Nanocomposites

Preparation and characterization of poly(ethylene terephthalate)/hyperbranched polymer nanocomposites by melt blending

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Abstract In this paper, nanocomposites of polyethylene terephthalate (PET) including polyesteramide-based hyperbranched polymer, or PET/Hyperbranched polymer nanocomposites, have been prepared via melt blending method with different hyperbranched polymer contents. In addition, morphology, surface structure, and thermal properties of these nanocomposites and virgin PET were studied by atomic force microscopy, attenuated total reflection Fourier transform infrared spectroscopy and differential scanning calorimetry (DSC), respectively. Dynamic mechanical analysis experiments in solid state were carried out to follow the effect of hyperbranched polymer on the dynamic mechanical properties of these nanocomposites. The structure of the nanostructured hyperbranched polymer was also studied by small-angle X-ray scattering. The rheometric mechanical spectroscopy results showed that the hyperbranched polymer as a modifier decreased the complex viscosity and enhanced liquid-like behavior. This happened more significantly by increasing the content of hyperbranched polymer. The DSC analysis results revealed that crystallinity and glass transition temperature decreased by adding the amount of hyperbranched polymer.

Keywords Polyethylene terephthalate (PET), Hyperbranched polymer, Nanocomposite, Melt blending

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Introduction

Polymer nanocomposites are a new class of engineering materials and a method of enhancing polymer properties using nanoscale modifiers, which have found many applications in various industrial fields such as automotive, construction, and packaging.¹ Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. They show extraordinary advantages in mechanical, thermal, optical, and chemical properties in comparison with virgin polymers or conventional macro- and microcomposites. These enhancements have attributed to the small size and high surface-to-volume ratio of the nanoscale materials.²,³ Melt intercalation (blending),⁴ solgel,⁵ and in situ polymerization⁶ are the different methods to prepare polymer nanocomposites. The melt blending method is the most useful approach for industrial applications due to the absence of environmentally harmful solvents, and compatibility with current industrial compounding and processing techniques. In this method, polymer and modifier are combined in internal batch mixer or in a twin screw extruder under shear and above the softening temperature of the polymer.⁷

Poly(ethylene terephthalate) (PET) is a linear polyester widely used in different applications such as food and beverage packing, textile fiber production, automotive components, and molded goods because of its relatively good physical, mechanical, barrier, and optical properties.⁸ Despite many excellent properties of PET, the disadvantages such as the lack of functional groups, hydrophobic nature, highly compact molecular structure, and relatively high crystallinity have limited its application. These deficiencies result in low dyeability⁹,¹⁰ as an important parameter in textile usages. Physical blending of PET with other polymers or additives containing functional groups with lower crystallinity has been the most frequent method of modification.¹² One of these approaches is incorporation of hyperbranched polymer as a modifier into the PET matrix in order to improve dyeability of PET.¹² Apart from the improvement in dyeability, the blend of this hyperbranched polymer with PET attained higher adsorption properties due to the formation of free volume between chains of
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PET that is related to the presence of hyperbranched polymer as a modifier.\textsuperscript{13,14} Hyperbranched polymers exhibit characteristics that are very different from those of linear polymers, for example, low viscosity, high solubility, and high density of the functional end-groups.\textsuperscript{15} These particulate polymers provide various kinds of functional end groups, from hydrophilic to hydrophobic and from reactive to non-reactive.\textsuperscript{16,17} The presence of numerous terminal groups is a typical characteristic of hyperbranched polymers. The terminal groups can affect the properties of the polymer and make such polymers attractive candidates for many material applications including targeted drug delivery, rheology modifiers, plasticizers, supporting material for catalysts, and versatile scaffolds for further synthesis.\textsuperscript{18,19} The content of the terminal groups in the hyperbranched polymer is a key index for polymer grafting, drug conjugation and catalyst supports.\textsuperscript{20} These polymers also have the ability of changing and disordering the crystalline structure of PET leading to change in physical and mechanical properties. Hence, it is a matter of great importance to study the effect of the modification process on the physical and mechanical properties of the final blends.

We have previously reported\textsuperscript{13,14} the adsorption properties of a disperse dye toward PET sheets modified using various loads of a hyperbranched polymer in terms of thermodynamic and kinetic parameters. According to these findings, the adsorption of the dye on the modified PET sheets was much higher than that of the virgin PET one. Eventually, the results indicated that the color yield of the virgin PET was improved by incorporating hyperbranched polymer.

In this study, PET nanocomposites with hyperbranched polymer were prepared via melt blending method using an internal mixer and the viscoelastic behavior, thermal and dynamic mechanical properties of these nanocomposites and virgin PET were investigated. The aim was to demonstrate the effect of adding various amounts of hyperbranched polymer on the morphology, thermal and dynamic mechanical properties of PET/hyperbranched polymer nanocomposites.

**Experimental**

**Materials**

In this work, polyethylene terephthalate chips (Zimmer Specification, Germany) with an intrinsic viscosity of 0.60 dl g\(^{-1}\), water content of 0.25 wt %, and melting point of 250 °C were purchased from Shahid Tondgoyan Petrochemical Company, Mahshahr, Iran.

Hyperbranched polymer (Hybrane H1500, \(M_n = 1500\), designated as H, possessing only hydrophilic hydroxyl end groups) was kindly supplied by DSM Company. Fig. 1 shows the schematic structure of this polymer.

All chemical reagents were of analytical grade and were used without further purification.

**Preparation of nanocomposites via melt blending method**

In this study, all the nanocomposites including 0.5, 1, 2, and 3 wt % of Hybrane H1500 with PET, which will be designated as PET + 0.5H, PET + 1H, PET + 2H, and PET + 3H were formed by melt blending method. Prior to any processing, all materials were dried for 24 h at 80 °C in an oven. Mixing was carried out using an internal mixer (Brabender Plasticorder W50, Germany), equipped with a Banbury type rotor design, which was maintained at a temperature of 250 °C, and a rotor speed of 60 rpm. Mixing continued until the rotor torque reached a constant value. The overall time of the mixing process was about five minutes. After having discharged, sheets with one mm in thickness were prepared by hot pressing the blended mixtures. Each sample was pressed for five minutes at a pressure of 140 bar and a temperature of 250 °C. The press was subsequently cooled to room temperature using cold water.

**Characterization**

**Atomic force microscopy**

Tapping mode atomic force microscopy (AFM) (Ambios Tech (USA)) was used to characterize the samples. A scanning probe microscope was operated under ambient conditions with commercial silicon microcantilever probes. Manufacturer’s values for the probe tip radius and probe spring constant were in the ranges of 5–10 nm and 20–100 N/m, respectively. Phase images were obtained using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of 60 ± 5 nm. This technique was used to study the homogeneity of the PET/H nanocomposites.

**Attenuated total reflectance**

Attenuated total reflectance (ATR-FTIR) measurements on samples were carried out on a Bomem Hartman & Braun FTIR Spectrophotometer. The samples were analyzed in the reflectance mode in the range of 400–4000 cm\(^{-1}\) at room temperature.

**Differential scanning calorimetry**

Thermal properties and crystallinity of virgin PET and PET/H nanocomposites were determined by a Mettler Toledo differential scanning calorimeter instrument under N\(_2\) atmosphere. The sample pan and the reference pan were heated from 0 to 300 °C at the rate of 10 °C/min. The glass transition temperature (\(T_g\)), the melting point (\(T_m\)), the cold crystallization (\(\Delta H_c\)), and the heat of melting (\(\Delta H_m\)) were determined from the differential scanning calorimetry (DSC) thermographs. The glass transition temperature and melting point were obtained from the midpoint of the transitions. The heat of melting, \(\Delta H_m\), and cold crystallization, \(\Delta H_c\), were determined by integrating...
the areas under the peaks. The percent crystallinity was then calculated from the following relation:

\[
\text{Crystallinity\%} = \frac{\Delta H_m - \Delta H_f}{\Delta H_{\text{f100\%}}} \quad (1)
\]

where heat of melting and cold crystallization are in J g\(^{-1}\). The term \(\Delta H_{\text{f100\%}}\) (135.8 J g\(^{-1}\)) was a reference value and represented the heat of melting of a 100\% crystalline PET.\(^{21}\)

**Dynamic mechanical thermal analysis in the melt state (rheometric mechanical spectrometry)**

A MCR300 rheometric mechanical spectrometer was utilized to perform the measurements in the melt state. The temperature was adjusted to 200 °C to equal the processing temperature. Parallel plate geometry was used and deformation was applied on the molten samples in the frequency range 0.1–500 s\(^{-1}\). The strain was kept at 10\% to keep the material in its linear viscoelastic region. Preliminary experiments confirmed the linearity.

**DMA in the solid state (dynamic mechanical thermal analysis)**

Dynamic mechanical thermal analysis (DMA) was carried out by means of a Tritec2000 in rotational mode, in order to study the thermal and mechanical properties of samples. Deformation was applied at a frequency of 1 Hz and strain of 0.1\%. The preliminary tests confirmed that the selected strain was in the linear viscoelastic zone. The temperature was increased at a rate of 5 °C/min from 0 to 250 °C.

**Small-angle X-ray scattering**

Small-angle X-ray scattering (SAXS) was used in order to study the size and shape of nanoparticles. SAXS works on the basis of difference in electronic density in materials. On the basis of this difference, X-ray beam in passing through material scattered in small angles. SAXS measurements were carried out using a 53-MICRO diffractometer (Hecus, Austria) equipped with a copper radiation source (\(\lambda = 0.154\) nm) operating at 40 kV and 49 mA. The beam was monochromated by a silicon monochromator and collimated by a set of slits defining pinhole geometry. A one-dimensional position sensitive detector was used to record the SAXS intensity as function of the modulus of the scattering vector. The data were recorded in the reflection mode over a 2θ range of about 0–10° at a rate of 0.04 °C/min.

**Results and discussion**

**Morphological analysis: atomic force microscopy results**

AFM is one of the most powerful techniques for nanoscopic characterization of surfaces. Usually, obtaining information on the sample's morphology is straightforward, since AFM images primarily contain topographical information.\(^{22}\) The AFM images which reported in Fig. 2 are the original scans without any filtering. The phase contrast image for virgin PET sheet showed the smooth and uniform surface without any nanoparticle. For nanocomposites using 1 and 2 wt % hyperbranched polymer, a few numbers of light-colored particles are observed indicative of the existence of hyperbranched polymer. These observations confirm that no aggregates are formed and there seems a complete homogeneous surface. However, some aggregations are seen in nanocomposite containing 3 wt % hyperbranched polymer. Accordingly, the PET/H nanocomposites containing up to 2 wt % hyperbranched polymer are more homogenous.

**Structural studies**

The ATR-FTIR spectra was recorded to assess structural changes, if any, made in the blended samples of the alteration of existing functional groups as a consequence of the presence of hyperbranched polymer. Fig. 3 shows the spectra of the virgin PET sheet (3b) and those of the pure hyperbranched polymer (Fig. 3a) as well as the blended samples. The ATR-FTIR results show that the presence of hyperbranched polymer is notable in all the nanocomposites. In almost all cases, the presence of the hyperbranched polymer is proved by the presence of the peaks at 1400–1500 and 1600–1700 cm\(^{-1}\) that is related to amide C=O stretching.

Moreover, virgin PET sheet shows a sharp peak for OH-stretching at 3400 cm\(^{-1}\) due to the presence of terminal hydroxyl groups in the chain. After blending, the intensity of this peak increased reflecting the increase in hydroxyl groups in the treated samples. Similarly, a broad peak at 3500–3600 and 3600–3770 cm\(^{-1}\) also increased in the treated samples, which indicates the enhanced hydrogen bonding among hydroxyl moieties existed in the samples containing hyperbranched polymer.

**Crystallinity and glass transition temperature: differential scanning calorimetry results**

The thermal properties of the blended PET samples may be changed when hyperbranched polymer as an additive was added to the virgin PET. This change can be possibly used to probe the existence of the hyperbranched polymer in the blended PET samples. Fig. 4 presents DSC diagrams for the virgin and blended PET samples during heating at a rate of 10 °C/min. It can be found from Fig. 5 that the glass transition temperature of virgin PET sheet was 80.07 °C and changed to 76.7, 73.96 and 72.49 °C when 0.5, 1 and 2 wt % hyperbranched polymer was added the virgin PET, respectively. It is concluded that as the content of hyperbranched polymer increased, the glass transition temperature decreased. This means that samples became more flexible upon addition of the amorphous hyperbranched polymer. For further investigations, the crystallinity for each sample was calculated from the heat of fusion during heating as shown in Fig. 5 and it decreased with the addition of hyperbranched polymer content in the virgin PET. As shown in Fig. 5, the crystallinity had reached 44% in virgin PET sheet. When 0.5, 1, and 2 wt % hyperbranched polymer was added to the virgin PET sheet, the crystallinity content of PET dropped to 41.65, 40, and 38\%, respectively.

**Dynamic mechanical thermal analysis in the melt state: RMS results**

Fig. 6 shows diagrams of the complex viscosity \(\eta^*\) and storage modulus \(G^*\) versus frequency of applied deformation, \(\omega\), for the virgin and blended PET samples. It is clear from the
ball-bearing effect and reducing free volumes between the matrix chains can be mentioned. In one study, the reduction of viscosity in blended samples with hyperbranched polymer has been attributed to two factors. The first factor involved the interference of physical entanglements between linear diagrams that virgin PET showed higher viscosity and modulus values compared with blended samples. The hyperbranched polymers as a subgroup of dendritic polymers were very well known for their reducing effect on viscosity. Different mechanisms have been proposed by researchers among which the

Figure 2  a–d AFM images a virgin PET, b PET + 1H, c PET + 2H, and d PET + 3H (right 1micron and left 5 micron)
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hyperbranched polymers due to their packed structure.24 The hyperbranched polymers also exhibit Newtonian behavior, indicating the absence of physical entanglements in these systems.25 Therefore, it is predicted that by adding hyperbranched polymer to PET, Newtonian behavior can be manifested. As can be seen in Fig. 6a, PET + 2H sample shows Newtonian behavior, that is, a constant viscosity, while virgin PET and PET + 1H samples show shear thinning trend.

Dynamic mechanical thermal analysis in the solid state: dynamic mechanical thermal analysis results

DMTA is one of the most versatile methods to simulate the conditions both on the production line and in operational use. Apparently, the viscoelastic behavior of the material obtained from the DMTA data originates from its nanoscale structure. Therefore, monitoring the nanostructure can provide valuable information to gain a better understanding of the mechanisms through which the properties have changed.23,26,27 DMTA can be used to predict and evaluate application performance of the nanocomposites. It was shown in the rheological studies that the hyperbranched polymers reduce the viscosity. In other words, these molecules facilitate motions of the PET chains on each other in the melt state. Utilizing the same logic, they had the same characteristics in the solid state as deduced from the reduced \( T_g \) of the blended samples. This means that hyperbranched polymers were spread between PET chains and reduced entanglements. As a consequence, the degree of freedom of the chains increased and the chains were more capable of moving. The DMTA results of all samples are presented in Figs. 7 and 8 in terms of temperature dependence of the loss factor (tan delta) and the storage modulus (\( G' \)), respectively. Fig. 7 shows that blended samples had only one relaxation peak, the primary relaxation peak associated with

![Figure 3](image-url) a–e ATR-FTIR spectra of virgin PET b, pure hyperbranched polymer a, PET + 0.5H c, PET + 1H d, and PET + 2H e.

![Figure 4](image-url) DSC diagrams of virgin and blended PET samples
increase in the hyperbranched polymer content, the glass transition temperature of blended PET sheets tended to shift towards lower temperatures. Thus, the decreased value of \( T_g \) resulting on the addition of the hyperbranched polymer confirms that the mobility of polymeric chains greatly increased which in turn affected the softer and more flexibility of the samples.

Storage modulus (\( G' \)) can be used to evaluate the hardness of polymer materials. Fig. 8 reports the storage modulus of samples versus temperature. The trends of storage modulus curves were qualitatively similar. All the storage modulus versus temperature curves experienced a gradual decline in storage modulus with temperature increasing from 0 to around 80 °C and then a decrease occurred in modulus for virgin PET and all the blended ones. Storage modulus indicates the strength of materials against deformation at different temperatures under oscillation forces. Therefore, higher storage modulus means that sheets can resist against deformation. As can be seen in Fig. 8, increasing hyperbranched polymer’s content decreases the storage modulus. This can be attributed to a more compacted structure of virgin PET sheet in comparison with blended PET sheets.

Small-angle X-ray scattering data evaluation

According to the SAXS theory, the SAXS signal is produced by electron density inhomogeneity in the sample. The angle between transmitted beam and scattered beam is scattering angle.28 The scattering intensity is proportional to the square of the density differences between the constituting phases. By plotting scattering intensity versus scattering vector in logarithmic scale, two regions are achieved. Very small angles are Guinier region and follows Equation (2):28

\[
I(q) \propto G \exp(-q^2 R_g^2/3)
\]

where \( I(q) \) is the scattering intensity, \( R_g \) is the gyration radius which indicates a measure of the mean square distance of the scattering centers within particle domains from the center of gravity and \( q \), the scattering vector is defined as Equation (3):28

\[
q = \frac{4\pi}{\lambda} \sin(\theta)
\]

where \( \lambda \) is the X-ray wavelength and \( \theta \) is the scattering angle. The \( R_g \) is related to the size of particle and could be calculated from the slope in the linear region of a plot of \( \ln(I(q)) \) versus \( q^2 \).

A log–log plot of SAXS data, called Porod plot, comforted in other region and could give an indication of the fractal nature of particle, specifically if the system displays a mass or surface fractal behavior.29 Porod formula30 is shown in Equation (4):

\[
I(q) \propto q^{-\alpha}
\]

where \( \alpha \) is the power exponent obtained from the slope in the linear region of a double logarithmic plot of \( \ln(I(q)) \) versus \( q^2 \). The power exponent is simply related to the fractal characteristics; thus, it is a measure of the compactness or shape of materials such as a sharp and smooth surface between the two regions of different electron density. An increase in the fractal dimension implies more compact structure of domains. For \( 1 < \alpha < 3 \), objects are considered as mass fractal in three-dimension and fractal dimension is determined by \( D = -\alpha \). Mass fractal
no particles exist in virgin PET. The Guinier plot and Porod plot of SAXS data for the blended PET showed a linear region (Figs. 9 and 10). The $R_g$ and $D$ are obtained from the slope of the curves. The power law exponent ($D$) and $R_g$ for blended PET dimensions are always less than the dimension of the space in which the fractal exists, which implies that the mass of the particulate increases less rapidly than the volume it occupies. For $3 < \alpha < 4$, objects are surface fractal with fractal dimension equal to $D_s = 6 - \alpha$. Fractal surfaces, on the other hand, have the property that the surface area $S$ varies as a non-integer power of the length. In other words, $D_s$ is a measure of surface roughness of the scattering particle. SAXS profile of virgin PET exhibited a very low scattering intensity and this means that fragments are always less than the dimension of the space in which the fractal exists, which implies that the mass of the particulate increases less rapidly than the volume it occupies. For $3 < \alpha < 4$, objects are surface fractal with fractal dimension equal to $D_s = 6 - \alpha$. Fractal surfaces, on the other hand, have the property that the surface area $S$ varies as a non-integer power of the length. In other words, $D_s$ is a measure of surface roughness of the scattering particle. SAXS profile of virgin PET exhibited a very low scattering intensity and this means that
were 2.48 and 12.6 nm, respectively. The power law exponent for the sample was lower than 3 and suggesting blended PET had mass fractal behavior. So based on this result, the shape of hyperbranched polymer can be imagined to look similar to Fig. 11.

Conclusion

Successfully, PET/hyperbranched polymer nanocomposites have been prepared via melt blending method. AFM studies were performed to examine the surface morphology for virgin PET and nanocomposites. According to the observations made by AFM, dispersion of the hyperbranched polymer in the nanocomposites containing 0.5, 1, and 2 wt % hyperbranched polymer was uniform, but some aggregations were observed in sample containing 3 wt % hyperbranched polymer. Thermal analysis by DSC was used to probe the effect of hyperbranched polymer on crystallinity and glass transition temperature of nanocomposites. The presence of the hyperbranched polymer decreased the glass transition temperature as well as the crystallinity of the nanocomposites compared with the virgin PET. It was concluded from the rheological data that the flowability of nanocomposites was enhanced. Solid-state DMA results clarified that microscopic properties such as \( T_g \) and viscosity were changed as a result of the melt blending process. SAXS measurements determined the size and shape of hyperbranched polymer in nanocomposites.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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