Theoretical Analysis of Fracture of Tetra-Needle-Like ZnO Whisker in Polymer Composite

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ABSTRACT: It is of practical importance to develop the tetra-needle-shaped ZnO whisker (T-ZnOw)-reinforced polymer composites that have isotropic properties. To give a guidance of material design and manufacture, it is necessary to have a theoretical analysis of the fracture mechanisms of this peculiar structure fiber in polymer composites. Based on previous investigations of the T-ZnOw-reinforced polymer composites, and from the viewpoint of materials mechanics, here we analyzed the distribution of stresses on different points of the tetra-needle-like crystal whiskers in a composite and calculated the total stress at the connection point. The results indicate that the stress on the connection point is proportional to the exerting force and correlates with the dimension, the size, and the location of the whiskers. According to the theoretical derivations, it was found that the stress at the connection point of the T-ZnOw is much larger than that at the others, leading to breakage on that point mainly or wholly, which is in accordance with the experimental observations. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2767–2771, 2011

Key words: T-ZnOw whisker; polymer-matrix composites (PMCs); fracture; theoretical analysis

INTRODUCTION

Polymer composites, usually containing polymeric matrix and inorganic fillers as the reinforcements, are increasingly becoming preferred structural materials for engineering applications. Different kinds of reinforcement fillers, including clays,[1] fibers,[2] nanoparticles,[3] and whiskers,[4,5] have been developed to reinforce various polymers. The structure, morphology, and size have distinct effect on the properties of the composites. Compared with other fillers, the whiskers are thought to be one kind of short fibers without internal defects such as crystalline dislocations. Thus, they display interesting prospects in a broad spectrum of applications, ranging from structural to functional materials, where they are exploited in the modification of polymer composites and related products.[6] The yield stress of whiskers tends to approach the maximum theoretical value.[4] For instance, the whiskers-reinforced polyamide-6 composites lead to marked increase in stiffness and strength.[4,5]

However, for one-dimensional whiskers or short fibers or both, an unavoidable problem is the orientation distribution of the fillers, owing to the shearing force during processing, which leads to anisotropic properties of the composites. For example, the composite exhibits higher strength, higher stiffness, less shrinkage, and lower strain-to-fracture along the direction of orientation than those in the perpendicular directions. Previous works demonstrate that the factors on improvement of properties in polymer composites include content,[7] orientation,[8] end spacing[7] of the fibers, and interfacial interactions between fibers and matrices.[9,10] Although anisotropy in mechanical property of fiber- and/or short fibers-reinforced polymer composites is applicable in a main direction of loading, it limits broad applications of such composites in the fields that need isotropic mechanical properties of the articles,[11] for instance, the application in manufacturing of gears.

The tetra-needle-shaped ZnO whisker (T-ZnOw) has four needle-like arms of single crystals extending symmetrically from the same center to four directions in three dimensions (Fig. 1). The combination of the well-proportioned morphology, single crystalline structure, and multifunctional behaviors of ZnO

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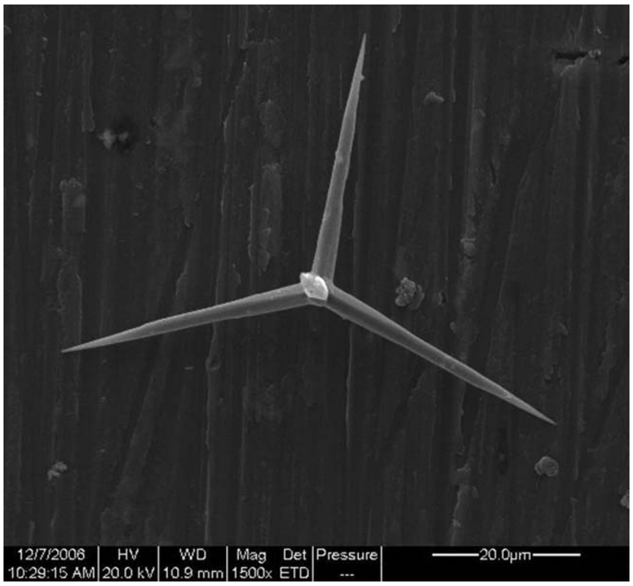

Figure 1 SEM image of T-ZnOw.

makes it a material that possesses lots of novel functions and properties such as isotropic reinforcement,[12] antistatic effect,[13] wear resistance,[14] vibration insulation,[15] microwave absorption,[16] etc. Thus, it is of practical importance in developing T-ZnOw-reinforced polymer composites as not only engineering materials, but also integrative materials for structural and functional applications. As an isotropically distributed microfiber with high strength, the T-ZnOw avoids the orientation in the flow field of processing, which endows the polymer composites display isotropic properties.[17,18] As a result, the T-ZnOw-reinforced polymer composites usually show a special fractured behavior and feature.[18] T-ZnO whisker-reinforced sample avoids the oriented distribution of T-ZnOw because of its three-dimensional structure, which endows the polymer composites the isotropic rather than the anisotropic properties; on the other hand, the concentrated stress at the tip of one needle of T-ZnOw will be transferred to other three needles, which leads to the homogeneous stress distribution in the composites.[19] Some works have been done to study the mechanism of the T-ZnOw-reinforced polymer composites, and different kinds and different dosages of coupling agents are introduced to treat the T-ZnOw to provide the corresponding interfacial interactions between T-ZnOw and matrix.[20,21] The results indicate that the surface modifications of T-ZnOw have a good effect on improving the compatibility of the polymer composites, and the modified T-ZnOw reinforces the rubber material isotropically even when most of the tetra-needles have been broken into single-handed crystal needles.[19,20] What is more, for the tetra-pod-shaped projection of morphology, the T-ZnOw displays multiple mechanisms, including crack-bridging, synergetic, and anchoring effects,[22] resulting in obvious disparity of tensile strength between the theoretical prediction and experimental data.[23] The key point of the discrepancy was ascribed to the ruptures and status of the whiskers in the composites, which lay on the shearing force during mixing process, and the multiconnected needles were speculated to decentralize the loading.

To give a practical guidance of material design, it is necessary to have a deep and theoretical understanding of the fracture mechanisms and related behaviors of the T-ZnOw in polymer composites. However, to the best of our knowledge, there is no convictional work concerning these kinds of problems; i.e., nothing of any rational mechanism. In this study, based on our previous investigations of the T-ZnOw-reinforced polymer composites, we analyzed the distribution of stresses on different points of the tetra-needle-like crystal whiskers in a composite and calculated the total stress at the connection point, hoping to give a fundamental hint for putting forward the fracture mechanism of said root-like fiber-reinforcing composites.

SCHEMATIC PROPOSALS

As shown in Figure 1, the T-ZnOw has a connection center from which symmetrically extend four needle-like arms of single crystals in four directions of three-dimensional space, and the angular separation of any two needles is 109°28′. Considering this isotropic structure, it is reasonable to suggest a root-like model for simulating the whisker's reinforcement. On the basis of this idea, we propound the following schematic proposals.

The spatial coordinates of T-ZnOw

It is of great importance to consider the spatial coordinates of T-ZnOw so that the azimuth resolution can be referred in the course of calculation. As a simplest situation, in the rectangular coordinate system as indicated in Figure 2, we let one of the needles, noted "1," lie exactly on the z-axis; another needle, noted "2," was located on the plane made up of x-axis and z-axis. Thus, the directional cosine of the four needles can be expressed as:

$$\begin{aligned}
1:&\quad (0,0,1)\\
2:&\quad (\cos 19^\circ 28', 0, -\sin 19^\circ 28')\\
3:&\quad \left(-\tfrac{1}{2}\cos 19^\circ 28', -\tfrac{\sqrt{3}}{2}\cos 19^\circ 28', -\sin 19^\circ 28'\right)\\
4:&\quad \left(-\tfrac{1}{2}\cos 19^\circ 28', \tfrac{\sqrt{3}}{2}\cos 19^\circ 28', -\sin 19^\circ 28'\right)
\end{aligned} \tag{1}$$

Analysis of the stress concentration at needle's tip

The stress at a tip of the needle is certainly depending on the localizing direction of the whisker.

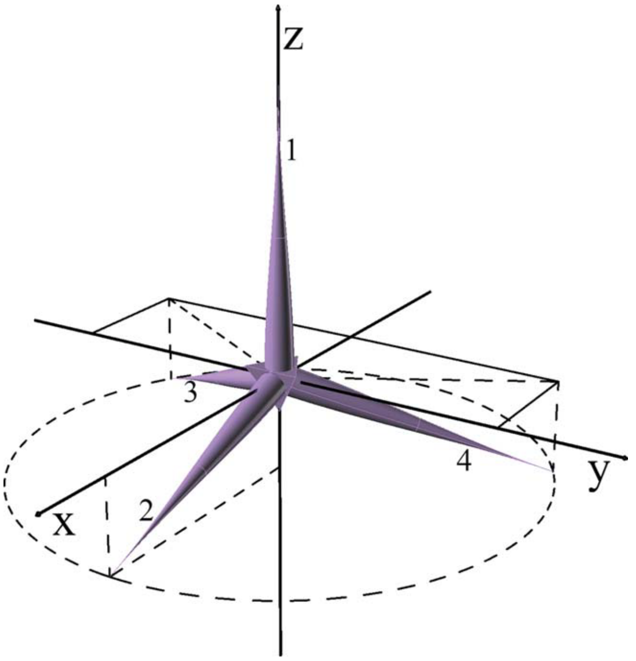

Figure 2 Spatial coordinates of T-ZnOw. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Further works will concentrate on the following aspects:

1. Supposing the direction of the loading force is along z-axis, for the whisker needle No. 1 in Figure 2, the stress at the needle's tip is $\sigma = 0$.
2. For the other needles, called off-axis needles, the stress concentration at the needle's tip can be obtained by limitation of a suitable distribution formula, which will be obtained from solid mechanics.
3. According to the experimental results,[14,23] we have found that the breaking of T-ZnOw usually takes place at the connection point (typical observation as shown in Fig. 3), meaning little consequence of the stress concentration at other places. Especially, after surface modification, the interfacial connection is good. Thus, it is not needed to consider special concentration of stress, and more attention will be paid to the stress transferring from the matrix (continuous phase) to the whiskers (disperse phase).

STRESS ANALYSIS OF T-ZnOw IN THE COMPOSITE

Hypothesis

To simplify the analysis of the man-made T-ZnOw with well-proportioned and symmetrical distribution in microstructure, we put forward the following hypotheses:

1. The tensile process is so slow that the distribution of the stress in the composites is homogeneous.
2. The size and structure of the T-ZnOw are uniform.
3. T-ZnOw has a good distribution in the composite.

The stress at the connection point of a whisker

Let us consider a special case, as illustrated in Figure 4, in which one of the four needles is supposed to be parallel to the loading force (called on-axis needle). When the tensile force, f in Figure 4, is exerted on the on-axis needle, it will lead to this crystal needle a tendency of moving along with the tensile force, and the compression force, noted as f', from the matrix will be formed and will act on the off-axis needles. The total compressing force on the three off-axis needles ($3f'$) and the tensile force (f) are equal in quantity and opposite in direction. As demonstrated in Figure 4, each compressing force (f') can be divided into two components of force: the one is vertical pressure (f_1) and the other is tensile force parallel to the off-axis needle, which can be expressed, respectively, as:

$$f_1 = \cos\theta \cdot f' = \frac{\cos\theta \cdot f}{3}$$
$$f_2 = \sin\theta \cdot f' = \frac{\sin\theta \cdot f}{3} \quad (2)$$

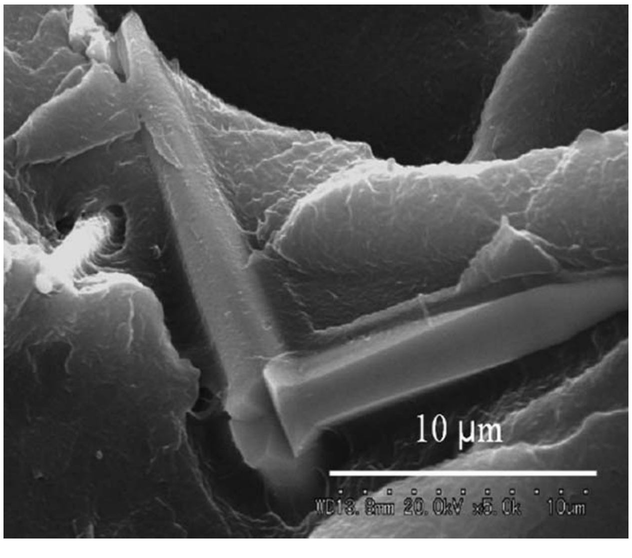

Figure 3 A typical T-ZnOw in a polymer composite after tensile fracture.

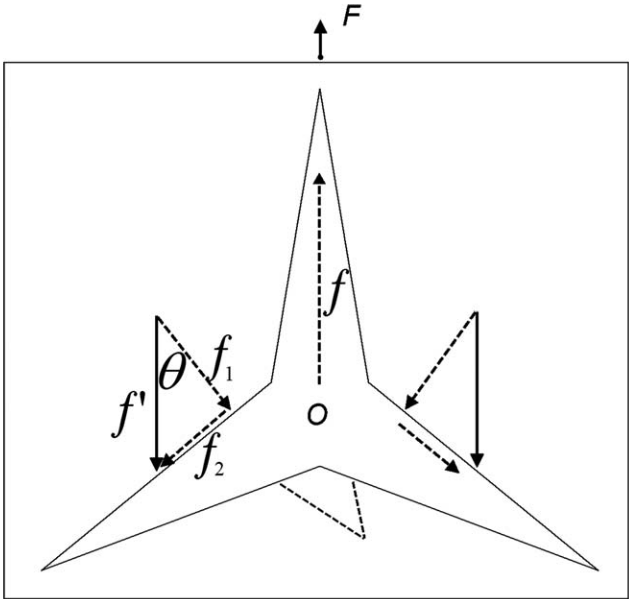

Figure 4 Analysis of the loading force on a T-ZnOw.

where $\theta = 109°28' - 90° = 19°28'$

Then, let us consider the stress at the connection point by vertical pressure. According to the moment expression[24]:

$$M = \frac{qx^2}{2} \tag{3}$$

where q is the distribution load, and x represents the distance from the connected point.

From the formula

$$q = \frac{f_1}{l} = \frac{f \cdot \cos\theta}{3l} \tag{4}$$

where f is the force exerted on the on-axis needle, l is the length of the needle, and $\theta = 109°28' - 90° = 19°28'$, the maximum moment can be expressed as

$$M_{\max} = \frac{q \cdot l^2}{2} = \frac{1}{6} l \cdot f \cdot \cos\theta \tag{5}$$

Suppose the cross-section of the whisker needle is circular and the diameter is d. Then, we get the second polar moment of an area

$$I_g = \frac{\pi d^4}{64} \tag{6}$$

The distribution factor can be obtained from the following formula

$$z = \frac{I_g}{\frac{1}{2}d} = \frac{\pi}{32} d^3 \tag{7}$$

Thus, we have the formula of the maximum stress at the connection point exerted by the moment of the vertical pressure on one of the off-axis needles

$$\sigma_{\max} = \frac{M_{\max}}{z} = \frac{16\cos\theta}{3\pi d^3} l \cdot f \tag{8}$$

The resultant tensile stress along with the whisker needle is illustrated in Figure 5(a), and the expression is noted as:

$$\begin{aligned} \sigma_1 &= \sigma_{\max} + \sigma_2 \\ &= \sigma_{\max} + \frac{f_2}{A} \\ &= \frac{4}{3\pi d^2}\left(\frac{4l}{d}\cos\theta + \sin\theta\right) \cdot f \\ &= \left(\frac{16l\cos\theta + 4d\sin\theta}{3\pi d^3}\right) \cdot f \end{aligned} \tag{9}$$

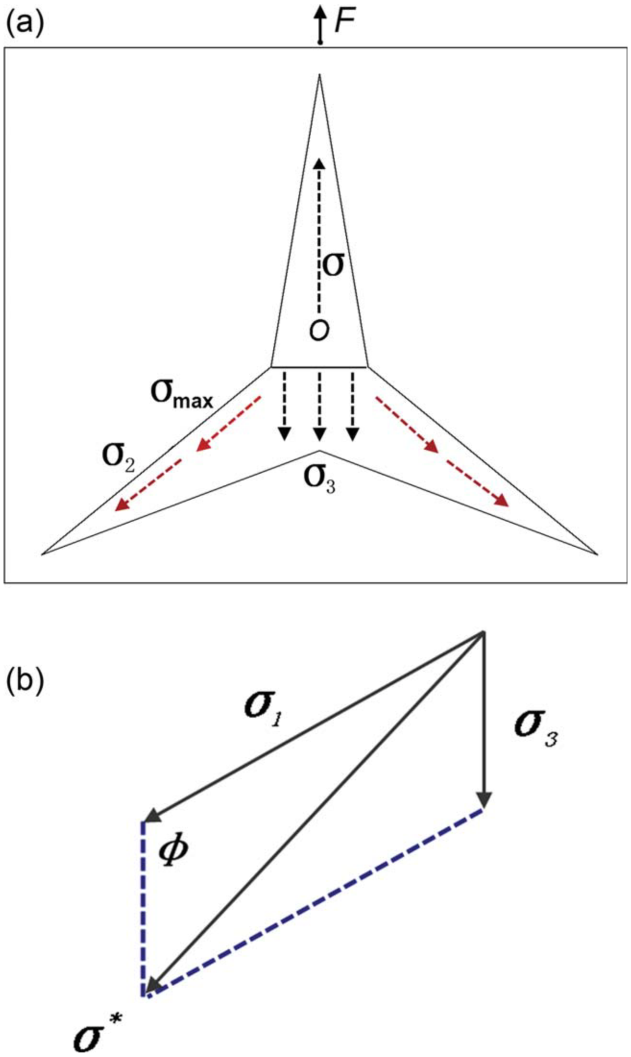

Figure 5 Analysis of stresses on T-ZnOw exerted by an external loading on the composite. (a) The total stress on T-ZnOw. (b) Illustration of the synthesizing stress at the central point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the connection point, the total stress will be the synthesis of compressive stress σ_3 and the tensile stress σ_1 ($\sigma^* + \sigma_2$). The compressive stress is equal in value and opposite in direction to the tensile stress on the on-axis needle. That is,

$$\sigma_3 = \frac{4f}{\pi d^2} \tag{10}$$

Thus, the total stress at the connection point from one needle is

$$\sigma^* = \sqrt{\sigma_1^2 + \sigma_3^2 - 2\sigma_1\sigma_3\cos\phi} \tag{11}$$

where $\phi = 109°28'$. The analysis of the stress synthesizing is demonstrated in Figure 5(b).

From the above formulae, we have

$$\begin{aligned} \sigma^* &= \frac{4f}{\pi d^2}\sqrt{\frac{(4l\cos\theta + d\sin\theta)^2}{9d^2} - \frac{(4l\cos\theta + d\sin\theta)\cos\phi}{3d} + 1} \\ &= \frac{4f}{\pi d^2}\sqrt{1.676\left(\frac{l}{d}\right)^2 + 0.037d^2 + 0.419\left(\frac{l}{d}\right) + 0.279d\cdot l + 1.037} \end{aligned} \tag{12}$$

where d and l are the basal diameter and needle's length, respectively, $\theta = 19°28'$, and $\phi = 109°28'$.

From eq. (12), we can find that the stress exerted on the connection point is proportional to the loading force and correlates with the dimension and size of the whiskers, particularly the basal diameter and the length. With regard to other positions of T-ZnOw azimuth, we suggest a consideration of changing the exerting direction of tensile force, from 0 to 109°28′ in three dimensions.

According to the above analysis and the theoretical derivations, we can see that the stress at the connection point (σ^*) is much larger than that at the others. Thus, we observe that the rupture takes place in the first place of this central point of the T-ZnOw. On the basis of this result, it is speculated that the flexibility of the multibranching or conjunction fibers may be a key factor for the system of the so-called root-like fiber-reinforcing composites.

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