December 2009 Volume 3 Issue 2

Trade Science Inc.

Nano Science and Nano Technology
An Indian Journal

Full Paper

NSNTAIJ, 3(2), 2009 [13-20]

Effect of T-ZnOw on the mechanical properties and morphology of PC/T-ZnOw composites

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Received: 9th December, 2009 ; Accepted: 19th December, 2009

ABSTRACT

In this work, the effects of treatment of tetra-needle-shaped zinc oxide whisker (T-ZnOw) on the mechanical properties and morphology structure of polycarbonate (PC) and PC/T-ZnOw composites were investigated by mechanical property test, scanning electron microscope (SEM), Fourier transform infrared (FTIR), and X-ray diffraction (XRD) analysis. The results show that untreated T-ZnOw seriously deteriorates the mechanical properties of PC, especially the impact strength due to the weak interfacial adhesion and poor compatibility between PC matrix and T-ZnOw. However, Young's Modulus of the composites with untreated or treated T-ZnOw gradually increases with increasing the content of the whiskers. Compared with the composites filled with untreated T-ZnOw, the treatment of T-ZnOw could remarkably improve the tensile and impact strength of PC/T-ZnOw composites due to the enhanced interfacial adhesion between polymer matrix and the whiskers. No new absorption peak is detected by FTIR. The results of XRD patterns show that T-ZnOw has little effect on the crystalline behaviors of PC, which indicates PC/T-ZnOw composites consist of two phase structures.

KEYWORDS

Polycarbonate;
T-ZnOw;
Composites;
Mechanical properties.

INTRODUCTION

Over the past decade in research and development, a great deal of attention has been paid to polymer matrix composites, especially polymer–filler composites. Polymer/fillers composites represent an attractive alternative to conventional filled polymer, because of their improved properties and potential of becoming a new class of high performance engineering materials[1-7]. The purpose of adding inorganic fillers are used to carry out a functional rule, such as increasing dimension stability, flame retardancy, hardness and toughening of polymer[8-11]. The properties of particulate filled polymer composites depend on the shape, particle size, loading, and distribution of filler particles in the polymer matrix and adhesion at the interface surface[12-15]. The interfacial interaction between polymer matrix and filler has influences on the physical, mechanical, and thermal properties of polymer. Ma et al.[16] investigated the effects of zinc oxide (ZnO) on the electrical and physical characteristics of the polystyrene (PS) composites. It was reported that ZnO improved the flexural modulus and reduced the flexural strength. The addition of coupling agents improved the flexural properties of the PS composites. The glass-transition temperatures and thermal degradation temperatures of the PS/ZnO composites increased with increasing the ZnO content. Chae et al.[17] also prepared PS/ZnO composites by solution mixing and studied the effects of ZnO on the physical properties of PS matrix. The results showed that the thermal stability of the PS matrix was improved with increasing the content of ZnO.

Polycarbonate (PC), as an engineering plastic, has recently attracted the attention of technologists because of the advantages that it provides over conventional materials, namely, the excellent combination properties of stiffness, strength, impact resistance, and transparency[18]. The mechanical properties, morphology, crystallization behavior, and color formation as well as thermal stability of PC/filler composites have been studied extensively. Results demonstrate that compounding with fillers is a feasible approach to enhance the tensile strength and Young's Modulus of PC matrix in contrast to that of pure PC, although the addition of clay leads to a decreased thermal stability and impact strength of PC matrix[19-21]. According to Carrio'n et al.[22,23], using small loadings of ZnO in PC matrix reduces both the wear rate and frictional coefficient of PC. The enhancement of PC properties is considered attractive in commercial products such as sporting goggles, automobile parts, audio discs, and so on.

Tetra-shaped zinc oxide whisker (T-ZnOw) has recently been the main subject of many researches because of its special spatial structure: four needles grow from one point and the angle degree between two needles is 109°28′[24,25]. It possesses good properties such as high strength, good wear resistance, microwave absorption, and antibacterial properties, etc. Recently, T-ZnOw has been widely used as both functional and structural materials[26-28]. In this work, T-ZnOw was dispersed into the PC matrix, and the influence of treatment of T-ZnOw on the mechanical properties, morphology, and structure of the PC/T-ZnOw composites were also discussed in detail.

EXPERIMENTAL

Materials

The materials used in this study were obtained from commercial products. Polycarbonate (PC) was supplied in trade name of PC–L1225L by Teijin Chemicals Ltd. (Japan). Tetra-needle-shaped zinc oxide whisker (T-ZnOw, density: 5.78g/cm^3) was prepared as our earlier reports[29]. Figure 1 showed the typical morphological structure of T-ZnOw, which indicates the whiskers have a typical three-dimensional tetra-needle-shaped structure. The length and basal diameter of the needles of the whiskers are about 15–20 and 1.5–6.6μm, respectively. Silane coupling agents, (3-glycidoxypropyl) trimethoxysilane (KBM803, density: 1.065–1.072g/cm^3, boiling point: 290°C) was obtained from Japan.

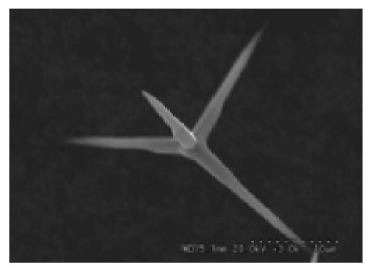

Figure 1 : The typical SEM morphology of T-ZnOw.

Surface treatment of T-ZnOw

The surface treatment of T-ZnOw was fulfilled as following steps: Firstly, the T-ZnOw was dried at 120°C for 16 h; Secondly, a certain amount of surface treatment agent was dissolved in ethanol and acetone; Thirdly, the solution was mixed with the powders of T-ZnOw, under stirring at 500 r/min for 3 h at 80°C; Finally the temperature of the mixture was increased up to 150°C, and the mixture was further stirred until ethanol and acetone was evaporated completely. The surface treated T-ZnOw was dried at 120°C for 16 h in a vacuum oven.

Preparation of samples

The PC/T-ZnOw composites were melt-compounding in desired compositions by using a Mixer-extruder (TSSJ-25) with the barrel temperature of 290°C and a screw speed of 90rpm. In this work, the loading of T-ZnOw was from 0 to 10 wt%. The content of coupling agent was 2 wt% of T-ZnOw. After blending adequately, the PC/T-ZnOw composites were injected into a mould of 4.2mm in thickness and 10.0mm in width for measurements and characterization.

Measurements and characterization

Mechanical properties

The tensile test of samples was performed at room temperature with a crosshead speed of 10 mm/min on a Material Test instrument (Model JIS K7113, Instron Co. Ltd. Series 3360). The dimensions of specimens were 30×5×2mm.

Notched impact test was performed according to the Chinese regulation GB1048 on a drop weight impact tester (Model ZBC-4B, made in Shenzhen, China). The dimensions of specimens were 60×10×4 mm. The notched depth is 2 mm and notch tip radius is 0.25mm.

Morphology

The morphology of the tensile fracture surfaces of samples were observed by a scanning electron microscopy (SEM) (Model high-technologies CO., S-4300). Gold sputter coated samples were examined using a Cambridge Stereoscan 250 with an accelerating voltage of 10 kV.

Fourier transform infrared spectrometer (FTIR)

Fourier transform infrared spectrometer (FTIR) (Nicolet 5700, America) was used to characterize the chemical absorption of pure PC and PC/T-ZnOw composites. The powders of PC and PC/T-ZnOw composites were mixed with KBr powders, and then the mixture was compressed into plates for FTIR spectra analysis.

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) spectra were collected on a Panalytical X'Pert PRO diffractometer (CuKα radiation, λ=1.54A°), equipped with computerized data collection and analytical tools. The X-ray source was operated at a voltage of 40kV and a filament current of 40mA. Samples were scanned in 2θ ranges from 5 to 90°.

RESULTS AND DISCUSSION

Tensile properties

Owing to the different shapes of inorganic fillers, their effects on the mechanical properties are different. In this work, the tensile strength and Young's Modulus of the PC/T-ZnOw composites with and without coupling agent as a function of composition are represented in figures 2 and 3. Adding inorganic particles into polymers often decreases the strength of the composites except for stiffening effect. When the interaction between polymer matrix and fillers is poor, tensile strength of composites is lower than that of pure polymer[30]. It is obviously seen from figure 2 that the values of the tensile strength decreased with increasing the untreated T-ZnOw content and, hence, untreated T-ZnOw does not improve the tensile strength of the PC composites prepared by extruder molding. The observed reduction in the tensile strength is mainly due to the poor compatibility between whiskers and the matrix in PC/T-ZnOw composites. On the other hand, compared with the PC/T-ZnOw composites with untreated T-ZnOw, the tensile strength of the PC composites with T-ZnOw treated by 2 wt% KBM803 exhibits different characters. The tensile strength gradually increases with increasing the treated T-ZnOw content, and then the value of the tensile strength decreases with further increasing the content of treated T-ZnOw. Although the tensile strength of PC/T-ZnOw/KBM803 composites decreases when the treated T-ZnOw content is above 6 wt%, the values of the tensile strength are higher than these of pure PC and PC/T-ZnOw composites without surface treatment agent. This indicates that the tensile strength of PC/T-ZnOw composites is greatly improved by using the coupling agent.

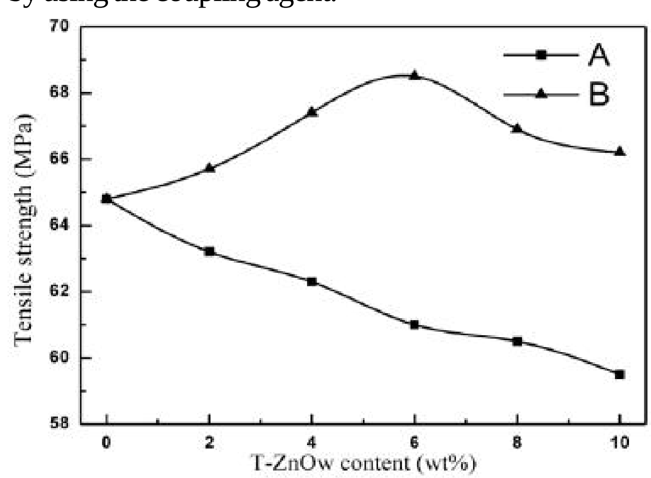

Figure 2 : Effect of T-ZnOw content on the tensile strength of PC/T-ZnOw composites: (A) Untreated T-ZnOw; (B) Treated T-ZnOw (T-ZnOw/KBM803=98/2).

Young's Modulus of the PC/T-ZnOw composites with untreated and treated T-ZnOw is showed in figure 3. Young's Modulus of PC/T-ZnOw composites with untreated and treated T-ZnOw increased with increasing the T-ZnOw content. In other words, addition of T-ZnOw endows PC/T-ZnOw composites better stiffness. This may be due to the increased interfacial area in the composites with the addition of whiskers. It is easy to be understood since the better interfacial interaction between PC matrix and whiskers is facilitated the stress transference from the matrix to whiskers in the initial stage during the tensing process. These results indicate that the addition of untreated or treated T-ZnOw can improve the rigidity of pure PC, which has much application on the engineering of plastic.

Impact strength

In this part, the effects of untreated and treated T-ZnOw on the notched impact strength of PC/T-ZnOw composites were discussed, and the results were showed in Figure 4. It can be seen from figure 4 (A) that the impact strength of PC/T-ZnOw composites with untreated whiskers decreases dramatically with increasing the content of untreated T-ZnOw, and then almost levels off with increasing up to T-ZnOw content of 6 wt%. These results are similar to previous observations on the mechanical properties of some polymer/rigid fillers dispersions[31], which indicates that rigid fillers have a negative effect on ductility and tensile strength. As the untreated T-ZnOw content increases, the composites exhibit higher Young's Modulus but lower impact strength. This suggests that the addition of untreated T-ZnOw with the special spatial structure as defects leads to the decrease of the impact strength of the PC composites.

Our previous studies[31-33] showed that it is necessary to improve the toughness of polymer-filler composites due to the poor interfacial adhesion between filler particles and polymer matrix. Silane coupling agent, (3-glycidoxypropyl) trimethoxysilane was firstly used to treat T-ZnOw. It can be seen from figure 4 (B) that the impact strength of PC/treated T-ZnOw composites still decreases with the addition of treated T-ZnOw, however, compared with PC/untreated T-ZnOw composites, PC/treated T-ZnOw composites show higher impact strength. For example, with increasing up to whiskers content of 8 wt%, the impact strengths of PC/T-ZnOw composites with and without coupling agent are 10 and 6.3kJ/m^2, respectively. It seems that the surface treatment agent is in favor of improvement for the toughness. A significant improvement in the impact strength of the PC composites is observed due to the increased energy absorption during impact process[34].

Morphology observation

In order to elucidate the effect of untreated and treated T-ZnOw on the mechanical properties of PC/T-ZnOw composites, SEM images of the tensile fractured surface of the PC composites were investigated, and the results were exhibited in figures 5-7. From fig-

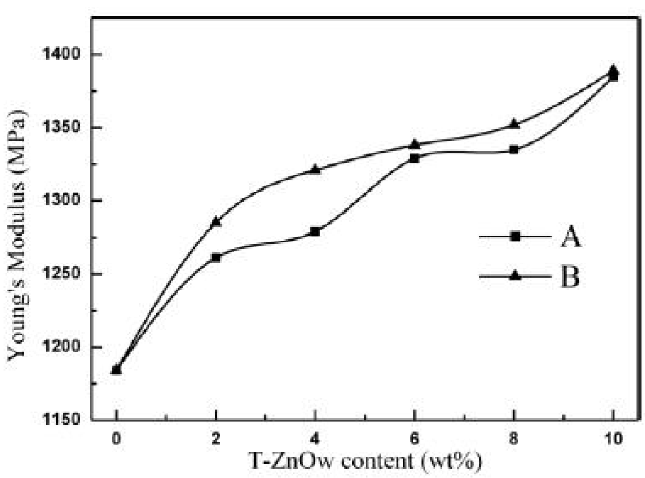

Figure 3 : Effect of T-ZnOw content on the tensile Young's modulus of PC/T-ZnOw composites: (A) Untreated T-ZnOw; (B) Treated T-ZnOw (T-ZnOw/KBM803=98/2).

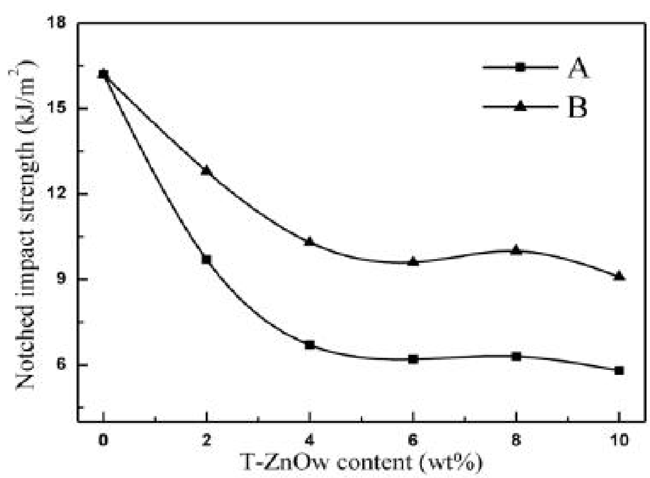

Figure 4 : Effect of T-ZnOw content on the impact strength of PC/T-ZnOw composites: (A) Untreated T-ZnOw; (B) Treated T-ZnOw (T-ZnOw/KBM803=98/2).

ures 5 and 6, it can be seen that the surfaces of untreated T-ZnOw without any coverage in the PC matrix are very smooth. Moreover, the interfaces between the PC matrix and T-ZnOw are very clear and no any blocking can be observed. This indicates that the interfacial adhesion and compatibility between the PC matrix and untreated T-ZnOw are very poor. The poor interfacial interaction leads to the decrease of mechanical properties.

From the micrographs of bulk specimens (Figures 5 and 6), it can be seen that the distribution of T-ZnOw is hardly uniform in PC matrix. At the same time, a small quantity of T-ZnOw agglomeration phenomena occurred in the PC composites. Most whisker needles are broken at the center crosspoint of T-ZnOw and some cavities formed, which could be seen on the fracture surfaces. In addition, the fractured surface of PC displays the sites from which T-ZnOw are pulled out during elongation and some exposed whiskers. This may be associated with absence of specific interfacial adhesion and the hardness of T-ZnOw. All these indicate that the PC composites loading with untreated T-ZnOw have low tensile strength.

In order to better understand the effect of surface treatment agent on the tensile fracture morphology, SEM images of PC/T-ZnOw composites with treated T-ZnOw have been focused on the tensile fracture surface region, and as shown in figure 7. Compared with untreated T-ZnOw filled PC composites, after being treated by surface treatment agent, the interfacial adhe-

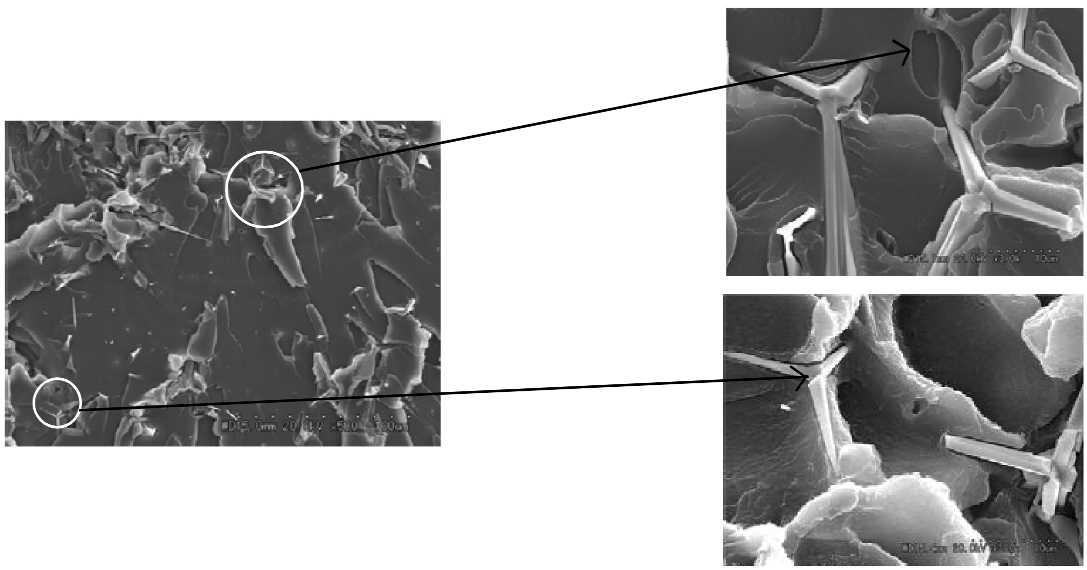

Figure 5 : SEM morphology of the tensile fracture surfaces of PC/T-ZnOw (98/2) composites.

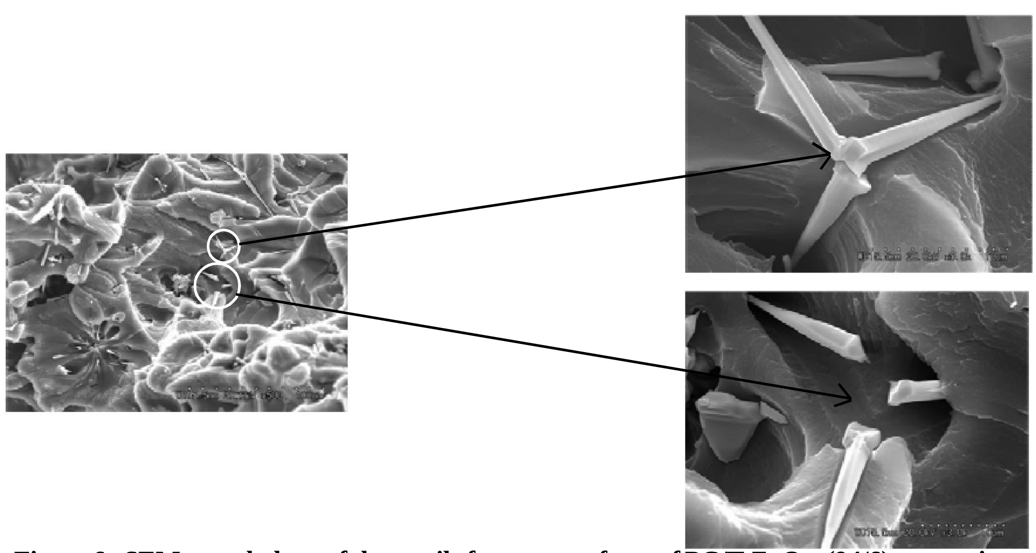

Figure 6 : SEM morphology of the tensile fracture surfaces of PC/T-ZnOw (94/6) composites.

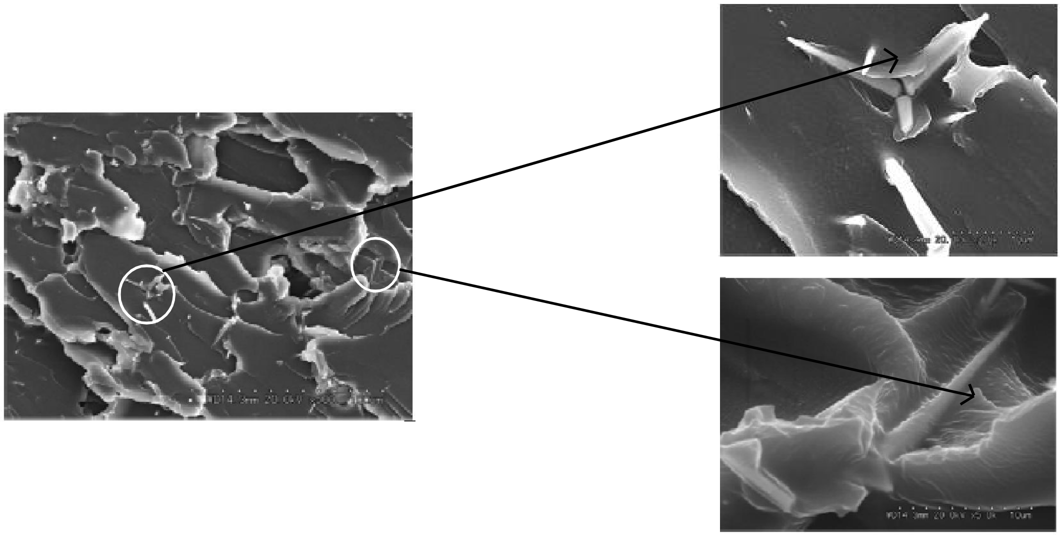

Figure 7 : Effect of surface treatments on the tensile fracture surfaces of PC/T-ZnOw (94/6) composites with 2wt% KBM803 treated T-ZnOw.

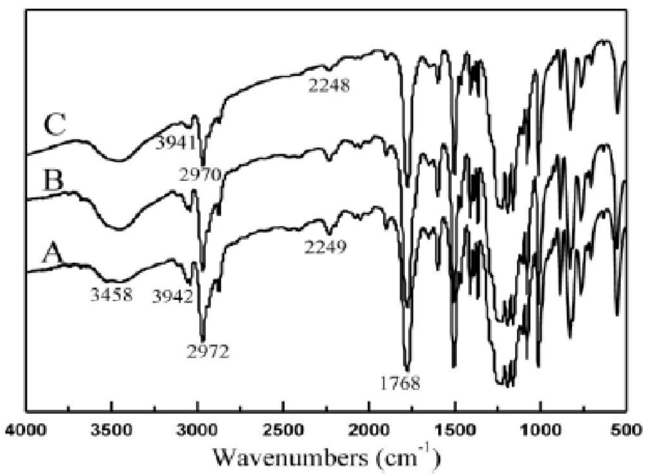

Figure 8 : FTIR spectra of PC and PC/T-ZnOw (94/6) composites: (A) Pure PC; (B) Untreated T-ZnOw; (C) Treated T-ZnOw (T-ZnOw/KBM803=98/2).

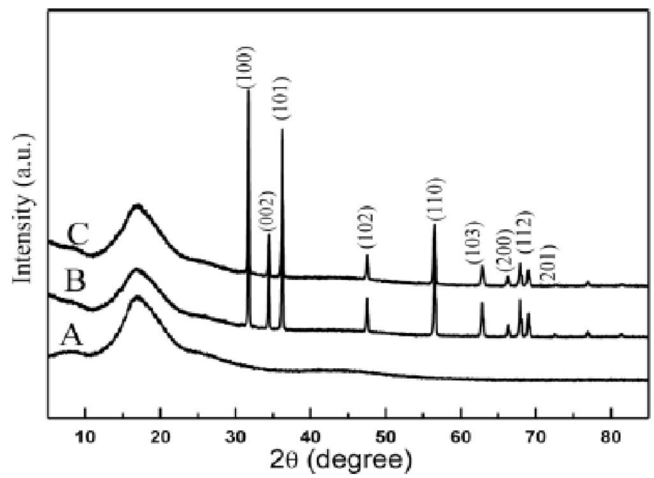

Figure 9 : XRD patterns of PC and PC/T-ZnOw (94/6) composites: (A) Pure PC; (B) Untreated T-ZnOw; (C) Treated T-ZnOw (T-ZnOw/KBM803=98/2).

sion between the PC matrix and whiskers obviously becomes much stronger. Treated T-ZnOw is covered by the PC matrix. The plastic deformation is also observed easily. However, a little localized plastic deformation of the fractured surface is invisible for untreated whiskers filled PC composites. The deformation would wear out a lot of energy when T-ZnOw acts as the stress concentration during tensile process. Furthermore, the plastic deformation around needles of whiskers is observed, indicating the stronger interfacial adhesion and better compatibility between the PC matrix and whiskers when T-ZnOw was treated by surface treatment agent. Obviously, the improvement of the tensile strength of PC/treated T-ZnOw composites is mainly attributed to the plastic deformation and the strong interfacial adhesion. The SEM results indicate that surface treatment agent coating enhances the interaction between T-ZnOw and the PC matrix, leading to increased tensile strength and Young's Modulus of PC/T-ZnOw composites.

FTIR spectra and XRD analysis

In order to evaluate the interface interaction between PC matrix and T-ZnOw, FTIR measurements were carried out. Figure 8 shows FTIR spectra of pure PC and PC/T-ZnOw (96/4) composites. The spectra of the samples clearly exhibit the characteristic absorption peaks corresponding to the polymer groups. For pure PC, very strong characteristic vibration bands at 1768 and 1221 cm^{-1} are observed, associated with C=O and C–O vibrational modes, respectively. The absorption bands ranging from 3200 to 2900cm^{-1} are assigned to aromatic C–H stretching. For PC/untreated T-ZnOw composites, neither shift nor sharpening of absorption band is detected, which indicates that there is poor interface interaction or no chemical linkage between PC and untreated T-ZnOw. However, there is a little difference between pure PC and PC/treated T-ZnOw composites. The characteristic peaks at 3941 and 2248cm^{-1} shift to lower frequency, and the intensities of absorption peaks decrease due to the presence of surface treatment agent. This indicates that the surface treatment agent was grafted onto the surface of T-ZnOw and the interface interaction between polymer matrix and whiskers is improved.

Figure 9 shows the XRD patterns of pure PC and PC/T-ZnOw (96/4) composites with and without surface treatment. On the one hand, it can clearly be seen from figure 9 (A) that a broad non-crystalline peak (10–30^{o}) of pure PC is obtained. On the other hand, the XRD patterns show sharp and increased diffraction peaks of T-ZnOw with the addition of T-ZnOw in the PC/T-ZnOw composites. The incorporation of T-ZnOw produces neither a new peak nor a peak shift with respect to PC, indicating that PC/T-ZnOw composites consist of two phase structures including polymer and inorganic filler. This further indicates that the interface interaction is poor between the polymer matrix and whiskers.

CONCLUSION

In this paper, PC/T-ZnOw composites with and without surface treatment were firstly prepared by melt mixing. The influences of untreated and treated T-ZnOw on the mechanical properties and morphology were measured and characterized. The results showed that untreated T-ZnOw seriously deteriorated the tensile strength and impact toughness but increased greatly the Young's Modulus. This indicates that the interfacial interaction is not strong enough to stand large mechanical forces. On the other hand, surface treatment of T-ZnOw could significantly improve the tensile strength, impact toughness, and hardness of PC/T-ZnOw composites due to the enhanced interfacial adhesion and good compatibility between the polymer matrix and whiskers.

ACKNOWLEDGEMENTS

The authors are grateful to Visiting Research Fellow Foundation of Japan, Science and Technology developing Project Foundation of Southwest Jiaotong University (2009-9), and Hope Star Foundation of Southwest Jiaotong University (2008–12) for financial supports of this work.

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