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Self-Extinguished and Anti-Dripping Intumescent Coating for Polyester and Polyester/Cotton Fabric via Layer-By-Layer Assembly

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Abstract: Intumescent coatings containing Branched-Polyethyleneimine (BPEI) and mixture of Ammonium Polyphosphate (APP) solution and aqueous kaolin clay were successfully applied on polyester and polyester/cotton fabric via layer-by-layer technique to enhance flame retardancy and anti-dripping of fabric. SEM micrographs of 3, 5 and 7 bilayers coated fabric affirmed that the coat layer on the fabric was rather thin. UL-94 rating of Vertical burning of Thin Material (VTM 0) showed that the flame retardancy of coated polyester and polyester/cotton fabric including self-extinguishing ability and anti-dripping were improved as compared with uncoated fabric. TGA thermogram also revealed that thermal stability of coated fabrics increased when the number of bilayer increased. The porous and slight expanded char layers of the char residue of the coating observed by SEM micrographs demonstrated that LBL coated fabric exhibited the typical structure of intumescent behavior. This research provides a basic method of intumescent coating for self-extinguishment and anti-dripping on polyester and polyester/cotton fabric.

Key words: Intumescent coating, layer-by-layer, branched-polyethyleneimine, ammonium polyphosphate, kaolin, polyester fabric, polyester/cotton fabric

INTRODUCTION

The intumescent system were first developed in 1938 (Grand and Wilkie, 2000) for coating application. It can protect the substrate against from fire or heat by forming the foam char as a barrier between substrate and heat or flame or combustible gas. This flame retardancy mechanism operates in the condensed phase and forms an insulating layer along the surface of substrate as the result of a foaming chemical reaction (Cain *et al*., 2014). The intumescent coating has been attracted as an efficient technique to improve flame retardancy and anti-dripping behavior of fabric due to the limited usage of halogen-containing flame retardants. The advantages of intumescent coating are the ability to protect fabric against fire while mechanical properties of the coated fabric will not be altered (Camino *et al*., 1985). It was reported that the flame retardant and/or anti-dripping properties of fabrics such as nylon (Li *et al*., 2009), cotton (Dahiya and Kumar, 2009; Chen and McCarthy, 1997) and polyester (Ma *et al*., 1997; Gao *et al*., 2006) were effectively enhanced by intumescent coating. Normally, the intumescent coating using non-halogen containing flame retardants was applied on fabric via conventional coating. Nevertheless, a coating still require high loading of non-halogen containing flame retardants for enhancing the flame retardancy of fabric. This affects the handle touch and mechanical properties of coated fabrics.

To further improve the handle touch of coated fabrics, the Layer-By-Layer (LBL) assembly technique is an alternative method. The LBL assembly is the simple surface modification by generating thin film on substrate by means of repeating an adsorption of different charged solution several times. The LBL assembly uses a low concentration of polyelectrolyte solution to build up the thin multiple cationic/anionic pairs of layer (known as bilayer, BL) on the substrate surface. LBL substrates can be of any size and shape. In addition, no stoichiometric control is necessary to maintain surface functionality of the substrates (Chen and McCarthy, 1997). The LBL assembly technique has been widely used to enhance properties of polymers and textiles such as oxygen barrier (Jang *et al*., 2008) and antibacterial (Fu *et al*., 2005), including to improve the flame retardancy of fabrics. LBL assembly technique is inexpensive and environmentally friendly treatment for flame retardation onto textiles (Zhang *et al*., 2014). This technique was applied to

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improve the flame retardancy of several types of fabrics such as cotton (Fang *et al*., 2015) ramie (Zang *et al*., 2013) and polyester (Carosio *et al*., 2011, 2013).

In this research, we presented a simple layer-by-layer assembly containing a carbonific compound, an acid source, a spumific compound and binder of the intumescent system. The LBL assembly of branched polyethylenimine, ammonium polyphosphate and kaolin was applied onto polyester and polyester/cotton fabrics. Branched-Polyethyleneimine (BPEI) is polymer that contain primary, secondary and tertiary amino group and has been used widely as positively charged surface in LBL assembly research. BPEI can serve as a carbonific compound to form carbonaceous char and also as a spumific compound to release gases such as ammonia for intumescent system at high temperature (Fang *et al*., 2015). Ammonium Polyphosphate (APP) is a non-halogen containing flame retardant which has been used widely in flame retardant for fabric. In intumescent system, APP can serve as an acid source which esterify the hydroxyl groups to form carbonaceous char (Zhang *et al*., 2014). Furthermore, kaolin is the mineral clay which can promote char formation (Tang *et al*., 2015). The mineral particles of kaolin will move to the upper surface of coated fabric and form a ceramic layer which act as the barrier to retard the combustion of fabric at high temperature (Zhang *et al*., 2014).

The objectives of this research were to improve flame retardancy and anti-dripping of polyester and polyester/cotton fabric by using intumescent coating with non-halogen containing flame retardants via LBL assembly and study the flame retardancy, melt dripping, thermal properties and morphology of coated fabrics. This work demonstrated the ability to apply the effective intumescent coating on polyester and polyester/cotton.

MATERIALS AND METHODS

Experimental: Two types of fabrics,100% polyester woven fabric with density of 160 gm^{-2} and blended woven fabric with density of 236 gm^{-2} (80% polyester/20% cotton: warp yarn is polyester fiber and weft yarn is cotton) were were purchased from PakNam Textile (Thailand) Co., Ltd., Samut Prakarn Province, Thailand. Branched Polyethylenimine (BPEI) (M_w = 25,000 M_n = 10,000), (105%) polyphosphoric acid and (28%) ammonium hydroxide were supplied by Sigma-Aldrich. Kaolin was provided by Nic Interchem Co., Ltd., Bangkok, Thailand.

Preparation of ammonium polyphosphate solution: Ammonium Polyphosphate (APP) was prepared by gently dropping 15 g of (28%) ammonium hydroxide solution into 30 g of (105%) polyphosphoric acid at room temperature. The obtained APP solution at pH 1.5 was then diluted to 10% wt and mixed with 0.5% kaolin solution (APP/K) at 9:1 ratio.

Layer-by-layer assembly: Prior to the deposition, the fabrics were washed with 5g L^{-1} standard soap at 40°C for 30 min and then dried at 80°C for 5 min. The fabrics were then immersed into the ionic aqueous solution, alternating between BPEI as cationic solution and APP/K solution as anionic solution (each cycle corresponding to one bilayer). The fabric was first immersed into 0.5% BPEI solution at pH 10 for 5 min and subsequently immersed into APP/K solution for 2 min. Each immersion was followed by padding fabric with 60% wet pick up then drying at 80°C for 5 min in the case of cationic solution and 110°C for 3 min in the case of anionic solution. This process was repeated until sample with 3, 5 and 7 Bilayers (BL) was accomplished.

Characterization: The surface morphology of uncoated and LBL coated fabrics before burning and of their char residue after burning were studied by using JEOL JSM-6480LV scanning electron microscope (SEM, Tokyo, Japan) operated at 10 kV for polyester fabric and 5 kV for polyester/cotton fabric. The thermal stability of uncoated and LBL coated fabrics were evaluated by thermogravimetric analysis using Mettler Toledo TGA/SDTA 851 (Greifensee, Switzerland) analyzer. Each sample was tested in nitrogen atmosphere (gas flow, 60 mL min^{-1}) from 50-800°C with the heating rate of 10°C min^{-1}.

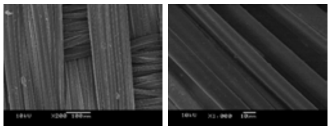
The flame retardancy was investigated by vertical burning test according to UL-94 VTM standard method. The samples, 50 mm in width and 200 mm in length, held 20 mm above burner were exposed to the flame for 3 sec and removed immediately. The first afterflame time and dripping behavior were recorded. The samples were then again exposed to the flame for 3 sec and removed immediately. The second afterflame time and dripping were recorded while a piece of cotton pad was placed under the burning sample to observe whether molten drips (with or without flame) could ignite and burn the cotton pador not.

RESULTS AND DISCUSSION

Morphology of the coated fabric: The morphology of the coatings created via layer-by-layer assembly was investigated by SEM micrographs as shown in Fig. 1

Table 1: UL94-vertical burning test data of uncoated and LBL coated polyester fabric and polyester/cotton fabric with BPEI (0.5%)/APP(10%): K(0.5%) (9:1)

Parameters	1st after flame time (sec)	2nd after flame time (s)	Dripping	Class
Uncoated polyester fabric	8.9	2.2	Yes	VTM 2
Coated polyester fabric, 3BL	0.3	0.4	No	VTM 0
Coated polyester fabric, 5BL	0	0	No	VTM 0
Coated polyester fabric, 7BL	0	0	No	VTM 0
Uncoated polyester/cotton fabric	37.4	-	Burn out	VTM 2
Coated polyester/cotton fabric, 3BL	2.5	2.2	No	VTM 0
Coated polyester/cotton fabric, 5BL	2.2	1.4	No	VTM 0
Coated polyester/cotton fabric, 7BL	0	1.4	No	VTM 0



Uncoated polyester fabric

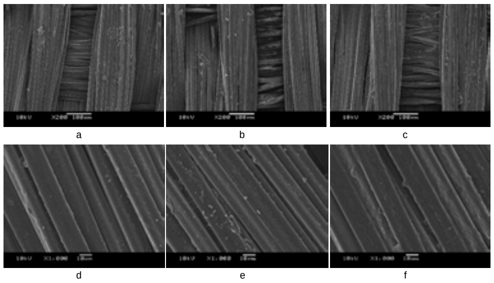
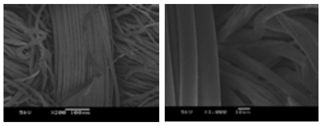


Fig. 1: SEM micrographs of uncoated polyester fabric with magnification of 200 and 1000×, coated polyester fabric using 0.5%BPEI/10%APP:0.5%K (9:1) via layer-by-layer assembly at 3(a), 5(b), 7(c)BL with magnification of 200× and at 3(d), 5(e), 7(f), BL with magnification of 1000×



Uncoated polyester/cotton fabric

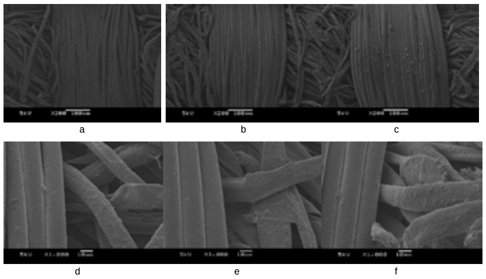


Fig. 2: SEM micrographs of uncoated polyester/cotton fabric with magnification of 200 and 1000×, coated polyester/cotton fabric using 0.5% BPEI/10%APP:0.5%K (9:1) via layer-by-layer assembly at 3(a), 5(b), 7(c), BL with magnification of 200× and at 3(d), 5(e), 7(f), BL with magnification of 1000×

and 2. The SEM micrographs of the uncoated fabric showed smooth and clean surface while those of coated fabric exhibited thick coating layers with rougher surface. The coating surface appeared thicker and more uniform when the number of coating layers increased from 3 Bilayers (BL) to 5 and 7 BL, progressively. It was observed that some particles were embedded in the bilayer. Moreover, SEM micrographs of coated fabric with magnification of 200× exhibited that the weave structure still appeared on the fabric after layer-by-layer assembly. This indicated that the coat layer on the fabric was rather thin.

Flame retardancy and morphology of char residue after burning: The vertical burning test data of uncoated and LBL coated fabric were shown in Table 1. Uncoated polyester and polyester/cotton fabric severely burned after removing the ignition source. The melted and flaming drips of uncoated polyester and polyester/cotton fabric ignited the underlying cotton pad and UL 94-rating VTM 2 was evaluated. While, all 3, 5 and 7BL coated fabric showed better flame retardancy without molten drip and UL 94-rating VTM 0 were evaluated.

Figure 3 showed SEM micrographs of char residue of uncoated and coated fabrics. Since the uncoated polyester/cotton fabric entirely burned, no char residue is subjected to investigate their morphology. However, the char residue of uncoated polyester fabric was rather smooth whereas char residue of all LBL coated polyester and polyester/cotton fabrics exhibited the intumescent behavior by displaying rough and porous char which is the typical structure of intumescent char.

Thermal stability: Thermal stabilities of uncoated and coated fabrics have been determined by thermogravimetry in nitrogen atmosphere. Figure 4 and 5 showed TGA thermogram of polyester and polyester/cotton fabric, respectively. Table 2 and 3 showed thermogravimetric data of coated polyester fabric and polyester/cotton fabric, respectively. The coated fabrics degraded at lower temperature in comparison with uncoated fabric. This

Table 2: Thermogravimetric data of uncoated and coated polyester fabric with 0.5%BPEI/10%APP:0.5%K (9:1)

Parameters	$T_{onset10\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	Residual char at T_{max} (%)
Uncoated polyester fabric	400	435	-	-
Coated polyester fabric, 3BL	336	425	750	12.9
Coated polyester fabric, 5BL	345	420	750	12.9
Coated polyester fabric, 7BL	340	417	750	15.9

Table 3: Thermogravimetric data of uncoated and coated polyester/cotton fabric with 0.5%BPEI/10%APP:0.5%K (9:1)

	$T_{onset\ 5\%}$ (°C)	$T_{max\ 1}$ (°C)	Residual char at T_{max1} (%)	$T_{max\ 2}$ (°C)	Residual char at T_{max2} (%)	Residual char at 700°C (%)
Uncoated polyester/cotton fabric	341	370	81.1	441	33.9	8.10
Coated polyester/cotton fabric, 3BL	220	248	91.3	440	37.3	11.3
Coated polyester/cotton fabric, 5BL	223	288	90.1	440	35.3	10.8
Coated polyester/cotton fabric, 7BL	227	248	91.9	440	34.1	16.5

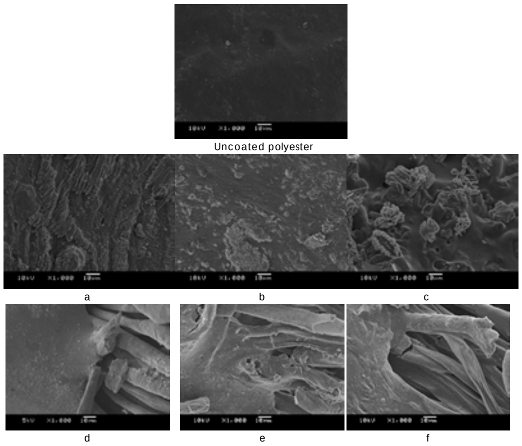


Fig. 3: SEM micrographs of char residue of uncoated polyester fabric, coated polyester fabric using 0.5%BPEI/10%APP:0.5%K (9:1) via layer-by-layer assembly at 3(a), 5(b), 7(c), BL and coated polyester/cotton fabric using 0.5%BPEI/10%APP:0.5%K (9:1) at 3(d), 5(e), 7(f), BL via layer-by-layer assembly with magnification of 1000×

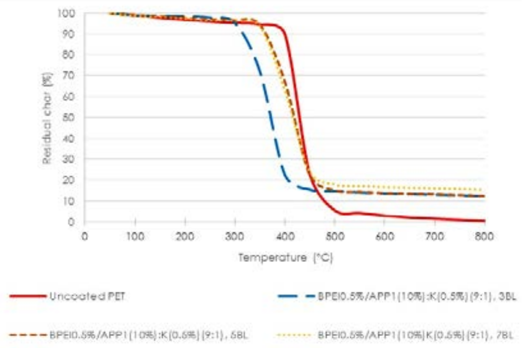


Fig. 4: TGA thermograms of uncoated and coated polyester fabric with 0.5%BPEI/10%APP:0.5%K (9:1)

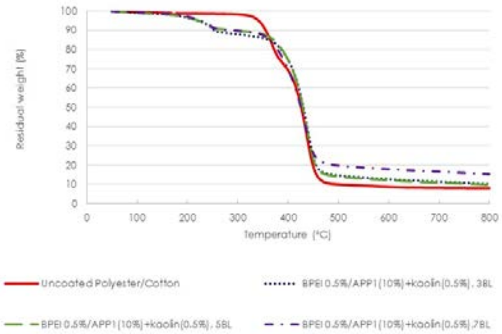


Fig. 5: TGA thermograms of uncoated and coated polyester/cotton fabric with 0.5%BPEI/10% APP:0.5%K (9:1)

is due to the reaction of dehydration to form the carbonaceous char in presence of APP (Fang *et al*., 2015). However, the coated fabric displayed more amounts of residual char than uncoated fabric on Tmax which indicating the improvement of thermal stability of coated fabrics. The porous and slight expanded char layers of the coating indicating the intumescent char behavior completely insulated the fabric. Accordingly, the flow of heat to fabrics was minimized. Moreover, this intumescent char contribute to decrease the melt drips and enhance thermal stability (Zhang *et al*., 2013; Ma *et al*., 2007).

CONCLUSION

The intumescent coating containing of Branched-Polyethyleneimine (BPEI) as polypositive charged surface and mixture of Ammonium Polyphosphate (APP) solution and aqueous kaolin as polynegative charged surface of 3, 5 and 7 bilayers were successfully applied on polyester and polyester/cotton fabric via layer-by-layer technique. SEM micrographs of 3, 5 and 7 bilayers coated fabric affirmed that the coat layer on the fabric was rather thin. UL-94 vertical burning rating VTM 0 of all 3, 5 and 7 BL coated fabrics in this study revealed that all LBL coated fabrics displayed better flame retardancy in terms of afterflame time and anti-dripping than those of uncoated fabrics. Moreover, the LBL coated fabrics could be self-extinguished after removing the ignition source. TGA thermograms of the coated fabrics degraded at lower temperature in comparison with uncoated fabric due to the dehydration reaction of APP to form carbonaceous char. In addition, the porous and slight expanded char layers of the coating observed by SEM micrographs demonstrated that LBL coated fabric exhibited the typical structure of intumescent behavior. Moreover, this intumescent char contribute to decrease the melt drips and enhance thermal stability.

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