Mechanical and Thermal Properties of Poly(acrylonitrile–butadiene–styrene) Copolymer Reinforced with Potassium Titanate Whiskers

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ABSTRACT: Potassium titanate ($K_2Ti_6O_{13}$) whisker treated with tetrabutyl orthotitanate was used to improve the mechanical and thermal properties of the poly(acrylonitrile–butadiene–styrene) (ABS) copolymer. The composites were prepared in a twin-screw extruder followed by injection molding. Static tensile measurements showed that both the modulus and breaking stress of ABS/$K_2Ti_6O_{13}$ composites increase considerably with increasing whisker content; the strain at break of ABS was almost unaffected by the incorporation of a whisker content up to 15 wt %. Izod impact tests indicated that the composites showed a decrease in the impact strength with increasing whiskers content. Thermogravimetric analysis showed that the $K_2Ti_6O_{13}$ whisker additions have little effect on the thermooxidative stability of ABS. Scanning electron microscopic observations revealed that the whiskers were aligned along the melt-flow direction in the thin surface layer, whereas the whiskers were oriented randomly as well as perpendicular to the injection direction in the thick core region of the composites. The Tsai–Halpin equation was used to evaluate the moduli of the ABS/$K_2Ti_6O_{13}$ composites. The theoretical calculations generally correlated well with the experiment data by assuming $K_2Ti_6O_{13}$ whiskers to have an aspect ratio of 12. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2985–2991, 1999

Key words: ABS; whisker; composite; stiffness; potassium titanate

INTRODUCTION

The acrylonitrile–butadiene–styrene (ABS) copolymer is a very successful rubber-toughened thermoplastic and has several attractive properties such as good processability, notch insensitivity, and low cost. So, ABS plastic has applications in sporting goods, home appliances, and electronic equipment, for example, in protective helmets, telephone switchboard panels, and screwdriver handles.[1] Furthermore, it is also widely used as a component material in the automotive industry because its surface finishes are relatively smooth and can be easily decorated. However, ABS has certain limitations, namely, low thermal stability and poor flame and chemical resistance. These shortcomings can be overcome by the incorporation of short fibers and fillers into ABS.[2–4]

Whiskers are generally known to exhibit high stiffness and strength. Their strengths are close to the maximum theoretical value expected from the theory of elasticity.[5] This is because whiskers are nearly free from internal flaws, owing to their small diameter. In this respect, whiskers have a specific advantage in compounding or molding, as there is less whisker breakage during processing than is experienced with large diameter fibers.

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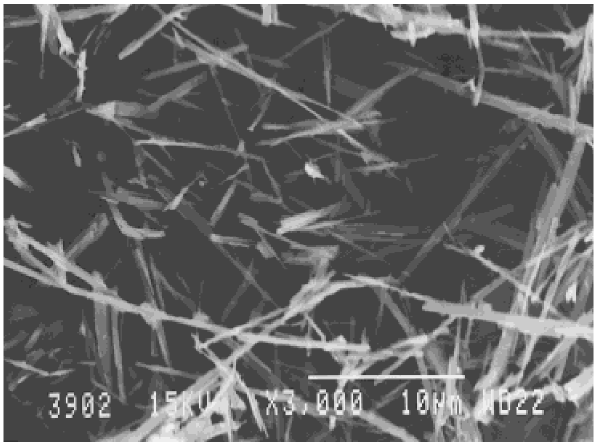

Figure 1 SEM micrograph of $K_2Ti_6O_{13}$ whiskers.

Moreover, whiskers can be well dispersed into a very thin or narrow region, thereby allowing one to manufacture smaller precision parts. These precision parts generally possess high strength, stiffness, and thermal stability and a smooth surface. For these reasons, whiskers have been used extensively as reinforcement materials in ceramic matrix composites, metal matrix composites, and polymer matrix composites.[6–20] The inorganic whiskers used include silicon carbide (SiC), potassium titanate ($K_2Ti_6O_{13}$), and aluminum borate ($Al_8B_4O_{33}$). Among these, SiC whiskers are used extensively in many reinforcement applications owing to their superior mechanical and physical properties.

However, the cost of SiC whiskers remains relatively high. Therefore, much effort has been spent by researchers in attempts to produce low-cost inorganic whiskers. For example, Suganuma et al.[15] reported that the price of potassium titanate whiskers ranges from one-tenth to one-twentieth of the cost of SiC whiskers. In this regard, it is more cost effective to use potassium titanate whiskers as reinforcement materials for polymer composites.

According to the literature,[21] property improvements with potassium titanate microfibers are comparable to those with glass fibers at equal loadings. Microfibers are discontinuous fibrous materials that range from 0.1 to 10.0 μm in diameter and approximately 30 μm in length and are polycrystalline or amorphous in structure. They are generally produced by fiber throwing or precipitation from solution. These processes produce fibrous products that generally contain many internal defects.[21] Hence, microfibers do not possess high mechanical strength as whiskers do. The stiffness of tinanate microfiber-reinforced plastic is generally higher than that of glass-fiber composites because the elastic moduli of titanates are more than four times that of glass fiber. More recently, we successfully incorporated potassium titanate whiskers into polyamide-6 (PA6) and polypropylene (PP) for the purposes of upgrading their mechanical and thermal performances. The experimental results showed 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] However, potassium titanate whiskers are found to be ineffective reinforcement materials for polycarbonate (PC) because these whiskers promote the chemical decomposition of PC during compounding.[22]

In general, the mechanical properties of filler-reinforced polymeric composites depend significantly on the interfacial adhesion between the polymer matrices and the reinforcing components. Therefore, surface treatments for fillers have been adopted in order to improve the interfacial interactions. For instance, the filler surface is treated with coupling agents such as "silane-" and "titanate"-based compounds[23,24] whose chemical structures allow them to react with both fillers and the polymeric matrix. The interfacial layer is formed via chemical bonds among the coupling agent, filler, and polymer matrix, thereby allowing a better shear-stress transfer between the fillers and the matrix. Consequently, the mechanical properties of the composites are dramatically improved. In this article, we attempted to use potassium titanate whiskers to reinforce ABS and to investigate the mechanical and thermal properties of the resultant composites.

EXPERIMENTAL

Materials

The ABS (type 100) used in this study was produced by Toray Plastics (Malaysia). This copolymer exhibits a melt-flow index of 13 g/10 min, a heat-deflection temperature of 87°C, a yield strength of 500 kg/mm^2, and a strain of break of 20%. Potassium titanate ($K_2Ti_6O_{13}$) whiskers were supplied by the Jinjian Composite Co. (Shenyang, China). The whiskers have a diameter range from 0.5 to 1.0 μm and exhibit a Mohs' hardness of 4. Their strength and stiffness are 7 and 280 GPa, respectively. Reagent-grade tet-

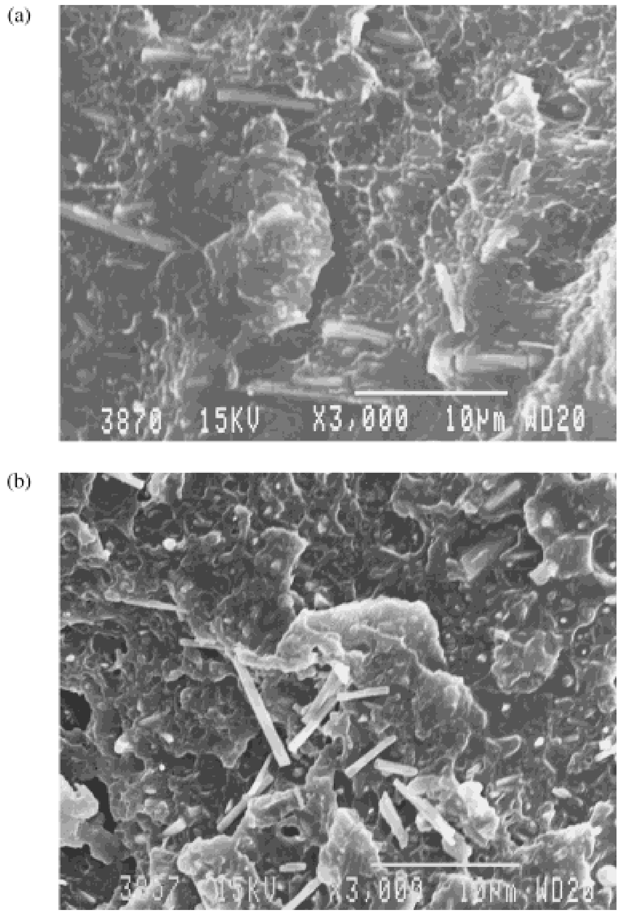

Figure 2 Fractographs of (a) thin skin layer and (b) thick core region for ABS/15 wt % $K_2Ti_6O_{13}$ composite.

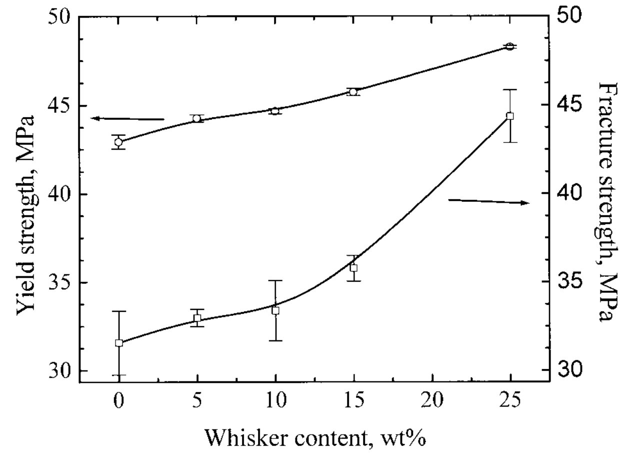

Figure 3 Variation of tensile strength with whisker content for ABS/ $K_2Ti_6O_{13}$ composites.

rabutyl orthotitanate was purchased from Fluka Chemie (Switzerland) and was used as the coupling agent for potassium titanate whisker.

Sample Preparation

Tetrabutyl orthotitanate was initially dispersed in acetone to form a 5 wt % solution. The solution was slowly poured into the whiskers and sufficiently blended by hand in a plastic box. 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 25 wt % whiskers were prepared in a twin-screw Brabender Plasticorder at 245°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 temperatures were set at 240, 245, and 240°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 reported.

Izod impact specimens with dimensions of 65 $\times$ 13 $\times$ 3.2 mm were cut from the midsection of the tensile bars. These specimens were sharply

Table I Effect of Tetrabutyl Orthotitanate Treatment on the Mechanical Properties of Composites

Sample	ABS	Untreated ABS/25 wt % $K_2Ti_6O_{13}$	Treated ABS/25 wt % $K_2Ti_6O_{13}$
Yield strength (MPa)	42.9 ± 0.4	46.0 ± 0.2	48.3 ± 0.1
Tensile strength at break (MPa)	31.6 ± 2.2	39.9 ± 1.1	44.4 ± 1.5
Young's modulus (MPa)	1372 ± 11	2103 ± 6	2365 ± 9
Strain at break (%)	16.4 ± 2.2	9.7 ± 1.3	6.5 ± 1.1
Impact strength (kJ/m^2)	18.3 ± 0.7	3.9 ± 0.2	3.9 ± 0.2

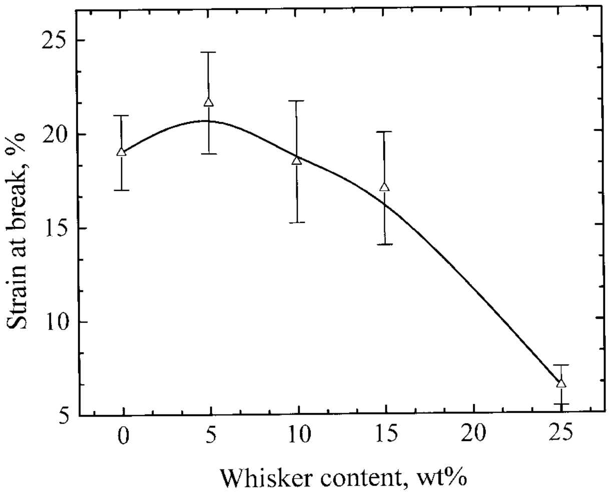

Figure 4 Variation of tensile strain at break with whisker content for ABS/$K_2Ti_6O_{13}$ composites.

notched with a V-shape knife. The radius of curvature for the notch was 0.025 mm. They were tested using a Ceast impact pendulum tester. At least five specimens were tested and the average values reported.

Dynamic mechanical analysis (DMA) of the injection-molded rectangular specimens with dimensions of 65 $\times$ 13 $\times$ 3.2 mm were conducted using a DuPont dynamic mechanical analyzer (Model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.4 mm. The mechanical properties were determined from 25 to 125°C with a heating rate of 4°C min^{-1}.

Thermal Analyses

Weight loss of ABS and its composites from 40 to 600°C was determined with a Seiko thermogravimetric analyzer (Model SSC/5200) at a rate of 10°C min^{-1} in a helium atmosphere. This instrument was also equipped with a differential thermal analyzer (DTA). The glass transition temperature (T_g) of the specimens was determined by DTA.

Morphological Observation

The morphologies of the surfaces of the blends and $K_2Ti_6O_{13}$ whiskers were observed in a scanning electron microscope (SEM, JEOL JSM 820). The blend specimens were cryofractured in liquid nitrogen. All the samples were coated with a thin layer of gold prior to SEM observations.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows an SEM micrograph of potassium titanate whiskers. This micrograph reveals that potassium titanate whiskers exhibit a large aspect ratio owing to their small diameter. Figure 2(a,b) shows SEM fractographs of the surface-treated ABS/15 wt % $K_2Ti_6O_{13}$ injection-molded composite. The fractographs indicate that the whiskers are oriented along the melt-flow direction in the thin skin layer of the composite, whereas the whiskers are oriented randomly as well as perpendicular to the injection direction in a thick core region. Some broken whiskers and considerable whisker pullout are evident in these fractographs. In the case of untreated $K_2Ti_6O_{13}$ whiskers, extensive whiskers pullout is observed.

Effects of Coupling Agent

In general, there are two approaches commonly applied to enhance the chemical/physical interaction between the reinforcements and polymeric matrices. The first route consists of the modification of the polymeric matrix structure via various chemical reactions, while the second approach employs coupling agents to modify the chemical nature of the filler surface. In this work, tetrabutyl orthotitanate was used as the surface modifier for potassium titanate whiskers. The typical mechanical properties of ABS and tetrabutyl orthoti-

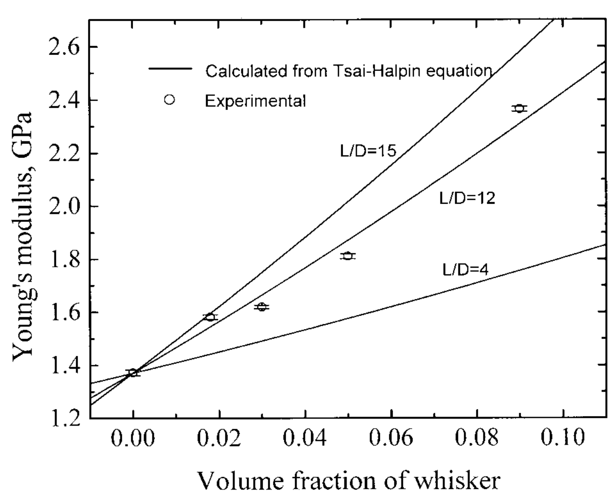

Figure 5 Variation of the Young's modulus with whisker content for ABS/$K_2Ti_6O_{13}$ composites. The modulus predicted by the Tsai–Halpin equation is also shown for the purpose of comparison.

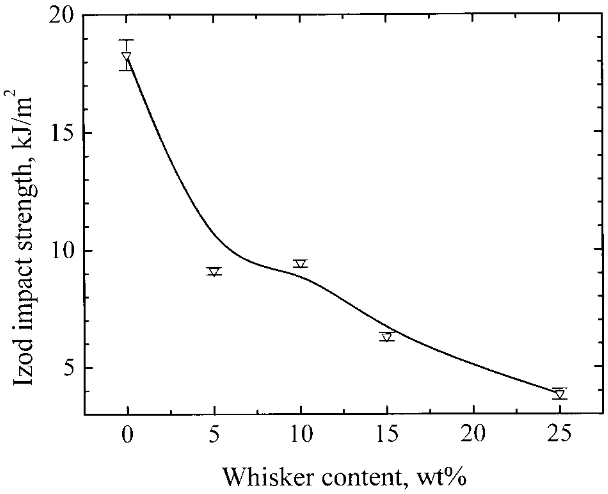

Figure 6 Variation of Izod impact strength with whisker content for ABS/$K_2Ti_6O_{13}$ composites.

tanate treated as well as untreated ABS/25 wt % $K_2Ti_6O_{13}$ composites are summarized in Table I. The results apparently indicate that tetrabutyl orthotitanate-treated whisker-reinforced composites exhibit much higher tensile strength and Young's modulus than those of the composite reinforced with untreated whiskers.

Mechanical Properties

Figure 3 shows the variations of the yield and fracture strengths with whisker content for the ABS/$K_2Ti_6O_{13}$ whisker composites. It reveals that

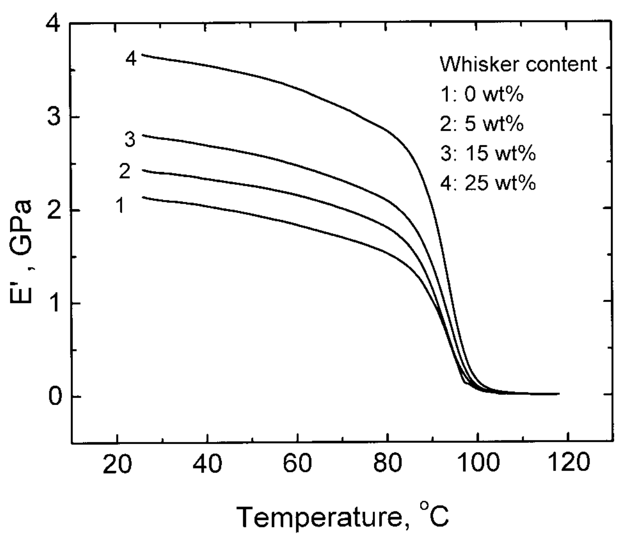

Figure 7 Storage modulus spectra for ABS and ABS/$K_2Ti_6O_{13}$ composites.

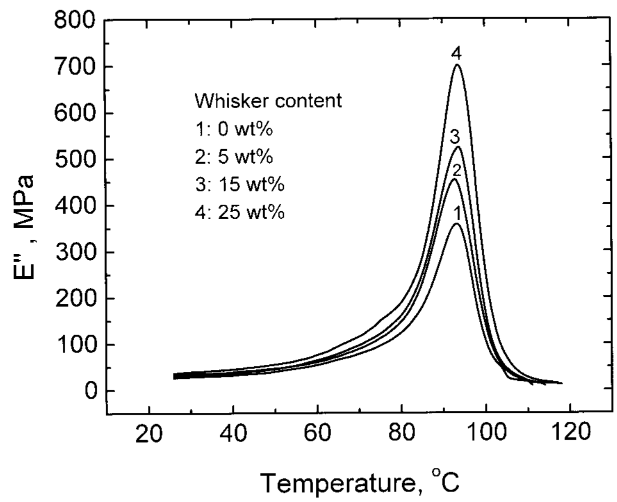

Figure 8 Loss modulus spectra for ABS and ABS/$K_2Ti_6O_{13}$ composites.

the yield strength of the ABS/whisker composites increases considerably with increasing whisker content. For the composite containing 25 wt % whiskers, the yield stress is 12.4% higher than that of the unreinforced polymeric matrix. The variation of strain at break of ABS/$K_2Ti_6O_{13}$ whisker composites with whisker content is depicted in Figure 4. It is noticed that the strain and stress at break are approximately constant up to 15 wt % whiskers. Afterward, the stress at break increases markedly with increasing whisker content (Fig. 3), whereas the strain at break drops sharply with increasing whisker content (Fig. 4). On the other hand, the Young's modulus of the composites tends to increase with increasing whisker content (Fig. 5).

We now attempt to correlate the stiffness data as shown in Figure 5 with theoretical predictions. The relationships most commonly used to predict the elastic modulus of a discontinuous short fiber-reinforced composite from the moduli of the individual components is the Tsai–Halpin equation,[25,26] which is based on the assumption of continuity of stress and strain along the fiber/matrix interface. The equation is given as follows:

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

where E_c and E_m are the elastic moduli of the composite and matrix, respectively, φ_r is the volume fraction of the short fibers, and η is given by

$$\eta = \frac{E_f - E_m}{E_f + \xi E_m} \tag{2}$$

Table II Thermal Properties of ABS and Its Composites

Specimen	$T_{E'=1.27}$ (°C)	T_g (°C)	$T_{-5\%}$ (°C)	T_{max} (°C)
ABS	87	102.2	381.4	417.0
ABS/5 wt % $K_2Ti_6O_{13}$	89	102.1	381.6	419.2
ABS/10 wt % $K_2Ti_6O_{13}$	90	102.5	381.7	420.9
ABS/15 wt % $K_2Ti_6O_{13}$	91	102.5	381.7	419.4
ABS/25 wt % $K_2Ti_6O_{13}$	93	102.1	384.9	420.1

where E_f is the modulus of the fibers and ξ is a constant associated with the aspect ratio L/D (length/diameter) and orientation of the fibers in the polymer matrix. The volume fraction φ_f of the fibers is defined as[27]

$$\varphi_f = \frac{W_f \rho_m}{W_f \rho_m + (1 - W_f)\rho_f} \tag{3}$$

where W_f, ρ_f, and ρ_m refer to the weight fraction of the fibers, the density of the fibers, and the density of the matrix, respectively. For ABS/$K_2Ti_6O_{13}$ composites, ρ_m = 1.04 (g/cm^3), E_m =1.37 (GPa), ρ_f = 3.3 (g/cm^3), and E_f = 280 (GPa). Scanning electron microscopic observations (Fig. 2) reveal that the whiskers in the ABS matrix are generally oriented along the melt-flow direction in the thin skin layer of the composites, whereas the whiskers tend to orient randomly in the thick core region. For randomly oriented discontinuous fiber-reinforced composites, ξ has different values dependent upon the aspect ratio of the reinforcement materials,[26] that is, $\xi = 2.08$ if $L/D = 4$, $\xi = 6.20$ if $L/D = 12$, and $\xi = 8.38$ if $L/D = 15$. The theoretical predictions, based on the Tsai–Halpin equation using various aspect ratios, are also shown in Figure 5 for the purpose of comparison. It can be seen that the experimental data correlate well with the theoretical prediction when $L/D = 12$. This aspect ratio is less than that of the actual $K_2Ti_6O_{13}$ whiskers prior to extrusion, that is, $\approx$ 30. This is because some $K_2Ti_6O_{13}$ whiskers are broken during blending with ABS as confirmed by SEM fractographs (Fig. 2). On the basis of SEM observations, our assumption of the aspect ratio $L/D = 12$ in the Tsai–Halpin equation seems reasonable for the estimation of the stiffness of ABS composites reinforced with mostly random-oriented whiskers.

Figure 6 shows the relationships between the Izod impact strength and the whisker content for the ABS/$K_2Ti_6O_{13}$ composites. The results indicate that the impact strength decreases with increasing whisker content. Figures 7 and 8 show the storage and loss moduli versus temperature for the ABS/$K_2Ti_6O_{13}$ composites. The figures reveal that both the storage and loss moduli increase considerably with increasing whiskers content. In addition, Figure 8 also indicates that the shape of the loss modulus peak almost remains unchanged with increasing whisker content. This result implies that the addition of $K_2Ti_6O_{13}$ whisker does not change the molecular structure of the ABS matrix during mixing. On the other hand, Tjong and Meng found that $K_2Ti_6O_{13}$ whiskers promoted the chemical decomposition of PC during compounding.[22]

Thermal Properties

As mentioned above, the heat-deflection temperature of ABS is 87°C. At this temperature, the storage modulus (E') of ABS equals 1.27 GPa (Fig. 5). To evaluate the heat resistance of the composites, we define the temperature at E' = 1.27 GPa as $T_{E'=1.27}$. Table II lists the $T_{E'=1.27}$ values for the ABS copolymer and its composites. The T_g of these specimens as determined by DTA are also tabulated. It is evident that $T_{E'=1.27}$ increases slowly with increasing whisker content. This behavior can be attributed to the amorphous structure of ABS and to the heat-deflection temperature of ABS (87°C) being somewhat lower than its glass transistion temperature (102°C). Consequently, the moduli of both ABS and its composites tend to drop sharply with increasing temperature as the temperature approaches the glass transition temperature of ABS. On the contrary, the storage modulus of crystalline polymers such as polyamide and PP is less affected by the temperature increment, particularly near the T_g and its vicinity. Therefore, the heat-resistance temperatures of $K_2Ti_6O_{13}$ whisker-reinforced PA and PP appear to increase rapidly with increasing whisker content.[19,20] From Table II, it is noted that the glass transition temperature for the ABS/$K_2Ti_6O_{13}$ compos-

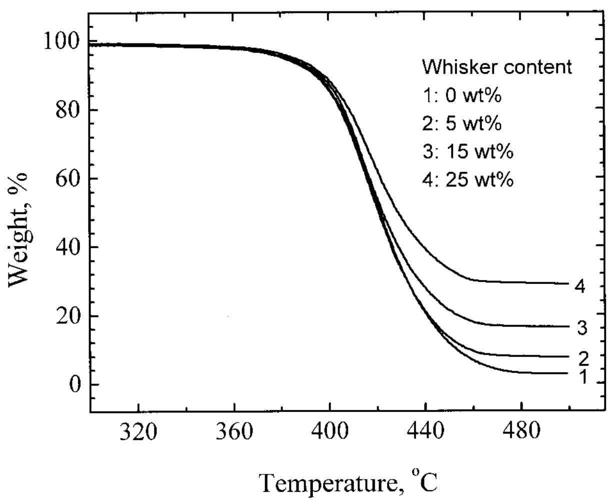

Figure 9 Weight loss versus temperature for ABS and ABS/ $K_2Ti_6O_{13}$ composites.

ite remains nearly unchanged with increasing whisker content, indicating that the $K_2Ti_6O_{13}$ whisker additions do not change the molecular structure of the ABS matrix during mixing. This result is in good agreement with the DMA measurement.

Figure 9 shows the weight loss versus temperature for the ABS matrix and its composites. The 5 wt % loss temperatures ($T_{-5\%}$) and maximum weight loss temperature $T_{\max}$ for these samples are also tabulated in Table II. The values of $T_{-5\%}$ and $T_{\max}$ for the ABS/whisker composites increase slowly with increasing whisker content. These results demonstrate that the $K_2Ti_6O_{13}$ whisker addition has little effect on the themooxidative stability of ABS.

CONCLUSIONS

The mechanical and thermal properties of ABS can be improved by the addition of $K_2Ti_6O_{13}$ whiskers. The fracture stress of the composite containing 25 wt % $K_2Ti_6O_{13}$ whiskers is 41% higher than that of the unreinforced ABS copolymer. In addition, the surface appearances of ABS/ $K_2Ti_6O_{13}$ whiskers composites are relatively smooth. Therefore, the introduction of $K_2Ti_6O_{13}$ whiskers into ABS can further extend the use of ABS for industrial applications.

The variation of the modulus of ABS/$K_2Ti_6O_{13}$ composites with the whisker content generally correlate well with Tsai–Halpin equation by assuming that $K_2Ti_6O_{13}$ whiskers to be randomly oriented and to have an aspect ratio of 12. SEM observations indicate that this assumption is appropriate to estimate the stiffness of whisker-reinforced composites.

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