

# Microstructural and mechanical characteristics of compatibilized polypropylene hybrid composites containing potassium titanate whisker and liquid crystalline copolyester

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## Abstract

Maleic anhydride (MA) compatibilized polypropylene (MPP) 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 molding. The surface of whiskers were treated with tetrabutyl orthotitanate before blending. Scanning electron microscopic (SEM) examination showed that elongated LCP fibrils are formed in the skin section of hybrids reinforced with whiskers of various concentrations. Consequently, the hybrids reinforced with both LCP fibrils and whiskers exhibited anisotropic mechanical properties. Tensile test showed that longitudinal Young's modulus and tensile strength of hybrids tend to increase with increasing whisker content. Moreover, the stiffness and tensile strength of hybrids were higher than those of MPP/ $K_2Ti_6O_{13}$  composites. Such enhancement in mechanical properties resulted from the compatibilizing effect of MA-grafted-PP, and from the hybrid reinforcing effect of LCP fibrils and  $K_2Ti_6O_{13}$  whiskers. Torque measurements revealed that LCP addition is beneficial in reducing the melt viscosity of MPP/ $K_2Ti_6O_{13}$ /LCP hybrids. The results of SEM observations generally correlate well with the mechanical measurements. The effects of MA compatibilization on the microstructure and mechanical properties of hybrids are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polypropylene; Hybrid composite; Compatibilization

## 1. Introduction

Isotactic polypropylene (PP) is widely used in different industrial sectors because of its attractive properties such as low price, low weight, shape and dimensions versatility. PP finds applications in the form of films, fibers and matrix of the polymer composites. In the latter case, various fiber reinforcements, whiskers and inorganic fillers are commonly incorporated into PP matrix [1–7]. Consequently, these composites generally exhibit superior stiffness, strength and thermo-oxidative stability than PP homopolymer. Recently, whiskers reinforced polymer composites have attracted considerable attention of many investigators [5,8–12]. This is because whiskers exhibit high stiffness and strength, and they are nearly free from internal flaws. In this respect, the strength of whiskers are close to the maximum theoretical value expected from the theory of elasticity [12]. Silicon carbide (SiC) whiskers have been used extensively as reinforcement materials in

the ceramic matrix composites and metal matrix composites [13–16]. More recently, Avella et al. have attempted to reinforce PP with SiC whiskers. They reported that the surface treated whiskers tend to disperse uniformly in PP matrix whilst uncoated whiskers show little tendency to be dispersed within PP matrix. As a result, the stiffness and impact fracture toughness ( $G_c$ ) of PP are improved considerably by the incorporation of surface treated SiC whiskers [5]. SiC whiskers are considered as expensive materials though their price has dropped dramatically in recent years. It is therefore of interest to find alternatives for SiC whiskers. Potassium titanate whiskers ( $K_2Ti_6O_{13}$ ) show promise as reinforcement materials owing to their price ranges from one-tenth to one-twentieth of the cost of SiC whiskers [17]. It is more cost effective to use potassium titanate whiskers to reinforce the metallic alloys [18] and polymers [9–11]. Tjong and Meng reported that the static tensile properties of polyamide 6 (PA6) improve with increasing potassium titanate whiskers content. Moreover, the heat resistance and thermo-oxidative stability of PA6 were enhanced greatly by the incorporation of potassium titanate whiskers [10].

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Table 1  
Properties of potassium titanate whiskers

Specific density (g cm <sup>-3</sup> )	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

It is generally known that the addition of short fibers or whiskers into thermoplastics can result in an increase in the viscosity of the materials. This leads to difficulties during processing of the composites. The melt viscosity of the fiber reinforced composites can be reduced dramatically by the incorporation of liquid crystalline polymers (LCPs) [19,20]. LCPs consist of long chain rod-like molecules that exhibit an ordered structure in the melt. The molecules within the nematic domains tend to align along the flow direction and such orientation can be preserved upon solidification from the melt. Kulichikhin et al. have investigated the effect of additions of liquid crystal copolyester (poly(ethylene terephthalate) and *p*-hydroxybenzoic acid) of various concentrations to glass fiber reinforced PP composites. They reported that the addition of LCP concentrations >20 w/w% leads to a decrease of blend viscosity [19]. He and coworkers observed a similar beneficial effect of LCP addition in reducing the melt viscosity of carbon fiber reinforced polyethersulfone (PES) composites [20]. These composites can be termed as in-situ hybrid composites. Conventional hybrid composites generally consists of different types of fibers and/or fillers in thermoplastic matrix. The broad variety of different fiber and matrix materials allows one to design hybrid composites with unique properties for specific applications [21,22]. The mechanical properties of conventional hybrid composites have been studied extensively [21–24]. However, less information is available on the mechanical performance and rheology of in-situ LCP hybrid composites [19,20]. More recently, Tjong and Meng [11] have studied the morphology, rheology and mechanical properties of in-situ hybrid PA6 composites containing K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> whisker and LCP. They reported that the tensile strength and modulus of the hybrid composites tend to increase with increasing whisker content. However, the tensile strengths of PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites were lower than the PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. This implies that the incorporation of LCP to PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites leads to a decrease in mechanical strength. This could be due to poor interfacial bonding between LCP phase and PA6 matrix.

Most LCP/thermoplastic blends are incompatible. These blends often have poor mechanical properties because of high interfacial tension, leading to poor adhesion between the components. It is well established that the interfacial adhesion between blend components can be enhanced through the addition of suitable compatibilizers [25]. The compatibilizers are block or graft copolymers which consist of segments capable of interactions with the blend components. The morphology and mechanical properties

of PP/LCP blends are well documented [26–28]. Generally, the PP/LCP blends exhibit improvement in the tensile modulus. However, they show little or no improvement in tensile strength when compared with PP homopolymer owing to the incompatibility between components [26,28]. As a result of the non-polar nature of PP in contrast to the more polar LCP, it is more appropriate to use functionalized PP as a compatibilizer. Maleic anhydride grafted polypropylene (MAP) has been used by some workers as a compatibilizer to improve the adhesion between the LCP and PP [29–32]. Their results indicated that fine and elongated LCP fibrils are formed in MAP compatibilized PP/LCP blends. In this regard, the tensile strength of compatibilized blends is improved dramatically [30,32]. The present article aims to investigate the effect of MAP compatibilization on the morphology, rheology and mechanical properties of in-situ PP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites.

## 2. Experimental

### 2.1. Materials

The whiskers used in this work were potassium titanate (K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>) supplied by Shenyang Jin-Jian Composite Co., China. Their physical and mechanical properties are tabulated in Table 1. The PP polymer (Profax 6331) with a melt flow index of 12 g per 10 min was purchased from Himont Company. The maleic anhydride (MA) supplied by Fluka Chemie and dicumyl peroxide (DCP) produced by Aldrich chemical company were used for the maleation of PP. The LCP used was Vectra A950, a copolymer composition based on 27 mol% of 2,6-hydroxynaphthoic acid (HNA) and 73 mol% of *p*-hydroxybenzoic acid (HBA). Reagent grade tetrabutyl orthotitanate was used as the coupling agent for whiskers.

### 2.2. Sample preparation

Tetrabutyl orthotitanate solution (5 w/w%) was prepared by dissolving it in acetone. The whiskers were treated with tetrabutyl orthotitanate solution, and the weight ratio of whisker to tetrabutyl orthotitanate was fixed at 98.5:1.5. Such a solution was poured into a plastic box filled with the whiskers. They were mixed thoroughly by hand, and subsequently dried in an oven at 80°C for 48 h.

Maleic anhydride-grafted PP (MAP) was prepared in a twin-screw Brabender Plasticorder at 220°C and 15 rpm by a one-step reaction of PP with MA in the presence of DCP. The weight ratio of PP, MA and DCP was fixed at 94:6:0.3.

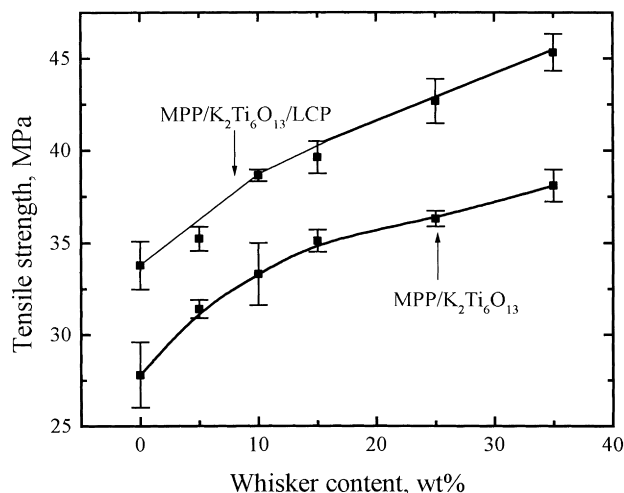


Fig. 1. Longitudinal tensile strength versus whisker content for MPP/ $K_2Ti_6O_{13}$  composites and MPP/ $K_2Ti_6O_{13}$ /LCP hybrids.

The extrudates were then pelletized. The blend containing 90 w/w% PP and 10 w/w% MAP was also extruded in Brabender at 220°C, and the extrudates were also pelletized. This binary blend is designated as MPP throughout this article.

The MPP blends containing 5, 10, 15, 25 and 35 w/w%  $K_2Ti_6O_{13}$  whiskers were prepared in Brabender extruder at 220–235°C. They were then pelletized upon exiting from the extruder. The LCP and MPP/ $K_2Ti_6O_{13}$  composite pellets were tumbled together in a container prior to injection molding. Subsequently, the MPP hybrid composites were injection molded directly from tumbled LCP and MPP/ $K_2Ti_6O_{13}$  composite pellets without any precompounding. The weight ratio of MPP/ $K_2Ti_6O_{13}$  to LCP is fixed at 85:15. Plaques with dimensions of 80 × 195 × 3 mm were also injection molded as pellets. The mold temperature was maintained at 40°C whilst the barrel zone temperatures were set at 285, 285 and 290°C. Longitudinal and transverse specimens with their axial axes parallel and perpendicular to the flow direction respectively were cut from these plaques.

### 2.3. Mechanical measurements

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

Longitudinal and transverse notched Izod impact specimens with dimensions of 65 × 12.7 × 3.2 mm were prepared from the injection molded plaques. Seven specimens were tested and the average values reported.

Dynamic mechanical analysis (DMA) of the injection molded composites was conducted with a Du Pont dynamic mechanical analyzer (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The

temperature studied ranged from -30 to 180°C with a heating rate of 2°C min<sup>-1</sup>.

### 2.4. Morphological observations

The longitudinal specimens after impact test were fractured in liquid nitrogen, and subsequently examined in a scanning electron microscope (SEM; JEOL JSM model 820). The fractured surfaces were coated with a thin layer of gold prior to SEM examination.

### 2.5. Torque measurements

Torque values for the MPP/ $K_2Ti_6O_{13}$  composites, MPP/ $K_2Ti_6O_{13}$ /LCP hybrids as well as MAP copolymer were determined using a Brabender Plasticorder batch mixer at 280°C and 30 rpm for 10 min. The chamber volume was 50 cm<sup>3</sup>. 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 analyzer (TGA; model SSC-5200) under a protective helium atmosphere (200 ml min<sup>-1</sup>). The heating rate employed was 10°C min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Mechanical properties

Fig. 1 shows the longitudinal tensile yield strength versus whisker content for both MPP/ $K_2Ti_6O_{13}$  composites and MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites. It can be seen that the tensile strengths of both composites tend to increase with increasing whisker content. Further, the tensile strengths of MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites are higher than those of MPP/ $K_2Ti_6O_{13}$  composites. This indicates that the LCP addition leads to an increase in the mechanical strength of MPP/ $K_2Ti_6O_{13}$  composites. This beneficial effect is believed to arise from the improvement of compatibility between the LCP phase and PP matrix because of MAP addition. Baird and coworkers reported that the functional groups of MAP react with the amide-end groups of the LCP. In this case, hydrogen bonding is responsible for the compatibilizing effect of MAP on PP/LCP blends [29,30]. Consequently, long and elongated LCP fibrils are formed in MAP compatibilized PP/LCP blends [30,32]. Indeed, long LCP fibrils are formed in the MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites as will be discussed in the morphology section. Therefore, hybridization of LCP fibrils and  $K_2Ti_6O_{13}$  whiskers in MPP/ $K_2Ti_6O_{13}$ /LCP composites have some advantages over using  $K_2Ti_6O_{13}$  whiskers alone in MPP matrix. It is noted that the tensile strength of hybrid composites depends significantly on the formation of elongated LCP fibrils. In the case where LCP does not deform

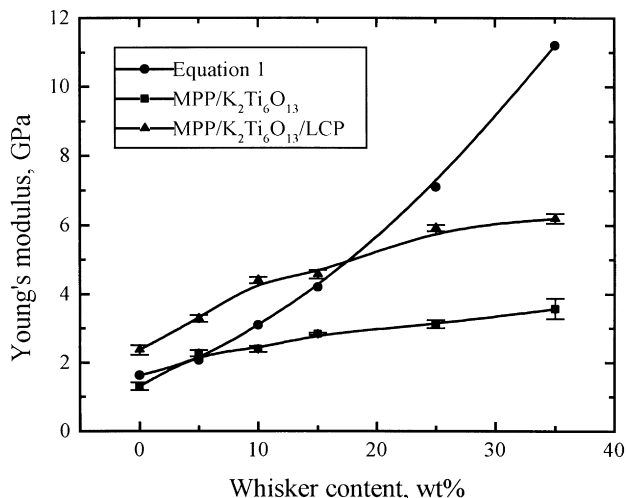


Fig. 2. Longitudinal Young's modulus versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids. The modulus of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites predicted from Tsai–Halpin equation is also shown for comparison purpose.

into fine and elongated fibrils, the hybrid reinforcing efficiency is relative low. He et al. reported the LCP fibrils formed in the carbon fiber/LCP/PES hybrid composites have low aspect ratios, which decreases the reinforcing effect of the fibrils. In this case, the major reinforcing effect comes from the carbon fibers [20]. In addition to the development of elongated LCP fibrils in hybrids, the adhesion between the LCP fibrils and polymer matrix also has a marked influence on the mechanical strength of the hybrids. Previous work has shown that the LCP phase and PA6 matrix polymer of hybrids have poor interfacial bonding, thereby the resulting tensile strengths of PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites are lower than those of PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. In that case, LCP fibrils are formed within the skin section of hybrid PA6/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP

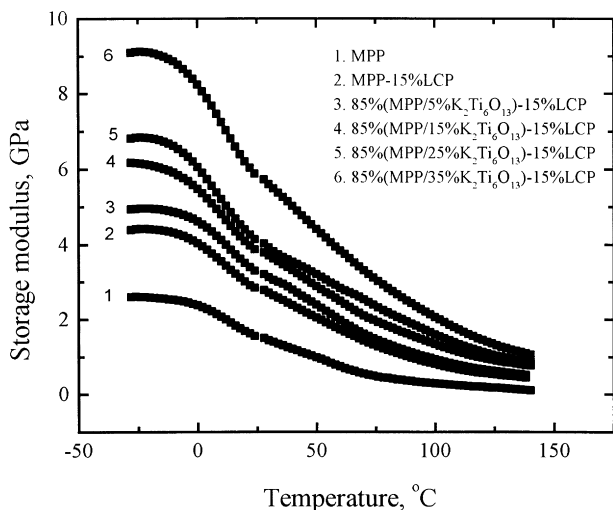


Fig. 3. Storage modulus versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

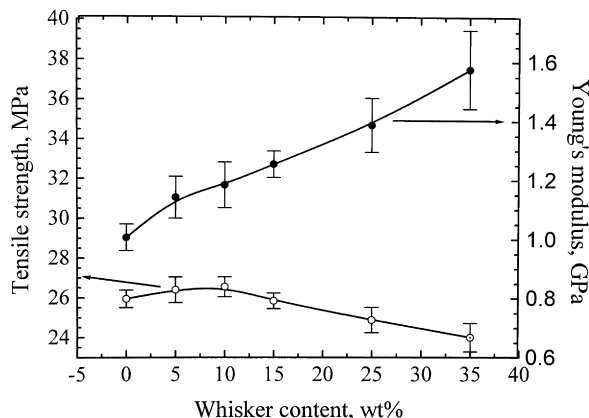


Fig. 4. Experimental transverse Young's modulus and tensile strength versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

composites containing whisker content  $\leq 10$  w/w%, whilst spherical LCP droplets are dispersed within the matrix of hybrid composites containing whisker content  $> 15$  w/w% [11].

Fig. 2 shows the variations of longitudinal Young's modulus with whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites. It is apparent from this figure that the longitudinal Young's modulus of both composites tends to increase with increasing whisker content. Further, the Young's moduli of hybrids are higher than those of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. The variation of storage modulus of hybrids with whisker content is shown in Fig. 3. Apparently, the storage modulus of hybrids also appears to increase with increasing whisker content. It is well known that the polymer composites reinforced with discontinuous short fiber exhibit anisotropic mechanical properties. This means that the values of longitudinal tensile modulus, tensile strength and impact energy are different from their transverse counterparts. Fig. 4 shows the variations of transverse Young's modulus and transverse tensile strength with whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites. It is evident that both the transverse stiffness and tensile strength of hybrids are considerably smaller than their longitudinal counterparts.

From Fig. 2, theoretical Young's modulus of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites determined from Tsai–Halpin equation is also shown for comparison purpose. Tsai–Halpin equation is frequently used to predict the elastic modulus of discontinuous short fiber reinforced composite from the moduli of the individual components. The equation assumes that the circular fibers are uniformly distributed throughout the matrix, and the continuity of stress and strain along the fiber/matrix interface [33]. Tsai–Halpin equation is given as follows:

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

where  $E_c$  and  $E_m$  are the elastic modulus of composite and matrix, respectively;  $\phi_f$  is the volume fraction of short

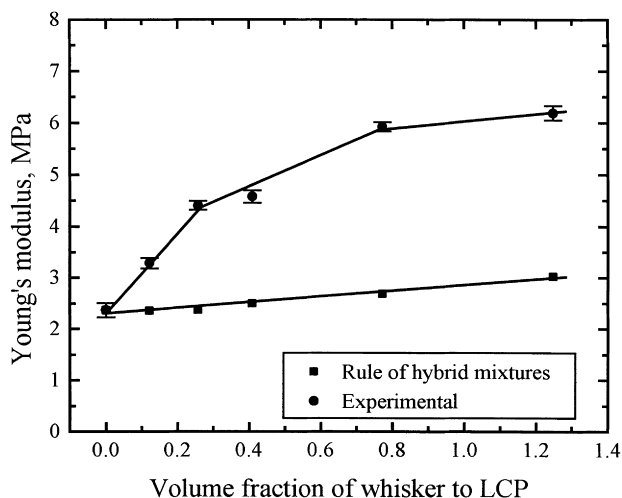


Fig. 5. Experimental longitudinal Young's modulus versus  $K_2Ti_6O_{13}$ /LCP volume fraction ratio for MPP/ $K_2Ti_6O_{13}$ /LCP hybrids. Theoretical values predicted from the rule of hybrid mixtures are also shown.

fibers. The constants  $\xi$  and  $\eta$  are defined as:

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

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

where  $L/D$  is the aspect ratio (length/diameter) of the reinforcing fibers, and  $E_f$  is the modulus of the fibers. It is noted that the average values of  $L$  and  $D$  (Table 1) are used for the calculation of  $\xi$  in Eq. (2). It can be seen from Fig. 2 that the experimental data of MPP/ $K_2Ti_6O_{13}$  composites with whisker content  $\geq 10$  w/w% deviate negatively from the theoretical values. However, experimental longitudinal Young's modulus of hybrids containing whisker content up to 15 w/w% deviate positively from the Tsai–Halpin equation. Thereafter, the experimental values are lower than those

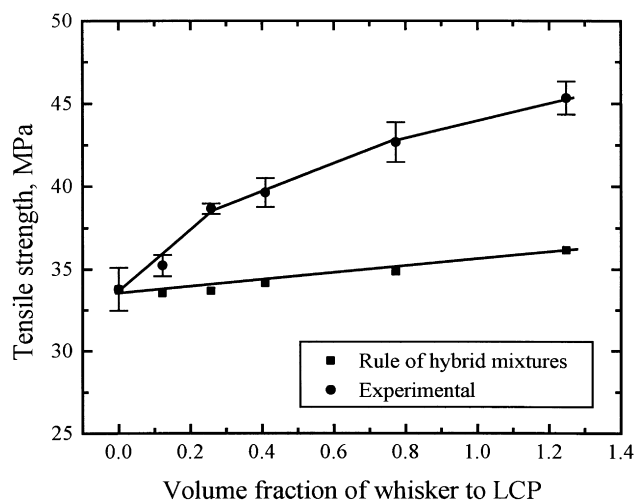


Fig. 6. Experimental longitudinal tensile strength versus  $K_2Ti_6O_{13}$ /LCP volume fraction ratio for MPP/ $K_2Ti_6O_{13}$ /LCP hybrids. Theoretical values predicted from the rule of hybrid mixtures are also shown.

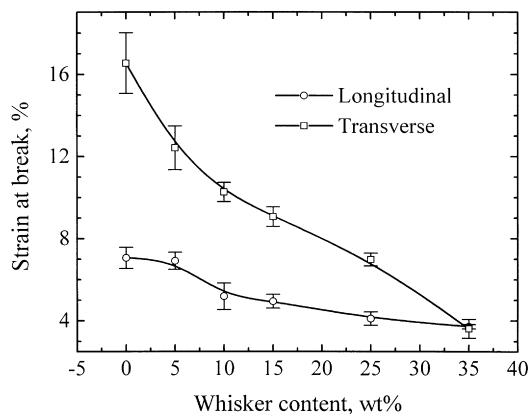


Fig. 7. Longitudinal and transverse strain-at-break versus whisker content for MPP/ $K_2Ti_6O_{13}$ /LCP hybrids.

predicted from Eq. (1). It should be noted that Tsai–Halpin equation is generally used to estimate the stiffness of composites containing only a single reinforcing component. As the MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites contain two kinds of reinforcements, it is more appropriate to express the variation of stiffness of the composites with volume fraction ratio of whisker to LCP, i.e. the rule of hybrid mixtures (Fig. 5). Hashemi et al. [22] have used the rule of hybrid mixtures to predict the mechanical properties of polyoxymethylene (POM) hybrid composites reinforced with short glass fiber (GF) and spherical glass beads (GB). They indicated that the flexural modulus, tensile strength and fracture toughness of POM/GB/GF hybrids can be estimated from the following equation:

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

where  $P_{POM/GF}$  and  $P_{POM/GB}$  are the measured properties of POM/GB and POM/GF composites, and  $\chi_{POM/GB}$  and  $\chi_{POM/GF}$  are the hybrid volume ratio of the glass bead and that of glass fiber, respectively [22]. Eq. (4) can be used to determine the Young's modulus and tensile strength of MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites because these hybrids contain two reinforcements, i.e. LCP fibrils and  $K_2Ti_6O_{13}$  whiskers. Fig. 6 shows the longitudinal tensile strength of hybrids versus volume fraction ratio of whisker to LCP. It is noticed from Figs. 5 and 6 that the measured Young's modulus and tensile strength of hybrids show positive deviation from the rule of hybrid mixtures. Thus synergistic reinforcing effect of LCP fibrils and  $K_2Ti_6O_{13}$  whiskers are very effective to improve the mechanical properties of hybrids. Moreover, it is worth noting that the strength and stiffness of hybrid composites are strongly influenced by the aligned fiber orientation. As LCP domains of hybrids tend to align along the flow direction and deform into elongated fibrils during injection molding, thus the composites with LCP are stronger and stiffer than those without.

Fig. 7 shows the variations of strain-at-break with whisker content for MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites. As

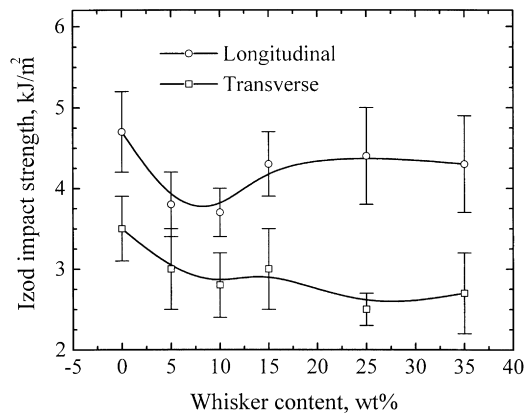
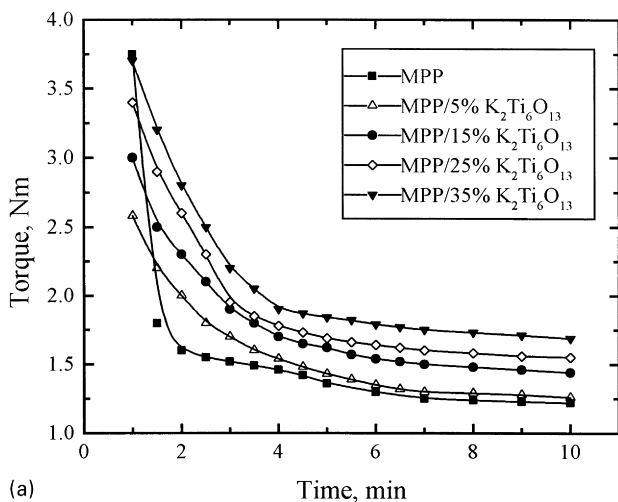
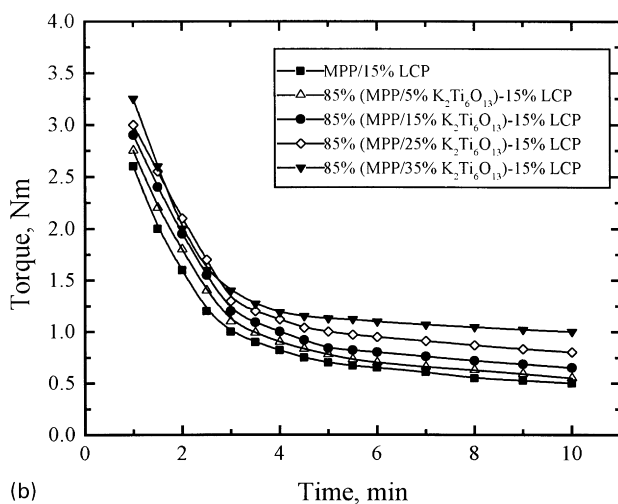


Fig. 8. Longitudinal and transverse impact strength versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

expected, the tensile ductility appears to decrease continuously with increasing whisker content. The reduction in tensile ductility with increasing whisker content in MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites are typical characteristics



(a)



(b)

Fig. 9. Torque values versus mixing time for: (a) MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and (b) MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

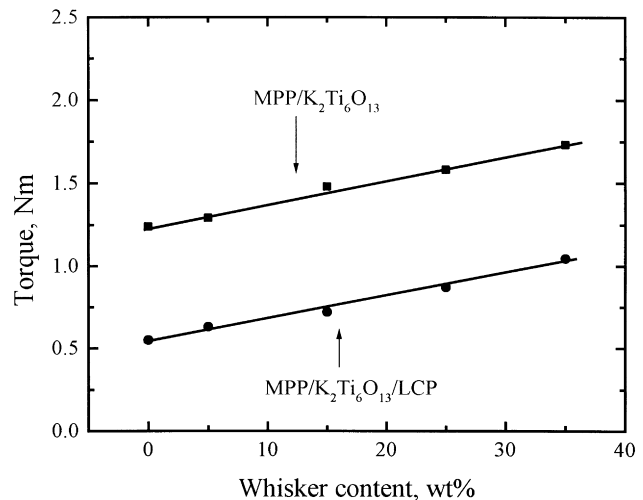


Fig. 10. Torque value at 8 min versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

of discontinuous fiber reinforced polymer composites. Fig. 8 shows the impact strength versus whisker content for longitudinal and transverse hybrid composites. It can be seen that the impact strength of longitudinal specimen initially decreases with increasing whisker content up to 10 w/w%, thereafter it increases steadily with increasing whisker content. This behavior can be attributed to the enhanced matrix plasticity at fiber ends in the crack tip region when the fibers are closely spaced [34]. However, the transverse impact strength of hybrids appears to decrease continuously with increasing whisker content (Fig. 8).

### 3.2. Torque properties

The torque during mixing is a measure of the viscosity and a good parameter for evaluating the processability of the polymer systems [35]. Fig. 9(a) and (b) shows the plots of torque value versus mixing time for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids, respectively. The torque values of both composite systems are relatively high during the initial materials loading period. They then decrease continuously with mixing time up to 4 min, followed by a steady decrease with further increase in the mixing time. Fig. 10 shows the variation of torque values at 8 min versus whisker content for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites and MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids. It can be seen that the torque values of both composites tend to increase with increasing whisker content. However, the torque values of hybrids are considerably lower than those of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. Thus the introduction of LCP into hybrids decreases the melt viscosity, thereby improving the processability of ternary blends.

### 3.3. Morphology

The injection molded in-situ composites generally exhibit a skin–core structure [36–38]. Fig. 11(a) and (b) shows typical SEM micrographs of the skin and core sections of

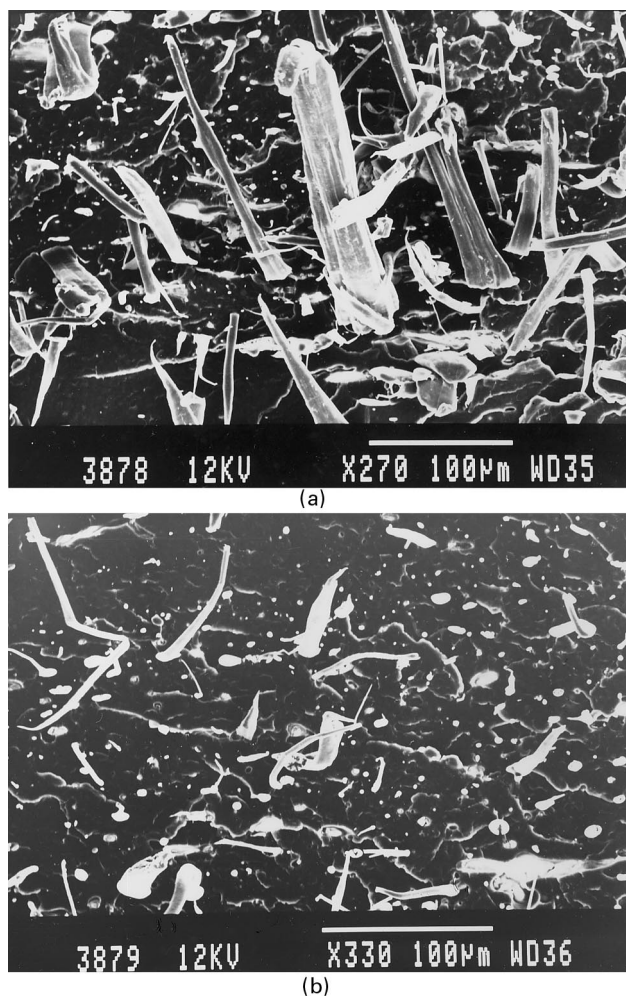


Fig. 11. SEM micrographs of MPP/LCP (85/15) composite showing formation of: (a) elongated LCP fibrils in the skin layer and (b) short fibrils in the core section.

the MPP/LCP (85/15) composite. Apparently, the LCP phase is deformed into elongated fibrils in the skin section of this composite. Moreover, short fibrils and spherical domains are observed in the core section (Fig. 11(b)). In the case of 85%(MPP/5% $K_2Ti_6O_{13}$ )-15%LCP hybrid composite, SEM micrographs show a similar fibrillar morphology in the skin and core layers (Fig. 12(a) and (b)). Further increasing the whisker content to 15% and above does not lead to microstructural changes of the fibrils (Figs. 13 and 14). As the addition of higher whisker contents to hybrids only leads to a slight increase in the torque values (Fig. 10), the LCP fibrils can still be developed in MPP/ $K_2Ti_6O_{13}$ /LCP composites with high whisker concentrations. However, the torque values of PA6/ $K_2Ti_6O_{13}$ /LCP hybrids with high whisker content are much higher than those containing low whisker content, LCP fibrils only formed in the skin layer of hybrids reinforced with low whisker content (10 w/w%). In other words, spherical droplets are observed in the skin and core sections of PA6/ $K_2Ti_6O_{13}$ /LCP hybrids containing whisker content

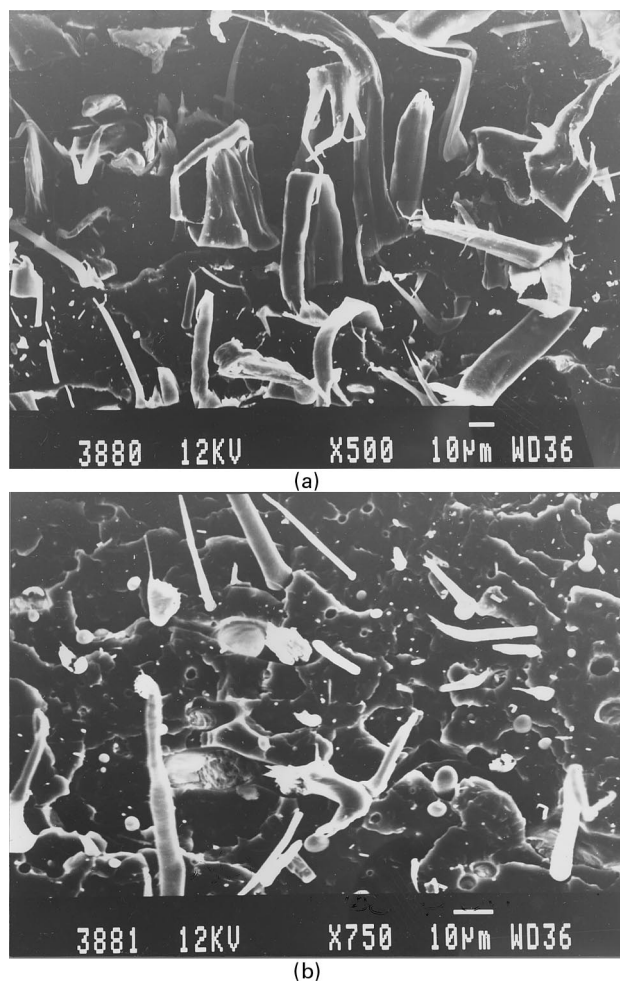
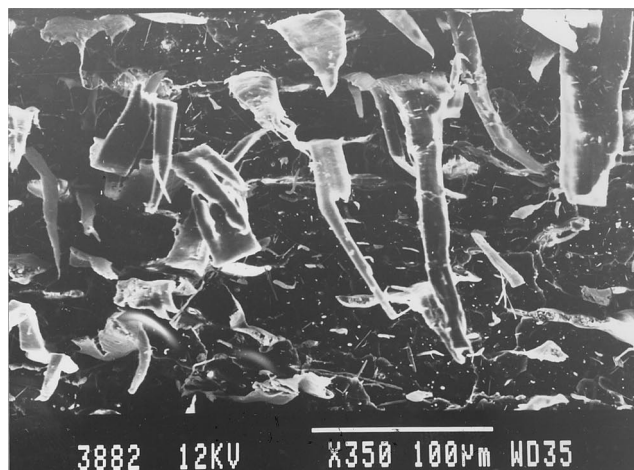


Fig. 12. SEM micrographs of 85%(MPP/5% $K_2Ti_6O_{13}$ )-15%LCP longitudinal composite specimen showing formation of: (a) elongated LCP fibrils in the skin layer and (b) short fibrils in the core section.

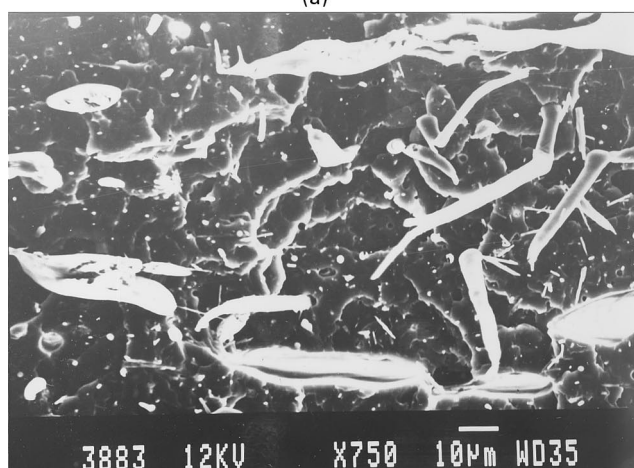
above 15 w/w% [11]. It should be noted that the MPP/ $K_2Ti_6O_{13}$ /LCP composites are compatibilized with MAP. And MAP permits the formation of elongated fibrils in MPP/ $K_2Ti_6O_{13}$ /LCP hybrids. However, the PA6/ $K_2Ti_6O_{13}$ /LCP hybrids contain no compatibilizer, hence LCP phase does not deform into fibrils for the hybrids with high whisker content [11]. The present SEM observations correlate well with the static tensile properties as shown in Figs. 1 and 2. Therefore, hybrid reinforcing effect of LCP fibrils and  $K_2Ti_6O_{13}$  whiskers are very effective to increase the tensile strength and stiffness of the hybrids.

### 3.4. Thermal properties

Fig. 15 shows the TG curves for MPP/ $K_2Ti_6O_{13}$ /LCP hybrid composites. The 5% loss temperatures ( $T_{-5\%}$ ) for the hybrids are listed in Table 2. In addition, the maximum weight loss temperatures ( $T_{max}$ ) determined from DTG curves are also given in Table 2. This table reveals that the addition of 15 w/w LCP to MPP leads to a marked increase in  $T_{-5\%}$  from 361.5 to 415.5°C. Moreover, the



(a)



(b)

Fig. 13. SEM micrographs of 85%(MPP/15%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>)-15%LCP longitudinal composite specimen showing formation of: (a) elongated LCP fibrils in the skin layer and (b) short fibrils in the core section.

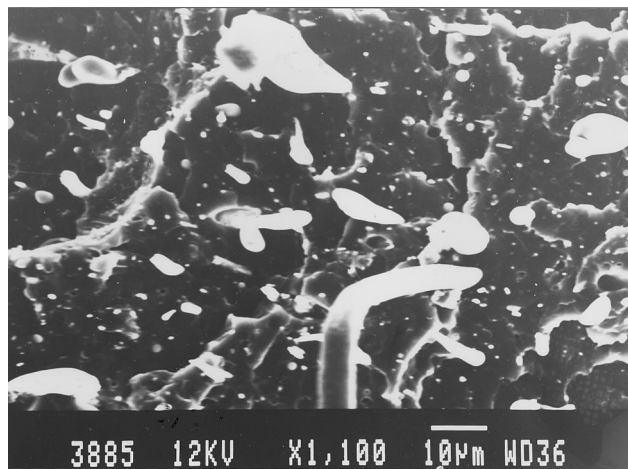


Fig. 14. SEM micrograph of 85%(MPP/25%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>)-15%LCP composite showing formation of elongated LCP fibrils in the skin layer.

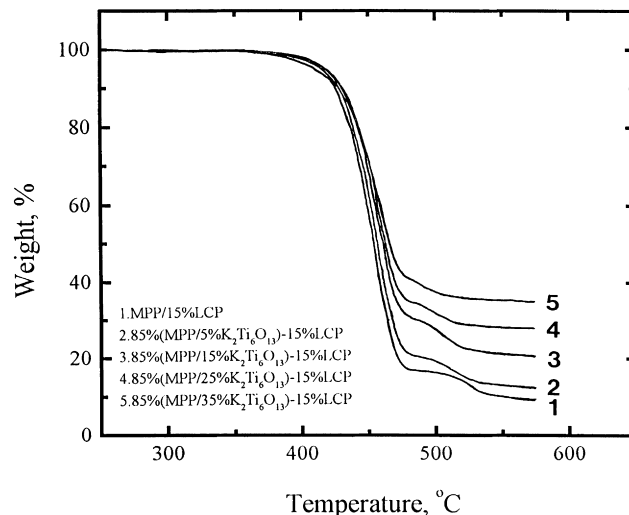


Fig. 15. TG curves for MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrids.

incorporation of a small amount of whisker content in 85%(MPP/5%K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>)-15%LCP hybrid results in a further increase in  $T_{-5\%}$  to 459.9°C. These data clearly indicate that both LCP and K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> whisker exhibit beneficial effect in improving the thermooxidative stability of MPP. Table 2 also shows that the  $T_{\max}$  of MPP/15%LCP is 456.2°C, and the incorporation of 5 w/w% K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> whisker into MPP/15%LCP leads to a decrease in  $T_{\max}$ . This is because the surface of whiskers are treated with tetrabutyl orthotitanate. As the boiling temperature of tetrabutyl orthotitanate is relatively low, thus  $T_{\max}$  of hybrids tends to decrease with the incorporation of K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> whiskers.

The glass transition temperatures ( $T_g$ ) of hybrids determined from DMA tests are summarized in Table 2. The  $T_g^1$  and  $T_g^2$  are the  $T_g$  of MPP and LCP, respectively. It appears that the difference in  $T_g$ s between MPP and LCP phases within the hybrids tend to decrease with increase in the whisker content, indicating that the compatibility between these two phases are improved with an increase in the whisker content. As tetrabutyl orthotitanate content in hybrids increases with an increase in the whisker content, it is believed that tetrabutyl orthotitanate can react with both MPP and LCP, thereby acting as a coupling agent between them. This results in an improvement of compatibility between MPP and LCP phases with an increase in the whisker content.

#### 4. Conclusion

Static tensile tests reveal that longitudinal Young's modulus and tensile strength of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites are higher than those of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites. Such enhancement in the mechanical properties of hybrids results from the improvement in the interfacial adhesion between LCP and PP matrix owing to the compatibilizing effect of MAP. Consequently, LCPs are aligned



Table 2  
Thermal properties of MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>/LCP hybrid composites

Specimen	$T_g^1$ (°C)	$T_g^2$ (°C)	$T_{-5\%}$ (°C)	$T_{max}$ (°C)
MPP	17.40	—	361.5	453.6
MPP/15%LCP	19.57	104.6	415.5	456.2
85%(MPP/5%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> )–15%LCP	19.08	107.5	459.9	419.9
85%(MPP/10%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> )–15%LCP	19.87	104.5	459.4	419.4
85%(MPP/15%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> )–15%LCP	20.14	108.3	459.8	418.1
85%(MPP/25%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> )–15%LCP	33.55	105.3	459.9	416.9
85%(MPP/35%K <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> )–15%LCP	33.52	104.8	461.1	412.2

along the flow direction and deform into elongated fibrils in the skin section of hybrids. This leads to the hybrids with LCP being stronger and stiffer than those without it. The longitudinal stiffness and tensile strength of hybrids deviate positively from the rule of hybrid mixtures. Moreover, the hybrid composites reinforced with both LCP fibrils and potassium titanate whiskers generally exhibit anisotropic mechanical properties. The values of the longitudinal tensile stiffness, tensile yield and fracture strengths as well as impact energy are considerably higher than their transverse counterparts. Torque measurements indicate that the addition of LCP into MPP/K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> composites decreases the melt viscosity, thereby improving the processability of such composites. Finally, TGA results show that both LCP and K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> whisker exhibit beneficial effect in improving the thermooxidative stability of MPP.

## References

- [1] Hashemi S, Koohgilani M. *Polym Engng Sci* 1995;35:1124.
- [2] Karger-Kocsis J. *Compos Sci Technol* 1993;48:273.
- [3] Thomason JL, Vlug MA. *Composites* 1997;28A:277.
- [4] Park BD, Balatinesc JJ. *Polym Compos* 1997;18:79.
- [5] Avella M, Martuscelli E, Raimo M, Partch R, Gangolli SG, Pascucci B. *J Mater Sci* 1997;32:2411.
- [6] Tjong SC, Li RKY, Cheung T. *Polym Engng Sci* 1997;37:166.
- [7] Tjong SC, Li RKY. *J Vinyl Additive Technol* 1997;3:89.
- [8] Taesler R, Wittich H, Jurgens C, Schulte K, Kricheldorf HR. *J Appl Polym Sci* 1996;61:783.
- [9] Kobayashi M, Takahashi T, Takimoto J, Koyama K. *Polymer* 1995;36:3927.
- [10] Tjong SC, Meng YZ. *Polymer* 1998;39:5461.
- [11] Tjong SC, Meng YZ. *Polymer* 1999;40:1109.
- [12] Courtney TH. *Mechanical behavior of materials*. New York: McGraw Hill, 1990. p. 83–84.
- [13] Wei GC, Becher PF. *Am Ceram Soc Bull* 1985;64:298.
- [14] Zheng L, Jin Y, Li P. *Compos Sci Technol* 1997;57:463.
- [15] Christman T, Suresh S. *Acta Metall* 1988;36:1691.
- [16] Xu XX, King JE. *Mater Sci Technol* 1996;12:911.
- [17] Saganuma K, Fujita T, Nihara K, Suzuki N. *J Mater Sci Lett* 1989;8:808.
- [18] Murakumi R, Matsui K. *Wear* 1996;201:193.
- [19] Kulichikhin VG, Parsamyan IL, Lipatov YS, Shumskii VF, Getmanchuk IP, Babich VF, Postema AR. *Polym Engng Sci* 1997;37:1314.
- [20] He J, Zhang H, Wang Y. *Polymer* 1997;38:4279.
- [21] Friedrich K, Jacobs O, Cirino M. In: Rohatgi PK, Blau PJ, Yust CS, editors. *Tribology of composite materials*. Materials Park, OH: ASM International, 1991. p. 277.
- [22] Hashemi S, Elmes P, Sandford S. *Polym Engng Sci*. 1997;37:45.
- [23] Fu SF, Lauke B. *J Mater Sci Technol* 1997;13:389.
- [24] Stricker F, Mulhaupt R. *J Appl Polym Sci* 1996;62:1799.
- [25] Xanthos M. *Polym Engng Sci* 1988;28:1392.
- [26] Seppala J, Heino M, Kapanen C. *J Appl Polym Sci* 1992;44:1051.
- [27] Holsti-Miettinen RH, Seppla J, Ikkala OT. *Polym Engng Sci* 1992;32:868.
- [28] Tjong SC, Liu SL, Li RKY. *J Mater Sci* 1995;30:353.
- [29] Datta A, Baird DG. *Polymer* 1995;36:505.
- [30] O'Donnell HJ, Baird DG. *Polymer* 1995;36:3113.
- [31] Kozłowski M, La Mantia FP. *J Appl Polym Sci* 1997;66:969.
- [32] Meng YZ, Tjong SC. *Polym Compos* 1998;19:1.
- [33] Halpin JC, Kardos JL. *Polym Engng Sci* 1976;16:344.
- [34] Shiao ML, Nair SV, Garrett PD, Pollard RE. *Polymer* 1994;35:306.
- [35] Sortino G, Scaffaro R, La Mantia FP. *Adv Polym Technol* 1997;16:227.
- [36] Nobile MR, Amendola E, Nicolais L. *Polym Engng Sci* 1989;29:244.
- [37] Tjong SC, Meng YZ. *Polymer* 1997;38:4609.
- [38] Tjong SC, Shen JS, Liu SL. *Polym Engng Sci* 1996;36:797.