

Surface Photografting: New Application for Flame Retardant Finishing of Polyamide6.6 (PA6.6) Fabric

Wei Liu,^{1,2,3} Sheng Zhang,^{1,2,3} Lihua Yu,¹ Xiaosui Chen,^{1,2} Lingyao Li,¹ Qingli Feng,¹ Xinjun Zhu¹

¹Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

²Beijing Key Laboratory on Preparation and Processing of Novel Polymeric Materials, College of Materials and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

³State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Received 18 October 2009; accepted 4 February 2010

DOI 10.1002/app.32319

Published online 20 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Surface photografting modification with maleic anhydride (MAN) under UV irradiation in association with a post reaction with triethanolamine has been used to improve the flame retardancy of polyamide6.6 (PA6.6) fabric in this study. The effects of irradiation time and monomer concentration on the fabric surface grafting were investigated. The flame retardancy and thermal decomposition behavior of the samples were characterized by limiting oxygen index test (LOI), thermogravimetric analysis (TGA), and differential scanning calorimetric (DSC), and the results indicate that flame retardancy of

the treated PA6.6 fabric samples has been significantly improved. The chemical structures of the treated samples' surface were characterized by attenuated total reflection infrared spectroscopy (ATR-FTIR), and the possible photochemical mechanisms were discussed. It is suggested that this could be the first time to use photografting technology to enhance the flame retardancy of PA6.6 fabric. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 66–72, 2011

Key words: flame retardancy; photopolymerization; polyamide6.6; surface modification

INTRODUCTION

Polyamide6.6 (PA6.6) fabric has been widely used in textile industry because of its excellent mechanical properties, good dyeability, resistance to shrinkage and stretch, pleasant aesthetics, etc. However, the inherent combustibility and melt dripping problems of PA6.6 fabric have been challenged by the increasing requirements of flame retardancy and antidripping in many application cases. Three main approaches, which are copolymerization with a flame retardant monomer, addition of flame retardants during fiber spinning and flame retardant finishing of PA fabric, have been used to improve the fire performance of PA fabric.^{1–11} Although effective flame retardancy can be achieved by both the incorporation of flame retardant into polyamide chain and adding flame retardant additives, much effort has been made to use flame retardant finishing to impart flame retardancy to PA fabrics due to the convenience and inexpen-

siveness during processing in the past three decades despite the fact that no successful commercial available finishing has been achieved so far. Thiourea-formaldehyde treatment is one of the most successful flame retardant finishing for PA fabric; however, its application is not desirable due to the formaldehyde emission during processing and use. With more strict related legislations (such as RoHS and REACH) taking into effect, to develop an environmental friendly and effective approach for flame retardant finishing of polyamide fabric is highly required.

Photografting is often used in fabric surface modification to improve the wettability,^{12–16} biocompatibility,^{17,18} and dyeability¹⁹ since it is an economical, environmentally sustainable and effective method for surface modification of materials without altering bulk properties. Some efforts have been made to introduce photopolymerization to flame retardant polymer. Yuan Hu and Kannan studied thermal behaviors of a series of novel UV cured flame retardant coatings and resins containing phosphorus, nitrogen and silicon prepared by photopolymerization.^{20–24}

This article reports a novel approach to improve flame retardancy of PA6.6 fabric. The fabric sample was firstly surface modified under UV irradiation

Correspondence to: S. Zhang (sheng1999@yahoo.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20774011.

with maleic anhydride (MAN) as grafting monomer, then further reacted with triethanolamine by a pad-cure procedure. It is suggested that the use of photografting techniques to enhance the flame retardancy of fabric samples has not been reported before.

EXPERIMENTAL

Materials

The 100% lustrous PA6.6 fabric, with an area density of 165 g/m², was provided by Chengdu Hairong Special Textile.

Irgacure 2959 was purchased from Ciba. MAN and acetone were obtained from Beijing Yili Chemical Reagent (Beijing, China). Triethanolamine was purchased from Fuchen Chemical Engineering Reagent Company (Tianjin, China). All the chemicals used were of reagent grade.

Sample treatment procedures

Surface photografting of PA6.6 fabric

The PA6.6 fabric sample was extracted with acetone for 24 h, and then washed with petroleum ether for 3 times. Some impurities, such as warp size residues comprising polyacrylate and polyvinyl alcohol and mineral oil pollution from processing are expected to be present on the surface of PA6.6 fabric, which are soluble or partly soluble in acetone and/or petroleum ether. Hence they can be removed by extraction and washing. Thereafter, it was soaked in 300 mL acetone solution containing 2 wt % Irgacure 2959 and 30 wt % MAN for 1.5 h. The sample was irradiated by a high intensity UV lamp with a UV intensity of 100 W/cm² for a fixed time. The reacted sample was rinsed thoroughly with water for 10 min, dried at room temperature, and then extracted with acetone for 24 h before it was finally dried in oven at 70°C for 20 min.

Post reaction of the grafted samples

The photografted fabric sample was soaked in 300 mL acetone solution containing 80 wt % triethanolamine at room temperature for 2 h, and then reacted in oven at 160°C for 5 h. The sample was then rinsed thoroughly with deionized water to remove the residual reagents.

The percentage grafting

The grafted PA6.6 fabric sample was subjected to Soxhlet apparatus with acetone for 24 h to remove the traces of unreacted chemicals and homopolymers. The sample weight was recorded after drying.

The weight percentage of the overall photopolymerization (PW%), the weight percentage of the photografting polymerization (GW%) and the grafting efficiency (E_g) were calculated according to the following equation:

$$\% \text{ Photopolymerization (PW\%)} = \frac{W_1 - W}{W} \times 100\%$$

$$\% \text{ Photografting polymerization (GW\%)} = \frac{W_2 - W}{W} \times 100\%$$

$$\text{Grafting efficiency (} E_g \text{)} = \frac{W_2 - W}{W_1 - W} \times 100\%$$

where W is the weight of untreated PA6.6 fabric sample extracted with acetone, W_1 and W_2 are the weight of grafted PA6.6 fabric sample before and after extraction in acetone, respectively. The weight of photopolymerization is the sum weight of both photografting polymer and homopolymer.

Tensile property

Tensile properties of PA6.6 fabric samples as functions of irradiation time were tested using GM T4104 electronic tensioner (Shengzheng, China) according to GB/T 3923.1-1997 with a drawing speed of 10 cm/min and a clamping distance of 20 cm.

Structural characterization

The surface structures of untreated and treated PA6.6 fabric samples were characterized by Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus 670), equipped with a variable-angle attenuated total reflection (ATR) accessory (PIKE ATRMax II) with ZnSe ($n = 2.43$) as internal reflection element wafer. The incident angle was 45°.

Absorbency

Absorbency of textile refers to the ability of textile to absorb a liquid in fiber, yarn, or fabric construction. The absorbency of the PA6.6 fabric sample was measured according to AATCC test method 79-2007. A distilled water or triethanolamine droplet from a 3 mL dropper fell from a fixed height onto the taut surface of sample. The required time for the specular reflection of the drop to disappear is defined as the wetting time.²⁵

Limiting oxygen index (LOI) tests

LOI tests were conducted on a JF-3 type instrument (Jiangning, China), according to GB/T 2403-1993.

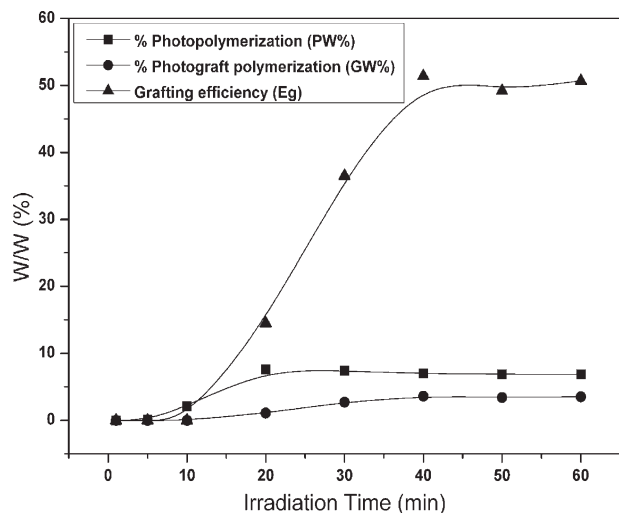


Figure 1 The effect of the irradiation time on photopolymerization (PW%), photograft polymerization (GW%) and grafting efficiency (E_g).

Thermal analysis

Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were performed using a HENVEN HCT-1 TG-DSC analyzer with the sample mass range of 3–5 mg in static air atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Surface photografting

PA6.6 fabric samples were grafted with MAN by using Irgacure 2959 as photoinitiator. The effects of irradiation time and monomer concentration on photopolymerization (PW%), surface photograft polymerization (GW%) and grafting efficiency (E_g) were investigated respectively. The effect of the irradiation time on surface photografting and photopolymerization is presented in Figure 1. Both PW% and GW% are zero when irradiation time is less than 1 min, indicating no involvement of both photopolymerization and grafting reaction during this period. PW% reaches its maximal value of 7.3% with the grafting efficiency of 15.1% in 20 min, indicating that most monomers have participated photopolymerization to form homopolymer. The longer is the irradiation time, the more is the GW%. This may suggest some homopolymer chains of MAN have attached on the surface of fabric samples by coupling reaction.²⁶ The GW% reaches its maximum value of 3.6% with the grafting efficiency of 51.4% when grafting time is 40 min. No increase for both PW% and GW% has been observed when the irradiation time is longer than 40 min. It is suggested that the formation of photografting polymerization can reach its equilibrium at this stage due to the steric hin-

TABLE I
Tensile Properties of PA6.6 Fabric Samples Before and After Irradiation

Sample	Irradiation time (min)	Tensile strength (MPa)	Elongation at break (%)
1	0	145.3	13%
2	10	143.9	13%
3	20	138.1	13%
4	30	117.8	13%
5	40	117.3	13%
6	50	116.8	12%
7	60	101.9	12%

drance, and hence the surface photografting parameters can not be increased when grafting time is longer than 40 min.

UV light irradiation could cause damage to the fabric structure, and hence affect the physical properties of PA6.6 samples. Table I presents the tensile strength and elongation data of untreated PA6.6 fabric sample irradiated at different times. The tensile strength and elongation at break of untreated PA6.6 fabric sample are 145.3 Mpa and 13% respectively. The tensile strength of all the irradiated samples is lower than that of the untreated sample. It is suggested that photo-oxidation occurred during irradiation could cause damage to the fibers. 20% decrease of tensile strength can be observed for the sample irradiated for 40 min, however, the decrease of elongation at break is minimal. Considering the damage caused by irradiation and the photografting efficiency (E_g), 40 min has been chosen as the irradiation time in the following study.

The effect of monomer concentration on surface photografting and photopolymerization is illustrated in Figure 2. It shows the monomer concentration can significantly affect the photografting of MAN onto

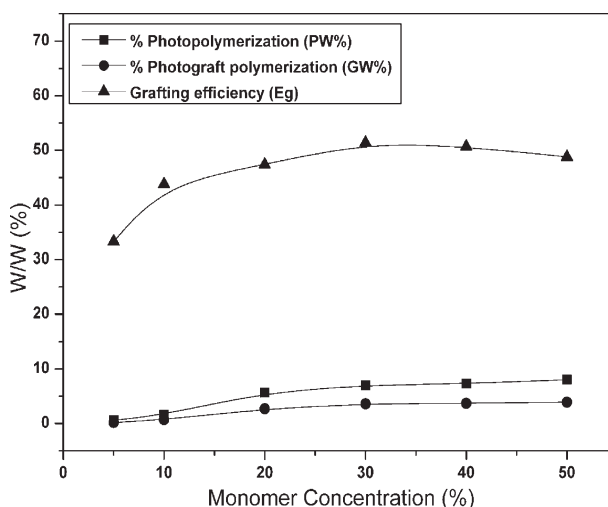


Figure 2 The effect of monomer concentration on photopolymerization (PW%), photograft polymerization (GW%) and grafting efficiency (E_g).

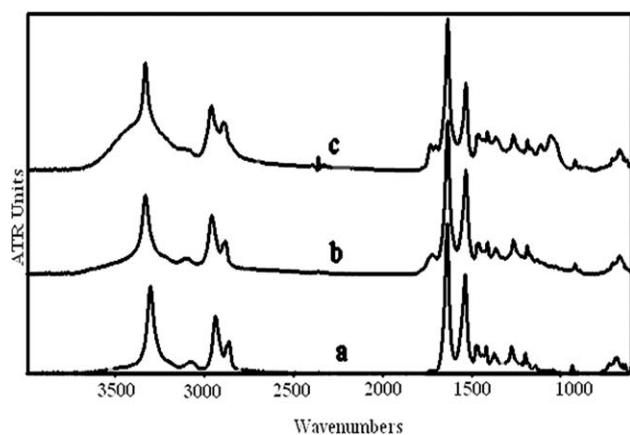
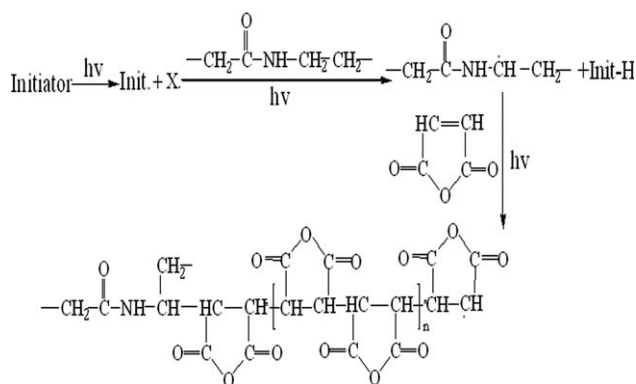


Figure 3 ATR-FTIR spectra of surfaces of PA6.6 fabric samples: (a) untreated PA6.6 fabric sample; (b) MAN-g-PA fabric sample ($C_g = 1.8\%$); (c) triethanolamine reacted MAN-g-PA fabric sample (Add-ons = 5.0%).

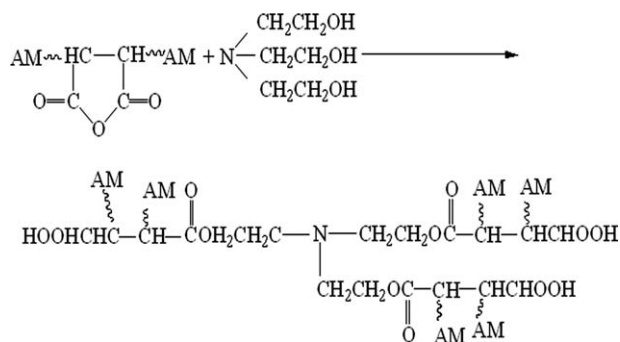
PA6.6 fabric. PW%, GW% and E_g all increase with the monomer concentration when MAn concentration is less than 30%. This is because the concentration controls the diffusion rate of monomer. PW% and GW% increase with monomer concentration, while E_g decreases when MAn concentration is more than 30%. The slow increase of GW% with irradiation time when MAn concentration is more than 30% is due to the steric hindrance caused by the already grafted polymer chains.

Structural characterization of PA6.6 fabric samples

The surface of treated and untreated PA6.6 fabric samples was characterized by ATR-FTIR. The results are shown in Figure 3. The amide characteristic peaks can be observed at 3301, 1636, and 1536 cm^{-1} in spectrum a, b and c, which can be assigned to $\nu_{\text{N-H}}$, $\nu_{\text{C=O}}$ and the combined absorption of both δ_{NH} and $\nu_{\text{C-N}}$, respectively.²⁷ Compared to spectrum a, spectrum b has an additional peak around 1722 cm^{-1} , which can be attributed to the characteristic



Scheme 1 The mechanism for PA6.6 fabric photografted with maleic anhydride (MAn) under UV irradiation.



Scheme 2 The esterification reaction of maleic anhydride (MAN) and triethanolamine (AM = the amide group of PA6.6).

peak of succinic anhydride groups. The intensity change of absorption peak at 1180 cm^{-1} which is assigned to the $-\text{CH}_2-(\text{NH})-$ groups in Figure 3(b) indicates the presence of MAN, and the proposed mechanism of photochemical reaction on the surface of PA6.6 fabric shown in Scheme 1.^{28–30} The absorption peaks at 1124 cm^{-1} and 1067 cm^{-1} in spectrum c can be assigned to C–O–C in ester bond and carbonyl groups, which are due to the esterification between the active anhydride groups from the surface of MAN-g-PA fabric and triethanolamine (see Scheme 2). The reduction in intensity of absorption peak at 1180 cm^{-1} in Figure 3 correlates with grafting. However, the intensity of the peak could also be influenced by the presence of other groups, such as methylene hydrogens from maleic anhydride (MA) and triethanolamine, and the photo-oxidation reaction between the methylene hydrogens from PA6.6 fabric and O_2 under UV irradiation. Therefore, the reduction in intensity of the peak is not proportional to the graft yield. The spectra of the surface of treated PA6.6 fabric samples before and after rinsing with water are presented in Figure 4. The

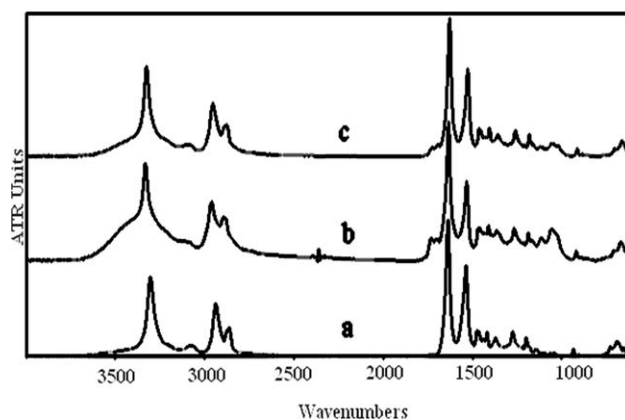


Figure 4 ATR-FTIR spectra of surfaces of PA6.6 fabric samples: (a) untreated PA6.6 fabric sample; (b) triethanolamine reacted MAN-g-PA fabric sample before rinsing; (c) triethanolamine reacted MAN-g-PA fabric sample after rinsing.

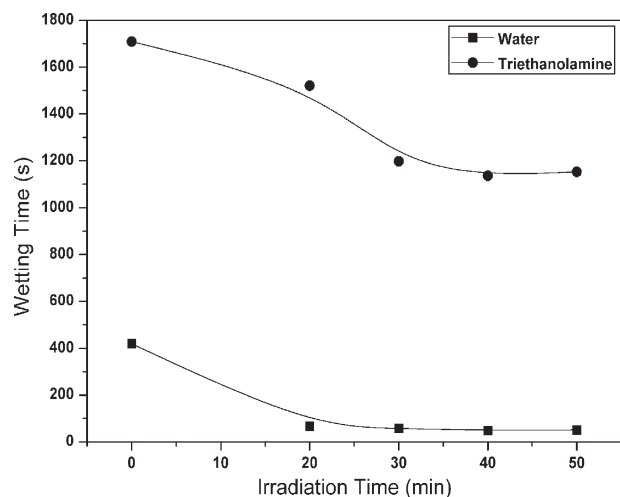


Figure 5 The absorbency of PA6.6 fabric samples with different irradiation time.

characteristic peaks at around 1124 and 1067 cm^{-1} , which may due to the esterification between the anhydride groups and triethanolamine, can still be observed after rinsing (see spectrum c) despite their reduced intensity, which suggests the monomer MAn and triethanolamine are attached with the polymer chain by chemical bonds.

Absorbency analysis

Polymaide 6.6 fibers are hydrophilic compared with polyester, and their moisture regains are about 4.5%. Figure 5 shows the absorbency of modified PA6.6 fabric samples as functions of irradiation time. The specular reflection of a water drop takes 419 s to disappear for the untreated PA6.6 fabric sample, whereas it takes only 49 s for the sample grafted for 40 min. Similar results can be obtained for triethanolamine drops shown in Figure 5. The specular reflection of a triethanolamine drop takes 1709 s to disappear on the surface of untreated PA6.6 fabric sample, whereas it takes only 1136 s for the treated sample. Table II shows the wetting time decreases with the degree of photografting. The absorption and spreading speed of both water and triethanolamine on the surface of untreated sample are much

TABLE II
Wetting Time of PA6.6 Fabric Samples With Different Irradiation Time

Sample	Irradiation time (min)	Wetting time (s)	
		Water	Triethanolamine
1	0	419	1709
2	20	66	1521
3	30	57	1198
4	40	49	1136
5	50	51	1153

TABLE III
Limiting Oxygen Index of Treated PA6.6 Fabric Samples

Samples	Add-ons (%)	Limiting oxygen index (%)
Untreated PA6.6 fabric	0	22.7
MAn-g-PA fabric	3.6	23.3
PA6.6 fabric with triethanolamine	0.9	26.8
Triethanolamine reacted MAn-g-PA fabric	6.6	29.1

slower than that of grafted samples. It is suggested that the introduction of the anhydride group through grafting can further improve the polarity and hydrophilicity of polyamide6.6 fibers, and hence can increase the absorbency of the grafted samples. Therefore, triethanolamine can be easily absorbed by the grafted fiber, which can improve the possibility to react with the modified polymer chain.

Flammability analysis

Table III shows the LOI values of different PA6.6 samples. It can be seen that the LOI value of MAn-g-PA fabric sample (23.3) is slightly higher than that of untreated PA6.6 fabric sample (22.7). The LOI value of the PA6.6 fabric sample treated with triethanolamine can reach 26.8, and the LOI value of MAn-g-PA fabric sample further reacted with triethanolamine can reach up to 29.1. Washing stability was further tested for treated PA6.6 fabric samples in both water and 0.5% commercial detergent solution at room temperature. The data are presented in Table IV. Flame retardancy of PA6.6 fabric sample treated with triethanolamine decreases significantly after 10 cycles of water rinsing, while flame retardancy of MAn-g-PA fabric sample reacted with triethanolamine can be well remained after 10 cycles of water rinsing. A LOI value of about 25.7 is still retained. However, MAn-g-PA fabric sample reacted with triethanolamine loses its flame retardancy after 10 cycles of washings with 0.5% commercial grade

TABLE IV
Limiting Oxygen Index of Treated PA6.6 Fabric Samples in Different Cleaning Agents

Cleaning agent	No. of washing cycles	Sample	LOI
Commercial grade detergent solution	10	Triethanolamine reacted	23.6
		MAn-g-PA fabric	22.0
		PA6.6 fabric with triethanolamine	
Water	10	Triethanolamine reacted	25.7
		MAn-g-PA fabric	22.5
		PA6.6 fabric with triethanolamine	

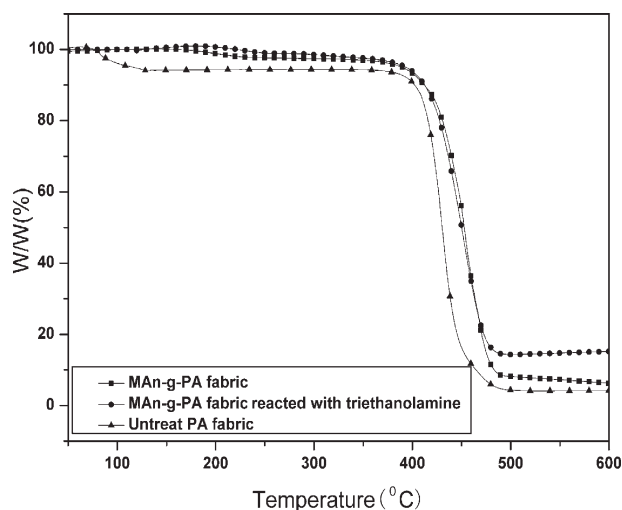


Figure 6 TGA curves of treated and untreated PA6.6 fabric samples.

detergent solution. It is suggested the grafted chain is easy to degrade in the commercial grade detergent solution because of the alkaline condition.

Thermal analysis

TGA curves of treated and untreated PA6.6 fabric samples under air atmosphere are shown in Figure 6. It can be seen that untreated PA6.6 fabric sample decomposes at 390°C. The initial decomposition temperatures of both MAn-g-PA fabric sample and triethanolamine reacted MAn-g-PA fabric sample are higher than that of untreated sample. Moreover, the residual char of treated PA6.6 fabric sample is significantly higher than that of untreated PA6.6 fabric sample. The residual char of triethanolamine reacted MAn-g-PA fabric sample could reach up to 13.1%. DTG curves of untreated PA6.6 fabric sample and triethanolamine reacted MAn-g-PA fabric sample are

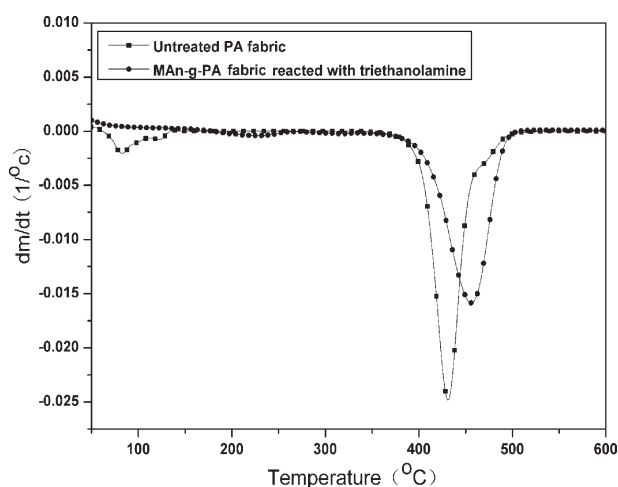


Figure 7 DTG curves of untreated PA6.6 fabric samples and triethanolamine reacted MAn-g-PA fabric samples.

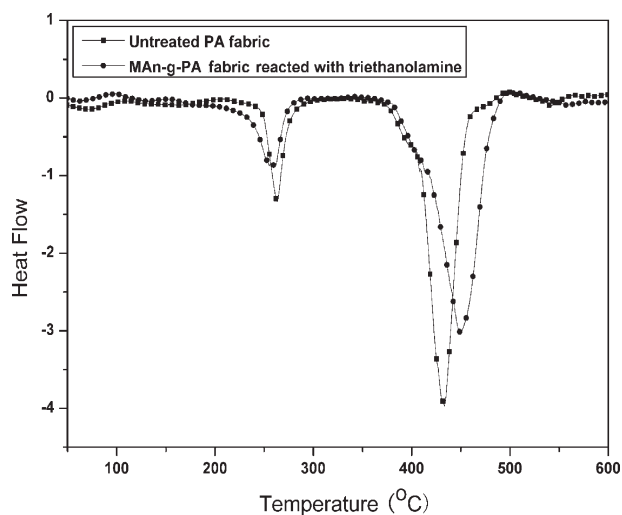


Figure 8 DSC curves of untreated PA6.6 fabric samples and triethanolamine reacted MAn-g-PA fabric samples.

illustrated in Figure 7. These show that the treated sample has higher maximal weight loss rate temperatures than that of untreated PA6.6 fabric sample. The maximal weight loss rate temperature of triethanolamine reacted MAn-g-PA fabric sample is 456°C, which is 30°C higher than that of untreated PA6.6 fabric sample. Figure 8 shows the DSC curves of treated and untreated PA6.6 fabric samples. Triethanolamine reacted MAn-g-PA fabric sample has an exothermic peak in the temperature range of 416–483°C, and it has a smaller and later exothermic peak than that of untreated PA6.6 fabric sample. This suggests that the presence of both triethanolamine and MAn could improve the thermal stability of the fabric samples. However, the melt-drip tendency of PA6.6 fabric has not been improved by the grafting. The enhancement of flame retardancy of MAn-g-PA fabric sample reacted with triethanolamine might be attributed to the release of nonflammable gas such as NH_3 and CO_2 during combustion, which can also dilute the concentration of the flammable gas from the degradation of PA6.6 fabric.

CONCLUSIONS

Surface photografting with MAn onto the surface of PA6.6 fabric has been shown to improve the absorption and penetration of triethanolamine into the fibrous structure as well as enhance the flame retardancy and thermal stability of polyamide6.6 fabric. It is confirmed that MAn has been photografted on the PA6.6 fabric surface. The esterification between the anhydride groups and triethanolamine could further improve the flame retardancy. The LOI value of reacted sample with 6.6% grafted add-on can reach up to 29.1. Efforts are undertaking in our laboratory to further improve the durability and flexibility of

treated fabric samples by using different monomers and will be discussed in the following publications.

References

1. Zhang, S.; Horrocks, A. R. *Prog Polym Sci* 2003, 28, 1517.
2. Zhang, S.; Horrocks, A. R. *J Mater Sci* 2003, 38, 2195.
3. Zhang, S.; Horrocks, A. R.; Hull, R. *Polym Degrad Stab* 2006, 91, 719.
4. Horrocks, A. R.; Zhang, S. *Fire Mater* 2002, 26, 173.
5. Liu, W.; Wang, Y. Z. *Polym Degrad Stab* 2007, 92, 1046.
6. Li, L. Y.; Chen, G. H.; Liu, W. *Polym Degrad Stab* 2009, 94, 996.
7. Mallakpour, S.; Taghavi, M. *React Funct Polym* 2009, 69, 206.
8. Hao, X. Y.; Gai, G. S.; Liu, J. P. *Mater Chem Phys* 2006, 96, 34.
9. Yang, H.; Yang, C. Q.; He, Q. L. *Polym Degrad Stab* 2009, 94, 1023.
10. Horacek, H.; Grabner, R. *Polym Degrad Stab* 1996, 54, 206.
11. Jou, W. S.; Chen, K. N.; Chao, D. Y. *Polym Degrad Stab* 2001, 74, 239.
12. Oechel, A.; Ulbricht, M.; Tomaschewski, G. *J Inf Rec Mater* 1994, 21, 633.
13. Wang, H. L.; Brown, H. R. *J Polym Sci Part A: Polym Chem* 2004, 42, 253.
14. Allm ear, K.; Hult, A.; R mby, B. *J Polym Sci Part A: Polym Chem* 1988, 26, 2099.
15. Janorkar, A. V.; Proulx, S. E. *J Polym Sci Part A: Polym Chem* 2006, 44, 6534.
16. Satoh, M.; Shirai, K. *J Polym Sci Part A: Polym Chem* 2005, 43, 600.
17. Yang, J. M.; Wang, M. C.; Hsu, Y. G. *J Membr Sci* 1997, 28, 133.
18. Yang, J. M.; Wang, M. C.; Hsu, Y. G. *J Membr Sci* 1998, 138, 19.
19. Shin, H.; Ueda, M.; Burkinshaw, S. M. *Dye Pigment* 1999, 41, 11.
20. Jiao, C. M.; Wang, Z. Z.; Chen, X. L. *Radiat Phys Chem* 2006, 75, 557.
21. Chen, X. L.; Hu, Y.; Jiao, C. M. *Polym Degrad Stab* 2007, 92, 1141.
22. Chen, X. L.; Hu, Y.; Jiao, C. M. *Prog Org Coat* 2007, 59, 318.
23. Chen, X. L.; Hu, Y.; Song, L. *Polym Eng Sci* 2007, 48, 116.
24. Kannan, P.; Murugavel, S. C. *J Polym Sci Part A: Polym Chem* 1999, 37, 3285.
25. AATCC test method 79 2007.
26. Xing, C. M.; Deng, J. P.; Yang, W. T. *Macromol Chem Phys* 2005, 206, 1106.
27. Wu, G. G.; Li, Y. P. *J Membr Sci* 2006, 283, 13.
28. Thanki, P. N.; Singh, R. P. *Polymer* 1998, 39, 6363.
29. Matsui, H.; Schehr, C. A. *Polymer* 2001, 42, 5625.
30. Thanki, P. N.; Singh, R. P. *Polym Degrad Stab* 2002, 75, 423.