Effect of Ethylene-Vinyl Acetate Copolymer on Properties of Acrylonitrile-Butadiene-Styrene/Zinc Oxide Nanocomposites

Sirirat Wacharawichanan*¹
Lalitwadee Noichin ¹
Sutharat Bannarak ¹
¹ Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand.
* e-mail: iamsirirat@yahoo.com

Mechanical and morphological properties of acrylonitrile-butadiene-styrene (ABS)/zinc oxide (ZnO) nanocomposites used ethylene-vinyl acetate copolymer (EVA) as compatibilizer were investigated. The ABS/ZnO nanocomposites without and with EVA 4 wt% were prepared by melting-blend with an internal mixer. The results showed that the addition of ZnO nanoparticles did not improve the mechanical properties of ABS/ZnO nanocomposites. The impact strength of the ABS/ZnO nanocomposites decreased with increasing ZnO content. The addition of EVA in ABS showed a decrease the impact strength but increased after adding ZnO in ABS/EVA matrix. The ABS/ZnO nanocomposites with EVA was higher the percent strain at break, but lower Young’s modulus, tensile strength and impact strength than the neat ABS and ABS/ZnO nanocomposites. The percent strain at break of ABS/ZnO nanocomposites increased with incorporation of EVA all ZnO compositions. However, the poor compatibility between ethylene in EVA and ABS matrix reduced as most of the mechanical properties of ABS/EVA/ZnO nanocomposites. The ZnO particle distributions in nanocomposites were studied by scanning electron microscopy (SEM), which observed that ZnO particles agglomerated in ABS and ABS/EVA matrix. The fractured surfaces of impact test samples were also observed through SEM and revealed that the ductile fracture of ABS was converted to brittle fracture with addition of ZnO.

Keywords : Acrylonitrile-Butadiene-Styrene, Ethylene-Vinyl Acetate Copolymer, Zinc Oxide, Polymer Nanocomposites, Mechanical Properties, Morphology
INTRODUCTION

Polymer nanocomposites represent a new and rapidly developing area of new materials. Nanoparticles are added as filler material to polymers to create nanocomposites with a good physical and mechanical properties. Because of their small size, nanoparticles have a high surface to volume ratio and provide high-energy surfaces, and the nanoparticles easily agglomerate (Pöllänén et al. 2010, Chae and Kim 2005, Kar et al. 2008, Yang et al. 2006). Achieving enhanced properties of nanocomposites also depends on a strong interaction between the nanoparticles and matrix. Most polymers are hydrophobic and metal oxide nanoparticles are hydrophilic, thus the compatibilizer is used to enhance compatibility between nanoparticles and polymers (Pöllänén et al. 2010). In polymer composites, ZnO nanopowder is one of the widely used filler. ZnO enhances the thermal, mechanical, UV resistance, as well as other relevant properties of the composites. Moreover, ZnO nanoparticles are non-toxic, stable, and highly thermostable inorganic filler (Deka and Maji 2012).

Acrylonitrile-butadiene-styrene (ABS) is a widely used thermoplastic material and prepared from acrylonitrile, butadiene, and styrene monomers. The advantage of ABS is that this material combines the strength and rigidity of the acrylonitrile and styrene polymers with the toughness of the polybutadiene rubber (Kar et al. 2008). Ethylene-vinyl acetate (EVA) copolymer is polar in nature due to vinyl acetate (VA) group and polarity of EVA increases with an increase in VA content. Various properties of EVA-based nanocomposites prepared by melt-blending technique were reported and showed that the polar VA group in EVA can affect the dispersion and interaction of nanoparticles within EVA (Ali et al. 2011).

The composites of ABS and metal oxides have been studied in the past literatures such as Kar et al. (2008) prepared ABS/α-alumina (Al₂O₃) nanocomposites and they reported that the ABS/Al₂O₃ nanocomposites were found to have slightly higher Young’s modulus, but lower tensile strength, percent strain at break, flexural and impact strength than the virgin ABS. But its flexural modulus increases with increasing Al₂O₃ content in ABS matrix. Wang et al. (2008) studied the properties of ABS/CaCO₃ and ABS/CaCO₃/EVA nanocomposites. The results showed that CaCO₃ nanoparticles could increase the flexural modulus of ABS/CaCO₃/EVA nanocomposites and maintain or increase their impact strength for a certain nano-CaCO₃ loading range. The tensile strength of the nanocomposites decreased by adding CaCO₃ nanoparticles.

This work studies the effect of EVA compatibilizer on the mechanical and morphological properties of ABS/ZnO nanocomposites. The nanocomposites were prepared by melt mixing technique in an internal mixer. The mechanical properties were investigated by tensile and impact test. The morphology of the nanocomposites was observed by scanning electron microscopy (SEM).
EXPERIMENTAL

Materials
ABS was supplied with the trade name of “INEOS” by INEOS ABS (Thailand) Company. The melting temperature of the ABS was around 105 °C and a melt flow rate of 38.2 g/10 min. EVA copolymer with a content of 18% vinyl acetate by weight and a melt flow index of 2.3 g/10 min was supplied as pellets by TPI Polene Company under a trade name of POLENE. ZnO in the form of a white powder with average particle sizes of 67 nm was produced by Aldrich Company.

Sample preparation
ABS, EVA pellets and ZnO particles were dried in an oven at 80°C for 3 hours before melt blending. The ZnO loading of nanocomposite samples was 1, 3, 5, 7 wt% based on ZnO contents. The ABS/ZnO nanocomposites without and with adding EVA 4 wt% were prepared by using an internal mixer at 170 °C and a screw speed of 50 rpm for 10 min and, finally, the nanocomposites were compression-molded in a hot press at 170 °C for 20 min for further characterization.

Sample Characterization
Tensile tests were conducted according to ASTM D 638 with a universal tensile testing machine (LR 50k from Lloyd instruments) at a crosshead speed of 50 mm/min. Izod impact strength tests were performed with an impact tester (Zwick/material testing August-Nagelstr.11.D-89079 Ulm) at room temperature. Each value obtained represented the average of five samples.

The morphology of impact-fractured surfaces of the ABS/ZnO nanocomposites without and with EVA compatibilizer and the dispersion of ZnO particles in the matrix were investigated by SEM instrument (Maxim 2000S, CamScan Analytical, England) with gold coated specimens.

RESULTS AND DISCUSSION

Mechanical Properties
The Young’s modulus for the nanocomposites of ABS/ZnO with and without EVA compatibilizer is presented in figure 1. The results found that Young’s modulus of ABS with EVA decreased considerably when compared to neat ABS.

![Fig. 1: Young's modulus of ABS/ZnO and ABS/ZnO/EVA nanocomposites](image-url)
However, Young’s modulus of ABS/EVA blends increased after adding ZnO. It was also observed from figure 1 that Young’s modulus of ABS/ZnO nanocomposites without EVA was higher than those of with EVA. It can be concluded that the incorporation of ZnO did not improve Young’s modulus of the reinforced nanocomposites. The addition ZnO showed the increase of Young’s modulus of ABS/EVA blends. This could be due to ZnO was mostly contained in EVA phase or ZnO particles are encapsulated by EVA. This conclusion will be further proven by the morphological investigation.

Figure 2 shows the variation of tensile strength of ABS/ZnO without and with EVA. The results found that the tensile strengths of both nanocomposites did not change significantly with increasing ZnO content. This result affected from the weak interfacial adhesion between ABS and ZnO nanoparticles was the main reason for the poor tensile strength. It can be seen from figure 6 that most of the nanoparticles existed in aggregates and had a poor compatibility with the matrix. The tensile strength of ABS/ZnO nanocomposites without EVA was higher than those of with EVA. This observation indicated that the addition of EVA caused a reduction of tensile strength of ABS/ZnO nanocomposites.

The percent strain at break for the nanocomposites of ABS/ZnO with and without EVA compatibilizer is presented in figure 3. The results found that the percent strain at break of ABS did not change when ZnO was added, but the addition of EVA caused an increase in percent strain at break of ABS and ABS/ZnO nanocomposites. The nanocomposites of ABS/ZnO with EVA had higher percent strain at break than those of without EVA. The presence of EVA improved the percent strain at break of the ABS/ZnO nanocomposites due to the elastomer effect of EVA.

The variation of impact strength of ABS/ZnO nanocomposites is shown in figure 4. From the figure, the impact strength decreased with increasing ZnO content but the incorporation of EVA showed the decrease and then increased after adding ZnO, and a maintain impact strength in a range of 1-7 wt% of ZnO. The obtained results led us to conclude that the addition of EVA induced the reduction of
Effect of Ethylene-Vinyl Acetate Copolymer on Properties of Acrylonitrile-Butadiene-Styrene/Zinc Oxide Nanocomposites

the impact strength of ABS which may be caused from the EVA had a low impact strength. Moreover, ABS/ZnO nanocomposite without EVA had impact strength small higher than ABS/ZnO nanocomposites with EVA. Additionally, the decrease of the impact strength may be affected from appeared porous in ABS matrix after adding ZnO particles, which confirmed by SEM observation. However, the poor compatibility between ethylene in EVA and ABS matrix reduced as most of the mechanical properties of ABS/EVA/ZnO nanocomposites.

Morphology

SEM micrographs of the impact-fractured surfaces of ABS and ABS/EVA are presented in figure 5. For the pure ABS, the fractured surface shows that ABS is ductile materials (Figure 5(a)) and undergoes a plastic deformation prior to fracture (Kar et al. 2008). While the fracture surface of the ABS matrix shifted from ductile to brittle.
with the incorporation of EVA as shown in figure 5(b).

The impact-fractured surfaces of the nanocomposites with and without EVA are presented in figure 6. It was observed that the pulled out sites of ZnO particles were usually observed in the both nanocomposites which indicated the interfacial interactions between the polymer matrix and the ZnO were rather poor and the incorporation of EVA did not improve the interfacial adhesion. The increasing the ZnO content in ABS nanocomposites led to be larger agglomerates. These observations are also in accordance with the fact that the available nanoparticles are generally in the form of agglomerates, and it is rather hard to be dispersed in their initial dimensions. This is due to the strong interaction among them (Kontou and Anthoulis 2007). Moreover, the fracture surface of the ABS nanocomposite prepared with the incorporation of 1, 3, 5, and 7 wt% ZnO indicated ductile fracture was converted to brittle fracture.
CONCLUSION

Mechanical and morphological properties of ABS/ZnO nanocomposites without and with EVA 4 wt% were studied. The results showed that the addition of ZnO nanoparticles did not improve the mechanical properties of ABS/ZnO nanocomposites. The impact strength of the ABS/ZnO nanocomposites decreased with increasing ZnO content. The addition of EVA in ABS showed a decrease the impact strength but increased after adding ZnO in ABS/EVA matrix. The ABS/ZnO nanocomposites with EVA was higher the percent strain at break than those of without EVA. The percent strain at break of ABS/ZnO nanocomposites increased with incorporation of EVA all ZnO compositions. However, the poor compatibility between ethylene in EVA and ABS matrix reduced as most of the mechanical properties of ABS/EVA/ZnO nanocomposites. SEM study observed that ZnO particles agglomerated in ABS and ABS/EVA matrix and the fractured surfaces of impact test samples revealed that the ductile fracture of ABS was converted to brittle fracture with addition of ZnO.

ACKNOWLEDGEMENTS

The authors would like to thank Silpakorn University Research and Development Institute (SURDI) for the financial support of this project.

REFERENCES