Thermal stability of polyacetal/ethylene-octene copolymer/zinc oxide nanocomposites

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Abstract. In this work we investigate binary blends of polyoxymethylene and ethylene octene copolymer (EOC) and their composites with nanostructured zinc oxide (ZnO). EOC content in the composites varies from 0 to 50 wt. %. The amount of ZnO filler in the composites is changed in the interval from 0 to 5 wt. %. Thermal properties of composites are investigated with thermogravimetric analysis and differential scanning calorimetry. It is observed that ZnO addition increases thermal stability of the investigated composites.

1. Introduction

Polyoxymethylene (POM), also known as polyacetal, is one of the engineering polymers used in many applications (industrial, transport, construction, house holding, medicine etc.) as an excellent alternative material for the replacement of metals due to its high strength and stiffness. However, range of POM application is limited due to some properties, for example, poor impact strength. To eliminate it many researchers have blended POM with elastomers such as styrene rubber [1], ethylene copolymer [2] and thermoplastic polymer TPU [3].

In recent years polymer- nanoparticle composites have attracted much interest because addition of small amount of nano-sized fillers can yield to considerable property increment, unachievable by using traditional micros-sized fillers. Many review reports testify about significant improvements of mechanical, barrier, electrical and magnetic properties of polymer nanocomposites [4-6].

In the current research the effect of nanosized ZnO on the thermal stability of ethylene-octene copolymer (EOC) modified POM is investigated.

2. Experimental

2.1. Materials

Polyoxymethylene copolymer with melt flow index of 42 g/10min, density of 1.41 g/cm^3, crystallinty of 60 % and melting peak temperature of 166 ^{0}C (POM: Kocetal 900, Kolon Plastics Inc.) was used as a matrix. Ethylene octene copolymer with α- octene content of 38 %, melt flow index of 5 g/10min, density of 0.87 g/cm^3, crystallinty of 14 % and maximum melting peak temperature of 60 ^{0}C (EOC: Engage 8200, The Dow Chemical Company) was used as a toughening agent.

The ZnO nanoparticles were prepared by evaporation of coarse grained commercially available zinc oxide (purity of 99.7 %) powder in a radio frequency discharge air plasma. The experimental apparatus consists of radio-frequency oscillator (5.28 MHz) with maximum plate power of 100 kW, water cooled cylindrical stainless steel reactor, heat exchanger, gas and powder supply systems, and

bag filter for collection of products. The flow rate of plasma forming gas air was 8.2 m^3/h and feed rate of powder was 1.2 kg/h. The raw powders were introduced into the plasma through 8 tubes with diameters of 2 mm by carrier gas. The growth of particles was controlled by introducing cold air at a distance of 25 μm below the introducing plane of ZnO.

Polyoxymethylene composites with various EOC and ZnO contents (0, 10, 30, 50 wt. % of EOC and 0, 2 and 5 wt. % of ZnO) were prepared by roll milling. POM based blends were processed at 170 ^{0}C, Blending time was 7 min.
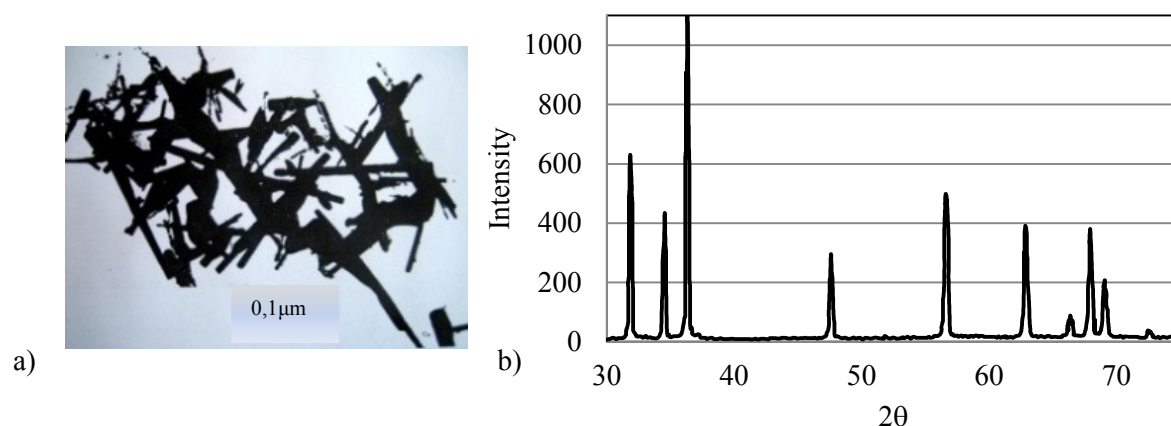
2.2. Characterization

Differential scanning calorimetry (DSC) was carried out by using DSC1/200W apparatus (Mettler Toledo). All measurements were made under N$_2$ flow. Samples of about 10 mg were heated from -100 up to 200 ^{0}C with a heating rate of 10 ^{0}C/min. Results of the second heating run were analyzed in order to earse thermal history of the sample.

Thermogravimetric analysis (TGA) was performed by using TGA1/SF thermogravimetric analyzer (Mettler/Toledo). Samples of about 10 mg were heated from 25 ^{0}C to 600 ^{0}C with a heating rate 10 of ^{0}C/min.

3. Results and discussion

Firstly synthesized ZnO particles were characterized. The obtained products were fine crystalline ZnO nanoparticles – plate-like and whisker-like particles (Fig.1. a) with length of 20–100 nm and diameter of ~20 nm. The specific surface of area of the powders was in the range of 24–32 m^2/g in dependence on the concentration of particles in the plasma flow and cooling rate of the formed ZnO particles. According to XRD analysis the prepared powders contained only ZnO phase (Fig.1. b).
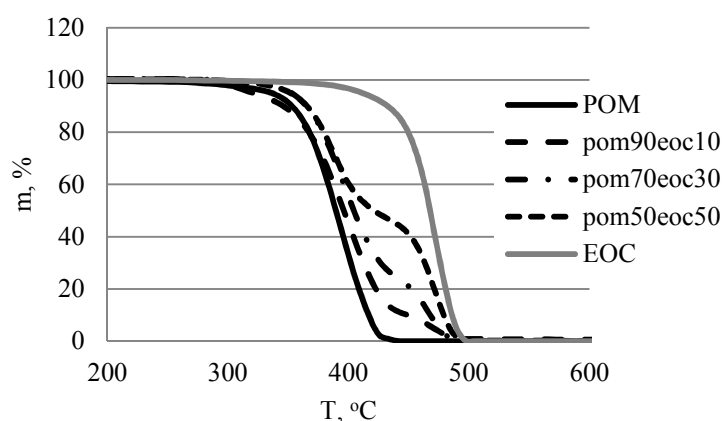

Figure1. Synthesized ZnO particles: a) TEM micrograph and b) XRD spectrum

Thermogravimetric curves of POM/EOC blends are shown in Fig.2. As one can see, POM and EOC, both degrade in one step; however, thermal degradation of EOC is observed 78 ^{0}C higher than POM testifying about higher thermal stability of the polymer, without any heteroatom in the hydrocarbon chain. Thermal degradation of POM macromolecule is initiated directly in the main chain by the scission of the -CH$_2$-O- linkages, which are the weakest points in the polymer macromolecule. In EOC macromolecule the weakest points are tertiary carbon atoms, at which breakage of the side-chains generally occurs. Consequently degradation process of EOC macromolecule is slower than that of POM macromolecule [8]. As we already expected, modification of POM with EOC, raised thermal resistance of the material. Besides it, two-step degradation behaviour is observed in the case of the investigated blends, the first degradation step being attributed to decomposition of POM, while the other one to degradation of EOC.

The effect of ZnO content on the degradation behaviour of all of the investigated blends is shown in Table1. The degradation temperatures are calculated at 5 %, 10 % and 20 % weight loss of the

nanocomposites. It can be seen that thermal stability of all of the investigated nanocomposites is higher than that of pure polymer matrix, most probably because of adsorption of polymer chains on the surface of ZnO particles resulting in decreased segmental mobility of macromolecular chains due to polymer matrix- nanofiller interactions, as demonstrated earlier in the case of CdS and Fe_2O_3 nanoparticles modified polymer composites [9]. Especially effective in respect to thermal stability of the investigated nanocomposites is addition of 2 wt. % of ZnO, which is most probably connected with higher surface area of ZnO because of smaller agglomeration and better distribution of the nanofiller in the polymer blend matrix.

Figure 2. Thermogravimetric curves of POM, EOC and their binary blends.

Table1. Characteristic degradation temperatures of ZnO modified POM/EOC blends.

POM, wt.p.	5 % weight loss			10 % weight loss			20 % weight loss		
	0% ZnO	2% ZnO	5% ZnO	0% ZnO	2% ZnO	5% ZnO	0% ZnO	2% ZnO	5% ZnO
1	324	342	340	345	358	355	369	378	373
0.9	311	345	340	347	365	355	368	378	373
0.7	347	318	347	366	346	368	379	364	380
0.5	344	363	345	366	381	361	380	394	386
0	402	431	432	434	449	450	450	459	457

In order to evaluate the effect of ZnO and EOC on the structural characteristics of POM, DSC thermograms of the investigated composites are analyzed. After erasing of thermal history investigated POM/EOC blends exhibit 2 separate melting peak temperatures, characteristic for incompatible heterogeneous systems. As shown in Table 2, difference between the component melting temperatures in the blend is higher than that between neat POM and EOC. Absence of melting peak of the elastomeric component for the composition with 10 wt. % of EOC evidently is due to its small crystallinity. As one can see there is no considerable effect of either POM content on the maximum melting temperature of EOC or EOC on the maximum melting temperature of POM. In the Table 2 one can however see that both components hinder each other's crystallization.

Interaction of the components in the amorphous phases of the blend can be evaluated by following the changes of it glass transition temperatures T_{gt}. According to the DSC measurements T_{gt} of POM, could not be detected, evidently due to high crystallinity degree of the polymer; T_{gt} of EOC is -55 ^{0}C. T_{gt} of EOC in the investigated blends, however, is hardly noticeable due to high crystallinity of the material as well as because the rate of relaxation of the material evidently is faster than heating rate used in the experiment.

Table 2.Melting peak temperatures (T_M) and degree of crystallinity (K_M) of POM and EOC and their fractions in the blend.

	Melting peak temperature, $^{\circ}C$		Difference between the component melting peak temperatures	Crystallinity degree, %	
POM, wt.p.	T_{M-EOC}	T_{M-POM}	$T_{M-POM} - T_{M-EOC}$	K_{M-EOK}	K_{M-POM}
0	64	-	-	8	-
0.5	64	164	100	5	58
0.7	63	164	101	2	62
0.9	Not observed	164	-	Not observed	60
1	-	163	-	-	67

Addition of ZnO nanofiller to either POM or EOC or their binary blends does not unambiguously change its crystallization behavior as melting peak onset, maximum and offset temperatures fluctuate within the range of couple of degrees. It should however be mentioned that addition of ZnO nanofiller to EOC causes increase in its glass transition temperature by $\sim 10\ ^{0}C$ thus testifying about certain interaction of EOC macromolecules in the vicinity of ZnO nanofiller. It should be, however, mentioned that in the blends the effect of ZnO on the T_{gt} of EOC is less expressed, which is evidently caused because of lower concentration of EOC, causing difficulties in T_{gt} detection.

4. Conclusion

In the current research effects of nanostructured ZnO filler on the thermal and calorimetric properties of POM, EOC and their binary blends are investigated.

Results of DSC investigations show that in the blends POM and EOC hinder each other's crystallization. Addition of ZnO nanofiller either to POM or EOC or their binary blends does not unambiguously change crystallization behaviour of the material. Addition of ZnO nanofiller to EOC, however, causes increase in its glass transition temperature by $\sim 10\ ^{0}C$ thus testifying about certain interaction of EOC macromolecules in the vicinity of ZnO nanofiller.

Results of TGA reveal that addition of EOC improves thermal stability of POM/EOC blends. Addition of ZnO either to POM or EOC or their binary blends cause further increase in the thermal resistance of the material.

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