Morphology and Performance of Potassium Titanate Whisker-Reinforced Polypropylene Composites

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ABSTRACT: Titanate whisker-reinforced polypropylene composites were prepared in a twin-screw extruder followed by injection molding. The whiskers were surface treated with tetrabutyl orthotitanate prior to blending. The static and dynamic mechanical properties, impact strength, and thermal properties of the composites were investigated. Static tensile measurements showed that the tensile strength and Young's modulus of the composites increased with increasing whisker content. However, the Izod impact tests indicated that the impact strength of longitudinal samples remained unchanged with the addition of whisker up to 10 wt %. Thereafter, it shows a continuous decrease with increasing whisker content. The thermogravimetric and dynamic mechanical tests demonstrated that the heat-resistance and thermooxidative stability for the composites also increased with increasing whisker content. Scanning electron microscopic observations revealed that the whiskers within the composites were oriented uniformly. The experimental data were compared with the well established mechanical models to evaluate the reinforcing efficiency. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 431–439, 1998

Keywords: polypropylene; whisker; potassium titanate; composite; coupling agent

INTRODUCTION

Polypropylene (PP) is a commodity plastic and one of the largest polyolefins consumed by the plastic industry. In terms of mechanical properties, it is close to engineering plastics widely used in significant load-bearing applications. To enhance its performance, various inorganic fillers such as talc, mica, clay, calcium carbonate, and fiber reinforcements, for example, glass fiber, are incorporated into polypropylene. Recently, natural fibers such as sisal fiber,[1] wood fiber,[2,3] and cellulosic fiber[4] also have been used to reinforce the polypropylene composites. These composites generally exhibit superior stiffness, strength, and heat distortion temperature with respect to unfilled polymer.

Whiskers are very attractive reinforcing materials for composites, because they combine high stiffness and strength. Owing to their small diameter, whiskers are nearly free of internal defects, thereby yielding a strength close to the maximum theoretical value predicted by the theory of elasticity.[5] Silicon carbide (SiC) whiskers have been used extensively in ceramic matrix composites[6,7] and metal matrix composites.[8–10] There has been growing interest in the development of new whiskers with high strength and toughness such as potassium titanate whiskers. These whiskers show promise as reinforcement materials owing to their relatively low cost. The price of potassium titanate whiskers ranges from

Table I   Properties of Potassium Titanate Whisker

Specific Gravity (g/cm^3)	Length (μm)	Diameter (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Melting Point (°C)	Heat Resistance (°C)
3.3	10 – 40	0.5 – 1.0	7	280	1370	1200

one-tenth to one-twentieth of that of SiC whiskers.[11] In this regard, potassium titanate whiskers have been used to reinforce the metallic alloys.[12,13] Compared with the whiskers reinforced MMCs, fewer attempts have been made to blend inorganic whiskers with thermoplastic polymers. Recently, considerable attention has been paid to upgrade the mechanical performance of polymers by reinforcing them with various inorganic and polymeric whiskers.[14–17]

It is well known that the mechanical properties of filler-reinforced polymeric composites significantly depend on the interfacial adhesion between the polymer matrices and reinforcing components. Therefore, surface treatments for fillers have been adopted to improve the interfacial interactions. For instance, the filler surface is treated with coupling agents such as "silane"- and "titanate"-based compounds,[18,19] whose chemical structures allow them to react with both fillers and polymeric matrix. The interfacial layer is formed via chemical bonds between the coupling agent, filler, and polymer matrix, thereby allowing a better shear stress transfer between the fillers and matrix. Consequently, the mechanical properties of the composites are dramatically improved.

In this article, the titanate whisker-reinforced polypropylene composites are extruded followed by injection molding. The static and dynamic mechanical properties, impact strength, and thermal properties are examined, and the orientation microstructure of the studied composites is viewed by scanning electron microscopy (SEM). The experimental data are compared with the well-established mechanical models.

EXPERIMENTAL

Materials

The whisker used in this work was potassium titanate ($K_2Ti_6O_{13}$) produced by Shen Yang Jinjian Composite Co., China. Their main properties are given in Table I. The PP is a commercial product of Himont (Pro-fax 6331) with a melt flow index of 12 g/min. The maleic anhydride (MA) was supplied by Fluka Chemie, and dicumylperoxide (DCP) produced by Aldrich Chemical Company was used for the maleation of the PP. Reagent-grade tetrabutyl orthotitanate was selected as the coupling agent for the whiskers.

Sample Preparations

Tetrabutyl orthotitanate was dissolved in acetone to form a 5 wt % solution. The whisker was treated with 1.5 wt % tetrabutyl titanate. The solution was slowly poured into a plastic box where the whisker was blended with the coupling agent solution. Subsequently, the treated whisker was dried in an oven at 100°C for 24 h.

The MA-grafted PP (MAP) was prepared in a twin-screw Brabender Plasticorder at 220°C and at 15 rpm by a one-step reaction of PP with MA and DCP. The weight ratio of PP, MA, and DCP was fixed at 94:6:0.3. The blend of 90 wt % PP and 10 wt % MAP was also extruded in the same extruder at 220°C and was designated as the PP-(MAP). It was used as the matrix for the whisker-reinforced composites.

The composites containing 5, 10 15, 25, and 35 wt % potassium titanate whisker were prepared in a twin-screw Brabender Plasticorder at 240°C. The extrudates were cut into pellets by a pelletizer. Both standard dog-bone tensile bars (ASTM D638) and plaques with dimensions of 147 × 80 × 6 mm^3 were injection molded from these pellets. The mold temperature was maintained at 40°C, and the barrel zone temperatures were set at 240, 250, and 250°C.

Morphological Observations

The fracture surfaces of the injection-molded composites after impact tests were coated with a thin layer of gold before the morphologies were examined using a scanning electron microscope (Jeol JSM 820).

Table II   The Effect of Tetrabutyl Orthotitanate on the Mechanical Properties of the Composites

Sample	PP(MAP)	Untreated PP(MAP)/15%$K_2Ti_6O_{13}$	Treated PP(MAP)/15%$K_2Ti_6O_{13}$
Yield strength (MPa)	28.20 ± 2.4	31.44 ± 0.8	36.44 ± 0.3
Tensile strength at break (MPa)	24.1 ± 3.1	27.77 ± 2.1	32.42 ± 2.7
Young's modulus (MPa)	1690 ± 98	2744 ± 82	2833 ± 71
Strain at break (%)	650 ± 47	19.18 ± 4.5	24.71 ± 3.8
Impact strength (longitudinal) (J/m)	38.4 ± 2.6	31.3 ± 2.7	32.0 ± 2.8
Impact strength (transverse) (J/m)	38.4 ± 2.6	27.2 ± 2.9	30.8 ± 2.8

Mechanical Properties

The tensile behavior of the specimens was determined using an Instron tensile tester (model 4206) at 23°C. A crosshead speed of 1 mm min^{-1} was used in the test. At least five specimens of each composition were tested and the average values reported.

Notched Izod impact specimens with dimensions of $65 \times 12.7 \times 6$ mm were prepared from the injection-molded plaques. Both longitudinal and transverse impact specimens were used in the tests. For the longitudinal impact specimens, the length direction was parallel to the mold filling direction while it was perpendicular to the mold filling direction for the transverse impact samples. Seven specimens were tested and the average values were reported.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) of the injection-molded specimens was conducted with a DuPont dynamic mechanical analyzer (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The temperature range was from −40–150°C, with a heating rate of 2°C min^{-1}.

Thermogravimetric Analysis (TGA)

The decomposition process of the specimens from 50–600°C under a protective helium-atmosphere (200 mL/min) was determined with a thermogravimetric analyzer (Seiko model SSC/5200). The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Effects of Coupling Agent

In general, there are two routes commonly applied to enhance the chemical/physical interactions between the reinforcements and polymeric matrices. The first route involves the modification of the polymeric matrix structure via various chemical reactions, and the second approach utilizes coupling agents to modify the chemical nature of the filler surface. In this work, tetrabultyl orthotitanate and MAP are used as the surface modifiers for potassium titanate whiskers and PP, respectively. For comparison, the typical mechanical properties of the PP(MAP), and tetrabultyl orthotitanate treated and untreated PP-(MAP)/15%$K_2Ti_6O_{13}$ composites are summarized in Table II. The results apparently indicate that the incorporation of potassium titanate whiskers into PP leads to an increase in both tensile strength and Young's modulus. Furthermore, tetrabultyl orthotitanate-treated whisker-reinforced composites exhibit much higher tensile strength and Young's modulus than those containing untreated whiskers. It is believed that tetrabutyl orthotitanate effectively decreases the surface tension between the whiskers and PP(MAP) matrices via chemical reactions, i.e., hydrolysis of tetrabutyl orthotitanate by both the —OH groups absorbed on the whisker surface[20] and —OH groups on PA(MAP) molecules. As a result of these reactions, ternary molecular products are formed according to the possible reaction scheme depicted in Figure 1. This scheme suggests that strong chemical bonds are established between
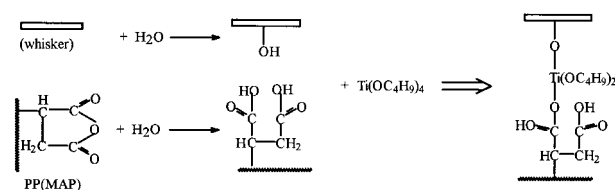

Figure 1   Possible reaction scheme of tetrabutyl orthotitanate with potassium titanate whisker and a PP-(MAP) matrix.
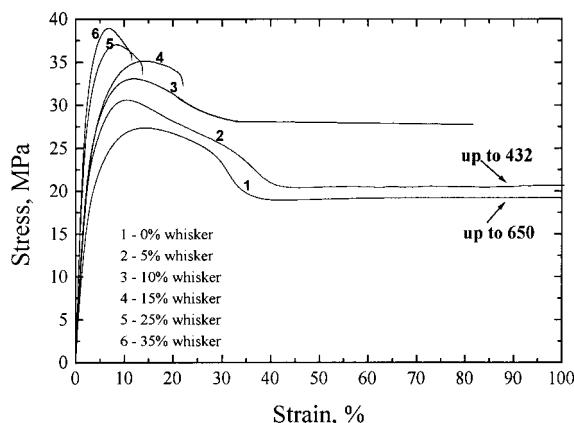
Figure 2 Typical stress–strain curves for PP/K₂Ti₆O₁₃ composites.

Figure 3 Yield and tensile strengths versus whisker content for surface-treated PP/K₂Ti₆O₁₃ composites.

the matrix and whiskers. Hence, the surface tension can be reduced considerably. From this point of view, the modified surface tension can, in turn, result in better adhesion and improved compatibility between the PP(MAP) matrix and whiskers. Finally, it is interesting to see that the impact strengths of samples in both longitudinal and transverse directions are slightly improved by the incorporation of a coupling agent. This implies that tetrabutyl orthotitanate treatment and MAP compatibilization for the composites can result in a considerable improvement in the mechanical properties.

Static Mechanical Properties

Figure 2 shows the typical stress–strain curves of PP(MAP) matrix and the PP(MAP)/whisker composites. In general, PP exhibits a ductile behavior during tension, i.e., it demonstrates the occurrence of necking followed by homogeneous drawing. On the basis of the stress–strain curves observation, it can be concluded that the composites containing a whisker content ≤15 wt % fracture in a ductile mode with obvious necking, while the composites containing more than 15 wt % whiskers exhibit yielding and fail in a brittle mode.

Figure 3 shows the variation of the yield and tensile strengths with whisker content for the PP(MAP)/whisker composites. Both the yield strength and fracture strength increase evidently with increasing whisker content. For the composite containing 35 wt % whiskers, the tensile strength (38.48 MPa) is 30% higher than that of unreinforced polymeric matrix. Similarly, the
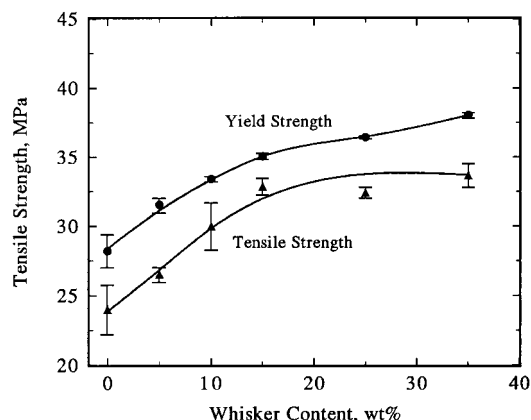
Young's modulus of the composites also tends to increase with increasing whisker content, as shown in Figure 4. The relationship most commonly used to predict the elastic modulus of a discontinuous short fiber-reinforced composite from the moduli of the individual components is the Tsai-Halpin equation,[21] which is based on the assumption of continuity of stress and strain along the fiber/matrix interface. The equation is as follows:

$$\frac{E_c}{E_m} = \frac{1 + \xi\eta\varphi_f}{1 - \eta\varphi_f} \tag{1}$$

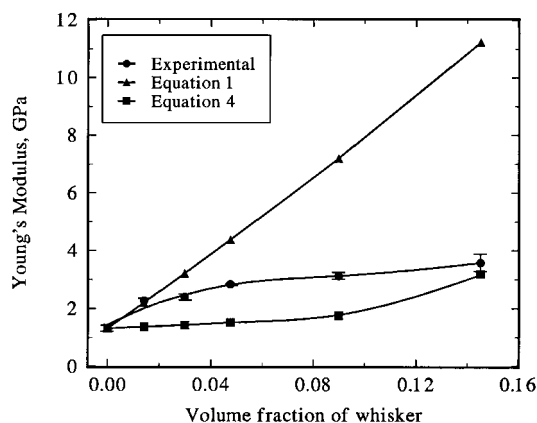where E_c and E_m are the elastic moduli of composite and matrix, respectively, and φ_f is the vol-

Figure 4 Young's modulus versus whisker content for surface-treated PP/K₂Ti₆O₁₃ composites. The moduli of discontinuous fiber and particulate-reinforced PP composites predicted from eqs. (1) and (4) are also shown.

ume fraction of short fibers. The constant ξ and η are given by

$$\xi = 2(L/D) \qquad (2)$$

$$\eta = \frac{E_f - E_m}{E_f + \xi E_m} \qquad (3)$$

where L/D is the aspect ratio (length/diameter) of the reinforcing fibers, and E_f is the modulus of the fibers. On the other hand, the simplest relationship to predict the Young's modulus of particulate reinforced composites was developed by Guth.[22] The equation reads

$$E_c = E_m(1 + 2.5\varphi_f + 14.1\varphi_f^2) \qquad (4)$$

where E_c and E_m are the elastic moduli of composite and matrix, respectively, and φ_f is the volume fraction of particulates. From Figure 4, the experimental data are lower than those predicted by eq. (1), but higher than those predicted by eq. (4). This is because the length and aspect ratio of the whisker is much shorter than that of short fiber. Hence, the reinforcing effect of whisker by means of a modulus is poorer than that of the short fiber. Generally, there exists a critical aspect ratio that allows the fiber reinforcements to effectively bear the external load transferred from the matrix. As aspect ratio of whiskers are larger than the particulates, the stiffness of the potassium titanate whisker-reinforced composites is higher than that calculated from eq. (4). It is interesting to note that the experimental data are closer to the theoretical values predicted from eq. (1) at lower whisker content (<10 wt %). This implies that the potassium titanate whiskers effectively reinforce PP at lower whisker content. Figure 5 shows the storage modulus versus temperature for the composites. Evidently, the storage modulus also increases with increasing whisker content.

More recently, Avella et al.[23] have investigated the mechanical properties of silicon carbide whisker-reinforced polypropylene composites. They reported that the incorporation of untreated whiskers to PP leads to an enhancement of the modulus, but a decrease in both the tensile strength and strain at break. In addition, the modification of the whisker surface also resulted in no improvement in the tensile strength. Taesler et al.[24] reported that the incorporation of poly(4-hydroxy-
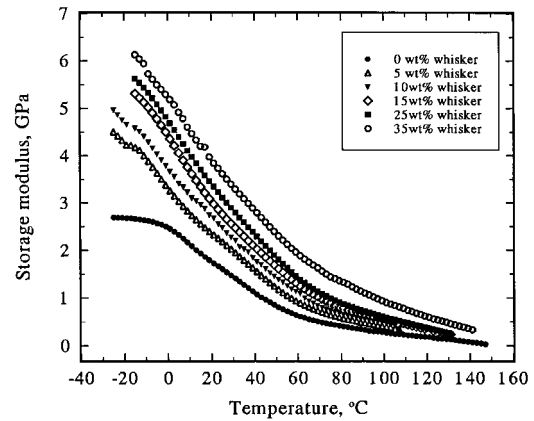

Figure 5 Storage modulus versus temperature for surface-treated $PP/K_2Ti_6O_{13}$ composites.

benzoate) (PHB) whiskers in PA6.6 leads to an increase in the elastic modulus but with decreases in both the tensile strength and strain at break. They pointed out that the reduction in the tensile strength of the composites resulted from the agglomeration of whiskers. These agglomerates were considered as the mechanical weak points because of poor wetting of the whiskers by the matrix. As discussed above, potassium titanate whisker-reinforce PP is effective, despite the fact that the reinforcing efficiency of the whiskers is lower than that of short fibers. It is believed that the reinforcing effect of potassium titanate whiskers used in this work arises from their specific crystalline and surface structure. Moreover, the proper surface treatment of the whiskers in this work is responsible for the effective reinforcement of the matrix. In previous work, we have also observed that potassium titanate whiskers effectively reinforce polyamide 6.[25]

The variation of the strain at break of composites with whisker content is depicted in Figure 6. It is apparent that the strain at break does not decrease sharply with the introduction of very low whisker content, i.e., 5 wt %. The strain at break drops significantly when the whisker content reaches 15 wt %. It is generally known that the typical characteristic of both fiber and filler-reinforced polymeric composites is that the strain at break decreases dramatically with the incorporation of very low whisker content (5 wt %) into matrices.

Impact Behavior

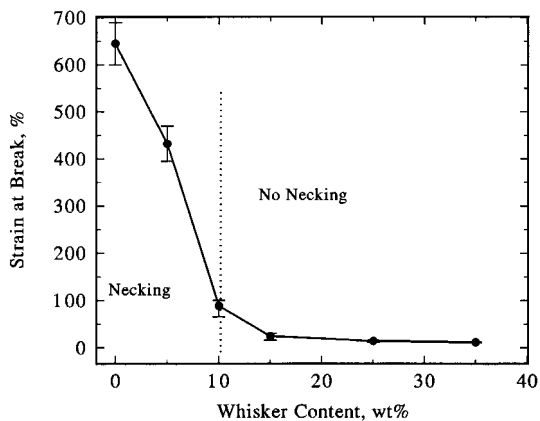Figure 7 shows the relationships between impact strength and the whisker content for the speci-

Figure 6 Strain-at-break versus whisker content for surface-treated PP/$K_2Ti_6O_{13}$ composites.

mens prepared from the longitudinal and transverse directions. The impact strength of the longitudinal specimens is higher than that of the transverse specimens. This is because the whisker orientation is parallel to longitudinal direction. These whiskers can inhibit crack propagation because a greater impact energy is absorbed when the whiskers are pulled out of the matrix. It should be noted that the impact strength of the longitudinal specimens decreases slightly with the addition of a whisker content up to 15 wt %. Afterwards, it levels off when the whisker content exceeds 23 wt %. In previous work, a brittle-to-ductile transition was observed in the polyamide-6/$K_2Ti_6O_{13}$ composites when the mean fiber-end spacing was less than about six times the fiber diameter. The behavior has been reported and
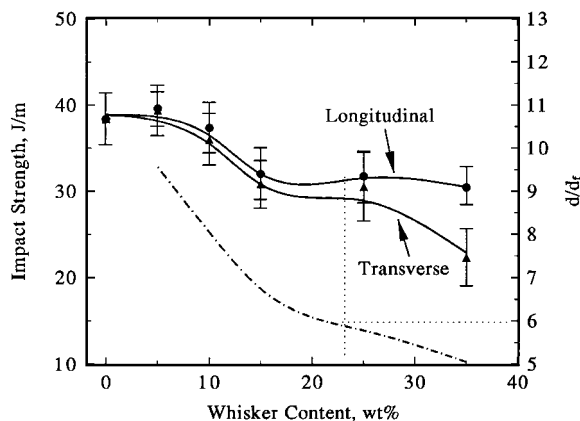
Table III Thermal Properties of PP(MAP) and Its Composites

Composite	$T_{E=0.47}$ (°C)	T_g (°C)	T_m (°C)	$T_{-5\%}$ °(C)
PP(MAP)	90	9.419	168.5	401.2
PP(MAP)/5%$K_2Ti_6O_{13}$	105	8.374	166.9	406.6
PP(MAP)/10%$K_2Ti_6O_{13}$	109	8.641	166.7	417.5
PP(MAP)/15%$K_2Ti_6O_{13}$	120	6.601	167.7	425.4
PP(MAP)/25%$K_2Ti_6O_{13}$	125	6.893	168.5	430.1
PP(MAP)/35%$K_2Ti_6O_{13}$	140	5.534	166.9	431.6

termed as fiber-end embrittlement effects[26] for short fiber-reinforced polyamide composites. In these systems, a brittle-to-ductile transition occurs when the mean fiber-end spacing is less than about six times the fiber diameter. The mean fiber-end spacing can be calculated based on the following equation:

$$d = \left(\frac{8\varphi}{\pi d_f^3 s} \right)^{-1/3} \quad (5)$$

where d is the mean fiber-end spacing, φ is the volume fraction, and d_f and S are the diameter and aspect ratio of the fiber,[26] respectively. The relationship between the calculated d/d_f and potassium titanate whisker content is also shown in Figure 7. It can be seen that the d/d_f value is less than six when the whisker content is higher than 23 wt. Conceptually, the impact strength would begin to increase at or above this whisker content. However, no brittle-to-ductile transition is ob-
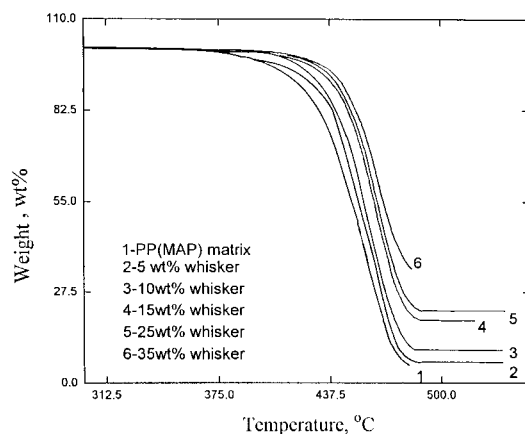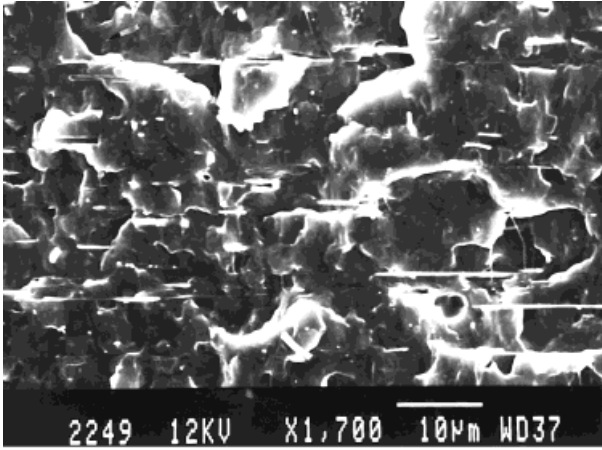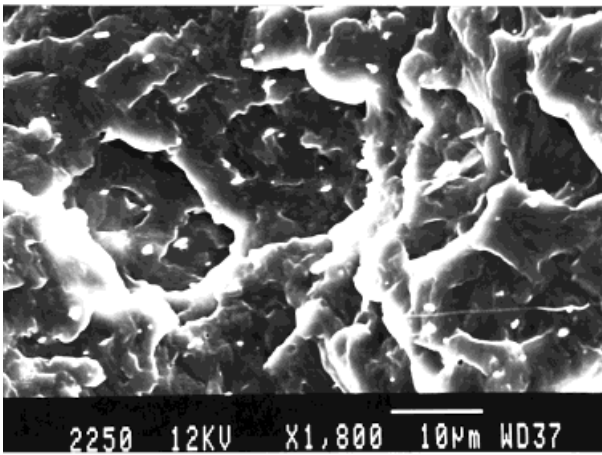

Figure 7 Longitudinal and transverse impact strengths versus whisker content for surface-treated PP/$K_2Ti_6O_{13}$ composites

Figure 8 Weight loss versus temperature for surface-treated PP/$K_2Ti_6O_{13}$ composites.

content. $T_E = 0.34$ for PP/35%$K_2Ti_6O_{13}$ composite is 60°C higher than that of pure PP, indicating that the heat resistance of PP is greatly enhanced by the addition of whiskers. It is noted that the glass transition temperature (T_g) for the composites decreases slightly with increasing whisker content. Lipatov[28] pointed that T_g for filled systems may be affected and is generally raised by the introduction of fillers. For polymers with low cohesion energy, however, T_g is practically independent of the filler content. It is believed that the decrease in T_g for PP/35%$K_2Ti_6O_{13}$ composites is due to the plasticizing effect of tetrabutyl orthotitanate on PP because T_g of the PP/15%$K_2Ti_6O_{13}$

(a)

(b)

Figure 9 SEM fractographs of the injection-molded and surface-treated PP/5%$K_2Ti_6O_{13}$ composite taken from (a) skin and (b) core sections of transverse sample after impact tests.

served for the longitudinal specimens because the impact strength levels off when the whisker content exceeds 23 wt %.
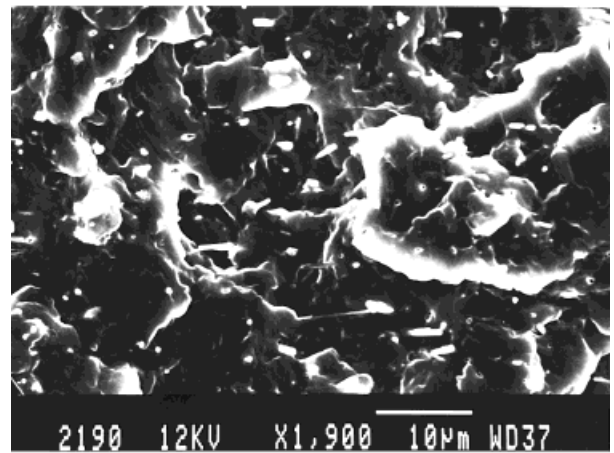
Thermogravimetric Analysis

To evaluate the heat resistance of the composites, we define the temperature at $E' = 0.34$ GPa as $T_E = 0.34$. The temperature for pure PP at $E' = 0.34$ GPa is 90°C, which is the same as the heat distortion temperature of pure PP.[27] Therefore, $T_E = 0.34$ can be used as a value to rate the heat resistance of the PP composite. $T_E = 0.34$ values of the composites are listed in Table III. We can see that $T_E = 0.34$ increases with increasing whisker
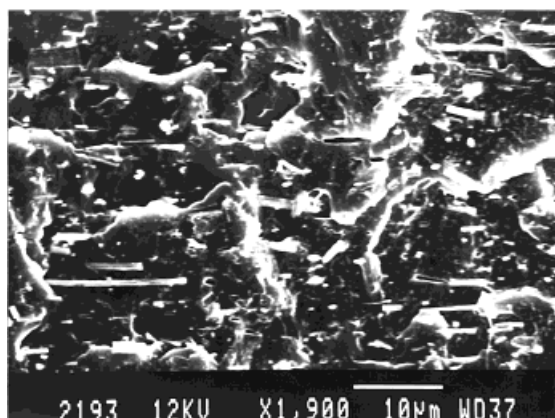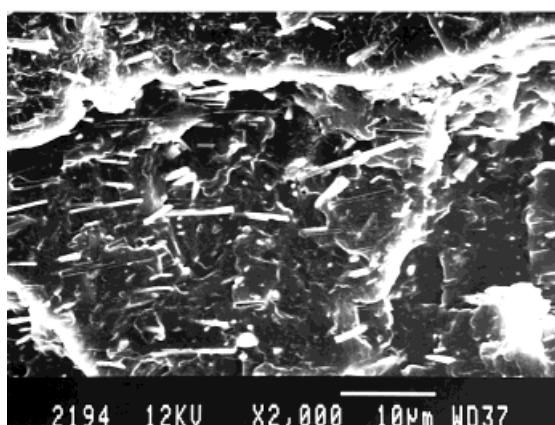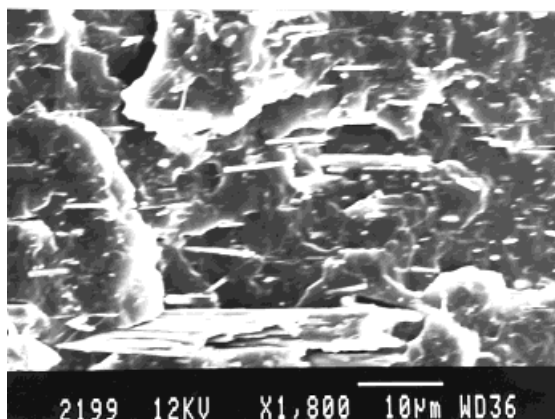

(a)

(b)

Figure 10 SEM fractographs of the injection-molded and surface-treated PP/10%$K_2Ti_6O_{13}$ composite taken from (a) skin and (b) core sections of transverse sample after impact tests.

(a)

(b)

(c)

Figure 11 SEM fractographs of the core section of transverse samples containing (a) 15 wt % (b) 25 wt %, and (c) 35 wt % whisker after impact tests.

composite (13.15°C) without tetrabutyl orthotitanate is higher than that of the surface-treated PP/15%$K_2Ti_6O_{13}$ composite (6.60°C).

Figure 8 shows the weight loss versus temperature relationship of the PP(MAP) matrix and its composites. The 5 wt % loss temperatures ($T_{-5\%}$) for these samples are also tabulated in Table III. It is apparent that the $T_{-5\%}$ values increase monotonically with increasing whisker content. This demonstrates that the thermooxidative stability of the composites is improved with increasing whisker content. The melting points (T_m) for the composites determined from the differential thermal analysis (DTA) are also listed in Table III. Apparently, the incorporation of whiskers into PP(MAP) exerts no effect on the T_m of the PP(MAP) matrix.

Morphology

It is well established that the injection-molded fiber-reinforced composites exhibit a typical skin-core morphology.[29,30] Figure 9(a,b) shows the SEM fractographs of the surface-treated PP/5%$K_2Ti_6O_{13}$ injection-molded composite. The fractographs indicate the formation of well-oriented whiskers in the skin section but random whiskers in the core section. SEM fractographs of PP/10%$K_2Ti_6O_{13}$ composite also show a similar skin-core microstructure [Fig. 10(a,b)]. As the whisker content of the composite is increased to 15 wt % or above, SEM micrographs shows well-oriented whisker microstructures in both skin and core sections [Fig. 11(a–c)].

CONCLUSION

Potassium titanate whisker-reinforced polypropylene composites were prepared in a twin-screw extruder followed by injection molding. The morphology, mechanical, and thermal properties of these composites were investigated. The results show that the compatibility between the whisker and PP(MAP) matrix is improved by the addition of a coupling agent. Therefore, the tensile strength and Young's modulus increase with higher whisker content. In addition, the composites containing lower whisker content (<15 wt %) exhibit necking behavior. The impact strength decreases slowly with increasing whisker content, and tends to level off when the whisker content is above 23 wt %. Moreover, the heat resistance of the composites investigated is greatly enhanced and the thermooxidative stability is improved by the incorporation of whiskers.

REFERENCES

1. K. Joseph, S. Thomas, and C. Pavithran, *Polymer,* **37,** 5139 (1996).
2. B. D. Park and J. J. Balatnecz, *Polym. Compos.,* **18,** 79 (1997).
3. R. T. Woodhams, S. Law, and J. J. Balatinecz, *Wood-Fiber/Polymer Composites,* M. P. Wolcott, Ed., Forest Products Society, Madison, WI, 1993.
4. Y. H. Zang and S. Sapieha, *Polymer,* **32,** 489 (1991).
5. T. H. Courtney, *Mechanical Behavior of Materials,* McGraw Hill, New York, 1990, p. 83.
6. G. C. Wei and P. F. Becher, *Am. Ceram. Soc. Bull.,* **64,** 298 (1985).
7. J. Homeny, W. L. Vaughn, and M. K. Ferver, *Am. Ceram. Soc. Bull.,* **66,** 333 (1987).
8. T. Christman and S. Suresh, *Acta Metall.,* **36,** 1691 (1988).
9. J. H. Kim, D. N. Lee, and k. H. Oh, *Scripta Metall. Mater.,* **29,** 377 (1993).
10. X. X. Xu and J. E. King, *Mater. Sci. Technol.,* **12,** 911 (1996).
11. K. Suganuma, T. Fujita, K. Nihara, and N. Suzuki, *J. Mater. Sci. Lett.,* **8,** 808 (1989).
12. M. Bai, Q. Xue, W. Liu , and S. Yang, *Wear,* **199,** 222 (1996).
13. R. Murakumi and K. Matsui, *Wear,* **201,** 193 (1996).
14. X. L. Wei, K. F. Zhao, T. J. Lu, Y. C. Xie, and Q. Zhu, *New Function Materials,* Chinese Chemical Engineering Press, Beijing, p. 125.
15. R. Taesler, H. Wittich, K. Schulte, and H. R. Kricheldorf, *J. Appl. Polym. Sci.,* **61,** 783 (1996).
16. M. Kobayashi, T. Takahashi, J. Takimoto, and K. Koyama, *Polymer,* **36,** 3927 (1995).
17. M. Avella, E. Martuscelli, M. Raimo, R. Partch, S. G. Gangolli, and B. Pascuci, *J. Mater. Sci.,* **32,** 2411 (1997).
18. G. Blinne, M. Knoll, D. Muller, and K. Schlichting, *Kunststoffe,* **75,** 29 (1985).
19. P. K. Mallick, *Fibre-Reinforced Composites,* 2nd ed., Marcel Dekker, New York, 1993, p. 71.
20. S. J. Monte and G. Sugarman, *Addtives for Plastics,* vol. 1, Academic Press, New York, 1981.
21. J. C. Halpin and J. L. Kardos, *Polym. Eng. Sci.,* **16,** 344 (1976).
22. E. Guth, *J. Appl. Physics,* **16,** 20 (1945).
23. M. Avella, E. Martuscelli, M. Raimo, R. Partch, S. G. Gangolli, and B. Pascuci, *J. Mater. Sci.,* **32,** 2411 (1997).
24. R. Taesler, H. Wittich, K. Schulte, and H. R. Kricheldorf, *J. Appl. Polym. Sci.,* **61,** 783 (1996).
25. S. C. Tjong and Y. Z. Meng, *Polymer,* to appear.
26. M. L. Shiao, S. V. Nair, P. D. Garrett, and R. E. Pollard, *Polymer,* **35,** 306 (1994).
27. I. I. Rubin, *Handbook of Plastic Materials and Technology,* John Wiley & Sons, Inc. New York, 1990, p. 441.
28. S. Lipatov, *Polymer Reinforcement,* Chem Tech Publisher, Toronto, 1995, p. 105.
29. S. C.Tjong and Y. Z. Meng, *Polymer,* **38,** 4609 (1997).
30. M. R. Nobile, E. Amendola, and L. Nicolais, *Polym. Eng. Sci.,* **29,** 244 (1989).-