



Effect of Mixing Conditions and Particle Sizes of Titanium Dioxide on Mechanical and Morphological Properties of Polypropylene/Titanium Dioxide Composites

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ABSTRACT

Particle sizes and melt processing of TiO_2 play an important role in thermoplastic systems. The mechanical and morphological properties of polypropylene (PP)/ TiO_2 composites were investigated by preparing the composite by melt mixing technique in a twin screw extruder. The results show that after adding TiO_2 particles of 42.3 nm (TD42.3) and TiO_2 130 nm (TD130) sizes, the tensile strengths of PP composites decreased with increasing filler content and their stress-at-break values increased after filler addition. The effect of particle size showed that TD130 improved the mechanical properties of PP in relation to TD42.3 of smaller size. TiO_2 of 130 nm size was added to PP using two different mixing conditions. PP composites prepared at screw speed of 50 rpm with 2 mixing cycles showed higher tensile strength, stress-at-break and Young's modulus relative to samples prepared by the same screw speed and 1 mixing cycle. The impact strength of the samples prepared by 2 mixing cycles was higher than those prepared by 1 mixing cycle. Apparently, the 2 mixing cycles improved the impact strength of the composites due to the improved interfacial interaction between TD130 and the matrix and increased energy absorption during the impact process. The higher screw speed led to low mechanical properties. The dispersion of TD130 particles was relatively good when operated at 50 rpm and 2 mixing cycles with less aggregations in PP matrix.

Key Words:

polypropylene;
titanium dioxide;
composite;
mixing condition;
mechanical properties.

INTRODUCTION

The purpose of adding inorganic mineral fillers into polymers is to fulfil their performance properties, such as increasing the stiffness, dimensional stability, heat distortion temperature, hardness, and toughening of the products [1-4]. The properties of particulate filled polymer composites depend on the particles size, shape, loading, dispersion, interfacial bonding, and surface treatment of the fillers [5-8]. The dispersion of fillers in

polymer matrix has influence on the physical, mechanical, and thermal properties of polymers. Among the various mineral fillers, calcium carbonate (CaCO_3) [5,9-11,12], zinc oxide (ZnO) [13] and titanium dioxide (TiO_2) [7,14] have been the most utilized materials. While the use of CaCO_3 has been due to its low cost [2,7-8,15], TiO_2 is mainly used as white pigment due to its brightness. In addition, TiO_2 can act as a flame retardant or

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antioxidant and help to improve the thermal stability of the final products [7,16-18].

PP as one of the most important commodity polymers is widely used in technical applications. Because of its good processability, relatively high mechanical properties, great recyclability, and low cost, PP has found a wide range of applications in the household goods, packaging, and automobiles [19].

Starkova et al. [14] studied the long-term tensile creep of polyamide 66 and its nanocomposites filled with 1 vol% TiO₂ nanoparticles of 21 and 300 nm in diameters. D unuzovic et al. [20] prepared poly-methyl methacrylate (PMMA)/TiO₂ nanocomposites by in situ radical polymerization of methyl methacrylate (MMA) in a toluene solution of TiO₂/6-palmitate ascorbic acid (6-PAA). The effect of TiO₂ nanoparticles on the thermal properties of the PMMA matrix was investigated using thermogravimetric analysis and differential scanning calorimetry [20]. It was found that glass transition temperature of the polymer was not changed by the presence of the nanoparticles while thermal stability was significantly improved.

The dynamic mixing under high-shear stress is preferred due to the ability to decrease the host polymer diffusion path length by breaking down the agglomerates and primary particles, efficiently. Another advantage of the melt process is its ability to increase the sample uniformity by strong distributive and dispersive mixing. However, although extrusion is currently the most common method in mixing polymers with particles, there are relatively few studies on the details of how the processing conditions will affect the nanocomposite formation [21].

Modesti et al. [4] studied the influence of processing conditions on the nanocomposites structure and on the enhancement of mechanical properties of PP nanocomposites. These nanocomposites were prepared using a twin screw extruder. In order to optimize processing conditions, both screw speed and barrel temperature profile were changed. The results obtained show that the barrel temperature is a very important parameter: using lower processing temperature, the apparent melt viscosity and, consequently, the shear stress are higher and, therefore, the exfoliation of clay is promoted. Even using optimized processing conditions, exfoliation of

clay can be achieved only when a high compatibility exists between polymer and clay.

Dennis et al. [22] investigated the effects of screw design and extrusion residence time on the extent of exfoliation of a nylon-6 montmorillonite clay system. Wang et al. [23] also studied the twin-screw compounding of PP/clay nanocomposites, where the feeding sequence and compatibilizer grade in a nanostructure formation were discussed in detail.

Hasook et al. [24] studied and analyzed the effect of different screw rotating speeds on the clay dispersion and mechanical properties of nanocomposites prepared by melt compounding of polylactic acid (PLA) with an organoclay in a co-rotating twin screw extruder. Polyamide 12 (PA12) was used as an additive. Two different screw rotating speeds of 65 rpm and 150 rpm were used in this study. According to the tensile strength data, the Young's modulus of the PLA/clay nanocomposites showed improvement at a screw rotating speed of 150 rpm. The Young's modulus was improved with the addition of an organoclay to PLA matrix, but decreased when PA12 was added to the PLA matrix. The tensile strengths of the PLA/organoclay nanocomposites increased for the higher screw rotating speed (150 rpm). The size of the clay aggregates in the PLA/PA12/clay nanocomposites was smaller than that of PLA/clay. Furthermore, the thermal stability of the PLA/clay nanocomposite increases with addition of PA12, while on the whole it had little effect on tensile properties.

Mina et al. [25] studied TiO₂ filled isotactic polypropylene (iPP) composites with various contents of TiO₂ which were first single-extruded by an extruder, and then double-moulded by compression moulding. Scanning electron micrographs show a better adhesion between iPP and filler in the extrusion and compression-moulded samples than the extrusion-moulded samples. X-ray diffraction and IR spectral studies reveal a structural change from a three-phase (α , β , and γ) crystalline system of neat iPP sample to only α -form due to inclusion of fillers. Microhardness increases rapidly and then levels off with increasing filler content and also shows variations with respect to moulding conditions. The thermal and electrical properties are found to be influenced by processing conditions.

Nanocomposites can be formed by melt processing and melt processing conditions have an important influence on the nature of the nanocomposite formed [22]. It is well known that TiO_2 particles are easy to agglomerate owing to their large surface energy. Improving the distribution of TiO_2 particles in PP/ TiO_2 composites is very important for enhancing the mechanical properties. In this work, the mixing conditions were imposed on the process of twin screw extruder of PP/ TiO_2 composites. The aim of mixing conditions was to improve the distribution of TiO_2 particles, which would lead to improved mechanical properties.

EXPERIMENTAL

Materials

Pure PP (Mophen HP400K) was supplied by HMC Polymers Co. Ltd. The melt flow rate of PP is 4 dg/min. TiO_2 , in the form of white powder with average particle sizes of 42.3 nm (TD42.3) and 130 nm (TD130) were purchased from Aldrich and S.R.LAB Co. Ltd, respectively.

Sample Preparation

Pure PP pellets and TiO_2 particles were dried in an oven at 100°C for 3 h before melt extrusion. The PP pellets and TiO_2 particles were compounded in melt with desired compositions in a twin screw extruder within the temperature range of 160°C and 220°C . Mixing cycles of 1 and 2 were set for screw speed of 50 rpm. One mixing cycle was set for each screw speeds of 50 rpm and 100 rpm. The extrudates were palletized at the die exit. After compounding, the blends were compression moulded into standard dumb-bell tensile bars and rectangular bars, the mould temperature was kept at 190°C .

Sample Characterization

Tensile tests were conducted according to ASTM D 638 with a universal tensile testing machine LR 50k from Lloyd instruments. The tensile tests were performed at crosshead speed of 50 mm/min. Each value obtained represented the average of five samples. Charpy impact strength tests were performed according to D 6110-06 standard at room

temperature. Each value obtained represented the average of five samples.

Scanning electron microscopy (SEM) was employed to study the morphology of the PP/ TiO_2 composites and to evaluate the dispersion quality of the TiO_2 particles. The impact-fractured surfaces of the PP/ TiO_2 composites obtained from impact tests were examined. All specimens were coated with gold before SEM observations.

RESULTS AND DISCUSSION

Effect of TiO_2 Particle Size on Mechanical Properties

We have studied the effect of particle size of TiO_2 on PP/ TiO_2 composites which can be found elsewhere [26]. However, the effect of particles size of TiO_2 still needed more explanations which are provided in the current work. The results presented in Figure 1 demonstrate the tensile strengths of the composite samples of PP/TD42.3 and PP/TD130 as a function of composite composition.

The trend in variation of the tensile strength of PP/ TiO_2 composites at various particle size of TiO_2 is presented in Figure 1. The values of tensile strength of PP/TD130 and PP/TD42.3 composites show small differences. The decreased changes in values of tensile strength are negligible with increasing TiO_2 content and, hence, TiO_2 does not improve the tensile strength of PP specimens prepared by compression moulding.

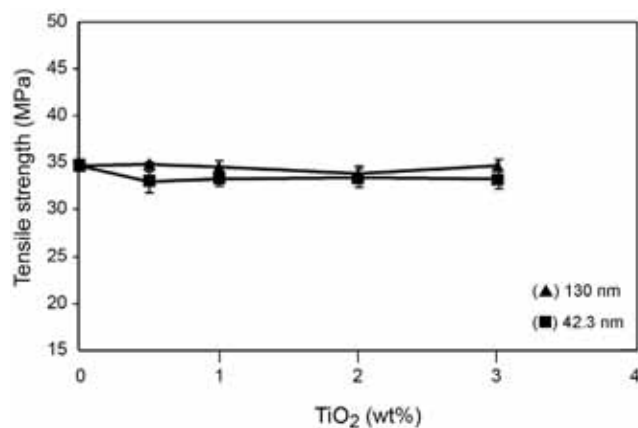


Figure 1. Tensile strength plots of pure PP and PP/ TiO_2 composites at various particle size of TiO_2 .

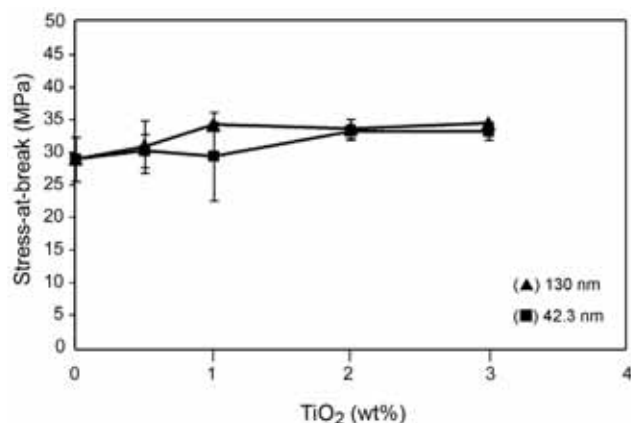


Figure 2. Stress-at-break plots of pure PP and PP/TiO₂ composites at various particle size of TiO₂.

It is well known that the tensile strength of a particulate composite is usually reduced with filler content following a power law in the case of a poor filler/matrix bonding. That means, the strength of the composite cannot be greater than that of the unfilled version because the filler particles do not bear any fraction of the external load [24]. It is seen that the presence of TiO₂ further reduces the tensile strength of the PP/TiO₂ composites. This is probably the result of the lower crystallinity of these samples compared to those of the corresponding pure PP.

Figure 2 presents the variation in the stress-at-break versus concentrations of TiO₂. It is observed that in PP/TiO₂ composites the stress-at-break increased with increasing TiO₂ content. The stress-at-break of PP/TD130 and PP/TD42.3 composites is not significantly different.

The Young's modulus of the PP/TiO₂ composites is presented in Figure 3. It is found that Young's modulus increases after adding a small amount of TD130. This may be due to the increased interfacial area in the composite with filler content, which promotes the stress transfer efficiency within a small strain range [25]. Moreover, it may be due to the brittle characteristics of fillers. An increase in Young's modulus of the composites with increasing filler content has also been observed in other filler-PP composites [27-30]. The PP/TD130 composites exhibit higher Young's modulus and stress-at-break than PP/TD42.3 composites. This may be due to the difference in the polarity mismatch of fillers and

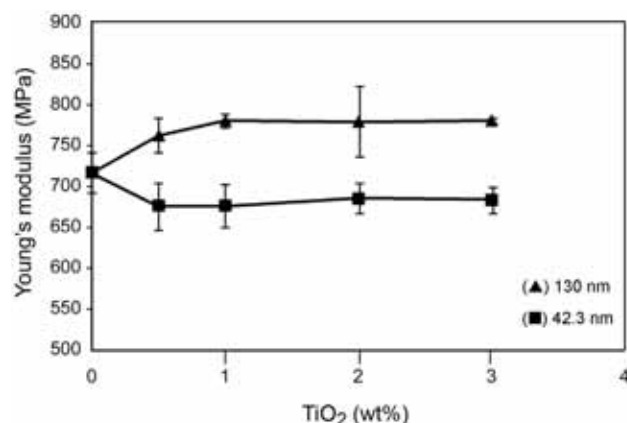


Figure 3. Young's modulus plots of pure PP and PP/TiO₂ composites at various particle size of TiO₂.

polymer matrix. Therefore, TD42.3 has higher surface area than that of TD130. This may induce agglomeration and poor adhesion between TD42.3 and polymer matrix and subsequently decrease the Young's modulus. From the above results, it is found that TD130 could improve the mechanical properties better than TD42.3. Thus, TD130 was chosen for studying the effect of processing conditions.

Effect of Particle Size of TiO₂ on Morphology

The morphology of the fractured surfaces of impact specimens of the composites was examined by SEM. Figures 4a-4f show the micrographs of the impact fracture surfaces of PP composites filled with 0.5, 1.0 and 3.0 wt% of TiO₂, respectively. It is observed that dispersion of TD42.3 on the polymer surface was non-uniform. This non-uniform dispersion led to local agglomeration of TD42.3 within the polymer. Moreover, the aggregation of TD42.3 particles in the polymer matrix increased with increasing TD42.3 content, and the dispersion of TD42.3 particles could have an influence on the mechanical properties of PP composites. The results show that the PP/TD42.3 composites caused greater agglomeration relative to PP/TD130 composites.

The SEM micrographs show that the dispersion of the TD130 particles was relatively good, only few aggregations exist as shown in Figure 4. This observation supports the results of the tensile tests where the PP/TD130 composites displayed higher stress-at-break and Young's modulus than the pure PP and

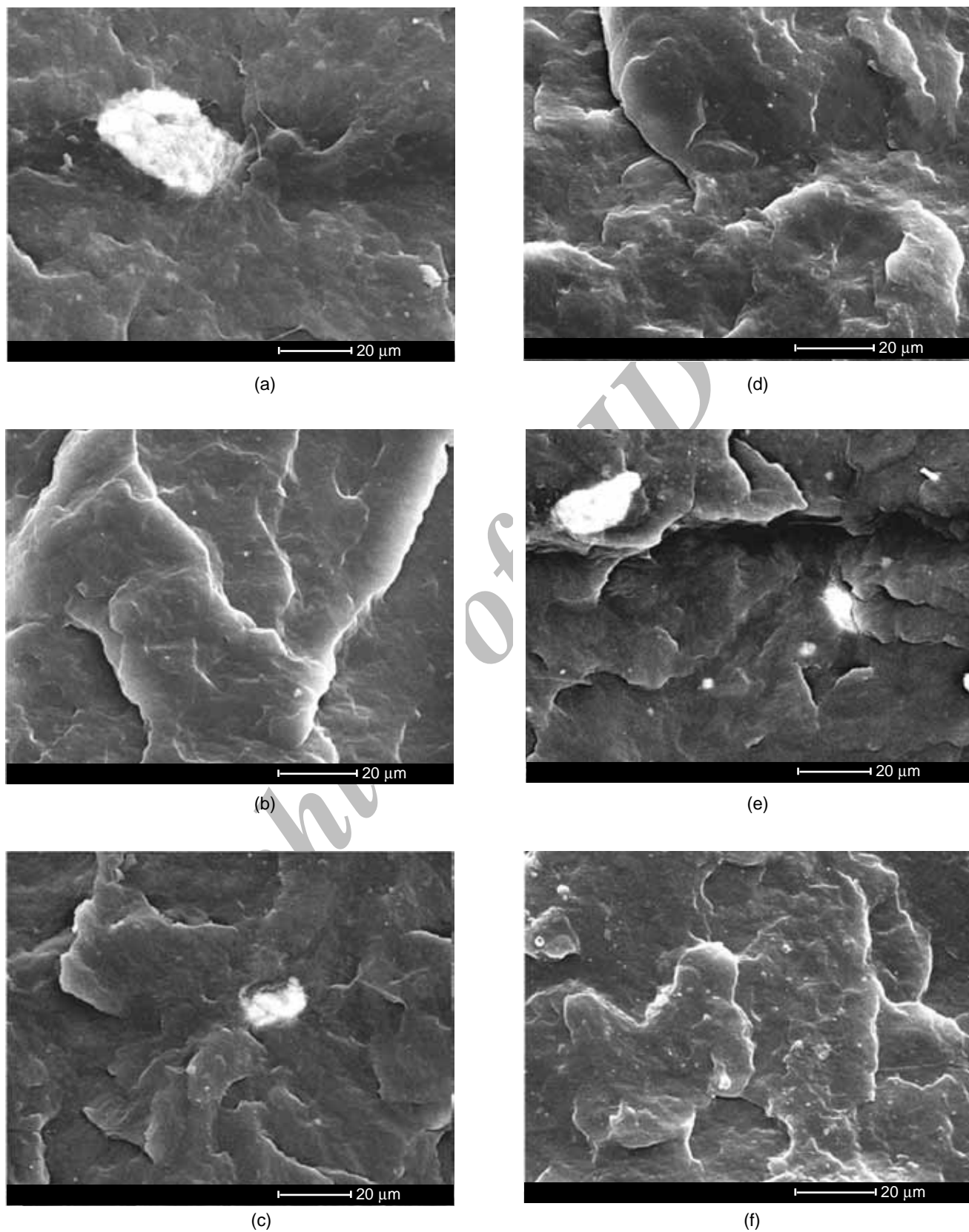


Figure 4. SEM micrographs of PP/TiO₂ composite samples after adding (a) 0.5 wt% of TD42.3, (b) 0.5 wt% of TD130, (c) 1.0 wt% of TD42.3, (d) 1.0 wt% of TD130, (e) 3.0 wt% of TD42.3, and (f) 3.0 wt% of TD130.

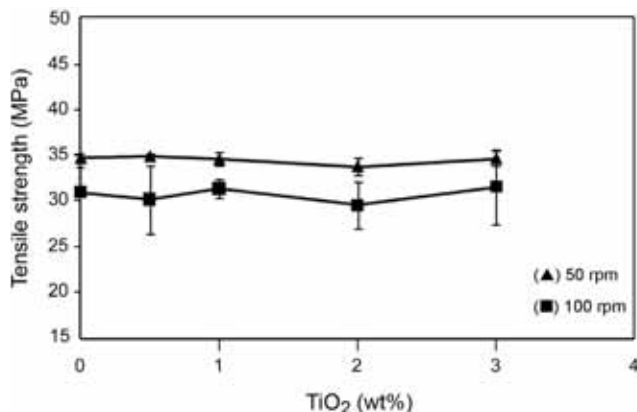


Figure 5. Tensile strength plots of pure PP and PP/TD130 composites at various screw speeds of mixing.

PP/TD42.3 nanocomposites.

Effect of Screw Speeds of Mixing on Mechanical Properties

The tensile strength for the composites of PP/TD130 as a function of composite composition and screw speed of mixing is represented in Figure 5. PP/TD130 composites mixed at screw speed of 50 rpm possessed higher tensile strength than those prepared by screw speed of 100 rpm. The stress-at-break and Young's modulus of PP/TD130 composites at various screw speeds of mixing are shown in Figures 6 and 7, respectively. Young's modulus of PP/TD130 composites at various screw speeds increased with increasing filler content. The stress-at-break and Young's modulus for PP/TD130 composites at screw speed of 50 rpm were higher than those of the

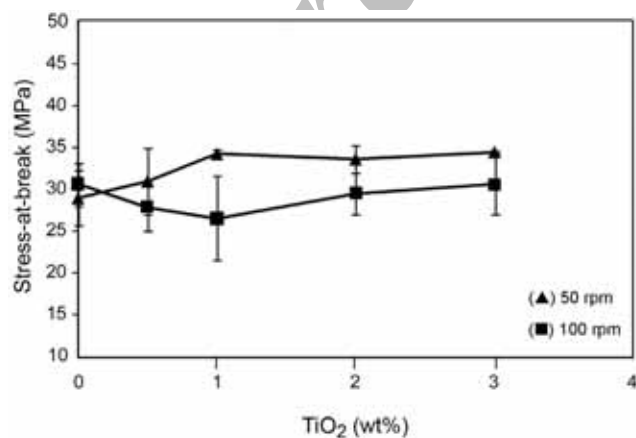


Figure 6. Stress-at-break plots of pure PP and PP/TD130 composites at various screw speeds of mixing.

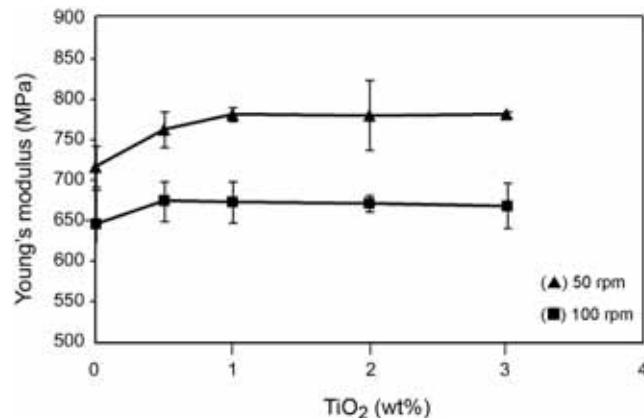


Figure 7. Young's modulus plots of pure PP and PP/TD130 composites at various screw speeds of mixing.

composites at screw speed of 100 rpm as shown in Figures 6 and 7. According to the tensile strength data, Young's modulus and stress-at-break of the PP/TD130 composites showed improvement at screw rotating speed of 50 rpm. This may be due to the higher mixing time or retention time in extruder mixing for screw speed of 50 rpm than screw speed of 100 rpm. Thus, the dispersion of TD130 increased at screw speed of 50 rpm.

Effect of Mixing Cycle on Mechanical Properties

The tensile strengths of the composites of PP/TD130 as a function of composite composition and mixing cycle are presented in Figure 8. PP/TD130 composites were mixed at 2 cycles had higher tensile strength than those prepared at 1 mixing cycle. The PP composites mixed at 2 cycles show higher tensile

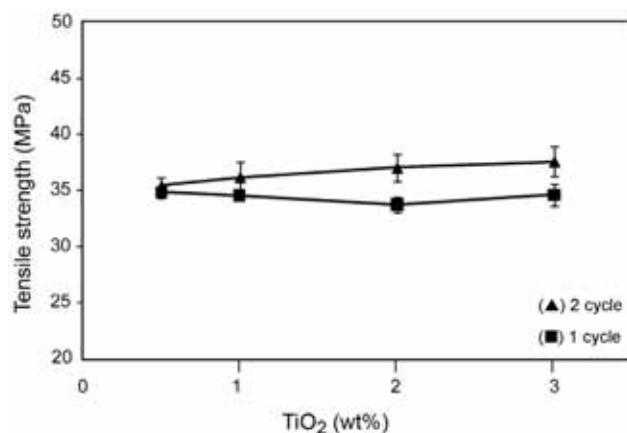


Figure 8. Tensile strength plots of pure PP and PP/TD130 composites at various mixing cycle.

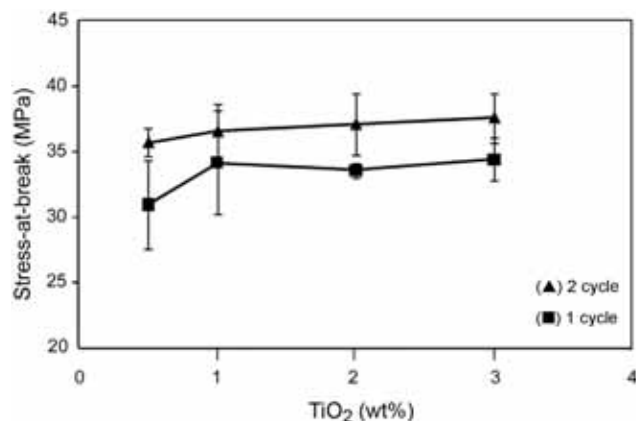


Figure 9. Stress-at-break plots of pure PP and PP/TD130 composites at various mixing cycle.

strength than pure PP and their tensile strength increased with increasing TD130 content. It is interesting to see that the tensile strengths of PP/TD130 composites samples, which were melt mixed at 2 cycles, have been increased. The tensile strengths of PP/TD130 composites also significantly increased with increasing TD130 content, probably due to the increased dispersion of TD130 in PP matrix by 2 mixing cycles. Efficient nanoparticle dispersion is critical for achieving improved strength and toughness. We have already shown that TD130 particles were uniformly distributed in this system [31].

The stress-at-break and Young's modulus of PP/TD130 composites mixed at 2 mixing cycle are higher than those of the composites prepared at

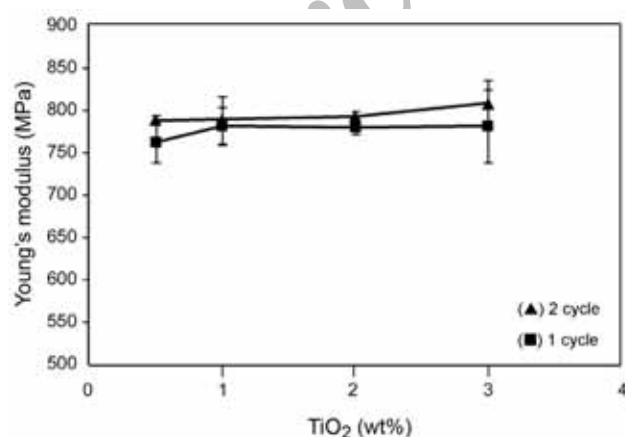


Figure 10. Young's modulus plots of pure PP and PP/TD130 composites at various mixing cycle.

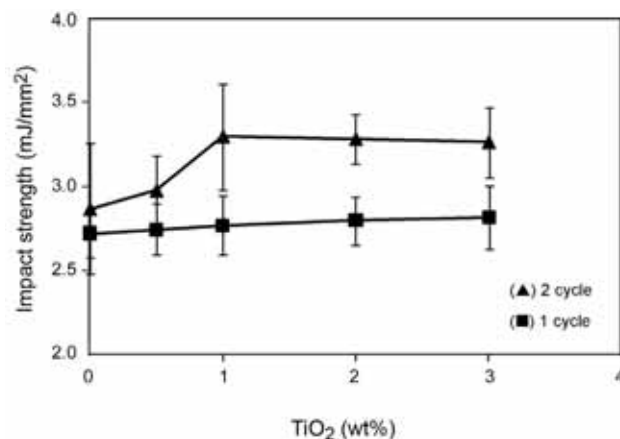


Figure 11. Impact strength plots of pure PP and PP/TD130 composites at various mixing cycle.

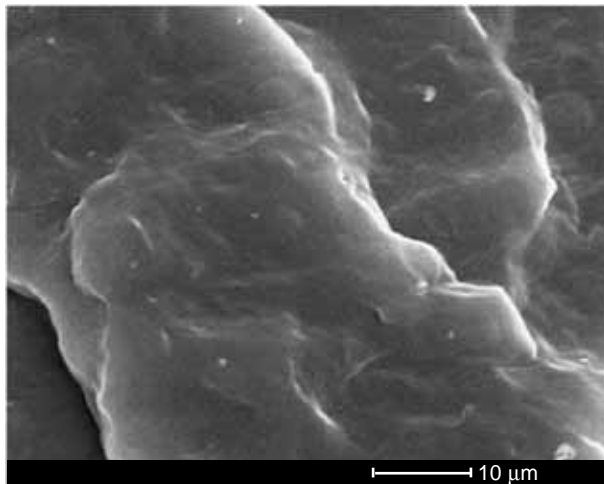
1 mixing cycle, as shown in Figures 9 and 10, respectively. This may be due to the good mixig of 2 mixing cycles compared with 1 mixing cycle, thus, dispersion of TD130 was increased at 2 mixing cycle.

The Charpy impact strength for the composites of PP/TD130 at various cycle is shown in Figure 11. It is observed that the impact strength of the 2 mixing cycles is higher than the 1 mixing cycle. Apparently the 2 mixing cycles improved the impact strength of the composites due to the improved interfacial interaction between TD130 and matrix and increased energy absorption during the impact process [32].

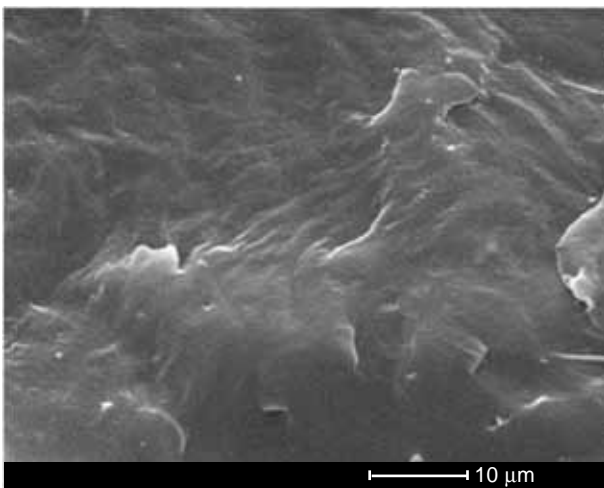
Effect of Mixing Cycle on Morphology

Figure 12 shows a comparison between the micrographs of the impact-fractured surfaces of PP/TD130 composites at various mixing cycle. Figures 12a and 12b show the micrographs of the impact fracture surfaces of PP composites filled with 0.5 wt% of TD130 at 1 and 2 mixing cycles, respectively. It can be seen that the composite sample mixed at 1 mixing cycle had more agglomeration than the sample prepared by 2 mixing cycles. It is observed that the dispersion of the TD130 at 2 mixing cycles on the polymer surface is uniform.

Therefore, the 2 mixing cycle times can improve the dispersion of TD130 particles. The aggregation of TD130 particles in the polymer matrix decreased with increasing mixing cycle, and the dispersion of TD130



(a)



(b)

Figure 12. SEM micrographs of PP after adding TD130 at various mixing cycle times: (a) 0.5 wt% of TD130 at 1 mixing cycle and (b) 0.5 wt% of TD130 at 2 mixing cycles.

particles could have an influence on the mechanical properties of PP composites.

CONCLUSION

PP/TiO₂ composites were prepared by melt compounding in a twin screw extruder. The PP/TD42.3 and PP/TD130 composites showed a decrease in tensile strength with increasing filler content. Stress-at-break of PP/TD42.3 and PP/TD130 composites increased with increasing filler content. The effect of particles size showed that 130 nm particle size (TD130) improved mechanical properties

of PP more than 42.3 nm (TD42.3). The PP composites prepared at screw speed of 50 rpm and 2 mixing cycles showed higher mechanical properties than those prepared at screw speed of 50 rpm and 1 mixing cycle. The dispersion of TD130 particles was relatively efficient when operated at 50 rpm and 2 mixing cycles and decreased the aggregates of TD130 particles in PP matrix. The results have indicated that the mixing conditions can improve the distribution of TiO₂ particles, leading to improved mechanical properties as well.

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REFERENCES

1. Zuiderduin WCJ, Westzaan C, Huetink J, Gaymans RJ, Toughening of polypropylene with calcium carbonate particles, *Polymer*, **44**, 261-275, 2003.
2. Chan C, Wu J, Li J, Cheung Y, Polypropylene/calcium carbonate nanocomposites, *Polymer*, **43**, 2981-2992, 2002.
3. Suwanprateeb J, Calcium carbonate filled polyethylene: correlation of hardness and yield stress, *Composites A*, **31**, 353-359, 2000.
4. Modesti M, Lorenzetti A, Bon D, Besco S, Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites, *Polymer*, **46**, 10237-10245, 2005.
5. Misra RDK, Nerikar P, Bertrand K, Murphy D, Some aspects of surface deformation and fracture of 5-20% calcium carbonate-reinforced polyethylene composites, *Mater Sci Eng A*, **384**, 284-298, 2004.
6. Bose S, Mahanwar PA, Effect of flyash on the mechanical, thermal, dielectric, rheological and morphological properties of filled nylon 6, *J Miner Mater Charact Eng*, **3**, 65-72, 2004.

7. Supaphol P, Thanomkiat P, Junkasem J, Dangtungee R, Non-isothermal melt-crystallization and mechanical properties of titanium(IV) oxide nanoparticle-filled isotactic polypropylene, *Polym Test*, **26**, 20-37, 2007.
8. Dangtungee R, Yun J, Supaphol P, Melt rheology and extrudate swell of calcium carbonate nanoparticle-filled isotactic polypropylene, *Polym Test*, **24**, 2-11, 2005.
9. Bartczak Z, Argon AS, Cohen RE, Weinberg M, Toughness mechanism in semi-crystalline polymer blends. II: high-density polyethylene toughened with calcium carbonate filler particles, *Polymer*, **40**, 2347-2365, 1999.
10. Osman MA, Atallah A, Suter UW, Influence of excessive filler coating on the tensile properties of LDPE-calcium carbonate composites, *Polymer*, **45**, 1177-1183, 2004.
11. Albano C, González J, Ichazo M, Rosales C, de Navarro CU, Parra C, Mechanical and morphological behavior of polyolefin blends in the presence of CaCO₃, *Compos Struct*, **48**, 49-58, 2000.
12. Thio YS, Argon AS, Cohen RE, Weinberg M, Toughening of isotactic polypropylene with CaCO₃ particles, *Polymer*, **43**, 3661-3674, 2002.
13. Chae DW, Kim BC, Characterization on polystyrene/zinc oxide nanocomposites prepared from solution mixing, *Polym Adv Technol*, **16**, 846-850, 2005.
14. Starkova O, Yang J, Zhang Z, Application of time-stress superposition to nonlinear creep of polyamide 66 filled with nanoparticles of various sizes, *Compos Sci Technol*, **67**, 2691-2698, 2007.
15. González J, Albano C, Ichaza M, Díaz B, Effects of coupling agents on mechanical and morphological behavior of the PP/HDPE blend with two different CaCO₃, *Eur Polym J*, **38**, 2465-2475, 2002.
16. Allen NS, Edge M, Corrales T, Catalina F, Stabilizer interactions in the thermal and photooxidation of titanium dioxide pigmented polypropylene films, *Polym Degrad Stab*, **61**, 139-149, 1998.
17. Turton TJ, While JR, Effect of stabilizer and pigment on photo-degradation depth profiles in polypropylene, *Polym Degrad Stab*, **74**, 559-568, 2001.
18. Titelman GI, Gonen Y, Keider Y, Bron S, Discolouration of polypropylene-based compounds containing magnesium hydroxide, *Polym Degrad Stab*, **77**, 345-352, 2002.
19. Yang K, Yang Q, Li G, Sun Y, Feng D, Morphology and mechanical properties of polypropylene/calcium carbonate nanocomposites, *Mater Lett*, **60**, 805-809, 2006.
20. D unuzovic E, Jeremic K, Nedeljkovic JM, In situ radical polymerization of methyl methacrylate in a solution of surface modified TiO₂ and nanoparticles, *Eur Polym J*, **43**, 3719-3726, 2007.
21. Liaw JH, Hsueh TY, Tan TS, Wang Y, Chiao SM, Twin-screw compounding of poly(methyl methacrylate)/clay nanocomposites: effects of compounding temperature and matrix molecular weight, *Polym Int*, **56**, 1045-1052, 2007.
22. Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, Paul DR, Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites, *Polymer*, **42**, 9513-9522, 2001.
23. Wang Y, Chen FB, Wu K C, Twin-screw extrusion compounding of polypropylene/organoclay nanocomposites modified by maleated polypropylenes, *J Appl Polym Sci*, **93**, 100-112, 2004.
24. Hasook A, Muramatsu H, Tanoue S, Iemoto Y, Unryu T, Preparation of nanocomposites by melt compounding polylactic acid/polyamide 12/organoclay at different screw rotating speeds using a twin screw extruder, *Polym Compos*, **29**, 1-8, 2008.
25. Mina F, Seema S, Matin R, Rahaman J, Sarker RB, Gafur A, Bhuiyan AH, Improved performance of isotactic polypropylene/titanium dioxide composites: effect of processing conditions and filler content, *Polym Degrad Stab*, **94**, 183-188, 2009.
26. Wacharawichanant S, Thongyai S, Siripattanasak T, Tipsri T, Effect of particles size of titanium dioxide on mechanical properties of polypropylene/titanium dioxide nanocomposites, *5th Thailand Mater Sci Technol Conf*, Bangkok, Thailand, 16th-19th Sep 2008.
27. Manchado MAL, Valentini L, Biagiotti J, Kenny JM, Thermal and mechanical properties of

- single-walled carbon nanotubes-polypropylene composites prepared by melt processing, *Carbon*, **43**, 1499-1505, 2005.
28. Ismail H, Edyham MR, Wirjosentono B, Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent, *Polym Test*, **21**, 139-144, 2002.
 29. Mwaikambo LY, Martuscelli E, Maurizio A, Kapok/cotton fabric-polypropylene composites, *Polym Test*, **19**, 905-918, 2000.
 30. Ruksakulpiwat Y, Suppakarn N, Sutapun W, Thomthong W, Vetiver-polypropylene composites: physical and mechanical properties, *Composites A*, **38**, 590-601, 2007.
 31. Mishra AK, Luyt AS, Effect of sol-gel derived nano-silica and organic peroxide on the thermal and mechanical properties of low-density polyethylene/wood flour composites, *Polym Degrad Stab*, **93**, 1-8, 2008.
 32. Domenici C, Levita G, Frosini V, Dielectric behavior of a rubber-toughened epoxy resin, *J Appl Polym Sci*, **34**, 2285-2298, 1987.

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