JOURNAL OF Applied Polymer SCIENCE

Fire Retardancy and Durability of Poly(*N*-benzyloxycarbonyl-3,4-dihydroxyphenylalanine)-montmorillonite Composite Film Coated Polyimide Fabric

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ABSTRACT: Polyimide (PI) fabric was coated with composite films composed of poly(*N*-benzyloxycarbonyl-3,4-dihydroxyphenylalanine) (PNBD) and montmorillonite (MMT), prepared via layer-by-layer assembly. Three coating recipes (changed by altering the concentration of PNBD solution) were used to study the growth of thin films. Scanning electron microscope showed that, after 20 times standard washing, PNBD-MMT film still coated on PI fiber, while MMT film coated on PI had been almost washed off. Thermogravimetric analysis indicated that, in nitrogen atmosphere at 900°C, the residue of uncoated PI was 36.62%, after 20 times standard washing, residue of PNBD-MMT coated PI (53.80%) was higher than that of MMT coated PI (50.08%). Vertical flame testing showed that the burning length of PNBD-MMT coated PI (7 mm) was much shorter than that of uncoated PI (30 mm) and MMT coated PI (17 mm) after 20 times standard washing. These results demonstrated the excellent flame retardancy and durability of PNBD-MMT film coated PI fabric. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39608.

KEYWORDS: clay; coatings; flame retardance; composites; self-assembly

Received 3 February 2013; accepted 1 June 2013

DOI: 10.1002/app.39608

INTRODUCTION

Layer-by-layer (LbL) assembly has become a popular method to fabricate multifunctional films in recent years.[1–10] LbL films have been studied for applications that include sensing,[11] antimicrobial surfaces,[10] biomedical applications, and oxygen barrier layers.[12–15] Phyllosilicate have been widely studied in LbL thin films, especially montmorillonite (MMT) and laponite,[15–18] because these platelet structures exhibit swelling and exfoliation in water. An individual MMT clay platelet is composed of two tetrahedral Si^{4+} layers intercalated by an octahedral Al^{3+} or Mg^{2+} layer in between. They typically organize face-to-face into aggregates, but in water dispersion, these faces become negatively charged and exfoliated as water intercalates the clay layers. Recently, it was reported that LbL assembly has been used as a surface treatment to impart flame resistance to cellulose by coating each individual fiber with a clay-polymer nanobrick wall.[15] However, the washing fastness (the ability of the coated polyimide (PI) fabric to retain its coating after standard wash) of these LbL film coated fabrics were not discussed.

PI fabric is a kind of primary high-temperature resistance fabric, and the fabric is soft hand and could be used to produce protective suit. Although PI fiber has the highest thermal decomposition temperature which is just about 600°C,[19] plenty of studies indicated that the temperature of fire could reach 800–1200°C.[20,21] Thus, it is a necessity to elevate heat-resistant property of PI. Various methods have been used to modify the combustion characteristics of textiles.[22] Halogenated and boron-containing additives continue to be the most commonly used flame retardants. Despite their effectiveness, the halogenated flame retardants have been reported to form toxins that can be harmful to health and the environment.[23] Boron-containing flame retardants are limited by the lack of durability.[24]

In the present work, MMT was deposited with poly(*N*-benzyloxycarbonyl-3,4-dihydroxyphenylalanine) (PNBD) to generate nanocomposite assemblies on glasses and PI fabrics. PNBD is a kind of adhesive polymer, which is prepared by introducing the essential functional components of the benzyl chloroformate (CbzCl) to L−3,4-dihydroxyphenylalanine (DOPA) (shown in Figure 1).[25–27] Pure MMT film and PNBD-MMT film were applied to PI fabric, the thermal stability and flame-retardant properties were studied by thermogravimetric analysis (TGA) and vertical flame testing. Additionally, the durability and mechanical properties of the coated fabrics were also discussed. The results showed that PNBD-MMT

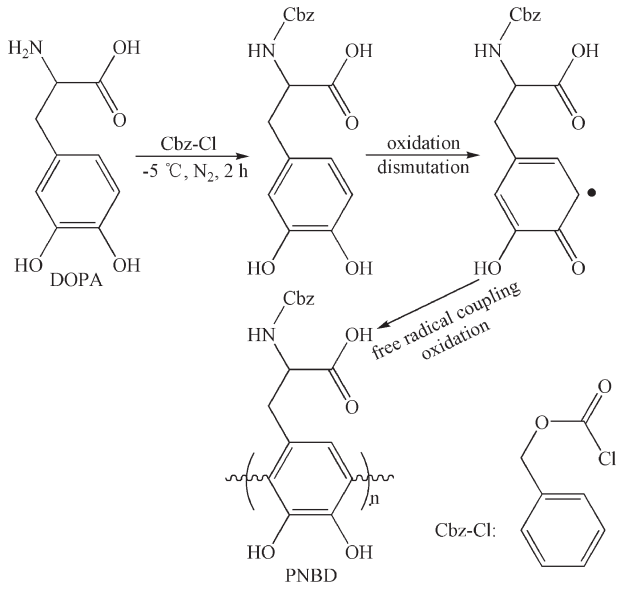

Figure 1. Preparation of PNBD.

composite film could improve fire retardancy of PI fabric with good washing fastness.

EXPERIMENTAL

Materials

Sodium MMT $((Na_x(H_2O))\{(Al_{2-x}Mg_x)[Si_4O_{10}]\ (OH)_2\}$ $(0.2 \leq x \leq 0.6)$, cation exchange capacity (CEC) = 90 mmol/100 g, Zhe Jiang Fenghong Chemical Co., Ltd., China) was exfoliated (0.20 wt %) in deionized water to produce MMT hydrosol. The pH value of MMT hydrosol was adjusted to pH 12 by adding 1*M* NaOH, and the pH was measured with a MODEL 6010 pH meter (JENCO, Quality Instruments, Shanghai). PNBD solutions were prepared by dissolving PNBD with a molecular weight of 6000 g/mol into acetone (0.02–0.10 wt %).

Glass slides (Cat. NO.7101, Sail Brand) were used as deposition substrates for films. Prior to deposition, glass slides were cleaned by immersion into "piranha" solutions (3 : 1 H_2SO_4/H_2O_2; dangerous if contacted with organics) for 1 h, followed by rinsing with deionized water. The PI fabric (Kegesi Filter material Co., Shanghai) used here was a kind of non-woven fabric with a weight of 500 g m^{-2}.

Preparation of LbL Film on Glasses and PI Fabrics

All films were assembled on a given substrate using the procedure shown in Figure 2. Each substrate was dipped into the deposition mixtures, alternating between the PNBD and MMT, with each cycle corresponding to one bilayer (BL). Each dip was followed by handling with a stream of filtered air for 60 s.

In the case of the fabrics, the drying step involved wringing the water out instead of air-drying. After achieving the desired number of BLs, the coated wafers and fabrics were dried in an oven at 40°C for 24 h.

Characterizations

Surface structures of films were imaged with a TM-1000 scanning electron microscope (SEM) (Hitachi Co., Japan) and film thickness could also be estimated by the scale of SEM. Cross-section of films were imaged with a JEOL 2100F transmission electron microscope (TEM) (Japan). Samples were prepared for imaging by embedding a piece of film in epoxy and sectioning it with a microtome equipped with a diamond knife. A small-angle X-ray scattering (XRD) (*D*/max2550PC, Japan) was used to investigate the microstructure of PNBD-MMT and MMT thin films.

The thermal stability of uncoated and coated PI fabrics was measured with a TG209F1 Thermogravimetric Analyzer (NETZSCH Instruments, Germany). Each sample was ~5 mg and was tested in air and nitrogen atmosphere, respectively, from room temperature to 900°C, with a heating rate of 10 °C/min. Vertical flame testing was performed on 8 cm × 15 cm sections of uncoated and coated PI fabrics. An automatic vertical flammability tester (YG(B)815D-I, Wenzhou Darong Textile Instrument Co.) was used to conduct this testing. Washing fastness of coated fabrics (8 cm × 15 cm) was measured with a washing fastness tester (Taiwan Rapid) at 60°C from 30 min to 600 min (according to ISO105-C03: 1989). The after-burn chars were characterized using Fourier transform Infrared Spectrometer (Avatar 380, Thermo Group, US) by KBr powder compression method. Structure of chars was imaged with a TM-1000 SEM (Hitachi Co., Ltd., Japan).

Physical property of the fabric was tested at H10k-S using ASTM D 5035-95 Standards. Coated and uncoated samples were tested three times. All fabrics were preconditioned at 21°C and 65% RH (according to ASTM D 1776) for 48 h before testing.

RESULTS AND DISCUSSION

LbL Thin Film on Glass Slides

MMT at 0.20 wt %, with PNBD at 0.02 wt %, 0.04 wt %, or 0.10 wt %, were used to prepare three different thin films. The influence of the concentration of deposition mixtures on the growth of the thin films was evaluated by SEM. Table I shows that the thickness of these films exhibited linear growth, the film made with lower PNBD concentration was thinner than those prepared at higher PNBD concentration. Films made with 0.10 wt % PNBD solution would achieve better coverage per deposition than films made with 0.02 wt % PNBD solution. Because PNBD is a kind of adhesive polymer, when the concentration of the polymer is high, it will provide more —OH

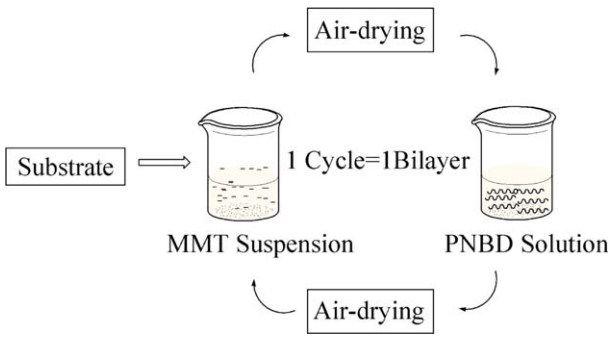

Figure 2. Schematic representation of LbL assembly. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Thickness as a Function of Bilayers Deposited for Films Made with Clay and PNBD (μm)

Sample	5 BL	10 BL	15 BL	20 BL
PNBD (0.02 wt %)-MMT film	1.43	2.15	2.86	3.23
PNBD (0.04 wt %)-MMT film	2.14	3.29	3.44	4.95
PNBD (0.10 wt %)-MMT film	2.78	3.53	4.44	6.45

groups to form hydrogen bonds with MMT, so much more MMT lamellae would be adhered to the substrate in the next layer. SEM results (Figure 3) showed the surface and cross-section of the films. The size of the MMT platelets looked uniform, and the surface texture and roughness was similar in all LbL films.

Figure 4 shows the cross-sections of PNBD-MMT film and MMT film. These films were deposited on glass slide substrates to facilitate sectioning. The PNBD-MMT film [Figure 4(b,d)] had a wavy cross-sectional microstructure, which maybe caused by the rearrangement of the uppermost layer when a new layer was adsorbed. The cross-sectional microstructure of MMT film [Figure 4(a,c)] shows a paralleled arrangement.

The XRD pattern in Figure 5 provided an additional evidence for MMT powder, MMT film, and PNBD-MMT films. The low-angle peak at 5.9° for MMT powder derived from a basal spacing of 1.50 nm, which was the periodic distance from platelet to platelet. Because the thickness of each platelet was 1.00 nm, the distance between the platelets was 0.50 nm (for the existence of interlayer adsorbed water). For the MMT film, the low-angle peak at 6.7° represented that the periodic distance between platelets was 1.30 nm. This was because during the preparation of MMT, most interlayer adsorbed water had been volatilized. In addition, the low-angle peak of PNBD (0.10 wt %)-MMT film at 6.0° indicated the film derived from a basal spacing of 1.39 nm. For PNBD-MMT films, the basal spacing was larger than that of MMT film, because of the intercalation with PNBD.[28,29]

LbL Thin Film Coated PI Fabrics

Microstructure of LbL Thin Film Coated PI Fabrics. PI fabric was coated with 20 BL of MMT film or PNBD (0.10 wt %)-MMT thin film. The coating weight was determined by weighing samples before and after coating. All samples were weighed only after oven-drying at 80°C for 2 h to remove moisture. Weight added to the fabric by each coating system is shown in Table II. The weight gain from coating on fabric was not the same as that on a glass slide by the same coating system, because the surface geometry and adhesion of the fabric was different from that of glass slide. All fabrics were imaged by SEM, before and after standard washing, to evaluate the surface morphology. Before standard washing, the coating on the fiber could be clearly seen in Figure 6(b,c). Fibers of the fabric were completely covered by the clay coating. After 20 times standard washing, the fiber surface of MMT coated fabric [Figure 6(d)] appeared cleaner and more smooth than that of the PNBD (0.10 wt %)-MMT coated fabric [Figure 6(e)]. Because the MMT film on the surface of MMT coated PI fabric was washed off. However, the laminated layers of MMT lamellae could be seen still coated on the fibers of the PNBD (0.10 wt %)-MMT coated fabric. The result demonstrated the excellent washing fastness of PNBD-MMT composite film. Because PNBD is a kind of adhesive polymer, the adhesive forces provided by hydrogen bonding between —OH groups of PNBD and C=O— groups of PI or —OH groups of MMT join them together.[25,30,31] So the PNBD made MMT lamellae adhere strongly to the surface of PI fiber.

Thermal Stability of LbL Thin Film Coated PI Fabrics. The thermal stability of PNBD (0.10 wt %)-MMT coated PI fabric, MMT coated and uncoated PI fabrics were tested by TGA, as shown in Tables II and III and Figures 7 and 8. In air

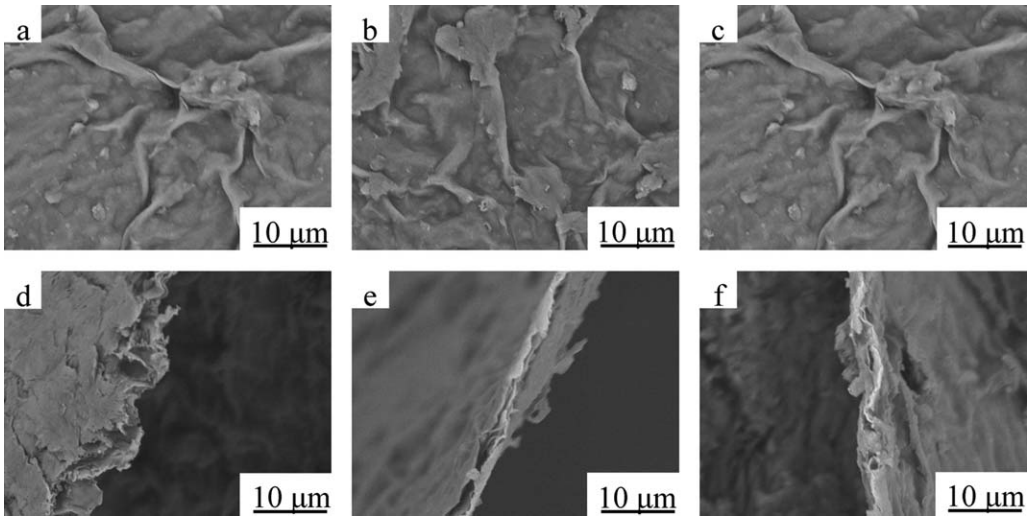

Figure 3. Front view of LbL film with different PNBD concentration (a) PNBD (0.02 wt %)-MMT film; (b) PNBD (0.04 wt %)-MMT film; (c) PNBD (0.10 wt %)-MMT film); cross-section of LbL film with different PNBD concentration (d) PNBD (0.02 wt %)-MMT film; (e) PNBD (0.04 wt %)-MMT film; (f) PNBD (0.10 wt %)-MMT film.

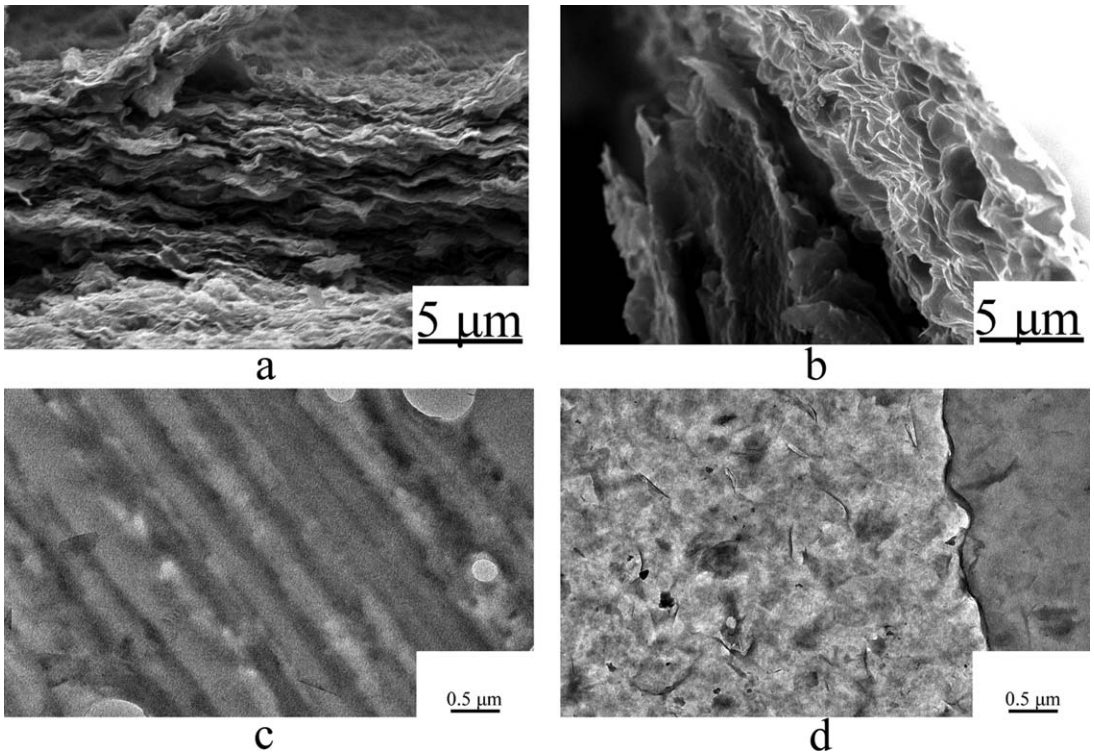

Figure 4. (a) SEM image of MMT film; (b) SEM image of PNBD-MMT film; (c) TEM image of MMT film; (d) TEM image of PNBD-MMT film.

atmosphere, the uncoated PI fabric began to degrade around 400°C and full degradation was near 650°C. The coated fabrics had degradation curves similar to the uncoated PI fabric, but they had shown less mass loss at 650°C. At 900°C, the residue of PNBD (0.10 wt %)-MMT coated PI fabric (3.28 wt %) after standard washing was larger than that of uncoated PI fabric (2.33 wt %) and MMT coated fabric (2.88 wt %). When the samples were heated to 900°C, all the organic polymers had decomposed, including PNBD (decomposition temperature of PNBD is nearly 200°C). The results demonstrated that there was more char left for PNBD (0.10 wt %)-MMT coated PI fabric after standard washing. And the temperature at 50% mass for all the samples were very close to one another.

To further understand the thermal stability of the samples, PNBD (0.10 wt %)-MMT coated PI fabric, MMT coated and uncoated PI fabrics were tested by TGA in nitrogen atmosphere. At 900°C, in nitrogen atmosphere, the residue of uncoated PI fabric was 36.62%. With 7.12 wt % PNBD (0.10 wt %)-MMT coated PI fabric, there was 54.54% (50.74% for PI) residue left before 20 times standard washing and 53.80% after. As for the MMT coated PI fabric (coating weight, 6.57 wt %), the residue was 57.36% (52.10% for PI) before 20 times standard washing and 50.08% after. For MMT coating system, the residue was greatly decreased after standard washing, but for PNBD-MMT coating system, the residue was almost the same before and after standard washing. Because the PNBD molecule existed in PNBD-MMT LbL coating could form hydrogen bonds with PI fabric and MMT to join them together, and the PNBD is hardly soluble in water.[25,31] So after 20 times standard washing, PNBD-MMT film could still coat on PI fiber and protect them. In summary, the thermal stability of PNBD-MMT coated PI fabric was excellent before and after standard washing.

Fire Retardancy of LbL Thin Film Coated PI Fabrics. The fire retardant property of these coated fabrics was put through vertical flame testing (GB/T 5455-1997). Figure 9 shows images of uncoated and coated fabrics after vertical flame testing. A more severe damage was observed on the uncoated fabric compared to the coated fabrics. The burning length of uncoated PI fabric was 30 mm, and that of MMT coated PI is 8 mm and 17 mm before and after standard washing, respectively. Because MMT film coated on PI fabric had been almost washed off and could

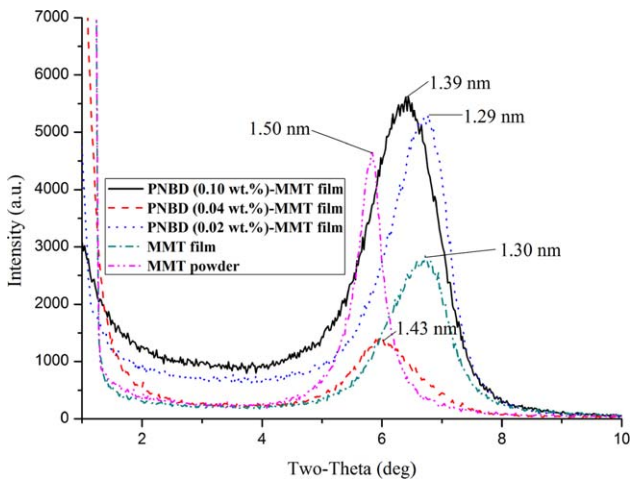

Figure 5. The low-angle XRD of samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermogravimetric Analysis of PI and Two Different Coated Fabrics Before Washing

		Air		N_2	
Coating systems	Add-on (wt %)	Temperature at 50% mass (°C)	900°C residue (%)	Temperature at 50% mass (°C)	900°C residue (%)
Uncoated PI	0	529.13	2.33	763.15	36.62
MMT coated PI	6.57	529.18	7.26	-	57.36 (52.10 for PI)
PNBD (0.10 wt %)-MMT coated PI	7.12	528.94	5.93	-	54.54 (50.74 for PI)

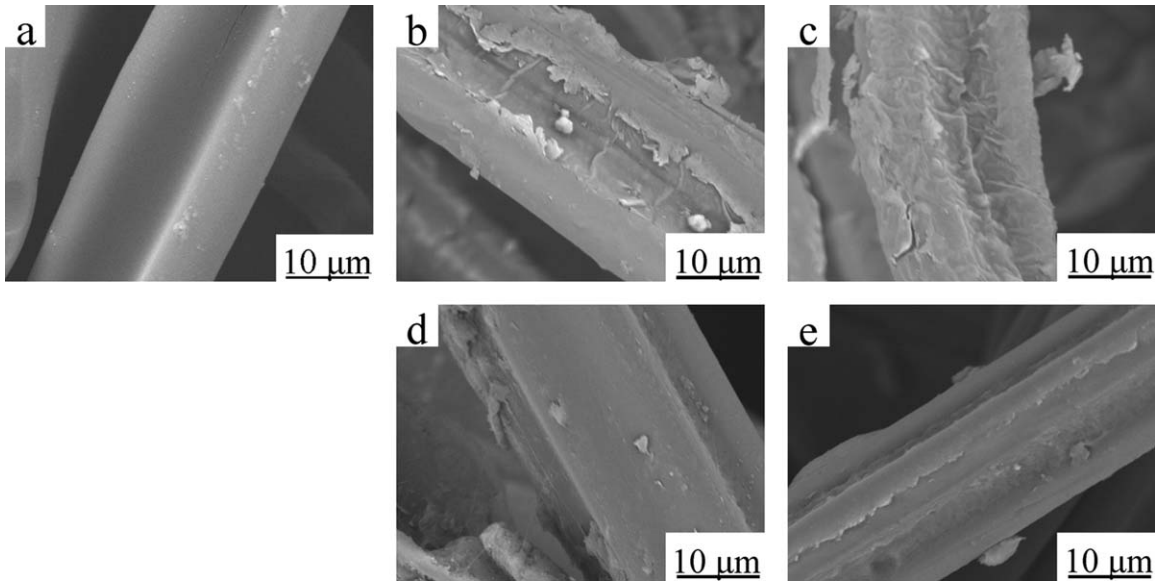

Figure 6. SEM images of samples before and after standard washing: (a) Uncoated PI; (b) PI coated with 20 BL MMT film before washing; (c) PI coated with 20 BL PNBD (0.10 wt %)-MMT film before washing; (d) PI coated with 20 BL MMT film after washing; (e) PI coated with 20 BL PNBD (0.10 wt %)-MMT film after washing.

not protect the fabric from burning any more. While the burning length of PNBD (0.10 wt %)-MMT coated fabric before and after standard washing was all 7 mm, because of the wonderful adhesion property of PNBD kept the MMT lamellae on the PI surface to protect the fabric from burning. In addition, the formation of char residue leads to a decrease in the amount and

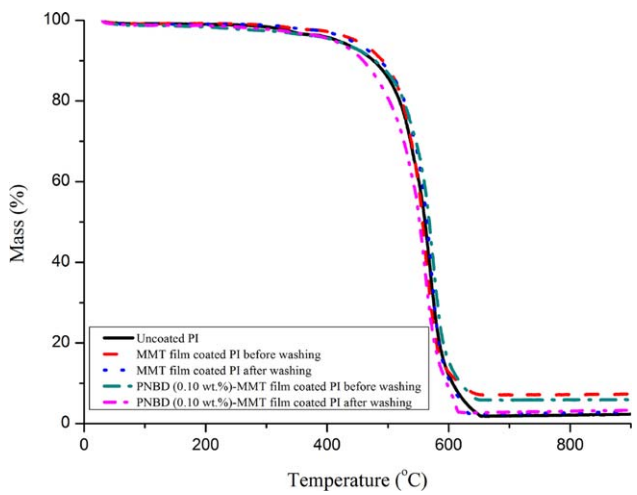

Figure 7. Mass loss as a function of temperature for uncoated and coated PI fabrics in air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

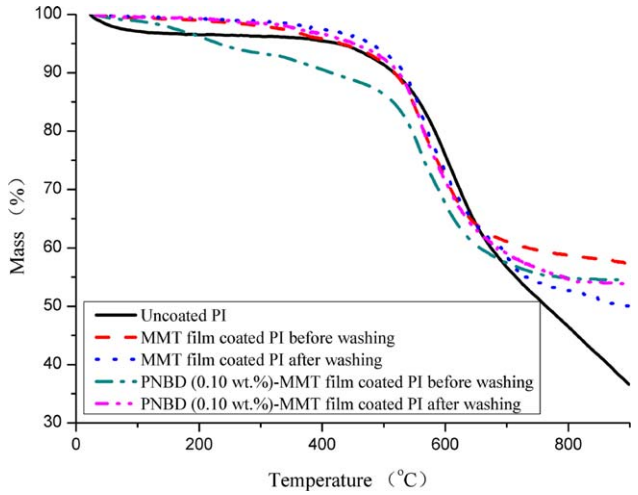

Figure 8. Mass loss as a function of temperature for uncoated and coated PI fabrics in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermogravimetric Analysis of PI and Two Different Coated Fabrics After Washing

		Air		N_2	
Coating systems	Add-on (wt %)	Temperature at 50% mass (°C)	900°C residue (%)	Temperature at 50% mass (°C)	900°C residue (%)
Uncoated PI	0	529.13	2.33	763.15	36.62
MMT coated PI	6.57	534.02	2.88	-	50.08
PNBD (0.10 wt %)-MMT coated PI	7.12	551.95	3.28	-	53.80

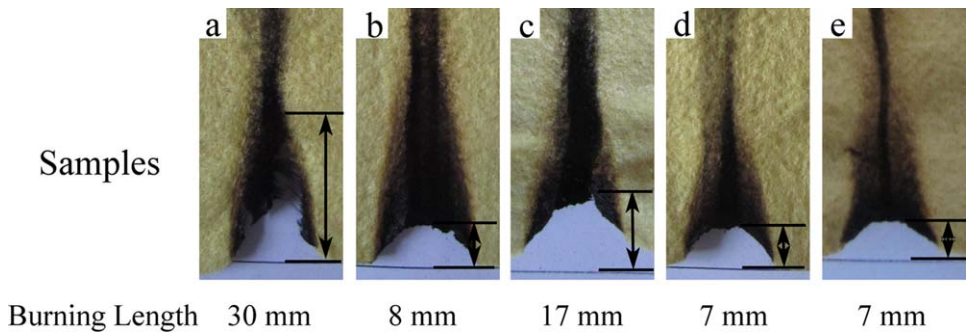

Figure 9. Samples after vertical flame testing: (a) Uncoated PI; (b) PI coated with MMT film before washing; (c) PI coated with MMT film after washing; (d) PI coated with PNBD (0.10 wt %)-MMT film before washing; (e) PI coated with PNBD (0.10 wt %)-MMT film after washing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

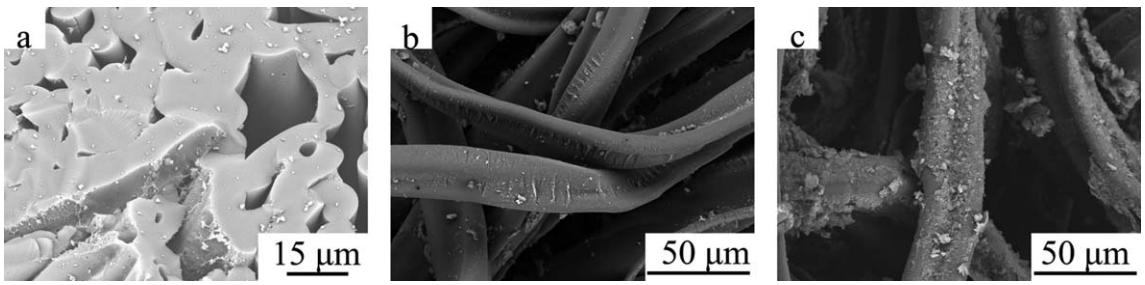

Figure 10. SEM image of residues: (a) Uncoated PI residue; (b) MMT coated PI (after standard washing) residue; (c) PNBD-MMT coated PI (after standard washing) residue.

rate of combustible volatile release, resulting in lower flammability.

In an effect to better understand the fire retardancy property of samples, afterglow residues were imaged with SEM, as shown in Figure 10. The fiber structure of PNBD-MMT coated PI (after standard washing) fabric was largely retained after vertical flame test. In addition, these PNBD-MMT coating did not alter the weave structure of the fabric prior to burning and no shrinkage of the PI thread was observed after vertical flame test. MMT coated PI (after standard washing) had slight deformation after vertical flame test. But uncoated PI after vertical flame test was completely consumed by direct flame.

To further elucidate the effects of the PNBD-MMT coating on the flame retardancy of PNBD-MMT coated PI fabric, the microstructure of the char after combustion was examined by FTIR. As shown in Figure 11, compared with pure PI, there was

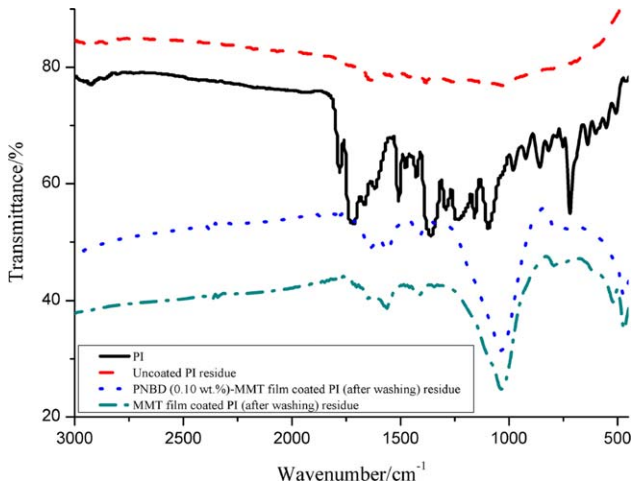

Figure 11. Infrared characteristic bands of residues. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Tensile Breaking Force of Uncoated and Coated PI Fabrics

Sample	BL number	Breaking force (N)		Elongation (%)	
		Horizontal	Longitudinal	Horizontal	Longitudinal
Uncoated PI	-	505.00	323.30	50.40	21.00
MMT coated PI	20	511.40	300.00	45.40	20.60
PNBD (0.10 wt.%)-MMT coated PI	20	550.60	321.10	43.40	29.40

no peak appeared in the FTIR spectrum of the char residue for pure PI, it means that the structure of PI was completely destroyed. But for the FTIR spectra of char for MMT or PNBD-MMT coated PI fabrics, the special absorption peaks of PI:imide ring around 1778 and 1772 cm^{-1}, phenylene around 1498 cm^{-1}, and aromatic ether around 1245 cm^{-1} still existed.[32] So these coatings could protect the PI from burning. In summary, the thermal stability of PNBD-MMT coated PI fabric was excellent before and after standard washing.

Physical Properties of LbL Thin Film Coated PI Fabrics. There was little difference in the appearance between the PNBD (0.10 wt %)-MMT coated and uncoated PI fabric. Even tactile assessment of the fabric (by touch of hand) was similar. In many cases, the addition of a flame retardant results in loss of strength,[33] so it is important to know whether this coating technology alters these properties.

A strip tensile strength test was used to determine the maximum force that could be applied to a material (sampled as a strip) until it fractured (ASTM D 5035). The results of tensile strength tests of coated and uncoated PI fabrics are summarized in Table IV. For MMT coated PI fabric, breaking strength in horizontal direction was increased, but breaking strength in longitudinal direction, elongation in horizontal, and longitudinal direction were decreased. For PNBD (0.10 wt %)-MMT film coated PI fabric, breaking strength in horizontal direction and elongation in longitudinal direction was increased, but breaking strength in longitudinal direction and elongation in horizontal direction were decreased. It was because the PNBD (0.10 wt %)-MMT film coated on PI fibers could reinforce the material providing greater breaking strength.[34,35]

The changes of breaking strength and elongation were all within 10%, the nature of these results suggested that the coating neither greatly improved nor harmed the fabric's mechanical strength. This is an improvement relative to traditional textile finishing that decreases the tensile strength of the fabric.

CONCLUSIONS

The PNBD-MMT thin films as flame-retardant coating system were successfully coated on PI fabrics by LbL assembly. From the SEM pictures of the coated fabric before and after standard washing, the PNBD-MMT composite film could be seen still coating on PI fiber after standard washing. The wonderful adhesive property of PNBD could keep MMT lamellae adhere to the surface of PI fiber after 20 times standard washing. The TGA results demonstrated that there was more char left for PNBD (0.10 wt %)-MMT coated PI fabric than that of uncoated PI and MMT coated PI after standard washing. During actual burning in the vertical flame test, the burning distance of uncoated and MMT coated fabric was larger than that of PNBD (0.10 wt %)-MMT coated fabric after standard washing. These results indicated the excellent thermal stability, flame retardancy, and durability of PNBD-MMT coated PI fabric. The physical properties of the fabrics did not show great differences between coated and uncoated fabrics, suggesting that the coating did not adversely affect the desirable properties of the fabric itself. The simplicity of the LbL process provides a convenient method for imparting flame resistance to fabrics using relatively benign ingredients.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China under grant 50673018, the National High-tech Research and Development Program (863 Program) under grant 2007AA03Z336, and the Program for New Century Excellent Talents in University under grant NCET-07–0174.

AUTHOR CONTRIBUTIONS

Dr. Tong Xu is the principal investigator of this study. Dr. Linping Zhang, Dr. Yi Zhong and Prof. Zhiping Mao participated in the design of the research, analysis of data and final versions. Prof. Zhiping Mao is corresponding author.

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