Internal stress and mechanical properties of epoxy resin coatings cured with acid catalyst in the presence of THF

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(Received 10 September 1991; revised 26 November 1991; accepted 16 December 1991)

Naphthalene-type epoxy resin was cured with u.v. irradiation in the presence of tetrahydrofuran (THF) using sulphonium salt as a curing catalyst. In this curing process, the epoxy resin was copolymerized with the THF. Thus, evaporation of THF was suppressed substantially. The suppression of solvent evaporation decreased shrinkage of the coatings in the curing process and thus reduced internal stress at the interface between the coatings and the adherend. Fracture energy of these cured films increased with the amount of THF added, and had a maximum value when 10 wt% of THF was added. This shows that the toughness of the cured resins increases with the introduction of the flexible chains which were formed by the ring-opening reaction of THF.

(Keywords: epoxy coatings; u.v. cure; internal stress; mechanical properties; toughness; reactive solvent)

INTRODUCTION

Epoxy resins are widely utilized for protection and decoration of various articles by virtue of their good adhesion and weathering resistance. However, epoxy resin coatings have usually been applied as solutions dissolved in organic solvents. Thus, in many cases, evaporation of the solvent during and/or after curing causes shrinkage and thus internal stress in the coatings. Another problem is that the glass transition temperature (T_g) and mechanical strength of coatings are decreased in the presence of residual solvent.

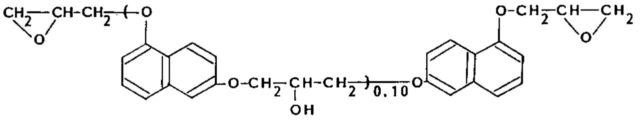
It is well known that tetrahydrofuran (THF), which is a good solvent for epoxy resin, is copolymerized[1–4] with epoxy resins if the resin is cured with a strong acid catalyst; mechanisms for this reaction have been proposed[3,4]. Okada *et al.*[5] reported that alicyclic ethers such as THF or dioxane are reacted with epoxy resin under electron beam irradiation. It is suggested in these reports that the THF added as a solvent reacts with epoxy resin through a ring-opening reaction, and would be introduced as a network segment into the cured resins. Thus, we consider that the shrinkage of the coatings will be considerably reduced if we are able to react the THF used as a solvent with epoxy resin. Moreover, it is also predicted that the toughness of the cured resins will be improved by copolymerization with THF, because the THF forms flexible aliphatic ether chains through the ring-opening reaction.

In this work, epoxy coatings having a rigid naphthalene ring were cured with strong acid by u.v. irradiation in the presence of THF. The effect of copolymerization, using THF as a solvent, on the mechanical properties, shrinkage and internal stress of the cured coatings, is investigated in detail.

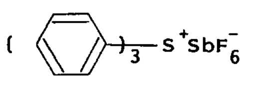
EXPERIMENTAL

Materials

The epoxy resin used was 1,6-naphthalene-type epoxy resin[6] (Epiclon, EXA-4032, epoxy eq.:147). A 50%



solution of triphenylsulphonium hexafluoroantimonate in propylene carbonate (General Electric Co. Ltd, UVE-1014) was used as a curing catalyst.



THF was used as a solvent for the epoxy resin. This solvent was EP grade material and was used with further purification. For comparison with THF, ethyl acetate, which was not reacted with epoxy resin, was also used as a solvent.

Curing of epoxy resin

Epoxy resin was degassed at 80°C under reduced pressure (< 3 mmHg) with stirring for 30 min. The curing catalyst and THF were added to the resin and stirred until they dissolved completely in the epoxy resin. This resin compound was uniformly coated with an applicator on a phosphor bronze plate (thickness 200 μm), which

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0032-3861/92/214550–06
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was previously surface-abraded, and then cured by u.v. irradiation. A mercury lamp (H400-P, Toshiba) was used for u.v. irradiation. The irradiation was carried out with a distance of 20 cm from the lamp to the specimen. The temperature of the coatings increased with u.v. irradiation and reached about 110°C, which is above the boiling point of THF.

Cured epoxy resin film was prepared by cutting and bending the coated substrate, which led to the peeling of coatings from the substrate.

Measurements

A diagram of the equipment used for measuring the internal stress of coatings[7] is shown in *Figure 1*. The phosphor bronze plate was used as the substrate. As the epoxy resins were cured, the substrate became curved due to the contraction or shrinkage of the coatings. The displacement (δ) of the substrate was measured by a laser displacement detector (Keyence Co. Ltd, LB-01) and reduced to the internal stress (σ_c) of the coatings using the equation[8]:

$$\rho = \frac{l^2}{8\delta} + \frac{\delta}{2} \fallingdotseq \frac{l^2}{8\delta}$$

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

where l is the distance from the support end to the measuring point on the specimen, h_1 and h_2 are the thicknesses of the phosphor bronze plate and the epoxy coatings, respectively, and E_1 is Young's modulus of the phosphor bronze plate. Since the cantilever method is used in the present work, l corresponds to twice the distance from the chucking point to the measuring point.

The flexibility of the coatings was evaluated by measuring the ultimate elongation of the coating in a tensile test. The phosphor bronze plate was machined as a dumb-bell shape and was coated with epoxy resin. A strain gauge (Kyowa Electric Co. Ltd, KFC-10-C-1-11) was embedded into the epoxy coatings. When a crack or delamination of the coatings was generated during the tensile test, the readout of the strain gauge indicated a catastrophic change. The elongation of coatings was measured from the readout of the strain gauge just before the catastrophic change.

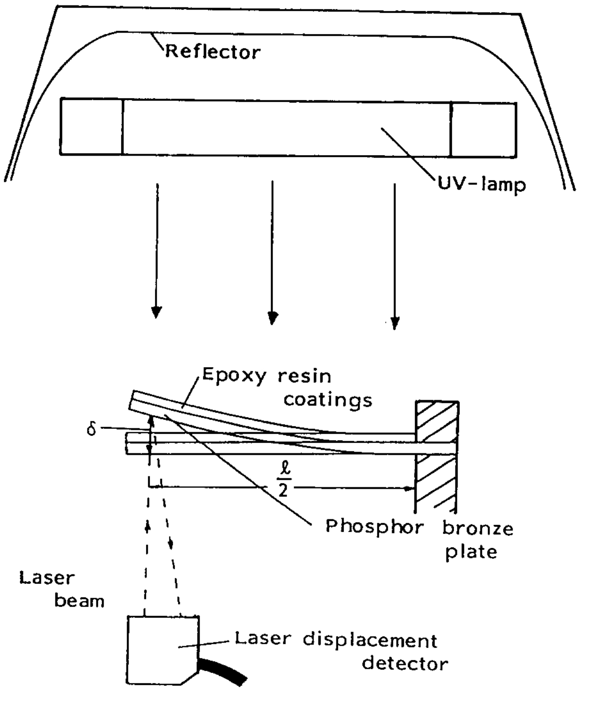

Figure 1 Schematic diagram of apparatus for measuring internal stress of coatings

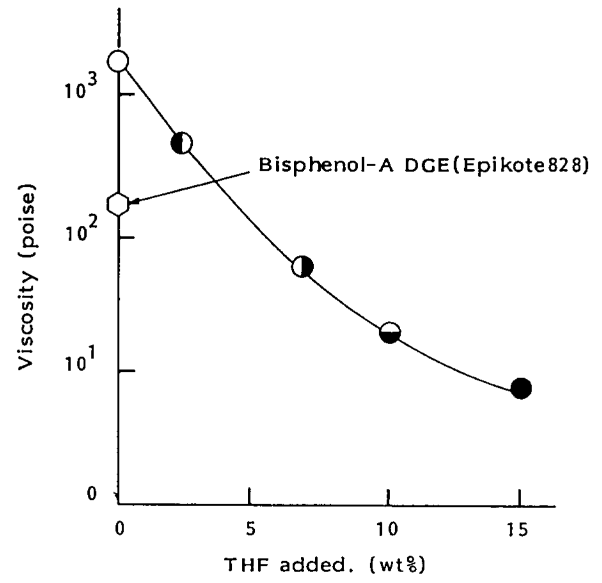

Figure 2 Effect of THF content on viscosity of epoxy resin compounds. THF added (wt%): ○, 0; ◐, 3; ◑, 7; ◒, 10; ●, 15

Dynamic mechanical properties were determined over the temperature range 30–270°C by a non-resonance, forced vibration viscoelastometer (Rheology Co. Ltd, DVE-3). The frequency for measuring was 1 Hz. The dimensions of specimens were 4 mm × 40 mm × 0.1 mm.

Mechanical properties were measured using an Instron-type tensile tester (Shimazu autograph, AGS-100A) at a crosshead speed of 10 mm min^{-1} according to ASTM-D-1708-72. Fracture energy was also calculated from the area under stress–strain curves of this mechanical test.

The chemical conversion of epoxy groups in the cured coatings was determined by the pyridine–HCl method[9] and the gel content was determined by Soxhlet extraction with THF as solvent[10]. The loss by evaporation of THF was evaluated from the change in weight of coatings as curing progressed. The concentration of network chains was calculated from the equation for ideal rubber elasticity[11].

RESULTS AND DISCUSSION

Preparation of naphthalene-type epoxy resin coatings

The change in viscosity of naphthalene-type epoxy resin with the addition of 0–15 wt% THF is shown in *Figure 2*. For comparison, the viscosity of a bisphenol-A-type resin, which is the most general epoxy resin, is also shown in this figure. The viscosity of the naphthalene-type resin is about one order of magnitude higher than that of the bisphenol-A-type resin and decreases with increasing the amount of THF added. The viscosity of the system to which 10 wt% THF was added was about two orders of magnitude lower than that of the original resin. These results show that the viscosity

Table 1 Conversion of epoxy group, gel fraction and THF evaporated for epoxy resin coatings

THF added (wt%)	THF evaporated (%)	Conversion of epoxy group (%)	Gel fraction (%)
0	–	90	97
3	0.1	92	98
7	1.1	92	97
10	1.6	90	97
15	3.3	91	98

of the epoxy resin could be controlled over a wide range by the addition of THF.

Five compounds of the naphthalene-type resin containing different amounts of THF were cured with u.v. irradiation in the presence of sulphonium salt. The amount of THF evaporated during the curing process, the chemical conversion and gel content of the coatings are summarized in *Table 1*. In this table, we assume that the weight of epoxy resin does not change with the progress of curing.

In all systems, the evaporation loss is much lower than the amount of THF added. This result shows that the THF added as a solvent remains in the coatings even after curing. As mentioned in the previous section, the temperature of coatings in the curing process rises above the boiling point of THF. Accordingly, it is reasonable to consider that the THF in the cured coatings remains as a result of copolymerization of the epoxy resin and THF. In practice, the gel content of the coatings is more than 97% regardless of the initial content of THF. From these results, it is concluded that most of the THF added as a solvent reacts with epoxy resin and thus is introduced as a network segment into the cured resin.

Mechanical properties of the epoxy coatings

The temperature dependence of the tensile storage modulus and glass transition temperature, T_g, for the five types of cured epoxy resin film are shown in *Figure 3*. The T_g of the cured resins shifted to a lower temperature and the tensile modulus in the rubbery region decreased with an increase in the amount of THF. These results mean that the concentration of network chains in the coatings decreases and the mobility of network segment in the rubbery region increases with increasing the content of THF, because the linear flexible chains are introduced into the epoxy networks as a result of the ring-opening copolymerization of THF.

The modulus in the glassy region also decreased with an increase in the content of THF. We consider that the introduction of flexible network chains, which have high mobility even in the glassy region, increases the free volume and thus decreases the storage modulus in this region.

In a previous paper[12], we reported that the storage modulus in the glassy region decreases with an increase of the modulus in the rubbery region[13,14]. We suggested that this behaviour is due to the decrease of the chain mobility in the rubbery region, which prevents the packing of network chains in the transition region. However, in this paper, linear aliphatic ether chains are formed by the reaction of THF with epoxy resin. It is reasonable to consider that the motion of this flexible chain is not frozen even in the glassy region. Indeed, we confirmed that the γ relaxation is observed near −130°C for the system with 15 wt% THF. We consider that the introduction of flexible chains, of which the motion is not frozen even in the glassy region, decreases the modulus in the glassy region as well as in the rubbery region, because of the increase of the free volume in both regions.

The relationship between the concentration of the network chains calculated from the rubbery modulus and the T_g of coatings is plotted in *Figure 4*. The T_g of the coatings decreased linearly with a decrease in the concentration of network chains. This is due to the

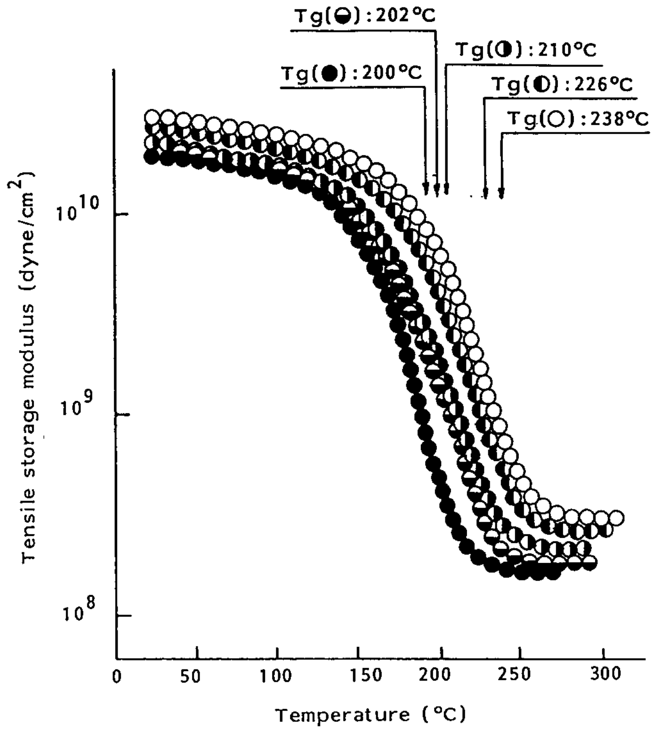

Figure 3 Tensile storage modulus of cured epoxy resin films. Notation as in *Figure 2*

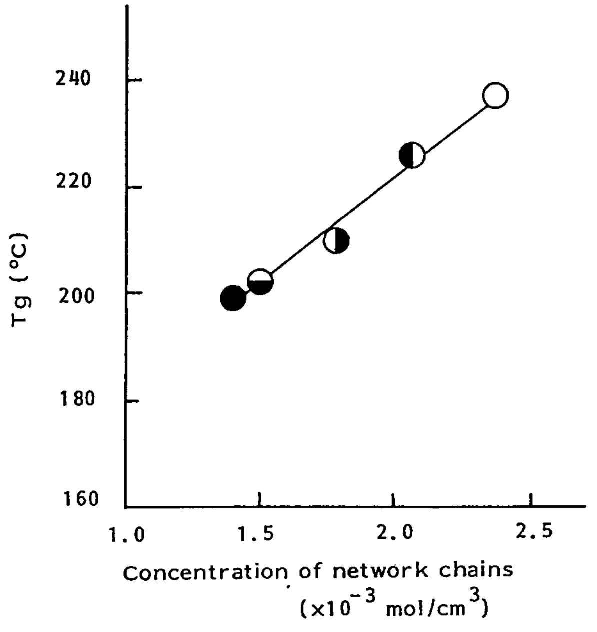

Figure 4 T_g *versus* concentration of network chains. Notation as in *Figure 2*

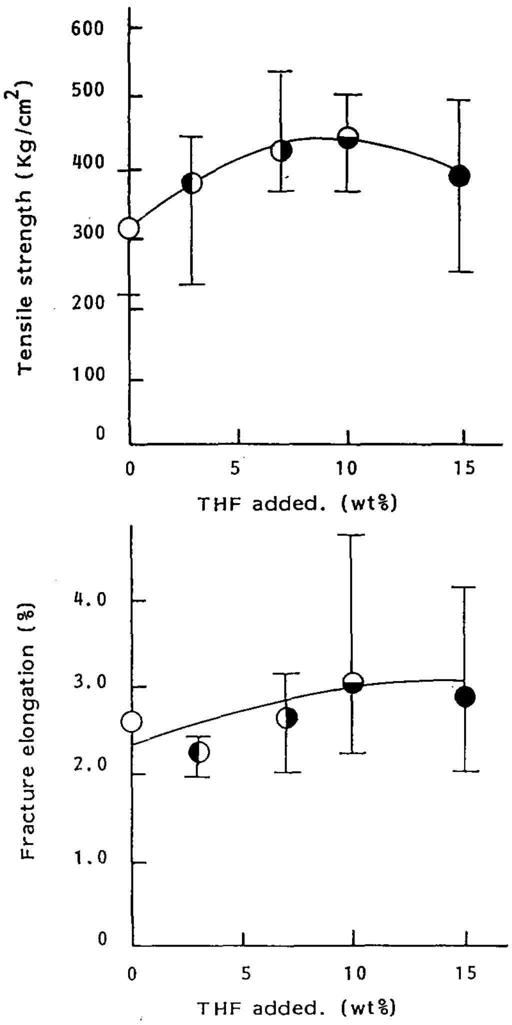

Figure 5 Mechanical properties of cured epoxy resin films. Notation as in *Figure 2*

increase in the mobility of the networks with the introduction of flexible chains formed by the reaction of THF.

Tensile strength and elongation at break for the cured films are shown in *Figure 5*. The tensile strength and the elongation of the system with no added THF had low values, less than about 300 kg cm^{-2} at 2.5%, respectively. These results show that the naphthalene-type epoxy coatings are extremely brittle. However, both the tensile strength and the elongation increased with an increase in the amount of THF. We consider from this result that the introduction of flexible chains by copolymerization with THF could improve the brittleness of the coatings. When the amount of THF was over 10 wt%, the tensile strength of the system decreased again. This is attributed to the decrease in the cohesive energy by the introduction of excess flexible network chains.

Fracture energy determined from the area under the stress–strain curves is shown in *Figure 6*. The fracture energy of the films has a maximum at 10 wt% THF. The T_g of this sample is about 202°C (*Figure 4*). Accordingly, we conclude that the copolymerization of THF to the naphthalene-type resin coatings is effective in improving toughness of the cured films with little decrease in heat resistance.

The effect of the amount of THF on the elongation of the epoxy coatings is shown in *Figure 7*. The elongation at break of the coatings also has a maximum peak at 10 wt% THF. The maximum value of elongation is twice as high as that of the control system. We conclude that the toughness and adhesion of the cured coatings are improved with the introduction of flexible chains formed from the ring-opening reaction of THF.

Stress at interface between epoxy resin coatings and adherends

As mentioned above, when the epoxy resins are cured with strong acids in the presence of THF, the copolymer of epoxy resin and THF is obtained as a cured resin. Thus, the evaporation of the solvent was not only suppressed substantially, but the toughness of the cured coatings was also improved.

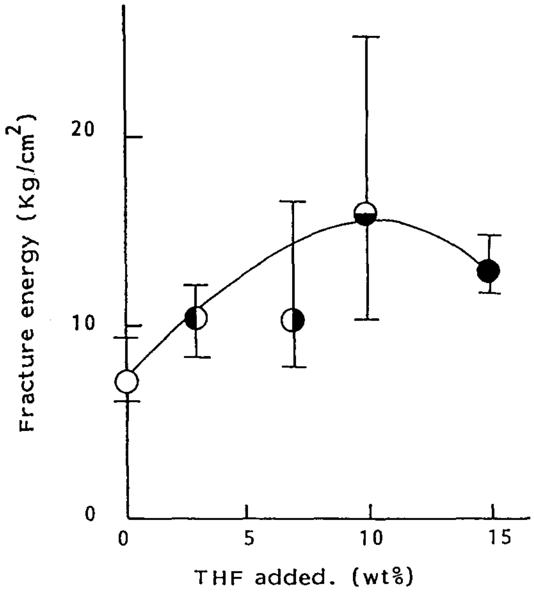

Figure 6 Fracture energy of cured epoxy resin films. Notation as in *Figure 2*

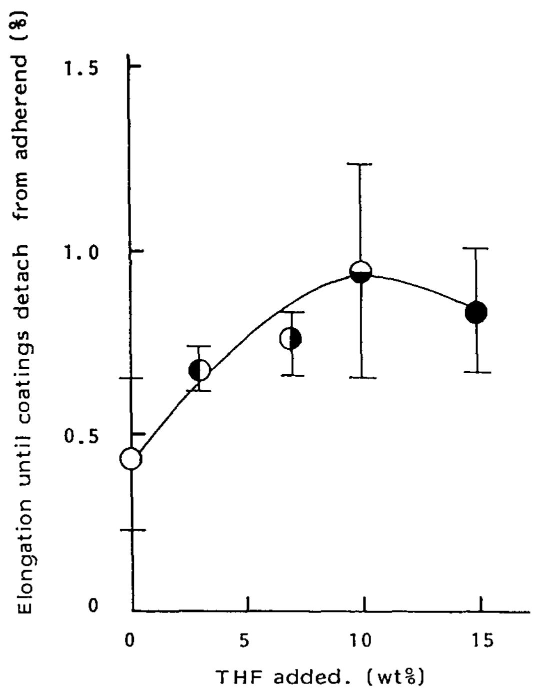

Figure 7 Elongation of epoxy resin coatings. Notation as in *Figure 2*

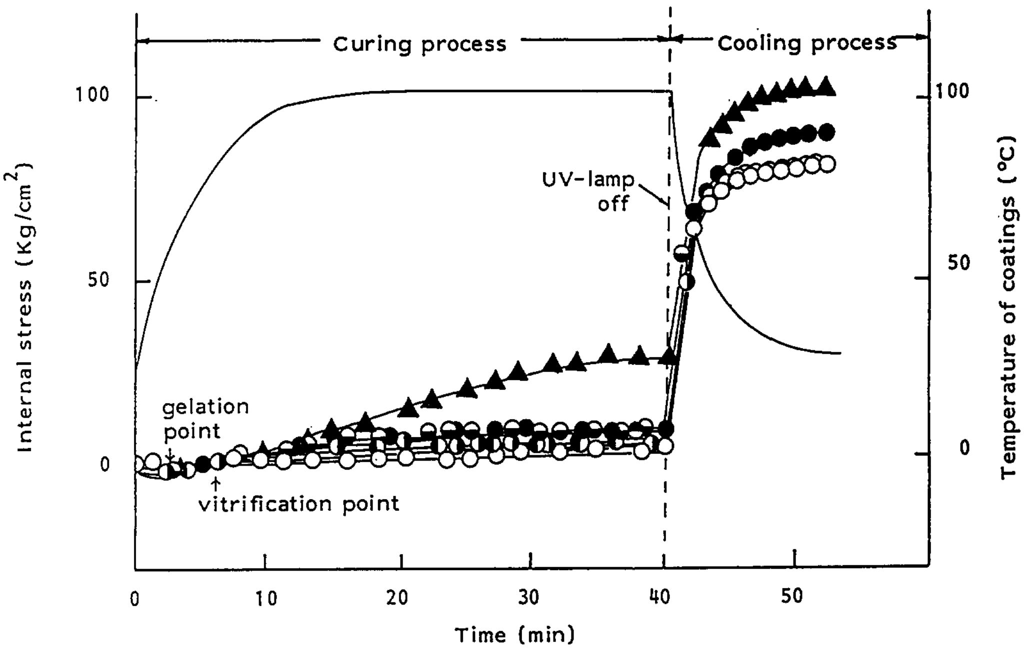

Figure 8 Internal stress and temperature of epoxy resin coatings cured by u.v. irradiation. Notation for added THF as in *Figure 2*; ▲, 15 wt% ethyl acetate added

It is expected that such suppression of the evaporation of solvent decreases the shrinkage of coatings during the curing process and thus reduces the internal stress at the interface between the cured coatings and the adherends. The internal stress and temperature of the five specimens during curing and cooling processes are shown in *Figure 8*. The stress for the system with ethyl acetate as a solvent is also shown in this figure. The temperature of the specimens increased rapidly with u.v. irradiation and finally reached almost 100°C. After curing, the specimens were rapidly cooled to room temperature.

In all systems, negative stress was observed at the beginning of curing. In these systems, gelation points were reached within 2 min. In addition, the coatings should be vitrified in the course of the curing process, as the T_g of the cured coatings ($\sim$200°C) was higher than the ambient temperature in the curing process ($\sim$100°C). Thus, the negative stress can be attributed to expansion of the coatings with increase in the ambient temperature.

The internal stress occurring in the system with ethyl acetate as a solvent was over three times greater than that in the system with THF. This is because the former coatings shrink considerably by evaporation of solvent after vitrification, since ethyl acetate could not react with epoxy resin. In other words, the values of internal stresses are very low in the system with THF as the THF reacts with the resin to reduce the shrinkage of the coatings after vitrification.

During the cooling process after curing, the internal stress of these systems increased rapidly with decreasing the ambient temperature. The internal stress in this process was much larger than that in the curing process and would not be affected by the type and amount of solvent. This result shows that the contraction of the coatings in the cooling process is larger than that after the vitrification point in the curing process. In addition, the contraction in this process should not be influenced by the evaporation loss of solvent. The value of the internal stress in the system with ethyl acetate was about 15 kg cm^{-2}, higher than that in the system with THF. This is due to the large internal stress in the curing process of the former system.

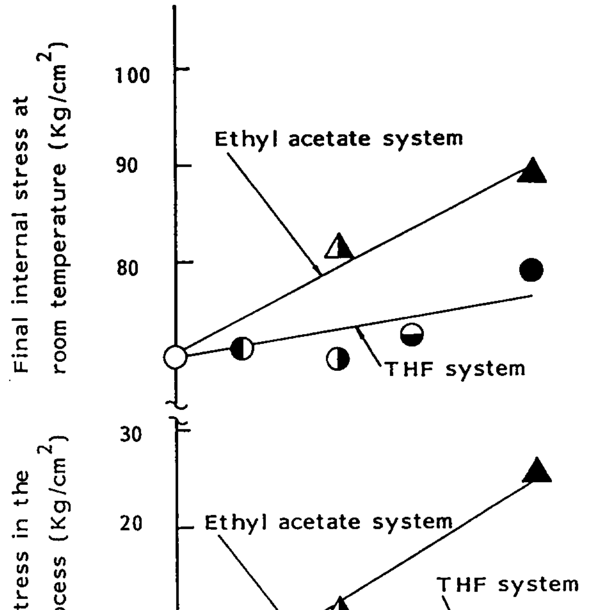

Figure 9 Effect of additional amount of solvent on internal stress. Notation for THF added as in *Figure 2*; ethyl acetate added (wt%): ◭, 7; ▲, 15

The relationship between the internal stresses at room temperature or in the curing process and the amount of solvent is plotted in *Figure 9*. The stress in the curing process of the system with THF hardly increases with the solvent content. But the stress of the system with ethyl acetate increases rapidly with the addition of solvent. Thus, the stress at room temperature in the former system was smaller than that of the latter system. This is due to the suppression of solvent loss as a result of the reaction between the epoxy resin and THF. Accordingly, we conclude that the reactive solvent, such as THF, is effective in decreasing the internal stress occurring at the interface between the coatings and the adherend.

CONCLUSION

Naphthalene-type epoxy resin dissolved in small amounts of THF was cured by u.v. irradiation in the presence of a sulphonium salt. The mechanical properties and internal stresses of these epoxy resin coatings were investigated and the following conclusions were reached.

1. The viscosity in the resin compounds was decreased by the addition of THF. The viscosity of the system with 10 wt% THF was about two orders of magnitude lower than that of the control system with no THF.
2. In these systems, the epoxy resin was copolymerized with THF through the ring-opening reaction of the furan ring. Thus, the evaporation of THF was suppressed substantially. Such a suppression of the solvent loss decreased the shrinkage of the coatings in the curing process and thus reduced the internal stress at the interface between the coatings and the adherend.
3. The toughness and the adhesion of the naphthalene-type epoxy resin coatings were considerably improved by copolymerization with THF. The improved toughness is explained as the result of the introduction of flexible chains into the networks through the ring-opening reaction of THF.

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