Residual Stress in Particulate Epoxy Resin by X-Ray Diffraction

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SYNOPSIS

Residual stress in particulate epoxy resin was investigated by X-ray diffraction. Microdeformation of incorporated Al and α-SiO_2 crystal, which was induced by the residual stress, could be detected as a shift of X-ray diffraction peak. The residual stress at the interface between the adherend and the particulate epoxy resin was found to decrease with the increase of volume fraction of filler. It was shown that the difference in the thermal expansion coefficients between the adherend and the particulate epoxy resin is much more effective on residual stress than the increment of Young's modulus owing to the incorporation of filler. When epoxy resin was cured on the Al plate, incorporated particles were subjected to a tensile stress; while cured on polytetrafluoroethylene sheet, particles were subjected to a compressive stress. The incorporation of some inorganic particles is considered effective to reduce the residual stress.

INTRODUCTION

Recently, with the demand of high-performance materials residual stress in composite material has become an important problem. Residual stress might cause cracks and deteriorate mechanical and electronic properties and weatherability. Many researchers have tried to reduce residual stress by modifying epoxy resin with rubbery components,[1] plasticizers,[2] or incorporation of inorganic particles.[3] There are a few methods that can be used to detect residual stress in terms of the *macro* deformation of adherend, such as the strain gauge method,[3,4] the bimetal method,[5,6] the laser[7] and X-ray[8,9] displacement method, and the layer removal procedure,[10] and so on.

In the previous paper,[11] we proposed a new technique—X-ray diffraction method—that can detect residual stress in terms of the *micro* deformation of crystal lattice. When epoxy resin is cured at high temperature and cooled to room temperature, the crystal lattice of adherend will be subjected to a stress (appears as a strain) owing to the difference in the thermal expansion coefficients between epoxy resin and adherend. This strain of crystal lattice would appear as a shift of diffraction angle 2θ, so the residual stress can be checked quantitatively by X-ray diffraction. It has been shown that this is an excellent method to detect the residual stress at the interface between resin and adherend *in situ* and nondestructively.

In this study, the X-ray diffraction method was applied to detect the residual stress of incorporated filler in the particulate epoxy composite material prepared on different adherends.

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)

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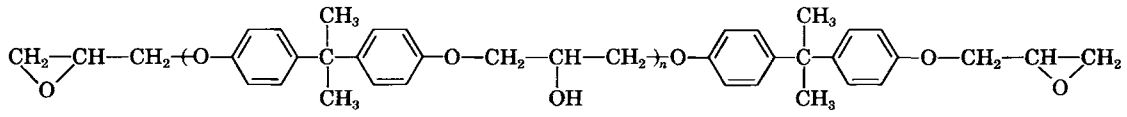
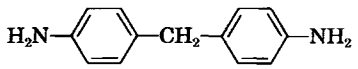


and 4,4'-diaminodiphenylmethane (DDM), an aromatic diamine curing agent



were chosen as the resin system in this study. The fillers used were Al particles with a purity of 99.5% and an average diameter of 10 μm, 100 μm, and crystalline silica particles (α-SiO_2) with an average diameter of 20 μm. Adherends used were commercial Al plate (50 × 70 × 4 mm) and polytetrafluoroethylene (PTFE) sheet. To get sharp peaks for X-ray diffraction and release internal residual stress, Al particles were heat treated at 500°C for 1.0 h. Al plate was mechanically ground and then also heat treated at the same conditions. It was degreased and treated with chromic acid, after which it was washed in running water followed by rinsing in deionized water (JIS 6848).

Preparation of Specimen

Epoxy resin was mixed with a stoichiometric amount of DDM (20.7 wt %) and filler at 100°C. Compounds were poured on adherend, degassed under vacuum, and precured at 80°C for 2 h, then cured at 180°C for 6 h. During the curing period, the specimen was turned upside down repeatedly to prevent sedimentation of filler. After curing, the specimen was cooled gradually to room temperature and preserved in a desiccator for over 24 h. The shape of the specimen has been presented in the previous paper.[11]

Glass transition temperature T_g of particulate resin was measured using a differential scanning calorimeter (Daini Seikosha, SSC-560S) at a heating rate of 10°C/min from room temperature to 200°C at ambient pressure. Sample weight was 10.0 mg. The system was calibrated with Indium.

Mechanical properties of samples 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 5 mm/min. Epoxy resin without incorporating silica particles showed a Young's modulus of 2.2 ± 0.1 GPa.

Thermal expansion coefficient β was measured by a thermomechanical analyzer (Rigaku Denki, TMA 8095B1) at a heating rate of 2.5°C/min from room temperature to 220°C using specimen with a shape of 20 × 5 × 0.5 mm.

Measurement of Residual Stress by X-Ray Diffraction

For a cured specimen, stress distribution will be very complicated as shear or peeling stress may exist at the ends of the interface. To simplify measurement, we have taken the center of the specimen as the measurement point. The shape of the specimen has been presented in the previous paper.[11] The specimen was set on a X-ray diffractormeter (Rigaku Denki, RAD-B system).

Al crystal is a cubic system (a = 4.0497 Å at 23°C) with a thermal expansion coefficient β of 2.386 × 10^{-5} K^{-1}. α-SiO_2 crystal is a hexagonal system (a = 4.913 Å, c = 5.405 Å) with a thermal expansion coefficient β of 1.333 × 10^{-5} K^{-1}. The thermal expansion coefficients of both Al and α-SiO_2 are far less than that of epoxy resin (β = 6.787 × 10^{-5} K^{-1}). When an epoxy resin is cured at high temperature and cooled to room temperature, crystal lattice of filler and adherend will be strained. These crystal strains would appear as a shift of diffraction angle 2θ, so the residual stress resided in filler and adherend can be checked out quantitatively by X-ray diffraction.[11-13] The crystal strain ϵ could be calculated in terms of the relation:

$$\epsilon = \Delta d/d_0 \qquad (1)$$

where d_0 denotes the initial lattice spacing for the (422) plane (2θ = 137.4° for $CuK_{\alpha 1}$) of Al crystal. Δd is the change in the lattice spacing induced by residual stress. The experimental error in measuring the peak shift is evaluated ordinarily to be less than 0.003° in an angle 2θ. Temperature was determined by attaching a thermocouple to the specimen, and the lattice spacings were converted into the values at 23°C by correcting with β. The measured strain ϵ is that in the direction perpendicular to the adherend surface. To get the information about the directionality of residual stress, the $\sin^2 \Psi$ method was adopted. In this method, the strains ϵ at different

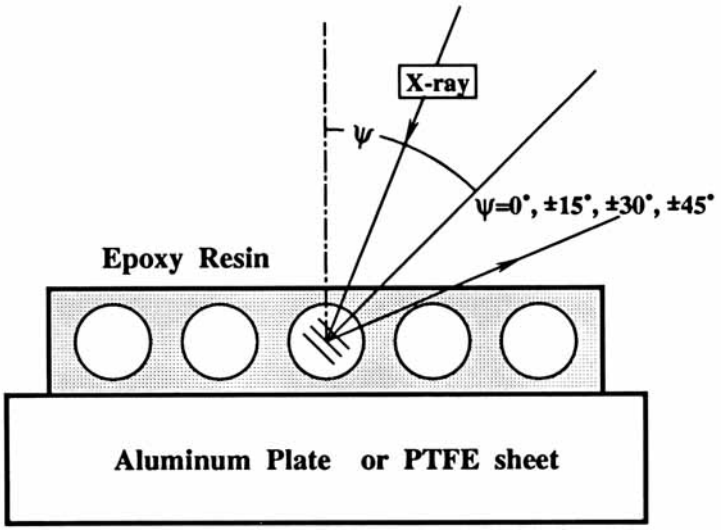


Figure 1 Schematic representation for residual stress measurement by X-ray diffraction.

Ψ, an inclination angle of the incident X-ray beam as shown in Figure 1, will be measured. When uniaxial residual stress σ exists, the relationship between ϵ and Ψ can be expressed as:

$$\epsilon = [(1 + \nu)\sigma/E]\sin^2 \Psi \qquad (2)$$

where E, ν are the elastic modulus and the Poisson ratio of crystal lattice, E being 75.5 and 83.8 GPa for Al and α-SiO_2, respectively. From the gradient of ϵ-$\sin^2 \Psi$ plot, we can get the information about the value and directionality of residual stress.

RESULTS AND DISCUSSION

Using a particulate epoxy resin cured on the Al plate with a volume fraction of Al particles (100 μm) ranging from 2–30 vol %, the strain ϵ of Al particles was measured at the different inclination angles Ψ.

Figure 2 shows the relationship between ϵ and $\sin^2 \Psi$ for these specimen. At any volume fraction of filler, $\epsilon < 0$ at $\Psi = 0°$, i.e., strain was minus in the direction perpendicular to the adherend surface. On the other hand, ϵ increased with increasing Ψ and became plus over 30° in Ψ. Plots in Figure 2 could be expressed with a straight line through $\epsilon = 0$ at $\Psi = 30°$ with a positive gradient. These indicate that incorporated Al particles were subjected to a uniaxial tensile stress. When epoxy resin is cooled from curing temperature to room temperature, the thermal shrinkage of cured resin below its glass transition temperature (167°C) was restricted by the Al adherend. This is considered to bring about a tensile stress to the incorporated particles through matrix resin. From Figure 2, the gradient decreased with the volume fraction of Al filler. This indicates

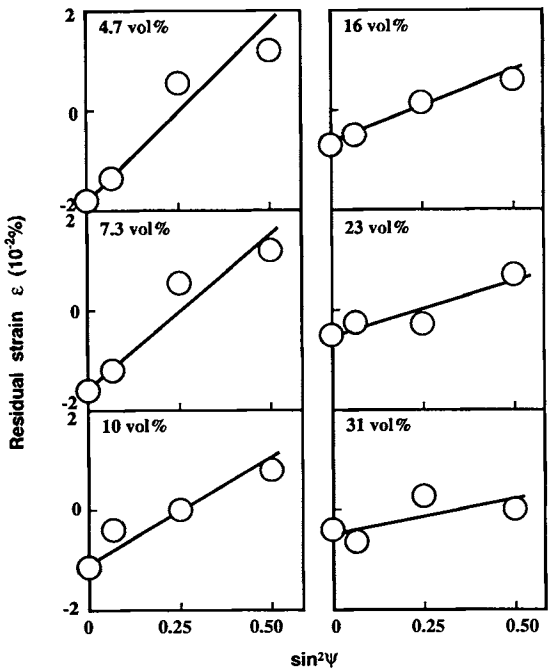


Figure 2 Relationship between residual strain (ϵ) of incorporated Al particles (ca. 100 μm) and $\sin^2 \psi$ for various volume fractions.

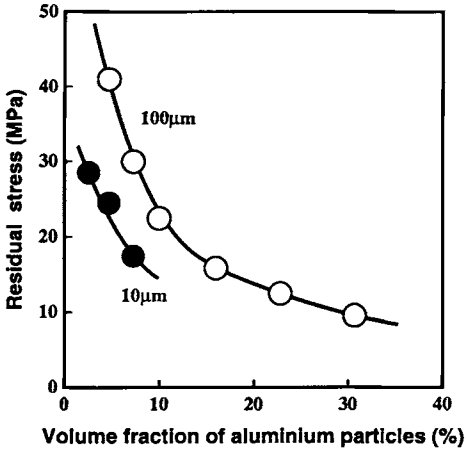


Figure 3 Relationship between residual stress σ and volume fraction of Al particles incorporated into resin cured on Al adherend.

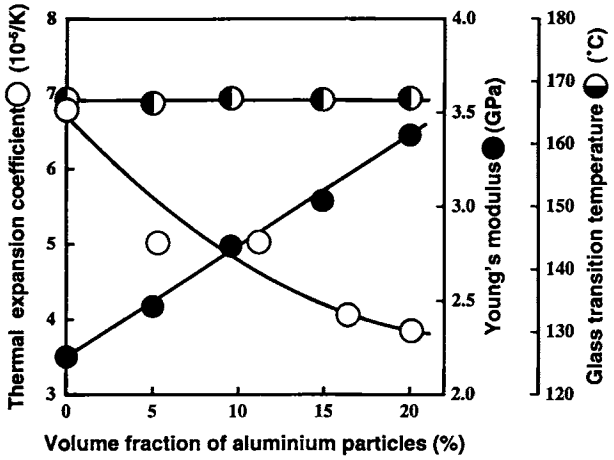


Figure 5 Relationships between Young's modulus, glass transition temperature, expansion coefficient, and volume fraction of Al particles incorporated into the epoxy resin.

that residual stress decreased by incorporating Al particles.

Figure 3 shows the relationship between residual stress and volume fraction of Al particles. Results on the epoxy composite incorporated with Al particles of its average diameter of 10 μm were also superimposed with filled circles on the figure. Residual stress decreased with the volume fraction of filler conspicuously. Further, residual stress was much lower for the specimen incorporated with Al particles of 10 μm. It is questionable whether these phenomena correspond to the decrement of residual stress at the interface between adherend and resin or not because here detected stress is that which resided in the incorporated particles and the detected position became far from the interface owing to the incorporation of Al particles. Accordingly, to measure stress that resided on both the adherend side and the incorporated particles side spontaneously

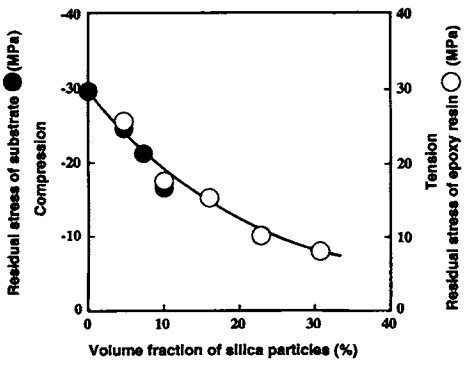


Figure 4 Relationship between residual stresses of both Al adherend side and incorporated SiO_2 side and volume fraction of filler.

silica particles, instead of Al particles, with an average diameter of 20 μm were incorporated into epoxy resin. The (225) and (502) planes (2θ = 143.2° for $CuK_{\alpha 1}$) of α-SiO_2 was used to measure strain resided on the incorporated silica crystal.

Figure 4 shows the relationship between residual stresses of both adherend side (filled circle) and incorporated SiO_2 particles side (open circle) and the volume fraction of filler. Residual stress on both sides decreased with increase of volume fraction of filler. This indicates that stress that resided at the interface between adherend and particulate resin also decreased by the incorporation of filler. Above 10 vol %, diffraction peaks of Al adherend could not be observed through the thick layer of incorporated SiO_2 particles. The interfacial residual stresses are considered to obey the law of action and reaction because the directionality of residual stress on both sides were opposite and the absolute values coincided.

As shown above, residual stress of particulate epoxy resin decreased by the incorporation of inorganic particles. It has been reported there are three main factors determining residual stress[4]: glass transition temperature T_g, Young's modulus of resin, and the difference in thermal expansion coefficients between epoxy resin and adherend. The decrement of any one of these three factors by incorporating particles will result in the decrement of residual stress.

Figure 5 shows the relationships between T_g Young's modulus, β of particulate epoxy resin, and the volume fraction of Al particles. T_g remained constant with increase of the volume fraction of filler. Thus, the incorporation of Al particles has

been proven to have no effect on the glass transition temperature. Young's modulus increased with the volume fraction of filler. The increment of Young's modulus will result in a large residual stress, which is against the present results. Meanwhile, β decreased with the volume of filler. Hence, it could be concluded that the decrement of the difference in thermal expansion coefficients between adherend and particulate epoxy resin is much more effective.

For the particulate epoxy composite cured on Al plate, the excellent adhesion with the adherend is considered to bring the residual stress to the incorporated particles. On the other hand, to investigate the influence of adherend on the residual stress of filler residual stress in the particulate specimen cured on PTFE plate was measured. PTFE plate has no adhesion to epoxy resin so particles incorporated in the epoxy resin could not be subjected to a stress from the adherend.

Figure 6 shows the relationship between ϵ and $\sin^2 \Psi$ for Al particles incorporated in the epoxy resin (10 vol %) cured on PTFE plate. Again, plots could be expressed with a straight line through $\epsilon = 0$ at $\Psi = 30°$; hence, it could be considered that the residual stress in the epoxy resin is uniaxial at the request of eq. (2). In this case, however, the line gradient is minus, in contrast with that cured on Al plate. This indicates that incorporated particles were subjected to a compressive residual stress. When cured on PTFE plate, the difference in the thermal expansion coefficients between incorporated Al particles and the matrix resin is considered to cause the residual stress.

Figure 7 shows the relationship between residual stress and volume fraction of Al particles incorporated in the epoxy resin cured on the PTFE plate.

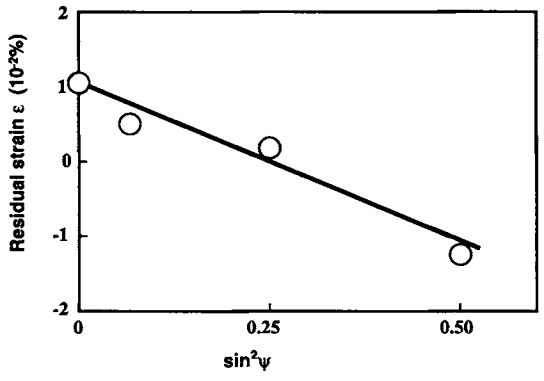


Figure 6 Relationship between residual strain (ϵ) of incorporated Al particles (ca. 100 μm) and $\sin^2 \Psi$. Epoxy resin was cured on PTFE sheet.

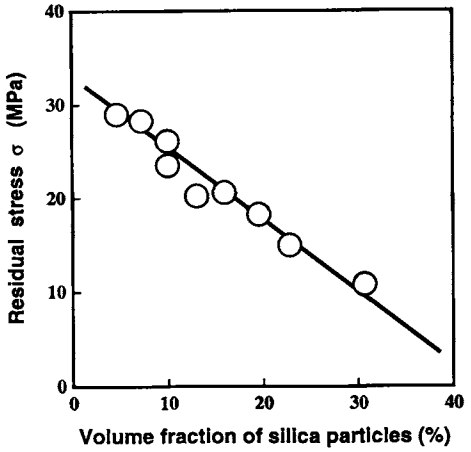


Figure 7 Relationship between residual stress σ and volume fraction of Al particles incorporated into epoxy resin cured on PTFE sheet.

Residual stress of Al particles reduced remarkably with the increase of volume fraction of filler. This suggests that the incorporation of some inorganic particles is effective to reduce residual stress.

The effects on residual stress of particle diameter, surface treatment, and heat history will be reported elsewhere.

CONCLUSION

Residual stresses in particulate epoxy resin cured on Al plate and PTFE sheet were investigated by X-ray diffraction. It was found that Al particles incorporated in epoxy resin cured on Al sheet were subjected to a tensile residual stress, whose value decreased with the volume fraction of the filler, and that smaller particles showed a better effect on the reduction of residual stress. Residual stresses on epoxy resin side and on adherend side were found to be equal in value but opposite in their directions. It was also found that Al particles in epoxy resin cured on PTFE sheet were subjected to a compressive stress, which also decreased with the volume fraction of Al particles. The incorporation of filler is considered effective to reduce residual stress. The X-ray diffraction method provides us with important information on residual stress in particulate epoxy resin.

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