

TENSILE PROPERTIES OF POLYPROPYLENE/METAL OXIDE NANO COMPOSITES

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Abstract

Polymers reinforced with nano metal oxides open up new pathways for engineering flexible composites that exhibit better mechanical and chemical properties. In this study, tensile properties of the polypropylene (PP) composites filled with nano titan dioxide (TiO₂) and zinc oxide (ZnO) were investigated. Nano particles were coated with maleic anhydride grafted styrene ethylene butylene styrene (SEBS-g-MA) and silane, respectively prior melt mixing for better surface adhesion and fine dispersion. Nano composites were obtained by using twin screw extruder at TiO₂ and ZnO loading of 1%, 3% and 5%. Firstly, thermal analysis was done to obtain melt temperature, crystallization temperature and degree of crystallinity. Then, tensile test was applied to obtain yield strength, tensile strength, elastic modulus and elongation of the composites. Due to the stiff structure of the metal oxides, all tensile properties except elongation were increased. On the other hand, although TiO₂ has higher hardness than ZnO, the elongation of the composites with TiO₂ was higher than that of with ZnO. This is probably due to the better compatibility of TiO₂ with SEBS-g-MA and this case induced more fine structure of TiO₂ with PP while ZnO particles agglomerated in some regions of the matrix which confirms the results of lower elongation and degree of crystallization.

Keywords: polypropylene, nanocomposite, titan dioxide, zinc oxide, tensile properties

1. INTRODUCTION

Polymers reinforced with nano metal oxides become popular every day because of their improved mechanical strength, flexibility in designing besides better chemical, electrical and optical properties (Breiner&Mark,1998; Omar,Ishak,Ismail& Fuad,1995; McCarthy & Mark,1998; Rong, Zhang, Zheng, Zeng & Friedrich,2001)

On the other hand, nano particles may agglomerate and thus degrade the properties of the nano composites. To overcome this problem, dispersant and coupling agents are being used (Tongpool, Kruenate & Panyathanmaporn,2004). Furthermore, the decreasing of the impact strength due to the stiffness of the inorganic material is another problem generally encountered. Researchers use elastomeric nature materials to increase the toughness of the composites (Bao&Tjong,2007;Ishak, Chow&Rochmadi,2008).In this work, tensile properties of the polypropylene reinforced with nano zinc oxide and nano titan dioxide were investigated. Improved tensile properties were obtained by using silane and SEBS-g-MA for better dispersion and surface adhesion between the metal oxide and the matrix.

2. EXPERIMENTAL WORK

2.1 Materials and Preparation of the Nano Metal Oxides

Polymer material used in this study was polypropylene copolymer (56M10, Sabic Company) with melt flow index of 6.2 g/10 min, density of 0.902 kg/cm³. Nano material was ZnO and TiO₂ (Nabond Company, China).

SEBS-g-MA (FG1901X, Kraton, Shell Company) and vinyltrimethoxysilane (VTMS, Aldrich) were used for coating the nano TiO₂ particles for better surface adhesion and dispersion.

The nano metal oxide particles were coated with them SEBS-g-MA and then silane, respectively. SEBS-g-MA was used as compatibilizer and by coating the powders with it, the coupling agent property of the SEBS-g-MA was thought to be more effective. Silane coating was for better dispersion of the SEBS-g-MA coated particles in the polymer matrix. Coating was applied by melt mixing of the nano particles with SEBS-g-MA which was dissolved in toluene in 48 hours at 25 °C. SEBS-g-MA coated nano powders were pulverized after drying the mixture at 50°C for 8 hours. Silane coating was applied by preparing a solution of 96% absolute alcohol and 4% distilled water with 1% silane. SEBS-g-MA coated nano particles was added slowly to this solution and mixed for 3 hours. The mixture was pulverized after drying at 50 °C for 8 hours.

2.2 Blending

The addition of the nano composites was applied in three different ratios as 1%, 3% and 5%. The coding of the composites was done as follows: PP/1TiO₂, PP/3TiO₂, PP/5TiO₂ and PP/1ZnO, PP/3ZnO, PP/5ZnO. The nano powders and the polymer were loaded into a twin screw extruder (Rondol MicroLab, England) with L/D ratio of 20. The operation temperature was set as 220, 200, 180, 120 and 75 °C and the speed of the screw was 60 rpm. The extrudate strands were granulized and dried at 80 °C under vacuum for two hours.

2.3 Differential Scanning Calorimetry (DSC)

The melting and crystallization behaviors were studied by differential scanning calorimetry (DSC, Perkin Elmer DSC-7) in nitrogen atmosphere. The samples (4-5 mg) were heated from 40 °C to 180 °C at 10 °C/min and held at 180 °C for 5 min and then cooled back to 40 °C at 10 °C /min and held 5 min at 40°C. Then, second heating cycle was performed to delete the thermal history of the samples. The melting temperature (T_m), crystallization temperature (T_c) and degree of the crystallization (X_c) were obtained. The fusion enthalpy of 100% crystalline phase of the PP was taken as 209 J/g in calculating the degree of the crystallization of the blends (Scheirs,2000).

2.4 Injection Molding

The dried granules of the composites were injection molded with a 40 tone injection molding machine. Tensile test specimens were obtained. The mold temperature was 40 °C, injection pressure was 65 MPa, holding pressure 45 MPa, holding time 15 s and cooling time was taken as 10 s.

2.5 Scanning Electron Microscope

Morphology of the fracture surface of the each specimen was analyzed by scanning electron microscope (JEOL JSM-5910 LV). The fracture surfaces obtained from the impact tests were etched with tetrahydrofuran (THF) and then washed with acetone and dried under vacuum. Finally, all the specimens were coated with gold.

2.6 Tensile Test

Tensile test was carried out by universal tensile machine (Zwick Z010) at room temperature according to ISO R-527. The speed of the cross head was 50 mm/min.

3. RESULTS AND DISCUSSION

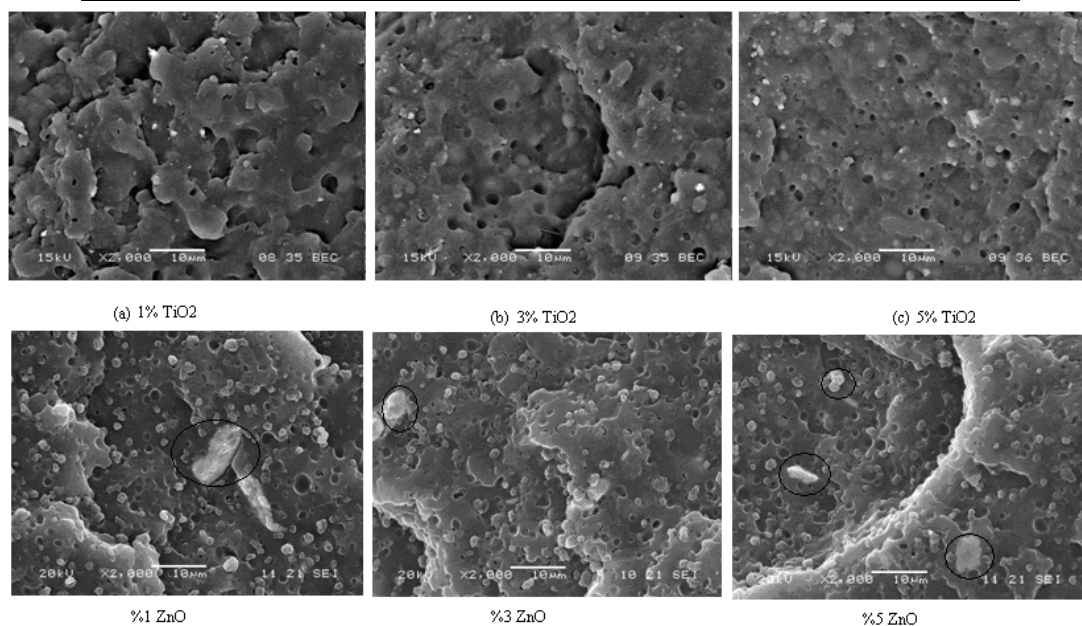
3.1 Thermal and Morphological Characterization

The DSC results of the composites are given in Table 1. Melt temperature (T_m) and crystallization temperature (T_c) did not change very much with the addition of TiO₂ and ZnO. On the other hand, ZnO addition reduced degree of crystallization more than that of TiO₂ which indicates that TiO₂ particles did not influence the stability of the PP. The retarding effect of zinc oxide on the PP crystals and the physical hindrance effect on the

molecular chains were more obvious in PP/ZnO composites. This effect is probably due to the better physical compatibility of TiO₂ with SEBS-g-MA and fine dispersion of the nano particles. There are many studies about the effects of nano particles on the degree of crystallization. Some of them accepted these particles as nucleating agents and some experimental observations showed diversified results (Chan,Wu,Li &Cheung,2002 ; Li,Wei&Sue,2002; Ma, Zhang,Qi,Li&Hu,2002). For example, for nano CaCO₃ filled PP, the increasing nanofiller content did not affect the crystallinity (Chan,Wu,Li &Cheung,2002).However, in other studies about clay/PP composites, crystallinity either increased (Li,Wei&Sue,2002) or decreased (Ma, Zhang,Qi,Li&Hu,2002). Also, Chandramaouleswaran et al (Chandramoulesswaran,Mhaske&Kathe,2007) found reduction in crystallinity of PP/nano ZnO composites similar to the obtained results in this study. Researches (Bahloul, Legare,David& Cassagnau,2010; Zebarjad,Sajjadi,Tahani&Lazzeri2006) on nano titan dioxide reinforced composites generally reported that TiO₂ did not affect degree of crystallinity very much or behaved as nucleating agent (Garcia,Vliet,Jain,Schrauwen,Sarkissov&Boukamp,2004; Wang,Wang& Zhang,2009). The possible agglomerates given in Fig. 1 within black circles strengthen the result of lower crystallinity of the ZnO composites. On the other hand, composites with reinforced TiO₂ gave more homogenous and fine dispersed morphological structures.

Table 1. Thermal properties of the composites

Blend	T _m (°C)	T _c (°C)	Enthalpy (J/g)	X _c (%)
Original PP	166,3	124,9	85,4	40,86
PP/1TiO ₂	165,8	122,9	82,7	39,57
PP/3TiO ₂	166,1	124,5	81,2	38,85
PP/5TiO ₂	166,5	125,1	83,1	39,76
PP/1ZnO	166,6	123,1	65	31,10
PP/3ZnO	165,9	123,4	63,42	30,34
PP/5ZnO	165,9	123,1	64,6	30,91

Fig. 1. SEM images of PP/TiO₂ and PP/ZnO nano composites

3.2 Tensile Properties

Metal oxides enhanced the mechanical properties of the polymer composites (Kruenate,Tongpool &Panyathanmaporn,2004).

Generally tensile properties such as tensile strength, elastic modulus, stress at break increase while elongation decreases(Bao&Tjong,2007; Garcia,Vliet,Jain,Schrauwen,Sarkissov&Boukamp,2004). Representative stress-strain curves obtained from the tensile test are shown in Fig. 2. Although ZnO has more ductile character than TiO₂, the elongation of the PP/TiO₂ composites found in this study was higher than that of PP/ZnO composites.

This is probably due to the elastomeric material of SEBS-g-MA. SEBS-g-MA showed more compatible structure with TiO_2 as discussed before in thermal properties. It is known that the interface between the polymer matrix and SEBS is strong due to the compatibility of their phases because SEBS could diffuse into the polymer under the formation of miscelles (Setz, Stricker, Kressler, Duscher & Mulhaupt, 1996).

Maleic anhydride functional groups grafted to the ethylene butylenes (EB) mid block of SEBS. Then, it becomes easier for the molecular chains of SEBS-g-MA and the polymer to bond with metal oxide. As result, the homogenous, fine dispersed structures can be obtained. However, according to the thermal analysis and tensile test results, SEBS-g-MA coated of ZnO particles were not dispersed as fine as TiO_2 particles. Fig. 3 gave the comparison of the effects of the two metal oxides on the tensile properties of the composites. Due to the stiff structure of the TiO_2 and better surface adhesion between the nano particle and the polymer matrix, yield strength, tensile strength and elastic modulus was higher than that of composites with ZnO. At 1% addition of the both metal oxides, an apparent increase was observed in the tensile properties except elongation. The increment in this ratio of the metal oxides was also very close to each other. At 3% and 5% loading of TiO_2 gave better results in every case.

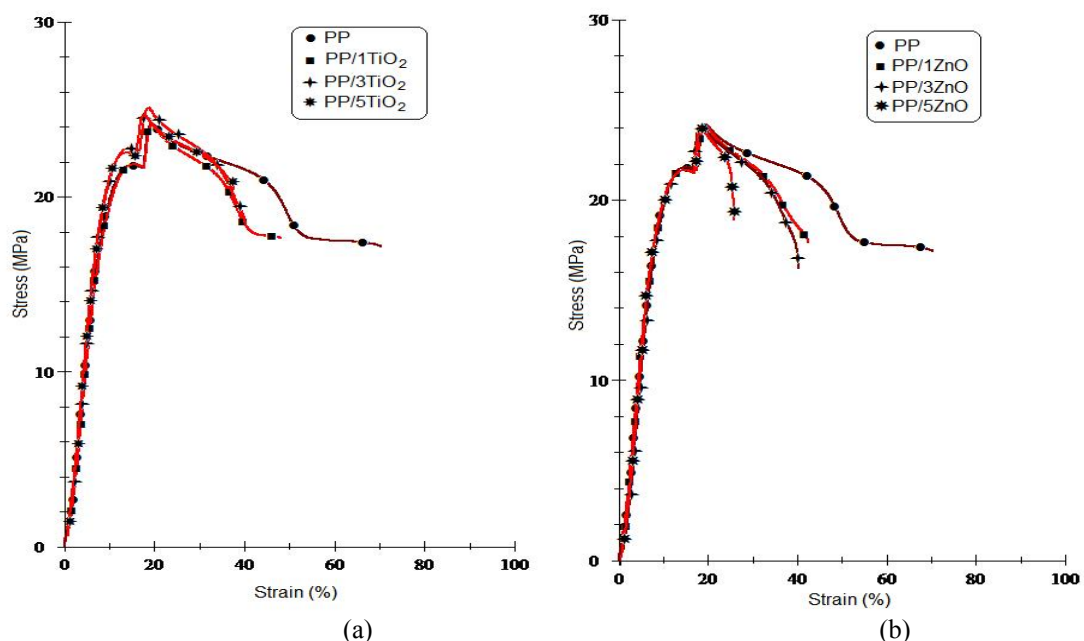


Fig 2. Stress-strain curves of the composites a) PP/ TiO_2 and b) PP/ ZnO

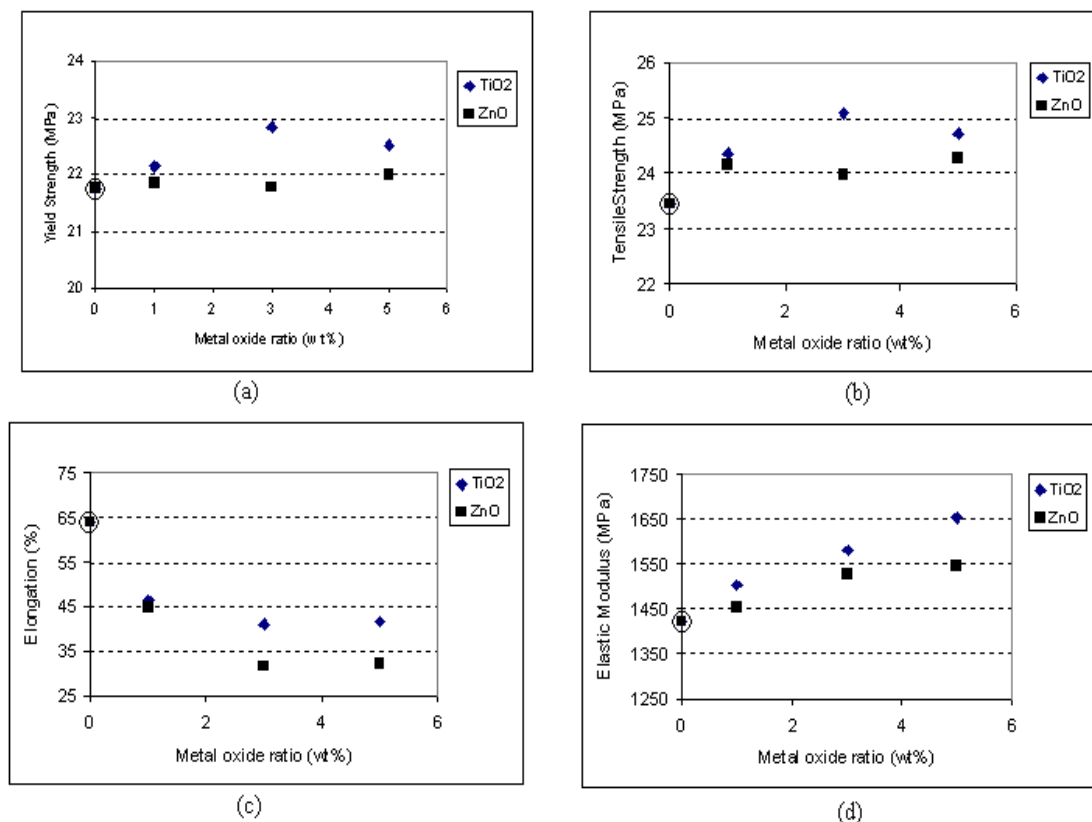


Fig. 3 Tensile properties of nano TiO₂ and ZnO reinforced PP (a-yield strength, b-tensile modulus, c- elongation d-elastic modulus), \odot : original PP

4. CONCLUSION

Metal oxides improve tensile properties but every metal oxide behaves different according to its physical, mechanical and chemical properties. In this study, two nano metal oxides were used as TiO₂ and ZnO for improving tensile properties of the polypropylene composites. SEBS-g-MA coating of the particles provided better surface adhesion besides fine dispersion together with silane. TiO₂ gave higher yield strength, tensile strength and elastic modulus due to its stiff structure and also its higher hardness than that of ZnO was effective in this result. On the other hand, elongation of the PP/TiO₂ composites was expected to be lower when compared with ZnO reinforced composites but just the opposite was obtained especially in the ratios over %1. This shows the compatibility of SEBS-g-MA was better with TiO₂ than ZnO. Furthermore, ZnO agglomerates appeared in some regions of the matrix reduced the tensile properties also crystallinity of the PP/ZnO composites.

5. ACKNOWLEDGMENT

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References

- Bahloul, W., Legare, V., David, L., & Cassagnau, P. (2010). Morphology and viscoelasticity of PP/TiO₂ nanocomposites prepared by in situ sol-gel method. *Journal of Polymer Science: Part B: Polymer Physics*, 48, 1213-1222.
- Bao, S. P., & Tjong, S. C. (2007). Impact essential work of fracture of polypropylene/montmorillonite nano composites toughened with SEBS-g-MA elastomer, *Composites: Part A*, 38(3), 78-387.

- Breiner, J. M., & Mark, J. E. (1998). Preparation, structure, growth mechanisms and properties of siloxane composites containing silica, titania or mixed silica-titania phases. *Polymer*, 39, 5486-5493.
- Chan, C. M., Wu, J. S., Li, J. X., & Cheung, Y. K. (2002). Polypropylene/calcium carbonate nanocomposites. *Polymer*, 43, 2981-2992.
- Chandramoulesswaran, S., Mhaske, S. T., & Kathe, A. A. (2007). Functional behaviour of polypropylene/ZnO soluble starch nanocomposites. *NanoTechnology*, 18(38).
- Fuad, M. Y. A., Ismail, Z., Ishak, Z., & Omar, A. K. M. (1995). Application of rice husk ash as fillers in polypropylene: effect of titanate, zirconate and silane coupling agents. *European Polymer Journal*, 31, 885-893.
- Garcia, M., Vliet, G. V., Jain, S., Schrauwen, B. A. G., Sarkissov, A., & Boukamp, B. (2004). Polypropylene/SiO₂ nano composites with improved mechanical properties. *Reviews on Advanced Materials Science*, 6, 169-175.
- Ishak Mohd, Z. A., Chow, W. S., & Rochmadi, T. T. (2008). Compatibilizing effect of SEBS-g-MA on the mechanical properties of different types of OMMT filled polyamide 6/polypropylene composites. *Composites: Part A*, 39, 1802-1814.
- Kruenate, J., Tongpool, R., & Panyathanmaporn, T. (2004). Optical and mechanical properties of polypropylene modified by metal oxides. *Surface and Interface Analysis*, 36, 1044-1047.
- Li, Y., Wei, G. X., & Sue, H. J. (2002). [Morphology and toughening mechanisms in clay-modified styrene-butadiene-styrene rubber-toughened polypropylene](#). *Journal of Materials Science*, 37(12), 2447-2459.
- Ma, J., Zhang, S., Qi, Z., Li, G., & Hu, Y. (2002). Crystallization behaviors of polypropylene/montmorillonite nanocomposites. *Journal of Applied Polymer Science*, 83, 1978-1985.
- McCarthy, D. W., & Mark, J. E. (1998). Synthesis, structure, and properties of hybrid organic-inorganic composites based on polysiloxanes. II. Comparisons between poly (methylphenylsiloxane) and poly (dimethylsiloxane), and between titania and silica. *Journal of Polymer Science, Part B: Polymer Physics*, 36(7), 1191-1200.
- Rong, M. Z., Zhang, M. Q., Zheng, Y. X., Zeng, H. M., & Friedrich, K. (2001). Improvement of tensile properties of nano-SiO₂/PP composites in relation to percolation mechanism. *Polymer*, 42(7), 3301-3304.
-] Scheirs, J. (2000). Compositional and failure analysis of polymers. *England: John Wiley&Sons Chapter 5*.
- Setz, S., Stricker, F., Kressler, J., Duscher, T., & Mulhaupt, P. (1996). Morphology and mechanical properties of blends of isotactic or syndioatactic polypropylene with SEBS block copolymers. *Journal of Applied Polymer Science*, 59, 1117-1128.
- Wang, Z., Wang, X., & Zhang, Z. (2009). Nucleating activation and aspherical crystals morphology of LLDPE/LDPE/TiO₂ nano composites prepared by non-isothermal crystallization. *Journal of Dispersion Science and Technology*, 30, 1231-1236.
- Zebarjad, S. M., Sajjadi, S. A., Tahani, M., & Lazzeri, A. (2006). A study on thermal behaviour of HDPE/CaCO₃ nano composites. *Journal of Achievements in Materials and Manufacturing Engineering*, 17(1-2), 173-176.