Journal of Metals, Materials and Minerals, Vol.20 No.2 pp.63-70, 2010

Study on Flame Retardancy and Anti-Dripping of Polyester Fabric Treated with Bentonite, Diammonium Hydrogen Phosphate and Aluminium Hydroxide

Panistha LERDKAJORNSUK[1] and Sireerat CHARUCHINDA[1,2*]

[1] *Center of Excellence in Textiles, Department of Materials Science, Faculty of Science, Chulalongkorn University, Phyathai Road, Patumwan, Bangkok 10330, Thailand*
[2] *Research Unit of Advanced Ceramics and Polymeric Materials, National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Patumwan, Chulalongkorn University,Bangkok 10330, Thailand*

Abstract

The purpose of this research was to improve flame retardancy and anti-dripping of polyester fabric by using bentonite, 3% (w/w) diammonium hydrogen phosphate (DA) and 5, 10% (w/w) aluminium hydroxide ($Al(OH)_3$) via pad-dry technique. The burning behavior of the treated polyester fabric was investigated according to ASTM D1230. The results showed that 10wt% of bentonite alone were capable of imparting anti-dripping. Nevertheless, the preparation of the slurry of bentonite (>10% (w/w)) caused high viscosity leading to difficulties for the preparation and finishing process. Thus, the addition of 4% (w/w) of sodium chloride (NaCl) to the suspension of bentonite (up to 25% (w/w)) resulted in lower viscosity of the slurry, which led to an easing of the preparation and finishing process. It was found that the flame retardancy and anti-dripping PET fabric treated with bentonite and NaCl could perform slightly better than the untreated one while the fabrics treated with DA or $Al(OH)_3$ alone exhibited no melt drips. However, the treated fabric with bentonite (over 10% (w/w) up to 20% (w/w)) mixed with 3% (w/w) DA or 10% (w/w) $Al(OH)_3$ mixed with bentonite showed safer flaming drip than the untreated one.

Key words: Anti-dripping, Bentonite, Flame retardancy, Polyester fabric, Aluminium hydroxide

Introduction

Polyester or Poly(ethylene terephthalate) (PET) fiber is synthetic fiber that has been produced in exceptionally large amounts. It has been used widely for its many advantages. Its applications are not only in automotive industries and civil engineering, but also in daily life for purposes such as textile garments, home textiles, medical textiles and sportswear. However, PET might not be safe in case of fire because it melts at 249-290^{o}C. Such molten PET could drip on underlying surfaces or human skin and be harmful to life. In addition, the heat from this molten polyester could ignite flammable materials in nearby areas rapidly and could thus damage life and property of consumers. For these reasons it is necessary to improve the fire retardant and anti-dripping properties of PET. Three main ways are used to endow PET with flame retardant. The first way is copolymerization of PET with a reactive flame-retardant monomer. The second way is addition of flame retardants into PET during processing, and the third way is flame-retardant treatment of PET fabrics. In fact, the flame-retardant treatment has been widely used to reduce the flammability of PET fabrics due to its relative convenience and inexpensiveness in comparison with the other two ways. Formerly, we favored finishing polyester fabric with halogen-based flame retardants since they possess high efficiency. However, some halogen-based flame retardants such as penta BDE and octa BDE pose threats due to their emission of toxic gases such as HBr and HCl during combustion, which are harmful to the human inspiratory system, their risks by emission of dioxins and furans (carcinogens) during incineration, and also their corrosivity. Consequently, EU regulations banned them from use in all applications in the EU market. Hence, halogen-free flame retardants have been increasingly sought after due to public interests concerning health, safety and environmental aspects.(1)

*Corresponding author Tel: +66 2218 5062; Fax: +66 2218 5561; E-mail: sireerat.c@chula.ac.th

Recently, several papers have reported on the improvement of flame retardancy and anti-dripping of polymer using montmorillonite.(1-2) It is believed that the presence of montmorillonite or nanoclays in PP or other polymers slow down burning and provide evidence of char enhancement.

In addition, Chen et al.(2005) used poly (2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate) (PPPBP) to improve flame retardancy and anti-dripping of poly(ethylene terephthalate) (PET) fabrics. FTIR spectra and SEM images of the residue of treated PET fabrics show that the structure and composition of the chars yielded during the decomposition of PPPBP have direct relationship with the enhancement in flame retardancy and anti-dripping of the treated PET fabrics.

Furthermore, Daimatsu et al.(2007) prepared hybrid material of PMMA and aluminum hydroxide surface-modified with phosphoric acid groups. They found that the flame resistance of the hybrid materials was improved in comparison with that of pure PMMA. These results suggest that the use of aluminium hydroxide surface-modified with phosphoric acid groups is an efficient method for obtaining good performance fire-resistant polymer materials. Aluminium hydroxide became aluminium oxide (which act as char barrier) and water when exposed to heat from flame as shown in equation 1.

$$Al(OH)_3 \longrightarrow Al_2O_3 + H_2O \quad (1)$$

In this study, the awareness of fire safety, human health and environment as mentioned above

Table 1. Formulations of flame retardant finishing on PET fabric.

Formulation	Amount (% (w/w))			
	NaCl (Na)	Bentonite (B)	Diammonium Hydrogenphosphate (DA)	Aluminium Hydroxide (Al)
untreated	-	-	-	-
B3	-	3	-	-
B5	-	5	-	-
B7	-	7	-	-
B10	-	10	-	-
Na	4	-	-	-
B10Na	4	10	-	-
B15Na	4	15	-	-
B20Na	4	20	-	-
B25Na	4	25	-	-
DA	-	-	3	-
B10NaDA	4	10	3	-
B15NaDA	4	15	3	-
B20NaDA	4	20	3	-
B25NaDA	4	25	3	-
Al5	-	-	-	5
B10NaAl5	4	10	-	5
B15NaAl5	4	15	-	5
B20NaAl5	4	20	-	5
B25NaAl5	4	25	-	5
Al10	-	-	-	10
B10NaAl10	4	10	-	10
B15NaAl10	4	15	-	10
B20NaAl10	4	20	-	10
B25NaAl10	4	25	-	10

drove us to utilize green products, namely bentonite clay as flame retardants and anti-dripping agents for the PET fabric. The fabric was treated with bentonite in various amounts by pad-dry technique. At a high amount of bentonite (10% over), sodium chloride was added to bentonite to lower viscosity of the suspension.(5) Moreover, aluminium hydroxide or diammonium hydrogen phosphate was used with bentonite (and sodium chloride). The effect of the mentioned compositions on the burning behavior was investigated.

Materials and Experimental Procedures

Materials

A bleached twill woven polyester fabric (PET fabric) with the density of 140 g/m^2 was kindly provided by Thainamsiri Intertek Co., Ltd. Bentonite (sodium montmorillonite) was also kindly supplied by Thai Nippon Chemical Industry Co., Ltd. Sodium chloride (NaCl) was supplied by Asia Pacific Specialty Chemicals Co., Ltd. Aluminium hydroxide ($Al(OH)_3$) was supplied by Chemmin Co., Ltd. Diammonium hydrogen phosphate (DA) was supplied by Wako pure chemical industries Ltd. These materials were used as received without further purification.

Suspension Preparation

Two types of bentonite suspension were prepared. The first type of suspensions was 0, 3, 5, 7 and 10% (w/w) bentonite alone without NaCl. The second type of bentonite suspensions with NaCl was 0, 10, 15, 20 and 25% (w/w) bentonite and 4% (w/w) NaCl. The latter type of suspension was prepared by adding bentonite into 4% (w/w) NaCl aqueous solution and continuous mixing at 100 rpm. 3% (w/w) Diammonium hydrogen phosphate (DA) or 5, 10% (w/w) aluminium hydroxide was further added. The viscosity of the prepared suspensions of bentonite and NaCl was then measured by Brookfield viscometer.

Flame Retardant Treatment

PET fabric was treated with suspensions prepared in 2.2 using a pad mangle set to a pressure nip at 90 percent wet pick up. The treated fabric was then dried at 60°C for 15 minutes.

Burning Test

Burning behavior and molten drip of untreated and treated PET fabric were investigated under standard test method of ASTM D1230 using the Atlas 45° Automatic Flammability Tester. In this study, the flame application time was set at 5 seconds, and a piece of cotton pad (weight: 700 mg, size: 64 cm^2, and thickness: 0.5 cm) was placed under the sample to observe whether molten drips (with or without flame) could ignite and burn the cotton pad or not. Experiments were conducted under condition of an ambient temperature of 30±2°C and 60±2% RH. The burning behavior was recorded by a digital video camera.

Results and Discussion

Viscosity

The viscosity of the suspension increased with the increase of bentonite. Especially when the amount of bentonite was over 10% (w/w), the suspension was too viscous to treat the fabric uniformly. However, the addition of sodium chloride was found to solve this problem in that it lowered the viscosity of the bentonite suspension as shown in Table 2.

It is seen that the viscosity of bentonite suspensions (10% w/w)) was markedly lower after adding NaCl at low concentrations due to the adsorption of chloride ion on the bentonite layer.(9) At sufficiently high ionic strength, aggregation of clay mineral particles increases so strongly that the networks transform into more or less isolated particles and the gel rigidity decreases.(10)

Burning Behavior of the Treated PET Fabrics

The burning behavior and molten drip of untreated and treated PET fabrics are shown in Table 3. In order to clarify this behavior, burning images of PET fabrics were also presented.

Table 2. Viscosity of bentonite suspension and suspension of bentonite with sodium chloride.

Formulation	B3	B5	B7	B10	B10Na	B15Na	B20Na	B25Na
Viscosity (cps)	20	40	284	2965	19	75	80	300

Table 3. Burning behavior and molten drip of untreated and treated PET fabrics (flame application time = 5 seconds).

Formulation	Add-on (%)	Afterflame time (s)	Char	Melt dripping	Time delay before melt dripping (s)	Cotton pad burning	After removing ignition source at 10 s	After dripping at 15 s
Untreated	-	11.3	No	Yes	3	Heavy		
B3	1.8	31	Yes	Yes	7	Heavy		
B5	3.1	32	Yes	Yes	12	Heavy		
B7	4.4	28	Yes	Yes	6	Heavy		
B10	5.4	26	Yes	No	-	Not ignited		
Na	2.8	23.8	No	Yes	9	Moderate		
B10Na	8.6	24	Yes	Yes	6	Moderate		
B15Na	12	25	Yes	Yes	7	Moderate		

Table 3. (continued)

Formulation	Add-on (%)	Afterflame time (s)	Char	Melt dripping	Time delay before melt dripping (s)	Cotton pad burning	After removing ignition source at 10 s	After dripping at 15 s
B20Na	15.5	20	Yes	Yes	8	Moderate		
B25Na	17.6	22	Yes	Yes	11	Heavy		
DA	2.3	1.3	No	No	-	Not ignited		
B10NaDA	10.8	20	Yes	Yes	14	Moderate		
B15NaDA	14	14.5	Yes	Yes	4	Moderate		
B20NaDA	16.8	26.2	Yes	Yes	17	Moderate		
B25NaDA	20.2	27.8	Yes	Yes	5	Heavy		
Al5	0.6	-	No	No	-	Not ignited		
B10NaAl5	9	25.6	Yes	Yes	17	Moderate		

Table 3. (continued)

Formulation	Add-on (%)	Afterflame time (s)	Char	Melt dripping	Time delay before melt dripping (s)	Cotton pad burning	After removing ignition source at 10 s	After dripping at 15 s
B15NaAl5	15.4	24.7	Yes	Yes	6	Heavy		
B20NaAl5	16.4	21.6	Yes	Yes	6	Heavy		
B25NaAl5	21	22	Yes	Yes	4	Heavy		
Al10	1.2	5	No	No	-	Not ignited		
B10NaAl10	10.8	20.4	Yes	Yes	10	Moderate		
B15NaAl10	12.8	35.2	Yes	Yes	8	Moderate		
B20NaAl10	16.3	29	Yes	Yes	7	Moderate		
B25NaAl10	20.3	29	Yes	Yes	10	Moderate		

No: No char or no drip Yes: Occurrence of char or drip

After removing the ignition source, untreated PET fabric was molten and its flaming drip led to severe burns of underlying cotton pad while char was not observed. Similarly, for the treated PET fabric with bentonite alone of up to 7% (w/w), the fabric was also molten and its flaming drip caused severe burns of underlying cotton pad. However, when 10%(w/w) bentonite was applied, the fabric burned without melting, but left a certain amount of char. Furthermore, there is no flaming drip at all. This indicates that incorporation of bentonite consisting layered silicate provides evidence of char formation, but it does not reduce ignition tendency; neither is it reduced after flaming. The higher amount of bentonite could increase the viscosity of the burning fabric resulting in decreasing tendency of drip with fire. The carbonaceous-silicate chars build up on the surface during burning and insulate the underlying material, slowing the mass loss rate of decomposition products.(6-7)

However, when the viscosity of the suspension of bentonite (over 10% (w/w), and up to 20% (w/w)) was decreased by the addition of NaCl, the burning behavior of the treated fabrics was different from the fabric treated with 10% (w/w) bentonite alone. The treated fabrics burned with melting, and still left a specific amount of char. In addition, the afterflame time was longer than that of the untreated fabric. Nevertheless, its flaming drip caused only moderate burns of the underlying cotton pad, which was a better performance than that of the untreated one. Moreover, it was noticeable that the dripping occurred in a slower rate than the treated one with bentonite alone, and the fabric was also consumed less.

The treated fabric with 3% (w/w) DA alone was molten in a small area, and the flame was self-extinguished right after removing the ignition source. There was neither dripping nor char formation. This observation can be explained by the fact that DA decomposes to phosphoric acid or polyphosphoric acid when fabrics are heated. These generated acids can form a molten and viscous surface layer. This layer acts as an insulation layer, protecting fabric from flame and oxygen and preventing further decomposition of the fabric.(8)

However, when the fabric was treated with the mixture of bentonite and DA, the treated fabrics burned with melting and still left a certain amount of char. In addition, the afterflame time was longer than that of the untreated fabric. Nevertheless, its flaming drip caused only moderate burns of the underlying cotton pad, which was a better performance than that of the untreated one.

Likewise, the treated fabric with $Al(OH)_3$ alone showed burning behavior similar to DA. Moreover, the treated fabric with bentonite and $Al(OH)_3$ at the amount of 10% w/w also showed similar burning behavior to DA, and better than that of 5% w/w of $Al(OH)_3$.

Conclusions

Bentonite with lower concentration could not promote the flame retardancy and anti-dripping of PET fabric, whereas 10% (w/w) bentonite could enhance anti-dripping of PET fabric while still leaving a sizeable amount of char. Sodium chloride addition could facilitate the application of bentonite suspension onto PET fabric. The treated fabrics with over 10% (w/w), and up to 20%, (w/w) bentonite and NaCl burned with melting; their flaming drip caused only moderate burns of the underlying cotton pad, which illustrates a better performance than the untreated one. Similarly, 3% (w/w) DA or 10% (w/w) $Al(OH)_3$ mixed with bentonite (over 10% (w/w), and up to 20% (w/w)) showed safer flaming drip than that of the untreated one.

Acknowledgments

The authors gratefully acknowledge the Center of Excellence in Textile, Chulalongkorn University, and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, for their financial support.

References

1. Kuenpong, P. & Charuchinda, S. (2009). Effects bentonite, sericin powder and phosphorus compounds on the thermal and fire properties of polyester nonwoven fabric. In : *Proceeding of the 10th Asian Textile Conference (ATC-10)*. September 7-9, Ueda, Japan : 150.

2. Song, L., Hu, Y., Tang, Y., Zhang, R., Chen, Z. & Fan, W. (2005). Study on the properties of flame retardant polyurethane/organoclay nanocomposite. *Polym. Degrad. Stabil.* **87(1)** : 111-116.

3. Chen, D. Q., Wang, Y. Z., Hu, X. P., Wang, D. Y., Qu, M.H. & Yang, B. (2005). Flame-retardant and anti-dripping effects of a novel char-forming flame retardant for the treatment of poly (ethylene terephthalate) fabrics. *Polym. Degrad. Stabil.* **88(2)** : 349-356.

4. Daimatsu, K., Sugimoto, H., Kato, Y., Nakanishi, E., Inomata, K., Amekawa, Y. & Takemura, K. (2007). Preparation and physical properties of flame retardant acrylic resin containing nano-sized aluminum hydroxide. *Polym. Degrad. Stabil.* **92(8)** : 1433-1438.

5. Carroll, P. W. (1995). Method for preparing high solids bentonite slurries. *US Patent 5,391,228.*

6. Hao, X., Gai, G., Liu, J., Yang, Y., Zhang, Y. & Nan, C.W. (2006). Flame retardancy and antidripping effect of OMT/PA nanocomposites. *Mater. Chem. Phys*. **96(1)** : 34-41.

7. Ge, X.G., Wang, D.Y., Wang, C., Qu, M.H., Wang, J.S., Zhao, C.S., Jing, X.K. & Wang, Y.Z. (2007). A novel phosphorus-containing copolyester/montmorillonite nanocomposites with improved flame retardancy. *Eur. Polym. J*. **43(7)** : 2882-2890.

8. Kashiwagi, T. & Gilman, J. W.(2000). Silicon-based flame retardants. In: A.F. Grand & C.A. Wilkie (Eds.). *Flame retardancy of polymeric materials*. New York, NY : Marcel Dekker : pp. 353-389.

9. Nash, V.G. (1960). Role of exchangeable cations in viscosity of clay suspensions. In : *Proceeding of the Seventh National Conference on Clays and Clay Minerals*. 333.

10. Benna-Zayani, M., Mgaidi A., Stambouli M., Kbir-Ariguib, N., Trabelsi-Ayadi, M. & Grossiord, J.L. (2009). Fractal nature of bentonite–water–NaCl gel systems evidenced by viscoelastic properties and model of gels. *Appl. Clay Sci*. **46(3)** : 260-264.