Studies on Mechanical Properties of Polymer Composites by X-Ray Diffraction. I. Residual Stress in Epoxy Resin by X-Ray Diffraction

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Synopsis

Residual stress in epoxy resin cured on Al plate was investigated by X-ray diffraction. Microdeformation of Al crystal can be detected as a shift of X-ray diffraction peak induced by the stress resided. Results show that Al plate is subjected to a uniaxial compressive stress of 29 MPa parallel to the adherend surface. In contrast to this, epoxy resin side (embedded particles) was found to be subjected to a uniaxial tensile stress. Experimental data have been compared with the calculated data and that obtained by the bimetallic method. On the basis of results, it is reasonable to conclude that T_g is a key factor determining the residual stress, and the difference of thermal expansion coefficients between Al plate and the cured epoxy resin from T_g to room temperature causes the residual stress. It has been shown that the X-ray diffraction method is useful to detect the stress at the interface between resin and adherend *in situ* and nondestructively.

INTRODUCTION

Recently epoxy resin has been widely used in many important fields, such as the electronic and aerospace industries, with its excellent electronic and mechanical properties. When epoxy resin is cooled down from curing temperature to room temperature, however, residual stress is known to arise because of the difference in thermal expansion coefficients of resin and adherend.[1-3] The residual stress reduces adhesive strength and induces cracks in materials. Further, when epoxy resins are used as sealing materials of IC and LSI, the residual stress might cause cracks, deteriorate electronic insulating properties, weatherability, and result in shorter lifetimes of IC and LSI.[4] Many researchers tried to reduce the residual stress by modifying epoxy resin, for example, with rubbery component,[5] plasticizers,[6] or by incorporating rubbery[7] and inorganic particles.[2]

A few methods detect the residual stress by using a strain gauge,[1-3] bimetal,[6,8] photoelasticity,[9] and layer removal procedures.[10] However, reported values of residual stress scattered widely for each investigator even though the same cured epoxy resin system was employed.

In this study, we propose a new technique, that is, the "X-ray diffraction method" to detect residual stress at the interface between resin and adherend.

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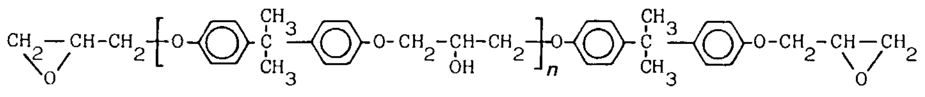
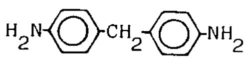
EXPERIMENTAL

Materials

A liquid diglycidyl ether of bisphenol A type epoxy resin (Epikote 828; Shell Chemical Co.; M_n 380, epoxy equivalent 190 ± 5);



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



were chosen as the resin system in this study. The filler used is Al particles with a purity of 99.5% and average diameters of 100 μm. The adherend used is commercial Al plate (50 × 70 mm × thickness 4 mm). In order to get sharp peaks for X-ray diffraction and release internal residual stress, the Al plate was mechanically ground and heat treated at 500°C for 1 h. It was degreased and treated with chromic acid, after which it was washed in running water followed by rinsing in deionized water (JIS K 6848).

Preparation of Specimen

Epoxy resin was mixed with a stoichiometric amount of DDM (20.7 wt %) and filler (when required) at 100°C. The compounds were poured on Al plates and precured at 80°C for 2 h, then cured at 180°C for 6 h. After curing, a specimen was cooled down gradually to room temperature and preserved in a desiccator for over 24 h. The shape and dimensions of the specimen for residual stress measurement are shown in Figure 1. The glass transition temperature

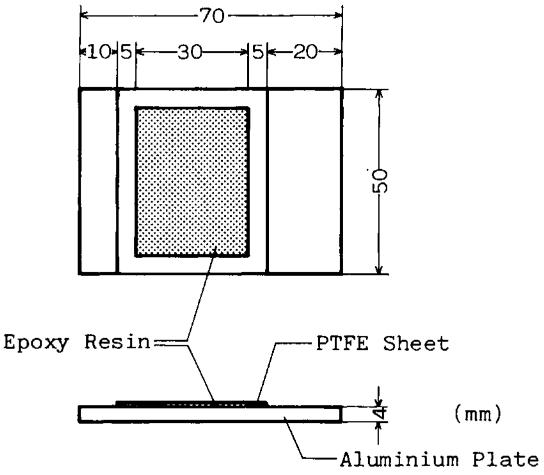


Fig. 1. Shape and dimension of the specimen for the residual stress measurement.

T_g of the specimen was determined to be 167°C, using a differential scanning calorimeter (Daini Seiko Sha, SSC-560S) at the heating rate of 10°C/min. The density of the cured specimen obtained by the flotation method (NaBr aqueous solution at 30°C) was 1.197 g/cm^3. Stress–strain curve for the cured epoxy resin was measured by a tensile tester (Shimadzu Autograph AD-100) at room temperature. The initial length of the specimen was 60 mm and the crosshead speed was 5 mm/min. The elastic modulus, tensile strength, and elongation at break are 2.4 GPa, 84.3 MPa, and 6.4%, respectively.

Measurement of Residual Stress by X-ray Diffraction

A cured specimen was set on an X-ray diffractometer (Rigaku Denki, RAD-B system) operated at a tube voltage of 40 kV, tube current of 20 mA for CuK$_\alpha$ radiation, with a divergence slit width of 0.5°. The Al crystal is a cubic system (a = 4.0497 Å at 23°C) with a thermal expansion coefficient (2.386×10^{-5} K^{-1}) far less than epoxy resin. When an epoxy resin is cured at high temperature and cooled down to room temperature, Al crystals of the adherend will be subjected to a residual stress because an epoxy resin adheres strongly to Al, which causes the strain in the Al crystal. This strain of Al crystal would appear as a shift of diffraction angle 2θ, so the residual stress can be checked out quantitatively by X-ray diffraction.[11-13] The strain ε of Al crystals could be estimated by use of the relation

$$\varepsilon = \Delta d / d_0$$

where d_0 denotes the initial lattice spacing for the (422) plane (2θ = 137.4° for CuK$_{\alpha 1}$) of the Al crystal, and Δd is the change in the lattice spacing induced by the residual stress. The experimental error in measuring the peak shift is evaluated ordinally 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 values at 23°C. Measured strain ε is that in the direction perpendicular to the Al plate. In order to get the information about the directionality of residual stress, the $\sin^2\psi$ method was adopted. In this method, the strain ε at different ψ, an inclination angle of

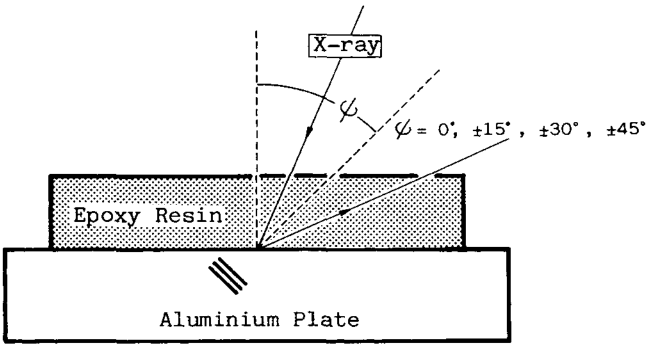


Fig. 2. Schematic representation for the residual stress measurement by X-ray diffraction.

incident X-ray beam as shown in Figure 2, will be measured. When uniaxial residual stress σ exists, the relationship between ε and ψ can be expressed as[13]

$$\varepsilon = \{(1+\nu)\sigma/E\}\sin^2\psi$$

where E and ν are the elastic modulus (75.5 GPa) and the Poisson ratio (0.33) of the Al crystal, respectively. From the gradient of $\varepsilon - \sin^2\psi$ plot, we get the information about the value and directionality of residual stress.

Measurement of Residual Stress by Bimetallic Method

Al plate (80 mm × 15 mm × thickness 0.1 mm) was coated with epoxy resin, then cured as mentioned in "Preparation of Specimen". When the sample was cooled down from curing temperature to room temperature, it curved due to the difference of thermal expansion coefficients between Al plate and the epoxy resin. By measuring the radius of curvature ρ, the residual stress can be calculated[8] by

$$\sigma = \frac{E_1 h_1^3}{12 h_2}\frac{2}{\rho H}\left[1 + \frac{1}{3}\left(\frac{h_1}{H}\right)^2\right]$$

where E_1 is elastic modulus of Al plate, h_1 and h_2 are thickness of Al plate and coated epoxy layer, respectively, and $H = h_1 + h_2$.

RESULTS AND DISCUSSION

Using an epoxy resin cured on the Al plate with a thickness of 0.6 mm, strain ε of Al crystal were measured by X-ray diffraction, and a relationship with $\sin^2\psi$ is shown in Figure 3. From this figure, $\varepsilon < 0$ at $\psi = 90°$, that is, in the direction parallel to the substrate surface; while $\varepsilon > 0$ at $\psi = 0°$, that is, in the direction perpendicular to substrate surface. Plots in Figure 3 can be expressed with a straight line through $\varepsilon = 0$ at $\psi = 30°$ with a minus gradient. This

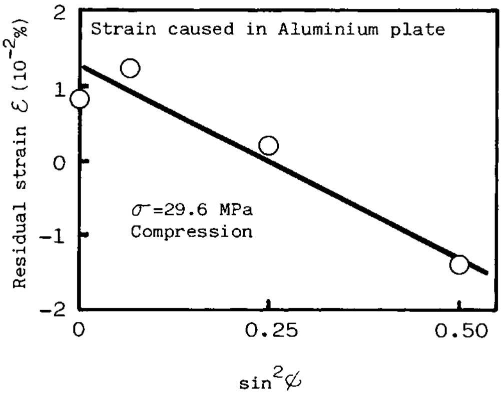


Fig. 3. Relationship between the residual strain (ε) of the Al plate and $\sin^2\psi$.

indicates that the Al plate is subjected to a uniaxial compressive stress of 29.5 MPa parallel to the adherend surface. These results can be explained in terms of the following phenomena. When the epoxy resin is cooled down from curing temperature to room temperature, it will shrink, as will the adherend. Epoxy resin, however, has a linear thermal expansion coefficient β_{ep} of 6.698×10^{-5} K^{-1}, measured by the dilatometric method, far greater than that of Al crystal ($\beta_{Al} = 2.386 \times 10^{-5}$ K^{-1}) and epoxy resin adheres strongly to Al adherend (they have a very excellent adhesion to each other), so the Al substrate surface is compelled to contract, and a compressive stress is brought about at $\psi = 90°$, while a poison deformation of Al crystal yields a strain $\varepsilon > 0$ at $\psi = 0°$.

Then the residual stress was measured for the specimens of different thickness of cured epoxy resin in order to know where residual stress arised.

Figure 4 shows the relationship between the residual stress and the thickness of cured epoxy resin layer. The residual stress in the Al plate is constant at about 29 MPa, having nothing to do with the thickness of epoxy layer up to 1 mm. Thus it can be said that the X-ray diffraction method detects the residual stress at the adhesion interface between the epoxy resin and the adherend.

In general, the residual stress in the cured system can be calculated from the products of the elastic modulus and the difference of the thermal expansion coefficients between the epoxy resin and Al.[1-5] The calculated values are listed in Table I together with the experimental value obtained by the X-ray diffraction, bimetallic, and strain gauge[2] methods. Residual stress of 29.5 MPa by X-ray diffraction is larger than the calculated one. This suggests that the residual stress at the interface between the epoxy resin and the adherend (X-ray diffraction method) is somewhat larger than that in the whole specimen (calculated value). Further, both in the bimetallic and strain gauge methods, the residual stress is smaller compared with both calculated value and that obtained by the X-ray diffraction method. In the X-ray diffraction method, the strain was measured directly as a microdeformation of lattice spacing of Al crystal, while in the bimetallic method, the strain was calculated from the curvature of the coated aluminum, that is, the macroscopic deformation. This is why the residual stress by the bimetallic method is smaller.

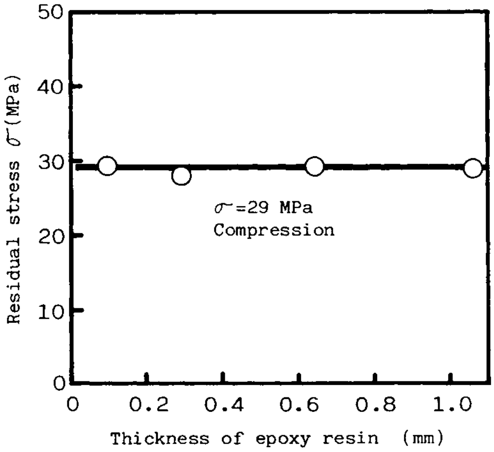


Fig. 4. Relationship between the residual stress and the thickness of cured epoxy resin layer.

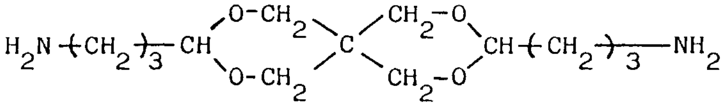
TABLE I
Calculated and Measured Value of Residual Stresses

Measurement	Residual stress MPa
X-ray diffraction	29.5
Bimetal	5.3
Strain gauge	8.8[a]
Calculated	17, 24.1[a]

[a] From Ref. 2.

In order to provide the residual stresses with a wide range of values, the content of curing agent DDM was changed for the cured epoxy resin.

Figure 5 shows the effect of the content of curing agent on (a) the residual stress on the Al plate and (b) the glass transition temperature T_g of cured epoxy resin. Both the residual stress and T_g increase abruptly with increasing content of DDM and reach the maximum value at the DDM equivalent content (▽), followed by gradual decreasing. The appearance of the change of residual stress corresponds to that of T_g. When the epoxy resin (Epikote 828) is cured with the room temperature curing agent (Epomate RX-3, Shell Chemical Co.; $M_n = 274$),



$$H_2N(CH_2)_3-CH\begin{smallmatrix}O-CH_2\\O-CH_2\end{smallmatrix}C\begin{smallmatrix}CH_2-O\\CH_2-O\end{smallmatrix}CH(CH_2)_3-NH_2$$

at room temperature for 24 h, both the residual stress (→) and T_g (→) are low. These indicate that T_g is the key factor to determine the residual stress,

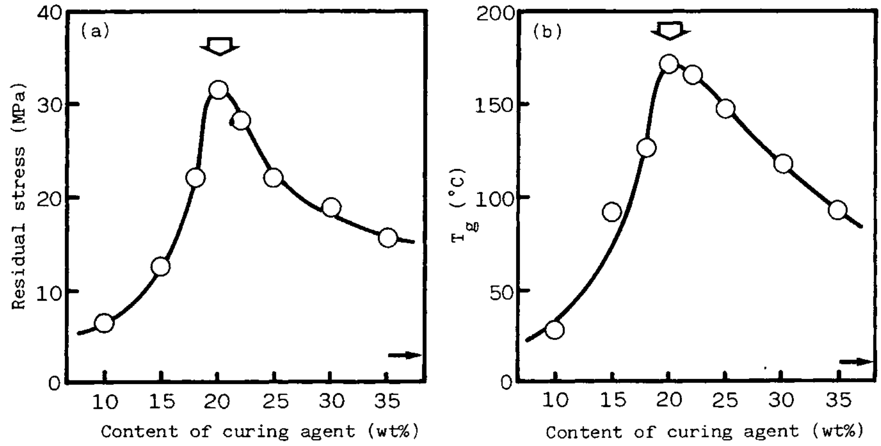


Fig. 5. Effect of the content of curing agent on (a) the stress resided on the Al plate and (b) the glass transition temperature T_g of cured epoxy resin. ▽ indicates the equivalent curing agent content and → indicates the results for the specimen cured with the room temperature curing agent.

and X-ray diffraction is a useful method to detect the residual stress in the epoxy resin/Al plate system.

The X-ray diffraction method is next extended to detect the residual stress in epoxy resin. To measure this residual stress, Al particles are embedded into the epoxy resin by 15 wt %, and the strain of the crystal of embedded Al particles is detected by X-ray diffraction.

Figure 6 shows the relationship between $\sin^2\psi$ and ε of the embedded particles. From this figure, plots can be expressed with a straight line through $\varepsilon = 0$ at $\psi = 30°$, hence it could be considered that the residual stress in the epoxy resin is uniaxial. In this case, the line gradient is plus, in contrast with that in the Al plate side. This indicates that the cured epoxy side (embedded particles) was subjected to a tensile residual stress of 35.4 MPa.

Figure 7 shows the strain of both sides in polar coordinates around ψ. It can be found that the epoxy resin side and the Al substrate side are subjected to tensile and compressive residual stress, respectively. This means that the residual stresses in the epoxy resin and the Al plate obey the law of action and reaction (equal value but opposite direction). Experimental results, however, turn out to be that the two values are not equal to each other. This is due to the embedding of the Al particle, which affects the residual stress, and the difference in β of the resin and the embedded particle influence the residual stress. Further investigation on the effect of embedded particles will be reported elsewhere.[14]

CONCLUSION

Residual stress in the epoxy resin cured on Al plate was investigated by X-ray diffraction. Since the epoxy resin has a thermal expansion coefficient much greater than the Al plate, when cooled down from curing temperature to room temperature, the Al plate was found to be subjected to a uniaxial compressive stress of 29.5 MPa. In contrast to this, the epoxy resin side (filled Al particle) is subjected to a uniaxial tensile stress. The X-ray diffraction method appears to be a useful method to detect the residual stress in the epoxy/Al plate system, *in situ* and nondestructively. Further, the X-ray diffraction method will be

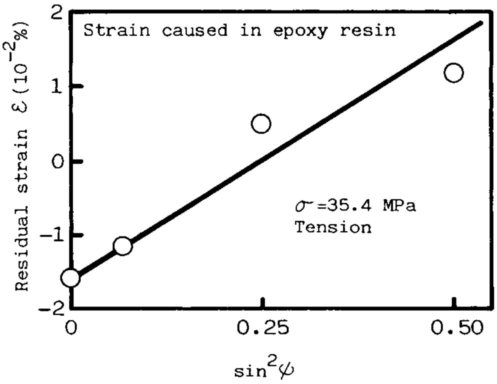


Fig. 6. Relationship between the residual strain (ε) of embedded Al particles and $\sin^2\psi$.

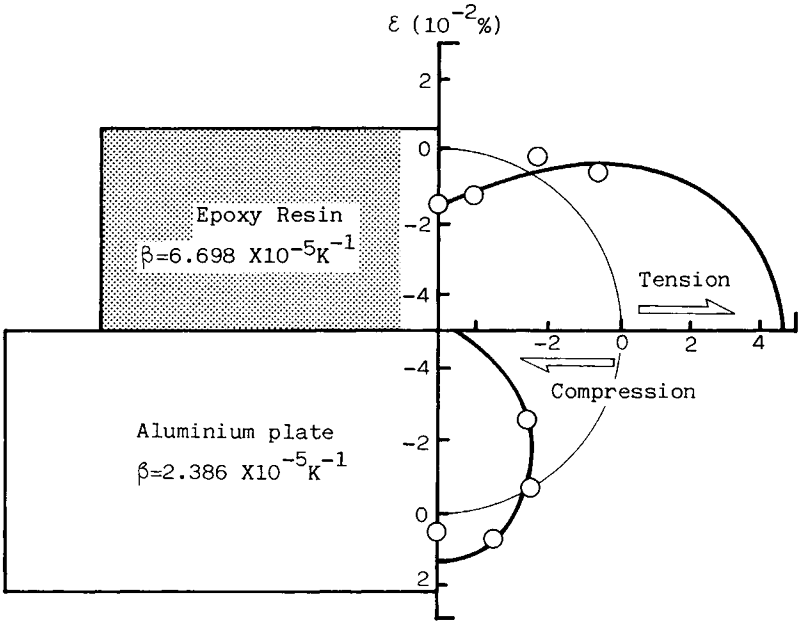


Fig. 7. Strain ε of both the epoxy resin side and the Al plate side in polar coordinates around ψ.

extended to measure the stress resident in polymer particulate composite materials.

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