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Composite materials reinforced with polyoxymethylene whiskers

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Various composite samples reinforced with polyoxymethylene (POM) whisker crystals were prepared and their Young's moduli were measured and analysed, on a theoretical equation, to estimate the modulus of the filler itself. Good reinforcement was obtained with matrix resins such as an epoxide and an unsaturated polyester, the results giving the modulus of the whisker to be approximately 1×10^{11} N m^{-2}, i.e., almost equivalent to the ideal crystal modulus of POM. Some acoustic properties were investigated for sheet composite materials prepared with a polyolefin polymer for matrix. The sonic velocity attained was more than twice that of the matrix polymer, at larger filler contents, while the internal dynamic loss was maintained at a reasonably high level. Loudspeakers carrying diaphragms of the composite sheets showed improved frequency characteristics in the high-frequency region. Some morphological observations were made for the crystals embedded in resins.

1. Introduction

In recent years much has been done to determine the nature of the needle-like polyoxymethylene (POM) crystals found in the cationic polymerization system of trioxane in solution [1–4]. Morphologically, the crystals, measuring 10 to 100 μm long and 1 to 3 μm diameter, have been revealed to be a kind of hexagonal, pencil-shaped single crystal, which may now be called the first polymer whisker. This first polymer whisker consists of molecular chains extended and aligned parallel with the long axis of the crystal and its crystalline perfection is extremely high, showing no significant broadening in X-ray reflection profiles. The molecular weight of the polymer chains comprising the original crystals was not clear, because severe conditions, which may well cause some chain scission, are required for dissolving the highly crystalline material in solvents. However, the value of a temporary measurement, of approximately 150 000 of the chain length of 1 μm, implies that crystal defects due to chain-ends exist in not more than one in several thousands of formaldehyde units.

Among the various properties characteristic of such a unique structure [5–8], the mechanical properties have been of particular interest. Although no direct method has been available for the mechanical testing of such a small specimen, a preliminary study for making composites [9] has shown that the whisker gives a good reinforcing effect for resins, in terms of the increase in Young's modulus, suggesting that the modulus of the whisker itself is remarkably high. This has also led to an interest in preparing sheet composite materials, for use for acoustic diaphragms, expecting a high specific modulus or a high sonic velocity.

In this study, some composite samples with random filler orientation have been prepared and their Young's modulus and data from previous measurements [9] have been analysed on the basis of a theoretical reinforcing equation [10] to estimate the modulus of the filler. The

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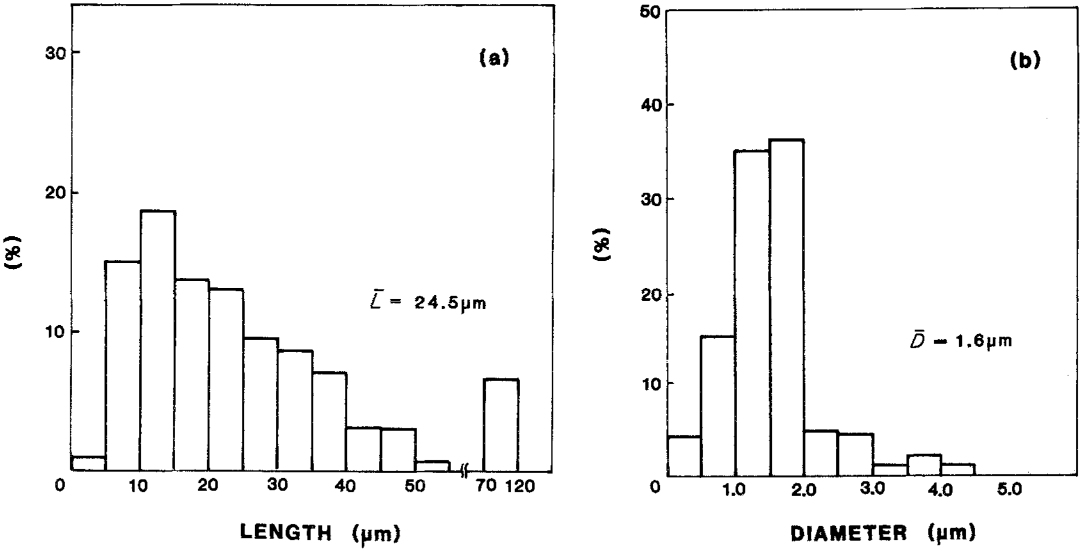

Figure 1 Length, L, and diameter, D, distributions of freshly prepared POM whiskers for the preparation of composite samples (Sampling number: 154). (a) Length, (b) diameter.

acoustic properties have also been investigated for composite sheets prepared with a particular matrix resin, polyolefin, and the frequency characteristics of a test loudspeaker is presented.

2. Experimental procedure

2.1. Whisker crystals

Whiskers used in this study were obtained from a 20-litre bench plant designed and constructed to produce 200 to 400 g crops per batch [11]. The quality of the products was as good as those obtained from a previous laboratory glass-ware apparatus. The whiskers were used either after treating with boron trifluroide to isolate single pieces or in the form of as-polymerized radial assemblies. As described before [3], the etching by boron trifluoroide takes place and proceeds selectively at both ends of the crystals, i.e., tips and roots, without damaging their side prism faces.

The size distribution of isolated whiskers was measured on scanning electron micrographs (see Fig. 1). The aspect ratio was calculated simply by calculating the ratio of the mean length to the mean diameter: 24.5 μm/1.6 μm = 15.3.

2.2. Preparation of composite samples

Two kinds of sheet composite materials were prepared with different matrix resins.

The one resin was an epoxide resin (Araldite CY230/HY956, 100/20 mixture, from Ciba-Geigy) for which a good affinity and adhesion to the filler was expected. Measured amounts of isolated whiskers and the resin were mixed in a beaker, the mixture was spread and sandwiched between glass plates and cured in an oven at 60° C for 4 h. In this way, composite sheet samples with various whisker contents, of 0.2 mm in thickness and with filler contents of up to 16 vol% were prepared.

The other resin used was a polyolefin polymer (SWP E620, from Mitsui Zellerback Co., Ltd) which was available in the form of a "pulp". The material was chosen mainly from the view-point of practical convenience in that, by applying the paper-manufacturing technique, dispersion of the filler in the matrix at large contents could be performed and sheets with a large area could be obtained. Thus, "papers" containing the whisker at various contents, up to 70 vol%, were prepared from aqueous dispersions and hot-pressed at 150° C to melt the matrix polymer and to form a solid composite. For preparing loudspeaker diaphragms, the hot-air press technique was applied with a pre-heated cone-shaped mould.

The orientation of the fillers in the matrices was checked by means of an optical microscope. For all the prepared samples, the orientation was, at least qualitatively, three-dimensionally random.

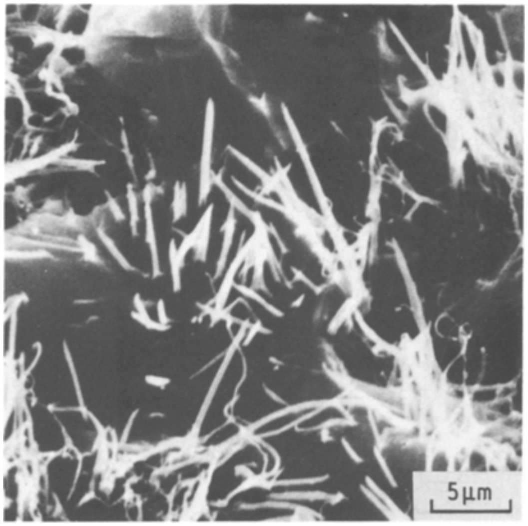

Figure 2 A fracture surface of an epoxide–POM whisker composite (scanning electron micrograph).

2.3. Measurement of the Young's modulus

The Young's modulus measurement of composite samples was made at room temperature using the vibrating reed method. The apparatus comprised a beat frequency oscillator (Model 1017, from Brüel and Kjaer) and other electronic components, to which rectangular specimens, 5 mm wide and 45 mm long (including a 20 mm clamping edge), cut from the composite sheets, were served. The modulus was calculated as usual from the resonant frequency and other parameters and, normally, for each sample, values from ten different measurements were averaged. To calculate the sonic velocity, the density was determined for each specimen from its weight and dimensions. The analysis of data was carried out as described in Section 3.2.

2.4. Additional Young's modulus data

Previously [9], some composite samples had been prepared and their Young's moduli were measured using the longitudinal oscillation method. The samples included the composites of POM whisker and an unsaturated polyester resin, POM whisker and a Celcon-type polyacetal resin, and a commercial silicon carbide whisker and an unsaturated polyester resin, the last having been prepared for reference. Some of the data were produced for the present analysis assuming appropriate values for the aspect ratios of the fillers, since these had not been measured in the original work.

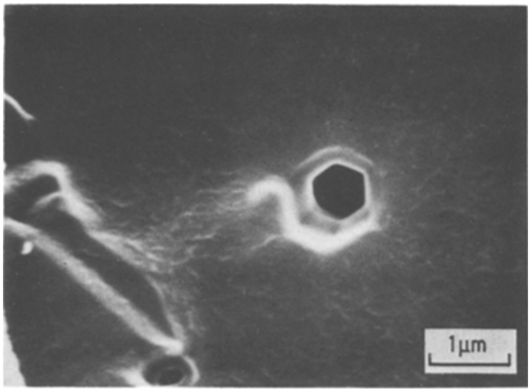

Figure 3 A "hexagonal hole" observed on the fracture surface of an epoxide–POM whisker composite (scanning electron micrograph), showing the cross-sectional shape of the whisker crystal.

3. Results and discussion

3.1. Morphological observation

First, the morphology of the polymer whiskers embedded in the resin matrices is examined. Fig. 2 shows a scanning electron-micrograph of the fracture surface of a whisker–epoxide composite, in which whiskers are seen either pulled out of the matrix or torn into fibrils, rather than being broken in the middle. (Similar observation was made earlier [1] with a different matrix.) Fig. 3 shows a "hexagonal hole" from which a whisker has been pulled out, confirming that the cross-sectional shape of the whisker single crystal was hexagonal [4] and that the wetting by the resin was good. The fibrillization of the whisker by mechanical deformation, such as observed above, is rather common. Fig. 4 shows an electron micrograph (surface replica) of a whisker which has been accidentally broken during, or prior to, the process of replication. In fact, the occurrence of fibrillization provides evidence that the molecules in the crystals are not short and are aligned parallel with long-axis of the crystal.

3.2. Young's modulus of composites and the filler POM whisker

The Young's moduli measured for various samples are listed in Table I. To describe the modulus of composite materials, E_c, a theoretical equation formulated by Halpin and Tsai and generalized by Nielsen [10] is most commonly used. The comprehensive theory assumes a solid adhesion between the filler and the matrix and relates the Young's modulus of matrix, E_m, the Young's modulus

TABLE I Young's moduli of composites and calculated moduli of fillers

Matrix–Filler	Filler content (vol %)	Modulus (10^9 N m^{-2})	Einstein coefficient	Filler modulus, calculation (10^9 N m^{-2})
Epoxide–POM whisker	0	2.77*	11.0	90.0 (±20)
	4	3.62		
	8	4.38		
	12	6.14		
	16	7.00		
Polyester–POM whisker	0	2.86†	≃16	121 (± 30)
	2.02	3.64		
	3.96	4.38		
	5.83	4.88		
Polyacetal–POM whisker	0	2.71†	≃16	107 (± 30)
	0.92	2.99		
Polyolefin–POM whisker	0	2.06*	11.0	23.7 (± 5)
	3.5	2.63		
	7.0	2.99		
	11.0	3.41		
	14.5	4.13		
	18.5	4.68		
	22.3	4.78		
Polyolefin–POM whisker‡	0	2.06*	≃11	22.7 (± 2)
	10	3.43		
	20	4.79		
	30	6.23		
	40	9.59		
	50	12.74		
	60	12.20§		
	70	10.53§		
Polyester–SiC whisker	0	2.86†	≃20	478 (± 100)
	0.94	3.66		
	1.87	4.05		
	2.78	4.29		
	3.67	4.65		

* Vibrating reed method.

† Longitudinal oscillation method (old data).

§ Omitted from the calculation.

of the filler, E_f, the volume content of the filler, V_f, the Einstein constant, K_E, and the maximum volume content of the filler, V^*. Thus, according to [10] the Young's modulus of a composite is given by

$$E_c = [(1 + A B V_f)/(1 - B p V_f)] E_m, \quad (1)$$

where $A = K_E - 1$, $B = (E_f - E_m)/(E_f + A E_m)$ and $p = 1 + [(1 - V^*)/V^{*2}] V_f$. V^* for the random orientation of short fibres is 0.52 and the Einstein constant, K_E, for fibrous fillers is calculated from the aspect ratio [10].

In order to examine the fitting of the experimental data and to estimate the Young's modulus of the whisker, curve fitting to Equation 1 was carried out on a computer, assuming various values for E_f. Fig. 5 shows the plot for the POM whisker–epoxide composites, in which optimum fitting was obtained for $E_f = 90.0 \times 10^9$ N m^{-2}. The results of fitting for other composite samples are only listed in the last column of Table I. With the polyester and the polyacetal matrices, the values obtained for the POM whisker were 121×10^9 and 107×10^9 N m^{-2}, respectively, values which are not much different from the one obtained above. For these matrix resins, the assumption of solid adhesion would not be unreasonable as their wettability was apparently good. For polyacetal resins, the occurence of epitaxy on the whisker surface has been previously observed [6, 7].

Figure 4 Replica of mechanically-damaged POM whiskers (transmission electron micrograph).

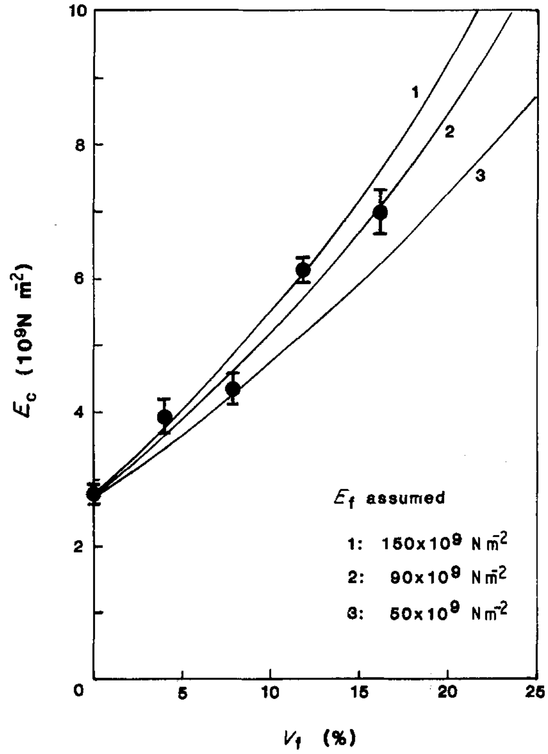

Figure 5 The Young's modulus of epoxide–POM whisker composite smaples plotted against filler content. Curves for various E_f-values have been calculated by fixing other parameters (see text).

(From the data of POM whisker–polyolefin composites, however, the curve-fitting gave very low E_f-values, of between 22×10^9 and 24×10^9 N m^{-2}. This should be attributed to poor adhesion of the matrix resin and the filler). The Young's modulus of the silicon carbide whisker of 478×10^9 N m^{-2}, deduced for the polyester-composites, agrees very well with the literature value of 490×10^9 N m^{-2} [12], supporting the usefulness of the present method for estimating the moduli of fillers.

During the curve-fitting operation, however, it was recognized that the optimum fitting value of E_f was sensitive to the scattering of data as well as to the assumed value of the Einstein constant. (The allowances for E_f, given in parentheses in the last column of Table I, are rough estimates and have no statistical significance.) In addition, the anisotropic nature of the POM whisker was not considered in the analysis. Taking these into account, 10^{11} N m^{-2} would be a reasonable estimate for the Young's modulus of the POM whisker. The crystal modulus of POM, given in the literature, deduced experimentally and calculated theoretically, ranges widely from 40×10^9 to 220×10^9 N m^{-2} (53×10^9, 189×10^9, 150×10^9, 220×109, 41×10^9, and 95×10^9 N m^{-2} in [13–18], respectively.) For a super-drawn poly-

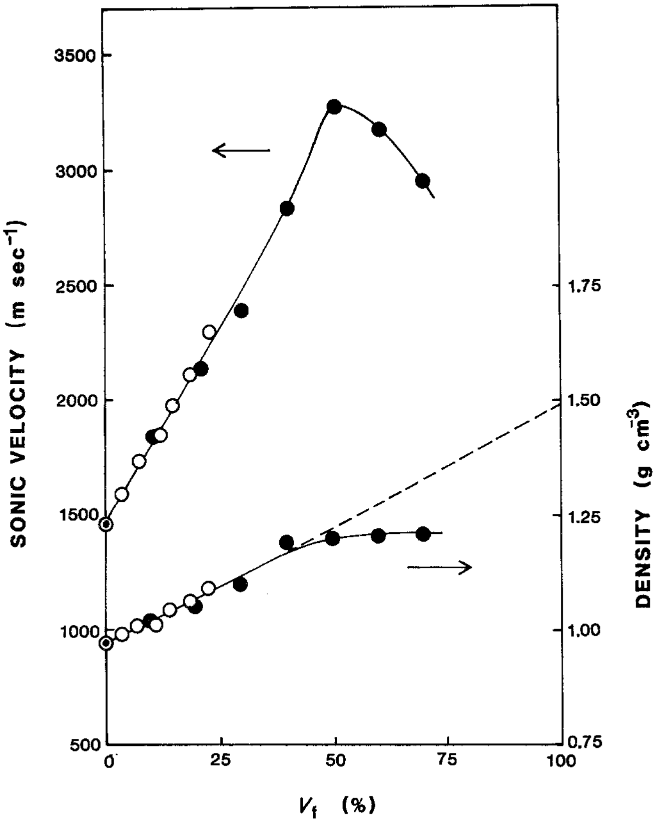

Figure 6 The sonic velocity and the density of polyolefin–POM whisker composite sheets plotted against filler content. o: isolated whiskers; •: unisolated whiskers. The broken line for the density is the theoretical relation expected from the densities of the filler and the matrix polymer, of 1.492 and 0.968, respectively.

acetal fibre and a fibrous material of solid-state polymerized trioxane, values of 35×10^9 and $47 \times 10^9\ \mathrm{N\,m^{-2}}$ are reported in [19, 20], respectively. In any case, the Young's modulus of the POM whisker is considered to be of the order of the theoretical value.

3.3. Acoustic characteristics of POM whisker–polyolefin composites

Reinforcement of the POM whisker by polyolefin was not as effective as the other matrix resins, but an increase in Young's modulus of as large as six times was attained with large filler contents (see Table I). The sonic velocity, calculated by the square-root of the Young's modulus divided by density, is plotted in Fig. 6 against the content of the filler. It was not clear whether or not the whiskers had been isolated into single pieces from the original radial assembly and how this affected their dispersibility in the matrix resins, but no significant differences were seen in the increases in sound velocity or Young's modulus. The curve showed a sudden decrease after the fifty per cent filler content. This is in accordance with the plot of the density, also made in Fig. 6, which deviated downwards from the expected line at around the same filler content. In practice, occlusion of air bubbles had been unavoidable when the filler content was higher. The point would correspond to the theoretical maximum volume content, of 0.52, for the random packing of short fibre-fillers in a space [10].

Besides sonic velocity, internal dynamic loss is an important parameter for a material to be used for acoustic diaphragms. The loss tangent, $\tan\delta$, obtained from the sharpness of the resonant peaks, was originally 6.9×10^{-2} at zero filler content and it decreased only gently with increasing filler content, for example, a value of 5.3×10^{-2} at 50 vol% filler. For this composite system, it could be understood that the fairly large internal loss, which did not drop seriously with increasing filler content, was due to the matrix polyolefin, whereas the improvement of the Young's modulus or the sonic velocity was due to the whisker.

Some cone-type loudspeaker diaphragms were prepared with the same composite sheets and test speaker units were constructed. In Fig. 7, an example of the frequency characteristics curves is demonstrated with a cone-type diaphragm

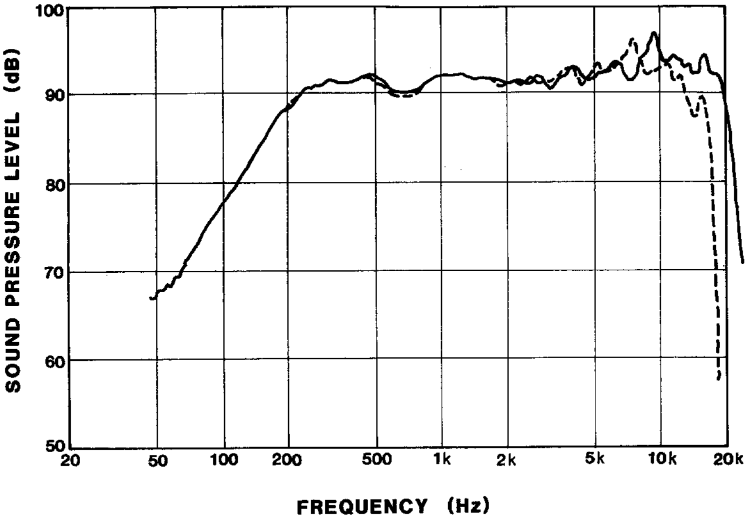

Figure 7 The frequency characteristic curves of test loudspeakers (7 cm diameter cone-type squawkers) carrying diaphragms of polyolefin sheets, unreinforced (broken line) and reinforced with 20 vol% POM whiskers (solid line). The sound pressure unit, dB, is converted to the SI unit, $\mathrm{N\,m^{-2}}$ by the factor $y = 2 \times 10^{0.05\,X - 5}$.

with a whisker content of 20 vol% and compared with the curve for a similar diaphragm constructed of unreinforced polyolefin sheet. The sound pressure level can be seen to have been improved by the addition of the whisker content in the high-frequency regions, i.e., above 10 KHz. The speakers exhibited an excellent audio performance, although this had nothing to do with materials science!

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