A New Nano-Structured Flame-Retardant Poly(ethylene terephthalate)

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A modified nano-hydrotalcite was used as inorganic flame-retardant fillers for poly (ethylene terephthalate) (PET) polymers. A flame-retardant compound was obtained from layered hydrotalcite (LDH) dispersed in brominated polystyrene (PBS) solution and then solvent evaporation from the dissolved PBS samples. The compound of PBS/LDH was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) and was found to have high aspect ratio LDH dispersed in the PBS matrix. Flame-retardant PET composite was prepared by melt-compounding the flame-retardant compound of PBS/LDH and PET. Improvement in the fire retardancy of the nano-flame-retardant PET composite obtained was found by measuring the oxygen index. The nanostructure of flame-retardant PET composite was chirecterized by scanning electron microscopy (SEM) of flame-retardant PET composite. The mechanical properties of the flame-retardant PET nano-composite were also characterized.

Keywords PET, inorganic, flame-retardant polymer, nano-, morphology, dispersion

Introduction

Flammability is an important concern that must be addressed before polymer materials are used in buildings, ships, aircraft, and clothing (1). The present generation of flame-retardant additives and flame-resistant polymers that are containing halogen, phosphorus, nitrogen, sulfur, and boron, however, has come under increasing public scrutiny because of the perception that they can contribute to environmental problems (2). This concern has spurred interests in the development of new and more "environmentally friendly" treatments to reduce polymer flammability. Inorganic flame-retardant additives are widely used to reduce polymer flammability and are considered as being more "environmentally friendly" treatments (3–5). LDH functions as flame-retardants in PET matrix by liberating their chemically combined water of hydration to cool the system, thereby delaying or inhibiting the ignition of PET polymer. The endothermic decomposition absorbs heat from the polymer and retards the rate of the thermal degradation. It is most important that magnesium oxide and alumina oxide, as the result of decomposition of LDH, can absorb toxic gases that are released from the halogenated flame-retardant. LDH is used,

in part, due to its relatively low cost as compared to antimony-halogen systems and phosphorus-containing flame-retardants. In addition, it is easy handling and relatively nontoxic. However, high concentrations of LDH are required to be effective, and there is a deleterious effect on mechanical properties. Surface modification aids in dispersion of modified nano-LDH (6–9), and it is reported that the flame retardancy of a polymer is increased without loss of mechanical properties by adding small amounts of both modified layered nano-LDH with surface modification and brominated polystyrene (PBS) as flame-retardant additives to a polymer matrix (10–12).

Experimental

Materials

The materials used for this program were from Great Lakes Co., America, PBS-64, Br concentration (mass fraction) is 64%, Yizheng Chemical Fiber Co., China, PET (intrinsic viscosities $[\eta] = 0.7, 0.9$) and Dalian Fumeida Co., China, LDH. The LDH was a nano-grade, suitable for fiber applications. New chemistries and processing parameters for further improvements are described in the following sections.

LDH Nano Flame-Retardant Compounds Preparation

To obtain the maximum flame-retardant improvement in polymer performance, it was desirable that the nano-LDH particles be homogeneously distributed throughout the PBS on the nano-scale. This distribution was governed by the interactions between the individual LDH platelets and the PBS chains. Surface modification was employed to improve the nano-dispersion of LDH in the PBS, as below:

Surface Modification of LDH

LDH was dried at 250°C for 24 h. The mixture of 100 g dried LDH, 2.5 g sodium oleate, and 500 ml pure alcohol were then stirred for 0.5 h, and filtered. The slurries of modified LDH were stored prior to use. Analysis of the LDH and dried LDH samples was performed using X-Ray powder diffraction (Figure 1), thermogravimetric analysis (TGA) (Figure 2) and transmission electron microscopy (TEM) (Figure 3).

Nano Flame-Retardant Compound Production

The process for producing a nano flame-retardant compound involved:

1. dissolving 100 g PBS in 500 ml toluene solvent by stirring for 0.5 h at a temperature of 60°C;
2. mixing 500 ml of the slurry of LDH and 500 ml the PBS solution, stirring for 2 h, at room temperature;
3. optionally filtering and drying the slurry at a temperature of 80°C;
4. milling the product to obtain a powder of flame-retardant compound with an average particle size (d50) of 0.3 micron.

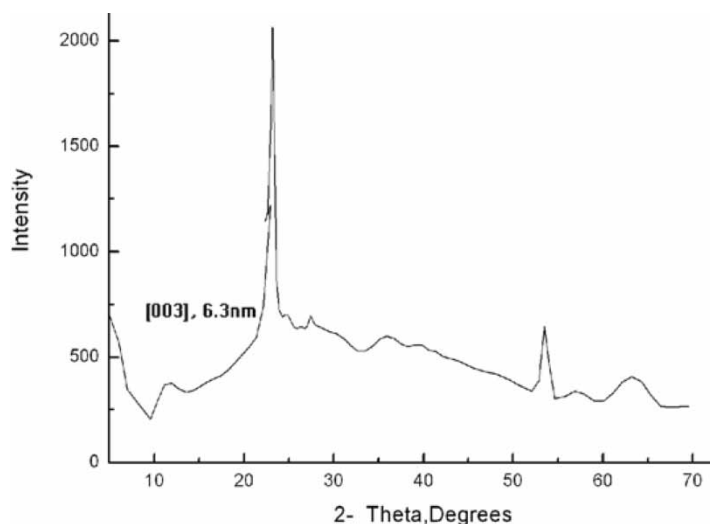Analysis of the samples was performed using transmission electron microscopy (TEM) (Figure 4).

Figure 1. XRD of dried LDH.

Flame-Retardant PET and Characterization

Both PET polymers and flame-retardant compounds were dried overnight at 100°C in a vacuum oven prior to sample preparation; proper moisture control is particularly important in the case of PET, which can change in molecular weight during melt extrusion. The dried polymers were tumble mixed to give blends ranging from 1 to 7.5% by weight of flame-retardant compound dispersed in PET.

Measured amounts of the different dry blends were fed to the hopper of a twin-screw extruder, and the two materials were melted, mixed and extruded into a water bath. The
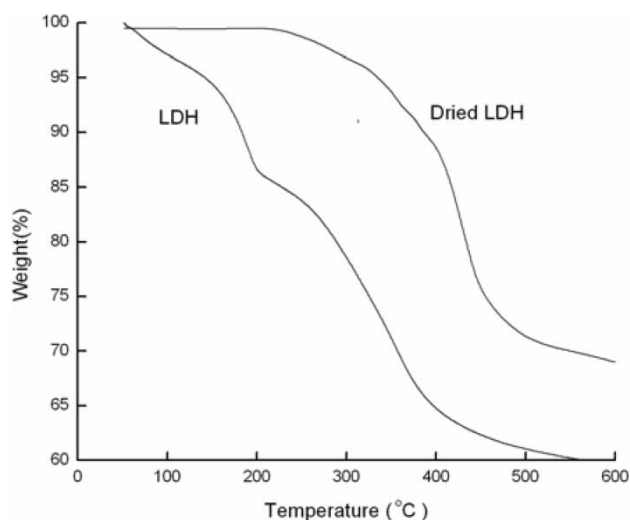

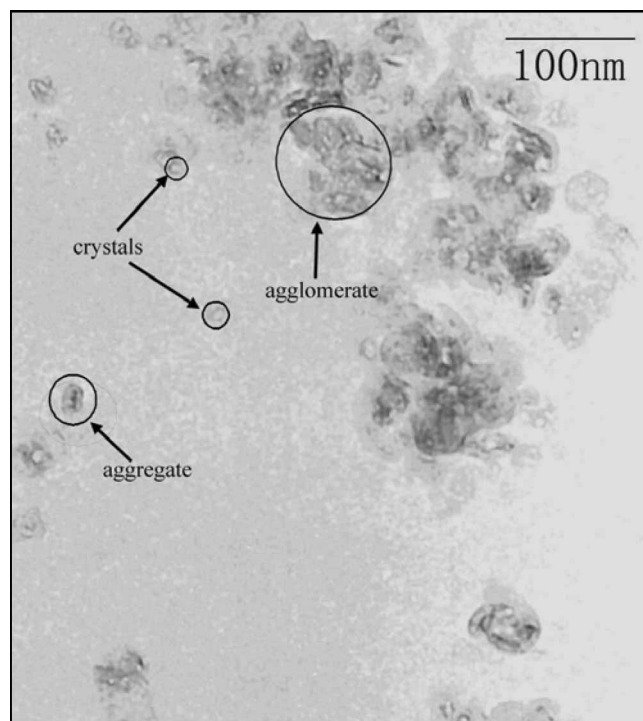**Figure 2.** TGA of LDH and dried LDH.

Figure 3. TEM micrograph of modified LDH.

extrusion temperature was measured to be 250°C–280°C for different samples with the extruder screw speed of 100–300 rpm.

In order to examine the morphology of the blends, a JEOL JSM-5600L scanning electron microscope was used. Samples of PET composites ($[\eta] = 0.7, 0.9$) were prepared by freezing the extruded strands immersed in liquid nitrogen and fracturing into small pieces using a pair of pliers. The sample surface was coated for 85 sec with a gold-palladium sputtering device to provide conductivity. The fracture surfaces that were then examined were aligned perpendicular to the flow direction through the die.

The flame-retardancy of PET ($[\eta] = 0.9$) was measured by the oxygen index. An ATSFAAR Cod.1004050 Oxygen Index by ASTM D2863-77 of the American Society was used. The results of the tests are shown in Table 1 and Figure 6.

The elastic modulus (E_t) was determined at a testing rate of 1 mm/min, and the other tensile properties at a testing rate of 50 mm/min with a Zwick 1464 type material testing machine (made in Germany) at a temperature of 23°C and a humidity of 50% according to ISO527–1 (DIN53455). The results of the tension tests are shown in Table 2.

Results and Discussion

XRD of the dried LDH in PBS matrix (Figure 1) showed that the interlayer space of the dried and modified LDH was 6.3 nm, lower than that of untreated LDH, suggesting that CO_3^{2-} and $-OH$ groups between the LDH layers were removed, and thus the interlayer space was decreased. TGA data (Figure 2) indicated that LDH decomposed over the temperature range of 180°C to 600°C, but the weight loss of dried LDH was lower than 5 wt%
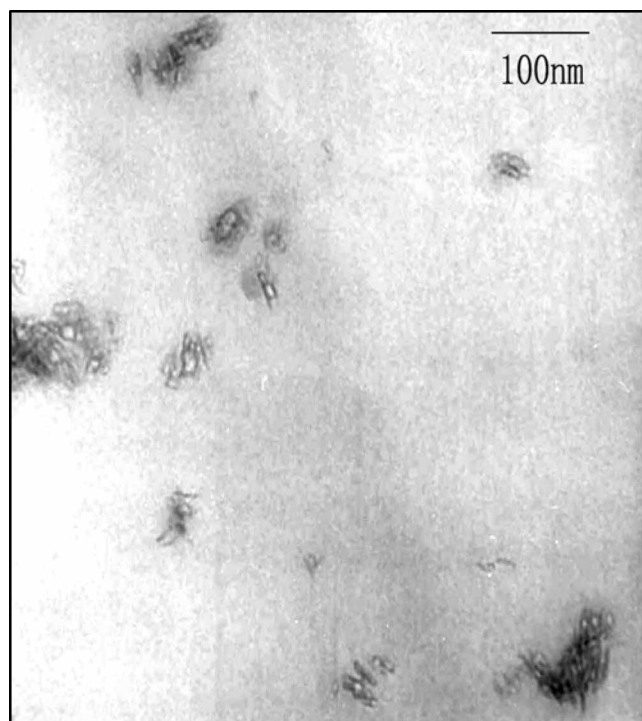
Figure 4. TEM micrograph of LDH and PBS compound.

below 300°C. Thus, it was a stable flame-retardant additive at PET processing temperature.

A TEM micrograph of LDH (Figure 3) showed that the size of the nano-LDH particles was ca.20 nm with the LDH agglomerates size being ca.200 nm. Because of surface treatment, the high surface tension of nano-LDH particles was reduced, and thus, the large size agglomerates were disrupted in the dried and modified LDH powder. In other words, the degree of dispersion was improved with these surface modifications due to the decrease in the number of aggregates; Thus the stability and processability of nano LDH were improved. In fact, the TEM micrographs of the dried and modified LDH showed three different species co-existing in the powder: crystals, aggregates, and agglomerates. Particle size analysis showed similar spectrum. The size of the dried and modified LDH was d(0.9): 200 nm, suggesting that most particles exist as agglomerates.

A TEM micrograph of LDH in the PBS matrix (Figure 4) showed the number of the large size LDH agglomerates was decreased, and the LDH particles were well-distributed

Table 1

The results of the flammability tests (used Oxygen Index)

LDH %wt	0	1	3	0	7	3	3.5
PBS %wt	0	1	3	7	0	4	4
OI of flame-retardant PET	20.9	22.9	27.1	26.8	23.5	29.4	29.8

Table 2

Mechanical properties of PET composites

Material	PET	PET (1 wt% LDH/3 wt% PBS)	PET (1.5 wt% LDH/2 wt% PBS)	
Tensile strength, Mpa	68.2	68.9	68.4	69.3
Tensile modulus, Gpa	1.32	1.37	1.33	1.42

in PBS matrix. We thought that the LDH agglomerates were disrupted by the interaction of LDH particles and PBS polymer chains. There was a strong interaction between LDH particles and PBS polymer chains because of the addition of surfactant, thus the decreased mobility of nano-LDH particles changed the probability of aggregation when the dried and modified nano-LDH was added to PBS solution.

Representative SEM micrographs of flame-retardant PET composites are shown in Figures 5(b–d), for a blend containing 7 wt% flame-retardant compound with different compositions dispersed in PET. As shown in Figures 5(b–d), the samples with high LDH particle concentrations exhibited the dot-pattern of aggregates of nano-LDH. This indicates that the extent of nano-LDH aggregate was dominated by the concentration of LDH. We believe that the increase of the LDH particle number leaded to an increase in size of LDH particles and thus a change of the interaction between LDH particles and polymer chains. Figures 5(a) and (e) show the morphology of polyblends containing 2 wt% and 4 wt% flame-retardant compound dispersed in PET, respectively. The micrographs show the nano-LDH particles were homogeneously distributed in the polymer matrix on the nano-scale, and the average size of LDH particles was lower than 50 nm. The fact of the good dispersion effect of the nano-LDH in the PET indicated that the concentration of flame-retardant compound and compositions of flame-retardant compound were important factors affecting the dispersion of nano-LDH in PET matrix. Comparing Figures 5(b) and (c), it could be shown the nano-LDH particles were more homogeneously distributed for the sample with the high intrinsic viscosity. This indicated that a high matrix intrinsic viscosity was also an effective factor to disperse nano-LDH in PET matrix.

Table 1 shows that the flame-retardancy of PET increased due to introduction of the nano-flame-retardant compounds. The PET composites with flame-retardant compounds (3 wt% LDH/3 wt% PBS, 3 wt% LDH/4 wt% PBS and 3.5 wt% LDH/4 wt% PBS) were flame-retardant materials. Figure 6 shows that nano-flame-retardant LDH/PBS compound could have a dramatic effect on oxygen index of PET composites. It was found that the flame-retardant PET composite with 3 wt% PBS and 1 wt% LDH had a similar oxygen index as that of with 5 wt% PBS. This shows that a smaller quantity PBS could improve the flame-retardancy of PET with 1 wt% LDH added. The toxic gases released from PBS decomposition would decrease with lower PBS concentration. This interference could be due to the formation of a stable interface of LDH particles and PBS chains.

Table 2 shows the mechanical properties of four different types of the PET composites. When flame-retardant compound was added to PET, the mechanical properties had almost no change. However, it should be noted that when the content of LDH was
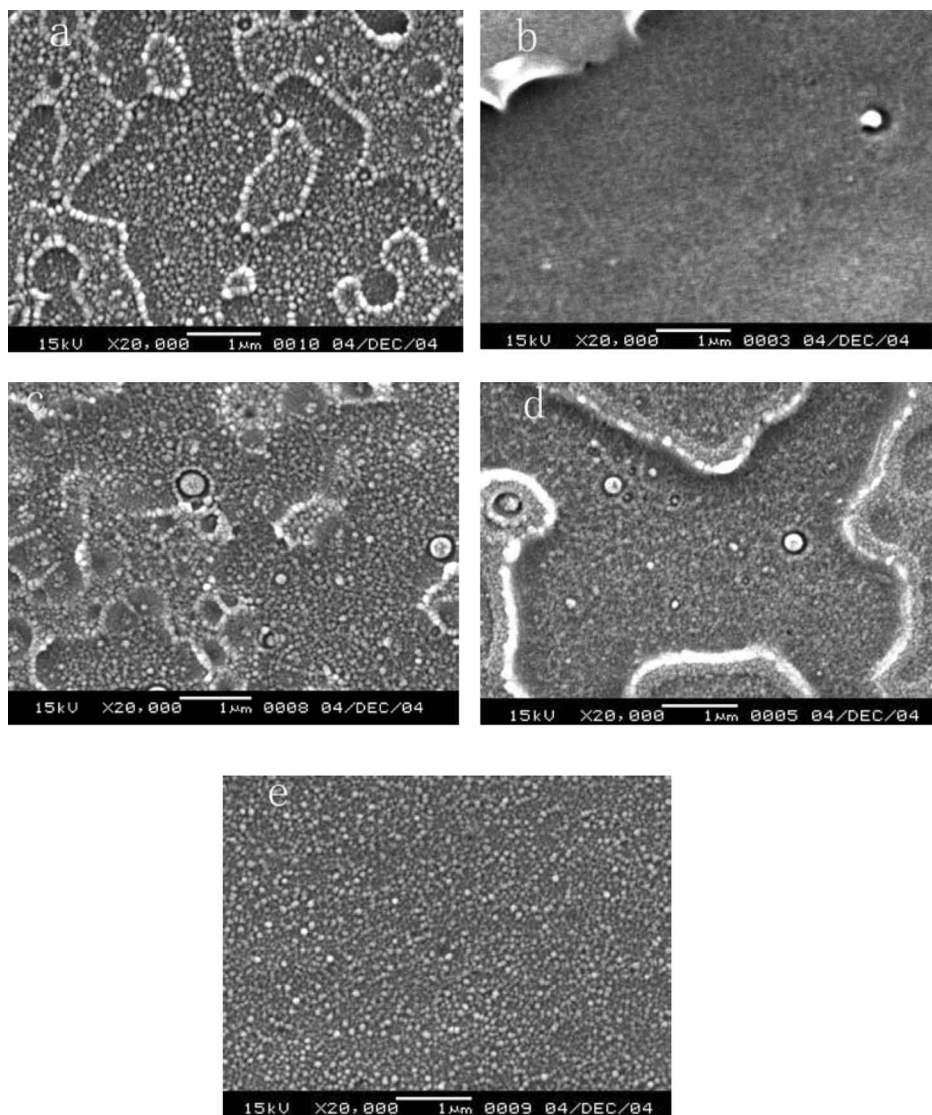
Figure 5. SEM micrographs of various blends (perpendicular fracture surfaces), flame-retardant compound (LDH/PBS) dispersed in PET, all with sodium oleate as coating agent of nano-LDH. Extruder rpm was $100 \sim 300$ and the processing temperature was $250°C–280°C$. (a) 2 wt% flame-retardant (LDH/PBS: 1/1 wt%), PET ($[\eta] = 0.9$); (b) 7 wt% flame-retardant (LDH/PBS: 5/2 wt%), PET ($[\eta] = 0.7$); (c) 7 wt% flame-retardant (LDH/PBS: 5/2 wt%), PET ($[\eta] = 0.9$); (d) 7 wt% flame-retardant (LDH/PBS: 3/4 wt%), PET ($[\eta]= 0.9$); (e) 4 wt% flame-retardant (LDH/PBS: 2/2 wt%), PET ($[\eta] = 0.9$).

only about 1 wt%, the tensile strength and tensile modulus of PET (LDH/PBS) composite were better than those of pure PET. The increased adhesion of nano-LDH with PET matrix by surface treatment and the improved dispersions of LDH could be the reasons.
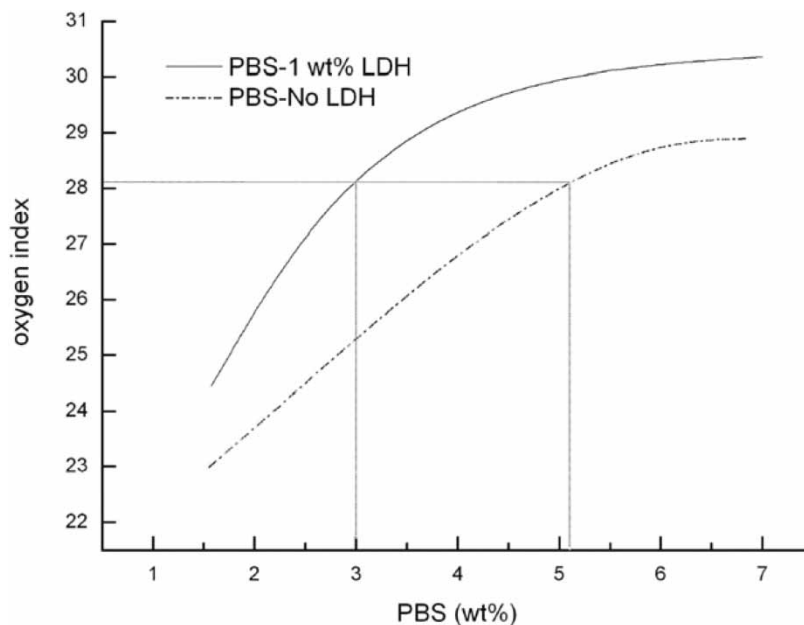
Figure 6. Oxygen index of flame-retardant PET vs. increased concentrations of LDH and PBS.

Conclusions

TEM observations of nano-structure of flame-retardant compound indicated that LDH particles were well-distributed in the PBS matrix. By melt-blending this nano-flame-retardant compound and PET polymer, the LDH particles were dispersed on the nano-scale. The dispersions of LDH particles were influenced by the LDH concentration, composition of flame-retardant compound and the intrinsic viscosity of PET. The concentration of LDH had an influence on the average size of agglomerates. Oxygen index tests of flame-retardant PET showed that LDH/PBS compound with the nano-dispersion of LDH, i.e., companying lower amount of PBS than PBS only, was an effective flame-retardant. Additionally, the mechanical properties of the flame-retardant PET composites had no obvious decrease with the addition of LDH/PBS compound.

Acknowledgements

References

1. Holmes, M. (2005) *Plastics, Additives and Compounding*, 7 (2): 3.
2. Brebu, M. and Bhaskar, T. (2004) *Fuel*, 83 (14–15): 2021–2028.
3. Kim, S. (2003) *J. Polym. Sci., Part B: Polym. Phys*, 41 (9): 936–944.
4. Lewin, M. (2003) *Fire and Materials*, 27 (1): 1–7.
5. Ulutan, S. and Gilbert, M. (2000) *J. Mat. Sci.*, 35 (9): 2115–2120.

6. McKenzie, A.L., Fishel, C.T., and Davis, R.J. (1992) *J. Catalysis*, 138 (2): 547.
7. Pukanszky, B. and Fekete, E. (1999) *Adhesion and Modification, Advances I Polymer Science*; Berlin: Springer; Vol. 139, 138–150.
8. Giannelis, E.P. (1999) *Appl. Organ. Chem.*, 12 (10–11): 675–680.
9. Caruso, F. (2001) *Advanced Materials*, 13 (1): 11–22.
10. Wei, W. and Manfred, H.W. (2003) *Coll. Polym. Sci.*, 281: 550–555.
11. Nakamuru, Y., Okabe, S., Yoshimoto, N., and Iida, T. (1998) *Polymer Composite*, 6: 407–414.
12. Pucciariello, R., Villani, V., Gorrasi, G., and Vittoria, V. (2005) *J. Macrom. Sci., Part B: Phys*, (44): 1/2005: 79–92.