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Properties and morphology of polyamide 6 hybrid composites containing potassium titanate whisker and liquid crystalline copolyester

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Abstract

Polyamide 6 (PA6) hybrid composites reinforced with potassium titanate whiskers ($K_2Ti_6O_{13}$) and liquid crystalline polymer (LCP) were prepared in a twin-screw extruder followed by injection moulding. The whiskers were surface treated with tetrabutyl orthotitanate prior to blending. Static tensile measurements showed that the tensile strength and modulus of the composites tend to increase with increasing whisker content. However, Izod impact tests indicated that the hybrid composites show little variation in the impact strength with the addition of whisker content up to 10 wt%, thereafter the impact energy shows an obvious decrease with increasing whisker content. Scanning electron microscopic observations revealed that the oriented LCP fibrils were formed in the skin section of hybrid composites containing whisker content < 10 wt%, whilst spherical droplets were dispersed in the skin section of hybrids containing whisker content ≥ 15 wt%. Torque measurements showed that the LCP is very effective in reducing the melt viscosities of PA6/$K_2Ti_6O_{13}$ composites. Finally, thermogravimetric analysis showed that the hybrid composites with higher whisker content exhibit good heat resistance properties. The hybrid effects of the two reinforcements on the mechanical properties and compatibility of these hybrid composites are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamide 6; Hybrid composite; Whisker

1. Introduction

Polyamide 6 (PA6) is used in a wide range of engineering applications because of its attractive combination of good mechanical properties and processability. In order to further upgrade the performance of PA6, various fibre reinforcements, e.g., glass, carbon, and natural fibre, are frequently added to polyamides [1–6]. Increasing attention is being directed toward composites with whisker reinforcement designed to increase the mechanical properties of polymers [7–11]. Whiskers are generally known to be free from the internal defects such as dislocations owing to their small diameter. Hence the yield strength of whiskers tends to approach the maximum theoretical value [12]. Potassium titanate whisker ($K_2Ti_6O_{13}$) is one of the most promising classes of reinforcement materials owing to their relative low cost, and superior physical properties. The price of potassium titanate whiskers ranges from one-tenth to one-twentieth of the cost of SiC whiskers [13]. In this regard, potassium titanate whiskers have been used to reinforce the metallic alloys [14,15] and polymers [7,11].

In general, the incorporation of discontinuous fibres or whiskers into polyamides leads to a dramatic increase in stiffness, strength, fracture toughness and heat-resistance, as well as melt viscosity. Thus fibre-reinforced polyamides pose significant processing problems owing to their high viscosity. Liquid crystalline polymers (LCPs) are well known for their unique mechanical and rheological properties. LCPs consist of linear rod-like molecules that are capable of forming a highly ordered molecular structure during processing. This implies that LCPs tend to form in situ reinforcing fibrils when blended with a thermoplastic under appropriate processing conditions. In addition, their spontaneous molecular orientation leads to low melt viscosity, with consequent improvement of processability. There have been numerous studies of in situ LCP/thermoplastic composites [16–25]. The morphology, rheology and mechanical properties of LCP/PA6 composites have been investigated by Tjong and Meng recently [23–25]. They reported that the processing steps and temperatures have a dramatic effect on the fibrillation of LCP in maleic anhydride compatibilized LCP/PA6 blends.

As the incorporation of whiskers into polyamides leads to an increase in the melt blend viscosity and stiffness whilst

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Table 1
Properties of potassium titanate whiskers

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

the introduction of LCP produces a reduction in viscosity, thus balanced properties could be reached by the introduction of LCP into the PA6/whisker system. More recently, He and co-workers have combined the concept of the in situ composite and hybrid composite, and introduced the concept of the in situ hybrid composite [26]. They have prepared the in situ hybrid polyethersulfone (PES) composites containing carbon fibres and LCP, and investigated the rheology and mechanical properties of such in situ hybrid composites.

In the present work, we attempt to prepare hybrid PA6/$K_2Ti_6O_{13}$/LCP composites in a twin-screw extruder followed by injection moulding. It is anticipated that such hybrid composites exhibit lower viscosity than whisker/PA6 composites. The main aim is to examine the morphology, rheology and mechanical properties of these hybrid PA6 composites, and to correlate the relationships between these properties.

2. Experimental

2.1. Materials

The whiskers used in this work were potassium titanate ($K_2Ti_6O_{13}$) obtained from Shenyang Jin-Jian Composite Co., China. Their main properties are listed in Table 1. Russian-made PA6 was used as the polymeric matrix. The LCP is Vectra A950 produced by the Hoechst Celanese Company. Reagent grade tetrabutyl orthotitanate was used as the coupling agent for the whiskers.

2.2. Sample preparation

Five wt% tetrabutyl orthotitanate solution was prepared by dissolving it in acetone. The whiskers were treated with 1.5 wt% tetrabutyl titanate. The tetrabutyl orthotitanate solution was slowly poured on to the whiskers and sufficiently blended by hand in a plastic box. Finally they were dried in an oven at 90°C for 48 h. The PA6 pellets were also dried at 100°C for 24 h prior to blending.

The PA6 blends containing 5, 10, 15, 25 and 35 wt% $K_2Ti_6O_{13}$ whiskers were prepared in a twin-screw Brabender Plasticorder at 265–285°C. The extrudates from the Brabender were cut into pellets by a pelletizer. The PA6/$K_2Ti_6O_{13}$ composite and LCP pellets were tumbled together in a container prior to injection moulding. Subsequently, the PA6 hybrid composites were injection moulded directly from tumbled PA6/$K_2Ti_6O_{13}$ and LCP pellets without any precompounding. The weight ratio of PA6/$K_2Ti_6O_{13}$ to LCP is fixed at 85/15. Standard dog-bone tensile bars (ASTM D638) were injection moulded from these pellets. The mould temperature was maintained at 40°C whilst the barrel zone temperatures were set at 290, 290 and 275°C.

2.3. Morphological observations

The samples after impact tests were examined in a scanning electron microscope (SEM). The fractured surfaces were coated with a thin layer of gold. The morphologies were observed in a JEOL JSM 820 SEM.

2.4. Mechanical measurements

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

Notched Izod impact specimens with dimensions of $65 \times 12.7 \times 3.2$ mm were prepared from the injection moulded tension bars. Seven specimens were tested and the average values reported.

Dynamic mechanical analysis (DMA) of the injection moulded composites was conducted with a Du Pont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The temperatures studied ranged from -30 to 200°C with a heating rate of 2°C/min.

2.5. Torque measurements

Torque values for the hybrid composites and pure polymers were measured using a Brabender Plasticorder batch mixer at 285°C and at 30 rpm for 5 min. The chamber volume was 50 cm^3. For each examination, 35 g material was added into the batch.

2.6. Thermal analyses

The decomposition process of the composites from 30 to 600°C was determined with a Seiko thermogravimetric analyser (TGA) (model SSC-5200) under a protective helium atmosphere (200 ml/min). The heating rate employed was 20°C/min.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the variations of tensile strength with

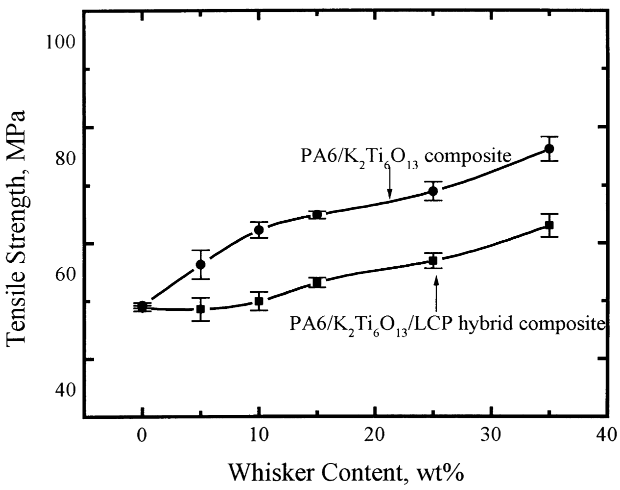

Fig. 1. Tensile strengths versus whisker content for PA6/$K_2Ti_6O_{13}$ composites and PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

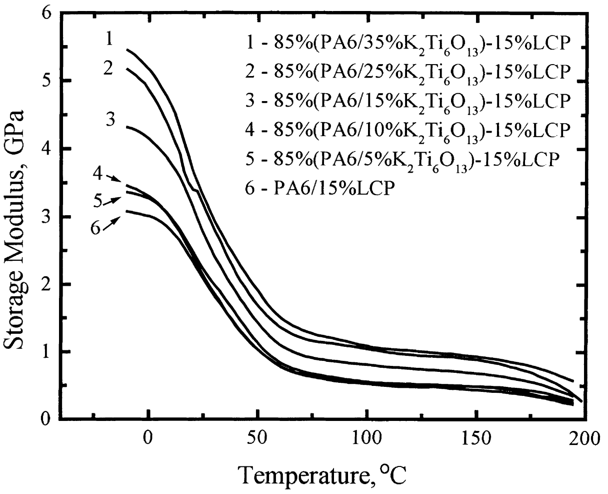

Fig. 3. Storage modulus versus temperature for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

whisker content for both PA6/$K_2Ti_6O_{13}$ composites and PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. Apparently, the tensile strengths tend to increase with increasing whisker content for two systems. Moreover, the tensile strengths of PA6/$K_2Ti_6O_{13}$ composites are higher than those of PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. This implies that addition of potassium titanate whiskers alone is more effective at reinforcing the PA6 matrix than combined potassium titanate whiskers and LCP reinforcements. This could be due to the poor interfacial bonding between the dispersed LCP phase and PA6 matrix. The poor interfacial bonding subsequently produces a lower mechanical strength for PA6/LCP composites [23]. Meanwhile, this also indicates that the LCP phase does not deform into long fibrils in the matrix. It is considered that the introduction of 15 wt% LCP into PA6/$K_2Ti_6O_{13}$ composites results in the decrease of whisker content and tetrabutyl orthotitanate concentration of composites accordingly. This decrement of whisker content in turn leads to a poor reinforcing efficiency. He et al. indicated that LCP fibrils formed agents in the hybrid PES/carbon fibre/LCP composites which have lower aspect ratios, thereby decreasing the reinforcing effect of the fibrils [25]. In that case, the short carbon fibres are the major reinforcing agents in the hybrid composites. In this work, the Young's modulus (Fig. 2) and storage modulus (Fig. 3) of hybrid composites also appear to increase considerably with increasing whisker content. Furthermore, the theoretical Young's modulus of the PA6/$K_2Ti_6O_{13}$ composite determined from the Tsai–Halpin equation is also shown for the purposes of comparison (Fig. 2). The Tsai–Halpin equation is commonly used to predict the elastic modulus of a discontinuous short fibre reinforced composite from the moduli of the individual components. The equation is based on the following assumption [27]:

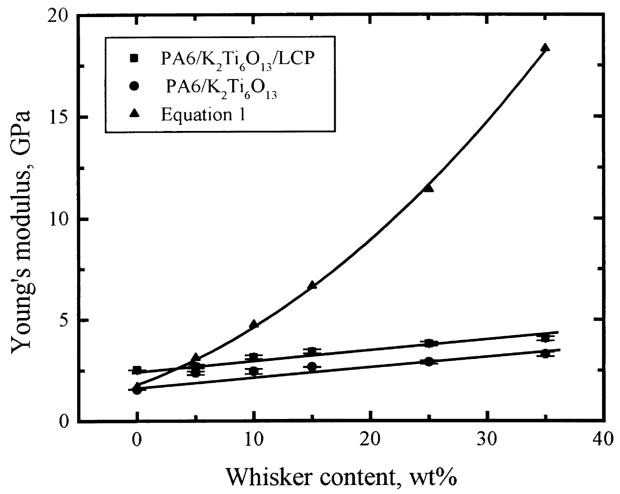

Fig. 2. Young's modulus versus whisker content for PA6/$K_2Ti_6O_{13}$ composites and PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. The modulus of PA6/$K_2Ti_6O_{13}$ composites predicted from the Tsai–Halpin equation is also shown for the purposes of comparison.

1. Fibre cross-section is circular.
2. Fibres are arranged in a square array.
3. Fibres are uniformly distributed throughout the matrix.
4. Matrix is free of voids.
5. The equation reads:

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

where E_c and E_m are the elastic moduli of composite and matrix, respectively; φ_f is the volume fraction of short fibres. The constants ξ and η are given by

$$\xi = 2(L/D) \tag{2}$$

$$\eta = \frac{E_f - E_m}{E_f + \xi E_m} \tag{3}$$

where L/D is the aspect ratio (length/diameter) of the reinforcing fibres, and E_f is the modulus of the fibres. The PA6/$K_2Ti_6O_{13}$/LCP composites satisfies Tsai–Halpin equation, although the length of $K_2Ti_6O_{13}$ whiskers is relatively short.

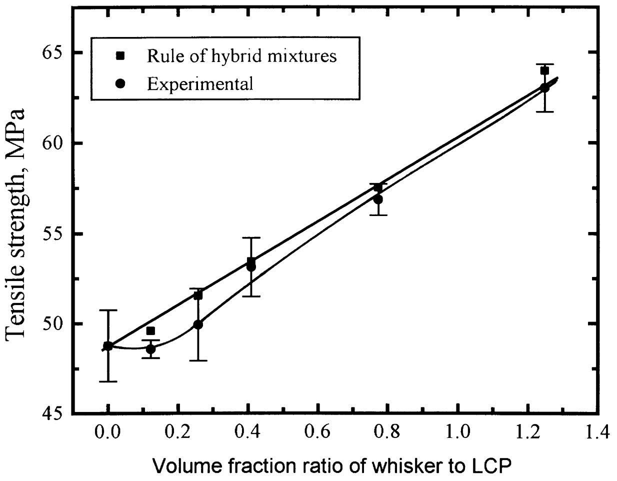

Fig. 4. Experimental tensile strengths versus $K_2Ti_6O_{13}$/LCP volume fraction ratio for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. Theoretical values predicted from the rule of hybrid mixtures are also shown.

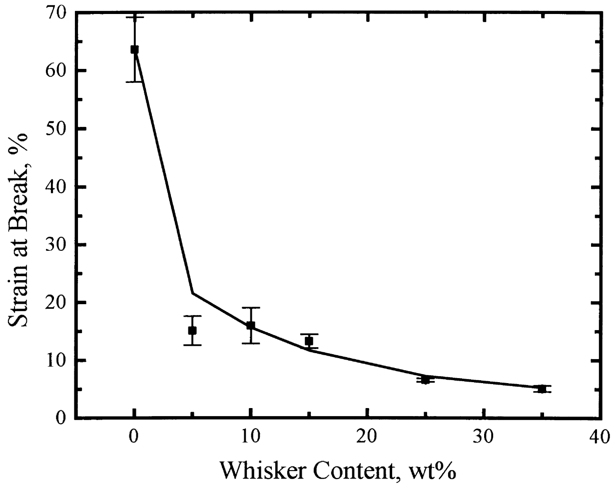

Fig. 6. Strain-at-break versus whisker content for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

Meanwhile, $K_2Ti_6O_{13}$ whiskers are oriented along the flow direction as reported in previous work [11]. The properties of used whiskers are listed in Table 1, and the average values of L and D are used for the calculation of ξ by Eq. (2). It can be seen from Fig. 2 that the experimental data of PA6/$K_2Ti_6O_{13}$ composites are much lower than those predicted from the Eq. (1). This is because the length and aspect ratio of the whiskers are shorter than the critical fibre length which is needed for effective load carrying capacity. Furthermore, the stiffness of hybrid PA6/$K_2Ti_6O_{13}$/LCP composites is slightly higher than that of the PA6/$K_2Ti_6O_{13}$ composite owing to the rigidity of the LCP phase. Hashemi et al. have investigated the fracture and mechanical properties of polyoxymethylene (POM) hybrid composites reinforced with short glass fibres (GF) and spherical glass beads (GB) [28]. They reported that mechanical properties of POM/GB/GF hybrid composites can be predicted from the following rule of hybrid mixtures

$$P_H = P_{POM/GF}\chi_{POM/GF} + P_{POM/GB}\chi_{POM/GB} \qquad (4)$$

where $P_{POM/GB}$ and $P_{POM/GF}$ are the measured properties of the POM/GB and POM/GF composites, and $\chi_{POM/GB}$ and $\chi_{POM/GF}$ are the hybrid volume ratios of the glass bead and that of glass fibre, respectively. Yilmazar [29] has used the rule of hybrid mixtures successfully to predict the ultimate tensile strength of acylonitrile–butadiene–styrene (ABS)/GB/GF hybrid composites [29]. Eq. (4) can also be applied for the hybridization with more than one type of filler or fibre in the same matrix [30,31]. As for the hybrid PA6/$K_2Ti_6O_{13}$/LCP composites, the mechanical properties can be estimated from Eq. (4) since these hybrids contain two different fibres, i.e., $K_2Ti_6O_{13}$ whiskers and short LCP fibrils. From Fig. 4, it can be seen that the tensile strengths of PA6/$K_2Ti_6O_{13}$/LCP hybrid composites are slightly lower than those predicted from the rule of hybrid mixtures. However, the experimental Young's modulus values of these hybrid composites are considerably higher than those predicted from the rule of hybrid mixtures (Fig. 5). This demonstrates that the hybrid reinforcing effect for Young's modulus is larger than that for tensile strength.

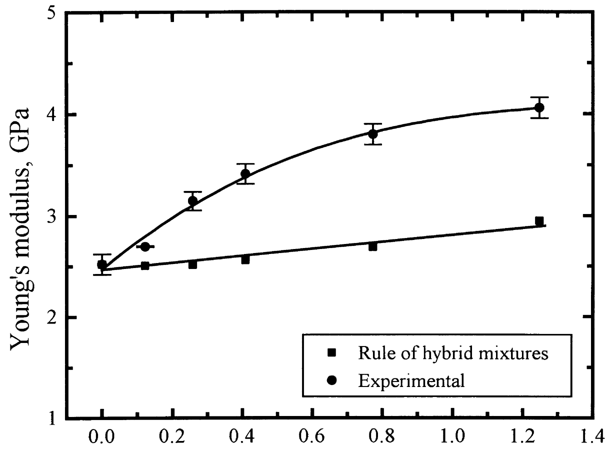

Fig. 5. Experimental Young's modulus versus $K_2Ti_6O_{13}$/LCP volume fraction ratio for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. Theoretical values predicted from the rule of hybrid mixtures are also shown.

The variation of strain-at-break of hybrid composites with whisker content is shown in Fig. 6. 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 the short fibre and filler-reinforced polymer composites.

We now consider the reinforcing effects of inorganic and polymer whiskers in thermoplastics. Taesler et al. [8] reported that the incorporation of PHB whiskers in PA6.6 leads to an increase in elastic modulus but a sharp decrease in tensile strength. They pointed out that the reduction in tensile strength of the composites was resulted from the agglomeration of whiskers. More recently, Avella et al.

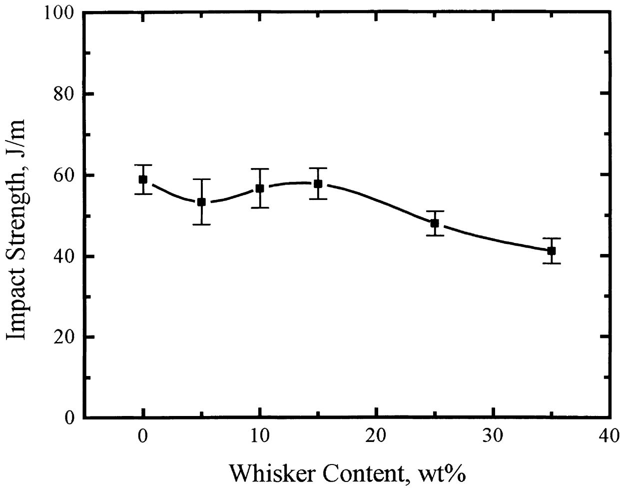

Fig. 7. Impact strengths versus whisker content for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

[10]. 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 tensile strength. In previous work [11], we have reported that the reinforcing effect of potassium titanate whiskers in PA6 is somewhat smaller than that in polyamide 6.6 [7]. On the other hand, the reinforcing effect of potassium titanate whiskers in PA6 is higher than that of poly(4-hydroxybenzoate) (PHB) whiskers [8] and silicon carbide whisker [10]. The reinforcing effect of potassium titanate whiskers in PA6 arises from their specific crystalline, surface structure, and proper surface treatment for whiskers [11]. Similarly, potassium titanate whiskers reinforce the hybrid PA6/$K_2Ti_6O_{13}$/LCP composites effectively despite the fact that the reinforcing efficiency for tensile strength is lower than that for Young's modulus.

3.2. Impact properties

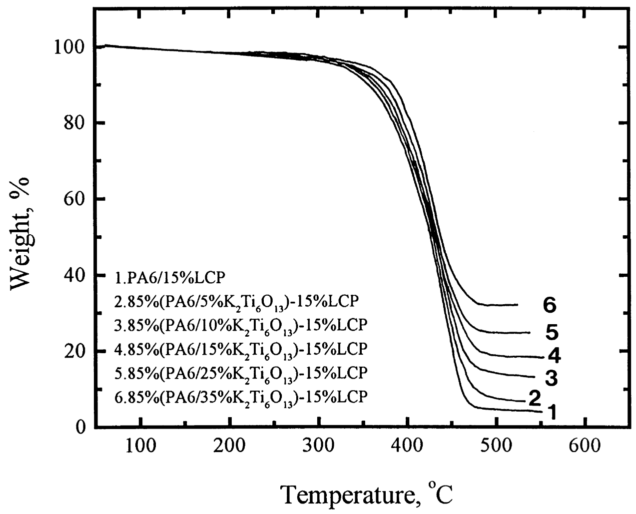

Fig. 8. Weight loss versus temperature for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

Fig. 7 shows the Izod impact strength versus whisker content for the PA6/$K_2Ti_6O_{13}$/LCP hybrid composite specimens. It can be seen that the hybrid composites show little variations in the impact strength with the addition of whisker content up to 15 wt%, thereafter it shows an obvious decrease with increasing whisker content. Compared with previous work [11], there exists no ductile to brittle transition in the impact strength versus whisker content for hybrid composites. On the other hand, a ductile to brittle transition tends to occur in the PA6/$K_2Ti_6O_{13}$ system when the fibre-end spacing is less than about six times the fibre diameter [11,32]. It is considered that the absence of such transition in this work is resulted from a decrease in the whisker content of hybrid composites due to the incorporation of LCP.

3.3. Thermal properties

Fig. 8 shows the weight loss curves versus temperature for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites. The 5% loss temperatures ($T - 5\%$) for these specimens are tabulated in Table 2. Meanwhile, the maximum weight loss temperatures (T_{max}) determined from DTG curves are also listed in Table 2. This table indicates that the addition of whiskers to the PA6/$K_2Ti_6O_{13}$/LCP hybrid composites results in a considerable increase in the $T_{-5\%}$ value. Thus the incorporation

Table 2
Thermal properties of PA6/$K_2Ti_6O_{13}$/LCP hybrid composites

Hybrid composite	T_g^1, °C	T_g^2, °C	T_g^3, °C	T_{max}, °C	$T_{-5\%}$, °C
PA6/15% LCP	39.25	—	94.49	451.4	322.3
85% (PA6/5% $K_2Ti_6O_{13}$)–15% LCP	36.42	—	105.0	439.6	337.4
85% (PA6/10% $K_2Ti_6O_{13}$)–15% LCP	37.55	60.93	104.9	435.8	341.4
85% (PA6/15% $K_2Ti_6O_{13}$)–15% LCP	38.35	59.09	105.2	433.1	346.3
85% (PA6/25% $K_2Ti_6O_{13}$)–15% LCP	33.55	60.95	105.3	430.7	346.5
85% (PA6/35% $K_2Ti_6O_{13}$)–15% LCP	33.52	57.81	104.8	419.1	350.2

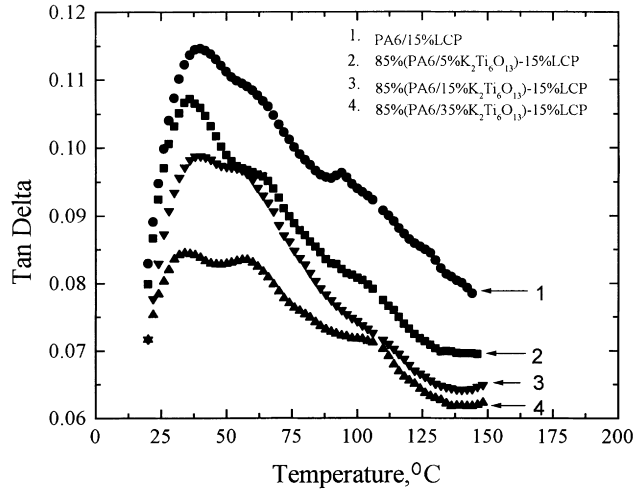

Fig. 9. Tan delta versus temperature for PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

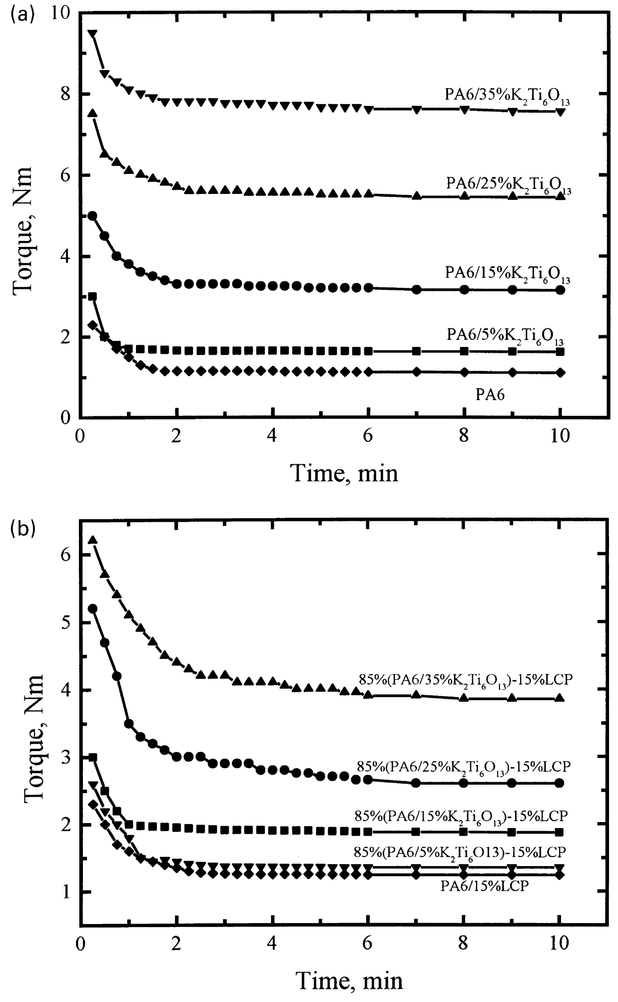

Fig. 10. Torque value versus mixing time for (a) PA6/$K_2Ti_6O_{13}$ composites and (b) PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

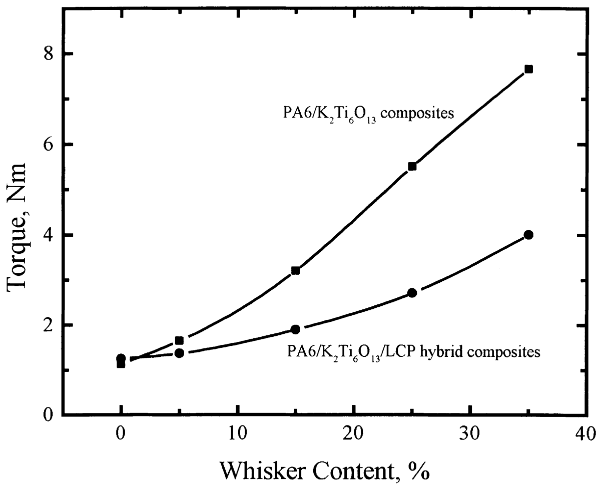

Fig. 11. Torque value at 5 min versus whisker content for PA6/$K_2Ti_6O_{13}$ composites and PA6/$K_2Ti_6O_{13}$/LCP hybrid composites.

of potassium titanate whiskers into PA6 is beneficial in improving the thermoxidative stability of PA6.

The glass transition temperatures (T_g) of hybrid composites determined from DMA measurements are also listed in

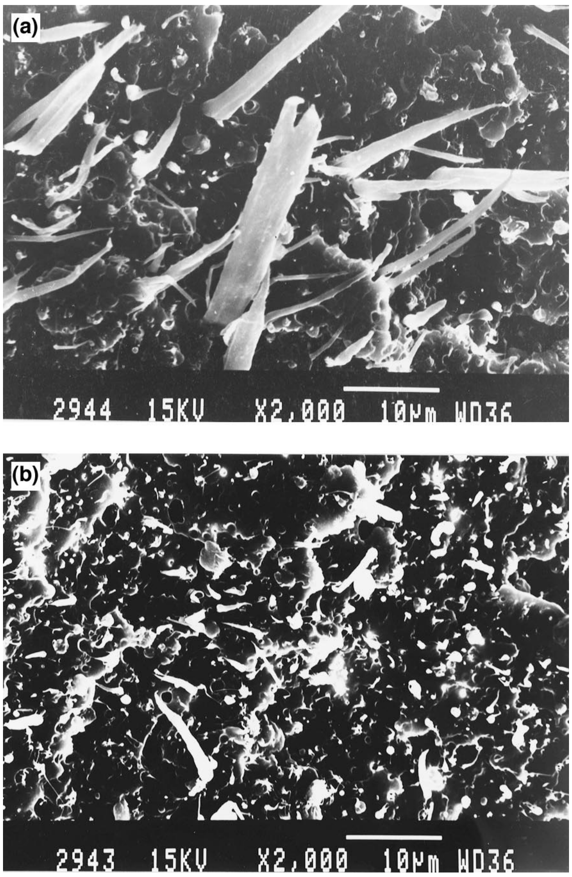

Fig. 12. SEM micrographs of PA6/LCP (85/15) composite showing formation of (a) elongated LCP fibrils in the skin layer and (b) short fibrils in the core section.

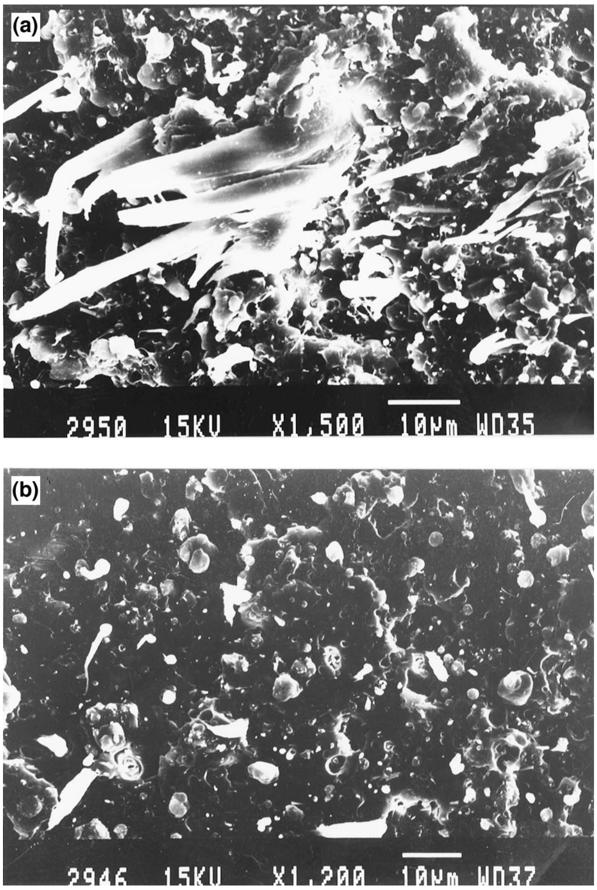

Fig. 13. SEM micrographs of 85% (PA6/5% $K_2Ti_6O_{13}$)–15% LCP hybrid composite showing formation of (a) elongated LCP fibrils in the skin layer and (b) short fibrils and ellipsoid domains in the core section.

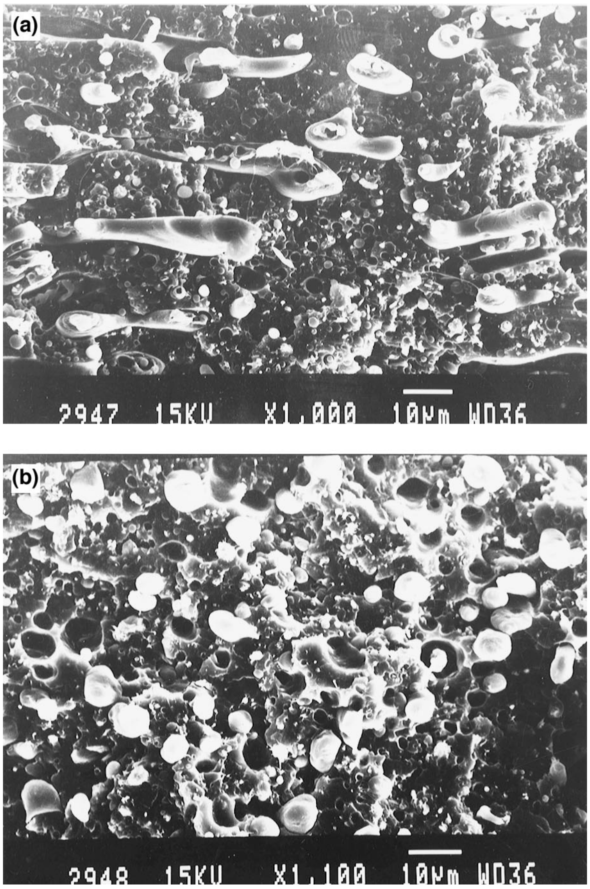

Fig. 14. SEM micrographs of 85% (PA6/10% $K_2Ti_6O_{13}$)–15% LCP hybrid composite showing formation of (a) elongated LCP ellipsoids in the skin layer and (b) spherical domains in the core section.

Table 2. The T_g^1 and T_g^3 represent the T_g of the PA6 and LCP phase within hybrid composites, respectively. The T_g values of pure PA6 and LCP are about 40 and 125°C, respectively [24]. It is interesting to see that the difference in T_g between the PA6 and LCP phases within hybrid composites tends to increase with the addition of whiskers (Table 2). A new T_g peak appears in the vicinity of 57–61°C with the introduction of whiskers (Fig. 9). This additional peak is considered to be associated with the T_g of a species formed at the PA6 and LCP interface owing to the tetrabutyl orthotitanate treatment.

3.4. Torque measurements

The relationships between the torque value and mixing time for PA6/$K_2Ti_6O_{13}$ and PA6/$K_2Ti_6O_{13}$/LCP hybrid composites are depicted in Fig. 10(a) and (b), respectively. For PA6/$K_2Ti_6O_{13}$ composites, the torque values tend to increase with increasing whisker content. The increase in torque value is resulted from the incorporation of inorganic whiskers into PA6 (Fig. 10(a)). Compared with PA6/$K_2Ti_6O_{13}$ composites, however, the torque values of the PA6/$K_2Ti_6O_{13}$/LCP hybrid composites are much lower than those of PA6/$K_2Ti_6O_{13}$ composites (Fig. 10(b)). This demonstrates that the introduction of LCP is very effective in reducing the viscosity of PA6/$K_2Ti_6O_{13}$ composites owing to the lower melt viscosity of LCP during shear processing. Fig. 11 shows the torque values at 5 min versus whisker content for PA6/$K_2Ti_6O_{13}$ and PA6/$K_2Ti_6O_{13}$/LCP systems. It is apparent that the difference in torque values between binary PA6/$K_2Ti_6O_{13}$ and hybrid PA6/$K_2Ti_6O_{13}$/LCP composites becomes larger as the whisker content increases. This implies that LCP exhibits higher efficiency for improving the processability of hybrid composites with higher whisker content.

3.5. Morphology

As stated previously, all the hybrid PA6/$K_2Ti_6O_{13}$/LCP composites are very brittle and exhibit low impact strength. In this case, the specimens after impact tests can be used for SEM observation since the fracturing process has no influence on the morphology of the dispersed LCP phase within the PA6 matrix. It is known that the injection moulded in situ composites exhibit typical skin-core morphology [33–35]. Fig. 12(a) and (b) show the typical SEM micrographs of the skin and core sections of PA6/LCP (85/15) composite. From Fig. 12(a), the LCP phase of the skin layer is oriented and

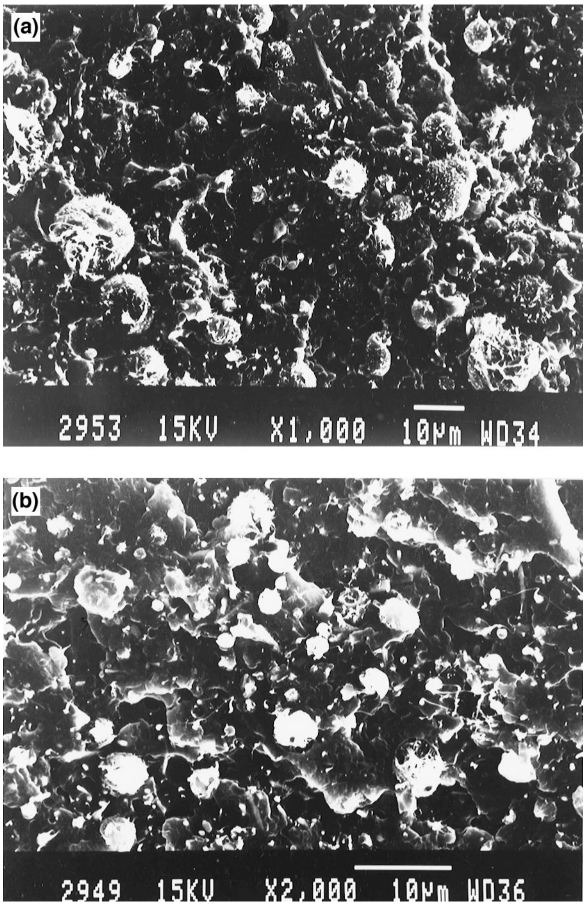

Fig. 15. SEM micrographs of (a) 85% (PA6/15% $K_2Ti_6O_{13}$)–15% LCP and (b) 85% (PA6/35% $K_2Ti_6O_{13}$)–15% LCP hybrid composites showing formation of LCP spherical domains in the skin section.

elongated into fibrils. Furthermore, short fibrils are formed within the core section of this composite (Fig. 12(b)). For 85% (PA6/5% $K_2Ti_6O_{13}$)–15% LCP hybrid composite, the SEM micrographs of the skin and core sections are similar to those of the PA6/LCP (85/15) composite (Fig. 13(a) and (b)). Thus the addition of a small amount of whiskers to the PA6/LCP composite produces no microstructural changes. As the whisker content of hybrid composites is increased to 10%, the LCP phase is deformed into an elongated ellipsoid in the skin section of 85% (PA6/10% $K_2Ti_6O_{13}$)–15% LCP hybrid composite (Fig. 14(a)) whilst the LCP domain retains a spherical morphology in the core section (Fig. 14(b)). With further increasing the whisker content of the hybrid composites to 15 wt%, there exists no skin-core or laminated morphology in the injection moulded PA6/$K_2Ti_6O_{13}$/LCP hybrid composites (Fig. 15(a) and (b)). In this case, only spherical droplets are observed. As stated above, the LCP phase becomes less likely to deform into oriented fibrils with increasing whisker content. It is believed that the spherical droplets result from a lower shear rate condition which prevails in the skin of hybrids containing higher whisker content during injection moulding.

4. Conclusions

Potassium titanate whisker and LCP-reinforced PA6 hybrid composites were prepared in a twin-screw extruder followed by injection moulding. Static tensile measurements showed that the tensile strength and modulus of the hybrid composites tend to increase with increasing whisker content. The tensile strengths of hybrid composites were slightly lower than those predicted from the rule of hybrid mixtures. However, the Young's moduli of these hybrid composites were considerably higher than those predicted from the rule of hybrid mixtures. Moreover, Izod impact tests indicated that the hybrid composites show a slight decrease in the impact strength initially with whisker content up to 15 wt%, thereafter it shows an obvious decrease when the whisker content reaches 25 wt%. Scanning electron microscopic observations revealed that the oriented LCP fibres are formed within the skin section of hybrid composites containing whisker content ≤ 10 wt%, whilst spherical droplets are dispersed within the hybrid composites containing whisker content >15 wt%. Torque measurements showed that the introduction of LCP leads to a small decrease in the melt viscosities of PA6/$K_2Ti_6O_{13}$ composites. Therefore, the processability of the hybrid composites can be improved by the incorporation of LCP.

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