Mechanical and Thermal Behavior of Polycarbonate Composites Reinforced with Aluminum Borate Whiskers

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ABSTRACT: Inorganic aluminum borate ($Al_{18}B_4O_{33}$) whisker was employed in this study to reinforce polycarbonate (PC). The composites were prepared in a single-screw extruder, followed by injection molding. The whiskers were pretreated with tetrabutyl orthotitanate prior to compounding. The tensile, dynamic mechanical, impact, and thermal properties of the composites were studied. Tensile results showed that the modulus of PC–$Al_{18}B_4O_{33}$ composites increased markedly with increasing whisker content. However, the tensile stress of the composite decreased slightly with the addition of 5 wt % whisker; thereafter, it increased slowly with increasing whisker content. Differential thermal analysis and thermogravimetric measurements showed that the glass transition temperature (T_g) and 5% weight loss temperature ($T_{-5\%}$) of the composite shift rapidly to lower temperature regimes with the addition of $Al_{18}B_4O_{33}$ whiskers up to 10 wt %. Thereafter, the T_g and $T_{-5\%}$ of PC–$Al_{18}B_4O_{33}$ composites tended to decrease slowly with increasing whisker content. The mechanical and thermal properties of PC–$Al_{18}B_4O_{33}$ composites were compared with those of PC–potassium titanate ($K_2Ti_6O_{13}$) whisker composites. The reinforcing effect of $Al_{18}B_4O_{33}$ and $K_2Ti_6O_{13}$ whiskers on PC was discussed and contrasted. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2247–2253, 1999

Key words: polycarbonate; whisker; composite; tensile strength

INTRODUCTION

Polycarbonate (PC) is a widely used engineering thermoplastic because it possesses several distinct properties, such as transparency, dimensional stability, flame resistance, high heat distortion temperature, and high impact strength. However, PC exhibits high notch sensitivity, and it is susceptible to crazing or cracking on exposure to various solvents. Moreover, PC is relative soft, and the surface of polymer can be easily scratched.[1] These disadvantages limit its use in some applications. The mechanical performance of PC can be improved either by the addition of small amounts of core–shell impact modifier,[2] or glass fiber reinforcements.[3,4] In the latter case, the glass fiber contributes to a dramatic increase in the tensile strength, modulus, and wear resistance of the resultant composites. But the introduction of glass fiber into PC can result in higher melt viscosity and breakage of the fiber.

It is generally accepted that whiskers exhibit high stiffness and strength. Their strength is close to the maximum theoretical value expected from the theory of elasticity.[5] This is because whiskers are nearly free from the internal flaws, owing to their small diameter. In this respect, whiskers have a specific advantage in compounding or molding. Therefore, whiskers have been used extensively as reinforcement materials for

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Table I Properties of Aluminum Borate and Potassium Titanate Whiskers

Material	Density (g/cm^3)	Diameter (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Moh Hardness
$Al_{18}B_4O_{33}$	2.93	0.5–1.0	8	400	7
$K_2Ti_6O_{13}$	3.3	0.5–1.0	7	280	4

the ceramic matrix composites, metal matrix composites, and polymer matrix composites.[6–20] These inorganic whiskers used include silicon carbide (SiC), potassium titanate ($K_2Ti_6O_{13}$), and aluminum borate ($Al_{18}B_4O_{33}$). Among these, SiC whiskers are used in many reinforcement applications, owing to their superior mechanical and physical properties. However, the cost of SiC whisker remains relatively high. Thus, much effort has been spent by researchers in attempts to produce low-cost inorganic whiskers. According to literature, the price of potassium titanate whiskers ranges from one-tenth to one-twentieth of the cost of SiC whiskers.[15] Also, the cost of aluminum borate whisker is significantly more competitive than the cost of SiC whisker (almost one-thirtieth).[18] More recently, we have incorporated potassium titanate whiskers into polyamide 6 (PA6) and polypropylene (PP), respectively, in order to upgrade their mechanical performance. The experimental results show that the stiffness, tensile strength, and thermal stability of PA and PP composites are remarkably higher than those of PA6 and PP homopolymers.[19–20] On the other hand, potassium titanate whiskers are found to be ineffective reinforcement materials for PC, owing to the fact that these whiskers promote chemical decomposition of PC during compounding.[21] In this article, we attempt to use the aluminum borate whiskers to reinforce PC and to study the mechanical and thermal properties of the resultant composites. The mechanical and thermal properties of PC reinforced with $Al_{18}B_4O_{33}$ and $K_2Ti_6O_{13}$ are compared and discussed.

EXPERIMENTAL

Materials

The PC used in this study was produced by Bayer Company (Germany) under the trade name Makrolon 2605. Aluminum borate ($Al_{18}B_4O_{33}$) whiskers were supplied by Jinjian Composite Co., Shenyang, China. Their main properties are listed in Table I. Reagent-grade tetrabutyl orthotitanate purchased from Fluka Chemie, Switzerland, was used as a coupling agent for the whiskers.

Sample Preparations

Tetrabutyl orthotitanate was initially dispersed in acetone to form a 5 wt % solution. The solution was slowly poured into a plastic box filled with whiskers. They were mixed thoroughly and subsequently dried in an oven at 80°C for 24 h. The weight ratio of whiskers to tetrabutyl orthotitanate was fixed at 98.5 : 1.5.

Composites containing 5, 10, 15, and 20 wt % whiskers were prepared in a single-screw Brabender Plasticorder at 250°C and 30 rpm. Standard dog-bone tensile bars (ASTM D638) were injection-molded from these pellets. The mold temperature was maintained at 40°C, while the barrel zone temperature was set at 240, 250, and 250°C.

Mechanical Measurements

The tensile behavior of the blends was determined using an Instron tester (model 4206) at room temperature under a crosshead speed of 5 mm min^{-1}. At least five specimens of each composition were tested, and the average values are reported.

Izod impact specimens with dimensions of 65 × 13 × 3.2 mm were cut from the midsection of tensile bars and were tested by a Ceast impact pendulum tester. These specimens were sharply notched with an V-shaped knife. At least five specimens were tested, and the average values are reported.

Dynamic mechanical analysis (DMA) of the injection–molded rectangular specimens with dimensions of 65 × 13 × 3.2 mm were conducted using 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

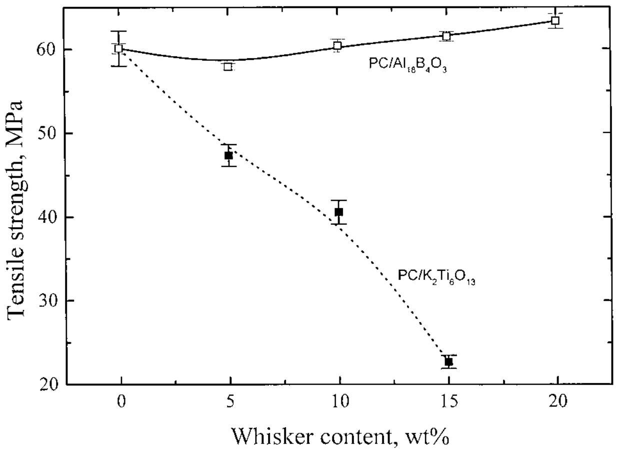

Figure 1 Variations of tensile strength with whisker content for PC–$Al_{18}B_4O_{33}$ composites. The tensile strength versus whisker content for PC–$K_2Ti_6O_{13}$ composites is also shown for the purposes of comparison.[21]

studied ranged from 40 to 140°C, and the heating rate employed was 4°C min^{-1}.

Thermal Analyses

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

Morphological Observation

The morphologies of the surfaces of the blend specimens and $Al_{18}B_4O_{33}$ whiskers were observed in a scanning electron microscope (SEM; Jeol JSM 820). The specimens were cryofractured in liquid nitrogen. All the samples were coated with a thin layer of gold prior to SEM observations.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the variation of tensile strength with whisker content for the PC–$Al_{18}B_4O_{33}$ whisker composites. In this figure, the tensile strength versus whisker content for PC composites reinforced with $K_2Ti_6O_{13}$ whiskers are also shown for the purposes of comparison.[21] Apparently, the tensile strength decreases continuously with increasing whisker content for PC–$K_2Ti_6O_{13}$ composites. This is due to the $K_2Ti_6O_{13}$ whisker promote the decomposition of PC during compounding.[21] However, it is interesting to note that the tensile strength decreases slightly with the addition of 5 wt % $Al_{18}B_4O_{33}$ whiskers to PC; thereafter, it increases considerably with increasing whiskers content. Furthermore, the strength of PC–$Al_{18}B_4O_{33}$ composites is higher than that of pure PC when the whisker content reaches 15 wt % and above. These results indicate that $Al_{18}B_4O_{33}$ whiskers can be used to improve the mechanical strength of PC, whereas $K_2Ti_6O_{13}$ whiskers do not. The variation of strain at break of composites with whisker content is depicted in Figure 2. It is noticed that the strain at break decreases sharply with the addition of only 5 wt % whiskers content for PC–$K_2Ti_6O_{13}$ composites. Compared to PC–$K_2Ti_6O_{13}$ composites, the strain at break of PC–$Al_{18}B_4O_{33}$ composites decreases slowly with the incorporation of 5 wt % whiskers content. However, the strain at break of PC–$Al_{18}B_4O_{33}$ composites drop sharply when the whisker content is greater than or equal to 10 wt %. This is one of the typical characteristics of polymer composites. Figure 3 shows the Young's modulus versus whisker content. Apparently, the stiffness increases considerably with increasing whisker content for both PC–$Al_{18}B_4O_{33}$ and PC–$K_2Ti_6O_{13}$ composites.

The relationship between Izod impact strength and whisker content for the PC–$Al_{18}B_4O_{33}$ and PC–$K_2Ti_6O_{13}$ composites is shown in Figure 4. It can be seen that the impact strength decreases dramatically with increasing whiskers content for

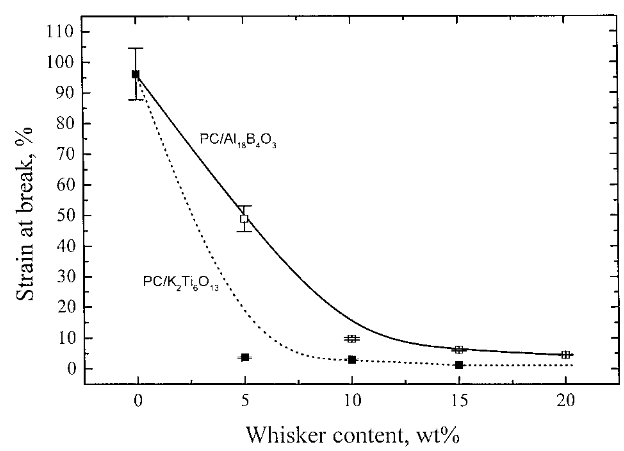

Figure 2 Variations of tensile strain at break with whisker content for PC–$Al_{18}B_4O_{33}$ composites. The tensile strain at break versus whisker content for PC–$K_2Ti_6O_{13}$ composites is also shown for the purposes of comparison.[21]

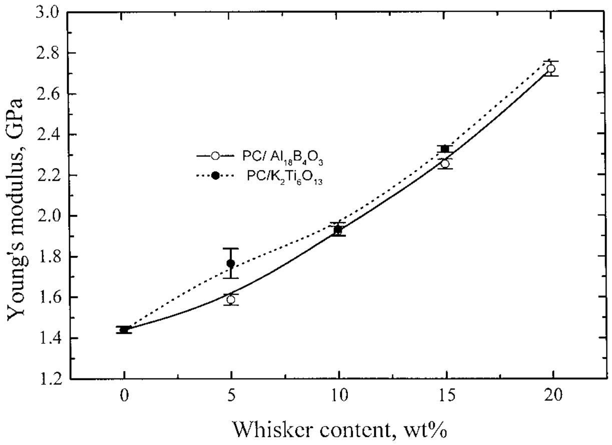

Figure 3 Variations of Young's modulus with whisker content for PC–$Al_{18}B_4O_{33}$ composites. The Young's modulus versus whisker content for PC–$K_2Ti_6O_{13}$ composites is also shown for the purposes of comparison.[21]

both PC–$Al_{18}B_4O_{33}$ and PC–$K_2Ti_6O_{13}$ composites. However, the impact strength of PC–$Al_{18}B_4O_{33}$ composites is slightly higher than that of PC–$K_2Ti_6O_{13}$ composites.

Figures 5 and 6 show the storage modulus and loss modulus versus temperature for PC–$Al_{18}B_4O_{33}$ composites. These figures show that both storage modulus and loss modulus tend to increase considerably with increasing whiskers content. Moreover, Figure 6 further indicates that the loss modulus peak does not shift to lower temperatures when the whisker contents are above 10 wt %. This implies that the glass transition temperature of PC remains unchanged when the $Al_{18}B_4O_{33}$ whiskers content is greater than 10 wt %. On the other hand, the decomposition of PC associated with the $K_2Ti_6O_{13}$ whisker additions leads to the DMA data of PC–$K_2Ti_6O_{13}$ composites becoming very unstable when the temperature approaches the T_g of PC.[21]

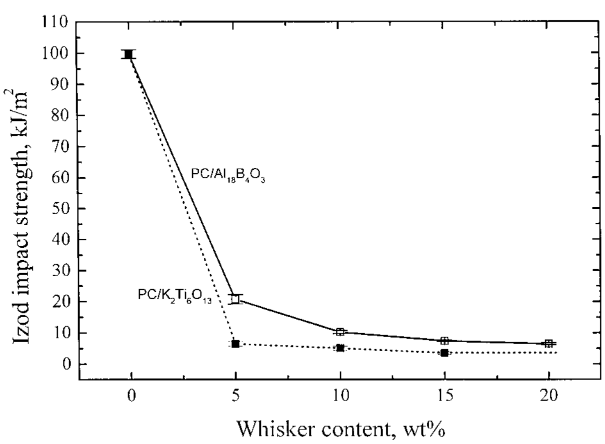

Figure 4 Variations of Izod impact strength with whisker content for PC–$Al_{18}B_4O_{33}$ composite. The Izod impact strength versus whisker content for PC–$K_2Ti_6O_{13}$ composites is also shown for the purposes of comparison.[21]

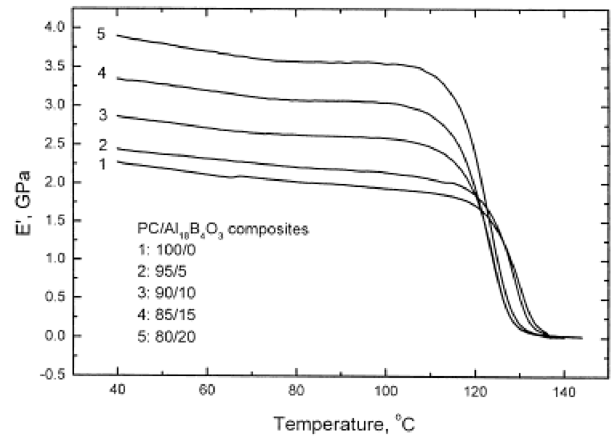

Figure 5 Storage modulus spectra of PC–$Al_{18}B_4O_{33}$ composites.

Thermal Properties

Figure 7 shows the effect of whisker additions on the glass transition temperature (T_g) of PC. The T_g was determined from DTA curves. It is noticed that the T_g of PC decreases sharply with the addition of only 5 wt % $K_2Ti_6O_{13}$ whiskers to PC; thereafter, it decreases continuously with increasing $K_2Ti_6O_{13}$ content. Compared to PC–$K_2Ti_6O_{13}$ composites, the T_g of PC appears to

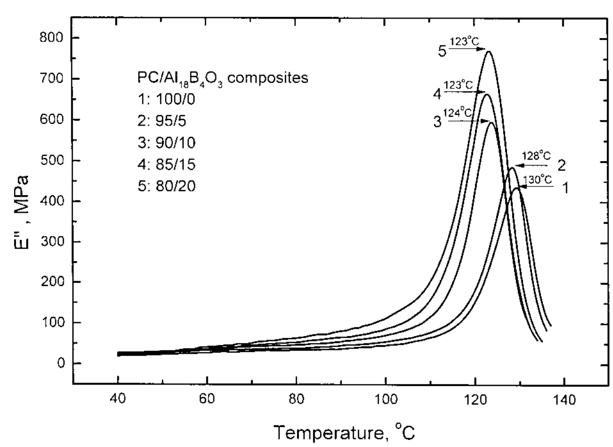

Figure 6 Loss modulus spectra of PC–$Al_{18}B_4O_{33}$ composites.

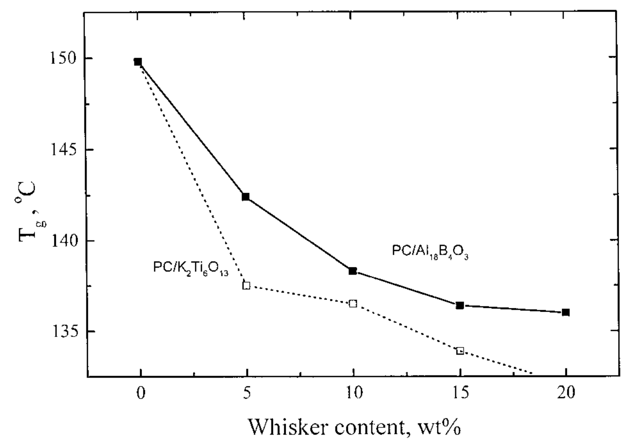

Figure 7 Variations of the glass transition temperature (T_g) of PC–$Al_{18}B_4O_{33}$ composites with whisker content. The glass transition temperature (T_g) of PC–$K_2Ti_6O_{13}$ composites versus whisker content is also shown for the purposes of comparison.[21]

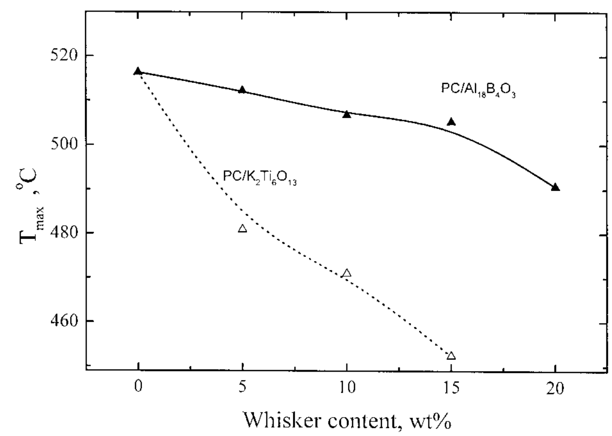

Figure 9 Variations of the maximum weight loss temperature (T_{max}) of PC–whisker composites with whisker content. The maximum weight loss temperature (T_{max}) of PC–$K_2Ti_6O_{13}$ composites versus whisker content is also shown for the purposes of comparison.[21]

decrease more slowly with increasing whisker content for PC–$Al_{18}B_4O_{33}$ composites, particularly when the whisker content reaches 10 wt % and above. This result is consistent with the DMA data, as discussed above. Figure 8 shows the 5% weight loss temperature ($T_{-5\%}$) of the composite versus whisker content determined from TGA measurement. It reveals that the $T_{-5\%}$ of PC–$K_2Ti_6O_{13}$ composites is remarkably lower than that of PC–$Al_{18}B_4O_{33}$ composites. Moreover, the $T_{-5\%}$ of PC–$Al_{18}B_4O_{33}$ composites drops slowly with increasing whisker content. Figure 9 shows

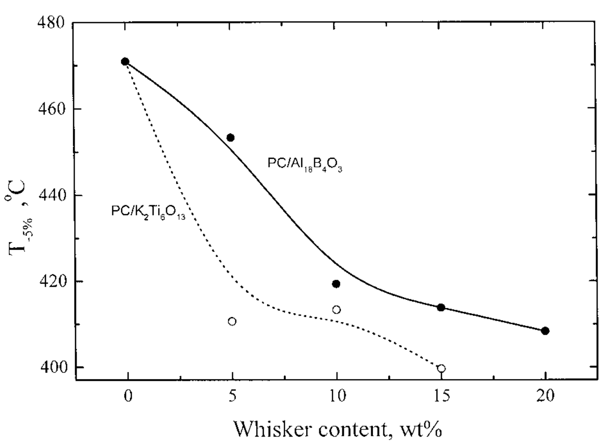

Figure 8 Variations of the 5% weight loss temperature ($T_{-5\%}$) of PC–$Al_{18}B_4O_{33}$ composites with whisker content. The 5% weight loss temperature ($T_{-5\%}$) of PC–$K_2Ti_6O_{13}$ composites versus whisker content is also shown for the purposes of comparison.[21]

the variation of maximum weight loss temperature (T_{max}) of the composites with whisker content. It can be seen that the incorporation of $Al_{18}B_4O_{33}$ whiskers up to 15 wt % to PC results in a small decrease of T_{max} from 512.3 to 505.2°C. On the other hand, T_{max} of PC–$K_2Ti_6O_{13}$ composites decreases significantly with increasing $K_2Ti_6O_{13}$ content.

From the above results, it is clear that both $Al_{18}B_4O_{33}$ and $K_2Ti_6O_{13}$ whiskers promote chemical decomposition of PC matrix during melt mixing, but the $Al_{18}B_4O_{33}$ whiskers have a smaller adverse effect in degrading PC than the $K_2Ti_6O_{13}$ whisker. And the degradation of PC due to whisker additions leads to a reduction in the molecular weight of PC. According to literature, the relationship between the glass transition temperature (T_g) and polymer molecular weight can be given by the following equation[22,23]:

$$T_g = T_g^0 - \mathrm{K}/M_n \tag{1}$$

where M_n is the number-average molecular weight of a polymer, K is a constant, and T_g^0 is the glass transition temperature when the polymer molecular weight approaches an infinite value. Rearranging eq. (1), we have

$$M_n = \frac{\mathrm{K}}{T_g^0 - T_g} \tag{2}$$

It is generally known that the molecular weight of polymers have a large effect on their strength.[24] Flory[25] proposed that the tensile fracture stress of a polymer (σ_P) can be related to the number-average molecular weight M_n, as follows:

$$\sigma_P = \mathrm{A} - \mathrm{B}/M_n \tag{3}$$

where A and B are constants. From the equations (2–3), we obtain

$$\sigma_P = \mathrm{A} - \frac{\mathrm{B}}{\mathrm{K}}\,(T_g^0 - T_g) \tag{4}$$

As mentioned above, the T_g of PC tends to decrease with increasing whisker content (Fig. 7). It is evident from eq. (4) that the decrease in T_g associated with the decomposition of PC could lead to a lower σ_p. Finally, the stress of a short-fiber-reinforced composite (σ_c) can be expressed as[26,27]

$$\sigma_C = V_f \sigma_f \frac{l}{2l_c} + (1 - V_f)\sigma_P \quad \text{for } l \le l_c \tag{5}$$

where V_f and σ_f are the volume fraction and stress of short fiber, and l and l_c are the length and the critical length of fiber, respectively. Combining eqs. (4)–(5) and the thermal analysis data of PC–whisker composites, we conclude that $K_2Ti_6O_{13}$ whisker with high strength reinforces PC via the σ_f factor, but it also reduces the value of σ_p, owing to chemical decomposition of PC. As the degree of degradation of PC increases with increasing $K_2Ti_6O_{13}$ whisker content, the tensile strength decreases sharply with increasing whisker content for PC–$K_2Ti_6O_{13}$ composites. On the other hand, PC degrades more slowly with increasing $Al_{18}B_4O_{33}$ whisker content, particularly when the whisker content reaches 10 wt % and above. In this case, the higher the whisker content, the higher the tensile strength of composites is (Fig. 1).

Morphology

Figure 10 shows the SEM micrographs of both aluminum borate and potassium titanate whiskers. These micrographs reveal that both aluminum borate whiskers and potassium titanate whiskers exhibit a large aspect ratio owing to their small diameter. Figure 11 show the typical SEM fractographs of PC–$Al_{18}B_4O_{33}$ (85/15) composite. This composite specimen fabricated by injection-molding exhibits a skin–core structure.

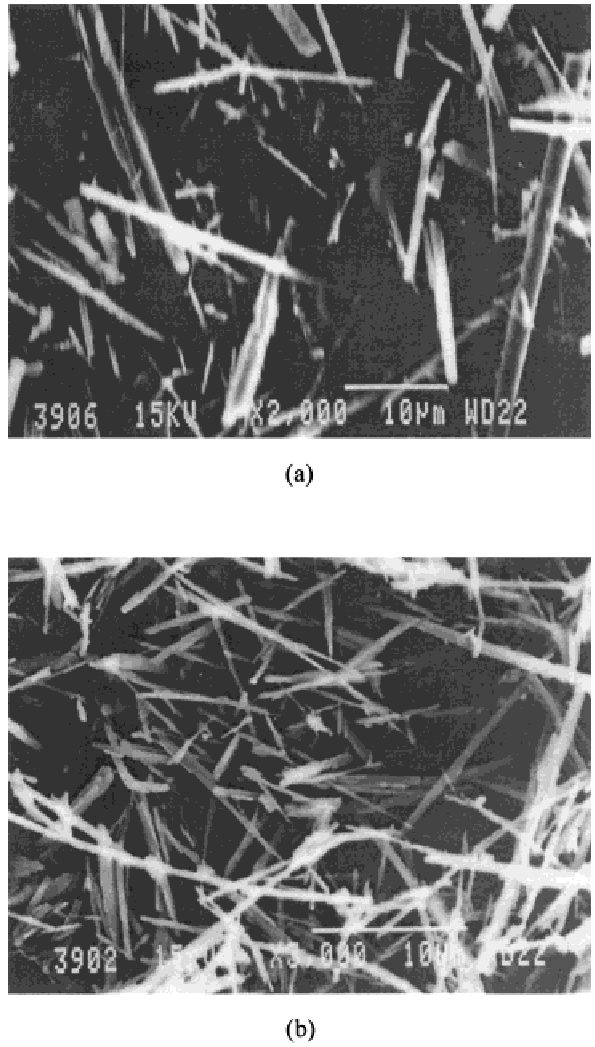

Figure 10 SEM micrographs of (a) $Al_{18}B_4O_{33}$ and (b) $K_2Ti_6O_{13}$ whiskers.

These fractographs indicate that the whiskers are well oriented in the skin sections, whereas the whisker tends to orient randomly in the core region.

CONCLUSION

Static tensile measurements showed that the modulus of PC–$Al_{18}B_4O_{33}$ composites increased markedly with increasing whisker content. However, the tensile stress of the composite decreased slightly with the addition of 5 wt % whisker; thereafter, it increased slowly with increasing whisker content. DTA and TGA results indicated that the glass transition temperature (T_g) and 5%

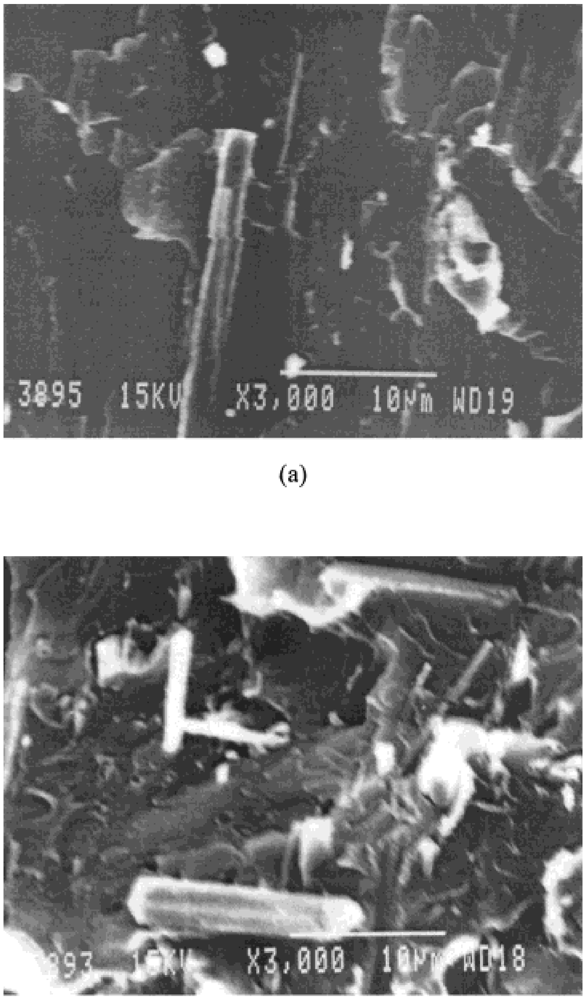

Figure 11 Fractographs of the (a) skin section and (b) core section for PC–15 wt % $Al_{18}B_4O_{33}$ whisker composite.

weight loss temperature ($T_{-5\%}$) of the composite shift sharply to lower temperature regimes with the addition of $Al_{18}B_4O_{33}$ whiskers up to 10 wt %. Thereafter, the T_g and $T_{-5\%}$ of PC–$Al_{18}B_4O_{33}$ composites tended to decrease slowly with increasing whisker content. The mechanical and thermal properties of PC–$Al_{18}B_4O_{33}$ composites were compared with those of PC–$K_2Ti_6O_{13}$ composites. In general, aluminum borate whiskers were found to be more effective to reinforce PC than potassium titanate whiskers. This was due to aluminum borate whisker additions do not promote extensive decomposition of PC during compounding.

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