

# Studies on mechanical properties of polymer composites by X-ray diffraction:

## 3. Mechanism of stress transmission in particulate epoxy composite by X-ray diffraction

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Stress on particles in an aluminium particulate epoxy composite under load was investigated by X-ray diffraction. The microdeformation of the aluminium crystal could be detected as a shift in the X-ray diffraction peak induced by the applied stress. When a tensile stress was applied to the particulate composite, incorporated particles were found to be subjected to a stress several times larger than the applied stress. This was considered to result in a mechanical reinforcement of the composite. The states for stress concentration onto particles depend on the volume fraction and particle size. An increase in the macroscopic Young's modulus with the incorporation of filler could be explained quantitatively by using the stress concentration factor.

(Keywords: particulate composite material; stress transmission; X-ray diffraction; epoxy resin; mechanical property)

### INTRODUCTION

Recently high-performance materials have been required in many important fields, while the various demands in each field could not be always fulfilled with materials consisting of only one substance. Thus, materials consisting of two or more substances, i.e. composite materials, have been designed for complying with the demands. Plastics, paints and rubbers have frequently been used with incorporating powdery fillers to improve mechanical properties. For these particulate composite materials, it is important to clarify the reinforcement effect of the fillers. A variety of studies have reported on the reinforcement effect in terms of macroscopic mechanical properties<sup>1,2</sup>. For example, the reinforcement effect has been discussed by evaluating the increase in the macroscopic elastic modulus of the composite material resulting from the incorporation of particles, using various kinds of mechanical models. However, there have been a lot of difficulties using theoretical analysis because of the uncertainty of the adhesion between the matrix and fillers, and the complex deformation in the composite. In order to investigate one of the factors which influence the mechanical properties, we have previously proposed the 'X-ray diffraction method' to detect *in situ* and non-destructively the residual stress at the interface between the resin and adherent<sup>3,4</sup>.

In this study, the stress on particles, i.e. the local stress in the particulate composite under load was measured *in situ* by X-ray diffraction, and the reinforcement behaviour was discussed from the microscopic point of view.

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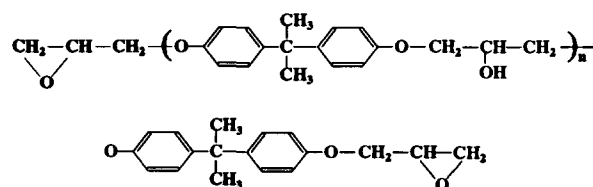
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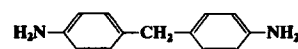
### EXPERIMENTAL

#### Materials

A liquid diglycidyl ether of bisphenol-A type epoxy resin (Epikote 828; Shell Chemical Co.;  $M_n$  380, epoxy equivalent  $190 \pm 5$ ,  $n = 0.1$ ) and 4,4'-diaminodiphenyl-



methane (DDM), an aromatic diamine curing agent,



were chosen as the resin system. The fillers used were aluminium particles with a purity of 99.5% and average diameters of 10 and 100  $\mu\text{m}$ . In order to obtain sharp peaks for X-ray diffraction, the aluminium particles were heat treated at 600°C for 1 h under  $\text{N}_2$  atmosphere and then gradually cooled. After heat treatment, a designated amount of aluminium particles was mixed with epoxy resin, degassed under reduced pressure at 120°C for 30 min, and then a stoichiometric amount of DDM was added. To prevent sedimentation of the filler which would bring about a cured specimen, the mixture was precured at 150°C for 10 min. The compound was then spread into a mould (80 × 60 × 0.5 mm) and cured at 200°C for 2 h.

The mechanical properties of the specimen were measured by a tensile tester (Shimadzu, Autograph SD-100) at 25°C. The initial length of the specimen was 40 mm and the extension rate was 5 mm min<sup>-1</sup>.

*Measurement of stress on particles by X-ray diffraction*

In order to know how much stress the particles would be subjected to, when the whole composite material was subjected to stress, the X-ray diffraction method was used. When a stress was applied to a specimen, it passed through the matrix, and was transmitted to the incorporated particles. The crystal lattice of the particles was strained by the stress and the crystal strains appeared as a shift in the diffraction angle 2θ. Consequently, the stress on the particles could be evaluated quantitatively by detecting the strain in the crystal by X-ray diffraction.

A cured specimen was set on a X-ray diffractometer (Rigaku Denki, RAD-B system) operated with a 2θ/θ scan and CuK<sub>α</sub> radiation. The aluminium crystal is a cubic system (a = 4.0497 Å at 23°C). The lattice plane of the crystal employed for the strain measurement was the (333)/(511) plane, and its diffraction angle was 162.5° for CuK<sub>α1</sub> radiation. Because of its high diffraction angle, the (333)/(511) reflection is very sensitive to the strain on the incorporated particles. The crystal strain ε was calculated from:

$$\epsilon = \frac{\Delta d}{d_0} \tag{1}$$

where d<sub>0</sub> denotes the initial lattice spacing for the (333)/(511) plane of the crystal, and Δd is the change in the lattice spacing induced by the constant stress applied. The experimental error in measuring the peak shift is evaluated ordinarily to be < ±0.003° for an angle 2θ. This corresponds to ~ ±0.1% strain. The strain measured is in the direction perpendicular to the applied stress. In order to obtain information about the strain distribution in the incorporated particles, strains at different inclination angles ψ of the incident X-ray beam were measured<sup>5,6</sup>.

Figure 1 shows a schematic representation of the measurement of stress on aluminium particles in a particulate composite by X-ray diffraction. For example, at ψ = 0°, the observed strain is in the direction perpendicular to the applied stress σ<sub>0</sub>, while from ψ = 90°, we can estimate the stress σ<sub>f</sub> on particles in the same direction as that of the applied stress σ<sub>0</sub>. Generally, the strain ε<sub>ψ</sub> at a given inclination angle can be expressed as:

$$\epsilon_{\psi} E = \sigma_f (\sin^2 \psi - \nu \cos^2 \psi) + P (\cos^2 \psi - \nu \sin^2 \psi) \tag{2}$$

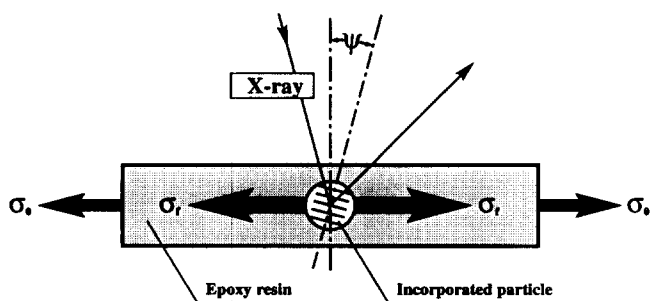


Figure 1 Schematic representation for the measurement of stress on particles by X-ray diffraction

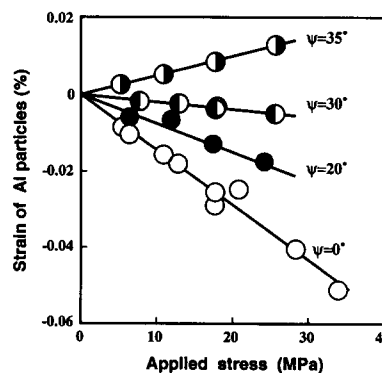


Figure 2 Relationship between the strain and the applied stress for aluminium (10 μm) particulate epoxy composite with a volume fraction of filler of 15.0%

where E and ν are the elastic modulus and the Poisson ratio of the aluminium crystal lattice, 75.5 GPa and 0.33, respectively, and P represents the pressure on the particles in the vertical direction to σ<sub>0</sub>. In these cases, shear stress might be brought about in the particles but its contribution is considered to be negligibly small. Thus, the principal stress of σ<sub>f</sub> and P are discussed here.

Matrix resin deforms much more than the incorporated particles since the Young's modulus of the former is usually much lower than that of the latter. Also, the matrix would contract much more than the incorporated particles in the direction perpendicular to the applied stress. The difference in strains between the matrix and the particles may cause a pressure P on the particles in the vertical direction to the applied stress.

When ε<sub>ψ</sub> is measured under various applied stresses at ψ = 0°, 20°, 30° and 35°, σ<sub>f</sub> could be determined by using equation (2) with the non-linear least square method.

RESULTS AND DISCUSSION

Figure 2 shows the relationship between strain ε<sub>ψ</sub> and the applied stress σ<sub>0</sub> of incorporated aluminium particles (average diameter 10 μm) at various inclination angles ψ for the particulate epoxy composite with a volume fraction of 15.0%. A linear relationship was observed between ε<sub>ψ</sub> and σ<sub>0</sub> for every inclination angle ψ. The strains were always reversible. At ψ = 0°, i.e. the direction perpendicular to the applied stress, the strain had negative values. This indicates that the incorporated particles were negatively strained in the direction perpendicular to the applied stress. The strain value increased gradually with increase in the inclination angle ψ, while over ψ = 35°, it became positive. From these results, we could estimate the stress of the aluminium particles using equation (2) and using the non-linear least square method. Because of the linear relationship between ε<sub>ψ</sub> and σ<sub>0</sub>, as shown in Figure 2, a strain value at a constant applied stress could be determined at every ψ.

Figure 3 shows the replot of Figure 2 for the relationship between the particle strain ε<sub>ψ</sub> and sin<sup>2</sup> ψ when σ<sub>0</sub> is 10 MPa. The value of ε<sub>ψ</sub> increased linearly with sin<sup>2</sup> ψ, which coincides with the prediction of equation (2).

In Figure 4, the strain ε<sub>ψ</sub> multiplied by the elastic modulus E of the aluminium particles is shown in polar coordinates around ψ for various applied stresses. Incorporated particles are subjected to a compressive

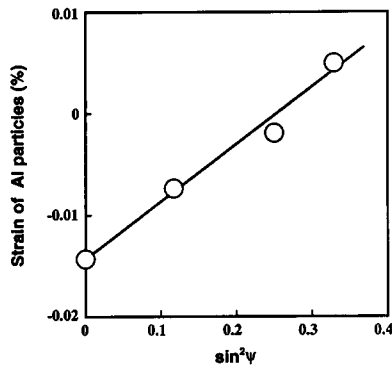


Figure 3 Relationship between the strain of aluminium particles and  $\sin^2 \psi$  for aluminium ( $10 \mu\text{m}$ ) particulate epoxy composite with a volume fraction of filler of 15.0%. The stress applied to the sample is 10 MPa

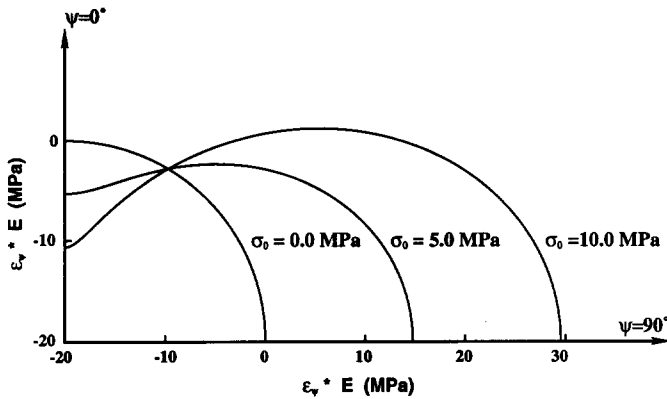


Figure 4  $\epsilon_{\psi}^* E$  of aluminium particles in polar coordinates around  $\psi$

strain in the direction perpendicular to the applied stress owing to the pressure  $P$  and the Poisson deformation of the crystallites. The stress  $\sigma_f$  on the particles increased with the applied stress, while with an applied stress of 10 MPa, the particles are subjected to a tensile stress of 29.2 MPa in the direction parallel to the applied stress, which is much larger than the applied stress. In other words, the stress concentrated on the incorporated particles is about three times higher than that of the applied stress. In contrast to this, the matrix resin of the composite would be subjected to less stress than the applied stress, which would result in reinforcement of the composite. Now the ratio of stress  $\sigma_f$  on the particles to applied stress  $\sigma_0$  is defined as a stress concentration coefficient  $\chi$  ( $= \sigma_f / \sigma_0$ ). The values of  $\chi$  for a specimen with different volume fractions of filler and different particle diameters of 10 and  $100 \mu\text{m}$  were measured.

Figure 5 shows the relationship between  $\chi$  and the volume fraction of filler for particulate epoxy composite. The stress concentration coefficient was larger than unity in all cases. This indicates that the reinforcement effect appeared up to a volume fraction of filler of 20.0%, though the value of  $\chi$  decreased with the volume fraction of filler. When the values of  $\chi$  for composites with different particle sizes incorporated were compared, the value of  $\chi$  was larger for the composite material incorporating aluminium particles with smaller diameters ( $10 \mu\text{m}$ ) for any volume fraction of filler. From these results, it may be predicted that the composite material incorporating aluminium particles with smaller diameters would show better mechanical properties. Since Young's modulus

corresponds to the deformation within a small strain region where non-linearity can be neglected, it is reasonable to focus on the Young's modulus in macroscopic mechanical properties.

Figure 6 shows the relationship between the macroscopic Young's modulus and the volume fraction of filler for the aluminium particulate epoxy composite. Young's modulus increased with the volume fraction of filler. Young's modulus increased from 2.15 ( $E_m$ ) to 4.51 GPa with increase in filler up to 20.0 vol% for the composite material incorporating aluminium particles with smaller diameters.

There have been a lot of reinforcement equations, from which the macroscopic Young's modulus could be estimated. Some of the equations are shown in Figure 6. For example, Kerner's equation<sup>7</sup> agreed with the result for the composite incorporating aluminium particles with larger diameters ( $100 \mu\text{m}$ ). However, it could not explain the reinforcement effect for the composite with smaller diameter ( $10 \mu\text{m}$ ) aluminium particles. Smallwood's equation<sup>8</sup> showed a better fitting with the observed Young's modulus, but neither of the equations fitted both experimental values<sup>9</sup>. These reinforcement equations can be divided into two types. One is constructed by considering mainly the volume effect of filler under various hypotheses such as homogeneous distribution of fillers, the complete adhesion at the interface between matrix and filler, etc. If these hypotheses were all satisfied, then the reinforcement effect could be evaluated on theoretical grounds. However, in practice, most of these hypotheses may not always be fulfilled, so when the

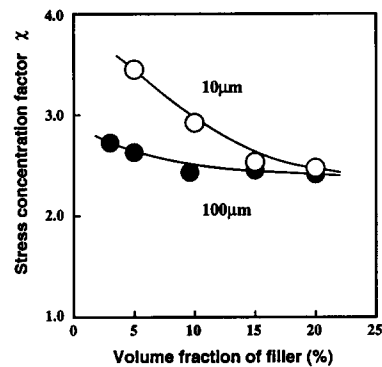


Figure 5 Relationship between the stress concentration factor  $\chi$  ( $= \sigma_f / \sigma_0$ ) and the volume fraction of filler for particulate epoxy composite

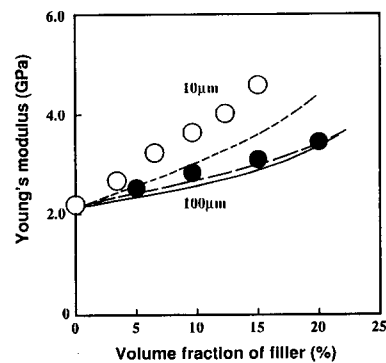


Figure 6 Relationship between Young's modulus and the volume fraction of filler for aluminium particulate epoxy composite: (—) Kerner's equation; (---) Guth's equation; (- - -) Smallwood's equation

equations are applied to the actual composite system, the calculated value is not consistent with the experimental value in many cases<sup>2</sup>, as shown in Figure 6. The other type is constructed by considering not only the volume effect of filler but also the surface effect, shape, diameter and hardness effects of filler, etc.<sup>10,11</sup>. There are also a large number of this type of equations. But in these cases, a lot of parameters are introduced in order to fit to the experimental value. Therefore the equations become empirical with little theoretical basis.

As shown in Figure 5, the stress concentration coefficient  $\chi$  had larger values when aluminium particles with smaller diameters were incorporated into the epoxy resin, and the smaller particles possessed a larger macroscopic Young's modulus, which is in accordance with the qualitative presumption. Next, we tried to obtain relationships between the macroscopic reinforcement effect, stress concentration coefficient  $\chi$  and the volume fraction of filler.

Particles incorporated in the composite material were subjected to a larger stress than the average stress as shown above, and the matrix was considered to be subjected to smaller stress. By using  $\chi$ , the average stress  $\sigma_m$  in the matrix can be expressed as follows:

$$\sigma_m = \sigma_o \frac{1 - \chi V_f}{1 - V_f} \tag{3}$$

where  $V_f$  represents the volume fraction of incorporated particles.

The strain of the matrix is restricted by the presence of the particles, and its distribution between two particles is shown schematically in Figure 7. The strain  $\varepsilon(l)$  at a position  $l$  ( $-L_o/2 \leq l \leq +L_o/2$ ) could be expressed by the following equation:

$$\varepsilon(l) = \varepsilon_{min} + (\varepsilon_{max} - \varepsilon_{min}) \times \left[ 1 - \exp\left(-\frac{L_o - 2l}{2\delta}\right) - \exp\left(-\frac{L_o + 2l}{2\delta}\right) \right] \tag{4}$$

where  $\varepsilon_{min}$  is the strain of the matrix at the particle surface,  $\varepsilon_{min} = \chi\sigma_o/E_f$ ,  $\varepsilon_{max}$  is the strain of the matrix with no restriction from particles,  $\varepsilon_{max} = \sigma_m/E_m$ ,  $L_o$  is the average distance between particle surfaces,  $L_o = \{(\pi/6)[(1 - V_f)/V_f]\}^{1/3}d$ , where  $d$  is the average diameter of particles (10 or 100  $\mu\text{m}$ ) and  $\delta$  is a position where  $\varepsilon_{max} - \varepsilon(l) = (\varepsilon_{max} - \varepsilon_{min})/\varepsilon$  (Figure 7). The experimental value of  $\delta$  is 2.50  $\mu\text{m}$  for the system studied.

The average strain  $\varepsilon_{av}$  for the matrix could be calculated from the following equation by integrating  $\varepsilon(l)$ :

$$\varepsilon_{av} = \left(\frac{1}{L_o}\right) \int_{-L_o/2}^{L_o/2} \varepsilon(l) dl \tag{5}$$

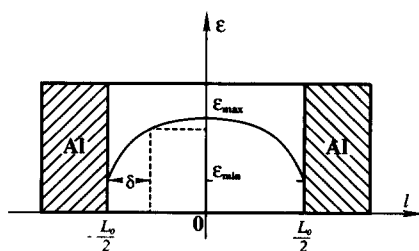


Figure 7 Schematic representation for the strain distribution of the matrix between two aluminium particles

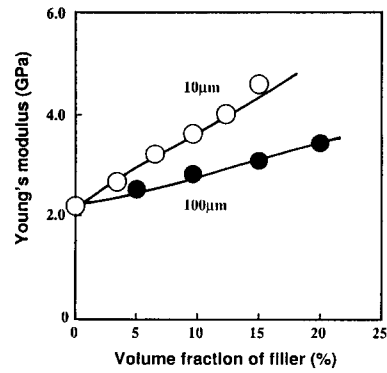


Figure 8 Relationship between Young's modulus and the volume fraction of filler for aluminium particulate epoxy composite. The solid line indicates the calculated result using equation (6)

With the average strain value  $\varepsilon_{av}$  the macroscopic Young's modulus  $E_c$  of the whole composite material could be calculated from the following equation:

$$\frac{1}{E_c} = \frac{\chi}{E_f} + \left[ \frac{1 - \chi V_f}{(1 - V_f)E_m} - \frac{\chi}{E_f} \right] \times \left\{ 1 - \frac{2\delta}{L_o} \left[ 1 - \exp\left(-\frac{L_o}{\delta}\right) \right] \right\} \tag{6}$$

For particles of large size, the restriction of the strain of the matrix by particles could be neglected, and equation (6) could be simplified into the following equation at a low volume fraction:

$$E_c = \frac{1 - V_f}{1 - \chi V_f} E_m \tag{7}$$

Figure 8 shows the calculated result from equation (6) with the observed Young's modulus in Figure 6. The calculated value agreed well with the experimental value. Accordingly, the increase in macroscopic modulus could be expressed quantitatively by considering the stress concentration on particles. The restriction of the deformation of the matrix by the incorporation of particles is concluded to bring the reinforcement effect to the composite. With the same volume fraction of fillers, reinforcement increased with decreasing particle sizes, because the distance between the interfaces of particles decreased with the decrease in particle sizes. This is the reason why the smaller particles are much more effective for the reinforcement of epoxy resin.

## CONCLUSIONS

The stress on particles in aluminium particulate epoxy composite under load was measured by the X-ray diffraction method. The stress on the particles was found to be several times larger than the applied stress. This indicates that the stress was concentrated on the incorporated particles, which is considered to bring about mechanical reinforcement in the composite. The ratio of the stress on the particles to the applied stress, defined as  $\chi$ , decreased with the increase in volume fraction and size of filler. By using the value of  $\chi$ , an increase in the macroscopic Young's modulus with the incorporation of filler could be quantitatively explained.

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