

Preparation and Cured Properties of Diallyl Phthalate Resin Modified with Epoxy Resin and Allyl Ester Compound Having Carboxylic Acid

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ABSTRACT: An epoxy resin was blended with a diallyl phthalate resin to improve the adhesive properties and the fracture toughness. A compatibilizer was used to reduce the decrease in heat resistance. An allyl ester compound [1,4-diallyloxycarbonyl-2,5-benzenedicarboxylic acid (DAPY)], which reacted with the diallyl phthalate resin and epoxy resin to have allyl groups and carboxylic acids on the end of the molecular chain, was synthesized as a compatibilizer by the reaction of pyromellitic dianhydride with allyl alcohol. These blends were cured with dicumyl peroxide and triethylamine. By modification with the epoxy resin and DAPY, the lap shear adhesive strength to steel increased up to about 3 times that of the diallyl phthalate resin. These results

suggest that the secondary hydroxyl group generated by the addition reaction of the epoxy resin and DAPY and the secondary hydroxyl group existing in the molecular chain of the epoxy resin formed hydrogen bonds with the hydroxyl group of water existing on a metal surface, and as a result, the adhesive strength to metal such as steel increased. The fracture toughness of the diallyl phthalate resin was increased by modification with the epoxy resin. The reason for this result was that the flexibility increased because the crosslinking density became small by modification with the epoxy resin. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 913–919, 2010

Key words: adhesion; blends; compatibility; thermosets

INTRODUCTION

Diallyl phthalate (DAP) resins, which are highly crosslinked thermosetting resins, are used as thermosetting reinforced plastics, molding compounds, and electronic devices that require high reliability under long-term adverse environmental conditions because of their excellent heat resistance, dimensional stability, and electrical properties.¹ Despite these excellent properties, the use of DAP resins is limited because of their poor adhesive properties to various metals and because of their brittleness.

There are a few approaches to the improvement of the adhesive properties for DAP resins in comparison with those of epoxy resins^{2–5} and polyimides.^{6–9} To improve their adhesive properties, DAP resins have been blended with epoxy resins superior in adhesive strength to metal.^{10,11} The peel strength of copper plating on a DAP resin increased through blending with an epoxy resin; however, the heat resistance of the DAP resin that was blended with the epoxy resin decreased markedly. In our previous ar-

icle,^{12,13} we reported that an epoxy resin and a vinyl ester resin that contained a hydroxymethyl group had excellent adhesive properties to metal because hydrogen bonds were formed between a hydroxymethyl group and a hydroxyl group of water existing on a metal surface. The lap shear adhesive strength to steel increased with increasing concentration of hydroxymethyl groups. Moreover, it was found that the lap shear adhesive strength of the DAP resin modified with a phthalic allyl ester having a hydroxyl group (HDAP) increased compared with that of the DAP resin.¹⁴ However, the heat resistance of the modified DAP resin decreased with increasing concentration of HDAP.

To improve their fracture toughness, DAP resins have been blended with polyarylate¹⁵ and reactive oligomers.¹⁶ Fracture energy and elongation increased with increasing concentration of polyarylate or reactive oligomers; however, other mechanical properties decreased markedly.

Epoxy resin is superior in adhesive strength to metal, and the distance between functional groups is longer than that of DAP resin. In this study, epoxy resin was blended with DAP resin to improve the adhesive properties and the toughness of the DAP resin. A compatibilizer was used to reduce the decrease in the heat resistance caused by the blending of the epoxy resin with the DAP resin. An allyl

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TABLE I
Structures of the Materials

Component	Structure
DAP	
Epoxy resin	
Dicumyl peroxide	
Triethylamine	

ester compound [1,4-diallyloxycarbonyl-2,5-benzenedicarboxylic acid (DAPY)], which reacted with DAP resin and epoxy resin to have allyl groups and carboxylic acids on the end of the molecular chain, was synthesized as a compatibilizer by the reaction of pyromellitic dianhydride with allyl alcohol. The lap shear adhesive strength of joints was tested to evaluate the adhesive properties of the modified DAP resin to steel. Moreover, the fracture toughness, thermal, mechanical, and electrical properties of the modified DAP resin were examined.

EXPERIMENTAL

Materials

Reagent-grade pyromellitic dianhydride, allyl alcohol, triethylamine, 2-butanone, toluene, and 4-methyl-2-pentanone were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and were used without further purification. Dicumyl peroxide (PERCUMYL D) as a catalyst was supplied by NOF Corp. (Tokyo, Japan). DAP monomer and DAP prepolymer (DAP A; number-average molecular weight = 6000, weight-average molecular weight = 41,600, iodine value = 55) were supplied by Daiso Co., Ltd. (Osaka, Japan). Bisphenol A based epoxy resin (JER 828, epoxy equivalent weight 186) was supplied by Japan Epoxy Resins Co., Ltd. (Tokyo, Japan). The chemical structures of the DAP, epoxy resin, dicumyl peroxide, and triethylamine are shown in Table I.

Synthesis of DAPY

The synthetic pathway for DAPY is shown in Scheme 1. A 2-butanone solution (200 mL) containing pyromellitic dianhydride (350 g), allyl alcohol (250 mL), and triethylamine (5.6 g) was added to a four-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The tempera-

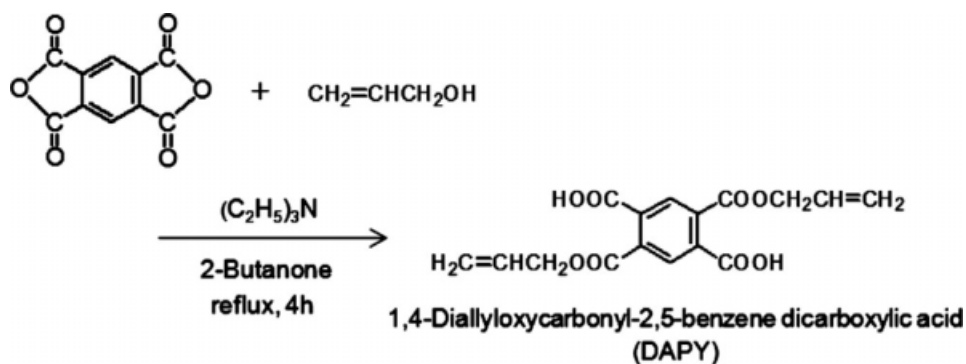
ture of this solution was refluxed with stirring for 4 h. From the reaction mixture, unreacted allyl alcohol and 2-butanone were removed by distillation under reduced pressure. The liquid solution after evaporation, which was dissolved in 4-methyl-2-pentanone, was washed several times with a 1N hydrogen chloride aqueous solution. Then, 4-methyl-2-pentanone was removed by distillation under reduced pressure after it was dried with anhydrous magnesium sulfate. A white solid of DAPY (520 g) was obtained. The chemical structure of DAPY was confirmed by Fourier transform infrared (FTIR) and ¹H-NMR spectroscopy.

Characterization

The ¹H-NMR spectrum was obtained with a Japan Electronic Co. (Tokyo, Japan), JNM-AL300 instrument operating at 300 MHz. Deuterated dimethyl sulfoxide (DMSO) was used as the solvent, and tetramethylsilane was used as the internal standard. FTIR spectra were obtained with a Thermo Fisher Scientific K. K. (Tokyo, Japan) Nicolet6700.

Preparation of the cured resin

Epoxy resin was blended with the DAP resin (7 : 3 wt % mixture of the DAP monomer and DAP prepolymer) at various weight ratios. The DAP resin/epoxy resin weight ratios were 100 : 0, 95 : 5, 90 : 10, and 80 : 20. Furthermore, DAPY was added to the epoxy resin (1 mol:1 mol). As a catalyst, dicumyl peroxide (1.5 wt % of the total weight of the DAP resin and DAPY) and triethylamine (1 wt % of the total weight of epoxy resin and DAPY) were mixed into each blend. The mixture was poured into a silicon mold, which was preheated at 120°C. The curing cycle was 1 h at 120°C, 1 h at 140°C, 1 h at 160°C, 1 h at 180°C, and 1 h at 200°C.



Scheme 1 Synthetic pathway for DAPY.

Measurements of the cured modified DAP resin

The lap shear adhesive strength of joints was measured to evaluate the adhesive properties of the modified DAP resin to steel. The lap shear adhesive strength was measured with an Autograph DSS5000 Instron-type universal testing machine (Shimadzu, Kyoto, Japan) at a crosshead speed of 5 mm/min, according to JIS K 6850. A steel plate (JIS G 3141 SPCC-SB) was used as a substrate. Steel plate was degreased with acetone, polished with abrasive cloth paper (#240), and then washed in an ultrasonic bath with toluene; this was followed by drying before curing.

The properties of the cured modified DAP resins were estimated by the fracture toughness, flexural properties, heat resistance, electrical insulation, and water absorption. The fracture toughness and flexural properties were determined according to ASTM D 5045 and JIS K 6911, respectively. The measurements were done with the Instron-type universal testing machine (Autograph DSS5000) running in compression mode. Single-edge notch specimens with dimensions of $46 \times 6 \times 3 \text{ mm}^3$ were used to measure the fracture toughness of the cured resins. A notch of 2.7 mm was made at one edge of the specimen. We made a natural crack by pressing a fresh razor blade into the notch. The center loading nose moved at a rate of 1 mm/min. The fracture toughness was expressed as the stress intensity factor (K_{IC}) and was calculated as follows:

$$K_{IC} = (PS/BW^{3/2}) \times f(x)$$

where ($0.45 < x < 0.55$)

$$f(x) = 3x^{1/2}[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)] / [2(1+2x)(1-x)^{3/2}]$$

where P is the load at the initiation of crack, S is the support span length, B is the specimen thickness, W is the specimen width, a is the crack length, and x is equal to a/W ($0.45 < x < 0.55$).

Rectangular specimens with dimensions of $100 \times 10 \times 4 \text{ mm}^3$ were used to measure the flexural strength and modulus of the cured resins. The center loading nose moved at a rate of 2 mm/min. The flexural strength (σ) and modulus of elasticity in bending (E) were calculated as follows:

$$\sigma = 3PL/2Wh^2$$

$$E = (L^3/4Wh^3) \times (F/Y)$$

where P is the maximum load in the load deflection curve, W is the specimen width, h is the specimen thickness, L is the support span length, and F/Y is the slope of the tangent to the initial straight-line portion of the stress-strain curve.

Heat resistance was estimated by the glass-transition temperature from dynamic mechanical analysis and by the thermal decomposition temperature from thermogravimetric analysis. Dynamic mechanical analysis was measured in three-point bending mode at 1 Hz with a heating rate of $2^\circ\text{C}/\text{min}$ on an SII NanoTechnology, Inc. (Chiba, Japan), DMS-110. The α maximum of the loss tangent curve was taken to estimate the glass-transition temperature.¹⁷ Thermogravimetric analysis was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with an SII NanoTechnology, Inc., TG/DTA 220. The thermal decomposition temperature was determined to be the temperature at which 10% weight loss was observed.

Electrical insulation was estimated with volume resistivity according to JIS K 6911. The volume resistivity was measured with a Hewlett-Packard Co., Ltd. (USA), HP4339A. The disk specimens (50 mm in diameter and 3 mm thick) were charged with 500 V of electricity, and after 1 min, the volume resistance was measured. The volume resistivity was calculated as follows:

$$\text{Volume resistivity} = \pi d^2/4t \times R$$

where d is the outside diameter of the inner circle of the face electrode, R is the volume resistance, and t is the specimen thickness.

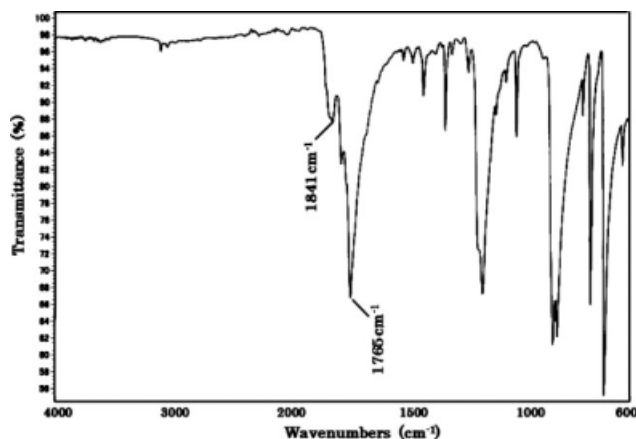


Figure 1 FTIR spectrum of pyromellitic dianhydride.

The water absorption test was determined according to JIS K 6911. The disk specimens (50 mm in diameter and 3 mm thick) were dried at 50°C for 24 h and then put in a desiccator for 1 h. After weight measurement, the specimens were immersed in boiling water for 1 h. Excess water was wiped off with a Kimwipe, and the samples were weighed immediately. The percentage water absorption was calculated as follows:

$$\text{Water absorption (\%)} = (m_2 - m_1)/m_1 \times 100$$

where m_1 and m_2 are the weights of the sample before and after immersion.

RESULTS AND DISCUSSION

Characterization of DAPY

The FTIR analyses of pyromellitic dianhydride and DAPY are shown in Figures 1 and 2, respectively. In the FTIR spectrum of pyromellitic dianhydride (Fig. 1), we observed peaks at 1841 and 1765 cm^{-1} (C=O stretching), representing the characteristic bands of the carbonyl peaks of dianhydride.

In the FTIR spectrum of DAPY (Fig. 2), the completion of the reaction of the pyromellitic dianhydride and allyl alcohol was confirmed by the disappearance of the carbonyl peaks of dianhydride observed at 1841 and 1765 cm^{-1} , whereas the carbonyl peaks of carboxylic acid (C=O stretching) at 1728 and 1693 cm^{-1} and the carbonyl broad peaks of carboxylic acid (C=O stretching) at 2500–3000 cm^{-1} were observed. In addition, the characteristic peak of allyl groups were observed at 1644 cm^{-1} (C=C stretching). The chemical structure of DAPY was confirmed by the $^1\text{H-NMR}$ spectrum. The detailed identification of the $^1\text{H-NMR}$ analysis is shown in Figure 3.

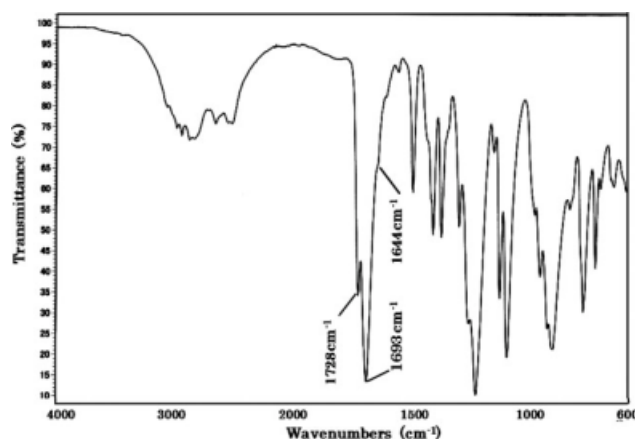


Figure 2 FTIR spectrum of DAPY.

Adhesive properties of the modified DAP resin

The lap shear adhesive strength of the modified DAP resin is shown in Figure 4. The lap shear adhesive strength increased by modification with the epoxy resin. With the addition of 10 wt % epoxy resin, the lap shear adhesive strength was about 3 times larger than that of DAP resin. Concerning the fracture mode, all of the joints showed a cohesive failure, not an interface failure. In general, cohesive failure happens when the interfacial adhesive strength of the adhesive and substrate is larger than the cohesive strength of the adhesive. Therefore, the interfacial adhesive strength of the modified DAP resin to steel improved by modification with the epoxy resin and DAPY. Scheme 2 shows the reaction thought to happen in this reactive system. The reaction thought to happen this reactive system included the following steps: (1) polymerization of the allyl group of DAP, (2) addition reaction of the epoxy group of the epoxy resin and carboxylic acid of DAPY, and (3) copolymerization of the allyl group of DAP and allyl group of DAPY. Many types of forces operate at the

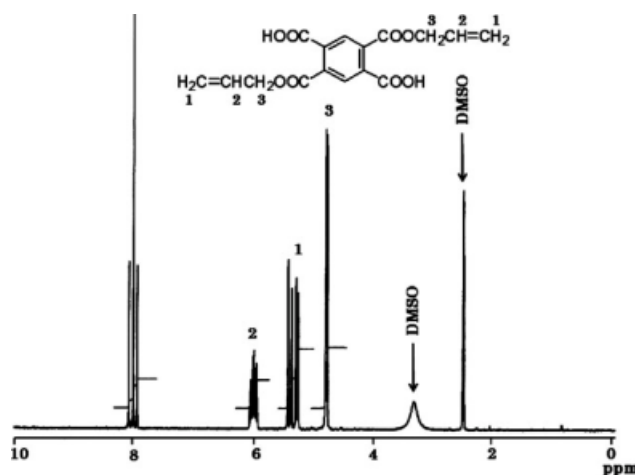


Figure 3 $^1\text{H-NMR}$ spectrum of DAPY.

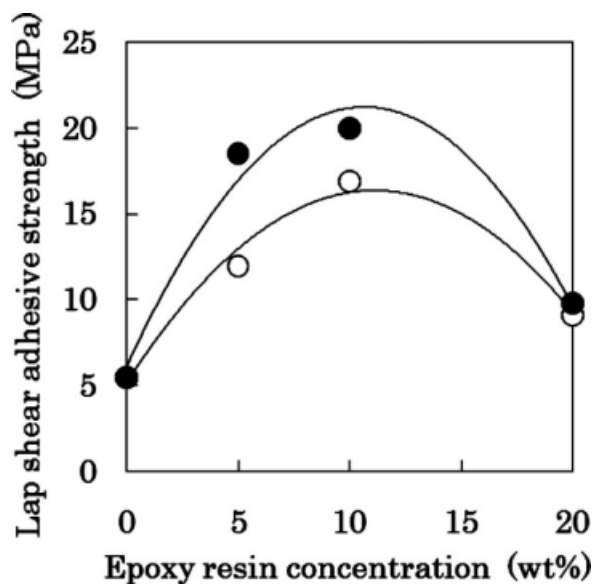


Figure 4 Lap shear adhesive strength of the DAP resin modified with epoxy resin versus the epoxy resin concentration: (○) epoxy resin/DAPY = 1 : 1 and (●) epoxy resin/DAPY = 1 : 2 (mol).

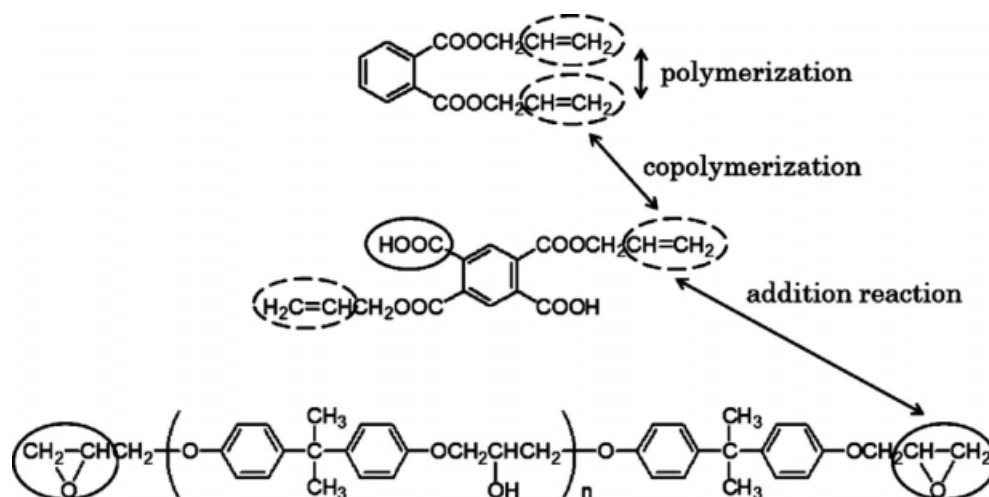
interface between the substrate and polymeric adhesive.^{18,19} Hydrogen bonding is formed between a polymeric adhesive and water existing on a metal surface in one of these forces. Nakamae et al.²⁰ reported that the adhesive strength to metal increased with increasing concentration of hydroxyl groups. Therefore, the reason for the aforementioned results is that the secondary hydroxyl group generated by the addition reaction of the epoxy resin and DAPY and the secondary hydroxyl group existing in the molecular chain of the epoxy resin formed hydrogen bonding to a hydroxyl group of water existing on the metal surface, and as a result, the adhesive strength to metal increased by modification with the epoxy resin and DAPY. Furthermore, to

examine the influence of the hydroxyl groups on the adhesive strength, DAPY was blended with the epoxy resin (1 mol : 2 mol) so that carboxylic acid of DAPY that reacted with the epoxy group of the epoxy resin might have become excessive. As a result, with the addition of 10 wt % epoxy resin, the lap shear adhesive strength was about 4 times larger than that of the DAP resin. The reason for this result is because the carboxylic acid of DAPY that remained without reacting with the epoxy group, and the hydroxyl group generated by the addition reaction of the epoxy resin and DAPY, contributes to the interfacial adhesive strength to the steel interface. As shown in Figure 4, the lap shear adhesive strength increased and passed through a maximum at 10 wt % addition and then decreased. In general, the lap shear adhesive strength indicated a large value by the adhesive hardness.²¹ It is thought that the lap shear adhesive strength decreased because the influence of the decrease in hardness was larger than the effect of the interfacial adhesive strength improvement by the blending amount increase of epoxy resin.

Properties of the cured modified DAP resin

K_{IC} of the DAP resin modified with the epoxy resin is shown in Figure 5. K_{IC} increased with increasing concentration of epoxy resin. The reason for this result is thought to be as follows: the distance between the functional groups of the DAP resin modified with the epoxy resin and DAPY was longer than that of DAP resin; as a result, the crosslinking density decreased, and then, the flexibility of the modified DAP resin was improved.

Figure 6 shows the flexural properties of the DAP resin modified with the epoxy resin. The flexural strength of the modified DAP resin decreased a little with increasing concentration of the epoxy resin. On



Scheme 2 Reaction of DAP resin, epoxy resin, and DAPY.

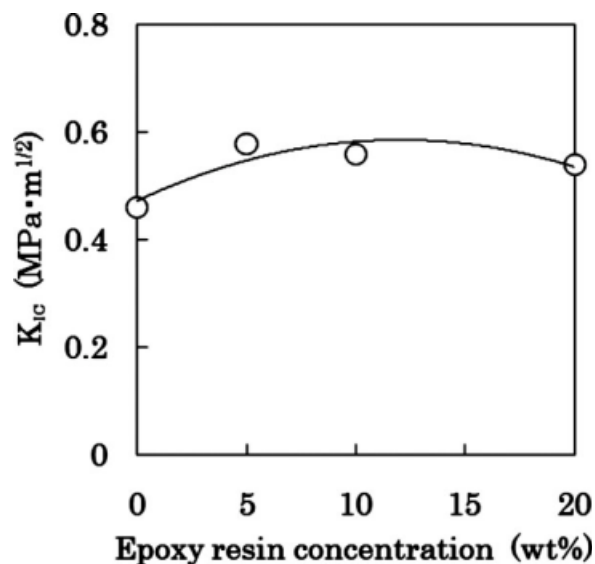


Figure 5 K_{IC} of the DAP resin modified with epoxy resin versus the epoxy resin concentration.

the other hand, the flexural modulus of the modified DAP resin was almost the same.

The glass-transition temperature and thermal decomposition temperature of the modified DAP resin are shown in Figure 7. The glass-transition temperature decreased slightly with increasing concentration of the epoxy resin. This result is due to a decrease in the crosslinking density of the modified DAP resin. On the other hand, the thermal decomposition temperature was almost the same as that of the DAP resin.

Table II shows the results for the electrical properties and water absorption. The volume resistivities of the modified DAP resin in all of the cured systems were almost the same as those of the DAP

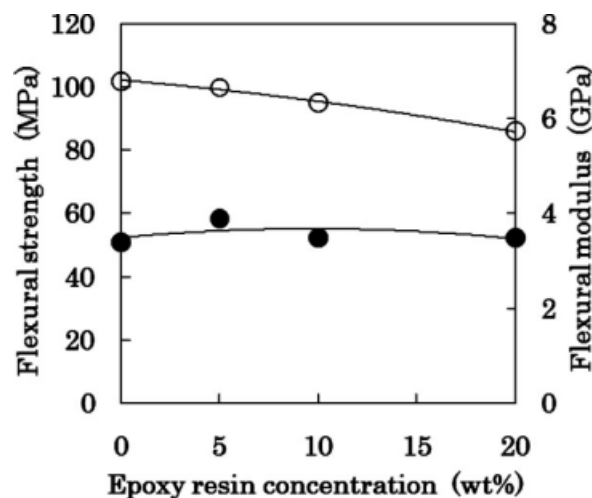


Figure 6 (○) Flexural strength and (●) flexural modulus of the DAP resin modified with epoxy resin versus the epoxy resin concentration.

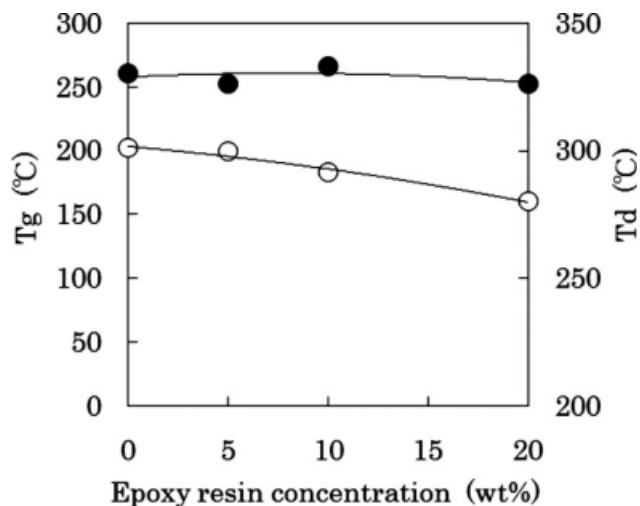


Figure 7 (○) Glass-transition temperature (T_g) and (●) thermal decomposition temperature (T_d) of the DAP resin modified with epoxy resin versus the epoxy resin concentration.

resin. The water absorption after boiling in water for 1 h increased with an increasing concentration of the epoxy resin. This result led to the conclusion that the secondary hydroxyl group of the modified DAP resin formed hydrogen bonds with water.

CONCLUSIONS

A DAP resin was modified with an epoxy resin to improve the adhesive properties and fracture toughness. DAPY, which reacted with the DAP resin and epoxy resin to have allyl groups and carboxylic acids on the end of the molecular chain, was used as a compatibilizer. The results showed that the lap shear adhesive strength to steel increased by modification with the epoxy resin and DAPY. We concluded that the secondary hydroxyl group existing in the modified DAP resin formed hydrogen bonds with a hydroxyl group of water existing on the metal surface. In our previous article,¹⁴ a phthalic allyl ester having a hydroxyl group (HDAP) was blended with DAP resin to improve the adhesive properties. When we compared the improvement in the adhesive properties of the HDAP blending

TABLE II
Electrical Insulation and Water Absorption of the DAP Resin Modified with Epoxy Resin

DAP/epoxy resin (weight ratio)	Volume resistivity (Ω cm)	Water absorption (%)
100 : 0	1.6×10^{16}	0.34
95 : 5	1.7×10^{16}	0.40
90 : 10	1.2×10^{16}	0.46
80 : 20	1.1×10^{16}	0.50

system in the previous study with that of the epoxy resin and DAPY blending system in this study, the lap shear adhesive strength improved greatly only by the addition of a small amount of epoxy resin in the epoxy resin and DAPY blending system. We concluded that the secondary hydroxyl group generated by the addition reaction of epoxy resin and carboxylic acid of DAPY, in addition to the secondary hydroxyl group existing in the molecular chain of the epoxy resin, existed in the epoxy resin and DAPY blending system; as a result, the interfacial adhesive strength to metal increased in the epoxy resin and DAPY blending system more than in the HDAP blending system. In addition, the distance between functional groups when the epoxy resin and DAPY were blended with DAP resin became long compared with that when HDAP was blended; then, the crosslinking density of the epoxy resin and DAPY blending system became small compared to that of the HDAP blending system. As a result, the internal stress when the epoxy resin and DAPY were blended with DAP resin was smaller than that when HDAP was blended. Therefore, we concluded that the adhesive properties when the epoxy resin and DAPY were blended from the aforementioned results were improved from when HDAP was blended.

The fracture toughness of the DAP resin increased by modification with the epoxy resin. The reason for this result is that the flexibility increased because the crosslinking density became small by modification with epoxy resin. The thermal decomposition temperature of the modified DAP resin was almost the same as that of the DAP resin. The glass-transition temperature decreased slightly with increasing concentration of the epoxy resin. However, the glass-transition temperature hardly decreased when the amount of epoxy resin blended with DAP resin was small. In addition, the electrical and flexural properties of the modified DAP resin were almost the same as those of the DAP resin.

As shown by the aforementioned results, we were able to improve the adhesive properties and the toughness without decreasing the heat resistance and flexural and electrical properties when a small amount of the epoxy resin and DAPY were blended with the DAP resin.

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