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Preparation and Flame Retardancy of Poly(ethylene terephthalate)/Montmorillonite Nanocomposites

S. Habibi, A. Rashidi*, S. Bazgir†, A.A. Katbab‡ and M. Montazer§
Department of Textile Engineering, Islamic Azad University
Science and Research Branch, Tehran, Iran
E-mail: rashidi50@yahoo.com

This paper presents the experiments on preparing nanocomposites based on poly(ethylene terephthalate) (PET) and montmorillonite *via* melt blending with different clay loadings to investigate their combustion behaviour. All the samples have intercalated structure by X-ray diffraction (XRD) and transmission electron microscopy. Their thermal stability and combustion behaviour were investigated by using thermogravimetric analysis (TGA), limiting oxygen index (LOI) and cone calorimeter. Peak heat release rate of nanocomposites decrease as the contents of clay increase compared to that of pristine poly(ethylene terephthalate).

Key Words: Poly(ethylene terephthalate), Nanocomposite, Flammability, Morphology, Thermal property.

INTRODUCTION

Polymer-layered silicate nanocomposites (PLSNs) has attracted great interest because of possibilities of concurrent improvements in the mechanical, thermal, barrier and flammability properties. Polymer-layered silicate nanocomposites are known as materials in which one dimension of a dispersed phase is in the nanometer range (typically 1-20 nm). The comparison of PLSNs with conventional filled polymers concluded that the property enhancements of PLSNs are granted *via* the addition of small amounts of clay[1-5]. Furthermore, significant improvements in flammability of polymer are reported with PLSNs. The improvements in flammability of polymer achieved with PLSNs are truly impressive since could become a ‘green’ alternative to conventional flame retardants. Recent reports about PLSNs flame retardant properties mainly demonstrate a significant decrease in the peak heat release rate (PHRR), a change in char structure and a decrease in the rate of mass loss during combustion in a cone calorimeter[6-9].

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†Department of Polymer Engineering, Islamic Azad University, Science and Research Branch, Tehran, Iran.

‡Department of Polymer Engineering, Amirkabir University of Technology, Tehran, Iran.

§Department of Textile Engineering, Amirkabir University of Technology, Tehran, Iran.

Poly(ethylene terephthalate) (PET) finds wide variety of applications, both as fiber and non-fiber because it combines low cost with good chemical resistance and good spinnability[10].

Poly(ethylene terephthalate) fibers have the higher production amount and wide usage among all the synthetic fibers. However, their combustibility and serious dripping during combustion, markedly limit their application. Therefore, the flame retardancy and the dripping resistance of PET have become an important subject to deal experimentally[11,12].

In this article PET based nanocomposites were prepared in the melt state with different clay loading levels. Poly(ethylene terephthalate) used in present experiment was fiber grade. The clay contents were 3 and 5 %. The morphology was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Thermal stability was conducted on samples by TGA. The flammability behaviour and dripping resistant of nanocomposites were evaluated by LOI and cone calorimeter.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET), fiber grade(intrinsic viscosity 0.64 dl/g) and in the form of pellets, was purchased from Tondgooian Petrochemical Complex. Organo-montmorillionite was obtained from Zhejiang Fenghong Clay Corp. with the commercial name DK2.

Poly(ethylene terephthalate)/montmorillionite (PET/MMT) blending: Poly(ethylene terephthalate)was dried at 110 ºC under vacuum for 24 h. Organo-montmorillionite (DK2) was dried at 80 °C for 8 h. The PET/MMT composites, with different contents of MMT (3 and 5 %), were obtained *via* melting process in a co-rotating twin screw extruder (Brabender ZSK25, l/d = 25) with a screw speed of 250 rpm. The residence time was in the range of 45-60 s and the thermal profile was 250-250-260-260-270-270 °C. Poly(ethylene terephthalate) was extruded in the same conditions without clay. The ratios of PET and organo-MMT are listed in Table-1.

TABLE-1
MASS RATIO OF PET/MMT COMPOSITES

Sample	PET	MMT(DK2)
PET	100	0
PET3C	97	3
PET5C	95	5

Characterization

X-ray diffraction analyses were performed at room temperature using a Philips X-ray diffractometer from 2θ(2° -10°), using CuKα with wavelength of 1.54 Å. Transmission electron microscopy (TEM) micrographs were carried out using EM208 Philips transmission electron microscope (Mag = 200,000). Ultrathin sections of about 30-60 nm thick were cut with UMU3-C Reichert ultra microtome equipped with a diamond knife and placed on a 400-meshed copper grid.

Thermal and flame tesing:

Thermogravimetric analysis (TGA): To perform thermogravimetric analysis, dimond TGA/DTG system was used. Samples were heated at 10 °C/min from 30 to 600 °C in a nitrogen atmosphere.

Limiting oxygen index (LOI): Limiting oxygen index was measured using a Toyoseiki instrument on samples (100 mm × 6 mm × 3 mm) according to standard ASTM D2863.

Cone calorimeter: A fire test technology (FTT) cone calorimeter was used to carry out measurements on samples (100 mm × 100 mm × 8 mm) following the procedure defined in International Standard ISO 5660. A heat flux of 50kW/m^2 was used for running the experiments.

RESULTS AND DISCUSSION

Characterization: Morphological studies carried out using XRD and results were confirmed by TEM. As shown in Fig. 1, the d001 peak of modified nanoclay is decreased from 2θ = 4.17 to about 2.6 nm (in accordance to Bragg's equation) for all samples indicating that interlayer distance is decreased from 2.16 nm for DK2 to 3.28 and 3.24 nm for nanocomposites with Organo-MMT contents of 3 and 5 %, respectively. Thus, the polymer molecules entered into the silicate layers of organo-MMT and formed intercalated nanocomposite rather than exfoliated one, due to existence of sharp diffraction peaks.

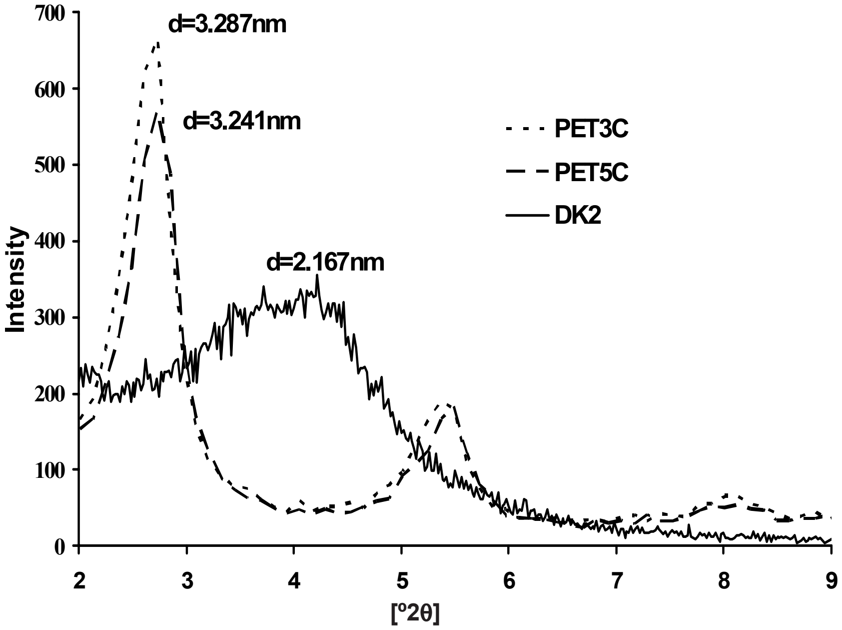
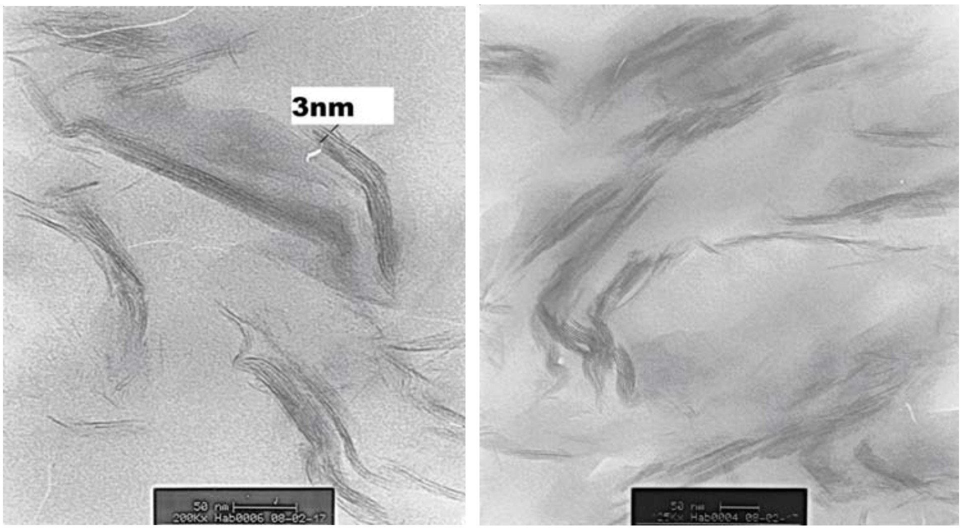


Fig. 1. XRD curve of DK2, PET3C and PET5C

Fig. 2(a-b) show TEM micrographs for PET3C and PET5C, respectively. These results demonstrate that the interlayer distance of dispersed clay is about 3 nm and confirm that polymer molecules have intercalated into the silicate layer galleries.



(a) (b)

Fig. 2. TEM micrographs of: (a) PET3C and (b) PET5C

Thermal stability: The TGA thermograms of PET and PET nanocomposites are presented in Fig. 3. The onset decomposition temperature of nanocomposites is 4 °C for PET3C and 11.5 °C lower than that of pristine PET. It is because of catalytic effect of clay to accelerating decomposition PET matrix. According to previous report, it can be due to (a) volatizing out of absorbed or bounded water in MMT; (b) catalytic effect of hydroxyl groups which acts as acidic active centers of sorptons[13]. The bigger loss of onset decomposition of PET5C compared with other samples, could be caused by the thermal degradation of organic treatment of the clay.

Flammability

Limiting oxygen index: Limiting oxygen index (LOI) values of samples are given in Table-2. As can be seen LOI values of nanocomposites samples increase compared to pristine PET. However, it is found out that as the content of organo-clay increases from 3-5 %, the LOI value decreases from 24 to 23.5. Since the presence of orgao-clay leads to formation of a barrier layer , it limits the propagation inside the sample but increases flame- spread over the surface of sample.

TABLE-2
THE LOI VALUES OF PET/MMT

Sample	LOI	Drip
PET	24.0	Heavy
PET3C	23.5	No
PET5C	23.5	No

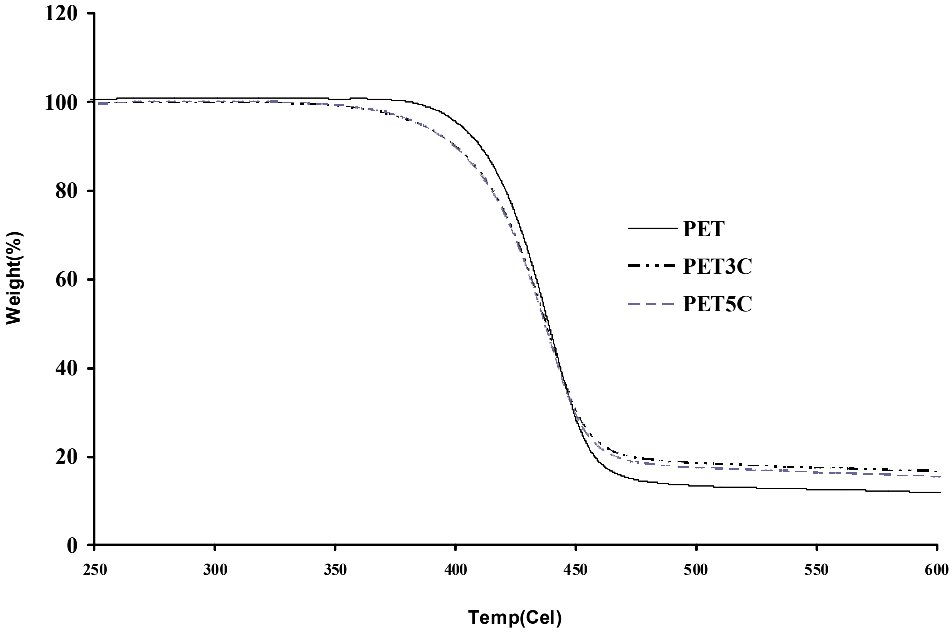


Fig. 3. TGA curves of pristine PET, PET3C and PET5C in nitrogen atmosphere (TGA heating rate : 10 °C/min)

Cone calorimeter test: The effect of varying organo-MMT loading in the heat release rate of nanocomposite samples is demonstrated in Fig. 4.

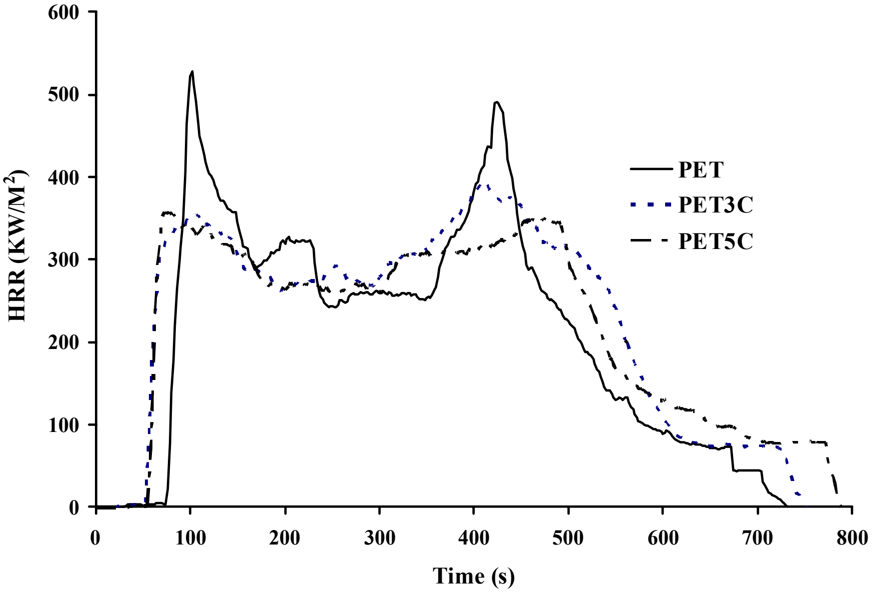


Fig. 4. Heat release rate (HRR) data for PET, PET3C and PET5C

The results indicate that the addition of MMT decreased the heat release rate of PET matrix. The greater the organo-MMT content, the lower the heat release rate. The peak of heat release rate values of PET3C and PET5C are reduced, respectively, about 25 and 32 % in comparison with pristine PET. The lower peak of heat release rate is due to barrier effect of clay in nanocomposite. According to previous studies[14,15], formation of carbonaceous char in the condensed phase leads to decrease in flammability of polymer/clay nanocomposites. The carbonaceous-silicate char acts as a barrier and insulates the underlayered polymer matrix. Thus, it slows down heat and mass transfer between the gaseous and condensed phases. Considering Fig. 4, it can be found out that the addition of MMT accelerates the ignition of the PET. Catalytic decomposition effect of MMT on polymer causes acceleration of the PET ignition which can be confirmed by TGA result.

Fig. 5. shows the mass loss rate results during the cone calorimetric experiments. Mass loss rate curves are almost identical to the heat release rate curves. Due to these observations, it can be concluded that the formation of coat-like carbonaceous char is responsible for the improvement in flammability properties.

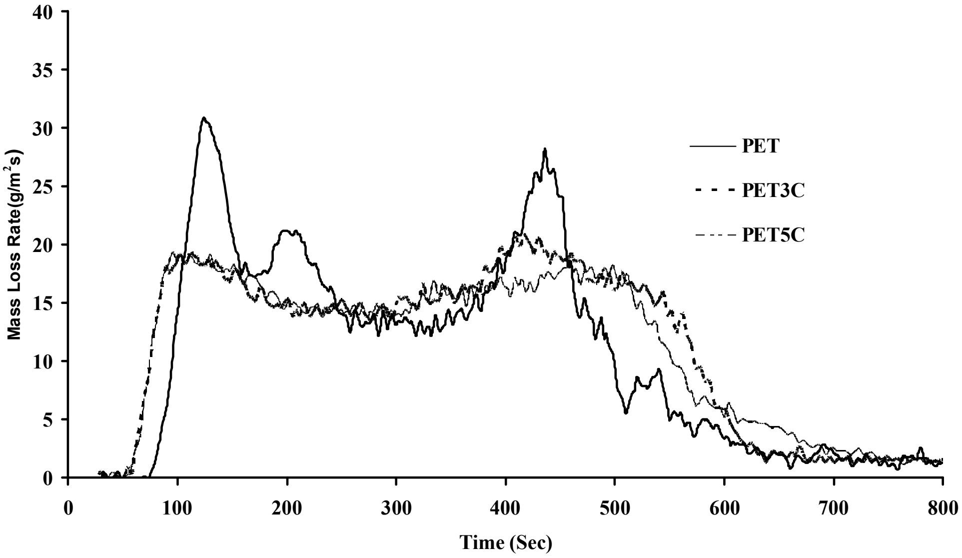


Fig. 5. Mass loss rate (MLR) data for PET, PET3C and PET5C

Some cone calorimetric data of pristine PET and its nanocomposites are listed in Table-3. As it can be seen, there is a small decrease in total heat release rate obtained.

CO production during the combustion of PET3C and PET5C was significantly lowered compared to pristine PET whereas no significant differences in the CO_2 release was evolved. Addition of clay greatly improved the amount of char residue from $W/W_0 = 0.11$ in case of pristine PET to 0.15 and 0.43 for PET3C and PET5C, respectively.

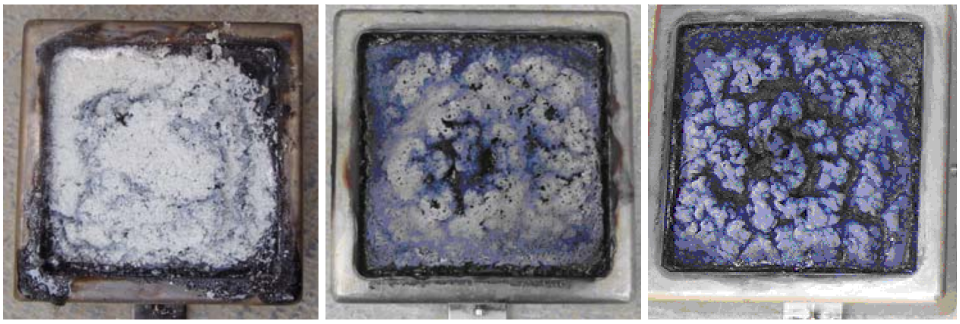
TABLE-3
CONE CALORIMETRY MEASURED PROPERTIES FOR PRISTINE PET AND ITS NANOCOMPOSITES

Sample	PET	PET3C	PET5C
Peak HRR (kW/m^2)	598.29	396.57	357.97
Total heat release rate (THR) (MJ/m^2)	188.70	171.70	169.10
Average EHC (MJ/kg)	18.12	17.45	17.41
Average SEA (m^2/kg)	269.53	287.25	304.68
Average CO yield (kg/kg)	0.0683	0.0346	0.0337
Average CO_2 yield (kg/kg)	1.94	1.79	1.77
Char residue (W/W$_0$)	0.11	0.15	0.43
Ignition time (s)	76	56	59

HRR = Heat released rate; EHC = Effective heat of combustion; SEA = Specific extinction area.

The effective heat of combustion (EHC) results of nanocomposites are similar to those of pristine PET.

The observation of the combustion phenomenon during the cone calorimetric measurements revealed that pristine PET sample melted and had a boiling surface followed by some large bubbles. At the end of combustion pristine PET left almost no residue as shown in Fig. 6. The nanocomposite with 3 % clay melted but it was more viscous than PET and small carbonaceous char formed on the surface with out covering it. The PET5C appeared more viscous and it did not melt. Addition of 5 % nano-clay inhibited bubbling process and formed a continuous solid coat-like carbonaceous char as it can be seen in Fig. 6. Thus, the protective carbonaceous char acts as a barrier and covers the surface. Hence, the exposure of the molten polymer to heat and oxygen and volatilization of nanocomposites will be reduced. Formation of network-structured protective layer during the burning was confirmed by LOI results, as it is given in Table-2. PET burns with heavy dripping while, PET3C and PET5C show dripping resistance. The residues of nanocomposites at the end of test is char like and for pristine PET is melt materials.



PET PET3C PET5C

Fig. 6. Residue images at the end of cone calorimetric test

Conclusion

In this research, PET/MMT nanocomposites with different contents of clay were prepared by melt blending. The intercalated morphology was confirmed by XRD and TEM. The catalytic decomposition effect of MMT is presented in TGA results. Cone calorimeter results present that flammability property of PET/MMT improves as the content of clay increases. A nanocomposite containing 5 % clay shows good flame retardancy and dripping resistance. According to LOI values the flame retardant property of nanocomposite samples improves compared to pristine PET. But increase in content of clay causes decrease in LOI.

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