

TOUGHENING AND STIFFENING EFFECTS OF T-ZnOw WHISKERS ON POLYSTYRENE*

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Abstract The main subject of this work is about the effect of T-ZnOw on the toughness and stiffness of polystyrene (PS). In order to avoid the rupture of T-ZnOw during the melt processing, T-ZnOw/PS composites were obtained *via* the combination of solution blending and injection moulding methods. Although the tensile strength of the composites decreases slightly, the impact strength and tensile modulus increase with the increase of the T-ZnOw content in the matrix. The stiffness and toughness of the composites are enhanced simultaneously. SEM results of the impact-fractured surface show more polymer avulsions, ridges and micro-cracks formed in the T-ZnOw/PS composites, companied with pullout of T-ZnOw from PS matrix and local yielding of PS matrix around T-ZnOw during the impact processing. The possible reasons for the toughness increment of T-ZnOw/PS composites are attributed to the interfacial debonding, pullout of T-ZnOw from PS matrix, anchoring effect of T-ZnOw's special three dimensional structure, local yielding of PS matrix and the formation and propagation of micro-cracks.

Keywords: T-ZnOw/PS; Toughness; Stiffness.

INTRODUCTION

Whisker is thought to be a very attractive reinforcing filler to improve the performance of polymers, because the yield strength of whisker tends to approach the maximum theoretical value^[1]. The whisker/polymer composite shows some special characteristics besides better mechanical and thermal properties than those of the pure polymer^[2–7]. For example, the dielectric properties of the composite with a certain whisker are improved under moist conditions^[8].

Normally, zinc oxide (ZnO) exists as sphere droplets with nano-scale or micro-scale and whiskers with length of 10–200 μm . By means of a special technology, whisker is also formed with a three-dimensional structure, namely, tetra-needle-shaped structure (so called 3d-whiskers). As a new kind of whiskers, the tetra-needle-shaped T-ZnOw whisker avoids the oriented dispersion in the flow field due to the three dimensional structure, which endows the polymer composites the isotropic rather than the anisotropic properties, so that T-ZnOw attracts much attention of researchers in recent years. Some work has been done to study the effects of T-ZnOw whisker on mechanical properties, conductivity and morphology of the polymer composites^[9–12].

Polystyrene is an amorphous glassy polymer with good transparency and has been used in a wide range. However, due to the high brittleness at room temperature, PS cannot be used in the field that needs certain degree of toughness. Addition of elastomers into PS is thought to be an efficient way to improve the toughness of PS at the cost of strength and modulus^[13–15]. So, how to improve the toughness and stiffness of PS

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simultaneously is a key issue to be solved.

In the present work, we attempt to introduce T-ZnOw into PS to study the effect of T-ZnOw on the mechanical properties of a glassy polymer. In order to avoid the rupture of T-ZnOw in the shear stress field, especially during the melt extruding process in which high shear stress could break T-ZnOw from the growth point of the whisker and leads to the formation of conventional whiskers, solution blending was used to obtain T-ZnOw/PS composites. Interestingly, the addition of T-ZnOw into PS induces the increase of toughness and stiffness of the composites simultaneously.

EXPERIMENTAL

Materials

In this work, PS and the coupling agent are commercially available. PS (666D, $M_w = 5.4 \times 10^4$, and melt flow rate is 4.3 g/10 min) was purchased from the Yan Shan Petroleum Chemical, China. Tetra-needle-shaped T-ZnOw whisker was prepared in our laboratory, and the detailed preparation can be seen in reference^[16], the typical morphology of T-ZnOw is shown in Fig. 1, which was obtained via scanning electronic microscope (SEM). Coupling agent γ -Aminopropyltriethoxy silane (KH-550, density: 0.946 g/cm³) used to modify the surface of T-ZnOw whisker in the work was obtained from Nanjing Shuguang Chemical Company, China.

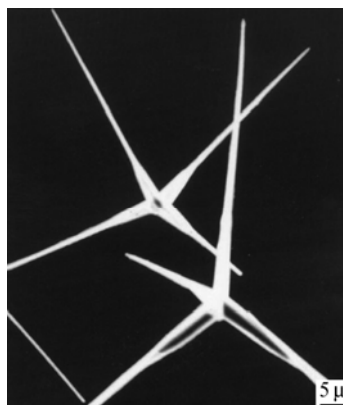


Fig. 1 Typical SEM photograph of tetra-needle-shaped zinc oxide whiskers (T-ZnOw)

Sample Preparation

The surface modification of T-ZnOw was carried out as follows: first, 2 wt% of coupling agent (relative to the weight of T-ZnOw) was dissolved in acetone (the volume ratio of coupling agent to acetone was 1:50), and the solution was stirred for 10 min; then the solution was ejected to the powder of T-ZnOw while continually stirred it; and then the T-ZnOw powder was dried in a vacuum oven at 120°C for 24 h to get the surface modified T-ZnOw.

A certain amount of PS was first dissolved in the solvent of benzene completely. Then the surface modified T-ZnOw was poured into the mixture of PS and benzene, continuously stirred at 60°C for 4 h. Then the mixture was heated to the boiling point of benzene, and the mixture was stirred until benzene was evaporated completely. At last the composite was dried in the vacuum oven at 80°C for one week to eliminate the remnant benzene. In this work, the weight fractions of T-ZnOw in the T-ZnOw/PS composites were 0 wt%, 3 wt%, 6 wt%, 9 wt%, 12 wt% and 15 wt%, respectively. T-ZnOw/PS composites were injected into a mould of 4.2 mm in thickness and 10.0 mm in width, using a PS40E5ASE injection moulding machine set at the temperature of 210–230°C from hopper to die, and the injection pressure was 30 MPa. For the sample of pure PS, it was injected and moulded in the same fashion as the composites.

Mechanical Properties Measurements

Tensile strength and tensile modulus of T-ZnOw/PS composites were measured by using an Instron 5567 Universal Testing Machine at room temperature according to GB/1040-92 standard method: the moving speed was 50 mm/min, and the measure temperature was 20°C. For impact strength measurements, a notch with 45° was made by machine and the retained width was 8 mm. The experiment was carried out on an XC-22Z Impact tester (China) according to ISO 179. The values of all the mechanical properties were calculated as averages of six to nine specimens for each composition.

Scanning Electron Microscope Measurements (SEM)

The impact-fractured surfaces of the composites were observed via an SEM instrument, Quanta 200, operating at 20 kV. In order to assure the consistent result, the same regions of all the impact-fractured samples were selected during the SEM experiments.

RESULTS AND DISCUSSION

Impact Strength and Impact-Fractured Surface Morphology

The impact strength of T-ZnOw/PS composites is shown in Fig. 2. The impact strength values were calculated as averages of six to nine specimens for each measurement. It can be seen that the impact strength of T-ZnOw/PS composites increases with increasing the content of T-ZnOw in composites. Although the toughness of T-ZnOw/PS composites is still worse than those of elastomers/PS blends in the same composition^[13, 14], here the toughness of PS is really improved. For example, the impact strength of T-ZnOw/PS (15 wt%) is increased from 6.3 J/m to 7.8 J/m, by about 24%, which suggests that the addition of T-ZnOw could really improve the toughness of PS. To our knowledge, if solvent remains in the polymer matrix, the toughness will be changed in a certain degree due to the plasticizing effect of the small molecules of solvent. In this work, although T-ZnOw/PS composites were obtained via the solution blending method, the solution of PS cooperated with T-ZnOw was heated up to the boiling point of benzene until it was evaporated out. In order to make assure that the remnant solvent was eliminated completely, the composites were dried in a vacuum oven for a long time. The TG measurement for the composites below the decomposition temperature of PS (heating up to 250°C) shows no weight loss during heating (not shown here), which means that solvent benzene is completely eliminated by the way used in the work. So, it can be deduced that the improvement of toughness of PS is attributed to the addition of T-ZnOw.

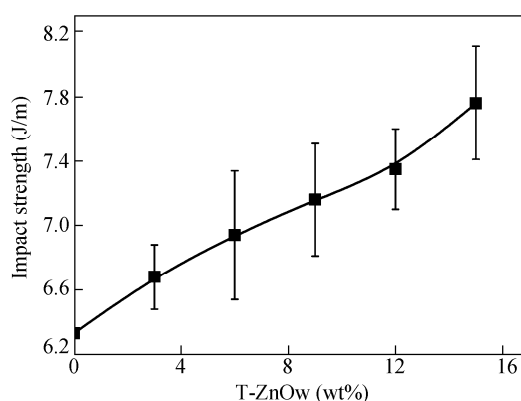


Fig. 2 Impact strength of T-ZnOw/PS composites as a function of T-ZnOw content

In order to understand the role of T-ZnOw on the toughness of PS, the impact-fractured surface of pure PS, T-ZnOw/PS (6 wt%) and T-ZnOw/PS (15 wt%) were characterized by SEM, and the results are shown in Fig. 3. For pure PS, the impact-fractured surface is very smooth, which is the typical character of brittle fracture during the impact process of glassy polymers without any toughening agent. However in the composite of T-ZnOw/PS

with 6 wt% surface modified T-ZnOw, the fractured surface becomes coarser and many polymer avulsions and ridges are observed on the surface due to the tearing role during the impact process. On the other hand, it also can be seen that the surface of the filled T-ZnOw whisker is not smooth but coarse covered with some PS, which means that the interfacial interaction between T-ZnOw whisker and PS is strengthened by surface modification effect of coupling agent. It should be noticed that in this image, only one needle of T-ZnOw is observed because the other three needles are embedded in PS matrix. With the increasing of T-ZnOw in the composites, the impact-fractured surfaces show more complicated morphologies. For example, for the composition of T-ZnOw/PS (15 wt%), besides the PS avulsions that are formed in the composites with lower T-ZnOw content are still observed here (shown as A in the Fig. 3c), the impact-fractured surface shows another type of morphologies. Some T-ZnOw whiskers are pulled out from PS matrix under the impact stress, which leaves a hole on the surface (shown as B), and other whiskers T-ZnOw are still wedging in PS matrix. On the other hand, some yielding zones are observed around the hole. Which means that during the pulling out of T-ZnOw, the good interfacial interaction between T-ZnOw and PS is facilitated the transfer of impact stress and induces the local yielding of neighbouring PS matrix. Furthermore, it is most interesting to observe some micro-cracks nearby the polymer ridges (shown as C), and the propagation direction is along the polymer ridges. The morphology of the region labelled by white circle in Fig. 3(c) under higher magnification is shown as Fig. 3(d). In this image the formation and propagation of the micro-cracks can be seen very clearly. Although the impact-fractured surface morphologies of all the compositions studied in this work are not shown here, analysis of these morphologies suggests that the number of the micro-cracks increases with the increasing of T-ZnOw in the composites, which means that the formation of these micro-cracks is related to the addition of T-ZnOw and is also related to the increase of toughness of the composites.

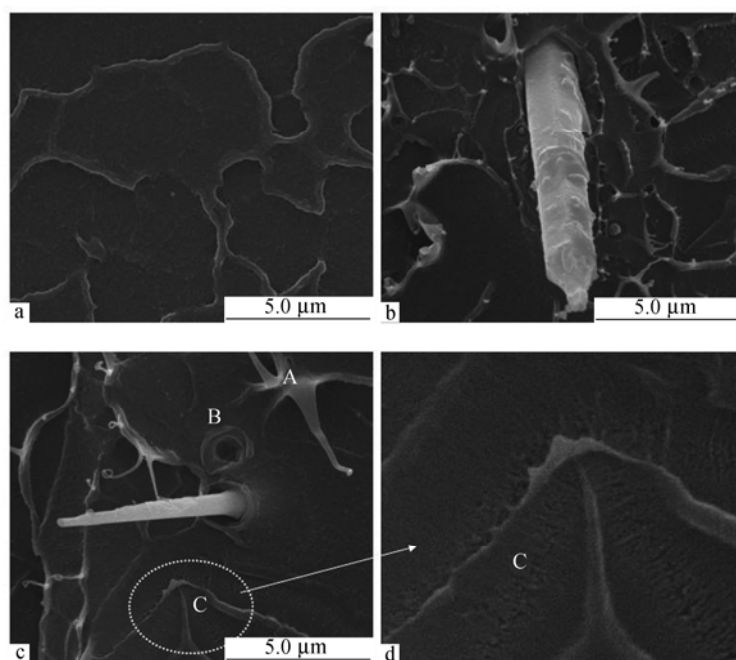


Fig. 3 SEM photographs of impact-fractured surfaces of T-ZnOw/PS composites with different content of T-ZnOw
a) Pure PS; b) T-ZnOw/PS (6 wt%); c) T-ZnOw/PS (15 wt%); d) Morphology of local region in (c) (shown by white circle) under higher magnification

Compared with polymer composites reinforced with short fiber such as glass fiber, carbon fiber and the like, whisker is also thought to be a short fibre with special structure. Thus the energy absorption mechanisms during the impact process of polymer composites reinforced by short fibre are still available for the whisker

intensified polymer composites. It is known to all that interfacial debonding and frictional sliding associated with the fiber pullout process are the two most important mechanisms to increase the toughness of fiber reinforced polymer composites^[17–20]. In more recent years, some researchers have paid much attention to the effect of fiber shape on the toughness of fiber reinforced polymer composites. The previous results show that polymer composites reinforced with the so called bone-shape short fiber provide a better fracture toughness increment compared with the conventional straight fiber reinforced polymer composites due to the anchoring effect of the fiber shape^[21–24].

In this work, the coarse surface of T-ZnOw in the composites observed from the impact-fractured surface suggests that there is a strong interfacial interaction between T-ZnOw and PS matrix, and the interfacial debonding happens during the impact process, which induces some energy absorption. Furthermore, the role of pullout of T-ZnOw from PS matrix during the impact process will also absorb some impact energy and enhance the toughness of the composite. On the other hand, T-ZnOw with the special three-dimensional structure can be thought to be a short fiber with special shape. For the impact-fractured surface morphology, only one needle of T-ZnOw can be seen, and the other three needles are embedded in PS matrix. So, it can be deduced that the anchoring effect is still reasonable for T-ZnOw during the impact process. Besides the above energy absorption mechanism, another two possible mechanisms are the yielding behavior of PS matrix around T-ZnOw and the formation and propagation of the micro-cracks along PS ridges during the impact process. Further work should be done to study the formation mechanism of the yielding region and the micro-cracks.

Tensile Modulus and Tensile Strength

Figure 4 shows the tensile modulus of T-ZnOw/PS composites as a function of T-ZnOw content. It can be seen that the tensile modulus increases with the increasing of T-ZnOw content. In other words, addition of T-ZnOw endows PS composites better stiffness. It is easy to be understood since the better interfacial interaction between T-ZnOw and PS matrix is facilitated the stress transference from PS matrix to T-ZnOw whisker in the initial stage during the tensile process. The tensile stress-strain curves and tensile strength of T-ZnOw/PS composites are shown in Fig. 5. It should be noticed that the tensile strength of the composites decreases slightly with the increase of T-ZnOw in the composites. Although the interfacial interaction is improved through the surface modification of coupling agent, the interfacial strength is still very weak compared with the polymer bulk. During the tensile process, especially in the later stage, the weak interfacial strength is not enough to transfer the stress from PS matrix to T-ZnOw whisker, and the debonding and pullout of T-ZnOw happen easily, which induces the decrease of tensile strength. On the other hand, with the increase of T-ZnOw, the fraction of the weak interfacial interaction compared with the polymer bulk enhances and finally results in the further decrease of tensile strength. Another surface modification method should be considered in further work to improve the interfacial interaction as possible so that the interfacial strength could be high enough to be favor to the stress transfer in the later stage during the tensile process, and in this condition T-ZnOw/PS composites with better tensile properties could be obtained.

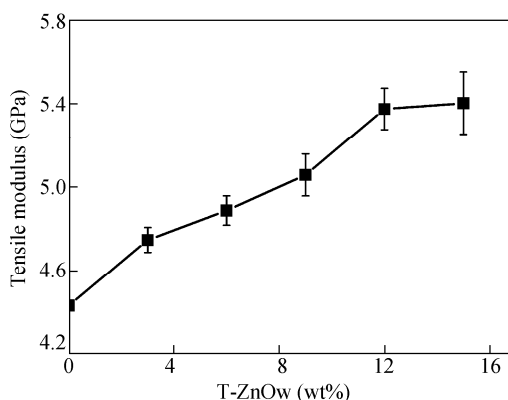


Fig. 4 Tensile modulus of T-ZnOw/PS composites as a function of T-ZnOw content

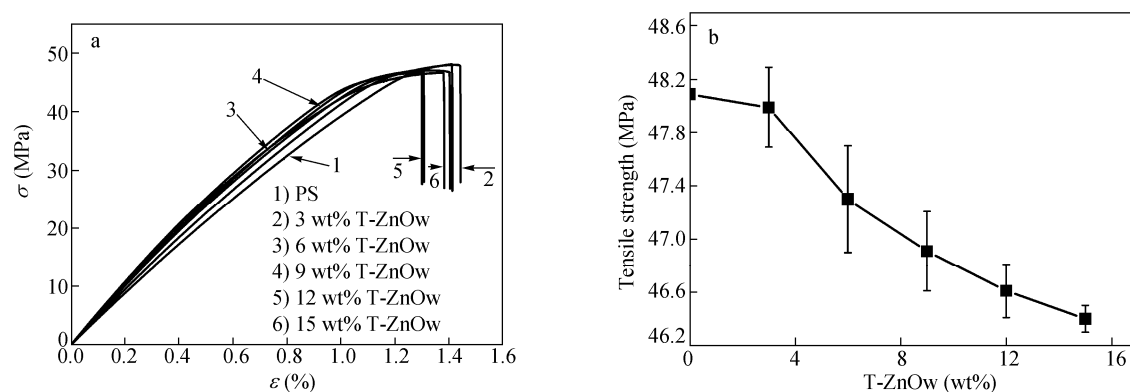


Fig. 5 (a) Tensile stress-strain curves of T-ZnOw/PS composites and (b) tensile strength of T-ZnOw/PS composites as a function of T-ZnOw content

CONCLUSIONS

In summary, to our knowledge, this work is the first time to introduce T-ZnOw whisker into the glassy polymer such as PS to investigate the variation of mechanical properties of the composites. By the surface modification of T-ZnOw and solution blending, T-ZnOw/PS composites show better impact toughness and stiffness simultaneously compared with the pure PS. Analysis to the impact-fractured surface morphology suggests that there are several possible mechanisms of energy absorption: debonding between T-ZnOw and PS matrix, pullout of T-ZnOw, anchoring effect due to the special structure of T-ZnOw, local yielding of PS matrix around T-ZnOw while T-ZnOw is pulled out from matrix and the formation and propagation of micro-cracks under the impact stress.

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