DOI: 10.1002/masy.201251122

Nanocomposites Based on ZnO Modified Polymer Blends

R. Merijs Meri,[*1] I. Bochkov,[1] A. Grigalovca,[1] J. Zicans,[1] J. Grabis,[2] R. Kotsilkova,[3] I. Borovanska[3]*

Summary: Ethylene-octene copolymer (EOC) modified polypropylene (PP) and polyoxymethylene (POM) were used as matrices for development of ZnO modified composites. EOC content in the composites was 10, 30 and 50 wt%, while ZnO content was 2 and 5 wt%. It was determined that addition of ZnO increased stiffness, strength and thermal resistance, as well as decreased coefficient of friction of the investigated composites. Somewhat greater increase of these characteristics was observed at 2 wt% of ZnO. Properties ZnO modified composites are also strongly affected by incompatibility of it ingredients, especially at higher EOC content.

Keywords: blends; mechanical properties; nanoparticles; polyolefins

Introduction

In recent years development of polymer nanocomposites have experienced significant breakthrough. Many review reports testify about significant improvements of mechanical, barrier, electrical and magnetic properties of polymer nanocomposites.[1–3] Considerable increase of stiffness of many polymer nanocomposites unfortunately is associated with prompt decrease of its toughness. Thus choice of appropriate polymer matrix plays an important role. Significant prerequisite of thermoplastic polymer matrix lays in its melt processability and recyclability. Blending of two thermoplastic polymers, in its turn, allows obtaining unique materials with specific set of properties, not characteristic for its individual components. Furthermore, use of polymer blends becomes more and more popular in many branches of national economy. Consequently this research is devoted to the choice of the most appropriate polymer-polymer composition for the development of novel nanocomposite materials of engineering significance.

Thermoplastic elastomer ethylene-α-octene copolymer is used as high molecular modifier of POM and PP. It is expected that addition of certain amounts of EOC will increase impact behaviour of POM and PP based binary composites, allowing their use in varying applications, where tough superelastic materials are required. On the other hand addition of EOC could compensate some property drop of PP and POM based nanocomposites.

Nanostructured ZnO filler is used in variety of applications due to its photocatalytic reactions, self-purification, antibacterial and other properties. In many researches it is shown that ZnO increases thermal stability,[4,5] mechanical stiffness and strength[5] of certain composites, as well as decreases their coefficient of friction.[6] In these researches, however, pure polymers are used as matrices. Meanwhile, there is practically no information about polymer blend usage as matrix for ZnO modified polymer nanocomposites.

---

[1] Institute of Polymer Materials, Riga Technical University, 14/24 Azenes Street, Riga, LV1048, Latvia
E-mail: remo.merijs-meri@rtu.lv
[2] Institute of Inorganic Chemistry, Riga Technical University, 34 Miera Street, Salaspils-1, LV2169, Latvia
[3] Department of Physico Chemical Mechanics, Institute of Mechanics, Bulgarian Academy of Science, Acad. G. Bontchev Street, Block 1, 1113, Sofia, Bulgaria

Experimental Part

In this research following commercial products were used: polyoxymethylene copolymer (POM), Kolon Plastics Inc., Kocetal K300; homopolymer of isotactic polypropylene (PP), Lyondell Basell, Moplen *HP456J*; thermoplastic elastomer of ethylene-α-octene copolymer (EOC) with alpha octene content 38%, The Dow Chemical Company, Engage 8200.

Nanostructured ZnO nanofiller with average crystallite sizes of around 70 nm was synthesized in the RTU Institute of Inorganic Chemistry (Salaspils, Latvia).

Polymer composites with various EOC and ZnO contents (0, 10, 30, 50 wt% of EOC and 0, 2, 5 wt% of ZnO) were prepared by using two roll mills. POM based blends were processed at 170 °C and PP based blends at 180 °C. Blending time was 7 min. Suitable melt processing method was used to prepare specimens corresponding to the testing requirements.

Density was determined by using a Sartorius AG density measurement kit YDK 01 equipped with Sartorius AG electronic balance KB BA 100 (with precision 1E-5 g).

Calorimetric properties were characterized by using Mettler Toledo DSC1/200W differential scanning calorimeter. All measurements were made under N_2 flow; samples of ~10 mg were heated from −100 up to 200 °C at a scanning rate of 10 °C/min.

Thermal resistance was characterized by using Mettler Toledo TGA1/SF thermogravimetric analyser. All measurements were made under N_2 flow; samples of ~10 mg were heated from 25 up to 800 °C at a scanning rate of 10 °C/min.

Tensile properties were investigated by using Zwick/Roell BDO FB-020FN universal testing machine (with a test temperature of 22 ± 2 °C; a test speed for modulus determination of 1 mm/min.; a test speed for determination of other stress-strain characteristics of 50 mm/min.).

Coefficient of friction (COF) was determined by using *CETR* Universal Material Tester UMT, Pin on Flat mode. Stainless steel metallic pin (D = 6.35; L = 25.4) contacted with the surface of flat polymer sample. All measurements were made under a load of 20 N, a force of 10 mm/s, and a distance of 10 mm.

Results and Discussion

Exploitation properties of multicomponent polymer systems strongly depend on mutual interaction of it ingredients. Interplay between the ingredients of the investigated nanocomposites is characterized in Figure 1 by means of experimental density deviations from theoretical ones, calculated here according to the rule of the mixtures.

As shown in Figure 1 deviations of the experimental densities from the theoretical

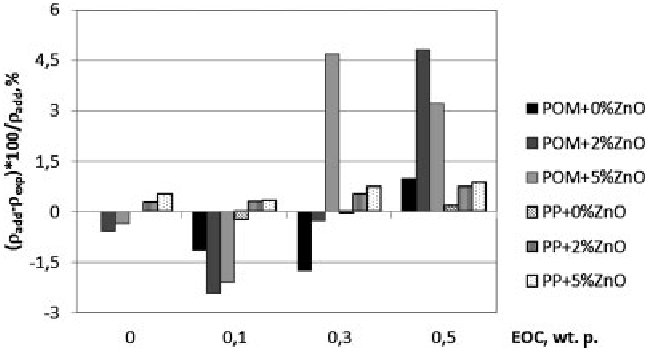

Figure 1.

Relative deviations of the experimental densities ρ_{exp} from the additive densities ρ_{add} of POM/EOC/ZnO and PP/EOC/ZnO composites as function of EOC weight content.

ones, representing both changed crystallinity and structural imperfectness (void content) of the investigated systems, are larger for POM based compositions. Probably this could be explained with less similar structure, and hence lower compatibility, between POM and EOC in comparison to that between PP and EOC.

Tensile stress-strain characteristics of the investigated compositions are shown in the Figure 2. As already expected addition of EOC lower stiffness and strength of the investigated compositions and raise their relative elongations to certain extent. Limited increase in relative elongation values of the compositions along with addition of EOC (observed only up to 30 wt%), most probably is connected with incompatibility of the blend components, which is especially pronounced in the case of POM/EOC blends.

Considering the effect of ZnO on the mechanical properties of thermoplastic matrices, it is reported[7] that the extent of stiffness and strength increase usually is highly dependent on the dispersion degree

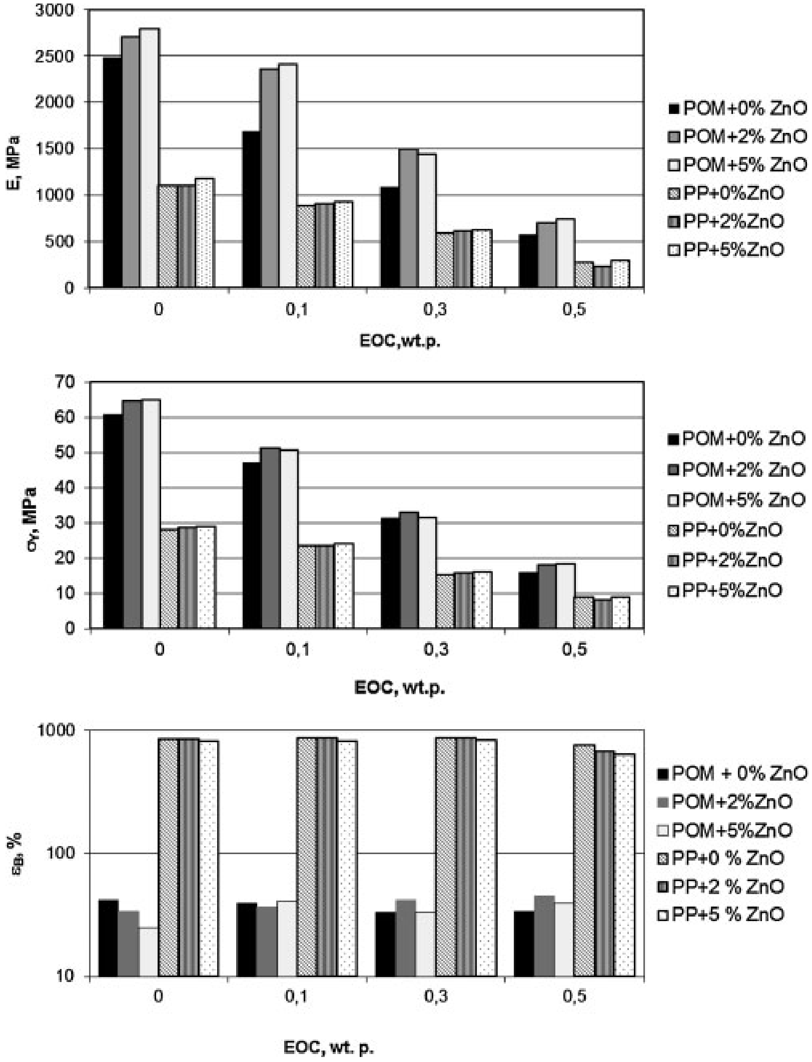

Figure 2.
Stress-strain characteristics of ZnO modified POM/EOC and PP/EOC blends as function of EOC weight content.

of the nanofiller. Similar statements evidently are true also in the case of the investigated blends. For an example, the modulus of elasticity of POM90/EOC10/ZnO5 is increased by ~40%, while that of POM70/EOC30/ZnO5 by ~30% in respect to the modules of respective binary blends. These changes can be explained also because of the effect of ZnO on the crystallinity degree χ of the above mentioned compositions; with raising nanofiller content up to 5 wt% χ is raised by 15% for both compositions. As in the case of PP based composites, these changes are smaller (~1 and 12% respectively for analogous compositions), and the effectiveness of ZnO addition is also smaller. It should be, however, mentioned that addition of 2 wt% of ZnO nanofiller is optimal for modification of the investigated polymer systems, independently from the polymer matrix used. At higher nanofiller content, reinforcing efficiency is somewhat reduced, especially in the case of POM based systems. This could be connected with greater agglomeration of ZnO in the matrix of POM based systems. Another factor that evidently influences the effectiveness of ZnO modifier is incompatibility of the blend components. Consequently reinforcing effectiveness of ZnO is higher for the blends with lower EOC concentrations.

Apart from evaluating stress-strain characteristics of the investigated POM/EOC and PP/EOC nanocomposites, the effect of ZnO on lowering of coefficient of friction (COF) of EOC modified thermoplastics is also assessed. It is demonstrated that addition of ZnO nanofiller allow successfully decrease COF of the materials investigated, starting from POM, already having excellent tribological properties (COF decreased by ~1.5% at maximum ZnO content), and ending with EOC, showing the highest COF (COF decreased by ~16% at maximum ZnO content). Besides it has been observed that addition of 2 wt% of ZnO ensures the most rapid decrease of the values of COF; at higher nanofiller content modifying effectiveness of ZnO nanofiller is evidently reduced, most probably due to increasing agglomeration trends, as it has been reported elsewhere.[5]

Good distribution of nanofiller in a polymer matrix is especially important for increasing thermal resistance of the materials. Consequently thermogravimetric curves of the selected POM and PP compositions, modified with 2 wt% of ZnO nanofiller, are shown in Figure 3.

As one can see addition of only 2 wt% of ZnO shifts thermogravimetric curves of the investigated compositions to higher temperatures by several degrees. It should however be remembered that thermogravimetric tests have been made in artificial conditions, i.e., in nitrogen atmosphere. It is expected that in oxidative atmosphere, at which processing of polymer composites is

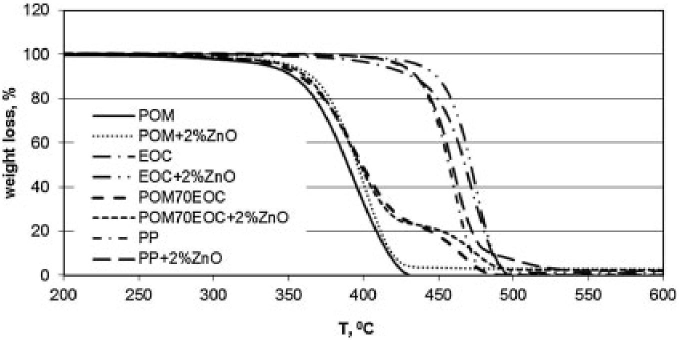

Figure 3.
Thermogravimetric curves of POM, PP, EOC, POM blend with 30 wt% of EOC and their respective composites with 2 wt% of nanostructured ZnO filler.

commonly performed, the protective effect of ZnO modifier will be much greater.

Conclusion

Results of the investigation show that certain amount of elastomer additive (up to 30 wt %) allows improving toughness of the composites based on either POM or PP matrices. Addition of optimal amount of ZnO nanofiller (2-5 wt%), in its turn, allows improve stiffness, strength and thermal resistance, as well as decrease coefficient of friction of the investigated nanocomposites. Somewhat greater increase of these characteristics is observed at 2 wt% of ZnO. Properties of ZnO modified composites unfortunately are strongly affected by incompatibility of it ingredients, especially at higher EOC content.

Acknowledgements: This research has been supported by the COST Action MP0701

[1] S. Pavlidou, C. D. Papaspyrides, *Prog. Polym. Sci.* **2008**, *33*, 1119.
[2] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, *Prog. Polym. Sci.* **2010**, *35*, 357.
[3] H. P. S. Abdul Khalil, A. H. Bhat, A. F. Yusra, *Carbohyd. Polym.* **2012**, *87*, 963.
[4] S. C. Liufu, H. N. Xiao, G. P. Li, *Polym. Degrad. Stabil.* **2005**, *87*, 103.
[5] S. Wacharawichanant, S. Thongyai, A. Phutthaphan, C. Eiamsamang, *Polym. Test.* **2008**, *27*, 971.
[6] F. J. Carrión, J. Sanes, M.-D. Bermúdez, *Wear* **2007**, *262*, 1504.
[7] S. Wacharawichanant, N. Thongbunyoung, P. Churdchoo, T. Sookjai, *Sci. J. UBU* **2010**, *1*, 20.