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Thermal characterization of polymer composites with nanocrystalline maghemite

Summary — Samples of multiblock poly(ether-ester) copolymer doped with magnetic γ -Fe₂O₃ nanoparticles (at small concentrations of 0.1 wt. % and 0.3 wt. %) have been investigated by DSC method to study the melting and crystallization behavior. Two forms of magnetic γ -Fe₂O₃ nanoparticle filler were used: solid-state grains and a suspension of γ -Fe₂O₃ with palmitic acid in toluene. Application of the solid filler caused formation of agglomerates of size of about 20 μ m while in the suspension form separate nanoparticles were in the range 10–20 nm. The thermal and thermo-oxidative stability of composites was analyzed by conventional TGA analysis. The DSC results showed that crystallization and, to a smaller extent, melting, were considerably affected by the introduction of magnetic nanoparticles. The main influence is a shift in the crystallisation temperature up to 20 °C and melting/glass transition shift up to 6 °C. Thermogravimetric analysis showed significant enhancement of thermal and thermo-oxidative stability of the composites with respect to pure PEE. The dependence of thermal parameters on the concentration of magnetic filler has shown that the largest agglomerates produced the biggest change in all thermal parameters.

Key words: magnetic nanoparticles, γ -Fe₂O₃, poly(ether-ester) multiblock copolymer, thermal transition, temperature, thermostability.

TERMICZNA CHARAKTERYSTYKA KOMPOZYTÓW POLIMEROWYCH ZAWIERAJĄCYCH NANOKRYSTALICZNY MAGHEMIT

Streszczenie — Próbkę multiblokowego kopolimeru eterowo-estrowego (PEE) domieszkowano magnetycznymi nanocząstkami γ -Fe₂O₃ (w ilości 0,1 % mas. lub 0,3 % mas.). Zastosowano dwie postacie napełniacza, mianowicie ziarna polikrystaliczne (tworzące aglomeraty o wymiarze ok. 20 μ m) lub zawiesiny nanocząstek γ -Fe₂O₃ w otocze kwasu palmitynowego w toluenie (wymiar ok. 20 nm). Metodą DSC zbadano wpływ tego nanonapełniacza na zjawiska topnienia i krystalizacji uzyskanych kompozytów (tabela 1, rys. 1) a do oceny stabilności termicznej i termooksydacyjnej wykorzystano analizę termogravimetryczną TGA (tabela 2, rys. 2, 3). Stwierdzono, że proces krystalizacji i, w mniejszym stopniu, także topnienia zostały znacznie zmodyfikowane przez obecne w kompozycie nanocząstki magnetyczne. Głównym efektem domieszkowania było podwyższenie temperatury krystalizacji aż o 20 °C i przesunięcie temperatury przemiany topnienia/zeszklenia o 6 °C. Analiza TGA wykazała istotniejszy wzrost stabilności termicznej i termooksydacyjnej kompozytów niż niemodyfikowanego PEE, przy czym wzrost ten jest tym wyraźniejszy im większe są aglomeraty.

Słowa kluczowe: nanocząstki magnetyczne, γ -Fe₂O₃, kopolimer multiblokowy eterowo-estrowy, przemiany termiczne, temperatura, termostabilność.

Materials containing magnetic nanoparticles are interesting from the point of view of their potential appli-

cations [1–6]. Magnetic nanoparticles, such as maghemite (γ -Fe₂O₃) nanoparticles, embedded in a nonmagnetic matrix, represent an interesting subject of fundamental research in magnetism [7–12]. Unique magnetic properties originated from the complex interactions among the intrinsic magnetic responses of individual particles, as determined by finite size and surface effects, make them distinctively different from those of the bulk counterparts. On the other hand, experimental work on γ -Fe₂O₃ nanoparticles with different surface coatings dispersed in polymeric matrices, has emphasized the contribution of surface effects and the diversity of mag-

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netic properties unveiling that the particle microstructure as well as the host medium can significantly affect the magnetic responses of these systems [7, 8, 11, 12]. Polymers may serve as excellent matrices for magnetic particles in order to synthesize nanocomposite materials that combine the polymer functionality and mechanical properties with those of the magnetic partners. The interactions of the particles with the supporting matrix become especially important for the determination of the magnetoelastic properties of these materials [13]. Related studies have shown that even a very small concentration of magnetic nanoparticles could significantly shift the glass transition temperature by more than 10 K. Equally important would be to study the influence of small concentration of magnetic nanoparticles on the melting point as well as on the crystallization process in polymer by applying the differential scanning calorimetry (DSC) method in the region of high temperatures [14—18].

This paper reports the influence of very low concentration of magnetic nanoparticles in different states of agglomeration on the melting temperature and crystallization processes of multiblock copolymers. Thermal properties of multiblock poly(ether-ester) (PEE) copolymers based on poly(oxytetramethylene) (PTMO) and poly(ethylene terephthalate) (PET) doped with γ -Fe₂O₃ magnetic nanoparticles at concentration of 0.1 wt. % or 0.3 wt. % were investigated by using DSC and thermogravimetric (TGA) analyses.

EXPERIMENTAL

Preparation of samples

Magnetic γ -Fe₂O₃ nanocrystalline particles with an average size of 10 nm were prepared according to a published method *via* oxidative transformation of an iron hydroxide gel using H₂O₂ as oxidant.

Composites, containing 0.1 wt. % or 0.3 wt. % of γ -Fe₂O₃ filler, were obtained by *in situ* polycondensation in the molten state during polymer syntheses [19]. As a polymer matrix the multiblock poly(ether-ester) copolymer based on poly(oxytetramethylene) and poly(ethylene terephthalate) 50:50 wt. % was used (the material is designated as PEE/0). Detailed information concerning the syntheses of similar block copolymers has been presented elsewhere [20].

Two forms of γ -Fe₂O₃ nanoparticles were used to prepare the polymer composites: a solid powder (the letter P stands for powder) producing samples PEE/0.1-P and PEE/0.3-P, and the other in the form of a suspension of γ -Fe₂O₃. Suspension is established simultaneously in one step by adding a toluene solution of palmitic acid and refluxing the toluene biphasic system [21] (letter L in sample designation) to produce samples PEE/0.1-L and PEE/0.3-L [11]. Details of the preparation of composites are given in [11].

Methods of testing

— The DSC technique was used to investigate the melting and crystallization behavior, degree of crystallinity and to determine the glass transition temperature T_g as a function of γ -Fe₂O₃ content and extent of agglomeration. Measurements were made using DSC-7 (Perkin-Elmer) apparatus. Samples were packed into hermetic aluminum DSC pans. The measurements were taken in the temperature range from -100 °C to 250 °C at a heating rate of 10 °C/min under nitrogen flow. The crystallization and melting temperatures (T_c , T_m) were measured at the maxima of the endo- and exothermic peaks during the heating and cooling cycles, and the glass transition temperature (T_g) was taken as the midpoint of the change in heat capacity ($\Delta c_p/2$). The enthalpies of melting and crystallization were determined by the area under the appropriate endo- and exothermic peaks and were normalised per gram of the sample. The degree of crystallinity (x_c) of the copolymer as a function of PET content was calculated as the ratio:

$$x_c = \frac{\Delta H_m}{\Delta H_m^o \cdot w_h} \cdot 100 \% \quad (1)$$

where: ΔH_m — heat of fusion of the examined sample, estimated from the 2nd heating scan, ΔH_m^o — heat of fusion of fully crystalline PET ($\Delta H_m^o = 140$ J/g) [22], w_h — its weight fraction in the copolymer.

— TGA analyses of PEE and composites were carried out using a STARAM TG 92-16 apparatus with a simultaneous system TG/DSC. The initial sample mass was 5 ± 0.1 mg. The experiments were carried out in an argon or a synthetic air (N₂:O₂ = 80:20 vol. %) atmosphere with a flow rate of 18 ml/min and heating rate 10 °C/min. The characteristic temperatures of thermal and thermo-oxidative degradation were determined.

RESULTS AND DISCUSSION

The PEE copolymers derived from PET and PTMO belong to the class of thermoplastic elastomers (TPE). These materials have multiblock chain architecture with alternating PET “rigid segments” and polyether (PTMO) “soft segments”. The thermoplastic and elastic behavior of these polymers arise from their multiphase structure, which is a consequence of the chemical nature and incompatibility of the two types of contributing segments (rigid and soft) building polymer chains. The PET-PTMO copolymers show an interesting combination of properties, such as high melting temperature (T_m), low glass transition temperature (T_g), high tensile and tear strengths, and ease of processing [23, 24]. The PEE is a semicrystalline polymer. The crystalline phase consists of PET rigid segments. Some hard segments do not crystallize and mix with the amorphous soft segments. The amorphous phase contains soft segments and non-crystalline rigid segments. It has a single glass transition that

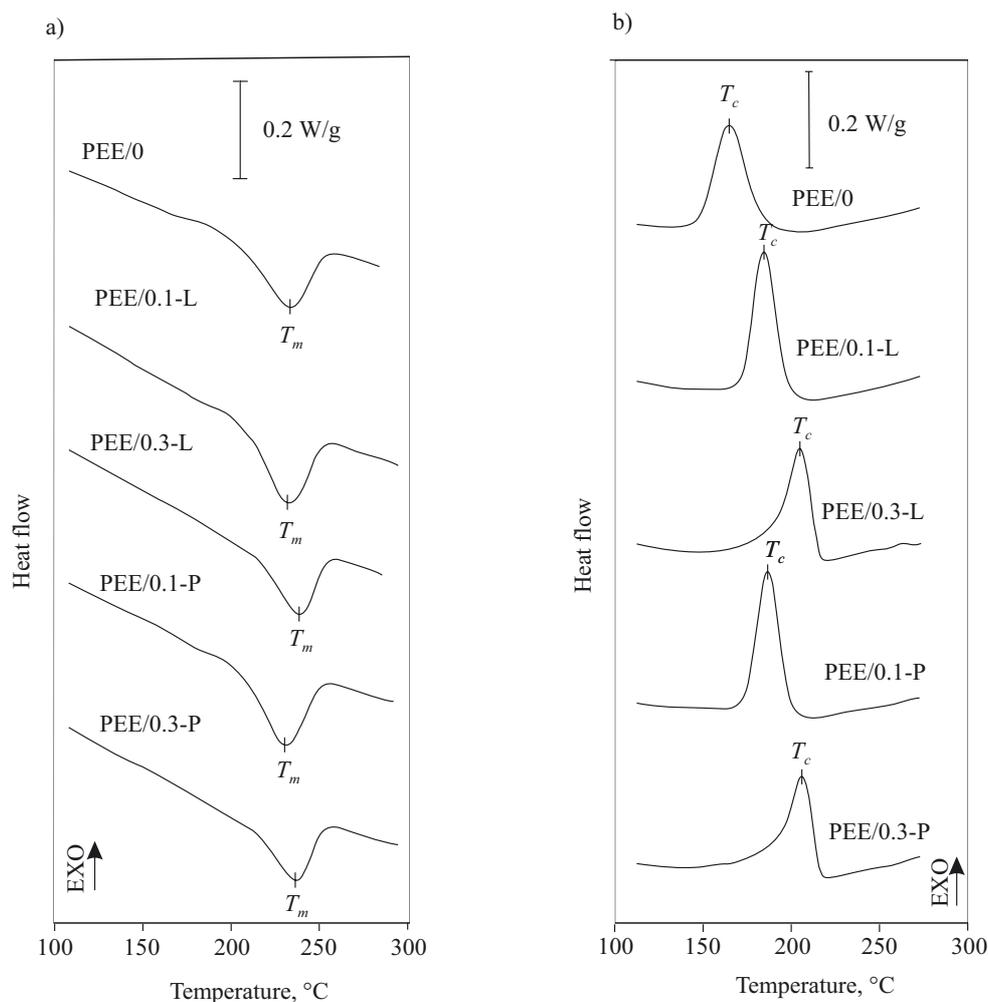


Fig. 1. DSC scans of PEE with different contents wt. % of $\gamma\text{-Fe}_2\text{O}_3$ in polymer at the heating (a) and cooling (b) rate cycles at $10^\circ\text{C}/\text{min}$ for PEE/0, PEE/0.1-L, PEE/0.3-L, PEE/0.1-P and PEE/0.3-P samples

is determined by the relative amounts of the two types of segments. The coexistence of a two-phase morphology of these polymers and composites derived from them is confirmed by DSC and AFM techniques.

Table 1. Results of DSC analyses of PEE sample and PEE composites filled with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles^{a)}

Sample	T_g , °C	Δc_p , J/g °C	T_m , °C	ΔH_m , J/g	T_c , °C	ΔH_c , J/g	x_c , %
PEE/0	-78.1	0.23	232.1	28.0	165.2	26.6	40.0
PEE/0.1-L	-74.9	0.33	230.7	28.3	184.8	26.9	40.1
PEE/0.3-L	-76.5	0.29	230.5	29.1	184.9	26.1	41.6
PEE/0.1-P	-73.6	0.30	238.1	27.1	203.6	24.1	38.7
PEE/0.3-P	-72.7	0.34	235.9	27.7	204.6	24.4	39.6

^{a)} T_g — glass transition temperature of soft phase; Δc_p — heat capacity of flexible segments; T_m , ΔH_m — temperature and enthalpy of melting of hard phase of polymer or composite; x_c — degree of crystallinity; T_c , ΔH_c — temperature and enthalpy of crystallization of polymer or composite.

As it was previously presented in [11], scanning electron microscopy (SEM) revealed an almost homogene-

ous distribution of agglomerates with a similar shape and size and a diameter over $20\ \mu\text{m}$ in complexes of P type samples, while Atomic Force Microscopy (AFM) images showed fine nanoparticles in the range of 10–20 nm, homogeneously distributed in L type samples.

The DSC thermograms of PEE polymer and its composites with $\gamma\text{-Fe}_2\text{O}_3$ recorded during heating and cooling runs are shown in Fig. 1. The heating scans show low temperature glass transition (T_g) due to polyether soft segments and multiple melting behaviour at about 230°C due to the crystalline rigid PET segments. The crystallization and melting temperatures are affected by the presence of low concentration of magnetic nanoparticles in PEE polymer (Fig. 1 and Table 1). The shapes of the endothermic peaks of the composites indicate that melting of the crystallites occurs in the range $160\text{--}260^\circ\text{C}$. The DSC parameters for pure PEE and composite samples were calculated from the obtained DSC curves and given in Table 1. The DSC results show: (a) no significant shift in the melting temperature to lower temperatures for PEE/0.1-L and PEE/0.3-L ($\Delta T_m = 1.4$ and 1.6°C) with increasing content of $\gamma\text{-Fe}_2\text{O}_3$ in the polymer, while for composites PEE/0.1-P and PEE/0.3-P the melt-

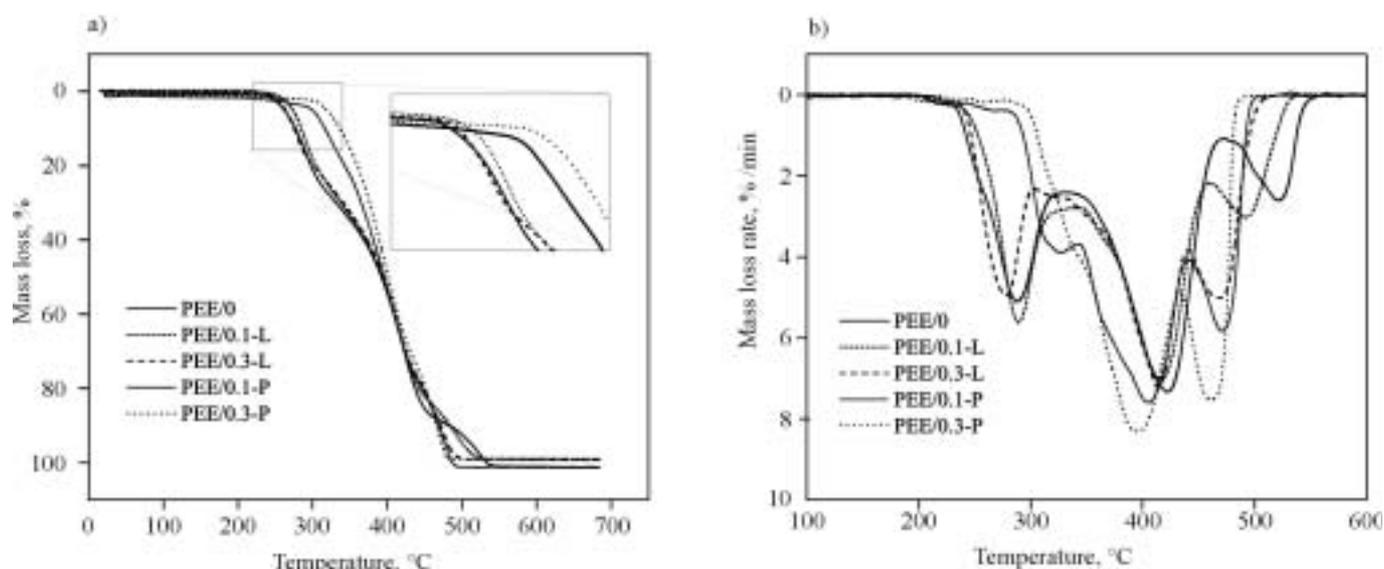


Fig. 2. TGA measurements in an air for PEE/0 and composite samples: a) weight loss (α), b) weight loss rate ($d\alpha/dt$)

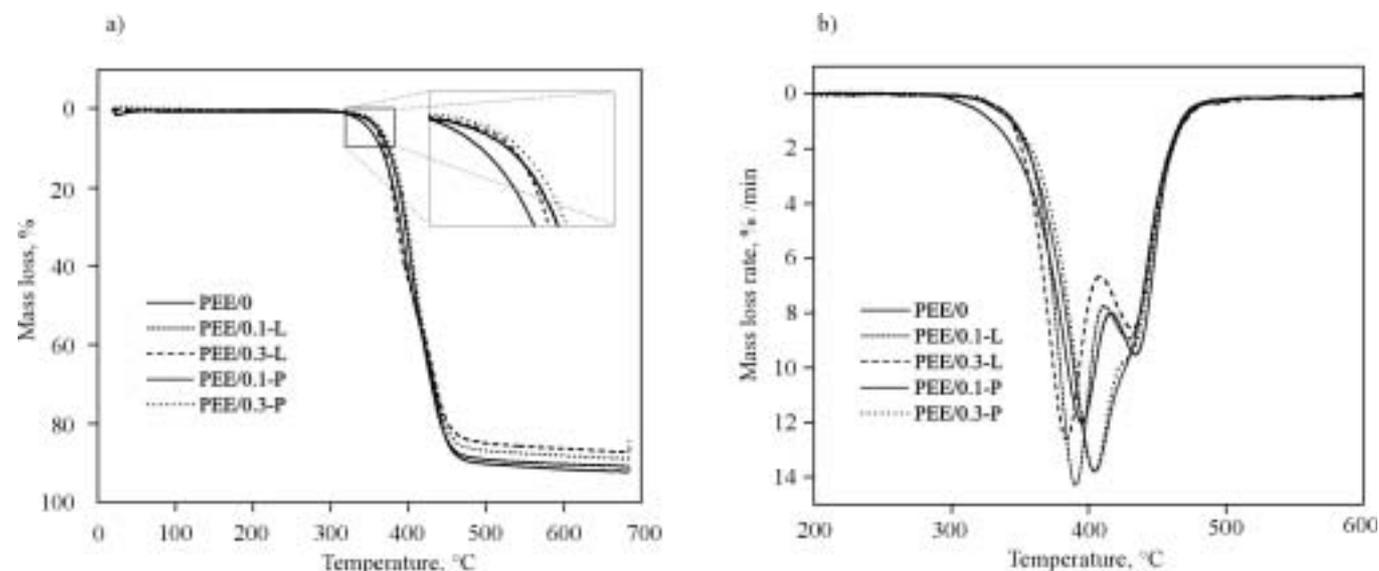


Fig. 3. TGA measurements in argon for PEE/0 and composite samples: a) weight loss (α), b) weight loss rate ($d\alpha/dt$)

ing temperature is about 6.0 °C and 3.8 °C higher than for pure PEE respectively; (b) degree of crystallinity of composites does not vary a lot (38.7—41.6 %) from the value of 40 % of the pure PEE because of the small γ -Fe₂O₃ content in the composites; (c) enthalpies of melting of crystalline hard phases of composites vary between 27.1 and 29.1 J g⁻¹; (d) for composites based on PEE, the glass transition temperature (T_g) of polyether soft phase is shifted to higher temperatures by 3.2 and 1.6 °C for PEE/0.1-L and PEE/0.3-L, and by 4.5 and 5.4 °C for PEE/0.1-P and PEE/0.3-P and this tendency is confirmed by dielectric measurements [13]; (e) larger values of the change in heat capacity Δc_p of composites indicate more intense phase separation in the composites than in PEE.

Two processes could be suggested to explain the shift in the melting point. The first involves an increase in the

bonding properties of the matrix and the other a magnetic dipole interaction that could form anti-parallel arrays of dipoles. In this respect, a ferromagnetic resonance study has shown that the values of internal magnetic field were different and the temperature dependence of magnetization for these samples revealed the existence of antiferromagnetic interaction [11, 12].

Magnetic nanoparticles dispersed in a copolymer could act as a nucleating agents and, thus, accelerate the crystallization of the composites. The crystallization behavior of the polymer could be changed significantly by increasing of the size of crystallites. Apparently, the polymer crystallization is interrupted by the presence of γ -Fe₂O₃ islands in the composite mass and this interruption increases with the size of the crystallites. Similar trend is observed for the temperature of crystallization that increases strongly with the insertion of magnetic

Table 2. Results of TGA analyses of PEE sample and PEE composites filled with γ -Fe₂O₃ nanoparticles^{a)}

Sample	In argon					In an air				
	$T_{\alpha=10\%}$, °C	$T_{\alpha=20\%}$, °C	$T_{\alpha=50\%}$, °C	T_{max} (d α /dt), °C		$T_{\alpha=10\%}$, °C	$T_{\alpha=20\%}$, °C	T_{max} (d α /dt), °C		
PEE/0	365.1	380.9	408.5	394.7	434.2	277.3	298.0	287.7	422.3	522.0
PEE/0.1-L	373.2	387.8	411.6	390.5	429.3	285.0	304.8	289.1	415.8	492.0
PEE/0.3-L	368.4	379.0	410.0	384.0	432.3	275.0	301.3	278.2	414.8	468.8
PEE/0.1-P	373.6	387.8	411.6	404.9	—	316.4	343.1	326.7	405.7	470.9
PEE/0.3-P	377.4	391.2	414.2	404.1	—	336.8	360.8	—	395.2	461.5

^{a)} $T_{\alpha=10\%}$, $T_{\alpha=20\%}$, $T_{\alpha=50\%}$ — temperature of degradation at which weight loss in 10 %, 20 % or 50 % respectively; T_{max} (d α /dt) — temperature at maximum weight loss rate.

articles with larger agglomerates causing higher temperature shifts. Also, in this case the crystallization of the polymer needs an extra energy to overcome the hindrance given by the magnetic nanocrystalline blocks. Dielectric measurements have shown a decrease in the transformation temperature to a glass state by up to 10 degrees [13]. The DSC peak at high temperature has shifted in a similar manner due to the presence of magnetic agglomerates as observed in dielectric studies. The temperature of crystallization has increased strongly with the introduction of magnetic nanoparticles and larger agglomerates shifted this temperature more strongly than smaller ones.

A similar effect of crystallization temperature increase was detected for multi-walled carbon nanotubes (MWCN) and poly(ethylene 2,6-naphthalate) (PEN) nanocomposites prepared by melt blending process [30]. For PEN the crystallization temperature was 203.8 °C, while for PEN with 0.1 wt. % of MWCN it increased to 228 °C. This was explained as follows: the MWCN acted as a strong nucleating agent in PEN matrix under non-isothermal crystallization conditions. The crystallization temperature shift to higher temperature implies that the supercooling of PEN/MWCN nanocomposites at a given cooling rate was decreased by MWCN [25].

The thermal and thermo-oxidative stability values of PEE- γ -Fe₂O₃ composites were examined by TGA response in an air (Fig. 2) and argon (Fig. 3) atmosphere. From the results (Table 2) it is evident that the thermal degradation of pure PEE and composites in an air is different from that in argon atmosphere. In an air we observed three distinct stages of degradation of PEE and composites while in argon only two of them.

The rate of the first step is strongly dependent on an atmosphere (inert or oxidative), which surrounds the sample. The oxidation of a block copolymer of PET and PTMO takes place on the carbon atom in α -position to the ether oxygen atom [26]. The ester groups, which are more resistant to oxygen attack than aliphatic ethers, are also oxidizable. The rate of the second step is not much dependent on the atmosphere and is similar to the rate of PET decomposition. Analysis of the thermal stability of PEE and composites (Table 2) expressed in terms of a low weight loss decomposition temperatures ($T_{\alpha=10\%}$, $T_{\alpha=20\%}$) and the temperatures corresponding to the first

and second maximum weight-loss decomposition rates indicate that pure PEE is characterized, as expected, by higher stability in argon than in an air. Finally, PEE/0.1-P and PEE/0.3-P composites with increasing concentration of γ -Fe₂O₃ in the polymer show significant enhancement (about 40—60 °C) in thermo-oxidative stability of the composites with respect to PEE.

CONCLUSION

DSC measurements have shown that low concentration of the magnetic γ -Fe₂O₃ nanoparticles could change considerably the thermal properties of a polymer composite in relation to pure PEE polymer. The largest changes of T_g , T_m and T_c values were observed usually in cases of greater magnetic agglomerates at higher concentration in the polymer matrix. The dipole interaction of magnetic nanoparticles could play a very important role in the melting and crystallization phenomena of the copolymer matrix. The composites show better thermo-oxidative stability in comparison with pure PEE and stability increases with higher concentration of nanoparticles and for larger sizes of agglomerates. The final conclusion is that the degradation time of a polymer can be extended essentially by introduction of a low concentration (0.1—0.3 wt. %) of magnetic nanoparticles to the polymer matrix.

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