristic DTG data analyzed in air and nitrogen are summarized in Table 7.2. As shown in Fig.7.1, it is evident that the treated samples lose weight much earlier than untreated sample. Accordingly decomposition peak in DTG shifts from 357°C of untreated cotton to 269°C of treated cotton before laundering. Similar situations are observed in nitrogen atmosphere. The char residue at 600°C increases from 16% of untreated fabrics to 40% of the treated fabric before laundering by 150% (Fig.7.4). The char residue decreases with the increase of laundering cycles, which is caused by the loss of HFPO during the laundering procedures.

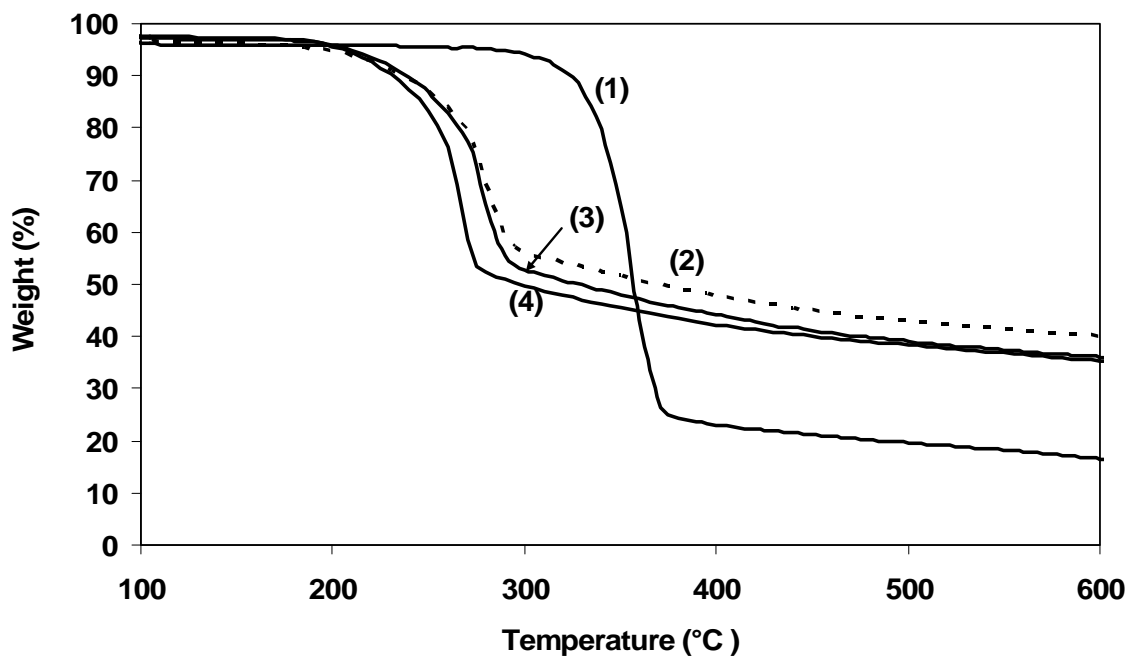


Fig.7.4 TG curves of the untreated and treated cotton determined at a heating rate of  $10^{\circ}\text{C}/\text{min}$  in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

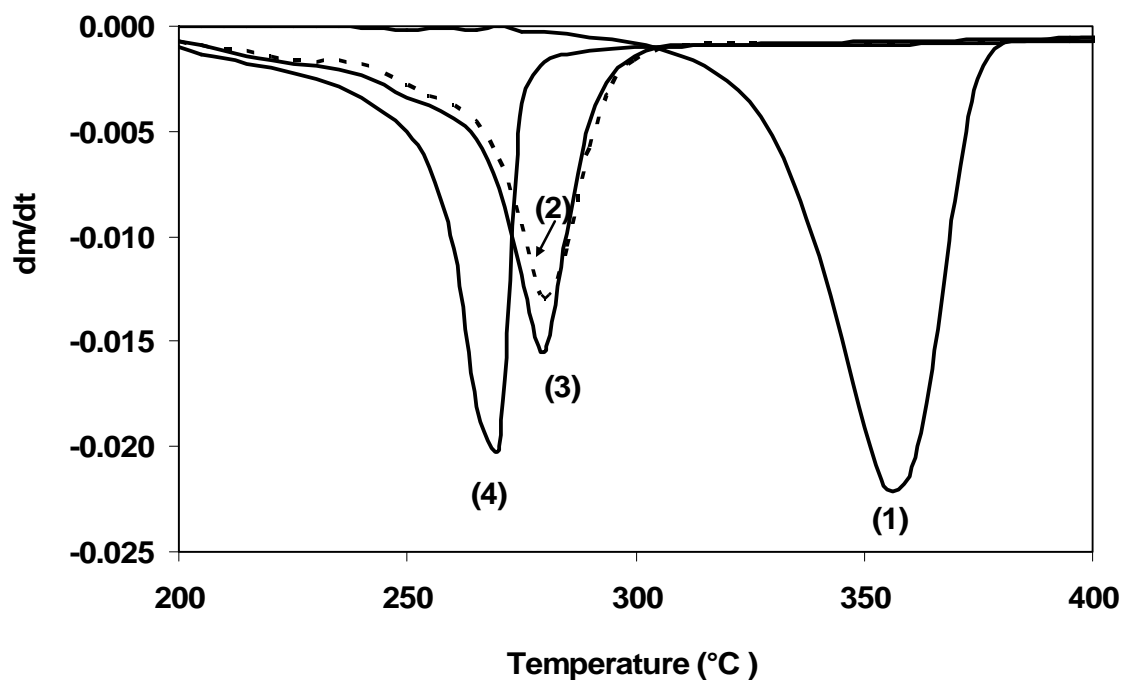


Fig.7.5 DTG curves of the untreated and treated cotton determined at a heating rate of  $10^{\circ}\text{C}/\text{min}$  in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

Table 7.2 DTG characteristic data for the cotton treated by HFPO after different home laundering cycles determined at a heating rate of  $10^{\circ}\text{C min}^{-1}$  analyzed in air and nitrogen.

Sample No.	In air	In nitrogen
Untreated	357	359
Treated, before wash	269	266
Treated, after 1 wash	281	276
Treated, after 10 wash	280	278

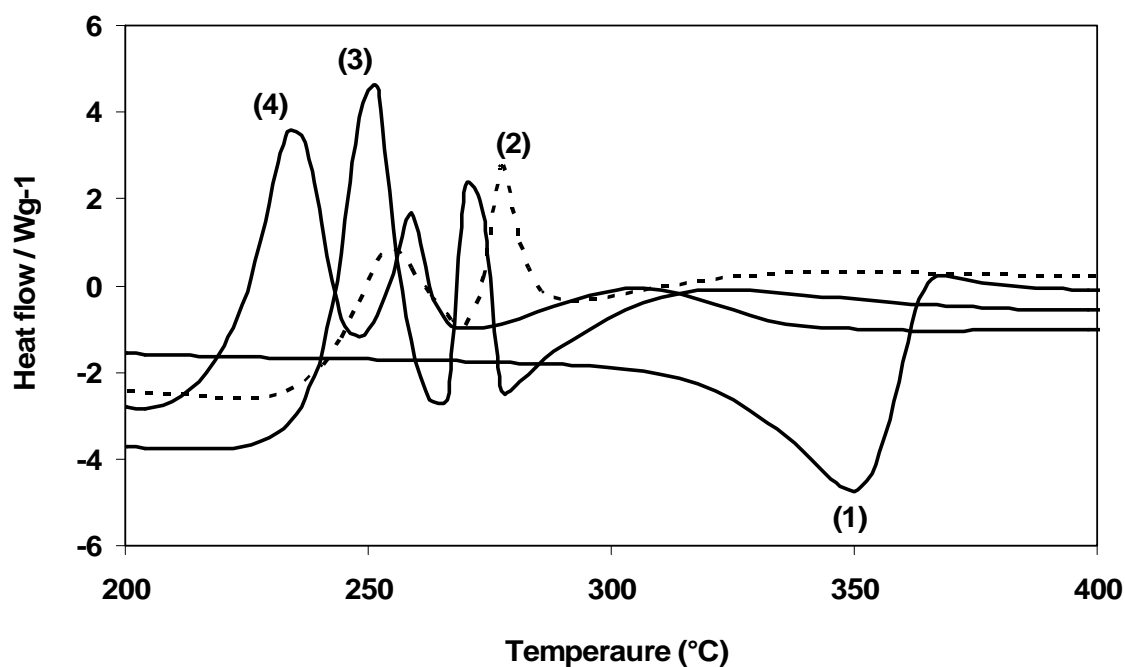


Fig.7.6 DSC curves of the untreated and treated cotton determined at a heating rate of  $10^{\circ}\text{C/min}$  in air: (1) untreated, (2) treated, after 10 wash, (3) treated, after 1 wash, (4) treated, before wash.

The corresponding DSC curves of the cotton fabrics with or without HFPO treatment are presented in Fig.7.6. Only one endothermic peak appears in the thermal degradation of untreated cotton, which is attributed to the depolymerization of cellulose. Two separate

exothermic peaks are observed in the cotton after flame retardant finishing where the endothermic peak of untreated cotton disappears. Fig.7.6 strongly indicates that dehydration of cotton cellulose becomes dominant while the depolymerization of cellulose seems insignificant after flame retardant finishing. In addition, it is clear that the peak of the decomposition temperature of treated cotton decreases with the increase of laundering cycles, which is attributed to the loss of flame retardant during laundering. Therefore, we can conclude that the flame retardant finishing not only decreases the decomposition temperature of cotton cellulose but also enhances the char formation. HFPO mainly acts through the condense phase mechanism on the cotton.

The TG and DTG curves of the untreated nylon6.6/cotton blend determined at a heating rate of 10°C/min analyzed under air atmosphere are compared with the corresponding expected curves in Fig.7.7. The expected TG and DTG curves are calculated by simple addition of individual weight loss data of cotton and nylon in Fig.7.1 and Fig.7.4 [7]. If no interaction occurs between cotton and nylon component during pyrolysis of the cotton/nylon blend fabric, the experimental curves should coincide with the expected curves [8]. However, obvious differences against assumption are observed in Fig.7.7 and Table 7.3. In contrast to the three peaks observed in the calculated DTG curve in Fig.7.7, only two peaks appear in the experimentally determined DTG curve, in which the first peak at the temperature 373°C might be assigned to the weight loss of cotton fiber. Due to the presence of nylon fiber in the blend, the peak of weight loss for the cotton component increases from 357°C to 373°C. However, the weight loss rate of the experimentally determined DTG curve seems the same as that of the calculated curve. The second peak centered on 441°C in experimentally determined DTG curve of

untreated blend fabric might be attributed to the weight loss of nylon-6.6 component. This suggests that the thermal degradation of the cotton component has a significant effect on the thermal degradation of the nylon-6.6 component in the blend fabric. Moreover, the char residue of experimentally determined TGA curve analyzed in air atmosphere at 600°C is 19.7%, which is significantly higher than 13.0% char residue of calculated TGA curve. The data presented above disprove the hypotheses of non-interaction between individual components in the nylon/cotton blend, and strongly indicate that some forms of interactions between individual components exist during thermal degradation of the nylon/cotton blend. The nylon/cotton blend has been classified as the interactive blend based on thermal behavior of 85%/15% nylon/cotton blend in the previous research [7]. The detailed interpretation for this interaction is rather complicated and further studies are needed to elucidate the interaction.

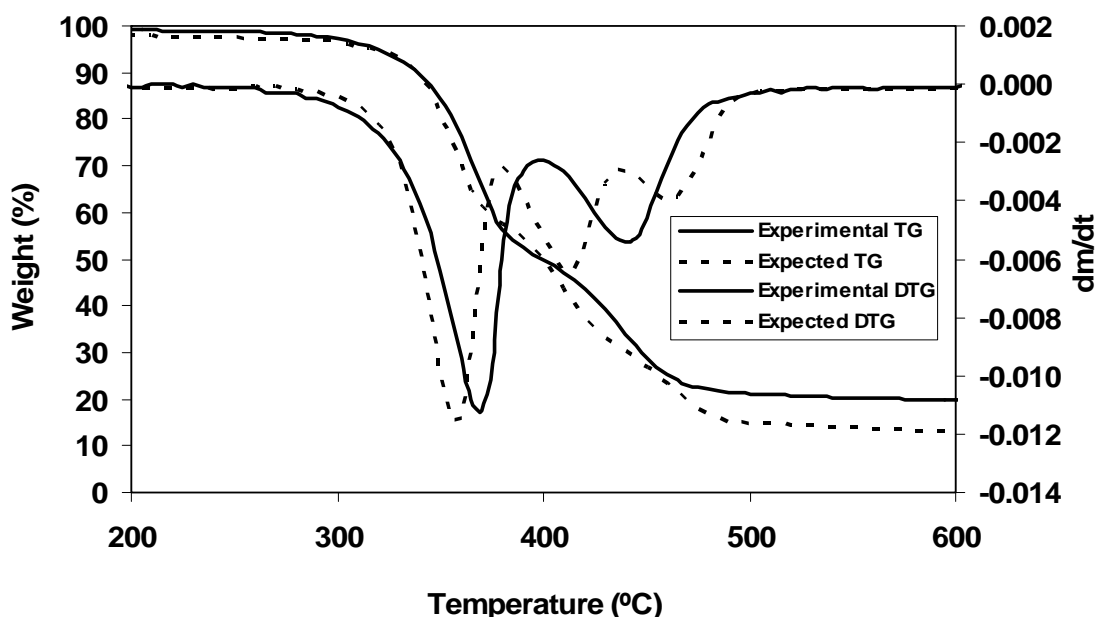


Fig.7.7 Experimentally determined and expected TG and DTG curves of the untreated nylon66/cotton blend determined at a heating rate of 10°C/min analyzed in air.

Table 7.3 DTG characteristic data for untreated 100% nylon-6.6, 100% cotton and 50%/50% nylon 66/cotton blend fabric determining at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  analyzed in air.

Fabric component	Peak I ( $^{\circ}\text{C}$ )		Peak II ( $^{\circ}\text{C}$ )		Peak II ( $^{\circ}\text{C}$ )	
	Temp	Char	Temp	Char	Temp	Char
0/100	357	16.5	--	--	--	16.5
100/0	--	--	412	--	460	9.4
50/50(Expected)	357	--	415	--	440	13.0
50/50(Experimental)	373	--	441	--	--	19.8

TG, DTG and DSC curves of the nylon/cotton blend fabric thus treated before wash are compared with those of the untreated nylon/cotton blend fabric in Fig.7.8, Fig.7.9 and Fig.7.10, respectively. Unlike the two decomposition peaks in the DTG curves of the untreated blend fabric, the treated nylon/cotton blend before wash breaks down into three stages. The first weight loss at around  $283^{\circ}\text{C}$  is assigned to the thermal degradation of the treated cotton component in the blend. The second weight loss takes place at  $368^{\circ}\text{C}$ , and the third weight loss occurs at around  $435^{\circ}\text{C}$ . Both of them are caused by the thermal degradation of the treated nylon-6.6 component in the blend. In comparison to the two decomposition peaks at about  $335^{\circ}\text{C}$  and  $540^{\circ}\text{C}$  in the corresponding DSC curves of the untreated blend, three separate peaks are observed in the DSC curve of the treated blend fabric before wash. The first peak at around  $325^{\circ}\text{C}$  is due to the melting of the nylon component. The second peak at around  $360^{\circ}\text{C}$  is an exothermic peak, which is caused by the dehydration of the cotton component. The third peak at around  $475^{\circ}\text{C}$  is assigned to the thermal degradation of the nylon component. This indicates that flame retardant finishing significantly alters thermal degradation of the blend fabric.

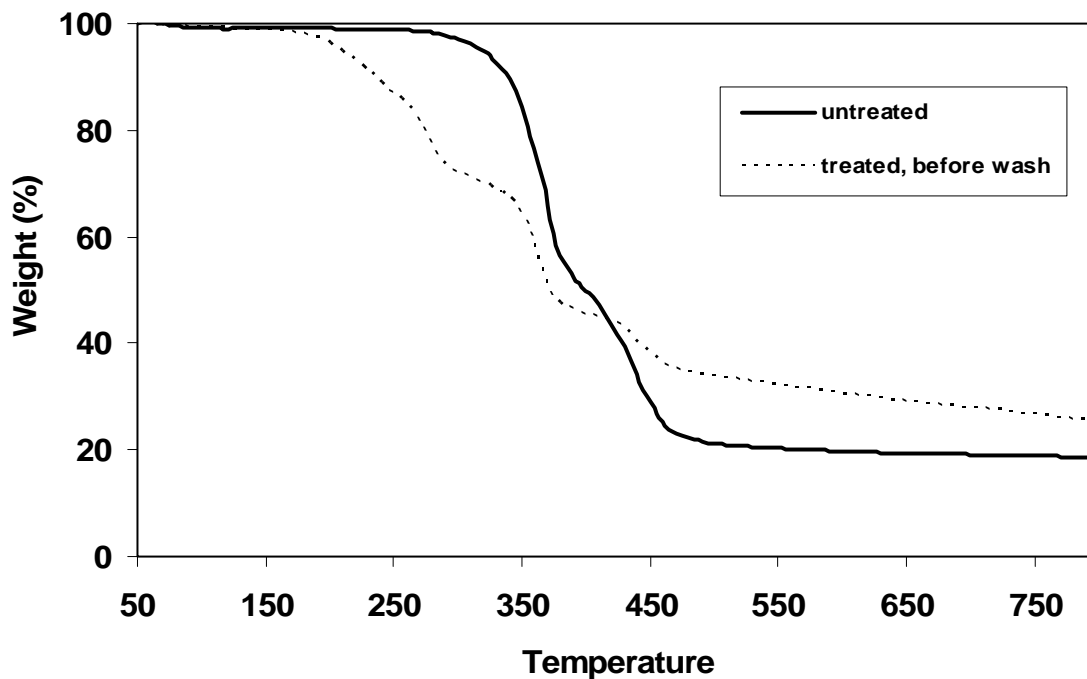


Fig.7.8 TG curves of the treated nylon/cotton blend fabric before wash and the untreated nylon/cotton blend fabric determined at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  analyzed in air.

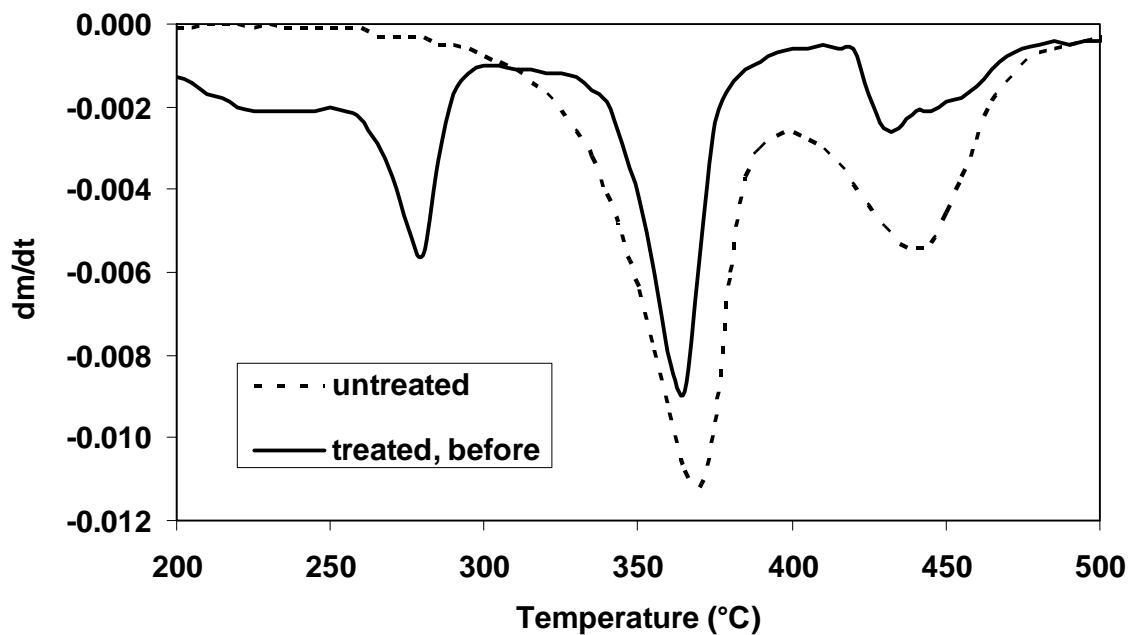


Fig.7.9 DTG curves of the treated nylon/cotton blend fabric before wash and the untreated nylon/cotton blend fabric determined at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  analyzed in air.

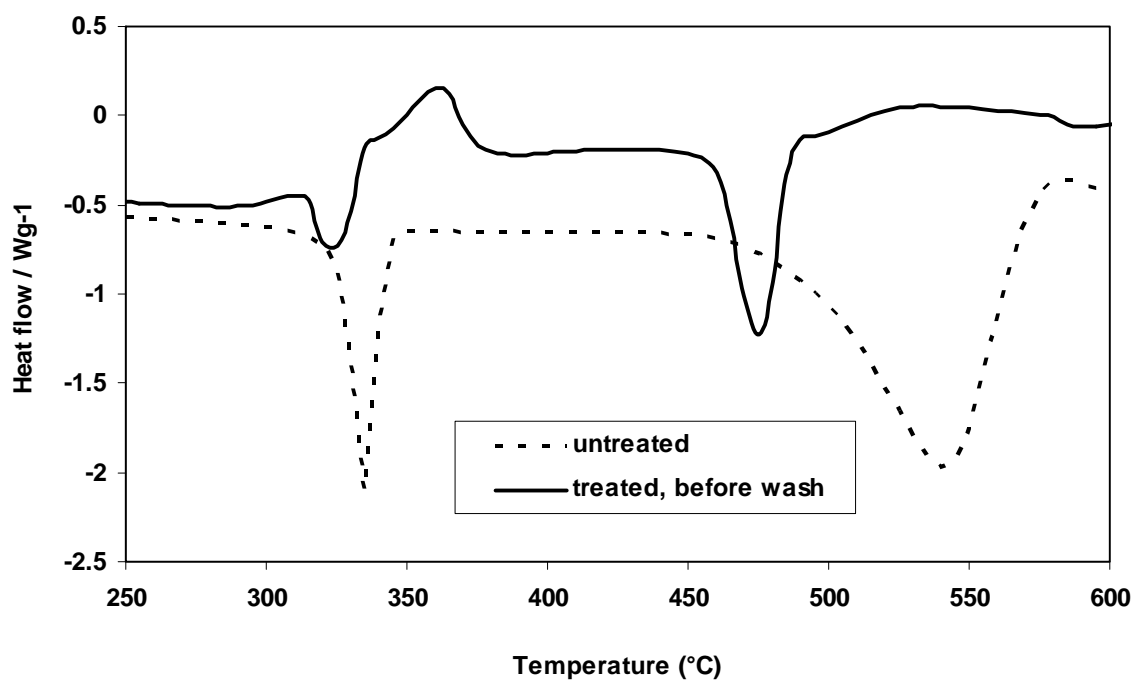


Fig.7.10 DSC curves of the treated nylon/cotton blend fabric before wash and the untreated nylon/cotton blend fabric determined at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  analyzed in air.

The TG and DTG curves of treated nylon/cotton blend after 1 wash determined at a heating rate of  $10^{\circ}\text{C}/\text{min}$  analyzed under air atmosphere are compared with the corresponding expected curves in Fig.7.11. The expected TG and DTG curves are calculated by simple addition of individual weight loss data of cotton and nylon in Fig.7.1 and Fig.7.4. Although both experimentally determined and calculated DTG curves have three peaks, obvious difference in the both peak of decomposition temperature and the rate of weight loss are observed. Therefore, some forms of interaction still occur during thermal degradation of the treated nylon/cotton blend after 1 wash.



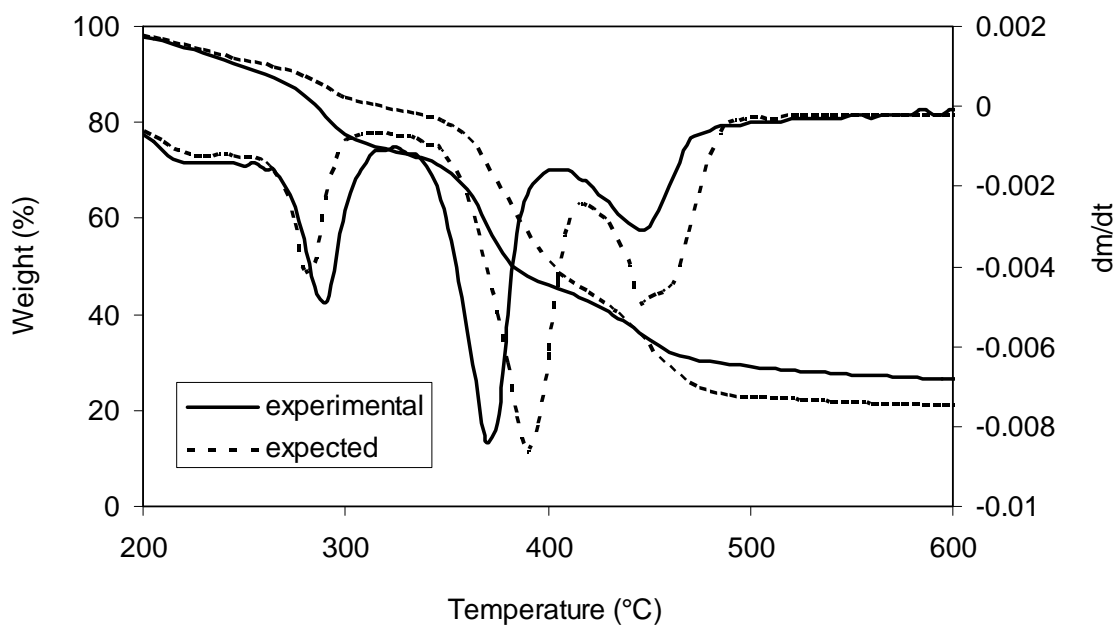


Fig.7.11 Experimentally determined and expected TG and DTG curves of the treated nylon/cotton blend after 1 wash determined at a heating rate of 10°C/min analyzed in air.

The nylon/cotton blend fabric was immersed in a finishing solution containing 40% HFPO and a mixture of 4.8% TMM and 3.4% XMM as a bonding system, then dried at 90°C for 3 min, finally cured at 165°C for 2 min. The fabric thus treated was subjected to 0, 1, 20 and 40 laundering cycles. Fig.7.12 and Fig.7.13 show the TG and DTG curves of the nylon fabrics thus treated measured at a heating rate of 10°C/min in the air atmosphere, respectively. DTG data of the treated blend fabric analyzed in air and nitrogen atmosphere are summarized in Table.7.4 and Table.7.5, respectively. Three distinct stages are observed in the DTG curves of treated blend fabrics. When the laundering cycle increases from 0 to 40, the peak of decomposition temperature at around 290°C increases from 283°C to 308°C, and the peak at around 370°C also increases from 368°C to 385°C (Fig.7.10 and Table.7.4). DSC curves in Fig.7.14 show two endothermic

peaks and one exothermic peak. It is very clear that all positions of peaks increase with the number of laundering cycles, which strongly indicates that flame retardant finishing decreases the decomposition temperature of nylon/cotton blend fabric. The char residue at 600°C is in the range of 29%-33%, which is notably higher than that (21%) of the untreated nylon/cotton blend (Fig.7.8).

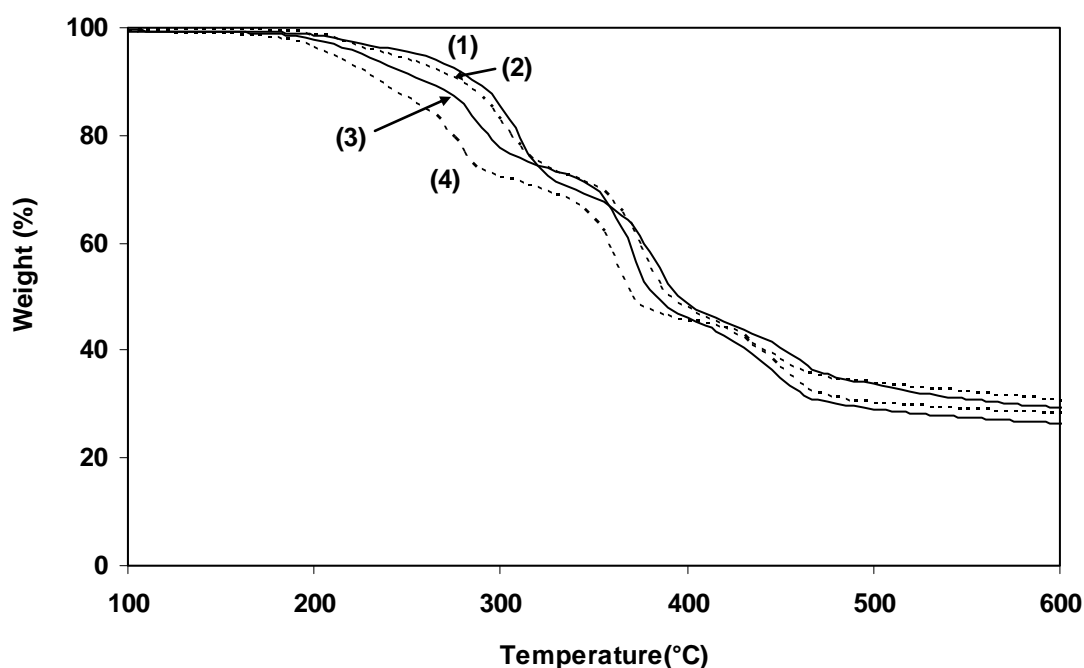


Fig.7.12 TGA curves of the treated nylon/cotton blend determined after different laundering cycles determined at heating rate of 10°C/min in air: (1) treated, after 40 wash, (2) treated, after 20 wash, (3) treated, after 1 wash, (4) treated, before wash.

The decomposition temperature of the first peak in the temperature range of 283-308°C in DTG (as shown in Fig.7.13) is plotted as a function of the phosphorus concentration on the treated nylon/cotton blend fabric in Fig.7.15. The position of decomposition peaks shifts from 308°C to 282°C as the phosphorus concentration of the treated nylon/cotton blend fabric increases from 1.39% to 3.93%. Therefore, it is evident that HFPO lowers the decomposition temperature of blend fabric.

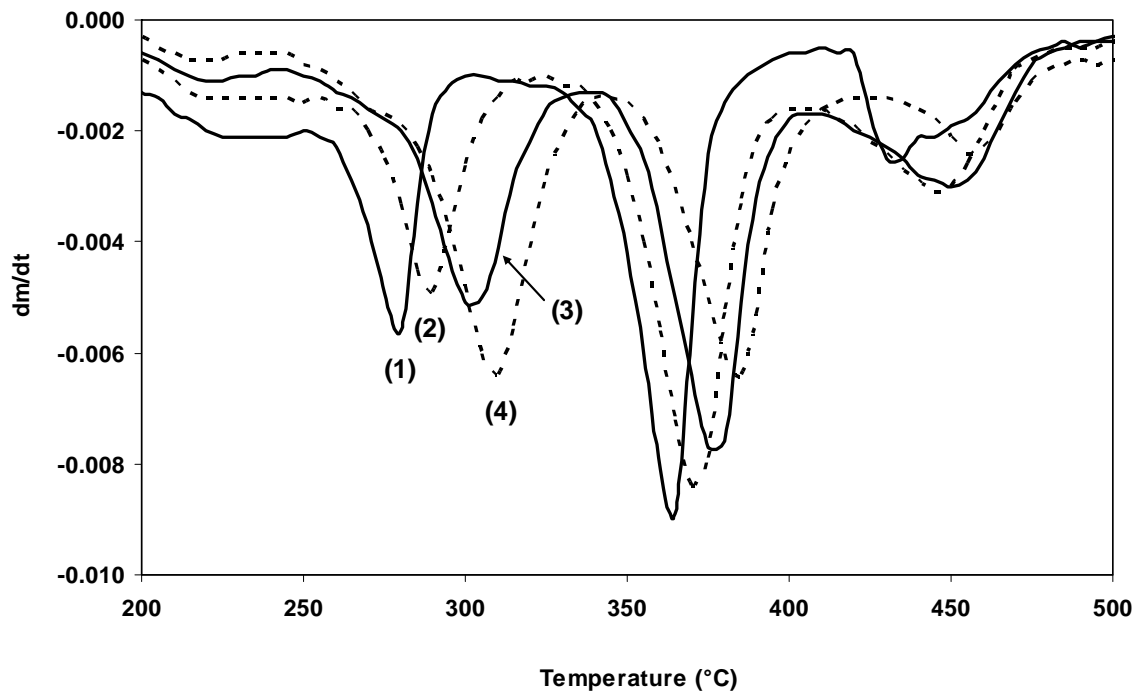


Fig.7.13 DTG curves of the treated nylon/cotton blend determined after different laundering cycles determined at heating rate of  $10^{\circ}\text{C}/\text{min}$  in air: (1) treated, after 40 wash, (2) treated, after 20 wash, (3) treated, after 1 wash, (4) treated, before wash.

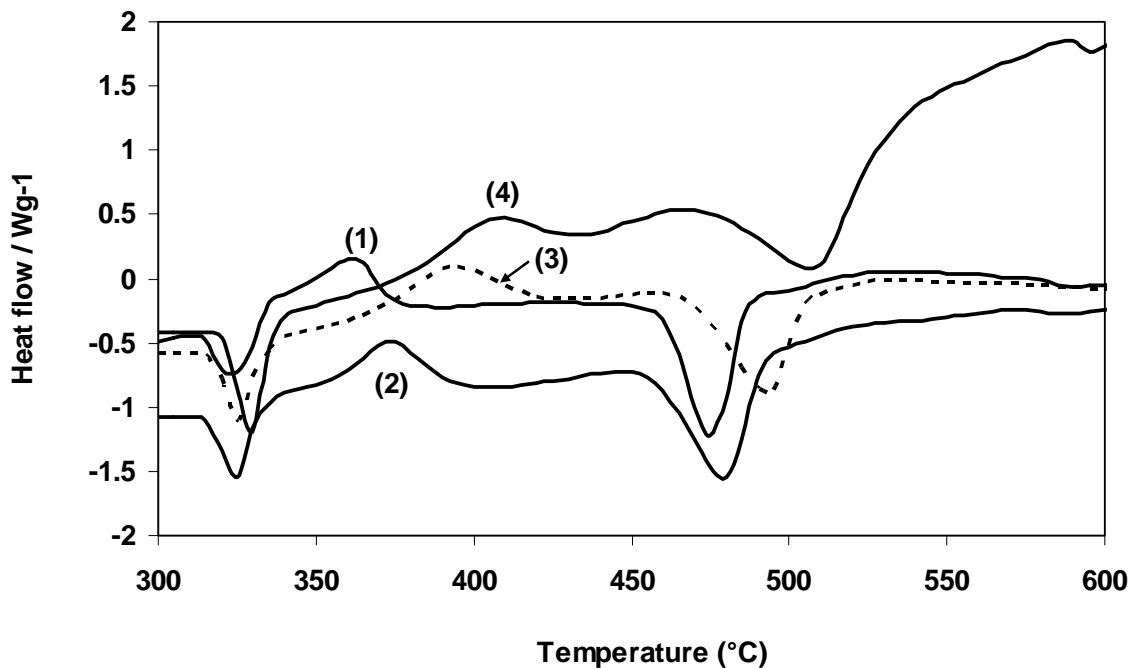


Fig.7.14. DSC curves of the treated nylon/cotton blend determined after different laundering cycles determined at heating rate of  $10^{\circ}\text{C}/\text{min}$  in air: (1) treated, after 40 wash, (2) treated, after 20 wash, (3) treated, after 1 wash, (4) treated, before wash.

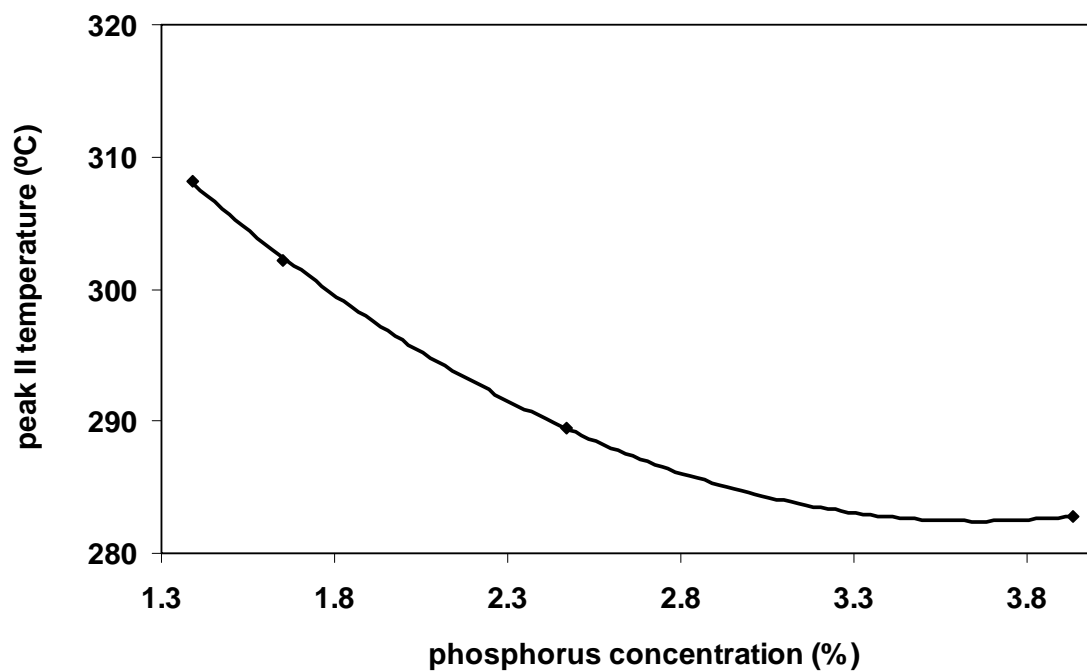


Fig.7.15 Relationship between the phosphorus concentration of the treated nylon/cotton blend fabric after launderings and the decomposition temperature of peak I as shown in Fig.7.13

## Conclusions

In the case of the nylon-6.6, flame retardant finishing lowers the decomposition temperature and also enhances the formation of char. It is found that flame retardant finishing acts in the condense phase on cotton. Flame retardant finishing not only enhances the char formation but also decreases the decomposition temperature of cotton cellulose. DSC experiments show that the dehydration of cellulose becomes dominant after flame retardant treatment. The interaction occurs between cotton component and nylon component when the blend is heated. Flame retardant treatment alters the thermal degradation of the nylon/cotton blend fabric, but some forms of interactions between individual components still exist. Like in individual fibers, flame retardant finishing lowers the decomposition temperature and enhances the char formation. Therefore, this flame retardant finish may function through the condense phase in the nylon/cotton blend fabric.

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**CHAPTER 8**  
**NON-FORMALDEHYDE FLAME RETARDANT FINISHING OF THE NOMEX/COTTON**  
**BLEND FABRIC USING A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS**  
**OLIGOMER**

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<sup>1</sup> Yang, H. and Yang, C.Q. Accepted by *Journal of Fire Science*. Reprinted here with permission of publisher, 07/11/2007.

### Abstract

Multifunctional carboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), have been used as durable press finishing agents to produce wrinkle-resistant cotton. In previous research, BTCA was used as a non-formaldehyde bonding agent in the flame retardant finishing systems based on a hydroxy-functional organophosphorus oligomer (HFPO) for cotton. In this research, I investigated the application of HFPO to the 65%/35% Nomex/cotton blend fabric using BTCA as a bonding agent and triethanolamine (TEA) as a co-reactant. I found that the addition of TEA in the flame retardant finishing system improves the hydrolysis-resistance of the HFPO bound to the Nomex/cotton blend and enhances the flame retardant performance of HFPO by means of the phosphorus-nitrogen synergism. Moreover, TEA reduces the deposit of calcium salt on the treated fabric during laundering by esterifying the free carboxylic acid groups on cotton. The Nomex/cotton blend fabric treated with the HFPO/BTCA/TEA system showed high levels of flame retardant performance at relatively low add-on levels. It is a completely non-formaldehyde flame retardant finishing system.

**Key Words:** BTCA; Cotton; Flame retardants; Multifunctional carboxylic acid; Nomex; Organophosphorus chemicals; Triethanolamine.

## Introduction

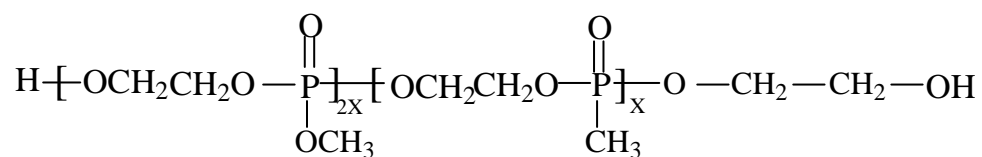
Nomex, a registered trade mark of Dupont for poly(m-phenylene isophthamide) fiber, has been commonly used to make fire-resistant protective clothing [1]. The high cost of Nomex, however, limits its wider uses. The low comfortability of Nomex due to fabric stiffness and low moisture regain is another disadvantage [2]. Blending Nomex with cotton not only reduces the cost but also improves its comfortability. Because cotton is a highly flammable fiber, the Nomex/cotton blend fabric containing more than 20% cotton is not self-extinguishable [3-4]. Therefore, a flame-retardant finishing treatment becomes necessary to make such Nomex/cotton blend fabric flame retardant if it contains more than 20% cotton.

Reactive organophosphorus chemicals, such as *N*-methylol dimethylphosphonopropionamide (MDPA) with the commercial name of “Pyrovatex CP” and “Pyrovatex CP New” (trade marks of Ciba) in combination with trimethylol melamine (TMM) as an additive, have been used to treat Nomex/cotton blend fabrics [4]. MDPA is an effective flame retardant for cotton, but it also has a number of limitations. The use of phosphoric acid as the catalyst makes it necessary to have multiple launderings after the treated fabric is cured. The strong and unpleasant odor of the “Pyrovatex” commercial products makes their uses very difficult and the treated fabrics also retain the odor [5, 6]. Tetrakis-(hydroxymethyl)-phosphonium chloride (“THPC”), commercially known as “Proban” (a trademark of Albright & Wilson), is another commonly used durable flame retardant for cotton [7-9]. The THPC system is effective and has exceedingly high laundering durability on cotton. But the THPC system requires the use of special equipment in its applications, and therefore is incompatible for most textile mills and significantly more

expensive. Both MDPA and THPC systems are based on formaldehyde as bonding agents for cotton, which must be considered as another disadvantage since formaldehyde has been classified as a carcinogen for human by World Health Organization recently [10].

Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), have been used as a formaldehyde-free crosslinking agent to produce wrinkle-resistant cotton fabrics and garments when sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ ) was used as the catalyst [11-12]. Previous research demonstrated that BTCA first forms a 5-membered cyclic anhydride intermediate, which then reacts with a cellulosic hydroxyl group on cotton, thus crosslinking cotton [13-17].

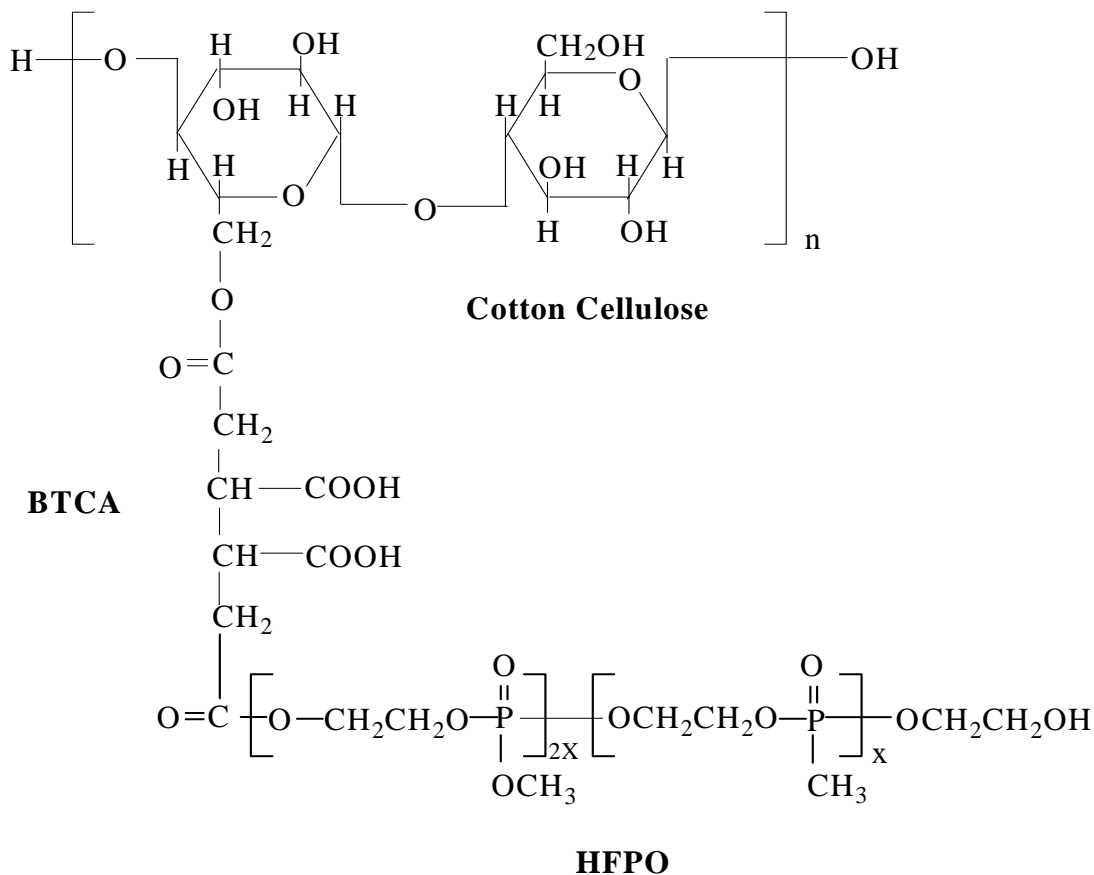
In previous research, a flame retardant finish system was developed for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO) shown in Scheme 8.1 [18-21]. Because HFPO does not have a reactive functional group for cotton, it is necessary to use a bonding agent such as TMM or dimethyloldihydroxyethyleneurea (DMDHEU) to form a covalent “bridge” between HFPO and cotton or to form a TMM/HFPO crosslinked network on cotton [18-21].



**Scheme 8.1.** The Hydroxy-Functional Organophosphorus Oligomer (HFPO)

BTCA was studied as a bonding agent for HFPO on cotton. BTCA is able to esterify the hydroxyl groups of both cotton cellulose and HFPO as shown in Scheme 8.2 [22, 23]. The flame retardant property of the cotton fabric thus treated deteriorated after a few laundering cycles because of the formation of calcium salt on the fabric [23]. It was also found that adding triethanolamine (TEA) in the finishing solution reduces the

amount of the calcium salt formed on the fabric, thus improving the flame retardant performance of the treated cotton fabric [23].



Scheme 8.2 HFPO bound to cotton by BTCA

In this research, I applied the HFPO/BTCA/TEA system to the Nomex/cotton (65/35) blend fabric and investigated the roles of TEA played in enhancing the flame retardant performance of the treated Nomex/cotton blend fabric. The performance of the Nomex/cotton blend treated with HFPO/BTCA/TEA was also evaluated.

## Experimental

### Materials

The cotton fabric used in this research was a scoured, bleached and desized cotton print cloth (Testfabrics Style 400) weighing 102 g/m<sup>2</sup>. The Nomex/cotton (65%/35%) blend fabric printed with woodland camouflage was a twill weave fabric weighing 219 g/m<sup>2</sup>. HFPO with the trade name of “Fyroltex HP” (also known previously as “Fyrol 51”, CA Registry No. 70715-06-9) was supplied by Akzo Nobel Functional Chemicals, Dobbs Ferry, New York. BTCA, TEA and hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>, as 50% aqueous solution) were reagent-grade chemicals supplied by Aldrich, Milwaukee, Wisconsin.

### Fabric Treatment and Laundering Procedures

The fabric was first immersed in a finishing solution, then passed through a laboratory padder with two dips and two nips, dried at 90°C and finally cured in a Mathis curing oven. All concentrations presented here are based on weight of bath (wob, w/w %). The wet pick-up of the cotton fabric was 118±4%. The wet pick-up of the Nomex/cotton blend fabric was 60±2%. After curing, the treated fabric was subjected to a specified number of laundering cycles using a standard reference detergent (“AATCC Detergent 1993”) according to AATCC Test Method 124-1996 (“Appearance of Fabrics after Repeated Home Laundering”). The water temperature for laundering was approximately 46°C. The fabric samples used in this study were subjected to one laundering cycle before being tested unless specified otherwise. The fabric samples that were not subjected to laundering were identified as “before wash”. The tap water used for home laundering in this study contained approximately 10ppm calcium.

### **Fabric Performance Evaluation**

The vertical flammability of the fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the fabric was measured according to ASTM Standard Method D2863-97. The tensile strength of the fabric was measured according to ASTM Standard Method D5035-95. The wrinkle recovery angle (WRA) was measured according to AATCC Standard Method 66-1996.

### **Infrared Spectroscopy Measurement**

The infrared spectroscopy has been successfully used for the qualitative and quantitative analysis of the esterified polycarboxylic acid on cotton in our previous research [24-26]. The diffuse reflectance infrared spectra of the treated cotton fabric were collected using a Nicolet Magna 760 FT-IR spectrometer with a Specac diffuse reflectance accessory, and they were presented in absorbance mode ( $-\log R/R_0$ ). Resolution for the infrared spectra was  $4\text{ cm}^{-1}$ , and there were 128 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 treated cotton fabric was first rinsed in water to remove the catalyst as well as the BTCA and TEA not bound to cotton, then treated with a 0.1M NaOH solution at the room temperature for 4 min to convert all free carboxylic acid groups on the cotton fabric to carboxylate anions. The cotton fabric sample thus treated was dried at  $90^\circ\text{C}$  for 5 min. To improve sample uniformity, a fabric sample was finally ground into powder in a Wiley mill before infrared spectroscopy analysis. The ester carbonyl band intensity in the infrared spectra was normalized against the  $1318\text{ cm}^{-1}$  band associated with a C-H bending mode of cellulose.

### **Determination of Phosphorus Concentration on the Treated Cotton Fabric**

Approximately 2g of the treated fabric taken from three different parts of a “10×12” fabric specimen was ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were added to 0.1 g fabric powder in a beaker. 10 ml of 30% H<sub>2</sub>O<sub>2</sub> were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO<sub>3</sub> vapor was produced. The completely digested fabric sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration.

## **Results and Discussion**

### **The Reaction between BTCA and TEA on Cotton**

The cotton fabric was treated with 10% BTCA and 3% H<sub>3</sub>PO<sub>2</sub> in combination with TEA at different concentrations. The pH of all the finishing solutions is adjusted to 2.8 using either 1M NaOH or 1M HCl solution depending on the amount of TEA in a solution. The fabric thus treated was cured at 180°C for 3 min, and then rinsed with 0.1M NaOH to convert the free carboxylic acid groups bound to cotton to carboxylate anions.

The infrared spectra of the fabric treated with 10% BTCA and 3% H<sub>3</sub>PO<sub>2</sub> without TEA are shown in Fig.8.1A. Two distinct carbonyl bands at around 1728 cm<sup>-1</sup> and 1585 cm<sup>-1</sup> are due to the carbonyl stretching modes of ester and carboxylate anion, respectively (Fig.8.1A). The ester band intensity increases and the carboxylate band intensity



decreases as the TEA concentration is increased from 1.0% to 6.0%, indicating that the amount of ester formed on the cotton fabric increases whereas that of carboxylate (anionic form of free carboxylic acid) decreases (Fig.8.1B-1E). One also observes that those two bands also shift slightly to higher frequencies at higher TEA concentrations (Fig.8.1B-1E), indicating the weakening of hydrogen-bonding of both ester and carboxylate carbonyls.

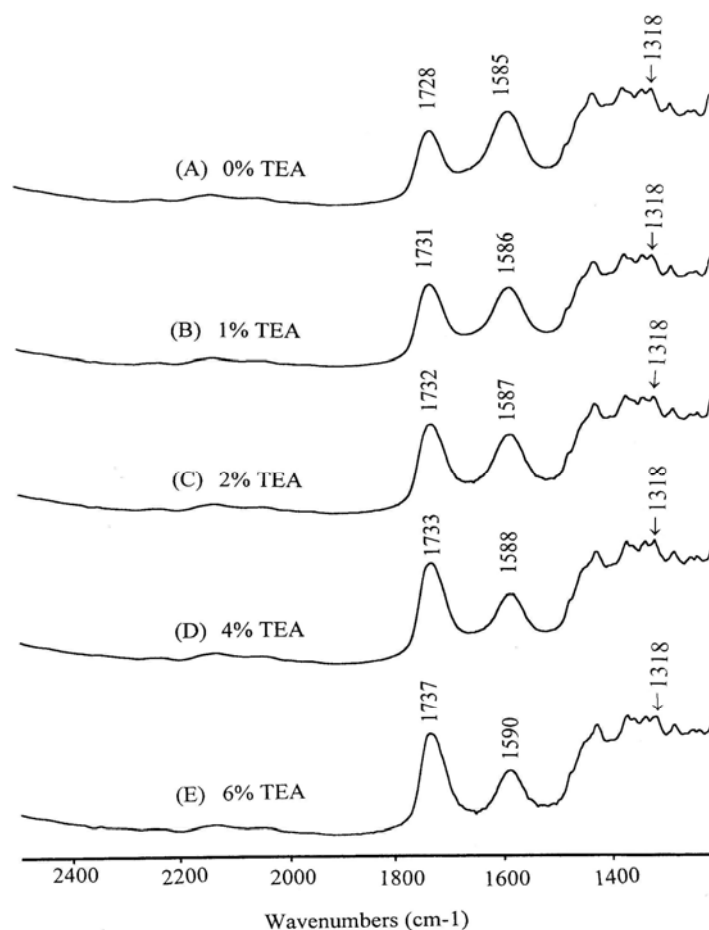


Fig.8.1 The infrared spectra of the cotton fabric treated with 10% BTCA and 3% H<sub>3</sub>PO<sub>2</sub> in combination with TEA at different concentrations and cured at 180°C for 3 min.

The intensities of the ester and the carboxylate carbonyl bands of the cotton fabric thus treated are plotted against the TEA concentration in Fig.8.2. The larger amount of

total ester formed on the cotton fabric at higher TEA concentrations shown in Fig.8.2 is evidently due to the esterification of the free carboxylic acid groups of BTCA bound to cotton by TEA. The intensity of the carboxylate carbonyl band is a measure of the amount of free carboxylic acid on cotton. The decrease in the amount of free carboxylic acid on cotton at increasing TEA concentrations, as shown in Fig.8.2, is a confirmation of the esterification of BTCA by TEA. Therefore, the infrared spectroscopy data presented here clearly demonstrate that TEA participates in the esterification of BTCA on cotton under the curing condition.

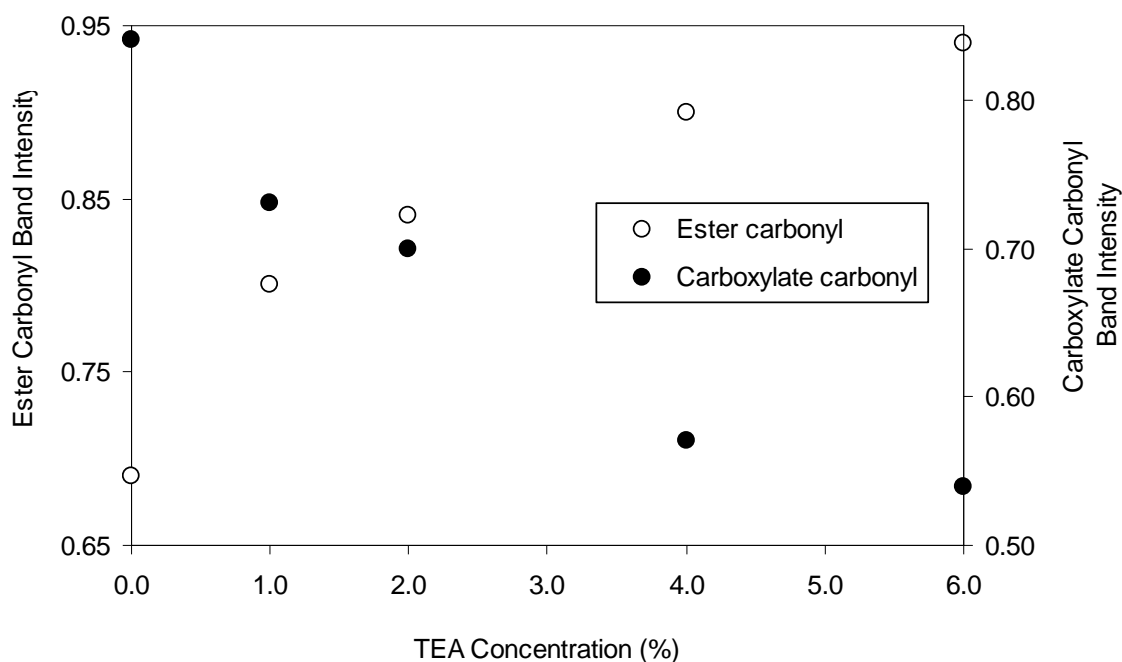


Fig.8.2 The ester and carboxylate carbonyl band intensities of the cotton fabric treated with 10% BTCA and 3%  $H_3PO_2$  in combination with TEA at different concentrations and cured at 180°C for 3 min, as a function of TEA concentration

The WRA of the cotton fabric thus treated with different TEA concentrations is presented in Table 8.1. WRA is a measure of the amount of the crosslinkages formed on

the treated cotton fabric by BTCA [27]. Table 8.1 shows that the WRA of the treated fabric decreases from 300° to 290° as the TEA concentration increases from 0.0% to 6.0%, thus indicating a slight decrease of the ester crosslinkages as the TEA concentration increases. As discussed above, the total amount of ester formed on cotton as shown by the intensity of the carbonyl band at 1728-1737  $\text{cm}^{-1}$  in Fig.8.1, which includes that formed by the reactions of BTCA/TEA and BTCA/cotton, increases as the TEA concentration increases. The data shown in Table 8.1 indicate that the amount of ester between BTCA and cotton decreases as the TEA concentration increases. So the amount of ester formed by BTCA/TEA increases as the TEA concentration increases. Thus, the data presented here prove that BTCA esterifies TEA on the treated cotton fabric and the amount of ester formed by the reaction of BTCA/TEA increases as the TEA concentration increases. Because both TEA and cellulose have hydroxyl groups, they compete to esterify BTCA. Consequently, the ester formed by BTCA/cotton decreases as the TEA concentration increases as shown in Table 8.1.

Table 8.1 The WRA of the cotton fabric treated with 10% BTCA and 3%  $\text{H}_3\text{PO}_2$  in combination with TEA at different concentrations and cured at 180°C for 3min.

TEA (%)	WRA (f+w, degree) *
0.0	300
1.0	297
2.0	295
4.0	292
6.0	290

- "f + w": combination of WRA at warp and filling directions.

### The Laundering Durability of the Treated Fabric Affected by TEA

The phosphorus concentration of the Nomex/cotton blend fabric treated with 24% HFPO, 8% BTCA and 2.5%  $H_3PO_2$  in combination with TEA at different concentrations and subjected to different laundering cycles is presented in Fig.8.3. After one laundering cycle, the phosphorus concentration on the treated Nomex/cotton blend fabric increases as the TEA concentration increases, and it reaches the maximum (1.60%) as the TEA concentration increases to 4.0% (Fig.8.3). The phosphorus concentration decreases as the TEA concentration increases further from 4% (Fig.8.3). After 10 and 25 laundering cycles, the maximum phosphorus concentrations on the treated fabric are also achieved when TEA concentration is 4.0% (Fig.8.3). The data presented here clearly show that the phosphorus concentration on the treated Nomex/cotton blend fabric first increases, then decreases as the TEA concentration increases in the range from 1.0% to 10.0% (Fig.8.3).

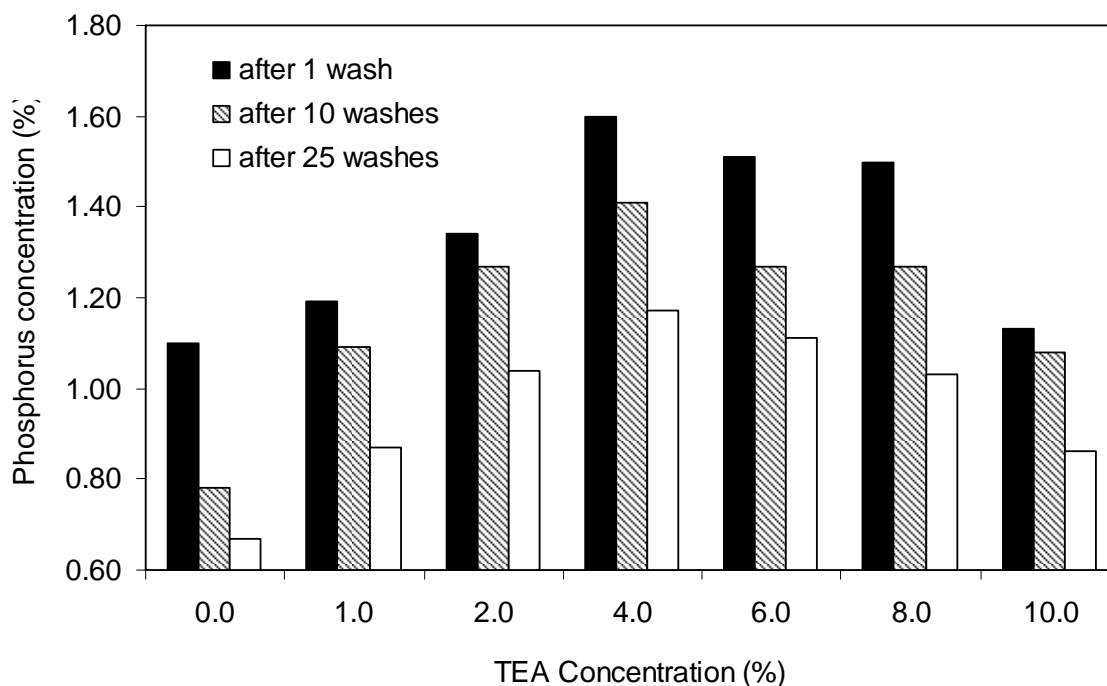
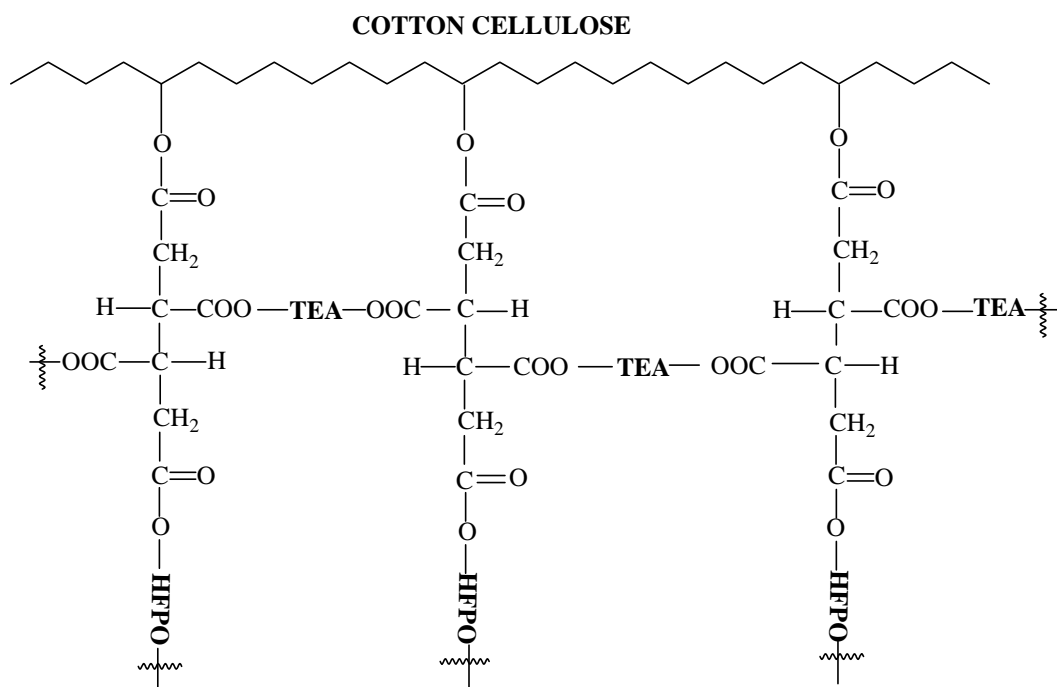


Fig.8.3 The phosphorus concentration of the Nomex/cotton blend fabric treated by 24%

HFPO, 8% BTCA and 2.5%  $\text{H}_3\text{PO}_2$  in combination with TEA at different concentrations, cured at  $180^\circ\text{C}$  for 3 min, and finally subjected to different numbers of laundering cycles, as a function of TEA concentration.

The data indicate that the use of TEA as a co-reactant in the flame retardant finishing solution increases the percent fixation of HFPO as well as the phosphorus retention on the fabric after multiple laundering cycles as the TEA concentration increases, and both percent fixation and phosphorus retention reach their maximum at 4% TEA. TEA has three hydroxyl groups in its molecule. It is possible for TEA to react with carboxylic acid groups of different BTCA molecules which also react with HFPO and cotton, to form a crosslinked network as shown in Scheme 8.3. The improved laundering resistance of the HFPO at increasing TEA concentrations shown in Fig.8.3 supports the hypothesis of the formation of the BTCA/HFPO/TEA crosslinked polymeric network.



Scheme 8.3 Formation of BTCA/HFPO//TEA crosslinked network on Cotton

The data presented in Fig.8.3 also show that further increasing TEA concentration from 4% to 10% reduces the fixation of HFPO and retention of HFPO after multiple launderings on the treated fabric. Because TEA, HFPO and cotton all have hydroxyl groups and they compete to react with BTCA, the presence of excessive amount of TEA reduces the reaction of BTCA with HFPO and cotton, thus reducing the both the fixation and the laundering durability of HFPO on cotton as shown in Fig.8.3.

### **The P – N Synergism Provided by TEA**

The cotton fabric was treated with 30% HFPO and BTCA at different concentrations. The cotton fabric thus treated was cured at 180°C for 3 min. The LOI of the treated cotton fabric (before wash) is shown in Table 2. The LOI of the cotton fabric thus treated is shows a very slight increase from 27.8% to 28.2% as the BTCA concentration increases from 0.0 to 10.0% (Table 8.2). The LOI of the cotton fabric treated with BTCA alone at concentration ranging from 0.0 to 10.0% (before wash) appears to be unchanged (Table 8.2). Little change is found in the LOI of the cotton fabric treated with TEA alone as the TEA concentration increases from 0 to 8% (before wash) (Table 8.2). Thus, we can conclude that both BTCA and TEA have no effect on the flammability of cotton.

Table 8.2 LOI of the cotton fabric treated with different formulas and cured at 180°C for 3 min.

HFPO (%)	BTCA (%)	TEA (%)	LOI (%)
30	0.0	-	27.8
30	2.0	-	28.0
30	4.0	-	27.9
30	7.0	-	28.1

30	10.0	-	28.2
-	0.0	-	17.5
-	2.0	-	17.3
-	4.0	-	17.3
-	7.0	-	17.4
-	10.0	-	17.6
30	10	0.0	28.2
30	10	2.0	29.3
30	10	4.0	30.3
30	10	6.0	30.7
30	10	8.0	31.4
-	-	0.0	17.5
-	-	2.0	17.2
-	-	4.0	17.3
-	-	6.0	17.4
-	-	8.0	17.6

The cotton fabrics treated with 30% HFPO, 10% BTCA and TEA at different concentrations was cured at 180°C for 3 min. The LOI of the treated cotton fabric (before wash) is also presented against in Table 8.2. The LOI of the treated cotton fabric increases from 28.2 to 31.4% as the TEA concentration is increased from 0.0 % to 8.0% (Table 8.2). Since the treated cotton fabric was not washed, all treated cotton fabric samples have same phosphorus concentration. Considering the fact that BTCA has no effect on the flammability of cotton fabric, the increase in LOI of the cotton fabric treated with HFPO/BTCA/TEA as the TEA concentration increases shown in Table 8.2 indicates that TEA enhances the flame retardant performance of HFPO on cotton. This elucidates the phosphorus-nitrogen synergism provided by TEA.

The Nomex/cotton fabric was treated with 24% HFPO, 8% BTCA, 2.5% H<sub>3</sub>PO<sub>2</sub> and TEA at different concentrations. The fabric thus treated was cured at 180°C for 3

min. The LOI of the fabric thus treated (before wash) is plotted against the TEA concentration in Fig.8.4. Without being subjected to laundering, all Nomex/cotton fabric samples have the same HFPO and  $H_3PO_2$  concentrations but different TEA concentrations. The LOI (%) of the fabric increases from 37.2 to 40.6 as the TEA concentration (%) increases from 0.0% to 8.0% (Fig.8.4). The data clearly demonstrate the phosphorus-nitrogen synergistic effect of TEA in the HFPO/BTCA/ $H_3PO_2$ /TEA system on the Nomex/cotton blend fabric (Fig.8.4).

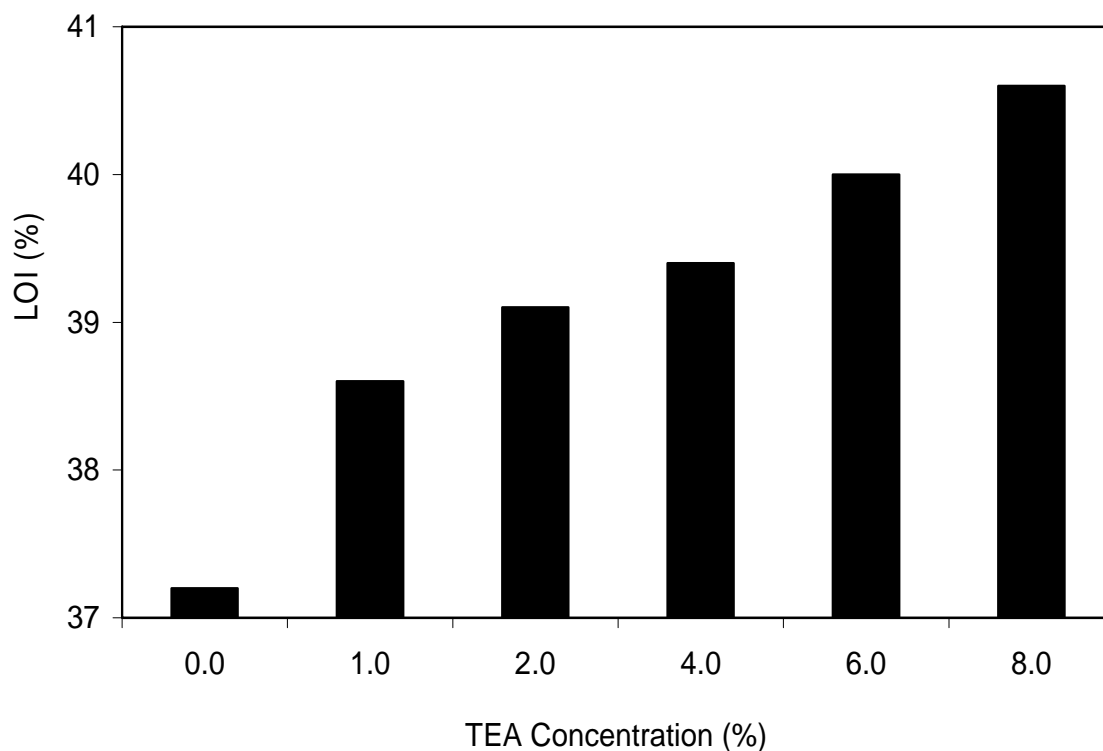
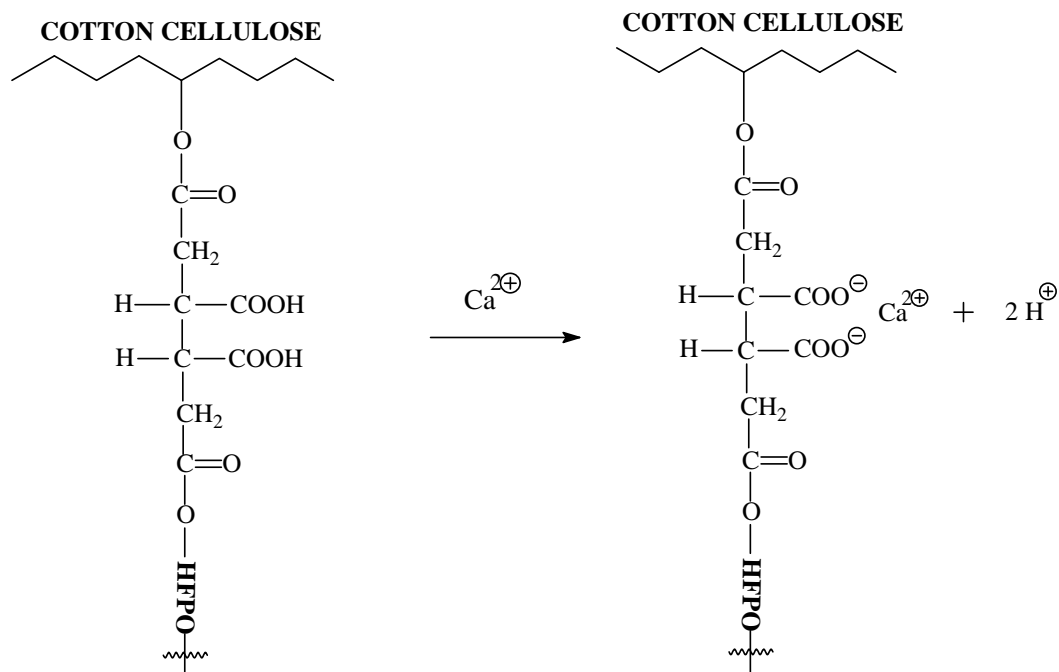


Fig.8.4 LOI of the Nomex/cotton blend fabric treated by 24% HFPO, 8% BTCA and 2.5%  $H_3PO_2$  in combination with TEA at different concentrations and cured at 180°C for 3 min, as a function of TEA concentration.



### **Formation of Calcium Deposit on the Treated Fabric Affected by TEA**

Previously, it was found that the calcium deposit formed on the cotton treated with HFPO/BTCA during laundering diminishes the flame retardant performance of the treated cotton fabric [23]. We studied the effects of TEA on the calcium deposit on the Nomex/cotton fabric treated with HFPO/TEA. The Nomex/cotton blend fabric was treated with 24% HFPO, 8% BTCA and 2.5%  $H_3PO_2$  in combination with TEA at different concentrations and cured at 180°C for 3 min. The fabric thus treated was subjected to different numbers of laundering cycles. The calcium concentrations of the treated Nomex/cotton blend fabric before laundering and after 10 laundering cycles are plotted against the TEA concentration in Fig.8.5. The calcium concentration on the fabric before wash is in the range of 0.06-0.09% (Fig.8.5). The calcium concentration on the fabric becomes significantly higher after 10 washes, but it decreases as the TEA concentration is increased to 10.0% (Fig.8.5). The increase in the calcium concentration on the treated Nomex/cotton blend fabric after multiple laundering is due to the formation of insoluble calcium salt of those free carboxylic acid groups of BTCA bound to cotton as shown in Scheme 8.4. The reduction of the calcium concentration on the treated Nomex/cotton blend fabric as a result of the presence of TEA in the finishing system is attributed to esterification of the free carboxylic acid groups of BTCA on cotton by TEA as shown in Scheme 8.3. The decrease in the calcium concentration on the fabric helps to restore the flame retarding performance of the treated fabric.



Scheme 8.4 Formation of Calcium Salt on the treated Nomex/Cotton Blend Fabric

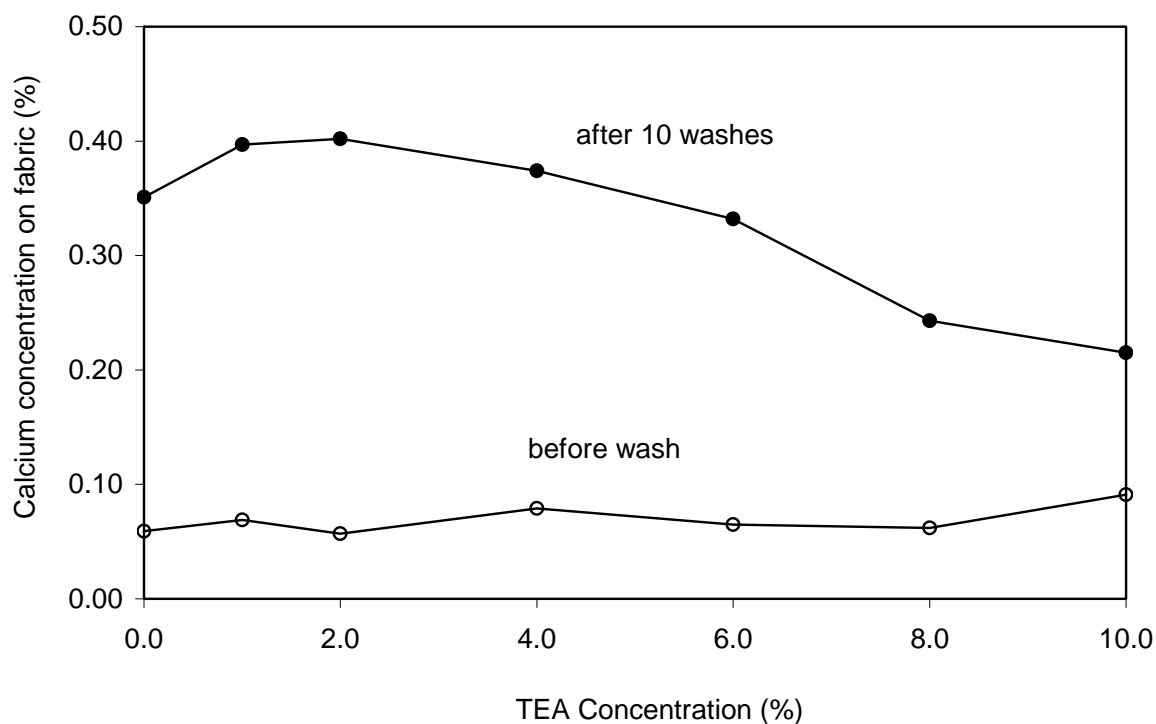


Fig.8.5 Calcium concentration of the Nomex/cotton blend fabric treated by 24% HFPO, 8% BTCA and 2.5%  $\text{H}_3\text{PO}_2$  in combination with TEA at different concentrations, cured at  $180^\circ\text{C}$  for 3 min, and finally subjected to different laundering cycles, as function of TEA concentration.

### Performance of the Nomex/Cotton Blend Treated with HFPO/BTCA/TEA

The Nomex/cotton blend fabrics were treated with 24% HFPO, 8% BTCA, 2.5% H<sub>3</sub>PO<sub>2</sub> and TEA at different concentrations. The initial pH value of all the finish solutions is presented in Table 8.3. Since TEA is a base with  $pK_b = 6.238$ , the pH of a finish solution increases as the TEA concentration increases (Table 8.3). The pH of all the finishing solutions was adjusted to ~2.8 using either a 1M NaOH or HCl solution. The Nomex/cotton blend fabric thus treated was cured at 180°C for 3 min and finally subjected to 1, 10 and 25 laundering cycles. The LOI (%) of the fabric thus treated is shown against the TEA concentration (Fig.8.6). After 1 laundering cycle, the LOI of the treated Nomex/cotton blend fabric first increases from 32.1% without TEA to its maximum (36.3%) when 6.0% TEA is used. Further increasing TEA concentration reduces the LOI of treated Nomex/cotton blend fabric (Fig.8.6). Similar trends are observed on the treated fabric subjected to 10 and 25 laundering cycles. The optimum TEA concentration for the finish solution is in the 4.0-6.0% range. After 25 laundering cycles, the LOI of the fabric treated using 6.0% TEA is 30.5%.

Table 8.3 The initial pH of the solutions containing 24%HFPO, 8%BTCA and 2.5% H<sub>3</sub>PO<sub>2</sub> in combination with TEA at different concentrations.

TEA (%)	Initial pH value
0.0	0.87
1.0	0.97
2.0	1.16
4.0	1.61
6.0	2.40
8.0	3.20
10.0	3.67

The char length of the Nomex/cotton blend fabric thus treated is shown in Table 8.4. The data clearly showed that the Nomex/cotton blend fabric treated with the finish solution without TEA fails the vertical flammability test after 20 laundering cycles. The use of TEA as a co-reactant in the finishing system significantly improves the flame retardant performance of the treated Nomex/cotton blend after multiple laundering cycles. All the fabric samples treated with HFPO/BTCA/TEA show excellent flame retardant performance after 25 laundering cycles. The data presented here also show that further increasing TEA concentration beyond 6.0% reduces LOI (Fig.8.6).

Table 8.4 The char length of the Nomex/cotton blend fabric treated with the finishing solutions containing 24%HFPO, 8%BTCA, 2.5% $H_3PO_2$  and TEA at different concentrations and cured at 180°C for 3 min.

TEA (%)	Number of home laundering cycles			
	after 1 wash	after 10 washes	after 20 washes	after 25 washes
0.0	30	40	>300	>300
1.0	25	45	44	51
2.0	31	34	33	35
4.0	33	34	36	43
6.0	30	35	34	31
8.0	30	29	40	30
10.0	33	33	43	30

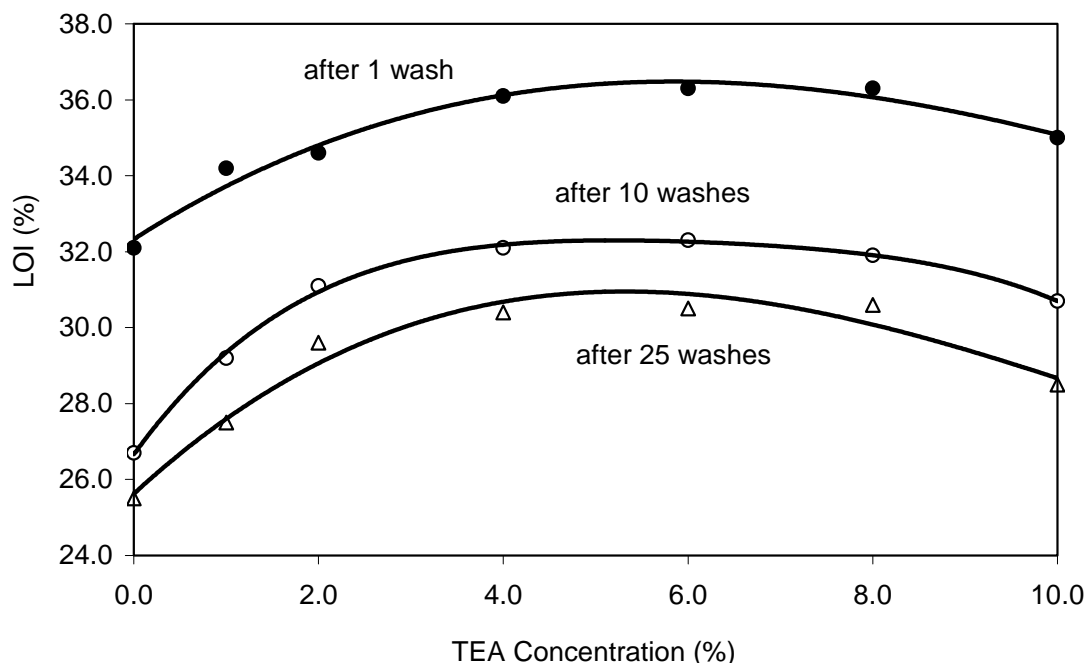


Fig.8.6 The LOI of the Nomex/cotton blend fabric treated by 24% HFPO, 8% BTCA and 2.5%  $H_3PO_2$  in combination with TEA at different concentrations and then cured at  $180^\circ C$  for 3 min, and finally subjected to different laundering cycles, as a function of TEA concentration.

The Nomex/cotton blend fabric was treated with the solutions containing 24% HFPO, 8% BTCA, 2.5%  $H_3PO_2$  and 6% TEA with their pH adjusted from 1.0 to 4.0 using either a 1M HCl or 1M NaOH solution, then cured at  $180^\circ C$  for 3 min. The LOI of the treated fabric subjected to 1 and 10 laundering cycles are presented against the pH in Fig.8.7. The LOI of the treated fabric after 10 laundering cycles appears to change very little in the pH range 1.0-2.8, but it decreases as the pH increases beyond 2.8 (Fig.8.7). The maximum phosphorus concentration was also achieved at pH=2.5 (Figure 8.8). The pH evidently plays an important role in the reactions associated with the bonding of HFPO to the fabric by BTCA/TEA. Because a finishing solution with lower pH causes more cellulose degradation and consequently more fabric strength loss [28, 29], we use 2.5 as the optimum pH for the HFPO/BTCA/TEA system.

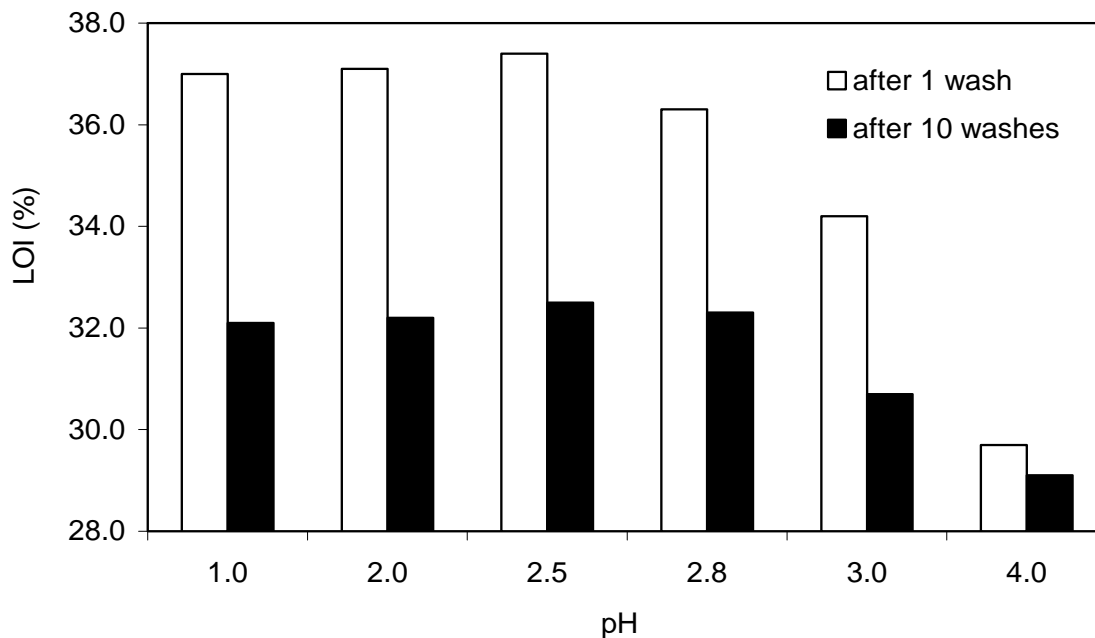


Fig.8.7 LOI of the Nomex/cotton blend fabric treated with 24% HFPO, 8% BTCA, 2.5%  $H_3PO_2$  and 6% TEA at different pH, cured at 180°C for 3 min, and finally subjected to 1 and 10 laundering cycles, as a function of the pH value.

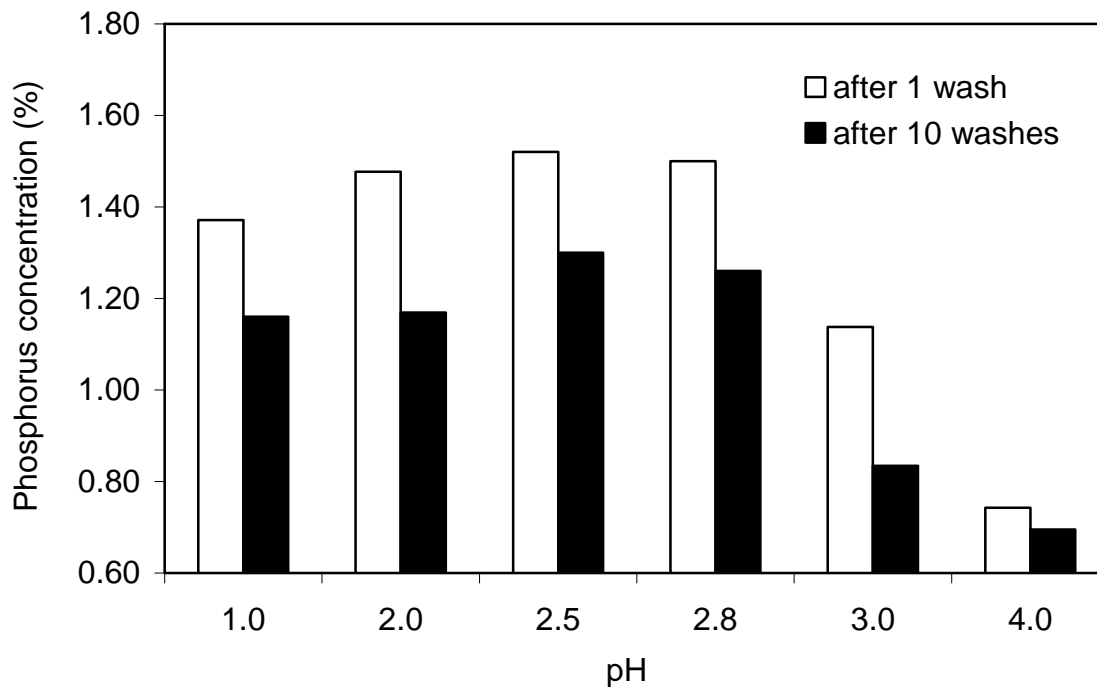


Fig.8.8 Phosphorus concentration of the Nomex/cotton blend fabric treated with 24% HFPO, 8% BTCA, 2.5%  $H_3PO_2$ , and 6% TEA at different pH, cured at 180°C for 3 min, and finally subjected to 1 and 10 laundering cycles, as function of the pH value.

The Nomex/cotton blend fabrics was treated with HFPO/BTCA/TEA (weight ratio:3.0/1.0/0.75) at different concentrations and curried at 180°C for 3 min. The HFPO concentration increases from 12% to 24%, and the BTCA and TEA concentration increases accordingly. The LOI, vertical flammability (char length) and phosphorus concentration of the treated fabric after different laundering cycles are presented in Tables 8.5, 8.6 and 8.7, respectively. The LOI of the Nomex/cotton blend fabric without treatment is 22.9% and it fails the vertical flammability test, indicating that the Nomex/cotton blend is not a flame-resistant fabric. All the Nomex/cotton fabric treated with the four HFPO/BTCA/TEA formulas passes the vertical flammability test after 30 laundering cycles (Table 8.6). The fabric treated with 12% (w/w) HFPO finishing solution (approximately 8% (w/w) HFPO on the fabric) has LOI of 26.5% and char length of 48 mm after 30 laundering cycles, demonstrating excellent flame retardant performance and superior laundering durability at a small add-on concentration on the fabric.

Table 8.5 The LOI of the Nomex/cotton fabric treated with HFPO/BTCA/H<sub>3</sub>PO<sub>2</sub>/TEA at the weight ratio of 24/8/2.5/6 and cured at 180°C for 3 min.

HFPO (%)	BTCA (%)	H <sub>3</sub> PO <sub>2</sub> (%)	TEA (%)	Number of home laundering cycles				
				before wash	after 1 wash	after 10 washes	after 20 washes	after 30 washes
12	4	1.25	3.0	35.7	32.7	27.9	27.1	26.5
18	6	1.88	4.5	38.8	35.7	31.1	30.1	28.5
24	8	2.50	6.0	40.7	37.2	32.5	30.5	29.4
30	10	3.13	7.5	40.6	37.8	33.0	32.0	29.5
Control				22.9				

Table 8.6 The char length of the Nomex/cotton blend fabric treated with HFPO/BTCA/H<sub>3</sub>PO<sub>2</sub>/TEA at the weight ratio of 24/8/2.5/6 and cured at 180°C for 3 min.

HFPO (%)	BTCA (%)	H <sub>3</sub> PO <sub>2</sub> (%)	TEA (%)	Number of home laundering cycles				
				before wash	after 1 wash	after 10 washes	after 20 washes	after 30 washes
12	4	1.25	3.0	37	34	41	44	48
18	6	1.88	4.5	28	29	43	27	35
24	8	2.50	6.0	27	31	35	34	31
30	10	3.13	7.5	27	31	30	38	32
Control				>300				

Table 8.7 Phosphorus concentration of the Nomex/cotton blend fabric treated with different concentration levels of HFPO/BTCA/H<sub>3</sub>PO<sub>2</sub>/TEA at the fixed ratio (24/8/2.5/6) and cured at 180°C for 3 min.

HFPO (%)	BTCA (%)	H <sub>3</sub> PO <sub>2</sub> (%)	TEA (%)	Phosphorus Concentration (%)				
				before wash	after 1 wash	after 10 washes	after 20 washes	after 30 washes
12	4	1.25	3.0	1.26	0.69	0.63	0.57	0.51
18	6	1.88	4.5	1.86	1.17	1.00	0.82	0.79
24	8	2.50	6.0	2.50	1.53	1.30	1.15	1.00
30	10	3.13	7.5	2.83	1.79	1.53	1.48	1.06

The tensile strength of the treated Nomex/cotton blend fabric is summarized in Table 8.8. The tensile strength retention is 73-77% at the warp direction and 77-82% at the filling direction (Table 8.8). The loss of fabric strength is due to the two factors: Acid-catalyzed cellulose depolymerization and crosslinking of cotton cellulose by BTCA [29-30]. Because the blend fabric only contain 35% cotton fiber, and its strength loss



after the flame retardant finishing process is modest. The effect of the treatment on the fabric hand property appears to be negligible.

Table 8.8 The tensile strength of the Nomex/cotton blend fabric treated with HFPO/BTCA/H<sub>3</sub>PO<sub>2</sub>/TEA at the weight ratio of 24/8/2.5/6 and cured at 180°C for 3 min.

HFPO (%)	BTCA (%)	H <sub>3</sub> PO <sub>2</sub> (%)	TEA (%)	Tensile Strength (N)		Strength Retention (%)	
				Warp	Filling	Warp	Filling
12	4	1.25	3.0	405	262	73	80
18	6	1.88	4.5	414	271	74	82
24	8	2.50	6.0	409	254	74	77
30	10	3.13	7.5	427	270	77	82
Control				556	329	-	-

## Conclusions

Using TEA as a co-reactant in the HFPO/BTCA flame retardant finishing system applied to the Nomex/cotton blend fabric significantly enhances the performance of this system on the Nomex/cotton blend fabric. TEA probably forms a crosslinked polymeric network with BTCA and HFPO on the treated fabric, thus improving the laundering durability of HFPO bound to cotton. It provides nitrogen to enhance the flame retardant performance by the phosphorus-nitrogen synergism. TEA also reduces the formation of calcium salts on the fabric by esterifying the free carboxylic acid group of BTCA bound to cotton. The Nomex/cotton blend fabric treated with HFPO/BTCA/TEA is able to achieve high levels of the flame retardant performance and laundering durability at relatively low add-on levels on the fabric. The treated fabric also shows limited strength loss and little change in hand properties. This flame retardant finishing system is a formaldehyde-free system and odor-free process.

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