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Original research

PET/Mica nanocomposites for food packaging: crystallization behavior and mechanical properties

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ABSTRACT

Nowadays polymer nanocomposites have introduced as a new class of food packaging materials due to their enhanced mechanical, thermal, and barrier properties. In this study PET nano composites were prepared by melt blending of poly (ethylene terephthalate) pellets and mica nanoparticles. The morphology of PET/mica nanocomposites was characterized by X-ray diffraction and transmission electron microscopy (TEM), showing exfoliated/intercalated structures for different concentrations of mica. The crystallization behavior was studied by differential scanning calorimetry (DSC). Incorporation of mica nanoparticles in PET matrix had pronounced effect on crystallization of poly (ethylene terephthalate). Both crystallization rate and degree of crystallinity increased due to nucleation effect of mica nanoparticles. The results of mechanical test indicated that addition of micas to PET matrix caused to slight diminish of tensile strength and ductility of polymer.

Keywords: Poly ethylene terephthalate; Somas if MAE; Crystallization; Nano composite; Transmission Electron Microscopy

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1. Introduction

Poly (ethylene terephthalate) (PET) is an engineering plastic which is widely used for many applications, such as stretch blowmolded packaging. It is commonly used as packaging material for drinking water, mineral water, carbonated beverages and edible oils, because of its excellent mechanical and barrier properties. However, even with its excellent properties for packaging applications there exists a growing demand for lighter and better barrier PET packaging material (Soon et al., 2009). Polymer/silicate nanocomposites, in which relatively small amounts of Nano scale particles (usually less than or equal to 5%) are dispersed in a bulk polymer matrix, offer the potential for reducing the weight and improving the barrier properties of packaging materials such as PET. Silicates like montmorillonite have been used as reinforcing materials for polymers owing to their high aspect ratio and unique intercalation/exfoliation characteristics. Nano composites of montmorillonite-polymer can be obtained by direct polymer 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 (Kawasumi et al., 1997; Liu et al., 1999). The mechanical properties of the products are affected by the degree of exfoliation, which depends on both processing conditions and clay chemical treatment. Successful melt exfoliation requires the presence of strong interactions between clay and macromolecules, a stress field and an adequate residence time of the stress field. Once exfoliated, the clay platelets dispersed in the polymer matrix present high stiffness and strength. Polyester-clay nanocomposites have been studied with regard to their crystallization properties (Ke et al., 1999). Non-isothermal crystallization dynamics show that the nano composites of PET have three times greater crystallization rates than that of pure PET. Modulus and HDT increase with clay concentration as much as threefold. The exfoliated clay particles play a nucleating role and have strong interactions with PET molecular chains. It is believed that the greater the interlamellar distance, the greater the interaction of PET with clay sheets. The increase of the apparent crystallinity with filler content also appears to result from the incidence of very rapid crystallization due to the nucleating effect of nanofillers (Sánchez-Solís et al., 2004). Most researches have been studied the effects of nanoscale natural montmorillonite on properties of polyethylene terephthalate. Synthetic micas have higher aspect ratio rather than montmorillonite particles (Yano et al., 1997) and could have different behavior in the polymer matrix. PET/mica nanocomposite has attracted much attention because of its expectable great improvement in better gas impermeability, thermal resistance, mechanical properties, etc (Imai et al., 2003; Tsai et al., 2005; Zhang et al., 2003). However, because of the complexity of

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PET/mica system, the effect of mica on the crystallization performance of PET is still poorly understood (Xu et al., 2002; Yuat al., 2004). In this study, the effect of Somasif-MAE (synthetic fluromica) on physical and mechanical properties of PET/mica nanocomposites has been investigated.

2. Material and Methods

Pure PET pellets (blow molding grade) with intrinsic viscosity of 0.82 dL/g were provided by Tondgooyan Petrochemical Company (Iran). Somasif MAE nanoparticles were supplied by CBC Co. (Japan).

2.1. Prepration of PET materials

PET nanocomposites containing 1, 3 and 5 wt% of nanomicas (coded as PET1%NM, PET3%NM and PET5%NM) were prepared via melt blending in a lab-scale counter- rotating twin-screw extruder (Collin ESC-T10 model) with screw diameter of 50 mm and L/D ratio of 15. The extruder has 5 heater zones and a die zone set at 250, 270, 275, 270, 265, and 265ºC and operated at a screw speed of 90 rpm. The components of nano composite were dried in an oven at 170°C for 5 h before extrusion process. The prepared profiles were water cooled and then milled in conventional milling equipment. Neat PET sample (coded as PET0) as reference material was prepared in the same procedure.

2.2. DSC analysis

The melting and crystallization characteristics of PET in the prepared samples were studied by differential scanning calorimeter (DSC 200 F3 Maia® NETZSCH, Germany).

The melting behavior of nanocomposite samples was determined using heating and cooling tests between 25-270 °C at a rate of ±10 °C/min. The first heating run was used to erase the thermal history and all reported data on melting characteristics of the prepared samples were obtained from the second heating curve of the DSC thermograms. The degree of crystallinity (Xc) of PET in the nanocomposites and the neat polymer specimens were calculated using the eq. (1):

$$X_C = \left(\frac{\Delta H_m}{\Delta H_{m0}} \right) \times 100 \tag{1}$$

Where ΔHm0 is the melting enthalpy of 100% crystalline PET, ΔHm0=105.97 J/g (Yamada at al., 2006) and ΔHm is the melting enthalpy of the samples.

2.3. X-ray diffraction (XRD)

The XRD patterns were recorded in an X-ray diffractometer (Simens D5000-Germany) at room temperature, using Cu Kα tube radiation with the wavelength of 1.5409 oA, generated at 30 kV and 30 mA. The samples were scanned in the range of 2θ = 2–10o with a step size of 0.04o. The angular and layer spacing values are related through the Bragg’s law:

$$\lambda = 2d \sin \theta \tag{2}$$

where d is spacing between diffraction lattice planes and θ is the measured diffraction angle.

2.4. Transmission electron microscopy

Ultra-thin sections (70–100 nm) of the nano composites were obtained with a microtome (Leica Ultracut UCT) equipped with a diamond knife. The morphology of PET/mica nanocomposites was studied by transmission electron microscopy (TEM, Philips-EM208S electron).

2.5. Tensile testing

Engineering stress-strain curves were prepared from uniaxial tension tests (following ASTM D638) on injection molded dumbbell-like specimens using a Galdabini Sun2500 tensile tester (Galdabini, Italy). The tensile tests were carried out at crosshead speed of 5 mm/min. At least five specimens for each sample were tested. The mechanical characteristics of the sample consisting of stress at break, strain at break, elastic modulus and dissipated energy determined from the test.

3. Results and Discussion

3.1. X-ray diffraction

To investigate Intercalation/exfoliation of micas in the polymer matrix WAXD measurements on pure nanoparticles and nanocomposites were performed. Fig. 1 shows the WAXD patterns for PET/mica nanocomposites. For mica powder, a peak appears at approximately 2θ= 4.84 (d 18.34 nm), corresponding to the basal interlayer spacing of the mica. Table 1 displays the parameters of XRD curves. The d-spacing of mica powder and nanocomposite sheets were determined by means of the Bragg’s equation. An efficient interaction between nanomica and polymer matrix allows the polymer chains to insert within the interlayer of the montmorillonite structure leading to intercalated/exfoliated structures.

The obviously larger interlayer distance of mica powder in PET nanocomposites demonstrates the efficiency of filling. A shift to lower angles of the characteristic diffraction peak in PET3%NM and PET5%NM suggests an increase in interlayer spacing or gallery of the mica, which is referred to as intercalation.

It seems that there would be a peak in 2θ < 2 for PET1%NM, which is not shown in 2theta range of 2-10, attributed to higher interlayer spacing of mica powder in PET nanocomposites containing 1% mica powder. By analyzing the spectra, it could be concluded that a part of mica stacks is well intercalated by polymer chains, resulting from higher 2theta values of these samples. So, the basal spacing of the layers (d-spacing) is not increasing for the filled systems. However, XRD should not be used as a stand-alone

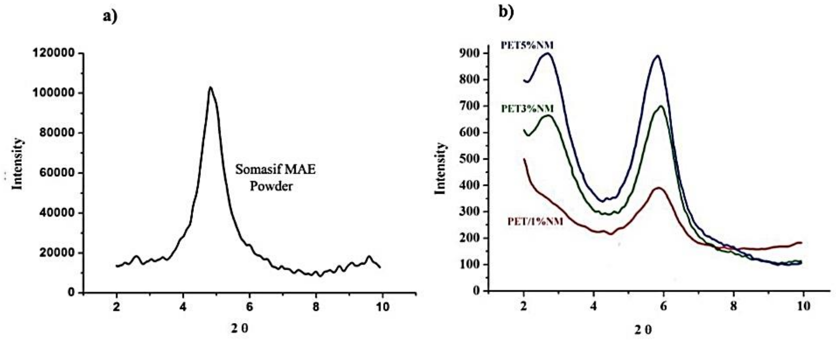


Fig. 1. WAXD analysis of mica powder (a) and PET/mica nanocomposites

Table 1. Values of 2theta and d-spacing for PET nanocomposites

	20	d-spacing (nm)
Somasif MAE powder	4.82	1.83
PET1%NM	5.84	1.51
PET3%NM	2.68 5.91	3.29 1.49
PET5%NM	2.65 5.81	3.33 1.52

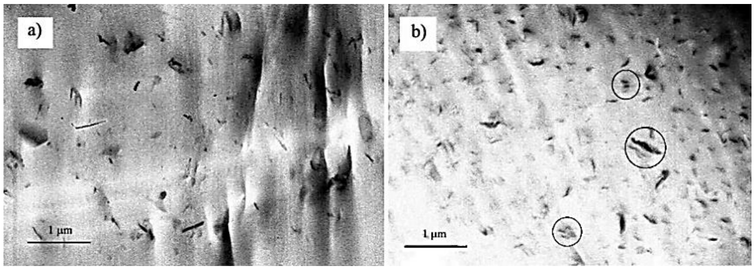


Fig. 2. TEM micrographs of PET nanocomposites containing 1 wt% (a) and 3 wt% (b) nano micas

characterization technique for polymer nanocomposites because it may give a misleading interpretation if there is a distribution of interlayer distances, a large amount of clay, uneven distribution of surfactant or random orientation of the clay (Vermogen et al., 2005; Masenelli-Varlot et al., 2007). The d-spacing may also be reduced if there has been surfactant degradation or compression of the polymer upon processing (Soon et al., 2009).

3.2. Morphology

TEM micrographs of PET nanocomposite films show a partially exfoliated/intercalated structure with dispersed tactoids. Intercalated structure of nanomicas in PET 3% NM sample indicated in a circle in (Fig. 2a). The individual delaminated silicate layers, especially at PET1%NM samples, reflect exfoliation structure. The micrographs of TEM confirm the results obtained by WAXD spectra.

3.3. Thermal analysis.

The values of glass transition temperature (Tg), melting temperature (Tm), crystallization temperature (Tc), enthalpy of crystallization (ΔHc), enthalpy of melting (ΔHm), and degree of crystallinity (Xc) are listed in Table 2. As shown in Table 1, the reduction of Tg for nanocomposites containing 1 and 3% mica nanoparticles is not very significant. Tg loss of PET5%NM nanocomposites could be attributed to slight degradation of the polymer matrix upon mixing with mica (Soon et al., 2009). Jordan et al. (2005) reported that incorporation of montmorillonite in the polymer matrix could cause a decrease on Tg of PET. Jordan et al. (2005) and Sunggi et al. (2007) reported that 2-3°C decrease in Tg of PET/clay nanocomposites could be related to molecular weight reduction of polymer after extrusion (Sunggi et al., 2007). The cooling and heating curves of the neat PET and its nanocomposites have shown in Fig. 3a and Fig. 3b, respectively. Compared to the neat PET, the crystallization temperatures (Tc) of nano composites shifted to higher temperatures. The characteristic values presented in Table 2 also show that the crystallization peak width (ΔTc) of the nanocomposites is narrower than the one of the neat PET. Similar results have been reported in the literature before for PET/clay nanocomposites. Bandyopadhyay et al. (2007) showed that addition of 1.3 and 2% organoclay Closite20A into PET matrix caused higher crystallization temperature compared to the neat polymer. Guan et al. (2008) showed that addition of 1, 2 and 3% MMT into PET matrix increased the crystallization temperature of nanocomposites. Another characteristic value of DSC analysis which considerably affected by mica nanoparticles is degree of crystallinity (Xc). PET nano composites containing 1% mica nanoparticles showed the highest Xc value (about 50% increase of Xc compared to the neat PET).

The results showed that when the concentration of modified mica nanoparticles elevated to 3 and then 5 wt %, Xc intended to decrease, suggesting that at high nano filler content, the mobility of polymer chain segments restricted. Dramatic increase of Xc and Tc of PET nanocomposites could be attributed to heterogeneous nucleation effect of mica nanoparticles which indeed reduce the need for meeting the barrier activation energy of thermal homogeneous nucleation. Therefore, crystallization process of nanocomposites can begin at higher temperatures than pure polymer and as a result of this phenomenon, the nucleation rate and consequently, the overall crystallization kinetics promotes. It is noteworthy that the crystallization behavior of nano composites depends on the nan filler loading content and its dispersion in the polymer matrix and is determined by the relative dominating status of the two aforementioned effects of nanoparticles on crystallization process i.e. nucleation effect and growth restriction effect. At low nanoparticle loading percent (≤1 wt% nanomica), the first effect dominates, Therefore, the Xc of these samples are the highest values among the others. While, increasing the nanofiller loading could alter the situation in which the hindrance of macromolecules motions become stronger. Another parameter which could affect the Xc of nanocomposites is intercalated/exfoliated structure of mica nanoparticles in the polymer matrix. Higher level of intercalation at PET3%NM and PET5%NM could hinder the polymer chains and diminish the polymer crystallinity.According to Fig. 3b, there was a slight increase in melting point of PET5%NM nanocomposites compared to the neat PET which could be related to wide crystallite size distribution of polymer matrix in the presence of high concentration of mica particles.

Table 2. The characteristic values of DSC analysis of neat PET and PET/Mica Nanocomposites

Sample	Tg (ºC)	Tm (ºC)	ΔHm (J/g)	Xc (%)	Tc (ºC)	ΔTc (ºC)	ΔHc (J/g)
PET0	80.50	249.20	35.48	33.48	187.50	24.3	37.73
PET1%NM	80.04	246.17	53.1	50.11	204.51	12.54	46.29
PET3%NM	79.68	249.48	44.61	42.10	207.60	11.20	43.34
PET5%NM	77.56	252.60	44.93	42.40	209.13	12.25	44.84

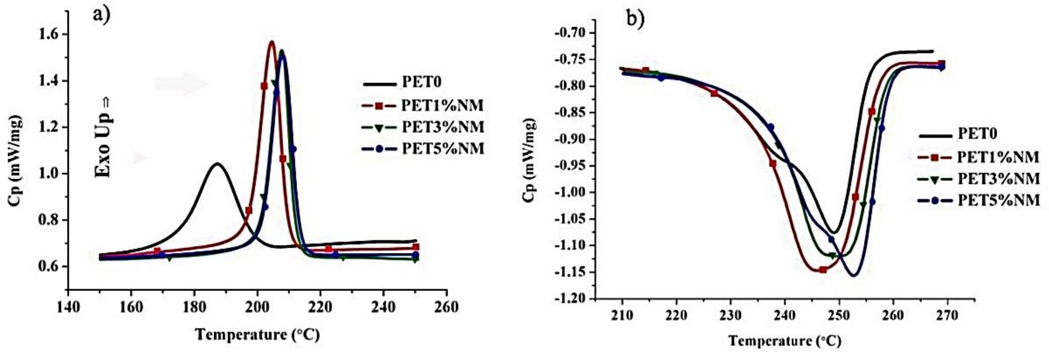
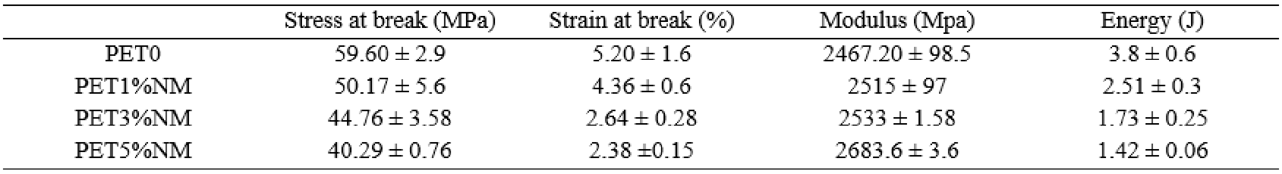


Fig 3. DSC curves of neat PET and its nanocomposites, cooling (a) and heating (b) processes

3.4. *Tensile testing*

The mechanical properties of the neat polymer and the prepared nanocomposites were listed in Table 3. It was expected that the elastic modulus of nano composites increases with the addition of mineral rigid mica nanoparticles, while the results show that there is not a significant difference in the magnitude of modulus. Although the modulus of nanocomposite showed a rising trend with increasing mica nanoparticles, but the large standard.

Table 3. Mechanical properties of neat PET and PET/Mica nanocomposites



	Stress at break (MPa)	Strain at break (%)	Modulus (Mpa)	Energy (J)
PET0	59.60 ± 2.9	5.20 ± 1.6	2467.20 ± 98.5	3.8 ± 0.6
PET1%NM	50.17 ± 5.6	4.36 ± 0.6	2515 ± 97	2.51 ± 0.3
PET3%NM	44.76 ± 3.58	2.64 ± 0.28	2533 ± 1.58	1.73 ± 0.25
PET5%NM	40.29 ± 0.76	2.38 ±0.15	2683.6 ± 3.6	1.42 ± 0.06

3.5. *Tensile testing*

The mechanical properties of the neat polymer and the prepared nanocomposites were listed in Table 3. It was expected that the elastic modulus of nano composites increases with the addition of mineral rigid mica nanoparticles, while the results show that there is not a significant difference in the magnitude of modulus. Although the modulus of nanocomposite showed a rising trend with increasing mica nanoparticles, but the large standard.

One of neat PET. It could be as a result of prevention effect of nanoparticles on strain hardening of the polymer chains after cold drawing. Strain hardening phenomenon plays a critical role in stabilizing polymers against strain localization and fracture, and reducing wear (Mergler et al., 2004). So, nano filler as heterogeneous solid nanoparticles could hinder the polymer stress induced crystallization and subsequently, decrease the resistance of polymer network against fracture. Another observed effect of the addition of nanoparticles on mechanical properties is the decrement of strain at break and dissipated energy or ductility (lost energy determined from the area under the stress-strain curve up to break). On the other word, the nano composite‘s ductility decreased with the addition of mica nanoparticles. Sanches-Solis et al. (2004) has shown that strain at break diminishes drastically for clay composites with their contents of 1, 2, and 3% for organo-modified and nonmodified montmorillonite (Sánchez-Solís et al., 2004). Higher intercalation level in PET3%NM and PET 5% NM nanocomposites compared to PET 1% NM samples would create more restrictions against polymer chains mobility and lead to lower ductility. These results reflect the behavior of fragile materials with generally small strain at break values. A comparison of the results reveals that mica nano fillers have a detrimental effect on the mechanical properties of the nano composites.

4. Conclusions

The results of DSC analysis showed that the crystallization temperature from the melt moved to higher temperatures with increasing nanoparticle loading. The degree of crystallinity first increases and then decreases with the incremental addition of nanoparticles. Both the crystallization rate and degree of crystallinity reach their maximum values in nanocomposite containing 1 %wt nanomicas. The results demonstrate that the addition of mica nano particles could significantly enhance the rate of crystallization of PET as a result of heterogeneous nucleation effect of nanofillers. The results of mechanical test indicated that addition of mica particles to polymer matrix caused to slight diminish of tensile strength and ductility of nano composites.

The shift of in characteristic diffraction peak to lower angles PET/mica nanocomposites related to intercalation/exfoliation structure. TEM results showed higher level of exfoliation in PET nanocomposites containing 1 wt.% mica nanoparticles, while with increasing the nanofillers from 1 wt.% to 3 and 5 wt.%, the level of intercalation increased.

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