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# *A Study on Morphology and Characterization of Polyethylene Terephthalate-Synthetic Mica Nanocomposites: Food Packaging Applications*

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*Abstract*—**Polymer nanocomposites are recently used for packaging materials because of their superior mechanical strength, increased heat-resistance and improved barrier properties against oxygen, carbon dioxide and water vapour. In this study, PET nanocomposites were prepared by melt blending of PET and synthetic micas (Somasof-MAE). The results of DSC analyses indicated that the influence of nanoparticles on crystallization of PET is considerable especially at 1 wt. % loading level of nanomicas. The addition of mica nanoparticles to polymer matrix caused to reduce of parameters elongation at break, tensile strength and dissipated energy. The results of WAXD analysis and TEM micrographs showed that when the content of nanomica in polymer matrix is 1 wt%, the mica layers partially exfoliated in the polymer matrix while at higher loading levels, the dominant morphology is intercalation.**

*Keywords-Poly(ethylene terephthalate); Somasif-MAE; Crystallization; Nanocomposite; Morphology*

## I. INTRODUCTION *(HEADING 1)*

Poly(ethylene terephthalate) (PET), produced from ethylene glycol and either terephthalic acid or dimethyl terephthalate, is commonly used as packaging material for drinking water, mineral water, carbonated beverages and edible oils. The strength and permeability properties of PET, its resistance to chemicals and its high degree of transparency are the main factors that make it superior than most of synthetic polymers. In the past decades polymers reinforced by micrometer fillers have been used to obtainhigher strength and stiffness, to improve solvent or fire resistance, or simply to reduce cost. However, the incorporation of these micro sized fillers had some drawbacks such as brittleness and opacity. Nanocomposites, for which at least one dimension of the filler is in the nanometer range, give an approach to overcome the limitations of traditional fillers. Besides, the mentioned properties improvements in nanocomposites are achieved at very low loadings of the nanoscale inorganic component (<5 wt %) while traditional microcomposites usually require much higher loadings (25-40 wt%) [1]. It is well-known that the structure, shape, size, concentration, specific surface area, concentration and adequate dispersion of nanoparticles impress the final properties of the nanocomposite [2]. PET/mica nanocomposite has attracted much attention because of its expectable great improvement in better gas impermeability, thermal resistance, mechanical properties, etc [3]. Because of the complexity of the PET/mica system, the effect of mica on the crystallization performance of PET is still poorly understood at present [4]. Most researchers considered that the nanoparticles dispersed in matrix acted as the nucleating agent for PET, so the crystallization rates of PET nanocomposites were increased [5, 6]. In this study, the effect of nanomicas on physical and mechanical properties of PET has been investigated.

## II. EXPERIMENTAL

### *A. Materials*

Pure poly(ethylene terephthalate)(PET) (blow molding grade) with intrinsic viscosity of 0.82 dL/g was provided by Shahid Tondgooyan Petrochemical Company (Iran). Somasif-MAE nanoparticles were supplied by CBC Company (Japan).

### *B. Methods*

PET nanocomposites containing 1, 3 and 5 wt% of nanomicas (coded as PET1, PET3 and PET5) were prepared via melt blending in a twin-screw extruder (Collin ESC-T10 model). 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 nanocomposite were dried in an oven at 170°Cfor 5 h before extrusion process. The prepared profiles were water cooled and then milled as pellets. Neat PET sample as reference material was prepared in the same procedure.

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 degree of crystallinity ($X_c$) of PET in the nanocomposites and the neat polymer specimens were calculated using (1):

$$X_c = (\Delta H_m / \Delta H_{m0}) \times 100 \qquad (1)$$

where $\Delta H_{m0}$ is the melting enthalpy of 100% crystalline PET, $\Delta H_{m0}$=105.97 J/g [7] and $\Delta H_m$ is the melting enthalpy of the samples.

The XRD patterns were recorded in an X-ray diffractometer (Simens D5000-Germany) at room

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temperature, using Cu Kα tube radiation with the wavelength of 1.5409oA, generated at 30 kV and 30 mA. The samples were scanned in the range of 2θ = 2–12owith a step size of 0.04o .The angular and layer spacing values are related through the Bragg's law:

$$\lambda = 2\ d \sin \theta \qquad (2)$$

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

Ultra thin sections (70–100 nm) of the nanocomposites 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).

Atomic Force Microscopy (AFM)

Tapping mode AFM micrographs were prepared using a Dualscope, DME Atomic Force Microscope (Denmark) equipped with a DS 95-50-E scanner and an AC probe.

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.

## III. RESULTS AND DISCUSSION

### A Thermal Analysis

The values of glass transition temperature ($T_g$),melting temperature ($T_m$), crystallization temperature ($T_c$), enthalpy of crystallization ($\Delta H_c$), enthalpy of melting ($\Delta H_m$), and degree of crystallinity ($X_c$) are listed in Table 1.

TABLE 1. THE CHARACTERISTIC VALUES OF DSC ANALYSIS OF NEAT PET AND PET/MICA NANOCOMPOSITES

| Sample | $T_g$ [°C] | $T_m$ [°C] | $\Delta H_m$ [J/g] | $X_c$ [%] | $T_c$ [°C] | $\Delta T_c$ [°C] | $\Delta H_c$ [J/g] |
|---|---|---|---|---|---|---|---|
| PET0 | 80.5 | 249.2 | 35.48 | 33.48 | 187.50 | 24.30 | 37.73 |
| PET1 | 80.04 | 245.07 | 53.10 | 50.11 | 204.51 | 12.54 | 46.29 |
| PET3 | 79.68 | 249.48 | 44.61 | 42.1 | 207.60 | 11.20 | 43.34 |
| PET5 | 77.56 | 252.60 | 44.93 | 42.4 | 209.13 | 12.25 | 44.84 |

As can be seen in Table 1, the reduction of $T_g$ for nanocomposites with increasing nanofiller content is not very significant except for PET5. Reduction of $T_g$ value in PET5 could be as a result of thermal degradation of polymer chains during the melt processing as well as high shearing forces of extruding process at the presence of rigid mica nanoparticles. Sunggi, et al. (2007) reported that 2-3°C decrease in $T_g$ could be related to molecular reduction of polymer after extrusion [8]. The cooling and heating curves of the neat sample and PET nanocomposites have shown in Figures 1 (a) and 1 (b), respectively.

Compared to the neat PET, the crystallization temperatures ($T_c$) of nanocomposites shift to higher temperatures. The characteristic values collected in Table 1 also show that the crystallization peak width ($\Delta T_c$) of the nanocomposites is narrower than the one of the neat PET. In this study, PET/mica nanocomposites showed the highest $X_c$ value at 1 wt% of nanomicas loading in the polymer matrix. However, when the content of nanomicas increases to 3 and 5 wt %, $X_c$ intends to decrease, suggesting that at high nanofiller content, the mobility of polymer chain segments is restricted significantly. Increase in $T_c$ could be due to the heterogeneous nucleation effect of nanoparticles surface on the crystallization of PET macromolecules which reduces 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. Consequently, the overall crystallization kinetics of nanocomposites promotes. According to Figure 1(b), there is a slight increase in melting point of nanocomposites compared to the neat PET.

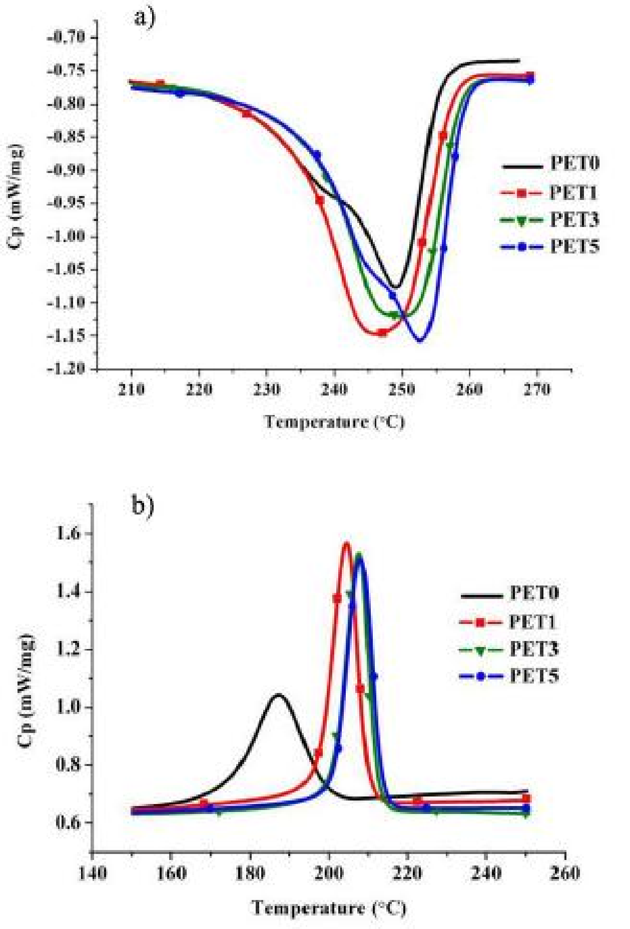

Figure 1. DSC curves of neat PET and its nanocomposites, cooling process (a), heating process (b)

### B. X-ray diffraction

To investigate Intercalation/exfoliation of micas in the polymer matrix WAXD measurements on pure nanoparticles and nanocomposites were performed. Figure 2 shows the

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WAXD patterns for the PET/mica nanocomposites. For mica powder, a peak appear at approximately $2\theta = 4.82$ (d 1.83 nm), corresponding to the basal interlayer spacing of the mica. Table 2 displays the parameters of XRD curves. The d-spacing of nanomicas and nanocomposite sheets were determined by means of the Bragg's equation. The obviously larger interlayer distance of nanomicas in PET nanocomposites demonstrates the efficiency of filling. A shift to lower angles of the characteristic diffraction peak in nanocomposites suggests an increase in interlayer spacing or gallery of the mica, which is referred to as intercalation.

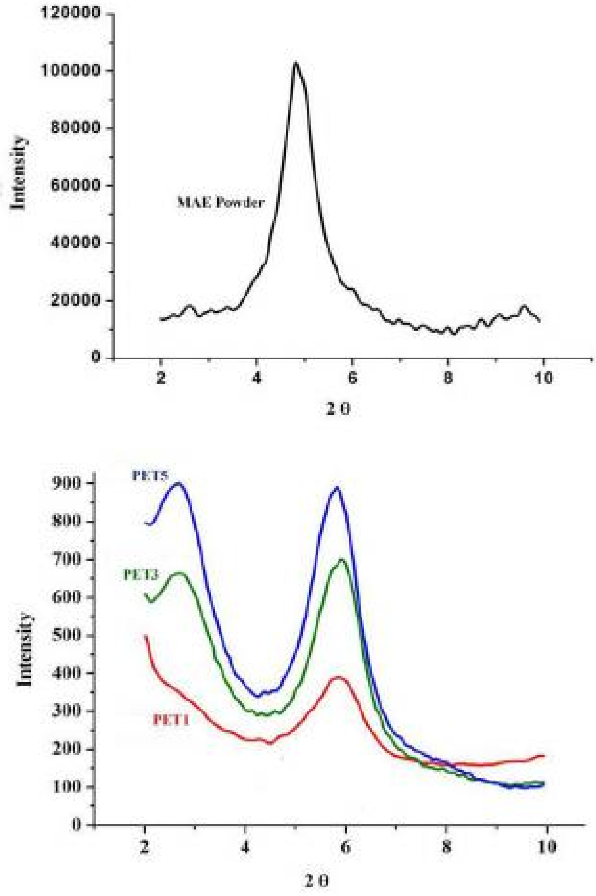

Figure 2. WAXD analysis of mica and PET/mica nanocomposites

It seems that there would be a peak at 2theta values lower than 2 for PET1 nanocomposites which could not be seen in this figure because of limited 2theta values range (2-12°). It could be referred as partially intercalation/exfoliation (intercalation of a certain number of tactoids) in the systems mixed with 1% of nanomicas. By analyzing the spectra, it could be concluded that a part of mica stacks are not well intercalated by polymer chains, resulting from higher 2theta values of these samples. So the basal spacing of the layers is not increasing for the filled systems.

TABLE 2. VALUES OF 2THETA AND D-SPACING FOR NANOMICA POWDER AND PET/MICA NANOCOMPOSITES

| | $2\theta$ | d-spacing (nm) |
|---|---|---|
| MAE Powder | 4.82 | 1.83 |
| PET1 | 5.84 | 1.51 |
| PET3 | 2.68<br>5.91 | 3.29<br>1.49 |
| PET5 | 2.65<br>5.81 | 3.33<br>1.52 |

XRD should not be used as a stand-alone characterization technique for polymer nanocomposites because it may give a misleading interpretation if there is a distribution of interlayer distances, a large amount of mica, uneven distribution of surfactant or random orientation of the mica [9]. The d-spacing may also be reduced if there has been surfactant degradation or compression of the polymer upon processing [10].

### C. *Morphology*

TEM micrographs of PET films containing 1 and 3 wt% Cloisite-20A nanoparticles show a partially exfoliated/intercalated structure with dispersed tactoids for PET3 samples.

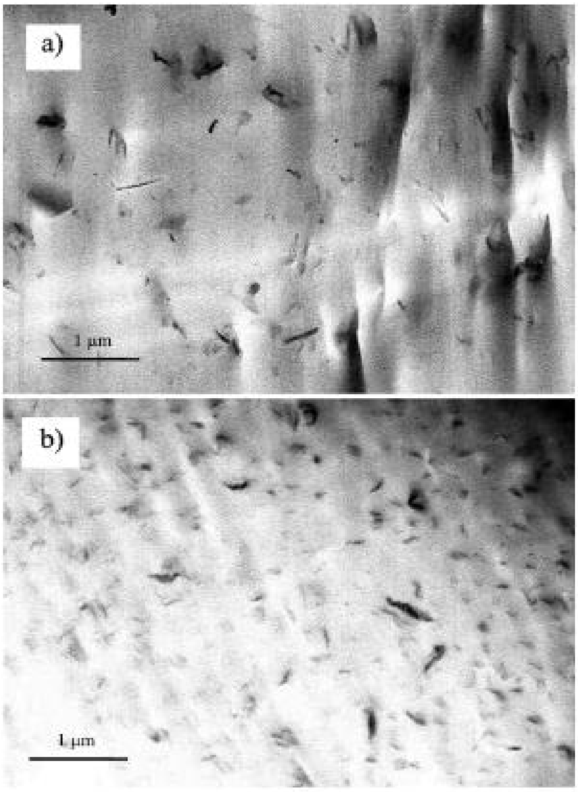

Figure 3. TEM micrographs of PET nanocomposites containing 1% (a) and 3% wt (b) nanomicas

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Intercalated structure of nanomicas in PET3 sample indicated in a circle in Figure 3 (b). The individual delaminated silicate layers, specially observed at 1% wt loading levels of nanomicas, reflect more exfoliated structure for PET1 samples. The micrographs of TEM confirm the results of WAXD analyzes.

One of the developments in tapping mode AFM is the use of the changes in phase angle of the cantilever probe to produce a second image, called a phase image or phase contrast image. This image often provides significantly more contrast than the topographic image and has been shown to be sensitive to material surface properties, such as stiffness, viscoelasticity, and chemical composition. In general, changes in phase angle during scanning are related to energy dissipation during tip-sample interaction and can be due to changes in topography, tip-sample molecular interactions and deformation at the tip-sample contact. In this study, the phase images of pure PET and its nanocomposite have been used to study polymer crystallization and nanomica dispersion, as well. Measurements were carried out in air at ambient conditions. Height and phase images were recorded simultaneously. Figures 4-6 show the height and phase images of PET nanocomposites. As it can be seen, phase image of samples exhibit three shade differences: black for amorphous phase of matrix, brown (light to dark) for the crystalline phase and matrix near the nanomica particles (interface region), and yellowish white for the nanomica phase. Cross-sectional lines were drawn over the scanned images to observe the size of crystals and mica nanoparticles (Figures 4c, 5c and 6c). These line spectra show some irregularities which indicate the variation in stiffness along the lines. The peaks of the PET1 spectrum in Figure 4c with y-values around 1.5V related to nanomica particles. The similar results observe in Figure 5 and 6 for PET3 and PET5, respectively. The bimodal peak in the line spectra of the nanocomposite confirms the presence of intercalated stacks in the bulk reflected the fact that the nanocomposite samples are not completely exfoliated.

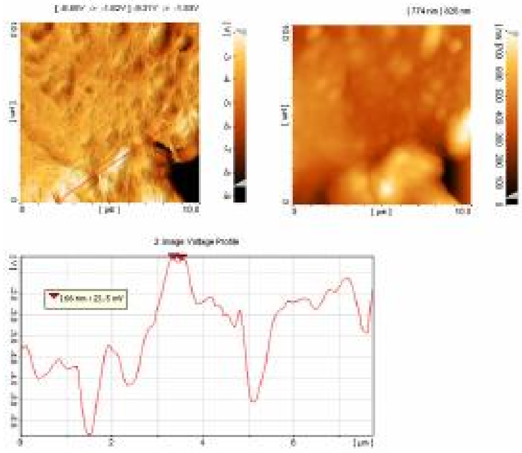

Figure 4. AFM phase image (a), height image (b) and the cross-sectional spectrum (c) of PET1

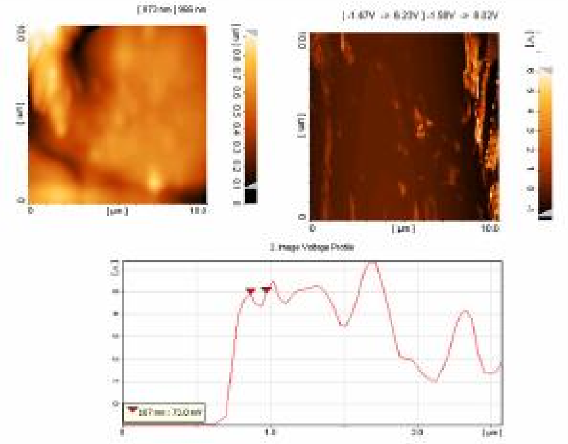

Figure 5. AFM phase image (a), height image (b) and the cross-sectional spectrum (c) of PET3

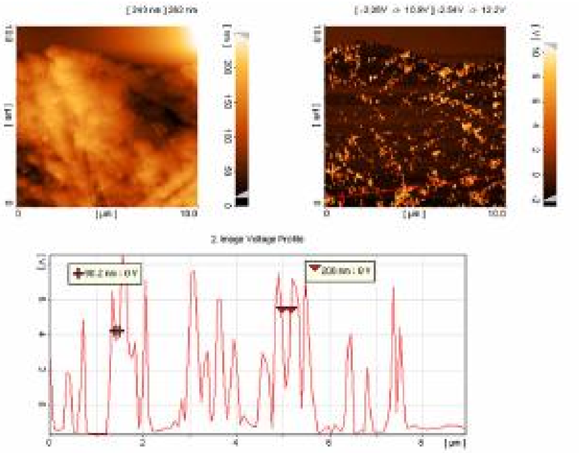

Figure 6. AFM phase image (a), height image (b) and the cross-sectional spectrum (c) of PET5

### *D. 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 nanocomposites increase with the addition of mineral rigid nanoparticle, 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 nanomicas loading, but the large standard deviation of the modulus causes the results to overlap each other.As can be found, the tensile strength of nanocomposites decreased compared with the 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. Nanofiller as heterogeneous solid nanoparticles could hinder the polymer stress induced crystallization and subsequently, decrease the resistance of polymer network against fracture.

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TABLE 3. MECHANICAL PROPERTIES OF NEAT PET AND PET/MICA NANOCOMPOSITES

| | Stress at break (Mpa) | Strain at break (%) | Modulus (Mpa) | Energy (J) |
|---|---|---|---|---|
| PET0 | 59.6 ± 2.9 | 5.2 ±1.6 | 2467.2± 98.5 | 3.8 ± 0.6 |
| PET1 | 50.17 ± 5.6 | 4.36 ± 0.6 | 2515.97 ± 97 | 2.51 ± 0.3 |
| PET3 | 44.765 ± 3.58 | 2.64 ± 0.28 | 2533.96 ± 1.58 | 1.73 ± 0.25 |
| PET5 | 40.29 ± 0.76 | 2.38 ± 0.15 | 2683.60 ± 3.6 | 1.42 ± 0.06 |

Another attractive 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 nanocomposite's ductility decreased with the addition of nanomicas. Sanches-Solis et al. has shown that strain at break diminishes drastically for nanocomposites with their contents of 1, 2, and 3% MMT nanoparticles [11]. These results reflect the behavior of fragile materials with generally small strain at break values. A comparison of the results reveals that nanofillers have a detrimental effect on the mechanical properties of the nanocomposites.

## IV. CONCLUSION

The results of DSC analysis showed that the crystallization temperature of nanocomposites increase compared to the neat PET. The percent of crystallinity first increases and then decreases with the incremental addition of nanoparticles. Addition of nanomicas could significantly enhance the rate of crystallization of PET as a result of heterogeneous nucleation effect of nanomicas. The results of mechanical test indicated that addition of nanomicas to polymer matrix caused to slight diminishes of tensile strength and ductility of nanocomposites. The XRD patterns showed a shift to lower angles of the characteristic diffraction peak in PET/mica nanocomposites. TEM results demonstrated that the ratio of intercalated to exfoliated structure increase with increment of loading level of nanomicas.

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