

Readily Decomposed Thermosetting Resins for Recovering and Reusing Resin-Embedded Materials

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ABSTRACT: To help recover the intrinsically valuable, reusable metal parts at the end of a product's life-cycle, we have used thermosetting (epoxy) resin that contains a small amount of thermoplastic polymer, polyethersulfone, which can be readily chemically decomposed. In a morphologically homogeneous modified thermosetting resin, the resin portion does not readily decompose when treated with an organic solvent, and chemical resistance equals the unmodified epoxy resin. A resin portion with thermoplastic polymer having continuous-phase morphology was finely broken down by treatment with an organic solvent, and the embedded metal parts were separated and recovered. Readily decomposed thermosetting resin can thus be ob-

tained by controlling the morphology of the thermoplastic polymer in the thermosetting resin to form a continuous phase. We also obtained a material having continuous variation in the phase morphology of a cured resin, from that with homogeneous morphology to that with continuous-phase morphology of the thermoplastic polymer: phase structure inclination material. We were thus able to control the decomposition rate by chemical treatment in one resin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1463–1470, 2006

Key words: alloys; microstructure; morphology; phase separation; recycling

INTRODUCTION

Epoxy, phenolic, and other thermosetting resins feature excellent electrical insulation, desirable mechanical properties, and thermal and chemical stability. They are used in electrical and electronic applications ranging from high voltage electrical equipment to semiconductor devices. Once such resins are cured, however, heating does not melt them, and they are insoluble in most organic solvents. At the end of the life-cycle of products in which they are placed, they cause disposal problems and invariably end up in incinerators or landfills. This problem is aggravated by the increasing demand for thermosetting resins. For example, in 1992 the Japanese market for epoxy resin was 163,000 tons, which rose to 197,000 tons in 2000. To use resources more effectively and to reduce the environmental impact of landfill disposal, we have developed a practical technology that facilitates recycling.

In materials recycling, a high proportion of fillers in thermosetting resins used for electrical and electronic devices means that the components using them have little intrinsic value. Metal and other parts with some value in many such devices are often embedded in

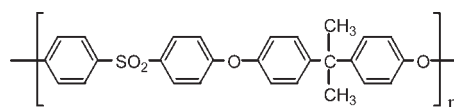
resins, and we attempted to develop a readily decomposable thermosetting resin that simplifies the recovery and reuse of embedded parts.

Thermoplastic polymer has been blended with the thermosetting resin to improve the thermosetting resin's performance.^{1–11} We also added a thermoplastic polymer (polyethersulfone) to the thermosetting resin (i.e., epoxy resin) to improve the heat resistance and the cured resin toughness¹. The phase morphology of the cured resin was controlled by changing the molding conditions. Therefore, this technology was applied to the development of a ready decomposition-type thermosetting resin.^{12–13}

EXPERIMENTAL

Materials and sample preparation

The thermosetting resin used was a biphenyl diglycidyl ether epoxy resin (YX4000: Japan Epoxy Resins). The curing agent was a phenol novolak resin (PSM4261: Gun Ei Chemical Industry), and the accelerator was triphenylphosphine (TPP). The thermoplastic polymer was an engineering plastic, polyethersulfone (PES: Solvay Advanced Polymer), whose structure is given below. The concentration of added PES was 20% by weight.



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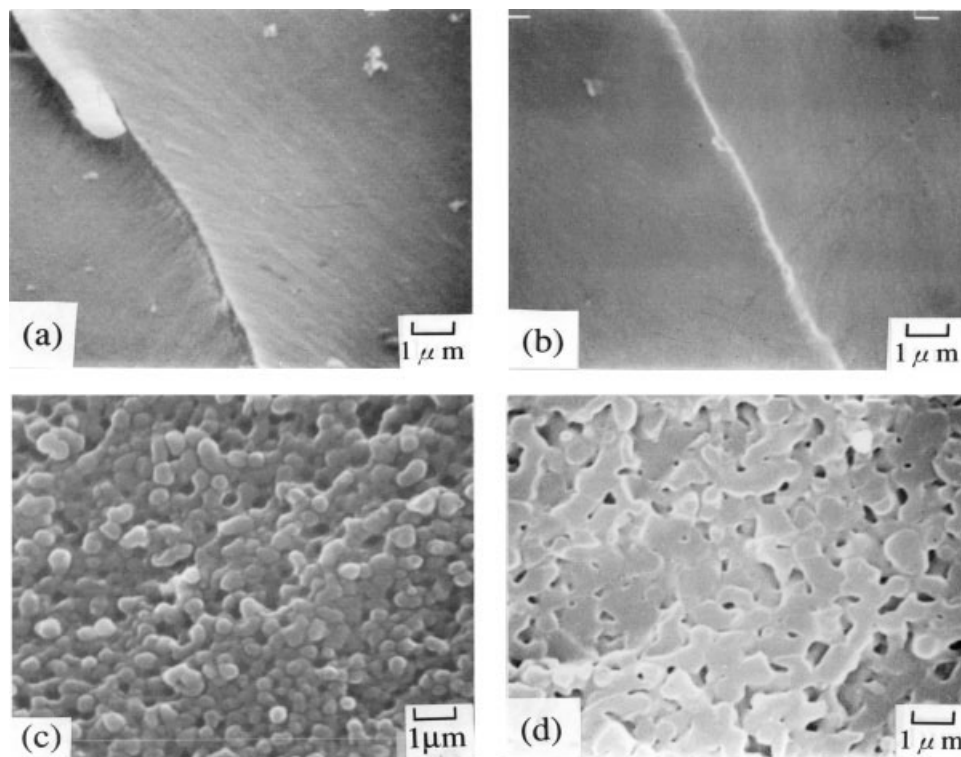


Figure 1 SEM micrographs of cured epoxy resins containing PES. Samples: (a) unmodified epoxy resin, (b)–(d) modified epoxy resins containing 20 wt % of PES. Molding temperatures: (a) 160°C, (b) 140°C, (c) 160°C, (d) 180°C.

The epoxy resin was compounded stoichiometrically with a curing agent, with one epoxy group corresponding to one hydroxyl group of the curing agent. The compound was stirred at 135°C until the PES dissolved homogeneously in a mixture of the epoxy resin and the curing agent. TPP was then added, and the mixture was rapidly removed from the apparatus. The mixture was formed in one of the two ways: at 140, 160, or 180°C for 10 min with a transfer press or while attaching a temperature slope from 140 to 180°C. Mixtures were then cured at 175°C for 7.5 h.

Measurements

The morphology of cured resins was observed using scanning electron microscopy (SEM; JSM-T20, Jeol). Cured resin surfaces were coated with a gold layer of about 200 Å thickness.

Adhesion properties of the encapsulants of the Fe–Ni 42 alloy were measured by extracting the specimen. In adhesion examinations, we used a specimen-embedded metal ($5 \times 20 \times 0.5 \text{ mm}^3$) 5 mm in the resin body ($10 \times 15 \times 5 \text{ mm}^3$). The metal portion of the specimen was pulled at 1 mm/min.

Heat resistance (T_g 's) of cured epoxy resins was measured by dynamic mechanical analysis (DMA) using nonresonance forced vibration viscoelastometry

(RDA, Rheometrics). Frequency was adjusted to 1 Hz at a heating rate of 2°C/min in air.

The decomposition of cured resins treated with an organic solvent was evaluated using a specimen from the pulled-out adhesion examination, a dumbbell sample ($1 \times 20 \times 150 \text{ mm}^3$), and model molding-parts. Dimethylformamide (DMF) was used as the organic solvent. Sufficient DMF was added to dissolve the thermoplastic polymer in the cured resin. The solvent was treated at 23, 50, 80, and 100°C.

RESULTS AND DISCUSSION

Decomposition evaluation of epoxy resin modified with PES

The epoxy resin/PES blends displayed a lower critical solution temperature phase diagram.² We observed the morphology of cured resins by fixing the PES content at 20 wt % and changing the molding temperature to 140, 160, and 180°C. Results are shown in Figure 1. PES was removed by extracting samples with dichloromethane prior to SEM. Unmodified epoxy resin to which no PES was added showed homogeneous morphology [Fig. 1(a)]. Even after epoxy resin was modified with PES, if formed at 140°C, the cured resin showed homogeneous morphology similar to unmodified epoxy resin [Fig. 1(b)]. Raising the mold-

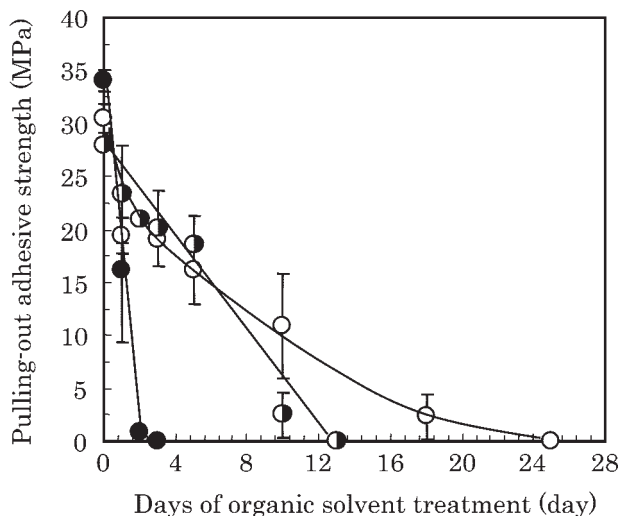


Figure 2 Decomposition of cured epoxy resins containing PES by chemical treatment. Samples: ○ unmodified epoxy resin, ●● modified epoxy resins containing 20 wt % of PES. Molding temperatures: ○ 160°C, ● 140°C, and ● 180°C.

ing temperature to 160°C distributed PES within the epoxy resin matrix as isolated globules [Fig. 1(c)]. Higher molding temperatures, that is 180°C [Fig. 1(d)], resulted in cocontinuous phase formation between the epoxy resin and the PES, indicating that the phase morphology of the cured epoxy resin modified with PES was controllable by changing the molding temperature, even using the same PES content. We then compared the decomposition characteristic by chemical treatment in the following three systems: unmodified epoxy resin, modified epoxy resin with homogeneous morphology (PES: 20 wt %; molding temperature: 140°C), and modified epoxy resin with continuous morphology of PES (PES: 20 wt %; molding temperature: 180°C).

The thermoplastic polymer, PES, used here was dissolved in special organic solvents such as dichloromethane and DMF. Then we treated the cured resin modified with PES with DMF and evaluated the decomposition using a specimen from the pulled-out adhesion examination. Figure 2 shows the relationship between the number of treatment dates of cured resins and pulled-out adhesion strength. Strength before treatment (0 days) showed the pulled-out adhesion strength of these cured resins. The pulled-out adhesion strength of the unmodified epoxy resin was about 30 MPa and that of modified resin with homogeneous morphology was 28 MPa, which equals the unmodified epoxy resin. The modified resin with continuous-phase morphology of PES showed improved adhesion strength to about 34 MPa, which is about 1.1 times greater than the unmodified epoxy resin, indicating that adding PES to the epoxy resin improves adhesion strength. When adhesion examination specimens of cured resins were treated with a solvent, the strength

decreased with the progress in the number of treatment days. The decrease rate of strength in individual cured resins differed greatly. In the modified resin with continuous-phase morphology of PES, strength decreased rapidly and immediately after the treatment started. In this system, the resin portion decomposed completely on day 2 after the treatment started, and metal substrates were dissociated from the resin portion and were recovered. In unmodified epoxy resin and modified resin with homogeneous morphology, however, strength on day 2 after the treatment started was 20 MPa or more, and high strength was maintained. In these cured resins, the strength decreased gradually after solvent treatment started. For modified resin with homogeneous morphology, the number of treatment days in which adhesion strength becomes 0 MPa was 13. At this time the adhesion strength of unmodified epoxy resin was still about 7 MPa, and it only became 0 MPa 25 days after the treatment started.

Figure 3 shows the relationship between the treatment temperature of the organic solvent and the time at which pulled-out adhesion strength became 0 MPa, in these modified resins. In every resin, the time in which the metal substrates are separated and recovered from the resin portion decreased with increase in the treatment temperature of the organic solvent. However, in modified resin with continuous-phase morphology of PES, when treatment temperature was raised to 100°C, metal substrates could be separated and recovered for only 2 h after the treatment started. On the other hand, in modified resin with homogeneous morphology, the time in which metal substrates

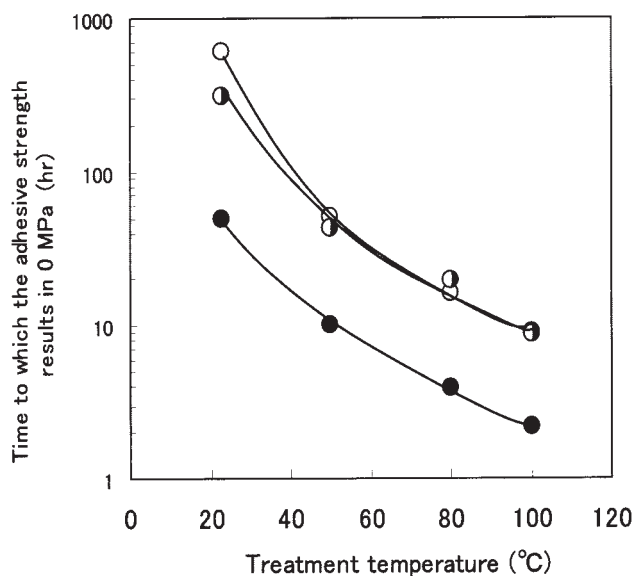


Figure 3 Relationship between treatment temperature in organic solvent and decomposition of epoxy resin modified with PES. Samples: ○ unmodified epoxy resin, ●● modified epoxy resins containing 20 wt % of PES. Molding temperatures: ○ 160°C, ● 140°C, and ● 180°C.

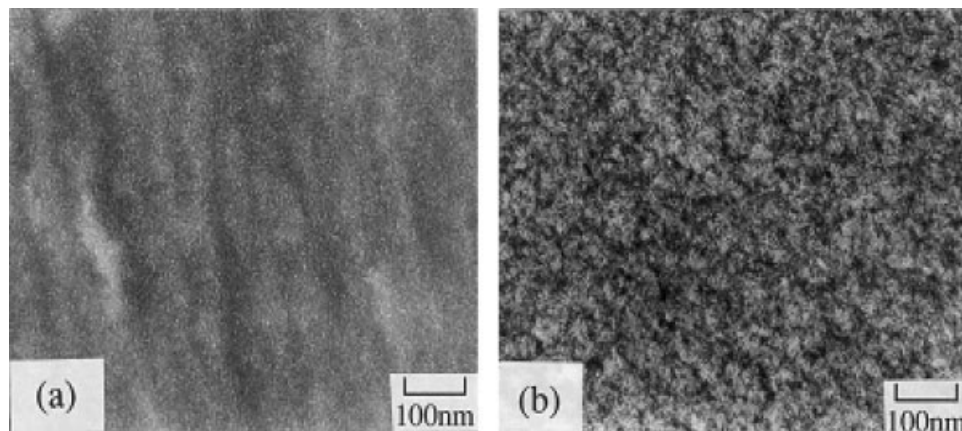


Figure 4 Transmission electron micrographs of modified resins with homogeneous morphology: (a) unmodified epoxy resin; (b) PES content 20 wt %.

are separated from the resin portion almost equaled to that of the unmodified epoxy resin. In these resins, the time in which metal substrates are separated at treatment temperatures of 100°C was about 10 h, which is equivalent to the time when being treated at 50°C in modified resin with continuous-phase morphology of PES.

To reveal why the chemical resistance of modified resin with homogeneous morphology equals the unmodified epoxy resin, modified resin with homogeneous morphology was observed in detail with a transmission electron microscope (TEM), and the results are shown in Figure 4. In these micrographs, the epoxy matrix was stained black by RuO_4 [Fig. 4(a)]. In the observations of resin containing 20 wt % PES [Fig. 4(b)], PES was dispersed in nano size on the entire epoxy matrix. It can be concluded, therefore, that chemical resistance equal to that of the unmodified epoxy resin attributes to the dispersion of PES in a nano order. If the dispersed state of PES is controlled from the dispersion of the nano order to the continuous-phase, it is possible to control from the portion readily decomposed by chemical treatment to the portion that has the same chemical resistance as that of the unmodified epoxy resin.

Next, metal substrates were recovered from the pulled-out adhesion sample having a resin portion with continuous-phase morphology of PES by treatment with organic solvent. The recovered metal substrates were embedded again into the resin portion with continuous-phase morphology of PES. We evaluated and compared the pulled-out adhesion strength (Fig. 5) with the pulled-out adhesion strength when virgin metal substrates were used and found that the adhesion strength using recovered metal substrates was almost identical to that using virgin metal substrates. Neither deterioration nor damage occurred in metal substrates recovered from the resin portion with continuous-phase morphology of PES by organic solvent treatment, and so the substrates were reusable.

Decomposition evaluation of phase structure inclination

The material in which phase morphology differs by the portion on one resin, as shown in Figure 6, was formed by attaching a temperature slope from 140 to 180°C at molding. In portion A in Figure 6, the cured resin is clear and uniform. In portion B, cured resin begins to become opaque and phase separation begins. Completely opaque cured resin is obtained in portion C.

Using SEM observation of portions A to C and dynamic mechanical analysis, we checked PES distribution.

In SEM observation of the phase structure inclination material (Fig. 7), PES completely dissolved into the epoxy resin, giving a homogeneous morphology to portion A. In portion B, PES separated from the epoxy resin matrix, forming a well-defined, dispersed phase.

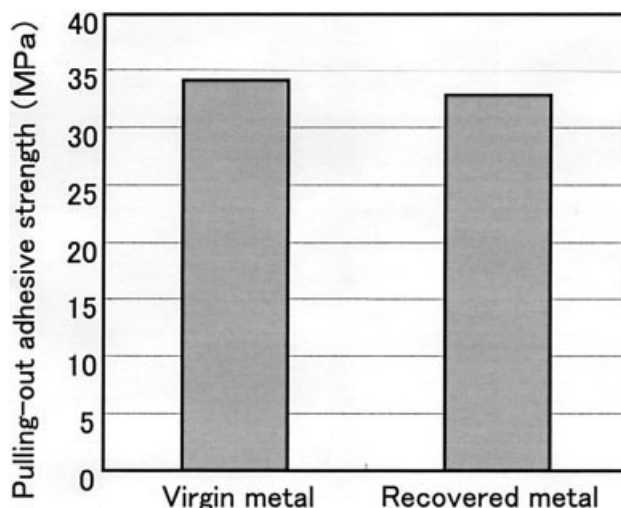


Figure 5 Comparison of pulled-out adhesive strength of modified epoxy resin with continuous phase of PES with recovered versus virgin metal.

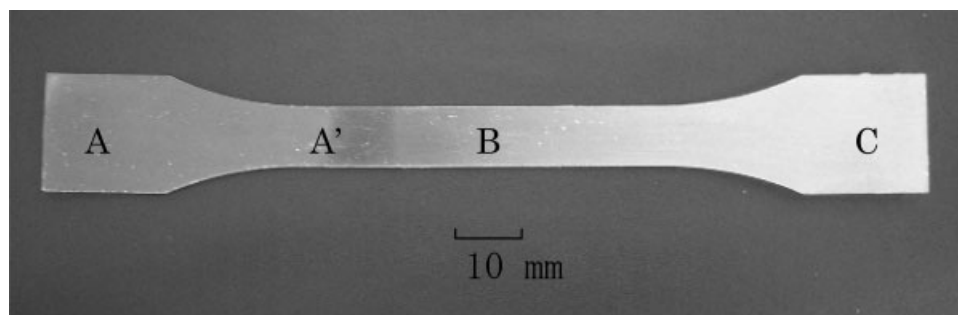


Figure 6 Phase structure inclination material. Sample: modified epoxy resins containing 20 wt % of PES. Molding temperatures: portion A, 140°C; portion C, 180°C.

In portion C, PES formed continuous-phase morphology. These results correspond to the phase structure in molding at each molding temperature in Figure 1.

Figure 8 shows the dynamic mechanical properties of resin portions A to C. Portion A' in the middle of portions A and B was also measured by dynamic viscoelastic analysis. Portion A shows a single $\tan \delta$ peak, indicating that PES has completely dissolved in the epoxy resin matrix. The T_g of portion A was 175°C, and the T_g of unmodified epoxy resin was 150°C. The T_g of portion A thus improved by 25°C compared to unmodified epoxy resin. The $\tan \delta$ of portion A' showed a peak at 175°C and a shoulder near 155°C, indicating that phase separation of PES begins to occur in portion A'. Two clear $\tan \delta$ peaks were observed at portion B: one based on T_g of epoxy resin at 154°C and the other on PES at 199°C, confirming PES phase separation from the epoxy resin matrix. It may also be assumed that PES slightly dissolved in the epoxy resin matrix, since the T_g of this system was slightly higher than the unmodified epoxy resin. Two clear $\tan \delta$ peaks occur in both portions B and C, and phase separation of PES progressed further in portion C, considering that T_g based on epoxy resin equals unmodified epoxy resin. The sample in Figure 6 was the phase structure inclination material from which the phase structure continuously changed. This is also the material that changed from portions A to C at about 25°C, also in T_g .

We then evaluated decomposability by organic solvent of the phase structure inclination material. Figure 9 shows the appearance change of the inclination material sample when treated with DMF solvent at 23°C. The material began to decompose from the portion in which PES formed continuous-phase morphology. After 20 h of solvent treatment, the portion of continuous-phase morphology of PES decomposed into large fragments, but the portion in which homogeneous morphology formed retained its original form. At 23 h after the treatment started, resin with continuous-phase morphology had finely broken down, as shown in Figure 9. The portion with homogeneous morphology retained its original form and size, although the outside of the resin was slightly decomposed. Phase structure inclination material thus has two portions: one that retains chemical resistance and one that decomposes readily with solvent.

A phase diagram of the mixture of epoxy resin and PES is demonstrated in Figure 10. Inclusion of a higher curing temperature produces further progress of the phase separation of PES from the epoxy matrix. However, the morphology is frozen when T_g exceeds the curing temperature. The final morphology reflects the competition between the molecular weight increase of the epoxy, which leads to phase separation, and simultaneous crosslinking, which suppresses it. In lower curing temperatures of 140°C (portion A), the resin mixture gels before the mixture is thrust into a

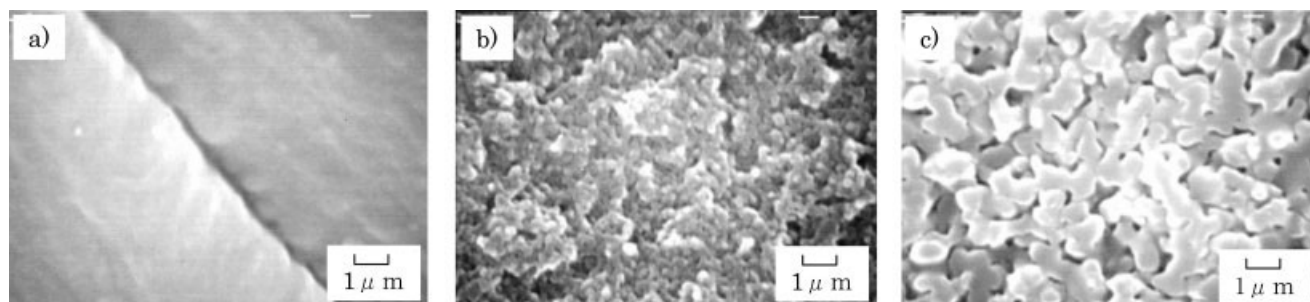


Figure 7 SEM micrographs of phase structure inclination material sample. Sample: modified epoxy resins containing 20 wt % of PES. Observed portion: (a) A, (b) B, (c) C.

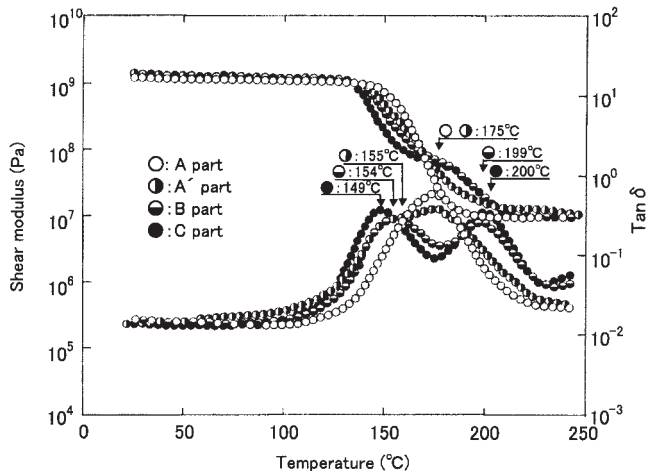


Figure 8 Dynamic mechanical properties of phase structure inclination material. Sample: modified epoxy resins containing 20 wt % of PES. Portion symbol: ○ A, ● A', ◐ B, ● C.

two-phase region. Therefore, PES was dispersed in a nano order, which leads to chemical resistance equal to that of the unmodified epoxy resin. At higher curing temperatures of 160°C (portion B) or 180°C (portion C), the mixture is thrust into a two-phase region, so phase separation occurs in the curing process. But a higher curing temperature forms cured resin with a longer periodic distance.² Therefore, the resin cured at 180°C has a longer periodic distance than the resin cured at 160°C, as shown in Figure 7. Thus, a solvent by chemical treatment easily advances inside the resin in the phase-separated resin with a long periodic distance and readily decomposes it.



Figure 9 Organic solvent treatment evaluation of phase structure inclination material. Sample: modified epoxy resins containing 20 wt % of PES. Organic solvent (DMF) treatment: 23 h at 23°C.

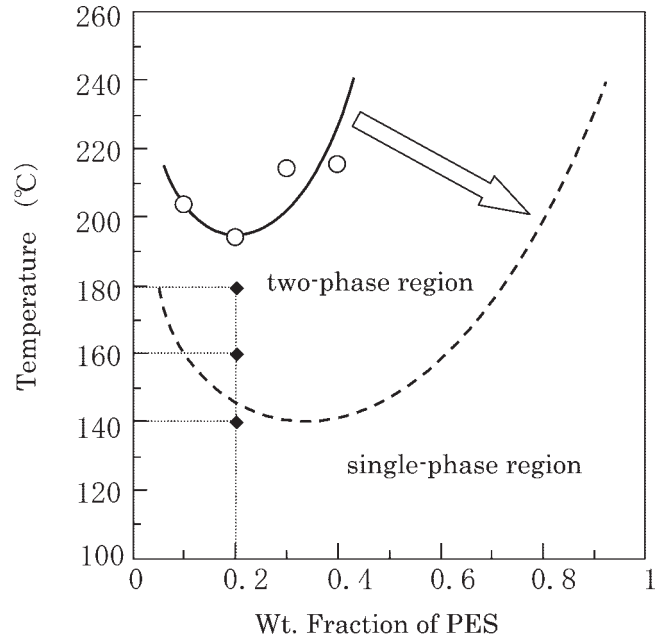


Figure 10 Phase diagram of epoxy/phenol resin/PES mixture. Schematic representation of variation of phase diagram with curing.

Thus, in one resin, we were able to control the decomposition rate by chemical treatment. Next we formed a model molding-part with a metal part embedded in the phase structure inclination material by controlling the temperature of the embedded metal at 180°C and the molding temperature at 140°C. Molding resin of this model formed continuous-phase morphology of PES near the embedded metal, and the

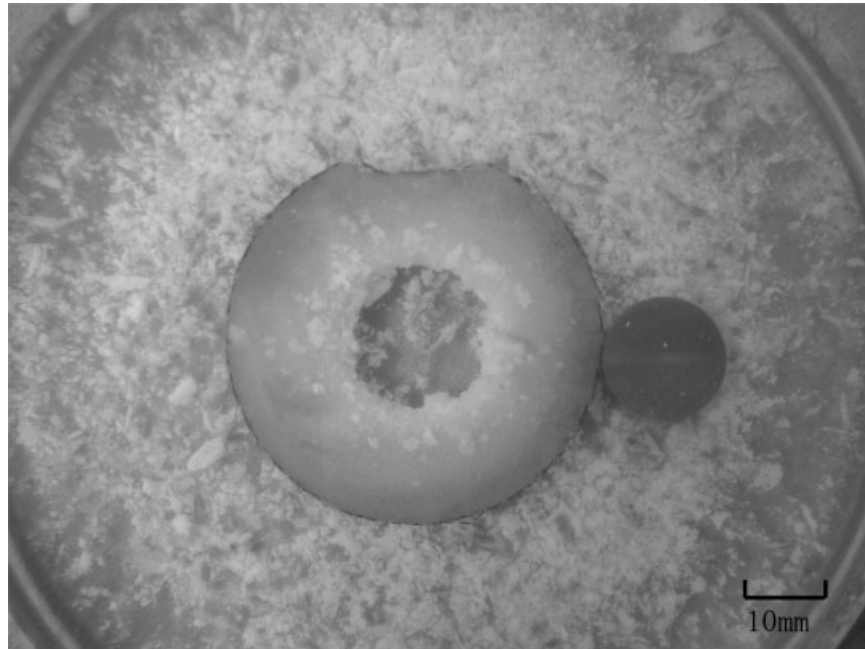


Figure 11 Organic solvent treatment evaluation of model part molded with phase structure inclination material. Sample: modified epoxy resins containing 20 wt % of PES. Organic solvent (DMF) treatment: 12 h at 23°C.

outer cover formed homogeneous morphology. We evaluated decomposition using this model molding-part (Fig. 11). In solvent treatment at 23°C for 5 h, the resin portion with continuous-phase morphology of PES near the embedded metal began to decompose, but the resin with homogeneous morphology at the outer portion remained unchanged. Ten hours after treatment started, decomposition of the portion in which PES formed continuous-phase morphology had considerably advanced. When solvent treatment was conducted at 23°C for 12 h, the embedded metal was separable from the resin, as shown in Figure 11. For the most part, resin with homogeneous morphology of the outer portion did not decompose. Thus, if the phase structure inclination material is used, only the portion to decompose can be readily decomposed.

The model a product with the application of phase structure inclination material is shown in Figure 12. Continuous-phase morphology of PES formed in the resin near the metal to be separated, and the homogeneous morphology of PES formed in the outside resin (that requiring chemical resistance) to which the solvent, etc., may adhere. Chemical resistance of the products during use is thus maintained, and easy separation and recovery of the valuable metal at the end of its life-cycle can be realized.

CONCLUSIONS

To help recover intrinsically valuable reusable metal parts at the end of a product’s life-cycle, we used

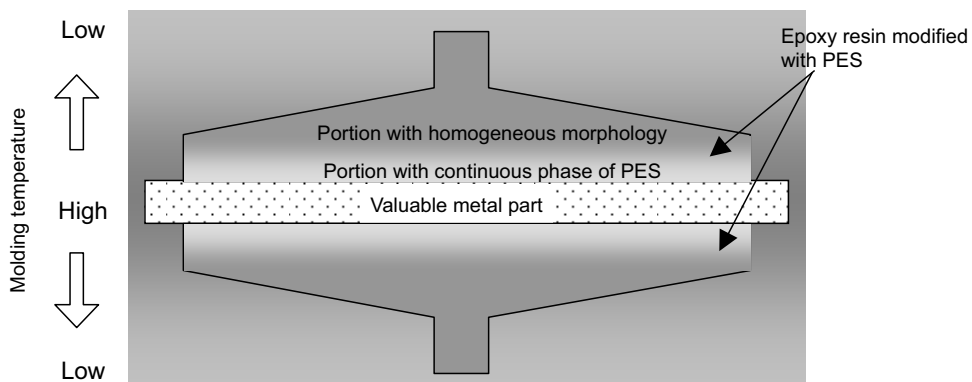


Figure 12 Coexisting improvement of chemical resistance of product during use and ready for decomposition at the end of the product’s life-cycle.

epoxy resin containing a small amount of PES that readily and chemically decomposed. The following results were obtained.

1. In modified epoxy resin with continuous-phase morphology of PES, the resin body decomposed readily when treated with organic solvent DMF. In decomposition evaluation with pulled-out adhesion sample embedded metal substrates, the resin portion decomposed in 50 h at 23°C. And the time in which metal substrates separated from the resin portion was only 2 h when treatment temperature was raised to 100°C.
2. In modified resin with homogeneous morphology, the time in which metal substrates are recovered from the resin portion almost equaled that of the unmodified epoxy resin. PES was dispersed in nano size on the entire epoxy matrix in the TEM observations of this resin. It is considered, therefore, that chemical resistance equal to that of the unmodified epoxy resin attributes to the dispersion of PES in a nano order.
3. By attaching a slope to the molding temperature of the sample, a material was created that has continuous variation in the phase morphology of cured resin from the portion with homoge-

neous morphology to the portion with continuous-phase morphology of PES: phase structure inclination material. Although the portion with continuous-phase morphology in this inclination material is readily decomposed, that with homogeneous morphology is not. Chemical resistance of a product during use and ready for decomposition at the end of its life-cycle can be achieved by forming the phase structure inclination material.

References

1. Mimura, K.; Ito, H.; Fujioka, H. *Polymer* 2000, 41, 4451.
2. Yamanaka, K.; Inoue, T. *Polymer* 1989, 30, 662.
3. Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, G. L.; Wilkes, G. L.; McGrath, J. E. *Polymer* 1991, 32, 2020.
4. Iijima, T.; Hiraoka, H.; Tomoi, M. *J Appl Polym Sci* 1992, 45, 709.
5. Kinloch, A. J.; Yuen, M. L. *J Mater Sci* 1994, 29, 3781.
6. Min, B.-G.; Stachurski, Z. H.; Hodgkin, J. H. *J Appl Polym Sci* 1993, 50, 1511.
7. Bucknall, C. B.; Gilbert, A. H. *Polymer* 1989, 30, 213.
8. Hourston, D. J.; Lane, J. M. *Polymer* 1992, 33, 1379.
9. Cho, J. B.; Hwang, J. W.; Cho, K.; An, J. H.; Park, C. E. *Polymer* 1993, 34, 4832.
10. Teng, K. C.; Chang, F. C. *Polymer* 1996, 37, 2385.
11. Iijima, T.; Tochimoto, T.; Tomoi, M. *J Appl Polym Sci* 1991, 43, 1685.
12. Mimura, K.; Ito, H. *J Appl Polym Sci* 2003, 89, 527.
13. Ito, H.; Mimura, K. *Mitsubishi Electric ADVANCE* 2003, 104, 13.