

# Performance of potassium titanate whisker reinforced polyamide-6 composites

S. C. Tjong\* and Y. Z. Meng†

*Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China*

*(Received 14 July 1997; revised 10 September 1997; accepted 5 November 1997)*

Composites of polyamide-6 reinforced with potassium titanate whiskers were prepared in a twin-screw extruder, followed by injection moulding. The whiskers were surface treated with tetrabutyl orthotitanate prior to blending. The tensile, impact, morphology and thermal properties of the injection moulded composites were investigated. Static tensile measurements showed that the tensile strength and modulus of the composites increased with increasing whiskers content. However, Izod impact tests indicated that the composites showed a decrease in the impact strength initially with whiskers content up to 25 wt%; thereafter they showed a slight increase when the whiskers content reached 35 wt%. Scanning electron microscopic observations revealed that the whiskers within the composites were oriented uniformly along the melt flow direction. Finally, thermogravimetric analysis showed that the heat resistance of the composites tended to increase with increasing whiskers content. The results were analysed and discussed in terms of established models of the behaviour of short-fibre reinforced composites. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: polyamide-6; composite; potassium titanate whiskers)**

## INTRODUCTION

Polyamide-6 (PA6) is a semicrystalline thermoplastic that has been widely used in engineering applications due to its outstanding mechanical properties and processability. However, PA6 also exhibits some disadvantages such as low heat deflection temperature, high water absorption and dimensional instability. In response to demands for high performance material, various fibre reinforcements, such as glass, carbon, natural fibre, liquid crystalline polymer, are frequently added to polyamides<sup>1–10</sup>. In general, the incorporation of discontinuous fibres into polyamides leads to a dramatic increase in stiffness, strength and fracture toughness<sup>11</sup>. Consequently, short glass fibre reinforced polyamides find applications for under-the-bonnet automobile parts<sup>12</sup> and in related industries where high performance materials are essential.

Recently, there has been considerable interest in upgrading the mechanical performance of polymers by reinforcing with whiskers<sup>13–16</sup>. Whiskers are generally recognized as being free from internal defects such as dislocations owing to their small diameter. Hence the yield strength of whiskers tends to approach the maximum theoretical value<sup>17</sup>. Silicon carbide (SiC) whiskers have been widely used as reinforcement in metal matrix composites (MMCs)<sup>18–21</sup>. However, potassium titanate whiskers show promise as reinforcement materials owing to their relatively low cost. The price of potassium titanate whiskers ranges from one-tenth to one-twentieth of the cost of SiC whiskers<sup>22</sup>. In this regard, potassium titanate whiskers have been used to reinforce metallic alloys<sup>23,24</sup>. Compared with whiskers reinforced MMCs, fewer studies have been conducted on the

mechanical performance of polymer composites reinforced with inorganic whiskers.

It is well established that the mechanical behaviour of fibre reinforced and filled polymers is closely related to the interfacial adhesion between the polymer matrix and the reinforcement<sup>25–29</sup>. When the interfacial bonding is poor, the loadbearing capacity of the polymer composite is limited. Therefore, many surface treatments for fibres and fillers have been applied to enhance the interfacial effects. For example, fibre and filler surfaces are treated with coupling agents based on silane and titanate compounds<sup>30,31</sup>, whose chemical structures allow them to react with the reinforcement and with the polymeric matrix. The interfacial bond created by silanes and other coupling agents allows a better shear stress transfer between fibres and matrix, thereby improving the tensile and interlaminar shear strengths of the composite<sup>31</sup>. In this paper, the morphology, static and dynamic mechanical properties, impact strength and thermal properties of PA6 composites reinforced with surface-treated potassium titanate whiskers are investigated.

## EXPERIMENTAL

### Materials

The whiskers used in this work were of potassium titanate ( $K_2Ti_6O_{13}$ ) obtained from Shenyang Jin-Jian Composite Co, China. Their main properties are listed in *Table 1*. Russian-made polyamide-6 was used as the polymeric matrix. Reagent-grade tetrabutyl orthotitanate was used as the coupling agent for the whiskers.

### Sample preparation

5 wt% tetrabutyl orthotitanate solution was prepared by dissolving it in acetone. The tetrabutyl orthotitanate solution was slowly poured into the whiskers and sufficiently

\* To whom correspondence should be addressed

† Y. Z. Meng is on leave from the Department of Polymeric Materials and Science, Dalian University of Technology, Dalian 116012, China

blended by hand in a plastic box. Finally the whiskers were dried in an oven at 100°C for 24 h. The PA6 pellets were also dried at 100°C for 24 h prior to blending.

Composites containing 5, 10, 15, 25 and 35 wt% whiskers were prepared in a twin-screw Brabender Plasticorder at 265°C. The extrudates exiting the Brabender were cut into pellets by a pelletizer. Both standard dog-bone tensile bars (ASTM D638) and plaques with dimensions of 147 × 80 × 6 mm were injection moulded from these pellets. The mould temperature was maintained at 40°C whilst the barrel zone temperatures were set at 265, 275 and 275°C.

*Morphological observations*

The injection moulded composites were cryofractured. The fracture surfaces were coated with a thin layer of gold. The morphologies were observed in a Jeol JSM 820 scanning electron microscope.

*Mechanical measurements*

The tensile behaviour of the composites was determined using an Instron tensile tester (model 4206) at 23°C. A crosshead speed of 1 mm min<sup>-1</sup> was used in the tests. Five specimens of each composition were tested and the average values reported.

Notched Izod impact specimens with dimensions of 65 × 12.7 × 6 mm were prepared from the injection moulded plaques. Both longitudinal and transverse impact specimens were used in the tests. For the longitudinal impact specimens, the length direction was parallel to the mould-filling direction, whilst it was perpendicular to the mould-filling direction for the transverse impact specimens. Seven specimens were tested and the average values reported.

Dynamic mechanical analysis (DMA) of the injection moulded composites was conducted with a DuPont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The temperature studied ranged from - 20 to 280°C, with a heating rate of 2°C min<sup>-1</sup>.

*Thermal analyses*

The decomposition process of the composites from 50 to 600°C was determined with a Seiko thermogravimetric analyser (model SSC-5200) under a protective helium atmosphere. The heating rate employed was 20°C min<sup>-1</sup>.

RESULTS AND DISCUSSION

*Effects of coupling agent*

The typical mechanical properties of pure PA6 and tetrabutyl orthotitanate treated PA6/25% K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites are summarized in Table 2. For purposes of comparison, the mechanical properties of untreated PA6/25% K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites are also listed in Table 2. It is apparent from Table 2 that the incorporation of potassium titanate whiskers into PA6 leads to an increase in both tensile strength and modulus. Furthermore, composites reinforced with tetrabutyl

orthotitanate treated whiskers exhibit much higher tensile strength and modulus than those containing untreated whiskers. It is believed that tetrabutyl orthotitanate effectively decreases the surface tension between the whiskers and the PA6 via hydrolysis reactions, i.e. interaction between -OH groups absorbed on the whisker surface and -NH or -OH groups of PA6<sup>32</sup>. This in turn results in better adhesion and compatibility between the whiskers and the PA6 matrix. On the other hand, it is interesting to see from Table 2 that the coupling agent has little effect on the impact strength of both longitudinal and transverse composite specimens. This means that tetrabutyl orthotitanate treatment does not lead to an improvement in the impact strength of the composites.

*Mechanical properties*

Figure 1 shows the variation of tensile strength with whisker content for the PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. Apparently, the tensile strength tends to increase with increasing whisker content. For the composite containing 35 wt% whiskers, the tensile strength is 50% higher than that of pure PA6. This implies that the potassium titanate whiskers reinforce PA6 effectively. Similarly, the Young's modulus

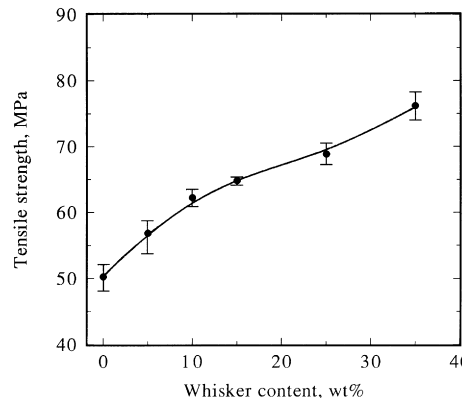


Figure 1 Tensile strength versus whisker content for surface-treated PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites

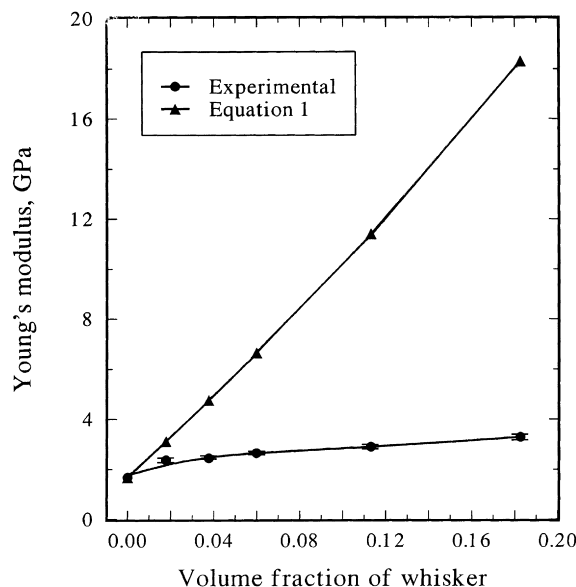


Figure 2 Young's modulus versus whisker content for surface-treated PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. The modulus of discontinuous fibre reinforced PA6 composites predicted from the Tsai-Halpin equation is also shown, for purposes of comparison

Table 1 Properties of potassium titanate whiskers

Specific density	Length	Diameter	Tensile strength	Tensile modulus	Melting point	Heat resisting temperature
g cm <sup>-3</sup>	µm	µm	GPa	GPa	°C	°C
3.3	10-40	0.5-1.0	7	280	1370	1200

(Figure 2) and storage modulus (Figure 3) of the composites also appear to increase considerably with increasing whisker content.

One of the relationships most commonly used to predict the elastic modulus of a discontinuous short-fibre reinforced composite from the moduli of the individual components is the Tsai–Halpin equation<sup>33</sup>. The equation is based on the assumption of continuity of stress and strain along the fibre/matrix interface, and reads:

$$\frac{E_c}{E_m} = \frac{1 + \xi\eta\varphi_f}{1 - \eta\varphi_f} \quad (1)$$

where  $E_c$  and  $E_m$  are the elastic moduli of composite and matrix, respectively, and  $\varphi_f$  is the volume fraction of short fibres. The constants  $\xi$  and  $\eta$  are given by

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

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

where  $L/D$  is the aspect ratio (length/diameter) of the reinforcing fibres, and  $E_f$  is the modulus of the fibres. From Figure 2, the experimental data are much lower than those predicted from equation (1). This is because the length of the whiskers is shorter than the critical fibre length which is needed for effective load-carrying capacity.

The variation of strain-at-break of composites with whisker content is depicted in Figure 4. It is noticed that the strain-at-break decreases dramatically with the incorporation of a very low whisker content into PA6, i.e. 5 wt%. Thereafter it shows a steady decrease with increasing whisker content. This is a typical behaviour of short fibre and filler reinforced polymer composites.

Wei *et al.*<sup>13</sup> reported that the tensile strength of PA6.6 increases sharply from 81 to 133 MPa when 30 wt% potassium titanate whisker is added. This means that the tensile strength of whisker reinforced composites is 64% higher than that of pure polyamide-6.6. The reinforcing effect of potassium titanate whiskers in the PA6 matrix in this work is somewhat smaller than that in the polyamide-6.6 matrix. On the other hand, the reinforcing effect of potassium titanate whiskers in PA6 is higher than that of poly(4-hydroxybenzoate) (PHB) whiskers<sup>14</sup>. Taesler *et al.*<sup>14</sup> reported that the incorporation of PHB whiskers in PA6.6

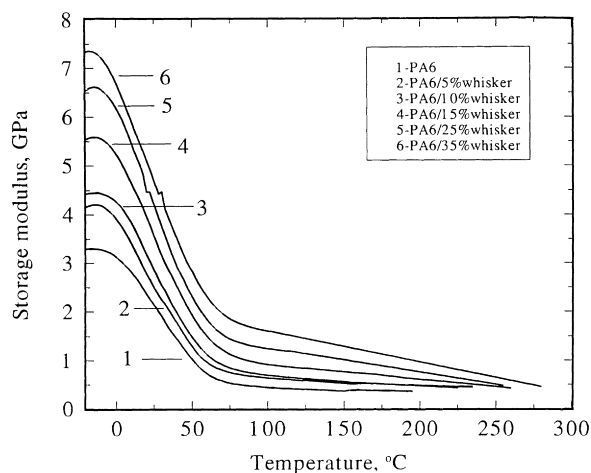


Figure 3 Storage modulus versus temperature for surface-treated PA6/ $K_2Ti_6O_{13}$  composites

led to an increase in elastic modulus but a sharp decrease in both tensile strength and strain-at-break. They pointed out that the reduction in tensile strength of the composites resulted from the agglomeration of whiskers. These agglomerates were considered as mechanical weak points because of poor wetting of the whiskers by the matrix.

More recently, Avella *et al.*<sup>16</sup> have investigated the mechanical properties of silicon carbide whisker reinforced polypropylene composites. They reported that the addition of untreated whiskers leads to an enhancement of the modulus but a decrease in both tensile strength and strain-at-break. In addition, the introduction of surface-treated whiskers resulted in no improvement of the tensile strength.

As discussed above, potassium titanate whiskers reinforce PA6 polymer effectively despite the fact that the reinforcing efficiency of the whiskers is lower than that of short fibres. It is believed that the reinforcing effect of the potassium titanate whiskers used in this work arises from their specific crystalline and surface structure. The  $K_2Ti_6O_{13}$  whiskers have a larger aspect ratio and surface area, which in turn leads to a stronger enhancing effect. Moreover, the proper surface treatment for whiskers in this work is responsible also for the effective reinforcement of the matrix.

#### Impact properties

Figure 5 shows the relationship between impact strength and whisker content for the specimens prepared from the longitudinal and transverse directions. It can be seen that the impact strength of the longitudinal specimens is higher than

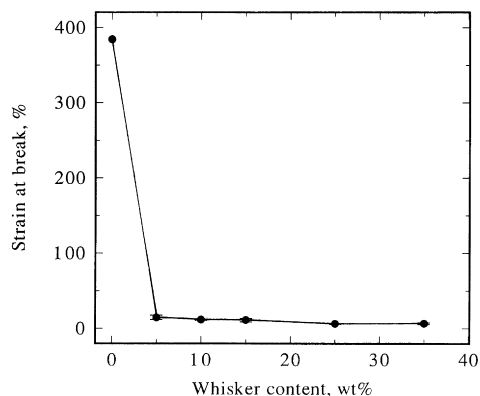


Figure 4 Strain-at-break versus whisker content for surface-treated PA6/ $K_2Ti_6O_{13}$  composites

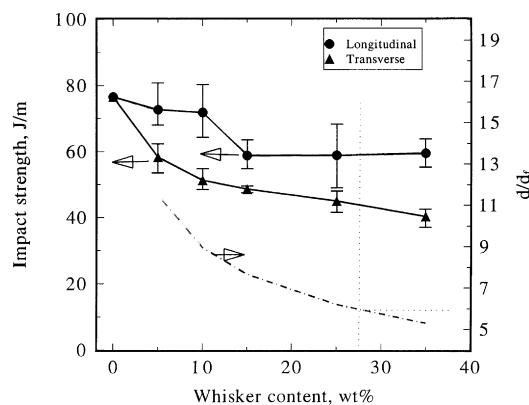


Figure 5 Longitudinal and transverse impact strengths versus whisker content for surface-treated PA6/ $K_2Ti_6O_{13}$  composites

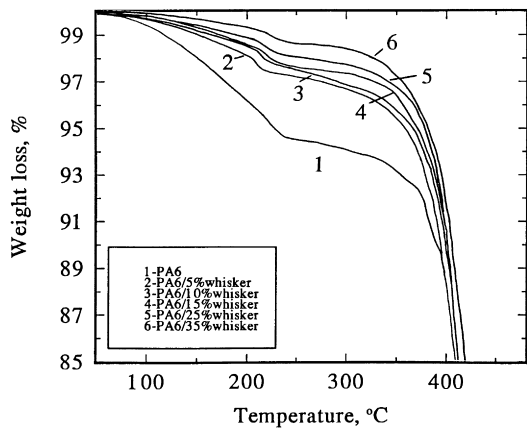


Figure 6 Weight loss versus temperature for surface-treated PA6/ $K_2Ti_6O_{13}$  composites

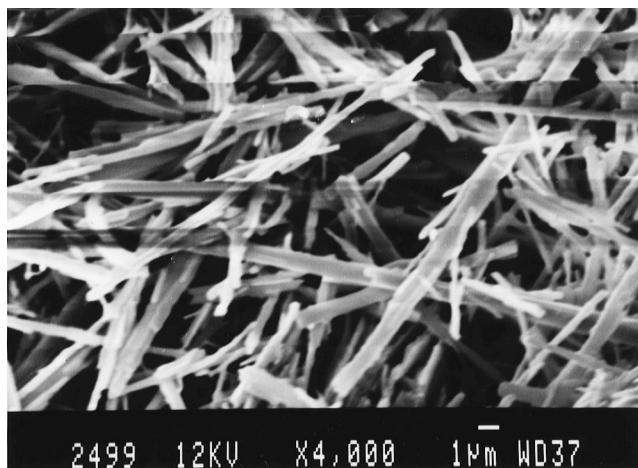


Figure 7 SEM micrograph of potassium titanate whiskers

that of the transverse specimens. This is because the whisker direction is parallel to the length direction for the longitudinal specimens. These oriented whiskers can inhibit crack propagation owing to the crack front being perpendicular to the whisker orientation. Furthermore, it is noticed from Figure 5 that the impact strength of longitudinal specimens initially decreases with whisker content up to 15 wt%, then levels off at 25 wt%. This behaviour is termed the fibre-end embrittlement effect in short fibre reinforced polyamide composites<sup>34</sup>. For those systems, a ductile-to-brittle transition occurs when the fibre-end spacing is less than about six times the fibre diameter. The mean fibre-end spacing can be calculated from the following equation:

$$d = \left( \frac{8\varphi}{\pi d_f^3 S} \right)^{-1/3} \quad (4)$$

where  $d$  is the mean fibre-end spacing,  $\varphi$  is the volume fraction,  $d_f$  and  $S$  are the diameter and aspect ratio of the fibre<sup>34</sup>. The calculated  $d/d_f$  value is smaller than six when the whisker content approaches 28 wt% and above. In this case, the impact strength of longitudinal specimens tends to increase slightly when the whisker content reaches 28 wt% and above.

#### Thermal properties

Figure 3 shows the variation of storage modulus with

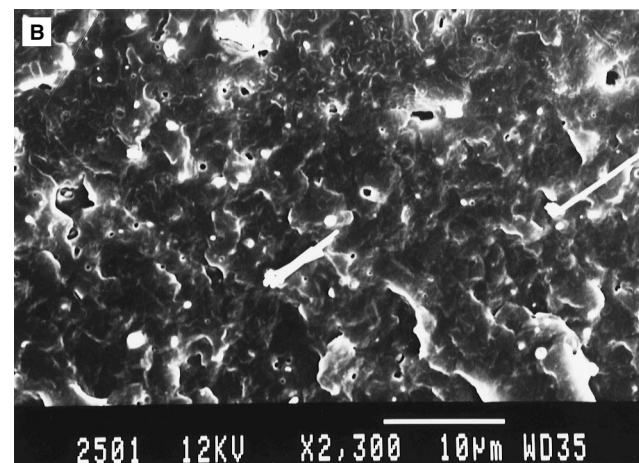
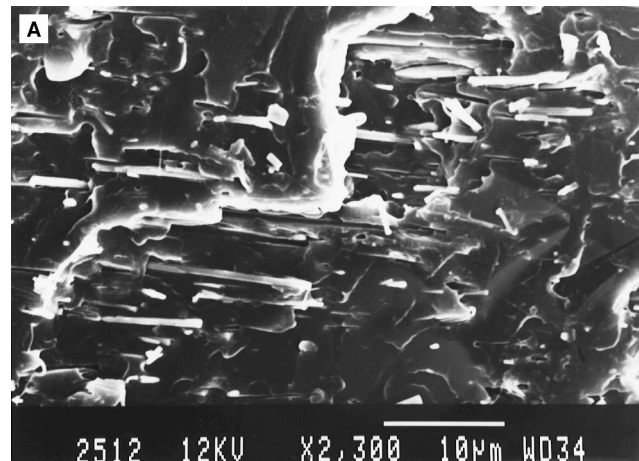


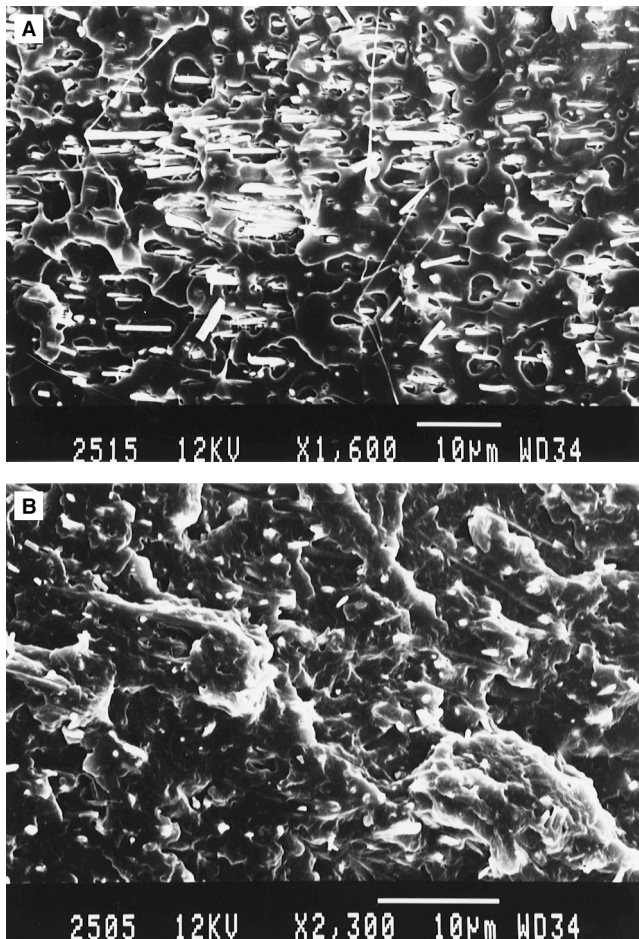
Figure 8 SEM fractographs of the skin section of injection moulded, surface-treated PA6/5% $K_2Ti_6O_{13}$  composite taken from (A) transverse and (B) longitudinal directions

Table 2 Mechanical properties of PA6, PA6/25% $K_2Ti_6O_{13}$  and tetrabutyl orthotitanate treated PA6/25% $K_2Ti_6O_{13}$  specimens

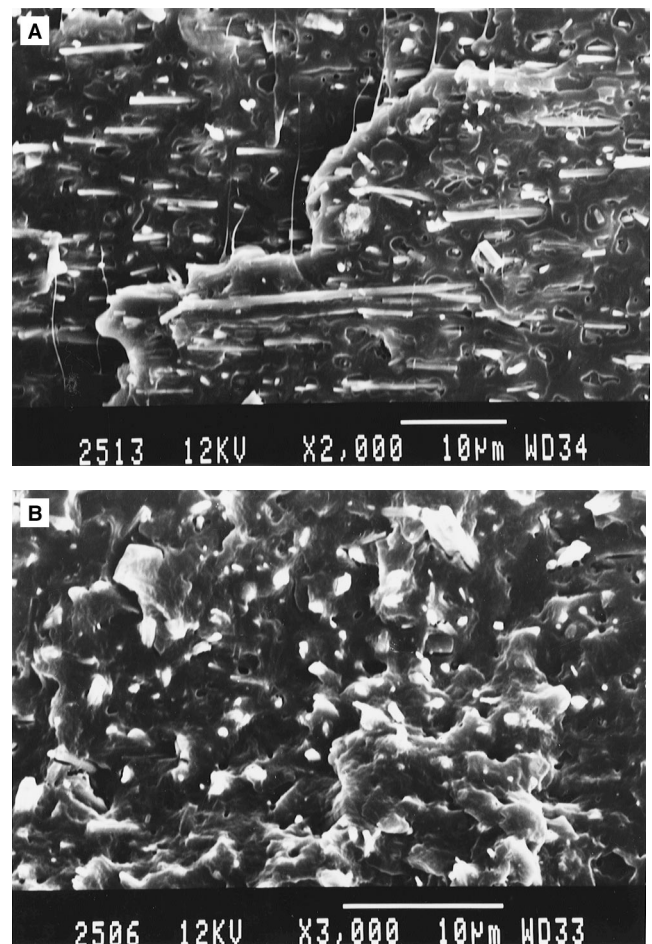
	PA6	Surface-untreated PA6/25% $K_2Ti_6O_{13}$	Surface-treated PA6/25% $K_2Ti_6O_{13}$
Tensile strength, MPa	50 ± 2.0	58 ± 3.1	69 ± 3.3
Young's modulus, MPa	1672 ± 76	2296 ± 86	2650 ± 102
Strain-at-break, %	384.4 ± 50	6.4 ± 1.3	8.4 ± 1.9
Longitudinal impact strength, J m <sup>-1</sup>	76.5 ± 4.9	59.5 ± 4.1	59.5 ± 4.4
Transverse impact strength, J m <sup>-1</sup>	76.5 ± 4.9	44.5 ± 1.5	45 ± 2.4

temperature for the PA6/ $K_2Ti_6O_{13}$  composites. In order to determine and to rate the heat resistance of PA6 and its composites, we define the temperature at  $E' = 0.47$  GPa as  $T_{E'=0.47}$ . From Figure 3, the  $T_{E'=0.47}$  for PA6 is 90°C, which is identical to the heat distortion temperature for pure PA6. Therefore, we can use the  $T_{E'=0.47}$  value to rate the heat resistance of polyamide composites. Values of  $T_{E'=0.47}$  for PA6 and its composites are listed in Table 3. From this table, one can see that  $T_{E'=0.47}$  tends to increase sharply with the addition of a small amount of whisker content, i.e. 5 wt%. In other words,  $T_{E'=0.47}$  of the PA6/5% $K_2Ti_6O_{13}$  composite is about 100°C higher than that of pure PA6. Further increase in the whisker content only leads to a considerable increase in  $T_{E'=0.47}$ .

It is interesting to see that the glass transition



**Figure 9** SEM fractographs of the skin section of injection moulded, surface-treated PA6/35%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composite taken from (A) transverse and (B) longitudinal directions



**Figure 10** SEM fractographs of the core section of injection moulded, surface-treated PA6/35%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composite taken from (A) transverse and (B) longitudinal directions

**Table 3** Thermal properties of PA6 and potassium titanate whisker reinforced composites

	$T_{E'=0.47}$ , °C	$T_g$ , °C	$T_{5\%}$ , °C
PA6	90	66.13	228.4
PA6/5%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	195	61.79	365.5
PA6/10%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	213	61.99	373.8
PA6/15%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	235	61.86	380.1
PA6/25%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	245	61.75	391.3
PA6/35%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub>	256	52.16	395.6

temperature ( $T_g$ ) of PA6 and its composites varies little with the whisker content (Table 3). Lipatov<sup>35</sup> pointed out that the  $T_g$  for a filled system can be represented by the following equation:

$$T_{g,c} = T_{g,m} + \Delta T\nu \quad (5)$$

where  $T_{g,c}$  and  $T_{g,m}$  are the  $T_g$ s for filled and pure matrix polymer, respectively.  $\nu$  can be determined from

$$\nu = 1 - \frac{\Delta G_c}{\Delta G_m} \quad (6)$$

where  $\Delta G_c$  and  $\Delta G_m$  are changes in heat capacity at  $T_g$  for filled and unfilled samples. From equation (5), it is readily seen that  $T_{g,c}$  varies linearly with  $\Delta T$ , which corresponds to the hole density of the cohesive energy of the polymer. For polymers with low cohesive energy, the magnitude of  $\Delta T$  in equation (5) is very small; thus the  $T_{g,c}$  value is close to  $T_{g,m}$ . This implies that  $T_{g,c}$  is not dependent on the filler content.

From Table 3, the  $T_g$ s of PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites remain constant up to 25 wt% whisker content, and their values are smaller than that of pure PA6. It is considered that the decrease in  $T_g$  is due to the plasticizing effect of tetrabutyl orthotitanate because the  $T_g$  of surface-untreated PA6/25%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites is close to that of pure PA6.

Figure 6 shows the weight loss curves versus temperature for PA6 and its composites. The 5% loss temperatures ( $T_{5\%}$ ) for these specimens are also tabulated in Table 3. This table indicates that the addition of 5 wt% whiskers to PA6 results in a dramatic increase in  $T_{5\%}$ . Further increasing the whisker content only leads to a small increase in  $T_{5\%}$  values. Thus the incorporation of potassium titanate whiskers into PA6 is beneficial in improving the thermoxidative stability of PA6.

#### Morphology

Figure 7 shows a typical SEM micrograph of the potassium titanate whiskers. This micrograph reveals that the whiskers exhibit a large aspect ratio owing to their small diameter. Figure 8A and B are SEM fractographs of the skin section of an injection moulded PA6/5%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composite taken from the longitudinal and transverse directions, respectively. The fractographs indicate the formation of well oriented microstructure of whisker within the PA6 matrix. As the whisker content of the composite is increased to 35 wt%, SEM micrographs also show a similar well oriented microstructure of whiskers in both skin and core

sections (Figure 9A–B and Figure 10A–B). There appears to be no skin-core or laminated morphology in the injection moulded PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites.

## CONCLUSIONS

Tetrabutyl orthotitanate treated potassium titanate whisker reinforced composites were prepared in a twin-screw extruder, followed by injection moulding. The morphology, mechanical and thermal properties of these composites were investigated. The results showed that the coupling agent effectively improved the compatibility between the whiskers and the PA6 matrix. In this case, the tensile strength and modulus of the composites tended to increase with increasing whisker content. Izod impact measurements indicated that the impact strength initially decreased with increasing whisker content, but appeared to increase slightly when the whisker content reached 35 wt%. Finally, the heat resistance and thermoxidative stability of PA6 were enhanced greatly by the incorporation of potassium titanate whiskers.

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