



Nanostructured zinc oxide filler for modification of polymer-polymer composites: structure and tribological properties

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Abstract. Self-lubricating behaviour of materials is very demanded in industry. In this study we investigated the effect of anisometric nanostructured ZnO filler (tetrapod shaped particles with arm length of 70–100 nm and diameter of 10 nm) and ethylene-1-octene copolymer on structure and tribological properties of isotactic polypropylene (PP). It was observed that addition of EOC caused the increment of roughness as well as of the coefficient of friction (COF) of the investigated composites. Addition of ZnO, in its turn, caused decrement of the COF and improvement of surface quality at certain nanofiller contents.

Key words: tribology, nanocomposite, polypropylene, ethylene-1-octene copolymer, zinc oxide.

1. INTRODUCTION

Polymer manufacturing and polymer material usage grows every year. In the last decade, polymer materials, especially in the form of composite materials, have “conquered” new areas of usage. Development of new composites and nanocomposites increases polymer materials perspectives because they are designed to possess enhanced structural, mechanical, thermal, thermomechanical, rheological, tribological, and other properties depending on the composition of the multicomponent system [1–8].

Self-lubricating systems become popular because of oil- and grease-free lubrication and non-toxicity for the environment. Principle of self-lubricating systems is based on a transfer of microscopic amounts of the material to the mating surface by creating a film that provides lubrication and reduces friction. Effectiveness of polymer self-lubricating systems in most cases is dependent on the nature of the added inorganic

materials. It is well known that carbon particles act as a lubricant absorbing moisture from the external environment. Zinc oxide (ZnO) particles contribute to improved tribological properties by changing thermal conductivity of nanocomposites [9–13]. In the current research the effects of anisometric nanostructured filler ZnO on the structure and tribological properties of polypropylene/ethylene-1-octene copolymer (PP/EOC) blends are investigated.

2. MATERIALS AND METHOD

We used commercial isotactic polypropylene (PP) Basell Moplen HP456J as a matrix material. As impact resistance additive we used ethylene-1-octene copolymer (EOC) Dow Chemical Engage 8200. As anisometric nanostructured filler we used zinc oxide (ZnO), synthesized in RTU Institute of Inorganic Chemistry by plasma torch [14]. In Fig. 1 obtained particles, possessing tetrapod shaped structure with arm length of 70–100 nm and diameter of 10 nm, are shown.

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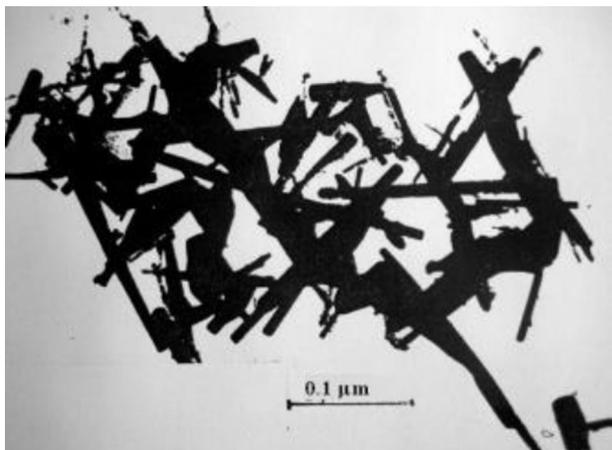


Fig. 1. TEM image of nanostructured anisometric ZnO particles.

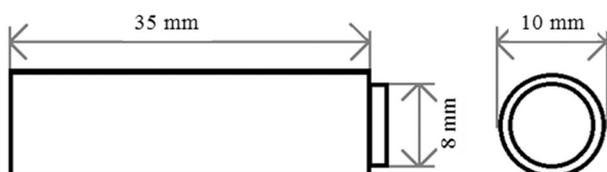


Fig. 2. Scheme of the used pin type sample.

Nanocomposites were obtained at 180°C by using Labtech Engineering Scientific Laboratory Two-roll mills LRM-S-110/T3E. Content of the elastomer EOC was 0, 10, and 30 wt%, but ZnO content was 0, 0.1, 0.5, 1, and 2 wt%. Obtained materials were cut into particles of the size ≤ 4 mm by using Retsch SM300 cutting mill. Test samples were obtained at 190°C by using MINIJECTOR 55 injection molding machine. Test samples represented cylinders with $d \times h$ 10 mm \times 35 mm. After injection molding, samples were milled to obtain the contact surface of 8 mm in diameter (Fig. 2). After

machining the samples were conditioned at room temperature ($23^\circ\text{C} \pm 2^\circ\text{C}$) for 48 h to allow relaxation to occur.

Tribological tests were provided on a Wazau TRM 500 system by using pin on disc test. Non-lubricated polymer samples were tested in contact with stainless steel 100Cr6 (bearing grade, $E = 21.98 \times 10^4$ MPa, 63–66 HRC) with prepared surface roughness of 0.10 ± 0.02 μm . Tests were performed at room temperature, sliding distance was 250 m, and applied load was 50 N.

Roughness of the samples was measured by using Mahr GD25 profilometer according to DIN EN ISO 4287:2010-07. Microscopic images were taken by using the Nikon Eclipse MA100 microscope; objective magnifications were 5, 10, 20, 50, and 100 times, while that of the camera – 100 times.

3. RESULTS AND DISCUSSION

Figure 3 represents surface morphology of the test specimens before subjecting to the wear test. As one can see, addition of the elastomer leads to increased surface roughness, i.e., if in the case of neat PP rather smooth surface with machined regular circular tracks is observed then in the case of the PP composite with 30 wt% of EOC machined tracks become more pronounced due to lower crystallinity and greater flexibility of the elastomer.

Due to complex structure of the investigated multi-phase polymeric systems it was necessary to choose appropriate wear conditions in order to avoid vibrations during the test. Consequently wear test was performed under different loading conditions. It was observed that at high force conditions ($F > 200$ N) samples showed vibration with jar, therefore loading force during the test was reduced to 50 N.

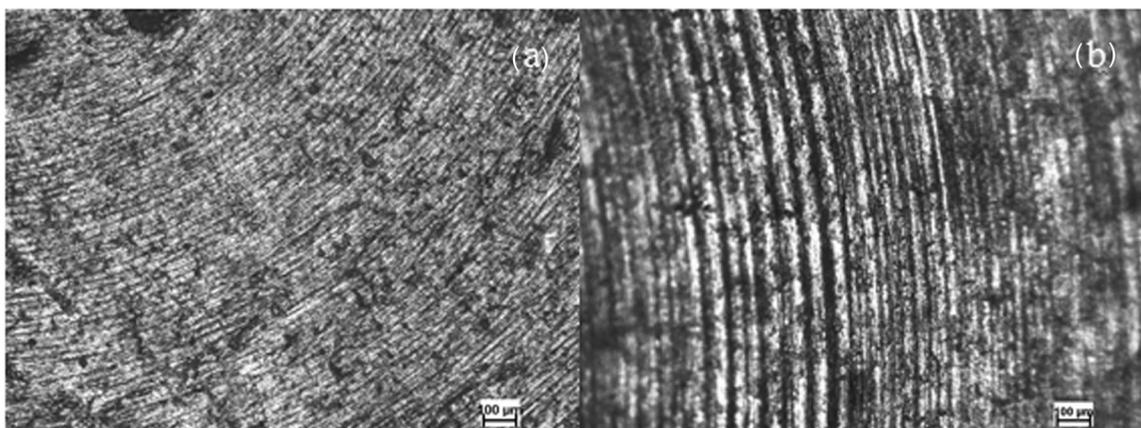


Fig. 3. Microscopic images of PP (left) and PP70/EOC30 composite (right) at 5 \times objective magnification.

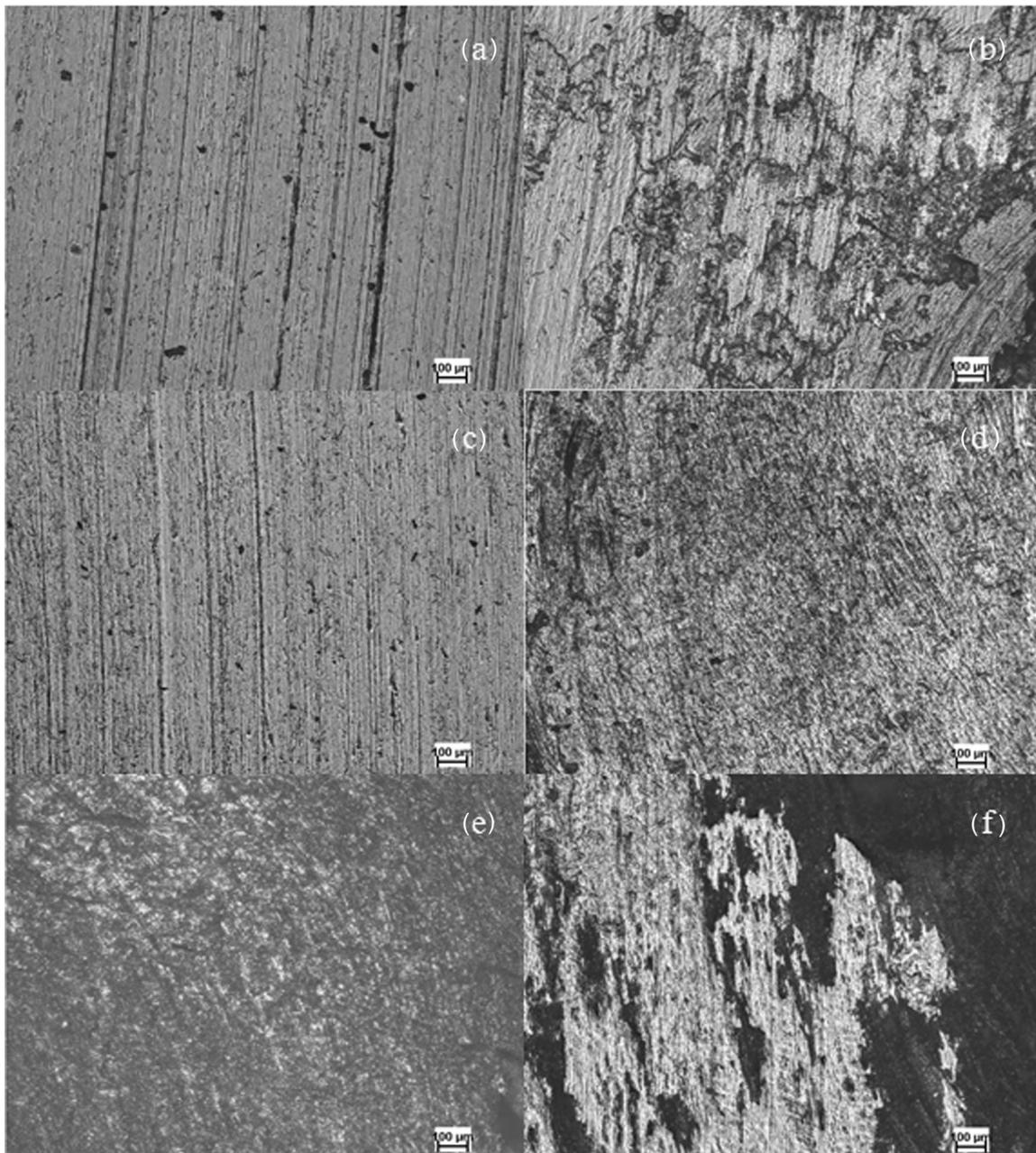


Fig. 4. Microscopic images of PP/EOC composites with 5× magnification: a – PP; b – PP with cleaved surface; c – PP90EOC10; d – PP90EOC10 with cleaved surface; e – PP70EOC30; f – PP70EOC30 with phase separated surface.

By evaluating surface morphology of the test samples after wearing, one can observe that neat PP samples show cleavage and cracks on the contact surface (Fig. 4b). Samples with 10–30 wt% of elastomer were less sensitive to cleavage and embrittlement (Fig. 4d) showing higher toughness of the composite as it has been also observed in [15]. In the case of the PP composites, containing 30 wt% of EOC, certain phase separation is observed, most probably due to insufficient compatibility between the two polymeric components.

In Fig. 5a, b phase separated surface of the PP/EOC30 composite is shown at greater magnifications allowing to distinguish the elastomer fraction deformed and pulled out of the PP matrix, evidently due to low melting temperature of EOC (about 60°C). Addition of ZnO to PP or PP blends with 10 wt% of EOC did not considerably influence surface morphology of the worn test samples. Addition of ZnO nanoparticles to the composites with higher EOC content (30 wt%) make the elastomeric phase stiffer. Consequently, no

pullout effect is observed on respective microscopic images (Fig. 5c, d).

Roughness after the wear test of the investigated PP based systems was also evaluated by means of the profilometer. As one can see from Fig. 6, in general the addition of the elastomer leaves greater effect on the composite roughness in comparison to ZnO. Roughness of the investigated PP matrix systems increase along with raising EOC content. For the composite containing 10 wt% and 30 wt% of the elastomer 4- and 40-fold increase is observed in comparison to the neat PP matrix. The effect of ZnO on the roughness of the investigated PP based systems is more complicated: up to certain ZnO concentration (0.1% for PP composites with 30 wt% of EOC and 0.5% for PP composites with 10 wt% of EOC) roughness of the investigated systems is decreased, while at higher nanofiller contents roughness is increased. The phenomenon could be explained by considering that at lower ZnO content better distribution of the nanofiller is expected, while at higher

ZnO content agglomeration of nanoparticles occur, yielding rougher surface.

By evaluating the changes of the coefficient of friction (COF) as a function of EOC content (Fig. 7) it was observed that addition of 10 wt% and 30 wt% of the elastomeric component to PP increased COF of the composite by 30% and 40%, respectively. This increase of COF along with raising the elastomer content is evidently connected with higher branching degree and lower crystallinity of EOC.

Contrary to the effect of EOC, addition of ZnO allows to reduce COF of the investigated polymer composite matrices. However, it should be mentioned that contribution of ZnO to the reduction of COF is greater at lower concentrations of the nanofiller in the polymer matrix. This phenomenon most evidently is connected with the fact that at smaller content ZnO nanofiller is more efficiently distributed in the polymer matrix yielding a higher surface area.

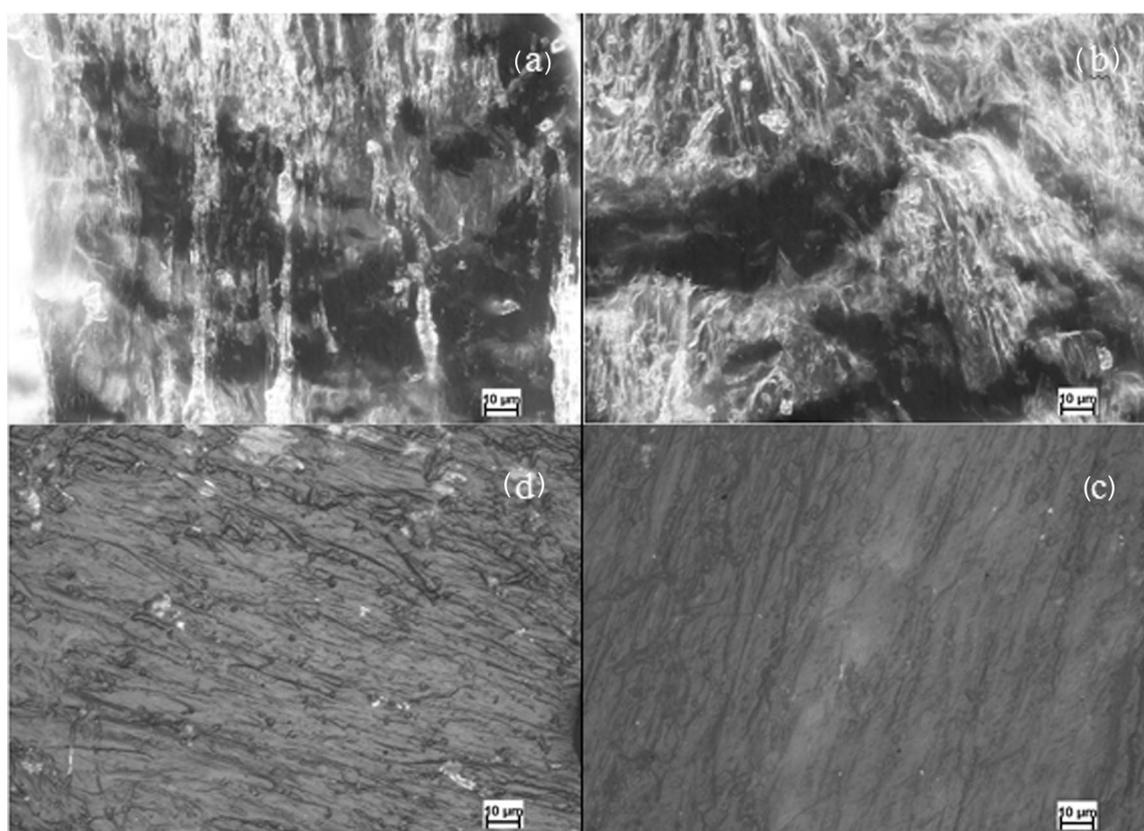


Fig. 5. Microscope images of PP/EOC/ZnO nanocomposites at 50× objective magnification: a, b – PP70/EOC30 composite; c – PP70/EOC30/ZnO0.1 nanocomposite; d – PP70/EOC30/ZnO2 nanocomposites.

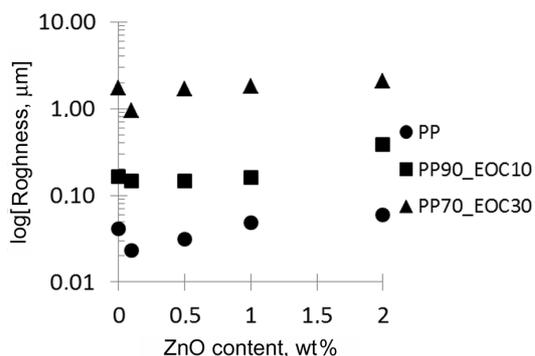


Fig. 6. Roughness after the wear test of PP/EOC/ZnO nanocomposites as a function of ZnO content.

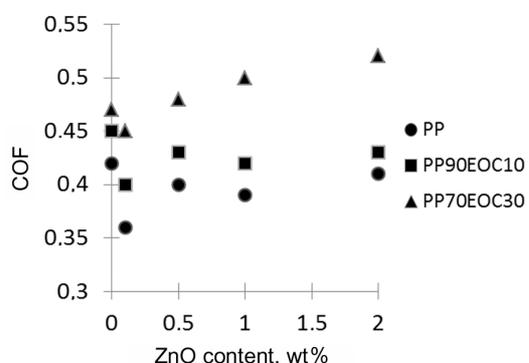


Fig. 7. Coefficient of friction of PP/EOC/ZnO nanocomposites as a function of ZnO content.

4. CONCLUSIONS

Investigations on the structure and tribological properties of ZnO and EOC modified PP have been performed. It has been determined that addition of EOC causes increment of the roughness as well as of the COF of investigated composites. Addition of ZnO in its turn assists in decreasing of the COF and increasing resistance to wear of the nanocomposites. It should, however, be mentioned that the effect of ZnO addition on the COF and surface roughness values of the investigated systems strongly depends on the dispersion quality of the nanofiller in the polymer matrix. Some structural and tribological features of PP/EOC/ZnO nanocomposites, such as dispersion of the nanofiller in the polymeric phases, stress relaxation after wearing, as well as the effects of other wear types on the surface quality and durability, needs further investigation.

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Nanostruktuurne ZnO täiteaine polümeer-polümeerkomposiitide modifitseerimiseks: struktuur ja triboloogilised omadused

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Materjalide isemäärivus on tööstuses hinnatud omadus. Käesolevas töös uuriti anisomeetrilise nanostruktuurse ZnO täiteaine (tetrapoodikujulised osakesed haru pikkusega 70–100 nm ja läbimõõduga 10 nm) ning etüleen-1-okteenkopolümeeri (EOC) mõju isotaktilise polüpropüleen (PP) struktuurile ja triboloogilistele omadustele. Täheledatai uuritud komposiitide pinnakareduse ja hõõrdumiskoeffitsiendi suurenemist EOC lisandi mõjul. ZnO lisand omakorda põhjustas teatud nanotäiteainesisalduste korral hõõrdumiskoeffitsiendi vähenemist ja pinna kvaliteedi paranemist.