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Mechanical properties of polyoxymethylene whiskers/polyoxymethylene resin composite films

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Polyoxymethylene (POM) needle-like crystals, whiskers, are known as trigonal crystals of very high perfection and are thought to have a high Young's modulus. In this study, composite films of the whisker were prepared as one possible method to utilize the whiskers as a new, high performance material. POM resin, i.e. a substance with the same chemical structure as the whisker, was selected as a matrix, having good adhesion with the filler (whisker). The whiskers were mixed with POM resin powder, prior to hot-pressing and made into the composite films, taking advantage of the difference of the melting points. The whisker content of the resulted film reached up to 70%. The Young's modulus of the composite film was increased up to about 14 GPa.

1. Introduction

Polyoxymethylene (POM) needle-like crystals, grown in the cationic polymerization system of trioxane in cyclohexane solution, are known as the first polymer whisker [1–3]. In recent years, much work has been done to characterize the nature of the needle-like crystals [4–8]. These needle-like crystals (whiskers) look like pencils in their shape, with a diameter of about 1 μm and a length of about 20–100 μm. The whisker is a single crystal of trigonal form with molecular chains of 9/5 helix (or 29/16 helix). The molecular chains are thought to be fully extended parallel to the long axis of the crystal. Their crystalline perfection has been proved to be very high by various experiments such as wide angle X-ray diffraction, differential scanning calorimetry (DSC), etc. [4, 6, 9]. The high crystallinity and high perfection of the whisker have been also proved by the vibrational spectroscopy [10, 11]. Through vibrational spectroscopic studies on the POM whiskers and related POM specimens, the extraordinary behaviour of the vibrational bands of POM have been found in relation to their morphology [10–13].

Because of their perfect crystal structure, the whisker is thought to have a high Young's modulus. The measurements of the modulus of the crystalline part [14, 15] and the theoretical calculations [16–18] predict a high Young's modulus (40–189 GPa). The utilization of the whisker with high Young's modulus and low density has been of interest. The acoustic diaphragm of a loudspeaker is an example of an industrial application for the POM whisker [19]. In this case, the whiskers were made into composite films with polyolefin and proved effective in improving the performance of the loudspeaker.

The whisker itself has a very high Young's modulus but it is too small to utilize this as a material. If many whiskers were stuck together with an adhesive, new high-performance materials would appear. POM resin is selected as an adhesive because adhesion would be good between the same chemical species, $(CH_2O)_n$. Fortunately, the whiskers have a very large crystallite size and high crystalline perfection and their physical nature is different from that of ordinary POM resin. For example, the melting point of the whisker is higher than that of the ordinary POM. The composite film of the whiskers and powder of the ordinary POM resin can be prepared by hot-pressing taking advantage of the difference in the melting points. Mechanical properties of the resulted POM whiskers/POM resin composite films are examined and discussed, where the whisker content is raised as much as possible.

2. Experimental details

2.1. Sample preparation

The POM whiskers were prepared in a cationic polymerization system of trioxane under similar conditions as published previously [2]. Some as-grown whiskers were etched by boron trifluoride to disrupt the original radial assembly [4]. Acetal resin (Delrin 500 of du Pont de Nemours) was used as the matrix. In order to make the powder, the resin was recrystallized from dilute bromobenzene solution at 130° C. After filtration and freeze-drying, the solution-grown crystals and whiskers were dispersed and mixed well in ethanol and the mixture was then filtered. As the whiskers are insoluble in boiling bromobenzene, Delrin 500 was also overgrown on the surface of the whiskers from dilute bromobenzene solution (0.5%) at 130° C and resulted in another mixture. The two

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kinds of mixtures of the whiskers and Delrin, prepared by both methods, were then pressed at about 180° C and made into POM whiskers/POM resin composite films. The whisker content of the films was up to 70 wt %.

2.2. Measurements

The resulting films were cut (5 mm × 60 mm, typically) and subjected to measurements. The Young's modulus (E) of the samples was measured by the vibrating reed method with Reska model RD-2B. The sonic velocity (c) was measured by H. M. Morgan model PPM-5R and the Young's modulus was also determined by the sonic velocity from $E = \varrho c^2$, where ϱ is the density of film.

DSC curves were measured using Perkin-Elmer model DSC-2. Differential thermal analysis (DTA) measurements under high pressure were performed with apparatus developed in our laboratory [20].

3. Results and discussion

3.1. Thermal properties and morphological observation

The DSC curves of the POM whiskers and other POM specimens are shown in Fig. 1. The melt-crystallized film and the solution-grown crystals melt below 180° C, while the whisker keeps solid state below 180° C. The melting behaviour confirms the large crystallite size and the high crystalline perfection of the whisker. This observation suggests that the POM whiskers/POM resin composite film could be made by hot-pressing at appropriate temperature. Fig. 2 shows the phase diagram of the POM whiskers and the solution-grown crystals measured by DTA under various pressures. Pressure dependence of the melting

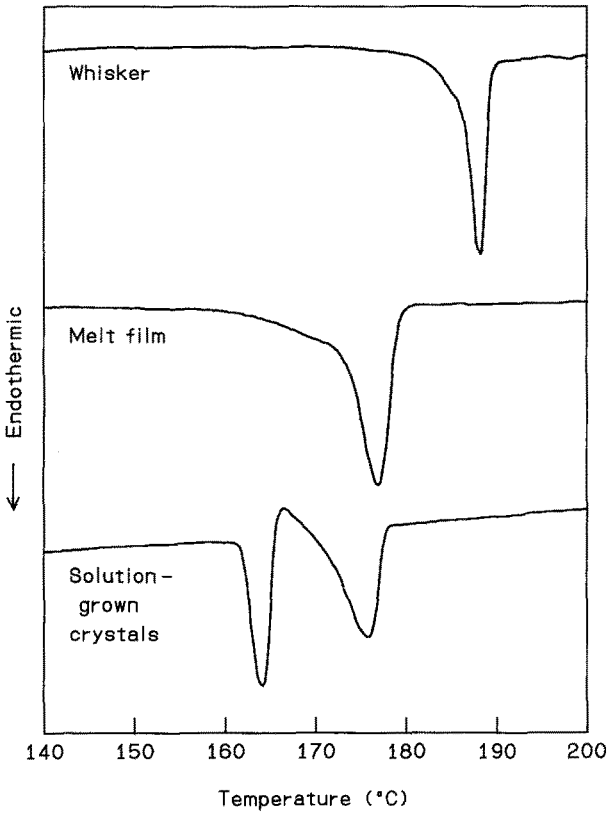

Figure 1 DSC curves of various POM specimens.

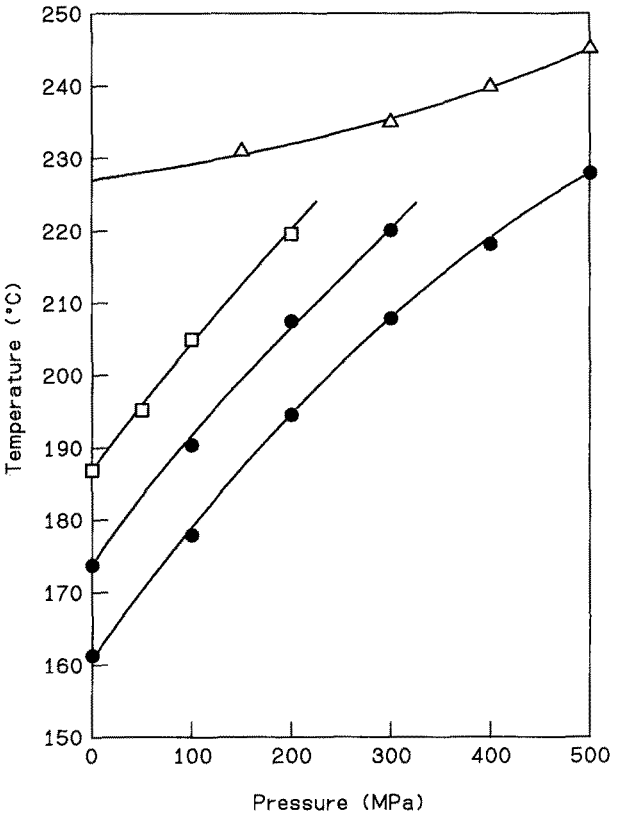

Figure 2 Phase diagram of POM whisker and solution-grown crystals. (△) Decomposition, (□) whisker, (●) solution-grown crystals.

point of both crystals is larger than that of decomposition. The melting point of the whiskers is about 15° C higher than that of the solution-grown crystals under a pressure up to at least 200 MPa, though the melting point of both crystals increases with pressure. The temperature of pressing, 180° C, adopted in this work, was determined from Fig. 2. At this temperature, the solution-grown crystals melt and the whiskers keep solid state through the hot-pressing.

In Fig. 3, the DSC curves of the mixture of the whiskers and the overgrown POM resin before hot-pressing (upper) and the resulting composite film after hot-pressing (lower) are shown. In the upper curve, a peak at around 190° C is due to the whiskers. The lower two peaks appear at almost the same temperature as those of the solution-grown single crystals. In the lower curve, the peak at 190° C is also found and only one peak appears in the lower temperature range. This means that the whiskers keep their highly ordered solid state structure during the hot-pressing. On the contrary, the two lower temperature peaks change to a single one through the hot-pressing, e.g. the overgrown POM resin melts during the hot-pressing and recrystallizes on cooling. The other mixture shows the same DSC curves as Fig. 3.

Scanning electron micrograph of the fracture surface of a POM whiskers/POM resin composite film is shown in Fig. 4. Some whiskers are pulled out from the matrix resin rather than being broken. This observation also suggests that the whiskers are not melted through the hot-pressing process and keep their morphology. Some whiskers seem to be bent, showing the good adhesion between the whiskers and melting POM resin.

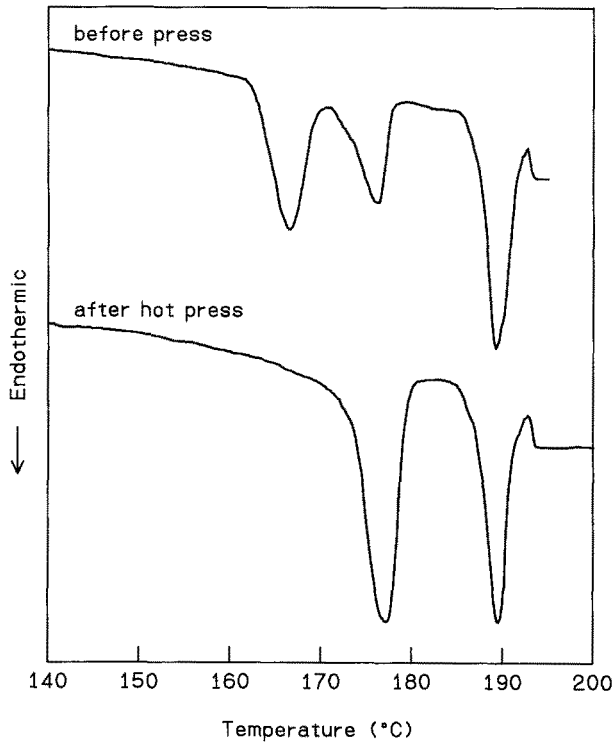

Figure 3 DSC curves of the POM whiskers/POM resin composite film.

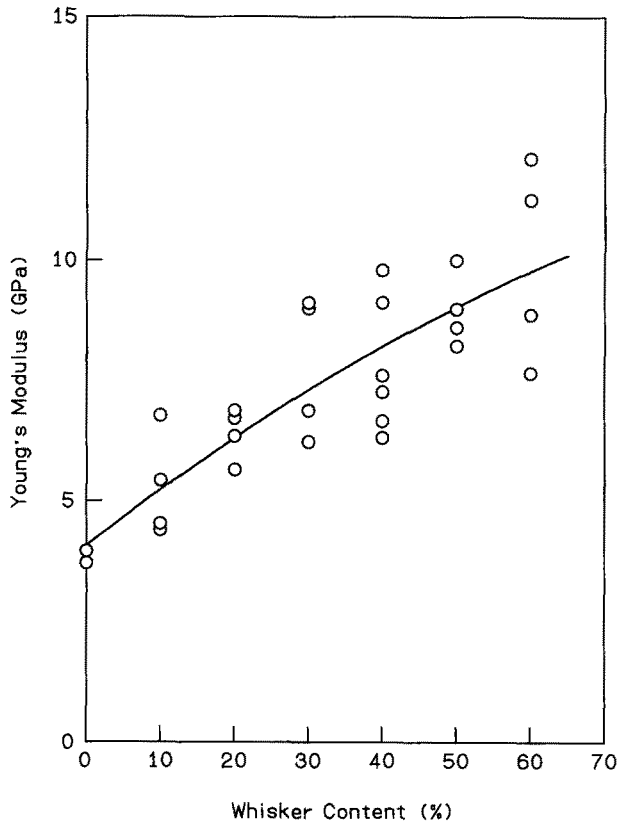

Figure 5 The Young's modulus of the POM whiskers/POM resin composite film measured by the vibrating reed method.

3.2. Young's modulus of the composite films

The Young's modulus of the POM whiskers/POM resin films measured with the vibrating reed method is shown in Fig. 5. The data of both films were plotted in the same figure, because the composite films prepared from the overgrown resin on the whiskers and from the mixture of the whiskers and the solution-grown crystals showed nearly the same values of Young's modulus within the accuracy of the measurement. The deviation of the data could be due to small sample size (about 0.5 mm × 5 mm × 50 mm) and/or the inhomogeneity of film. Though the data are so scattered, the Young's modulus of the POM whiskers/POM resin films is seen to be raised at least up to 10 GPa.

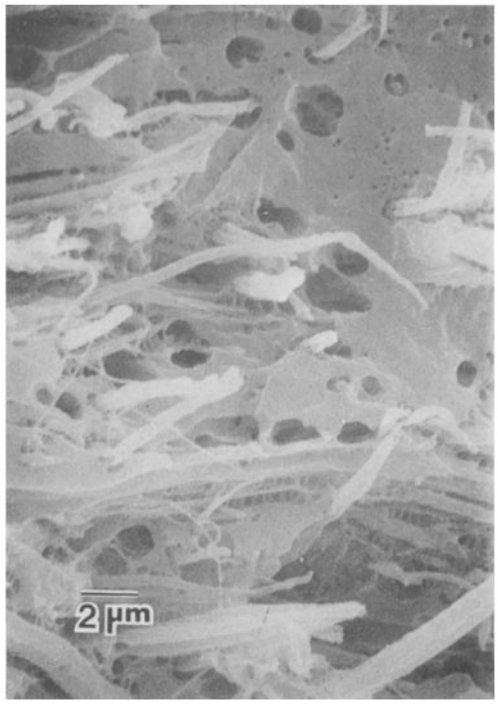

Figure 4 A fracture surface of the POM whiskers/POM resin composite film.

Fig. 6 shows the sonic velocity and the Young's modulus derived from the sonic velocity. As no significant difference was found between the Young's modulus of the films of different origins (see Fig. 5), the sonic velocity was measured only for the films made from the mixture of the whiskers and the solution-grown crystals. Though the data are also scattered as well as the vibrating reed method, it is clear that the Young's modulus of the sample films becomes higher, up to 14 GPa, than the pure Delrin (POM resin) film (3 GPa).

The equation, formulated by Halpin and Tsai and generalized by Nielsen [21, 22] is commonly used to describe the modulus of composite materials with rather low filler content. The Young's modulus of composite, E_c, is given by

$$E_c = [(1 + ABV_f)/(1 - BpV_f)]E_m \qquad (1)$$

where $A = K_E - 1$, $B = (E_f - E_m)/(E_f + AE_m)$, $pV_f = 1 - \exp[-V_f/(1 - V_f/V^*)]$, E_m the Young's modulus of matrix, E_f the Young's modulus of filler, V_f the volume content of the filler, K_E the Einstein constant and V^* the maximum volume content of the filler.

Since the Young's modulus of whiskers (filler) is not yet known precisely, the modulus of the composite film is calculated with Equation 1 for various values of the Young's modulus of the whisker. The relation between the filler content and calculated Young's modulus of the composite film are shown in Fig. 7.

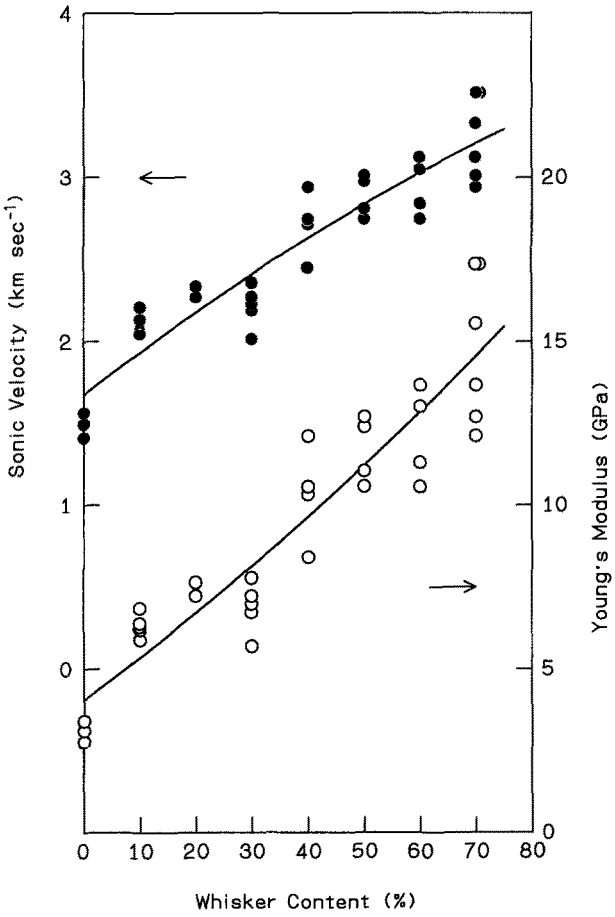

Figure 6 The sonic velocity and derived Young's modulus of the POM whiskers/POM resin composite films.

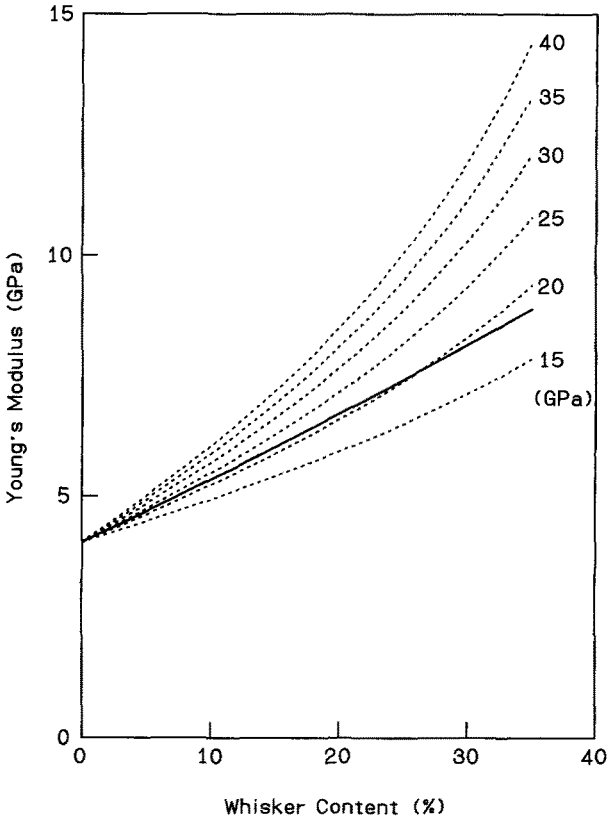

Figure 7 Observed (——) and calculated (– – –) Young's modulus of the POM whiskers/POM resin composite films.

The solid line represents the observed Young's modulus of sample films (from the sonic velocity measurement) and the broken lines are the calculated curves for various E_f, i.e. Young's modulus of the whiskers. The values (in GPa) of E_f assumed in calculations are written on the right hand side of the broken lines (in Fig. 7). The observed modulus does not fit well with the calculated lines, especially for the films of high filler content. From the curves in the low filler content range, the Young's modulus of the whiskers could be estimated to be about 20–30 GPa. This value is small compared to the previously determined value, i.e. 100 GPa [19], or the theoretically calculated values (40–150 GPa) [16–18].

This might be due to the anisotropic modulus of the whisker, e.g. the modulus parallel to the *c*-axis is much higher than that perpendicular to the *c*-axis and the theoretical calculations are concerned with the modulus along the *c*-axis. Another possible reason is the presence of inhomogeneities and/or voids in the sample films. The temperature of pressing is not much higher than the melting point of the matrix resin. At such temperature, the viscosity of melted POM resin might be rather high and the inhomogeneity or voids in the films could not be removed completely. As a result, the determined modulus of the whisker is lower than the theoretically expected value.

4. Conclusion

The composite films of the POM whisker and the POM resin, having the same chemical structure $(CH_2O)_n$, were prepared by hot-pressing at 180° C, where the resin powder melted while the whiskers remained in the solid state.

The Young's modulus of the composite films is improved by an increase in the filler (whisker) content. But improvement in the modulus did not reach the theoretically expected value at the higher filler content region. This might be due to the anisotropy of modulus in the POM whiskers or to the inhomogeneities and/or voids in the sample films.

Precisely-controlled film making apparatus would be needed to make the POM whiskers/POM resin composite films with a high performance.

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