

Effect of Clay on Degradation of Poly(ethylene terephthalate)/ Montmorillonite Nanocomposites

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Poly(ethylene terephthalate)/montmorillonite nanocomposites, with different contents of montmorillonite (1, 3 and 5 wt %), were prepared *via* melt compounding. The dilute solution viscosity technique was used to evaluate the intrinsic viscosity of poly(ethylene terephthalate)/montmorillonite nanocomposites. The incorporation of clay reduces the intrinsic viscosity of polymer matrix. Their thermal stability were investigated by using thermogravimetric analysis. Their nano-dispersion morphology were confirmed by X-ray diffraction and transmission electron microscopy.

Key Words: Nanocomposite, Poly(ethylene terephthalate), Thermal degradation, Montmorillonite, Intrinsic viscosity, Morphology.

INTRODUCTION

It has been proved that reinforcement of polymer with nanosized particles is a promising technique that affords to enhanced performance of the materials. Among all nanoparticles one of the most favourable is montmorillonite (MMT) because of its natural occurrence and beneficial properties. Incorporation of nanodispersed clay may lead to a broad range of applications such as imparting improvements in the mechanical, thermal, barrier and flammability properties¹⁻⁶.

Polymer-layered silicate nanocomposites (PLSNs) are prepared *via* three general routes: solvent method, *in situ* polymerization and melt intercalation where the polymer chains diffuse into the space between the clay galleries. This process can be carried out through a conventional melt-compounding process. Melt blending is an economically favourable process and some experiments have been demonstrated. Poly(ethylene terephthalate) (PET) is a thermoplastic, semi crystalline polymer with low cost and high performance and has variety of applications in textile in form of fibers and films in food packaging and soft drink bottles⁷. However, it is drastically prone to degradation in case of being melt compounded. In case of fiber, the final properties of nanocomposite fibers, such as mechanical properties are highly influenced by degradation during the production process. In this research,

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PET/MMT nanocomposites, with different contents of MMT (1, 3 and 5 wt %), were prepared *via* melt compounding. The dilute solution viscosity technique was used to evaluate the intrinsic viscosity of PET/MMT nanocomposites. The thermal degradation behaviour of samples was investigated by thermogravimetric analysis (TGA). Their nano-dispersion morphology was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

EXPERIMENTAL

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

PET/MMT compounding: Poly(ethylene terephthalate) was dried at 110 °C under vacuum for 24 h. Organo-MMT (DK2) was dried at 80 °C for 8 h. The PET/MMT composites, with different contents of MMT (1, 3 and 5 %), were obtained *via* melting process in a co-rotating twin screw extruder (Brabender ZSK25) with a screw speed of 250 rpm with the thermal profile of 250-250-260-260-270-270 °C. PET 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
PET1C	99	1
PET3C	97	3
PET5C	95	5

X-Ray diffraction (XRD): XRD analyses were performed at room temperature using a Philips X-ray diffractometer from $2\theta(2^\circ-10^\circ)$, using $\text{CuK}\alpha$ with wavelength of 1.54 Å.

Transmission electron microscopy (TEM): 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.

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

Intrinsic viscosity (IV): Intrinsic viscosity values were obtained at 25 °C according to Zimmer method using an Ubbelohde viscometer (Ecoline). A mixture of phenol and 1,2-dichloro benzene (3:2 parts by weight) was used. Any residual moisture would be influenced on the value of relative viscosity. Hence, samples were dried at 80 °C for 20 min.

RESULTS AND DISCUSSION

Characterization: The XRD patterns of organo-clay (DK2), PET1C, PET3C and PET5C are shown in Fig. 1. As it can be seen, the d001 peak of modified nanoclay has decreased from $2\theta = 4.17$ - 2.60 nm (in accordance to Bragg's equation) for all samples indicating that interlayer distances has increased from 2.12 nm for DK2 to 3.31, 3.33 and 3.24 for nanocomposite with organo-MMT content of 1, 3 and 5. Thus, the polymer molecules have entered into the silicate layers of organo-MMT and formed intercalated nanocomposite rather than exfoliated one, due to existence of sharp diffraction peaks. As it can be seen from TEM micrograph shown in Fig. 2 the interlayer distance of dispersed clay is about 3 nm which confirms that polymer molecules have intercalated into the silicate layer galleries.

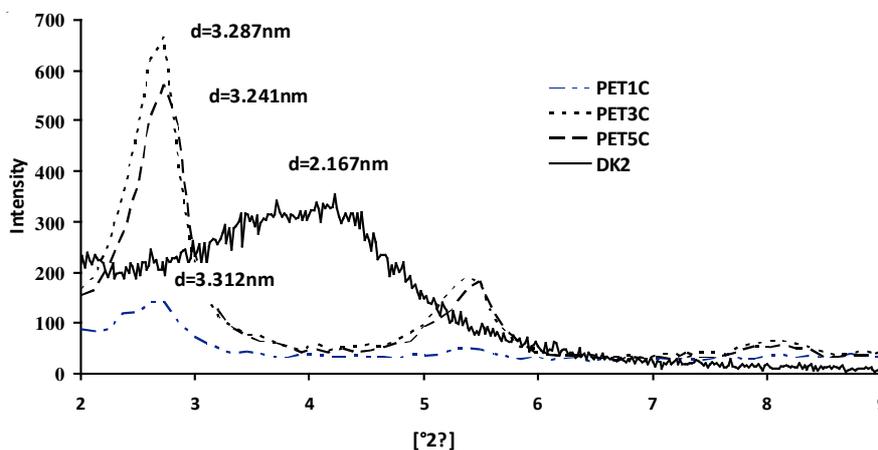


Fig. 1. XRD curve of DK2, PET, PET1C, PET3C and PET5C



Fig. 2. TEM image of PET3C

Thermal stability: The TGA thermograms of PET and PET nanocomposites are presented in Fig. 3. The onset decomposition temperature of nanocomposites is 3 °C for PET1C, 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 work on thermal degradation of polymer/clay nanocomposites, it can be due to (a) volatilizing out of absorbed or bounded water in MMT; (b) Catalytic effect of hydroxyl groups which acts as acidic active centers of sorptions⁶. The bigger loss of onset decomposition of PET5C compared with other samples could be caused by the thermal degradation of organic treatment of the clay⁸⁻¹².

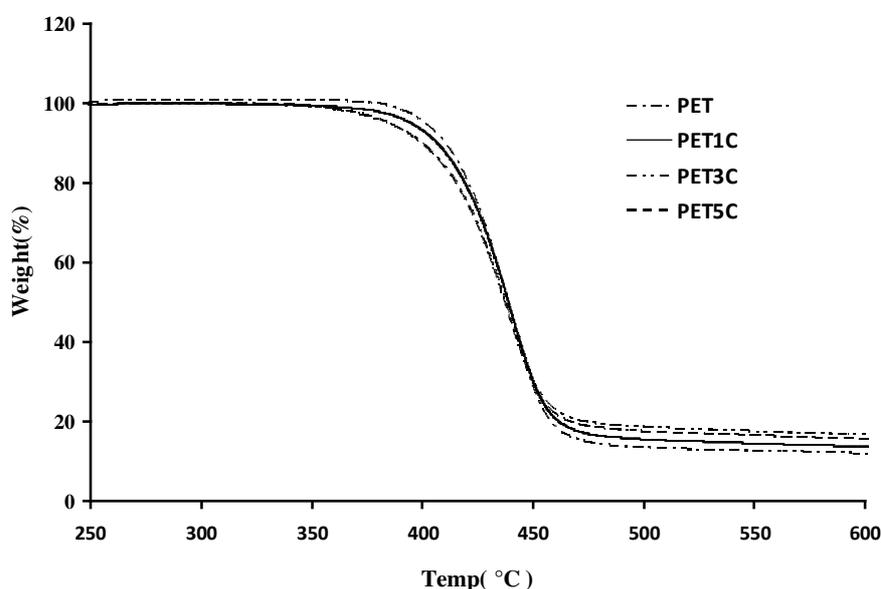


Fig. 3. TGA curves of pristine PET, PET1C, PET3C and PET5C in N₂ atmosphere (TGA heating rate: 10 °C/min)

Intrinsic viscosity: As it can be observed in Tables 2 and 3, the extrusion of PET resulted in high reduction of intrinsic viscosity (η), which is 33 % for extruded PET (PET. ext) compared to virgin PET. During extrusion, the following processes may occur simultaneously: (1) hydrolysis and condensation (the predominating process depends on water content); *trans*-esterification, cycle formation; (3) thermal degradation by decomposition of weak points (diethylene glycol); chain resulting of oxidation at high oxygen concentration and (6) cross linking resulting of oxidation at low oxygen concentration. All materials were dried in vacuum oven before melt compounding. It must be noted that the moisture and oxygen during process had not been removed¹²⁻¹⁵.

The nanocomposite samples experienced much more degradation as the content of clay increased from 1-5 % because the hydroxyl groups acted as Bronsted acidic sites to accelerate polymer degradation. Thus, the nanocomposite with larger amount

TABLE-2
INTRINSIC VISCOSITY OF VIRGIN, EXTRUDED AND NANOCOMPOSITE SAMPLES

Samples	Intrinsic viscosity (dL/g)	Samples	Intrinsic viscosity (dL/g)
PET	0.64	PET3C	0.44
PET.ext	0.43	PET5C	0.41
PET1C	0.57	–	–

TABLE-3
PERCENTAGE REDUCTION OF IV OF NANOCOMPOSITE AND
EXTRUDED SAMPLES WITH RESPECT TO VIRGIN PET

Samples	Percentage variations (%)	Samples	Percentage variations (%)
PET.ext	33.0	PET1C	10.94
PET3C	31.2	PET5C	36.00

of organo-clay experienced much more degradation compared to virgin PET, depending upon acidic sites produced by Hofmann elimination reaction of ammonium.

Conclusion

(1) XRD and TEM results indicate that intercalated PET/MMT can be produced *via* melt compounding. The best dispersion is when MMT content is 1 %. (2) Results imply that PET nanocomposites are more sensitive to degradation than virgin PET which leading to reduction on intrinsic viscosity and the onset decomposition temperature. Nanocomposite with 5 % of MMT shows more reduction on η and T_{onset} ^{15,16}.

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