Mechanical and Thermal Properties of Polycarbonate Composites Reinforced with Potassium Titanate Whiskers

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ABSTRACT: Polycarbonate (PC) composites reinforced with potassium titanate ($K_2Ti_6O_{13}$) whiskers were blended in a twin-screw extruder followed by injection molding. The surface of whiskers was treated with tetrabutyl orthotitanate prior to blending. The effects of potassium titanate whisker additions on the tensile, impact, and thermal properties of PC were investigated. Tensile tests showed that the stiffness of composites markedly improved with increasing whisker content. However, potassium titanate whiskers were ineffective to reinforce PC because these whiskers promoted chemical decomposition of PC matrix during compounding. Consequently, the torque values of PC/$K_2Ti_6O_{13}$ composites were much lower than that of PC. Moreover, torque measurements revealed that titanate coupling agent also facilitated decomposition of PC during blending. The mechanisms responsible for the degradation of PC matrix of the surface-treated PC/$K_2Ti_6O_{13}$ composites are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 501–508, 1999

Keywords: whisker; decomposition; coupling agent; PC; tensile strength; potassium titanate

INTRODUCTION

Polycarbonate (PC) is an amorphous and polar thermoplastic polymer. It possess outstanding properties such as dimensional stability, flame resistance, and high impact strength. However, PC is susceptible to crazing or cracking on exposure to various solvents. Moreover, PC is relatively soft, and the surface of polymer is easily scratched.[1] To upgrade the performance of PC, short glass fibers are incorporated into PC to form polymer composites. In this case, the tensile strength, stiffness, and surface finish of PC are improved dramatically.[2,3] Thus, short glass fiber-reinforced PC can be used as a material in many structural applications. Recently, there has been growing interest in upgrading the mechanical properties of polymers by reinforcing them with whiskers.[4–8] Whiskers are attractive because they exhibit high yield strength and high stiffness, and are free from internal defects such as dislocations owing to their small diameter.[9] For example, inorganic whiskers such as silicon carbide (SiC) have been used by Avella et al. to reinforce polypropylene (PP).[6] They reported that uncoated SiC whiskers show little tendency to be dispersed within the PP matrix, thereby resulting in a diminution of both tensile strength and elongation of break with the addition of uncoated whiskers. However, SiC whiskers coated with acrylate-grafted polydivinylbenzene tended to disperse uniformly within the PP matrix modified with maleic anhydride. Thus, the stiffness and impact toughness of PP were improved accordingly. Such improvement in mechanical proper-

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Table I Properties of Potassium Titanate Whiskers

Material	Specific Gravity, g/cm^3	Length, μm	Diameter, μm	Tensile Strength, GPa	Tensile Modulus, GPa	Moh Hardness
$K_2Ti_6O_{13}$	3.3	10–40	0.5–1.0	7	280	4

ties resulted from stronger interface interactions between the whisker coating and the matrix.[6]

SiC whiskers are considered to be an expensive material, although its cost has fallen sharply in the past few years. Other prospective inorganic whiskers that can be used to reinforce the composites include potassium titanate and aluminum borate ($Al_{18}B_4O_{13}$).[10] Potassium titanate ($K_2Ti_6O_{13}$) whiskers show promise as a reinforcement material, owing to its good physical and mechanical properties as well as low cost. The price of $K_2Ti_6O_{13}$ whiskers ranges from one-tenth to one-twentieth of the cost of SiC whiskers.[11] Consequently, several workers have attempted to reinforce metallic alloys[12] and polymers[5,7,8] with $K_2Ti_6O_{13}$ whiskers. In the former case, $K_2Ti_6O_{13}$ whiskers provided an effective reinforcement and improved the wear resistance of copper composites.[12] As the hardness of $K_2Ti_6O_{13}$ whiskers is not as high as SiC whiskers, the machinability of potassium titanate whisker-reinforced metal matrix composites is improved considerably. In terms of polymer-based composites, $K_2Ti_6O_{13}$ whiskers have the potential for engineering applications in watch-gears, audiovisual housings, bumpers, etc., because these whiskers can reinforce the narrow space of the components.[12] Most recent studies of the morphology, mechanical, and thermal properties of $K_2Ti_6O_{13}$ whiskers reinforced semicrystalline thermoplastics, for example, PP and polyamide 6 (PA6) have been conducted by Tjong and Meng.[7,8] They reported that the tensile strength and modulus, as well as heat resistance of composites, tend to increase with increasing whisker content. This implies that the $K_2Ti_6O_{13}$ whiskers additions are beneficial in improving the mechanical and thermal properties of semicrystalline thermoplastics. As part of our study on the improvement and upgrading the performance of thermoplastics by reinforcing with $K_2Ti_6O_{13}$ whiskers, this article presents the first report on the mechanical and thermal properties of an amorphous PC polymer containing $K_2Ti_6O_{13}$ whisker additions.

EXPERIMENTAL

The whiskers used in this study were of potassium titanate ($K_2Ti_6O_{13}$) purchased from Jinjian Composite Co., Shenyang, China. Their properties are listed in Table I. The PC (Makrolon 2605) was supplied by Bayer Company, Germany. Reagent-grade tetrabutyl orthotitanate, purchased from Fluka Chemie, Switzerland, was used as the coupling agent for the whiskers.

Tetrabutyl orthotitanate was initially dispersed in acetone to form a 5 wt % solution. The surface of $K_2Ti_6O_{13}$ whiskers was treated with tetrabutyl orthotitanate prior to blending. The weight ratio of whiskers to tetrabutyl orthotitanate was fixed at 98.5 : 1.5. The solution was slowly poured into a plastic container filled with whiskers. They were thoroughly mixed by hand, and subsequently dried in an oven at 80°C for 24 h.

PC was mixed with varying amounts of $K_2Ti_6O_{13}$ whiskers to produce composites with whisker contents of 5, 10, 15, and 25% by weight. Blending was performed in a Brabender twin-screw extruder at 250°C. The extrudates were subsequently pelletized. These pellets were then injection molded to produce dumbbell-shaped tensile bars (ASTM D-638) and plaques with dimensions of $147 \times 80 \times 6$ mm^3. The mold temperature was kept at 40°C while the barrel zone temperatures were maintained at 240, 250, and 250°C.

For the purposes of comparison, the $K_2Ti_6O_{13}$ whiskers were also surface treated with a si-

Table II Thermal Properties of PC and Its Composites

Specimen	T_g, °C	T_{max}, °C	$T_{-5\%}$, °C
PC	149.8	516.3	470.9
PC/$K_2Ti_6O_{13}$ 95/5	137.5	480.9	410.6
PC/$K_2Ti_6O_{13}$ 90/10	136.5	471.0	413.3
PC/$K_2Ti_6O_{13}$ 85/15	133.9	452.4	399.6
PC/$K_2Ti_6O_{13}$ 75/25	132.7	444.0	408.0

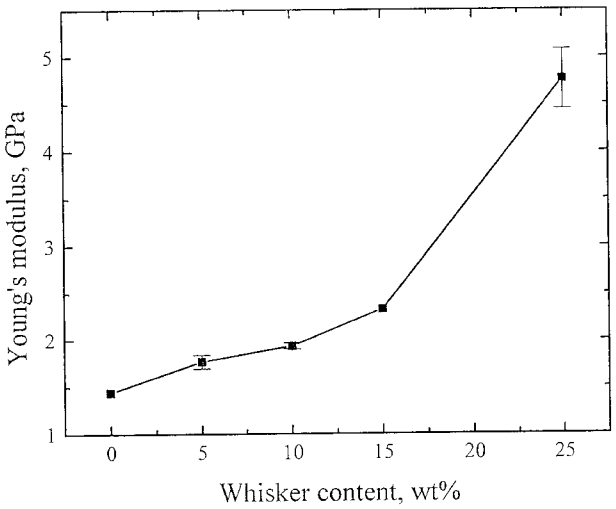

Figure 1 Variation of Young's modulus with whisker content for PC/$K_2Ti_6O_{13}$ composites.

lanization agent, $CH_3Si(OCH_3)_3$. PC composites reinforced with silane-treated whiskers were also prepared under similar processing conditions as outlined above.

Torque values for PC homopolymer and the composites were measured using a Brabender Plasticorder batch mixer at 250°C and 30 rpm for 10 min. The chamber volume was 50 cm^3. For each measurement, 35 g material was added into the chamber.

The tensile properties of the composites were determined using an Instron tensile tester (model 4206) at room temperature at the strain rate of 1 mm min^{-1}. This facility is equipped with a computerized data acquisition system. Reported values were averaged from the tensile data of five specimens.

The notched Izod impact tests were determined using a Ceast instrumented pendulum-type testing machine (model 6545). Longitudinal impact specimens with dimensions of 65 × 12.7 × 6 mm were cut from the injection-molded plaques. At least seven specimens were tested to give each data point reported. Impact specimens were prepared with their length parallel to the mold-filling direction (MFD). The fractured surfaces of impact specimens were examined in a JEOL JSM-820 scanning electron microscope (SEM). The samples for SEM were sputtered with a thin layer of gold prior to observation.

Thermal analysis was carried out in a Seiko thermogravimetric analyzer (model SSC/5200). This instrument was also equipped with a differential thermal analyzer (DTA). Weight loss against temperature was measured at a rate of 10°C min^{-1} in helium atmosphere, from 50 to 600°C.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the variation of Young's modulus vs. whisker content for PC/$K_2Ti_6O_{13}$ composites. Apparently, the stiffness of the composites tends to increase with increasing whisker content. The improvement in stiffness is expected, because the incorporation of inorganic fillers into thermoplastics generally leads to an increase in Young's modulus. However, the tensile strength of the inorganic filler-reinforced thermoplastics is significantly influenced by their compounding conditions, types of filler and polymer matrix used, and interfacial bonding between the filler and matrix. Figure 2 shows the tensile strength vs. whisker content for PC/$K_2Ti_6O_{13}$ composites. It can be see from this figure that the tensile strength decreases almost linearly with increasing whisker content up to 15 wt %. Thereafter, the tensile strength appears to decrease steadily. In other words, $K_2Ti_6O_{13}$ whiskers reduce the mechanical performance of PC: the tensile strength of PC decreases sharply with increasing whisker additions. In a previous study, Tjong and Meng[7] reported that $K_2Ti_6O_{13}$ whiskers are very effective to increase the tensile strength and stiff-

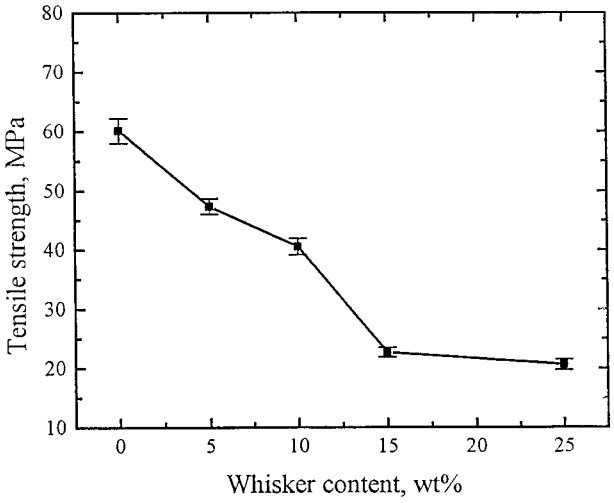

Figure 2 Variation of tensile strength with whisker content for PC/$K_2Ti_6O_{13}$ composites.

Table III Properties of PC Composites Reinforced with Silane and Orthotitanate-Treated Whiskers

Specimen	Young's Modulus, MPa	Tensile Strength, MPa	Strain at Break, %
PC/$K_2Ti_6O_{13}$ 95/5 (silane-treated)	1674 ± 5	15.6 ± 0.8	0.98 ± 0.05
PC/$K_2Ti_6O_{13}$ 95/5 (orthotitanate-treated)	1765 ± 74	47.3 ± 1.3	3.67 ± 0.24
PC/$K_2Ti_6O_{13}$ 90/10 (silane-treated)	1944 ± 44	6.9 ± 0.6	0.38 ± 0.07
PC/$K_2Ti_6O_{13}$ 90/10 (orthotitanate-treated)	1931 ± 33	40.6 ± 1.4	2.94 ± 0.31

ness of PP/$K_2Ti_6O_{13}$ composites. The whisker surface is also treated with tetrabutyl orthotitanate, and MA-grafted PP is used as a compatibilizer for that composite. The improvement in tensile strength associated with whisker addition in this case is attributed to a strong interaction existing between the functional group of MA-grafted PP and the titanate coupling agent. This allows a better shear stress transfer between the whiskers and matrix, thereby improving the tensile strength dramatically.[7] In the present work, it seems that the $K_2Ti_6O_{13}$ whisker does not exhibit a reinforcing effect becayse this filler can result in the degradation of PC during compounding. In other words, the $K_2Ti_6O_{13}$ whisker promotes the chemical decomposition of PC during the blending process, causing deterioration of the polymer mechanical properties. Furthermore, the tetrabutyl orthotitanate coupling agent also facilitates the degradation of PC during processing. To assess the effect of coupling agents on the mechanical performance of PC, the $K_2Ti_6O_{13}$ whisker was also surface treated with a silanization agent, $CH_3Si(OCH_3)_3$. From Table III, it is noticed that the silane-treated composites exhibit even lower tensile strength and ductility than those of the orthotitanate-treated composites. The composites containing silane-treated whisker $\geq$15 wt % cannot be injection molded, owing to the excessive degradation of PC during processing. On the basis of these results, it is apparent that the occurrence of chemical reactions between the $K_2Ti_6O_{13}$ whisker and PC matrix during processing, and the ease of the formation of these reactions in the presence of coupling agents, are the main factors leading to the deterioration in the mechanical strength of PC.

Figure 3 shows the tensile strain at break vs. whisker content for the PC/$K_2Ti_6O_{13}$ composites.

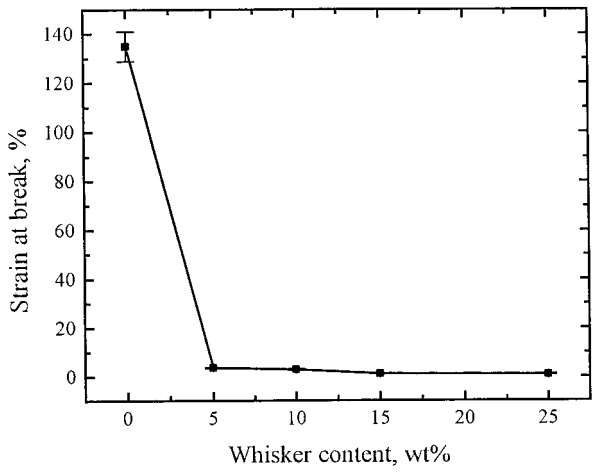

Figure 3 Variation of tensile strain at break with whisker content for PC/$K_2Ti_6O_{13}$ composites.

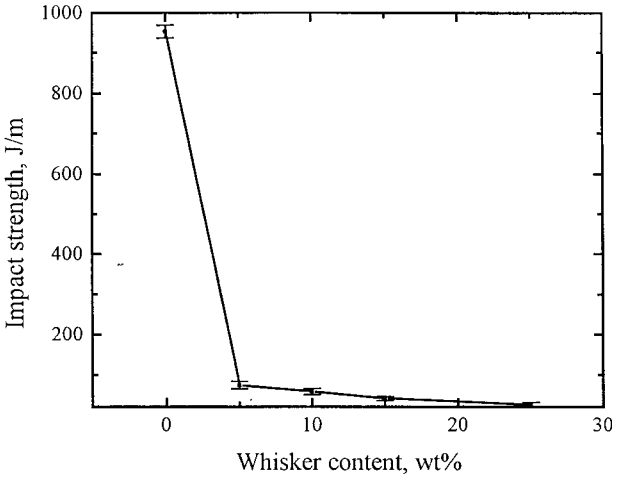

Figure 4 Variation of Izod impact strength with whisker content for PC/$K_2Ti_6O_{13}$ composites.

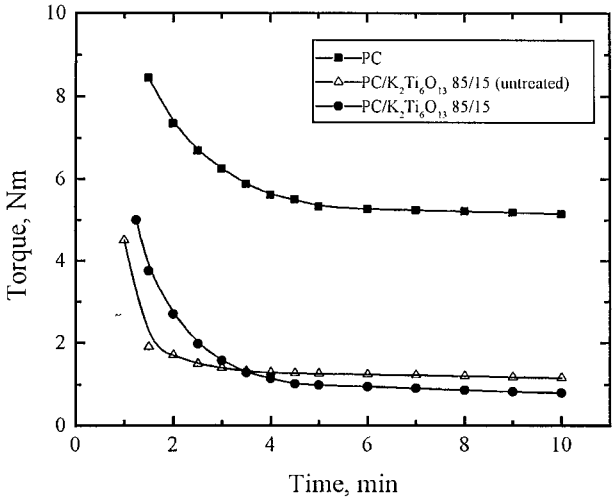

Figure 5 Variation of torque with mixing time for PC, tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ 85/15, and untreated PC/$K_2Ti_6O_{13}$ 85/15 specimens at 250°C.

It is evident that the tensile ductility decreases sharply with the addition of whiskers ≥5 wt %. The Izod impact strength also exhibits a similar decreasing trend with whisker content (Fig. 4). This is a typical characteristic of polymer composites.

Decomposition of PC

Figure 5 shows a torque-time plot for the PC polymer, tetrabutyl orthotinate-treated PC/$K_2Ti_6O_{13}$ 85/15 composite, and surface-untreated PC/$K_2Ti_6O_{13}$ 85/15 specimen at 250°C. The torque is related to the viscosity of the polymer blends during blending. It can be used to assess whether scission of the molecular chain associated with degradation of the polymers takes place during compounding. Chain scission generally results in

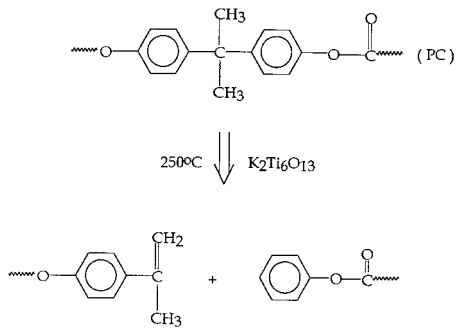

Figure 6 Possible chemical reaction leading to degradation of PC in the presence of $K_2Ti_6O_{13}$.

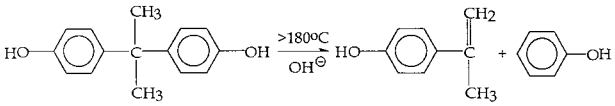

Figure 7 The decomposition of bisphenol A in an alkaline environment at temperatures above 180°C.

polymers having a lower molecular weight, thereby giving rise to lower torque values. From Figure 5, the torque values of both surface-treated and untreated PC/$K_2Ti_6O_{13}$ 85/15 composites are relative high during the initial material loading period, they then decrease steadily with increasing mixing time. Similar behavior is observed for the PC homopolymer. However, the steady-state torque value of the PC/$K_2Ti_6O_{13}$ 85/15 composite is markedly lower than that of PC, indicating that the $K_2Ti_6O_{13}$ whisker addition promotes scission of the PC molecular chain. Furthermore, the steady-state torque value of the tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ 85/15 specimen is slightly lower than that of its untreated counterpart. This implies that the titanate coupling agent can result in further decomposition of PC during mixing.

It is generally known that PC has poor resistance in an alkaline environment, particularly at high temperatures. $K_2Ti_6O_{13}$ consists of strong base and weak acid components, and PC is susceptible to degradation upon exposure to such an alkaline component during blending. The possible reaction leading to the fragmentation of PC polymer in the presence of $K_2Ti_6O_{13}$ is shown in Figure 6. This reaction is based on the results of previous work concerned with the synthesis of copoly(ether sulfone)s containing

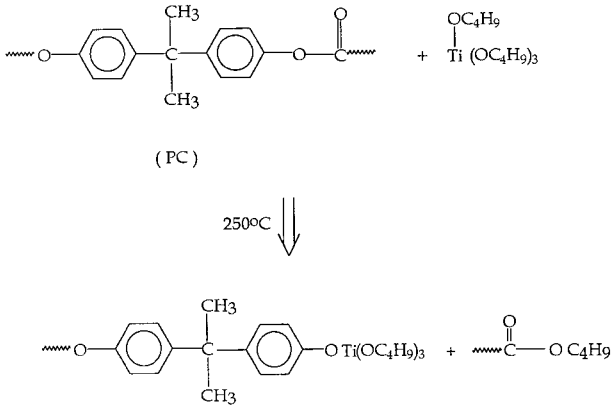

Figure 8 Possible chemical reaction between PC and tetrabutyl orthotitanate.

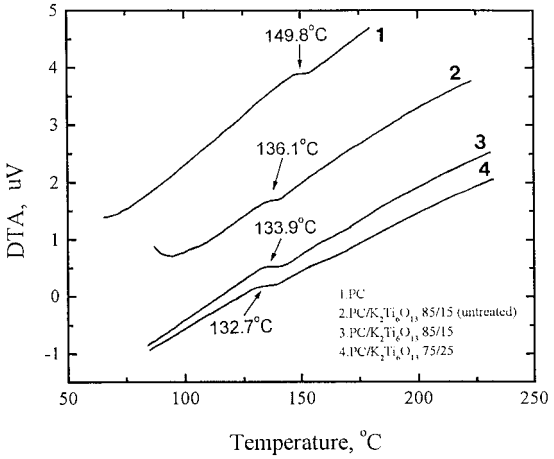

Figure 9 DTA curves for PC and PC/ $K_2Ti_6O_{13}$ composites.

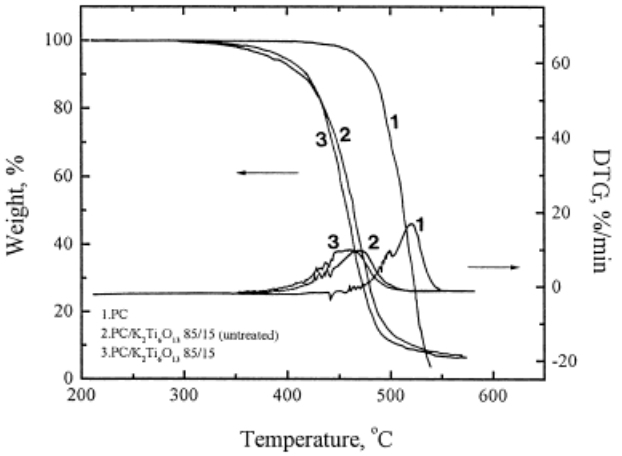

Figure 10 TG and DTG curves for PC, tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ 85/15, and untreated PC/ $K_2Ti_6O_{13}$ 85/15 specimens.

bisphenol A.[13] Meng et al. reported that the synthesis temperature of copoly(ether sulfone)s containing bisphenol A must be below 180°C to avoid the decomposition of bisphenol A (Fig. 7). Indeed, such a decomposition reaction can be used to prepare 4-isopropenylphenol. This reaction is considered to be appropriate to explain the decomposition of PC as shown in Figure 6. It is noted that the surface of whisker pretreated with the tetrabutyl orthotitanate coupling agent also facilitates the decomposition of PC. This is because the nucleophilicity of the phenoxy is greater than that of the the butoxy group. In addition, soft acid (phenoxy) and soft base (titanate) tend to react preferentially. This exchange reaction is very similar to the transesterification reaction between polyester and PC.[14–16] From this viewpoint, the possible reaction of PC with tetrabutyl orthotitanate leading to the scission of the PC molecular chain is shown in Figure 8.

Thermal Properties

Figure 9 shows typical DTA curves for PC and PC/$K_2Ti_6O_{13}$ composites. The glass transition temperature (T_g) for PC and composites determined from DTA measurements are listed in Table II. Figure 10 shows the TG curves for PC, the tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ 85/15 composite, and the surface-untreated PC/ $K_2Ti_6O_{13}$ 85/15 specimens. This figure also shows the DTG curves for these specimens. The maximum weight loss temperature (T_{max}) of PC determined from the DTG curve is 516.3°C, and the T_{max} for the untreated PC/$K_2Ti_6O_{13}$ 85/15 composite is decreased to 464.1°C. Moreover, the T_{max} of the tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ 85/15 composite is further decreased to 452.4 °C, as expected. The TG and DTG curves for other tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ composites are shown in Figure 11. The T_{max} for PC and its composites are given in Table II. It can be seen that T_{max} decreases sharply with increasing whisker content. This is due to the composites with higher whisker content containing more titanate coupling agent and $K_2Ti_6O_{13}$, which facilitate the decomposition of PC. The 5% loss temperatures ($T_{-5\%}$) determined from TG curves are also summarized in Table II. It is apparent that $T_{-5\%}$ of PC also

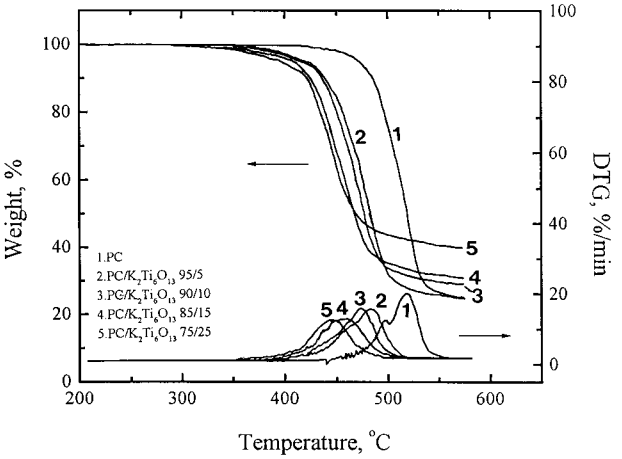

Figure 11 TG and DTG curves for tetrabutyl orthotitanate-treated PC/$K_2Ti_6O_{13}$ composites.

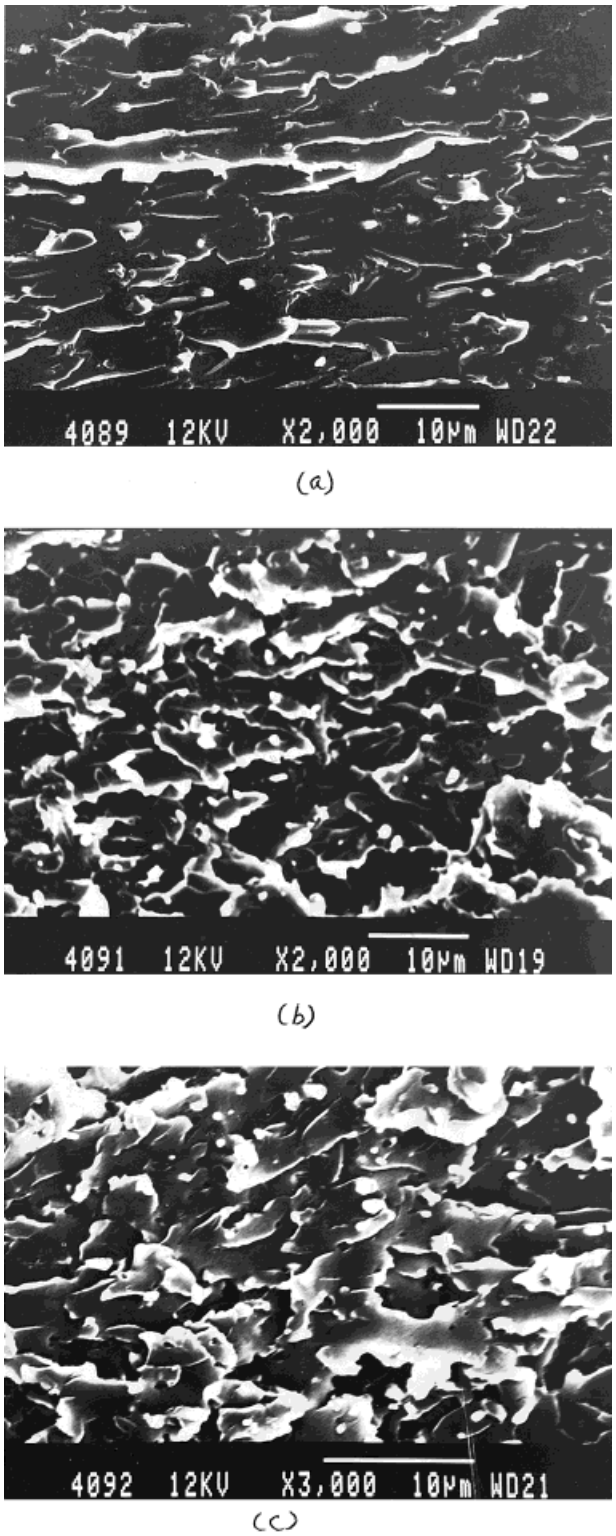

Figure 12 SEM micrographs showing the fracture surfaces of (a) PC/$K_2Ti_6O_{13}$ 95/5, (b) PC/$K_2Ti_6O_{13}$ 85/15, and (c) PC/$K_2Ti_6O_{13}$ 75/25 composites. The fractographs were taken from the midsection of specimens.

decreases markedly with increasing whisker content.

Morphology

It is generally known that the morphology of injection-molded specimen consists of a skin-core structure. Figure 12(a)–(c) show the SEM fractographs of the PC/$K_2Ti_6O_{13}$ 95/5, 85/15, and 75/25 composites, respectively, after impact tests. Generally, no skin-core structure can be observed in this particular injection-molded PC/$K_2Ti_6O_{13}$ composite. The whiskers tend to align along the MFD. This is because the degradation of PC during injection molding results in a lower melt viscosity, thereby favoring the whiskers to orient easily along the MFD.

CONCLUSION

In this study, we attempted to prepare PC/$K_2Ti_6O_{13}$ composites by means of injection molding, and to study their mechanical and thermal properties. The whisker was pretreated with a tetrabutyl orthotitanate coupling agent. Tensile tests showed that the $K_2Ti_6O_{13}$ whisker additions improve the stiffness of PC dramatically. However, $K_2Ti_6O_{13}$ whiskers were very ineffective to raise the tensile strength of PC. The tensile strength of PC decreased sharply with increasing whisker content. This was due to the $K_2Ti_6O_{13}$ whisker promoting the decomposition of PC during compounding. Furthermore, tetrabutyl orthotitanate also facilitated the decomposition of PC. Torque measurements, and TG tests provided substantial evidence for the decomposition of PC in the presence of the $K_2Ti_6O_{13}$ whisker and tetrabutyl titanate coupling agent.

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