Fabrication of polymer matrix composites reinforced with controllably oriented whiskers

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Polyvinyl chloride (PVC) reinforced with controllably oriented potassium titanate whisker (PTW) has been prepared. The preparation includes wet-spinning a polymer solution that contains the whiskers, placing the resultant precursor fiber in a die and hot-pressing to form composite. The whiskers are highly aligned along the axis of the fiber as the result of extrusion and drawing in spinning. Therefore, the whisker orientation in the composite can be closely controlled through controlling the directions of the precursor. The degree of whisker alignment is found to depend strongly on drawing ratio, and a simplified mathematical relation is presented. The mechanical properties of the PTW reinforced PVC are reported. The applications of the composite processing technique described above in functional composites are also discussed.

1. Introduction

Chopped glass fibers are usually used as reinforcing agents in short fiber reinforced plastics (SFRP). However, their low elastic modulus, poor wear-resistance and environmental sensitivity preclude their applications in many areas. In recent years, inorganic whiskers have been increasingly utilized to replace glass fibers in some critical applications. A whisker is a nearly perfect single crystal, and exhibits strength significantly higher than the corresponding polycrystalline material and sometimes close to the theoretical value. Their other merits over glass fibers are high modulus, wear resistance, chemical and thermal stability. Whiskers also give composites better processability and surface finish than glass fibers as the result of their much smaller dimensions. However, in most composites, whiskers are placed randomly and their full potential has not been reached.

The maximum Young's modulus (E) and strength (σ) of SFRP are given by the rule of mixtures [1, 2],

$$E = \alpha E_f V_f \left(1 - \frac{L_c}{2L}\right) + E_m V_m \quad (L > L_c)$$

$$\sigma = \alpha \sigma_f V_f \left(1 - \frac{L_c}{2L}\right) + \sigma_m V_m \quad (L > L_c)$$

where f stands for fiber, m for matrix, L for fiber length and L_c for the critical fiber length, and α is a material constant, determined by the degree of the preferred orientation of the fibers. For instance, $\alpha = 1$ when the fibers are in parallel; $\alpha \approx \frac{1}{3}$ when the fibers are plane-random-oriented; $\alpha \approx \frac{1}{6}$ when the fibers are randomly distributed. Accordingly, it is generally accepted that the full value of whiskers can be realized only when their orientations are closely controlled.

Aligned SFRP is by no means a rarity in the nature, for example animal bones or wool. Under the microscope, animal bones are made up of tiny inorganic single crystal needles bonded by protein. The crystals are so ingeniously oriented that they endow bones with a perfect combination of strength, rigidity and fracture toughness as well as the necessary biological functions. A wool fiber is made of a large number of 'fibrils'. They align along the fiber axis, and give the fiber excellent strength and feel. Most of the commercial inorganic whiskers have diameters of 0.1–3 μm and lengths of 10–100 μm. The tiny size makes the alignment or even uniform dispersion extremely difficult. Much effort has been made in the past to orient whiskers through tape casting [3] or extrusion [4] or liquid carrier routes [5]. However, the whiskers are only partially aligned because all these processes rely mainly on the shear stress generated in fluid extrusion as the driving force for whisker movement.

We have previously reported [6] a new method for the controllable alignment of whiskers. It is a modified industrial solution spinning process. Briefly, polymer fluid containing whiskers is extruded through a spinneret orifice and solidified. The resultant filament is then drawn, dried and finally wound to give a precursor fiber, in which the whiskers are highly aligned along the fiber axis. In this paper, the effects of spinning conditions on whisker orientation are analyzed. Composites that contain aligned potassium titanate whiskers are fabricated and characterized.

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2. Experimental procedure

Commercial potassium titanate whisker (chemical formula $K_2O{\cdot}6TiO_2$ or $K_2Ti_6O_{13}$) was used as the reinforcement. Its major properties are listed in Table I. PVC was selected as the matrix because of its availability and good processability. Tribasic lead sulfate (5%, based on the PVC, all by mass below unless stated otherwise) and barium stearate (1%) were added as the thermal stabilizers. PVC tends to decompose during composite fabrication after prolonged exposure to high temperature in the absence of thermal stabilizing agents, resulting in serious reduction in its mechanical properties. NDZ-101 (a titanate ester, Shu Guang Chemical Co., Nanjing), was used as coupling agent between the polymer and the whisker.

The PTW was surface-treated prior to use by being immersed into a 2% NDZ-101 isopropyl alcohol solution. After 15 min soaking, they were filtered out and dried at 80°C. The surface treated whiskers are much easier to disperse and have a better stability in DMF (N,N-dimethyl formamide, solvent for PVC) than non-treated ones. To prepare spinning dope, the PTW and the thermal stabilizers (∼10 μm powder) were dispersed in DMF by vigorous stirring with a heavy-duty shear mixer (Silverson Machine Ltd., Model L2R) at 3000 revolutions per minute for 5 min. The PVC powder was then added and completely dissolved. The mixture was stirred with a common mechanical stirrer at 300 revolutions per minute for 30 min to give a homogeneous fluid. These procedures can ensure the absence of large agglomerates of the PTW or the insoluble PVC additives in the dope, whose presence would block the spinneret and make continuous spinning impossible. Before use, the spinning dope was filtered with copper-gauze of 100 mesh and then left undisturbed for 60 min for deaeration. For an appropriately prepared fluid, no whiskers or stabilizers should be filtered out.

Wet spinning was utilized to make fiber precursor under the conditions listed in Table II. All the spinning runs were conducted using a laboratory wet spinning apparatus described in detail elsewhere [7]. The drawing ratio was defined here as the ratio of winding speed to extrusion speed. No spinneret blockage or whisker accumulation on the spinneret was experienced during spinning, suggesting that the whiskers were well dispersed and the size of any agglomerates were limited below the fiber diameter (∼100 μm). Composites were made by placing the fibers in parallel in a steel die, followed by die pressing at 190°C and 0.5 MPa for 3 min.

The whisker distribution in the fiber precursor and the composites was observed with scanning electron microscopy (SEM). Prior to examination, the polymer matrix was removed through oxidation at 600°C for 30 min. A semi-quantitative assessment was also carried out using X-ray diffraction (XRD) on polished composite surface, with the intended whisker orientation parallel to the surface. PTW grow mainly in ⟨200⟩ or ⟨201⟩ directions. Therefore, the whiskers that lie parallel to the sample surface will not contribute to these two peaks. In other words, the intensity of the (200) or (201) peak will decrease with increased degree of whisker orientation. Consequently, the disappearance of the (200) and (201) reflections is expected for perfect whisker alignment. Mechanical properties of the composites were tested using a universal-testing machine on rectangular specimens. The gauge length was 45 mm in tensile testing and the span 40 mm in flexural testing. The testing speed was 1 mm·min^{-1} in both cases.

TABLE I Selected properties of potassium titanate whisker

Density (kg·m^{-3})	3100	Tensile strength (GPa)	7
Diameter (μm)	0.1–1.0	length (μm)	10–40
Elastic modulus (GPa)	280	Elongation to failure (%)	4
Melting point (°C)	1300	Mohs hardness	4

TABLE II Wet spinning conditions

Spinneret	Single hole, ϕ250 μm
Coagulation tank	70% DMF, 30% distilled water (by volume), 50°C
Drawing tank	Boiling water
Drawing ratio	12
Winding speed	65 m·min^{-1}

3. Results and discussion

A typical fiber precursor has an essentially circular cross-section and a smooth surface. Its strength decreases with increasing whisker content, because of the increase in micro-porosity. However, the fiber containing up to 40% PTW, the highest loading in this work, was still quite strong to allow normal handling. In order to simplify the fiber-forming process, the spinning conditions were designed mainly to ensure the optimum whisker alignment, rather than to obtain very strong fibers. The fibers were used only as the composite precursor and their densification would eventually be realized in the subsequent hot-pressing stage. The magnified picture of the fiber surface, taken after the removal of the polymer matrix, is shown in Fig. 1. The whiskers are almost unidirectional along the fiber axis. Such excellent alignment has never been reported before to our knowledge. The whisker placement in the composites

Figure 1 SEM micrograph of the precursor fiber taken after the removal of polymer matrix.

was very similar, indicating that the composite processing had not disturbed the whisker arrangements of the precursor.

XRD analysis was performed on the polished surfaces of two composites (Fig. 2). The whiskers were aligned in one composite, but essentially random in the other. Melting and cooling a mixture of PTW and PVC powder forms the composite with the PTW randomly distributed. The intensities of the (200) (two theta $= 11.54°$) and (201) (two theta $= 13.86°$) peaks are among the strongest in Fig. 2 (b), but very close to zero in Fig. 2 (a). The difference is attributed to the different degree of whisker orientation. The whiskers will not produce (200) or (201) reflections unless these planes are parallel to the sample surface. For randomly placed whiskers, there are always some planes meeting such a condition. For whiskers aligned parallel to the sample surface, however, the (200) and (201) planes are perpendicular to the sample surface and will not contribute to these reflections. Therefore, the absence of the (200) and (201) peaks is the direct consequence of the excellent whisker alignment observed by SEM. Similar XRD profiles were also found in the other composites of this study.

The excellent whisker alignment in the as-spun fibers is the result of fluid extrusion and fiber drawing. During spinning, the dope flows along a narrow duct before it reaches the spinneret and extrudes through the spinneret orifice. In this process, the whiskers tend to rotate and orient toward the direction of flow. A mathematical analysis indicates that the whiskers rotate fastest next to the wall of the spinneret hole and slowest in the center. Consequently, the whiskers near the fiber surface align better than the whiskers near the center. However, as the fluid duct is thick and the length (thickness) of the spinneret orifice is small (~0.3 mm), the flow of the spinning dope could only produce limited whisker alignment. In this work, the preferred orientation was mainly due to the drawing in the coagulation bath and the hot water bath. For the most conservative estimation, a completely random whisker distribution is assumed in the extruded filament at the exit of spinneret orifice. Suppose that a fiber is stretched λ times, its length changes from L_0 to L, and diameter from D_0 to D, then $\lambda = \frac{L}{L_0}$.

During drawing, the solvent inside the fiber and the non-solvent in the baths will counter-diffuse, usually resulting in volume reduction. Let V_0 and V be the volume of the fiber before and after drawing, and $\beta = \frac{V}{V_0}$, then $\beta = L\frac{\pi D^2}{4}/L_0\frac{\pi D_0^2}{4}$, or $\frac{D}{D_0} = \sqrt{\frac{\beta}{\lambda}}$. Also, assume that a whisker inclines at angle θ with the fiber axis, projecting b and h along the axis and diameter, then $\tan\theta_0 = \frac{h_0}{b_0}$, $\tan\theta = \frac{h}{b} = h_0\frac{D}{D_0}/b_0\lambda = \beta^{\frac{1}{2}}\lambda^{-\frac{3}{2}}\tan\theta_0$. Thus, the average angle ($\tilde{\theta}$) after drawing is given by:

$$\tilde{\theta} = \frac{2}{\pi}\int_0^{\frac{\pi}{2}} \beta^{\frac{1}{2}}\lambda^{-\frac{3}{2}}\tan\theta_0\,\mathrm{d}\theta_0 \qquad \text{in radian}$$

$$= \frac{360}{\pi^2}\int_0^{\frac{\pi}{2}} \beta^{\frac{1}{2}}\lambda^{-\frac{3}{2}}\tan\theta_0\,\mathrm{d}\theta_0 \qquad \text{in degree}$$

This complex calculus equation has no exact solutions, but it can be readily solved with computer. Fig. 3 gives the average angle as a function of drawing ratio, where the volume change during drawing is ignored ($\beta = 1$). Clearly, whisker alignment increases rapidly with drawing ratio. At $\lambda = 1$ (no drawing), the average angle is 45°, but at $\lambda = 10$, the average angle is less than 5°. When the whisker rotation in extrusion and the volume contraction of the precursor fiber in drawing are also taken into consideration, the angle is much smaller.

The statistical analysis of Fig. 1 also shows that the whisker damage (reduction of average aspect ratio) and agglomeration are negligible, two important advantages of the present composite processing technique over the industrial methods. In industrial plastic production, dry whiskers are normally mixed with polymer melt. Because the viscosity of molten polymers is usually very high (>100 Pa·s), intensive compounding or twin-screw extrusion is indispensable for homogenization. Breaking of whiskers is inevitable during these processes, seriously decreasing their reinforcing efficiency [8]. Large whisker agglomerates often remain

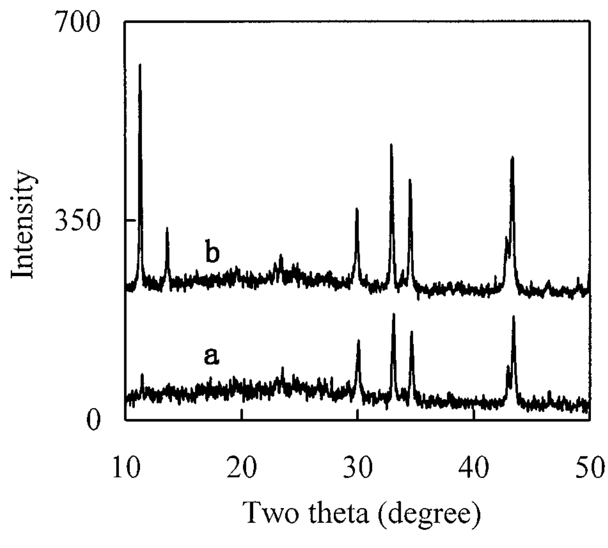

Figure 2 XRD profiles of the composites containing (a) aligned and (b) randomly oriented whiskers.

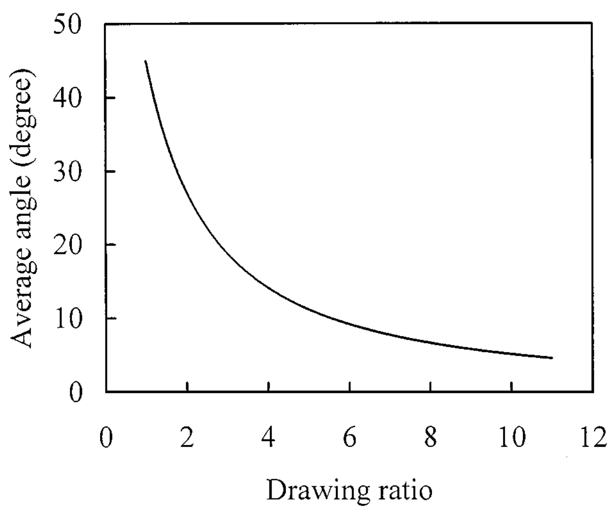

Figure 3 Average angle ($\tilde{\theta}$) of whiskers with fiber axis as a function of drawing ratio (λ).

after mixing. They behave like cracks in composites and act as the possible initiating points of mechanical failure. The uniform dispersion normally becomes more difficult with the increasing content of additives. The maximum whisker content is usually limited to ~30%; above this, the composite strength drops rapidly. In the present work, however, polymer solution rather than polymer melt was used. It has a much lower viscosity (~10 Pa·s). Through the proper surface treatment and the selection of liquid medium, the whiskers can be uniformly dispersed simply by mechanical stirring, keeping the whisker damage to a minimum.

Industrial SFRP are normally isotropic, however, they are often used to make components suffering from axial or plane stress, such as member bars or pressure vessels. In these situations, the service efficiency of the composites has not been fully realized. When the directions of the reinforcing fibers are controlled so that the mechanical properties of the composite match the stress such as in bones, much material will be saved. The precursor fiber is analogous to wool. The whiskers are similar to the 'fibrils', lying parallel and giving the fiber the optimum properties along its axis. When a number of filaments weave into different patterns, the resultant cloth can be made suitable for service in any spatial stress conditions.

The mechanical properties of the unidirectional whisker-reinforced composites are shown in Fig. 4. Both tensile and flexural strength increases with whisker content. An increase of over 250% in tensile strength and 300% in flexural strength is achieved for the composite containing 40% PTW. The fracture surface shows extensive whisker pullout. A close examination has found that the fiber ends are clean. This indicates that the interface of the whisker and matrix is weak and the composite fractures as the result of interfacial shear failure. If the interface is improved, further increase in the mechanical properties is possible. We notice that, although the precursor fibers that form the composite appear to have fused together completely by SEM, repeated bending of the composite invariably results in de-bonding at the interfaces of the precursor. What effect this has on strength is not clear yet, but it seems to be beneficial in preventing catastrophic failure of the composite. The precise reasons of the de-bonding are to be investigated.

Finally, the composite processing technique described above might also find important applications in functional composites. The preferred whisker orientation can improve the desired properties in given directions. We have used it in the preparation of barium titanate whisker reinforced piezoelectric composites and obtained some very interesting results. The detailed information will be presented separately.

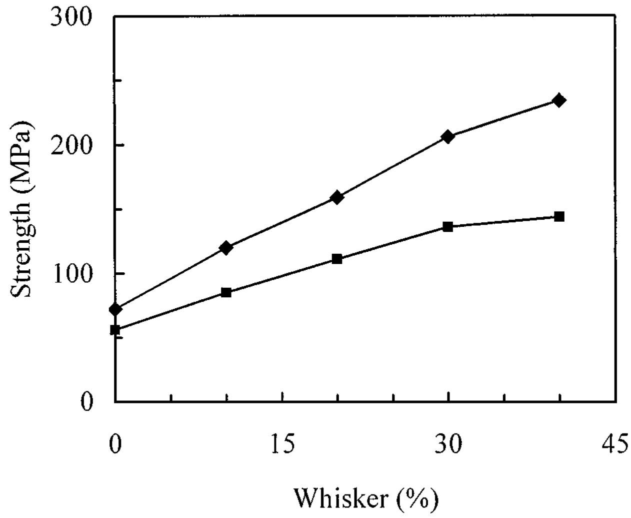

Figure 4 Tensile (●) and flexural (♦) strength as a function of whisker content.

4. Conclusions

Polyvinyl chloride (PVC) reinforced with controllably oriented potassium titanate whisker (PTW) was prepared by hot-pressing the precursor fibers that contained the whiskers. The close control of the whisker directions was realized through placing the fibers in a predetermined pattern. A drawing ratio of 10 is sufficient to give a nearly unidirectional whisker alignment in the precursor. In comparison with the industrial methods, the present composite processing technique offers the advantages of better whisker dispersion and minimum whisker damage. The strength of the composites reinforced with the aligned whisker increases with whisker content up to 40%, the highest loading studied in this work.

References

1. A. A. BERLIN, S. A. VOLFSON and S. S. NEGMATOV, "Principles of Polymer Composites" (Springer-verlog, New York, 1986).
2. D. HULL, "An Introduction to Composite Materials" (Cambridge University Press, Cambridge, London, 1981).
3. M. WU and G. L. MESSING, *J. Am. Ceram. Soc.* **77** (1994) 2586.
4. M. J. FOLKES and D. A. M. RUSSELL, *Polymer* **21** (1980) 1252.
5. P. W. MANDERS and T. W. CHOU, in Proc. ICCM-IV, edited by T. Hayashi, K. Kawata and S. Umekawa (North-Holland Publishing Co., Oxford, 1982) p. 1075.
6. L. F. CHEN and C. LEONELLI, *J. Mater. Sci.* **32** (1997) 627.
7. G. Y. GAO and L. F. CHEN, *J. Chinese Ceramic Society* (in Chinese) **1** (1999) 888.
8. T. J. LU, X. L. WEI *et al.*, *Engineering Plastics and Applications* (in Chinese) **23** (1995) 5.

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