

Effect of ZnO Type and Concentration on the Morphology, Thermal, and Mechanical Properties of Poly(ether ester)/ZnO Composites

Hande Celebi,¹ Goknur Bayram,² Aydin Dogan³

¹Department of Chemical Engineering, Anadolu University, Eskisehir 26555, Turkey

²Department of Chemical Engineering, Middle East Technical University, Ankara 06800, Turkey

³Department of Materials Science and Engineering, Anadolu University, Eskisehir 26555, Turkey

Correspondence to: H. Celebi (E-mail: handed@anadolu.edu.tr)

ABSTRACT: Poly(ether ester) (PEE) copolymers were synthesized in a two-stage process involving transesterification and polycondensation. The synthesized copolymer and the zinc oxide (ZnO) were used in composite preparation by melt compounding. The influence of ZnO type and concentration on the morphology, thermal and mechanical properties of the composites were studied. DSC and XRD analyses indicated that crystallinity of composites was slightly reduced with ZnO content. Homogeneous dispersion of fillers in the polymer matrix was observed through morphological analyses. While in general tensile strength and elongation at break values of the composites decreased with increasing ZnO content, elastic modulus values increased with the addition of ZnO. Moreover, ZnO particles were modified with poly(*N*-vinyl pyrrolidone) and a slight improvement in mechanical properties was observed, respectively over the composites containing unmodified particles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3417–3424, 2013

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INTRODUCTION

Thermoplastic elastomers, a class of engineering polymers, possess the properties of vulcanized rubbers and can be processed like typical thermoplastic elastomers.¹ These elastomers are commercially produced worldwide and their application areas range from automobile parts and structural materials of sports equipments to industrial rollers and hoses.²

A series of thermoplastic elastomers consisting of amorphous noncrystalline poly(tetramethylene oxide) (PTMO) and semi-crystalline poly(butylene terephthalate) (PBT) have found uses in which they combine good mechanical properties, low temperature flexibility, thermooxidative stability up to high temperatures, creep resistance, melt stability and resistance against many chemicals.^{3,4} These copolymers are named as poly(ether ester)s, PEEs that contain two segments: soft and hard segments formed by PTMO and PBT chains, respectively. The domains of the crystalline hard segments act as physical crosslinks and are interconnected by a matrix of soft segments.³ Each segment reveals its own characteristic properties in the copolymer.¹

Zinc oxide (ZnO) is a potential candidate for filler selection in polymer composites due to its versatile properties, ease of preparation and low cost. It has outstanding physical and chemical properties; chemical stability, low dielectric constant, high lumi-

nous transmittance, high catalytic activity, antibacterial effect, intensive ultraviolet, and infrared absorption. Therefore, with these properties, zinc oxide is preferred in various applications, which include catalysts, semiconductors, varistors, surface acoustic wave devices, gas sensors, transducers, sunscreens, and dye-sensitized solar cells based on ZnO films, antibacterial and UV-shielding materials.^{5,6}

Incorporation of inorganic fillers into the poly(ether ester) is an effective route for preparing new materials with enhanced properties. Because of the developments in nanotechnology, the concern in the studies has become on how the properties of polymer matrices change with the size of incorporated filler.⁷ However, obtaining a uniform dispersion in the composite is a difficult issue to solve because of the poor interfacial adhesion between the matrix and the filler. To overcome this problem and also to improve the properties of the composite, surface of the fillers are modified with a properly selected coupling agent. Zhou et al. used three different silane coupling agents and a titanate coupling agent to modify ZnO whiskers.⁸ Hong et al. treated the ZnO particles with a silane coupling agent which was followed by grafting polymethyl methacrylate onto the ZnO particles.⁹

Amorphous poly(*N*-vinyl pyrrolidone) (PVP) is soluble in water and alcohol and it has high diffusion/sorption ability compared

with the polymers with the same group, $[-NH-]$.¹⁰ Because of the basic nature of its functional group, PVP is a strong proton acceptor. On the other hand, PTMO is a proton donor like polyethylene glycol (PEG) since it has two hydroxyl groups at the chain ends. It has been reported by some authors that hydrogen bonding is formed between the hydrogen atom of PEG terminal group and oxygen atom of carbonyl group of PVP chains and that results in PVP-PEG miscibility.^{11,12} At the same time, formation of a hydrogen bond between the oxygen in the amide group of PVP and hydroxyl group on the surface of ZnO is expected so that agglomeration of ZnO particles is prevented.

The studies in the literature were mainly on PEE/carbon nanotube composites.^{13,14} Furthermore, magnetic nanocrystallines were embedded in PEE matrix and magnetic interactions in these nanocomposites were studied.¹⁵ Also, PBT-PTMO polymer composites containing carbon-covered nickel (Ni/C) were synthesized.¹⁶ The effect of the Ni/C filler on the thermal and mechanical properties of the polymer was presented. Zhou and Burkhart investigated the thermal and mechanical properties of PEE-based thermoplastic elastomers, which were filled with titanium dioxide (TiO₂) nanoparticles.¹⁷ To the best of our knowledge, there has been no previous study in the open literature on the effect of ZnO size and concentration on the structural properties of PEE/ZnO composites.

In this study, the poly(ether ester) composite materials were prepared by the addition of ZnO fillers into the PEE matrix, which was synthesized by melt polycondensation in the molten state. Two kinds of ZnO at different sizes were commercially obtained, namely, nano scale ZnO (n-ZnO) and submicron scale ZnO (m-ZnO). Moreover, ZnO particles (s-ZnO) were synthesized by homogeneous precipitation method. These particles were modified with PVP to improve the compatibility between the filler and the matrix and named as pvp-ZnO. The mechanical, thermal properties, and morphologies of the resulted composites were investigated.

EXPERIMENTAL

Materials

In this study, dimethyl terephthalate (DMT), poly(tetramethylene oxide) (PTMO) and 1,4-butanediol (BD) were used for the synthesis of copolymer. Some of the physical properties and manufacturer information of these materials are shown in Table I. The synthesis took place in the presence of a catalyst, tetra-*n*-butyl orthotitanate and a thermal stabilizer, Irganox B 225.

The reaction was carried out in a one liter stainless steel reactor (Parr Instruments, USA) with a nitrogen inlet, a condenser and a mechanical stirrer.

Synthesis of PBT-PTMO Copolymers and ZnO Particles

PEE's were synthesized by condensation polymerization in two stages, e.g., (i) transesterification of DMT with hydroxyl groups of PTMO and 1,4-BD (ii) low pressure melt polycondensation at high temperature.¹⁸

ZnO nanoparticles were synthesized by the homogeneous precipitation method by mixing aqueous solutions of zinc nitrate (Zn(NO₃)₂) and hexamethylenetetramine (HMT).⁵ Commercially available reagents for ZnO synthesis were purchased from Merck and used as received. In ZnO precipitation reaction, the Zn²⁺ ions were produced from the dissociation of the starting material, Zn(NO₃)₂ in aqueous solution. HMT was an ammonium-hydroxide source in the formation of zinc hydroxide. ZnO was formed from the Zn²⁺ cations surrounded by OH⁻ ions followed by condensation. Furthermore, the synthesized particles were modified with PVP to increase the interaction between the polymer and nanoparticles. The sizes of synthesized ZnO (s-ZnO) and PVP modified ZnO (pvp-ZnO) were measured using a Malvern Zetasizer Nano Instrument (UK) as 315 and 350 nm, respectively. Aside from synthesizing new particles, ZnO particles at different sizes were purchased. Their dimensions and manufacturers are listed in Table II.

Preparation of PEE/ ZnO Composites

ZnO particles were added into the PEE matrix in weight ratios of 3, 5, 10, and 15% of the total. They were mixed in a 15 mL twin-screw micro compounder (DSM Xplore 15 mL Micro-compounder – The Netherlands) at 220°C and 150 rpm. Residence time was adjusted by the recirculation of the melt for 3 min. The compounded melt was shaped via a 12 mL injection molding machine (DSM Xplore 12 mL Injection Molding Machine – The Netherlands) according to ISO 527–2 5A tensile test specimens. The sample holder and mould temperatures were 240 and 30°C, respectively.

Characterization of the PEE Copolymer and PEE/ZnO Composites

The melt flow index of the copolymer was determined using an Omega Melt Flow Indexer at 210°C under 2.16 kg load according to the ASTM D1238 standards. A capillary viscometer was used to measure the intrinsic viscosity of the PEE in *m*-cresol at 25°C. The average of three measurements was used to verify the intrinsic viscosity.

Table I. Some of the Properties of the Components Used in Polymer Synthesis

Specifications	Material			
	1,4 Butanediol	PTMEG	DMT	Tetra- <i>n</i> -butyl orthotitanate
Molecular weight (g/mol)	90.12	1000	194.2	340.36
Purity (%)	99	≥99	≥99	≥98
Density (g/ml)	1.017 (25°C)	0.974 (25°C)	1.350 (20°C)	0.990 (20°C)
Melting point (°C)	16	25–33	139–141	–40
Supplier	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Merck

Table II. The Dimensions and Manufacturers of ZnO Particles

ZnO	n-ZnO	m-ZnO
Dimension	50 nm	<1 μm
Manufacturer	MTI Corporation	Sigma-Aldrich

Fourier Transformation of Infrared Spectroscopy (FTIR) analysis was performed by using a Bruker Tensor 27 FTIR Spectrometer. The effect of ZnO particles on the chemical structure of the polymer matrix were evaluated through ATR-FTIR analyses. The measurements were done at 4000–600 cm⁻¹ spectral range with a resolution of 4 cm⁻¹. Sixteen scans were averaged per spectrum.

Differential scanning calorimetry (DSC) analyses were conducted on PEE matrix and the composites using Perkin Elmer Diamond DSC equipment under nitrogen atmosphere. Firstly, the samples were heated up to 250°C. At this point they were kept for 2 min to remove their thermal history before cooling to -70°C. Finally they were heated again to 250°C. The cooling and heating rates were the same as 20°C/minute. The crystallinity temperature (*T_c*, °C) was read from the cooling curve and melting temperature (*T_m*, °C), melting enthalpy values were determined from the second heating curve. % crystallinity values (*X_c*) were found by using eq. (1) where Δ*H_m* is melting enthalpy of the polymer (J/g) and Δ*H_f* is theoretical melting enthalpy of 100% crystalline polymer.^{19,20} The theoretical value of melting enthalpy for 100% crystalline poly(butylene terephthalate) homopolymer is 140 J/gram²¹ and *w* is the mass ratio of polymer matrix in the composite.

$$X_c = (\Delta H_m / \Delta H_f) \times w^{-1} \times 100 \quad (1)$$

X_c value gives the total amount of crystallinity in the polymer. By taking, the ratio of *X_c* and mass fraction of PBT segments in the copolymer (*w^{PBT}*), the mass fraction of hard segments incorporated into the crystallites (*X_c^{PBT}*) was found from eq. (2).²²

$$X_c^{PBT} = X_c / w^{PBT} \quad (2)$$

The chemical structure of the PEE copolymer was given in Figure 1. The average length of *x* (degree of polymerization) of the hard PBT segment was calculated according to one mol of the soft segment (*y* = 1).¹⁹ The degree of polymerization of the hard segment and the mass fraction of PBT segments were determined as 6.4 and 0.56, respectively.

The X-ray Diffraction (XRD) analysis of PEE/m-ZnO and PEE/n-ZnO composites with varying ZnO concentrations were carried out using a Rigaku Rint 2200 X-Ray Diffractometer with

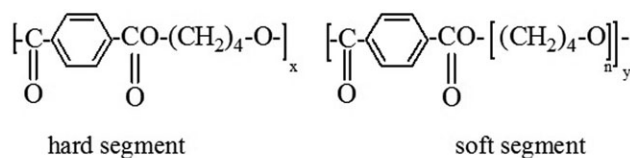


Figure 1. The hard and soft segments of PBT-PTMO copolymer.

CuK_α (λ = 1.54 Å) radiation at 40 kV and 40 mA. The diffraction angle, 2θ was scanned from 5° to 40° at the scanning rate of 2°/min.

Dynamic mechanical thermal analysis (DMA) was done using a Gabo Qualimeter Eplexor 500 N in tensile mode. The samples with 40 mm length and 2 mm thickness were cut from dog bone shape test specimens used in the mechanical measurements. The resonant frequency was 10 Hz at room temperature, measurements were conducted from -120 to 180°C, and heating rate was 3°C/min.

The morphologies of PEE copolymer and the composites containing ZnO were investigated by scanning electron microscopy using a Zeiss Supra™ 50 VP. Before the investigation, samples were coated with gold-palladium to provide the conductivity on the surface.

The effect of the type and concentration of ZnO fillers on the tensile properties of the composites were determined using an Instron-Mechanical Testing Machine 5581 equipped with 2 kN load cell according to the ASTM D638 standard. Strain rate was set to 50 mm/min. The arithmetic mean of five samples and their standard deviations were reported.

RESULTS AND DISCUSSION

Characterization of PEE Copolymers

The PEE copolymers, synthesized by a two-step condensation polymerization method, having 0.75 dL/g intrinsic viscosity were obtained. The melt flow index of copolymer was determined as 22.7 g/10 min at 210°C and under 2.16 kg load.

The FTIR analysis of PEE copolymer is presented in Figure 2. The peaks at 1720 cm⁻¹ (C=O stretching in ester group) and 726 cm⁻¹ (ring C-H vibration) are assigned to the hard segment. C-H asymmetric stretching and C-H symmetric stretching appear at 2938 and 2854 cm⁻¹, respectively and they are assignable to the soft segment. The peak at 1600 cm⁻¹ belongs to the characteristic of the terephthalic benzene ring. The C-O bonds of both segments are observed at 1100 cm⁻¹.^{2,23}

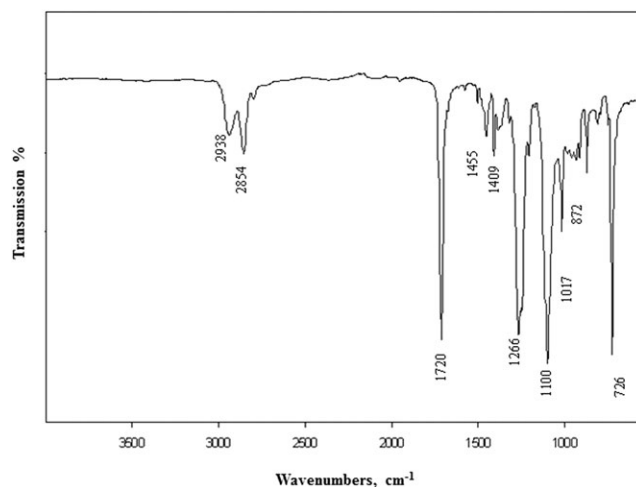


Figure 2. The ATR-FTIR spectrum of PEE copolymer.

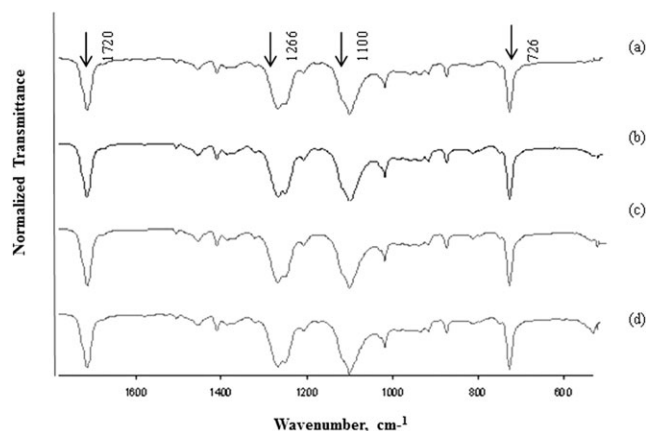


Figure 3. Normalized transmittance ATR-FTIR spectra of polymer composites containing n-ZnO at a concentration (a) 0%, (b) 5%, (c) 10%, (d) 15%.

Characterization of PEE/ZnO Composites

FTIR Analyses. The ATR-FTIR spectrum of PEE/n-ZnO composites with varying filler concentration is illustrated in Figure 3. When compared with neat polymer, no effect of ZnO is seen on the structure of composites. On the spectra of composites neither a new transmission band nor a peak shift is appeared that could be attributed to the formation of a new chemical bond between the polymer matrix and ZnO.

The ATR-FTIR spectrum of PEE/pvp-ZnO is shown in Figure 4. The characteristic peaks of PVP do not appear in the spectrum. This may be due to the small amount of PVP in the composite. However, the carbonyl peak of PEE at 1720 cm^{-1} shifts to the lower wavenumber of 1711 cm^{-1} . This was probably caused by the interactions between the carbonyl groups of the polymer and the amide group of PVP.^{24,25}

DSC Analysis. DSC analysis of neat PEE and the composites were done in the temperature range from -70 to 250°C . T_c , T_m , ΔH_m , and X_c values are summarized in Table III. A single T_m rather than two values for the two segments was detected.

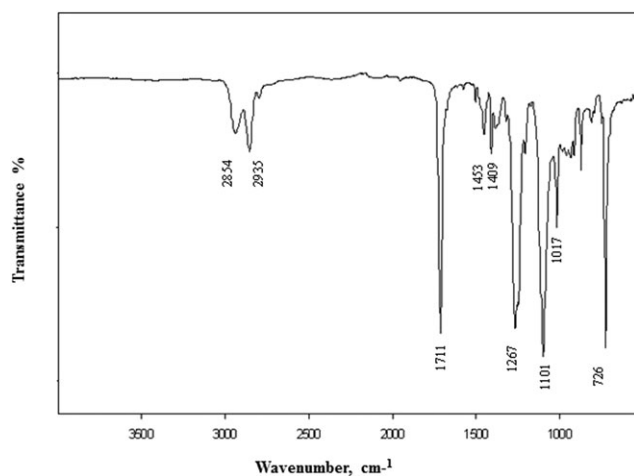


Figure 4. The ATR-FTIR spectrum of the polymer composite containing 15% pvp-ZnO.

Table III. T_c , T_m , ΔH_m , and X_c Values of the Neat Polymer and Composites

Sample	T_c ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	X_c (%)
PEE	167	196	20.4	14.6
PEE/n-ZnO % 3	169	196	19.6	13.6
PEE/n-ZnO % 5	163	197	19.0	12.9
PEE/n-ZnO % 10	169	197	20.4	9.5
PEE/n-ZnO % 15	169	196	15.1	9.2
PEE/m-ZnO % 3	166	196	17.3	11.9
PEE/m-ZnO % 5	166	196	17.4	11.8
PEE/m-ZnO % 10	167	196	17.6	11.3
PEE/m-ZnO % 15	168	195	13.8	8.4

The total degree of crystallinity (X_c) and crystalline fraction (X_c^{PBT}) of neat PEE were calculated as 14.6 and 26.1, respectively. This means that all of the hard segments did not crystallize completely. Only 26% of these segments crystallized and the remaining portion was incorporated into the amorphous matrix. This result is in agreement with the earlier studies described for thermoplastic poly(ether ester)s.^{19,26,27} The rate of crystallization is low as expected because of slow cooling of polymer to room temperature after the synthesis.

It is remarkable that adding ZnO nanofillers to the polymer matrix does not have any significant effect on the T_c and T_m values. On the other hand, it is observed that there is a slight decrease in X_c values with increasing filler content. Addition of the fillers may result in the hindrance of polymer chain mobility and slowdown the crystal growth. This may also cause imperfect crystals to grow up in the structure.^{28,29}

In this study, T_g values of the neat matrix and the composites could not be detected by DSC analysis. Although it is a convenient method to determine the T_g , it is not very sensitive. If the specific heat capacity (C_p) changes are small and take place over a broad temperature interval, it is difficult and uncertain to determine the T_g values. In this case, dynamic mechanical, or dielectric measurements are more suitable.³⁰

XRD Analysis. Figure 5(a,b) shows the diffraction patterns of PEE/n-ZnO and PEE/m-ZnO composites, respectively. XRD pattern of the neat copolymer matrix displays an amorphous polymeric structure. In the pattern of PEE/ZnO composites, the peaks at $2\theta = 32^\circ$ and 36° are corresponding to the zinc oxide. The increase in the zinc oxide concentration results in the decrease of intensity of these peaks, i.e., crystallinity of composites. The same trend is also seen from DSC analysis (Table III). The use of fillers should restrain the movement of polymer chains and therefore composites may possess less perfect crystals or a wide distribution of crystallite size, and it is observed as a decrease in the crystallinity. A review on the polymer nanocomposites noted that the incorporated nanoparticle can replace for the absence of primary nuclei and competes with the enclosed crystallization. At higher filler concentrations the increased viscosity (decreased chain diffusion rate) decreases the crystallization.³¹

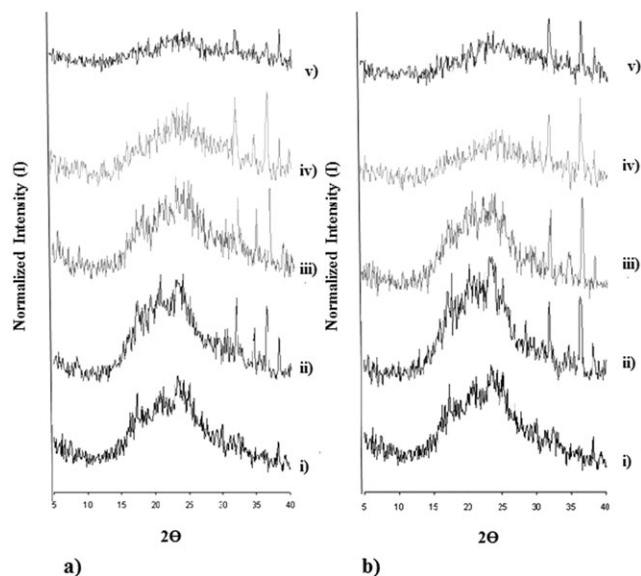


Figure 5. XRD patterns (with normalized intensity) of (a) PEE/n-ZnO composites (b) PEE/m-ZnO composites (zinc oxide concentration, wt % (i) 0, (ii) 3, (iii) 5, (iv) 10, (v) 15).

DMA Analysis. The viscoelastic properties such as storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) of the neat polymer and composites were investigated using DMA analysis. Figures 6 and 7 show the temperature dependent E' and E'' , respectively, of neat polymer and m-ZnO, n-ZnO, and s-ZnO composites with 15 wt % ZnO concentration. In comparison to PEE copolymer, the incorporation of ZnO to the matrix increases the modulus of composites. In other words, zinc oxides as reinforcing particles cause an increase in the stiffness particularly at low temperatures, which indicates that the effect of the ZnO addition is mainly active in the amorphous phase of the polymer.²¹

T_g values of composites containing 15 wt % ZnO were determined from the maximum of $\tan \delta$ curve (Figure 8). The PEE copolymer shows only one T_g value because of the occurrence

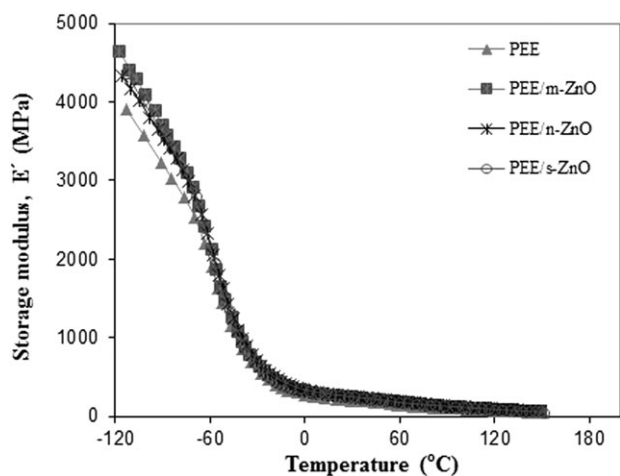


Figure 6. Storage modulus of the PEE copolymer and composites vs. temperature.

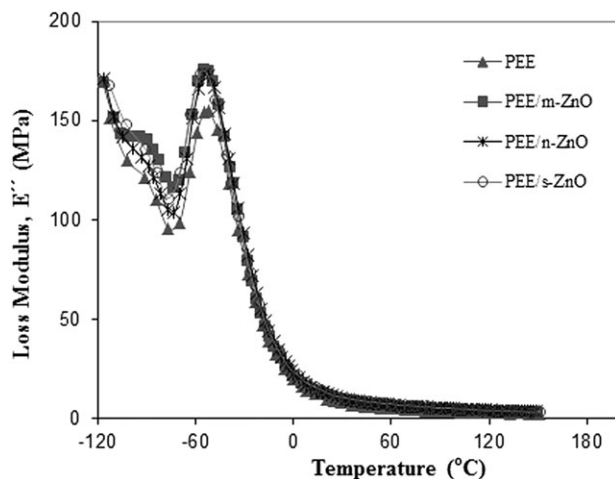


Figure 7. Loss modulus of the PEE copolymer and composites vs. temperature.

of glass transition in the noncrystalline phase which is composed of the soft segments and noncrystalline hard segments.³² Neither T_g (-86°C) of neat PTMO nor T_g of neat PBT (30 – 60°C) can be observed in the figure.^{33,34} Moreover, a single T_m was detected in DSC analysis. This result reveals that the synthesized polymer is a random copolymer.³⁵

It is evident that the glass transition temperature is almost the same for all the samples. It indicates the lack of attractive interactions between the polymer matrix and the unmodified nanofiller.

SEM Analysis. The morphology of the composites and also the filler dispersion in the composites were characterized through scanning electron microscopy. The SEM micrograph of the composite filled with n-ZnO nanoparticles is shown in Figure 9(a). It seems that the nanoparticles have a tendency to agglomerate. The small spherical particles on the surfaces are not ZnO; in fact, they are due to the gold-palladium coating of the surfaces before the SEM analysis. The image of PEE/m-ZnO composite [Figure 9(b)] shows that the particles are well dispersed in

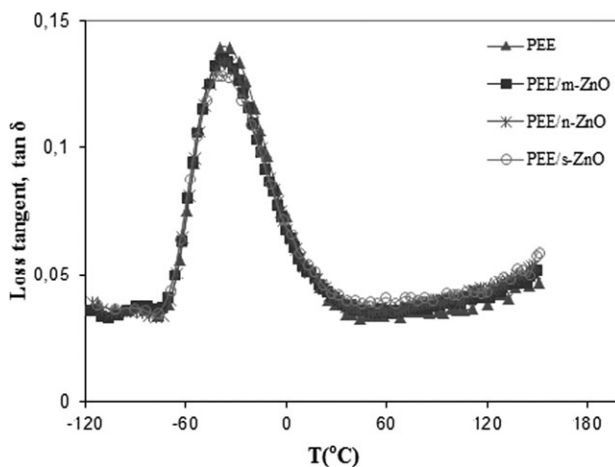


Figure 8. The loss tangent ($\tan \delta$) of the PEE copolymer and composites vs. temperature.

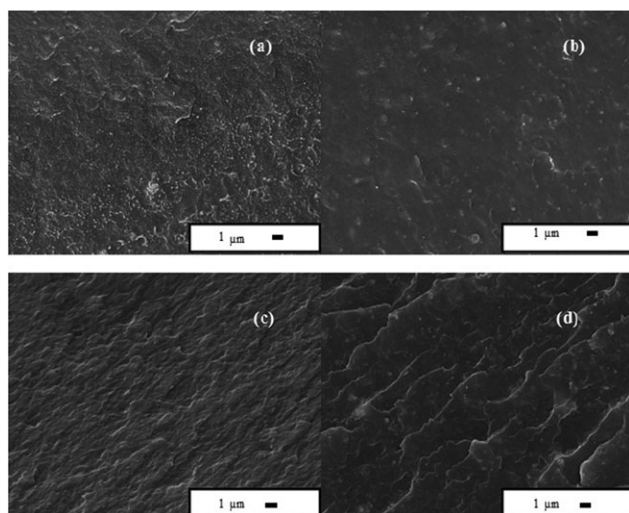


Figure 9. SEM micrographs (x10,000) of the fractured surface of composites containing 15% (a) n-ZnO, (b) m-ZnO, (c) s-ZnO, (d) pvp-ZnO.

the matrix in their original sizes. The fracture surface of the composite filled with s-ZnO particles turns to a more torturous structure [Figure 9(c)]. The synthesized particles, previously determined as 315 nm in diameter, are uniformly distributed in the matrix. It proves that there is little or no agglomeration of the fillers. When the surfaces of the s-ZnO particles are modified with PVP, there exists possibility of interaction with the hydrogen bonds of PTMO and ZnO. If the micrographs of the composites with modified [Figure 9(d)] and unmodified ZnO [Figure 9(c)] are compared, the tortuous crack propagation paths become more evident on the surface of the composite, which is filled with PVP modified ZnO particles. This may indicate the enhancement of interaction between the matrix and the particles [Figure 9(d)].

Mechanical Testing

The tensile strength values with different ZnO type and concentration are given in Figure 10. It is observed that in general the tensile strength decreases with the increasing concentration of the fillers. Hereby filler-matrix interaction is the most important

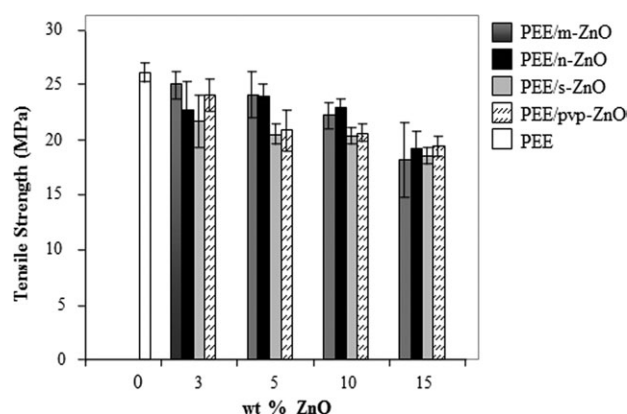


Figure 10. Tensile strength of composites with varying ZnO concentration.

factor. The addition of ZnO with poor interaction into the polymer matrix decreased the tensile strength, regardless of the filler concentration or size. At low ZnO concentrations PEE/m-ZnO composites have higher tensile strength values as compared to other nanocomposites. However, by further filler addition there is a sharp decrease in the tensile strength of PEE/m-ZnO composites. The tensile strength of composites with n-ZnO fillers reaches a maximum value at 5 wt %. The nanoparticles, which are commercially available, are usually in the form of agglomerates. In SEM micrograph [Figure 9(a)] of PEE/n-ZnO composites it is observed that the particles are homogeneously distributed in the matrix, however, they have a tendency to agglomerate. The limited shear force applied during mixing may be insufficient for dispersing them efficiently in the matrix. At higher filler content, weak interfacial interaction between the nanoparticles and the matrix could be the reason for the decrease in the tensile strength of composites.

Figure 11 reveals that the addition of ZnO fillers increases the elastic modulus of composites. Inorganic fillers have considerably higher modulus than polymers and therefore they increase the modulus of the incorporated polymer. High surface area and anisotropy are the other factors that provide higher modulus.³⁶ At higher concentrations, n-ZnO particles have higher elastic modulus in comparison to m-ZnO particles because of the increase in interfacial region area of nanoparticles. In general, the modulus of composites increases as the size of fillers decreases.⁷ The reason for the increase in the elastic modulus with the incorporation of synthesized ZnO may be due to the high anisotropy of synthesized particles. The modification of particles increases elastic modulus slightly when compared to the composites with unmodified fillers due to the possibility of the interactions between the composite constituents.

The decrease in elongation at break values with the increase of ZnO concentration designates the mechanical restriction applied by the particles to the matrix (Figure 12). However, a small increase in the elongation at break values of composites consisting ZnO modified particles (pvp-ZnO) is observed. The viscoelastic deformation at the interface and flow in the matrix may lead to increase in these values.³⁷

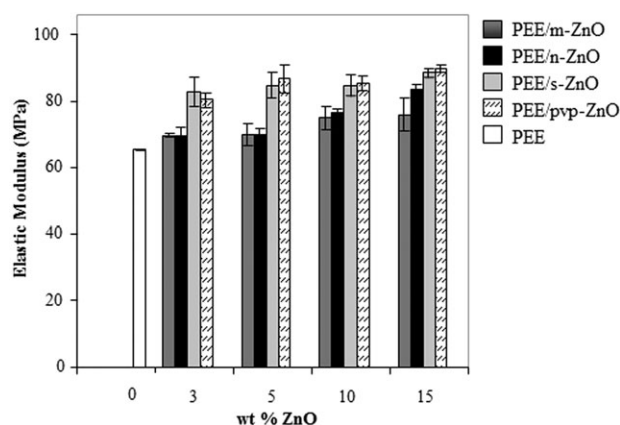


Figure 11. Elastic modulus of composites with varying ZnO concentration.

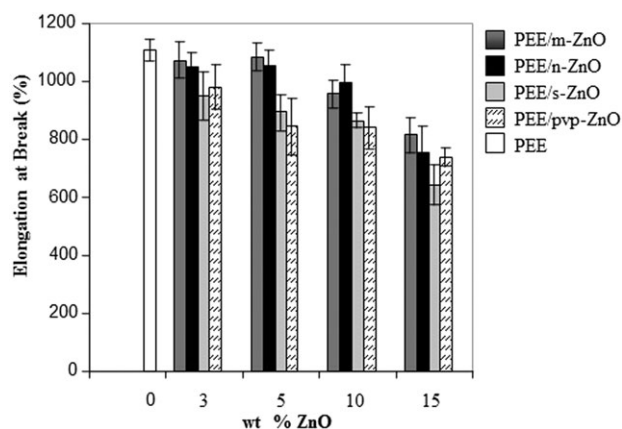


Figure 12. Elongation at break of composites with varying ZnO concentration.

The modification of nanoparticle surface with low molecular weight polymer, PVP can be considered as an efficient way to disperse the particles in the matrix. Because of its low molecular weight it can easily penetrate into the agglomerated particles and may form chemical or physical bonding with the particles and the polymer matrix. Jordan reports that for the composites filled with treated fillers there exists an improvement in strength as well as in toughness.⁷ In this study, the expected effect of the modification is slightly seen on tensile strength, elastic modulus and elongation at break values of PEE/pvp-ZnO composites when compared to PEE/s-ZnO composites containing unmodified particles.

CONCLUSIONS

Segmented PBT-PTMO copolymers were synthesized by the polycondensation reaction. The single glass transition temperature intermediated between the glass temperatures of PBT and PTMO showed that the copolymers were random copolymers. The PEE copolymers were used as polymer matrix in the PEE/ZnO composites prepared by melt blending. The effect of type and concentration of ZnO on the crystallization of copolymer were studied through DSC analysis, which revealed that the crystallinity of composites decreased slightly with ZnO concentration. The same results were also supported with XRD analyses. The addition of ZnO particles induced a slight increase of storage modulus under T_g . This may result from the stiffening effect of ZnO. SEM investigations showed that ZnO fillers were homogeneously dispersed in the PEE matrix. The torturous structures became more evident on the fractured surface of the matrix with the incorporation of the modified ZnO fillers. The tensile strength of the composites decreased with increasing filler content. On the other hand, the elastic modulus values of the composites increased with the incorporation of ZnO particles. It was found that there was a sharp decrease in elongation at break values with increasing filler content. The reason was probably due to the mechanical restriction applied by fillers in the polymer matrix. In comparison to the PEE/s-ZnO composites, a slight increase was seen in mechanical properties of the PEE/pvp-ZnO composites as the interaction of the filler-matrix was improved by the modification of ZnO particles with PVP.

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