Properties of Diallyl Phthalate Resin Modified with Phthalic Allyl Ester Having a Hydroxyl Group

Keiko Ohtsuka, Akihiro Matsumoto, Hajime Kimura

Osaka Municipal Technical Research Institute, 6-50, 1-Chome, Morinomiya, Joto-Ku, Osaka, 536-8553 Japan

ABSTRACT: A phthalic allyl ester having a hydroxyl group [2-(2-hydroxy-3-allyloxypropanocarbonyl)-allylphthalate (HDAP)] was synthesized by the reaction of phthalic monoallyl ester with allyl glycidyl ether. HDAP was added to a diallyl phthalate resin to a concentration of 30 wt % to improve the adhesive properties. These blends were cured with dicumyl peroxide. The lap shear strength of joints was measured to evaluate the adhesive properties of the modified diallyl phthalate resin to steel and copper. The lap shear strength of the diallyl phthalate resin was increased by modification with HDAP. By modification with HDAP, the lap shear strength to steel increased up to about 2.5 times that of the diallyl phthalate resin. Moreover, the lap shear strength to copper was about 3.0 times larger than that of the diallyl phthalate resin upon the addition of 30 wt % HDAP. These results suggested that the secondary hydroxyl group of HDAP (used as a modifier) formed a hydrogen bond to a hydroxyl group of water existing on the metal surface, and as a result, the adhesive strength to metals such as steel and copper increased. The thermal decomposition temperature of the modified diallyl phthalate resin was almost the same as that of the diallyl phthalate resin; on the other hand, the glass-transition temperature of the modified diallyl phthalate resin decreased with an increasing concentration of HDAP. The electrical properties of the modified diallyl phthalate resin were almost the same as those of the diallyl phthalate resin. On the other hand, water absorption after boiling increased with an increasing concentration of HDAP. This result led to the conclusion that the secondary hydroxyl group of HDAP (used as a modifier) formed a hydrogen bond to water. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1517–1522, 2008

Key words: adhesion; additives; crosslinking; thermosets

INTRODUCTION

Diallyl phthalate (DAP) resins, which are highly crosslinked thermosetting resins, are used as thermosetting reinforced plastics, moldings, and coatings for electronic devices, such as electrical connectors and insulators, requiring high reliability under long-term adverse environmental conditions because of their excellent heat resistance, dimensional stability, and electrical properties.[1] However, the use of DAP resins is restricted because of poor adhesive properties to various metals and brittleness.

Recently, the trend of integrated circuit packaging has shifted from conventional insertion-mount devices to surface-mount devices. For the mounting of semiconductor parts, both the semiconductor and the printed circuit board have to be exposed to high temperatures during the reflow soldering process. Furthermore, the use of lead-free solder is better from the viewpoint of environmental protection in this field, but for lead-free solder, the reflow temperature rises to 260°C from 240°C in comparison with conventional solder because the melting point of lead-free solder is high. On the other hand, DAP resins have attracted attention with the expansion of the use of lead-free solder, but they are not used in the encapsulation of semiconductor devices and materials of copper-clad laminates because of their poor adhesive strength to metal and fracture toughness. Therefore, if the adhesive strength to metal and the fracture toughness of DAP resins are improved, it is thought that demand for DAP resins in this field could be expected.

There are a few approaches to the improvement of adhesive properties for DAP resins in comparison with those of epoxy resins[2–6] and polyimides.[7–10] To improve their adhesive properties, DAP resins have been blended with epoxy resins with excellent adhesive strength to metal.[11,12] The peel strength of copper plating on a DAP resin was increased through blending with a epoxy resin; however, the heat resistance of the DAP resin that was blended with the epoxy resin decreased markedly.

In our previous article,[13] we reported that an epoxy resin that contained a hydroxymethyl group had excellent adhesive properties to metal because a hydrogen bond was formed between the hydroxymethyl group and a hydroxyl group of water existing on a steel surface. The adhesive strength to steel

Correspondence to: K. Ohtsuka (ohtsuka@omtri.city.osaka.jp).
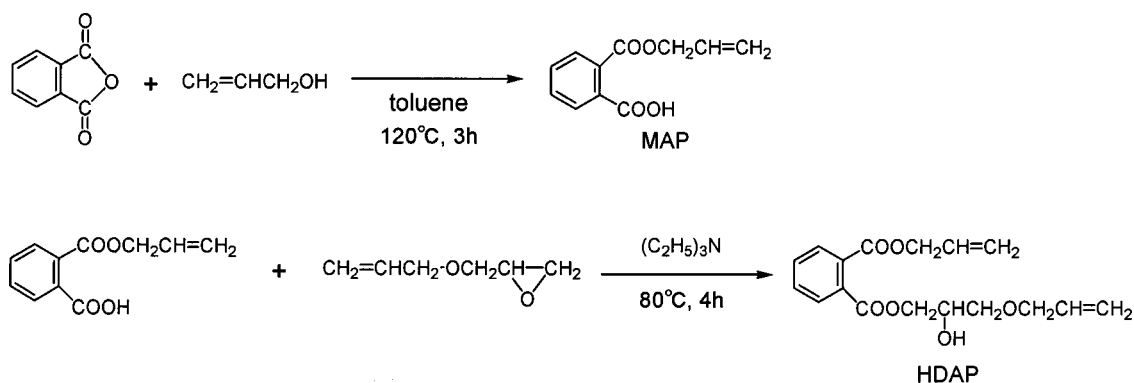
Scheme 1 Synthetic pathway for HDAP.

increased with an increasing concentration of the hydroxymethyl group. In this study, a phthalic allyl ester having a hydroxyl group [2-(2-hydroxy-3-allyloxypropanocarbonyl)-allylphthalate (HDAP)] was synthesized by the reaction of phthalic monoallyl ester with allyl glycidyl ether. It was used as a modifier of a DAP resin because it was predicted that a hydrogen bond would be formed between the hydroxyl group of HDAP and a hydroxyl group of water existing on a metal surface. The lap shear strength of joints was tested to evaluate the adhesive properties of the modified DAP resin to steel and copper. Moreover, the thermal, mechanical, and electrical properties of the modified DAP resin were examined.

EXPERIMENTAL

Materials

Reagent-grade phthalic anhydride, allyl alcohol, and allyl glycidyl ether were acquired from Nacalai Tesque, Inc. (Kyoto, Japan), and used without further purification. Reagent-grade triethylamine and dicumyl peroxide as a catalyst were obtained from Kanto Chemical, Inc. (Tokyo, Japan), and used without further purification. Toluene as a solvent was distilled before use in a routine manner. DAP was supplied by Daiso Co., Ltd. (Osaka, Japan).

Synthesis of 2-allylphtalate (MAP)

The synthetic pathway for MAP is shown in Scheme 1. A toluene solution (180 mL) containing phthalic anhydride (148 g) and allyl alcohol (80 mL) was added to a three-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The temperature of this solution was refluxed with stirring for 3 h. From the reaction mixture, unreacted allyl alcohol and toluene were removed by distillation under reduced pressure. The liquid solution after evaporation, which was dis-

solved in diethyl ether, was washed several times with a 5% NaHCO$_3$ aqueous solution and a 1N HCl aqueous solution. Then, diethyl ether was removed by distillation under reduced pressure. A transparent, viscous fluid of MAP (180 g) was obtained. The chemical structure of MAP was confirmed by Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopy.

Syntheses of HDAP

The synthetic pathway for HDAP is shown in Scheme 1. MAP (206 g), allyl glycidyl ether (148 mL), and triethylamine as a catalyst (4 g) were added to a three-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The temperature of this solution was raised to 90°C with stirring for 3.5 h. From the reaction mixture, unreacted allyl glycidyl ether was removed by distillation under reduced pressure. The liquid solution after evaporation, which was dissolved in toluene, was washed several times with a 5% NaHCO$_3$ aqueous solution and a 1N HCl aqueous solution. Then, toluene was removed by distillation under reduced pressure. A transparent, viscous fluid of HDAP (235 g) was obtained. The chemical structure of HDAP was confirmed by FTIR and ^{1}H-NMR spectroscopy.

Characterization

^{1}H-NMR spectra were obtained with a Japan Electronic Co. (Tokyo, Japan) JNM-AL300 operating at 300 MHz. Deuterated chloroform (CDCl$_3$) was used as the solvent, and tetramethylsilane was used as the internal standard. FTIR spectra were obtained with a Nicolet Japan Co., Ltd. (Kanagawa, Japan), Impact 400.

Preparation of the cured resin

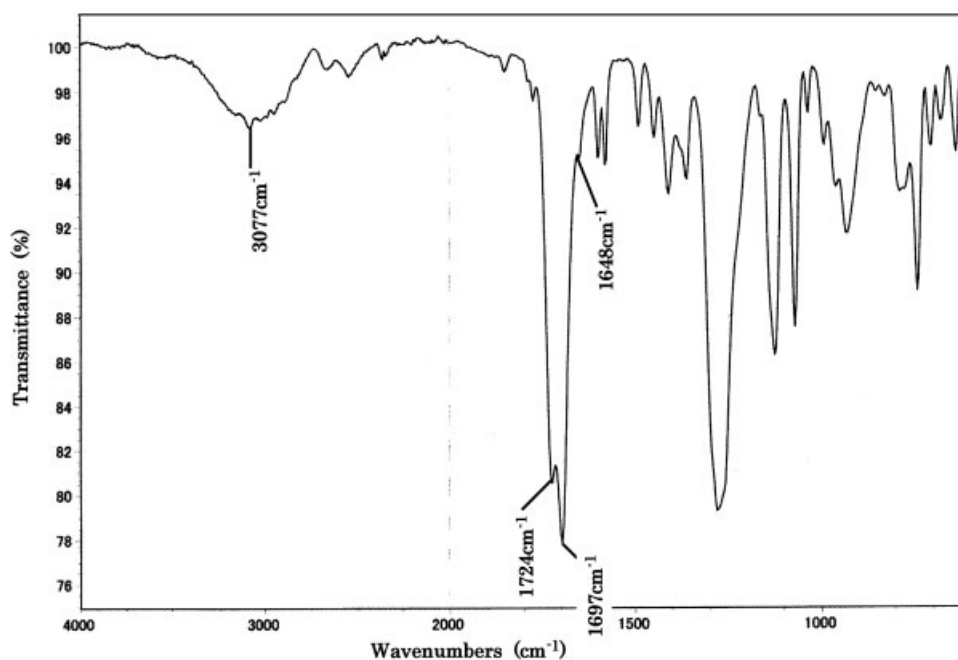HDAP was blended with DAP in various weight ratios: 100/0, 90/10, 80/20, and 70/30. Dicumyl

Figure 1 FTIR spectrum of MAP.

peroxide (1.5 wt %) as a catalyst was mixed into each blend. The mixture was poured into a silicon mold, which was preheated at 100°C. The curing cycle was 1 h at 120°C, 1 h at 140°C, 1 h at 160°C, and 1 h at 180°C.

Measurements of the cured resin

Heat resistance was estimated by the glass-transition temperature on dynamic mechanical analysis and by the thermal decomposition temperature on thermogravimetric analysis. Dynamic mechanical analysis was measured in a three-point bending mode at 1 Hz with a heating rate of 2°C/min on a Seiko Instruments, Inc. (Chiba, Japan), DMS-110. The α maximum of the loss tangent curve was taken to estimate the glass-transition temperature.[14] Thermogravimetric analysis was carried out with a heating rate of 10°C/min under a nitrogen atmosphere with a Seiko Instruments TG/DTA 220. The thermal decomposition temperature was determined to be the temperature at which 10% weight loss was observed.

The flexural properties of the cured resins were obtained with an Instron-type universal testing machine (Autograph DSS5000, Shimadzu Co., Kyoto, Japan). The flexural strength and modulus were obtained at a crosshead speed of 2 mm/min according to ASTM D 790-86.

Electrical properties were estimated by the volume resistivity and dielectric constant. The volume resistivity was measured with a Yokogawa–Hewlett–Packard Co., Ltd. (Tokyo, Japan), instrument. The

dielectric constant was measured at 1 MHz with an Ando Electric Co., Ltd. (Tokyo, Japan), TR-1100.

A water absorption test was carried out through the immersion of the cured resins in boiling water for 1 h. The cured resins were removed and cooled to the ambient temperature and then were wiped dry and weighed to the mass after water absorption.

The lap shear strength of joints was measured with an Instron-type universal testing machine (Autograph DSS5000, Shimadzu) at a crosshead speed of 5 mm/min according to ASTM 1002-72. Steel and copper plates were used as substrates. 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. Copper plate was polished with abrasive cloth paper (#240), washed with acetone, treated with a 25% HNO_3 aqueous solution, and then washed with water; this was followed by drying before curing.

RESULTS AND DISCUSSION

Characterization of MAP and HDAP

FTIR analysis of MAP is shown in Figure 1. In the FTIR spectrum of MAP, we can see peaks at 3077 and 1648 cm^{-1} (C=C stretching) representing the characteristic band of the allyl group, and carbonyl broad peaks of carboxylic acid can be observed at 2500–2700 and 2700–3300 cm^{-1} (C=O stretching). In addition, the carbonyl peak of carboxylic acid
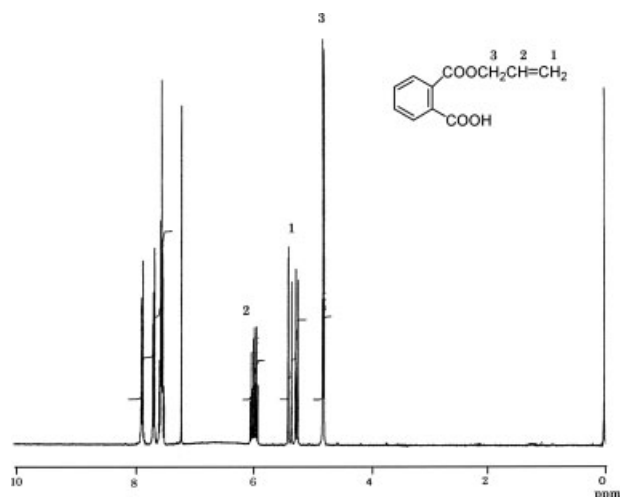
Figure 2 ^{1}H-NMR spectrum of MAP.

appears at 1697 cm^{-1}, next to a carbonyl peak attached to the allyl group at 1724 cm^{-1}. ^{1}H-NMR analysis was conducted with CDCl$_3$ to confirm the chemical structure of MAP. The detailed identification is shown in Figure 2.

FTIR analysis of HDAP is shown in Figure 3. In the FTIR spectrum of HDAP, the completion of the reaction of MAP and allyl glycidyl ether is confirmed by the disappearance of carbonyl peaks of carboxylic acid observed at 2500–2700, 2700–3300, and 1697 cm^{-1}, whereas the absorption peak of the secondary hydroxyl group appears at 3200–3600 cm^{-1} (OH stretching). The chemical structure of HDAP is conformed by the ^{1}H-NMR spectrum. The

detailed identification of ^{1}H-NMR analysis is shown in Figure 4.

Adhesive properties of the modified DAP resin

The lap shear strength of joints was measured to evaluate the adhesive properties of the DAP resin modified with HDAP. The lap shear strength of the modified DAP resin is shown in Figure 5. The lap shear strength of the modified DAP resin increased by modification with HDAP with both steel and copper as substrates. On the addition of 20 wt % HDAP with steel as the substrate, the lap shear strength was about 2.5 times larger than that of the DAP resin. In the case of copper as the substrate, the lap shear strength increased with increasing HDAP; in particular, it was about 3.0 times larger than that of the DAP resin on the addition of 30 wt % HDAP. Concerning the fracture mode, all of the joints showed cohesive failure. Many types of forces operate at the interface between the substrate and polymeric adhesive.[15,16] Hydrogen bonding is formed between a polymeric adhesive and water existing on a metal surface in one of these forces. Nakamae et al.[17] reported that the adhesive strength to metal increased with an increasing concentration of hydroxyl groups. Therefore, it is thought that the reason for the aforementioned results is that the secondary hydroxyl group of HDAP (used as a modifier) formed a hydrogen bond to a hydroxyl group of water existing on the metal surface, and as a result, the adhesive strength to the metal increased by modification with HDAP.
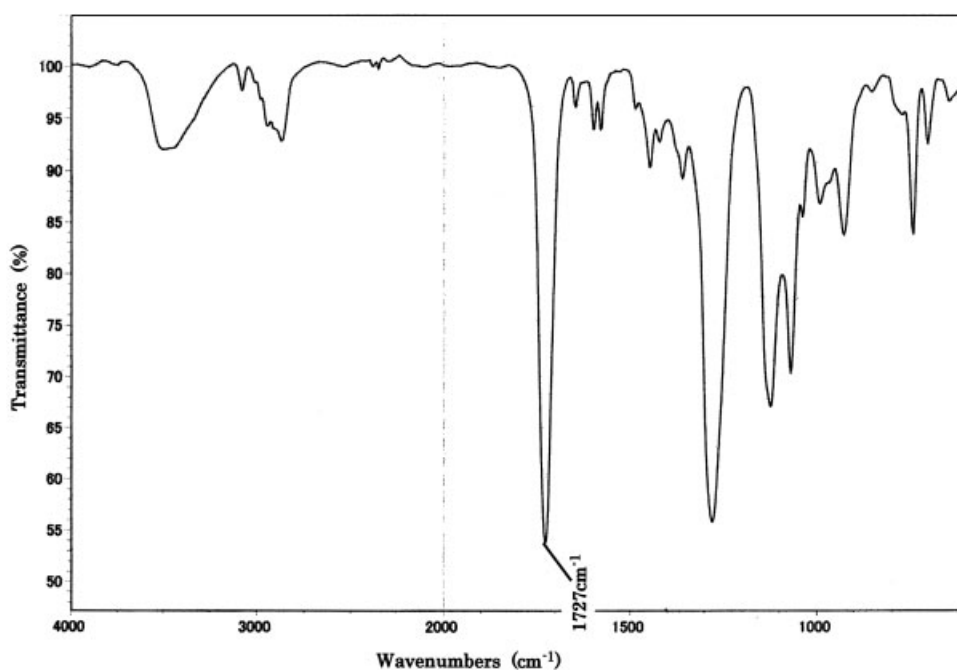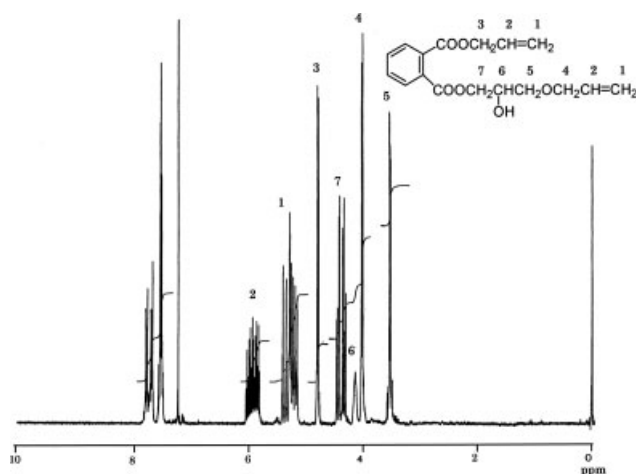

Figure 3 FTIR spectrum of HDAP.

Figure 4 ^{1}H-NMR spectrum of HDAP.

Figure 6 Glass-transition temperature (T_g) and thermal decomposition temperature (T_d) of the DAP resin modified with HDAP versus the HDAP concentration: ($\bigcirc$) T_g and ($\bullet$) T_d.

Properties of the cured resin

The glass-transition temperature and thermal decomposition temperature of the DAP resin modified with HDAP are shown in Figure 6. The thermal decomposition temperature of the modified DAP resin was almost the same because the DAP resin modified with HDAP and the DAP resin have similar structures. On the other hand, the glass-transition temperature decreased with an increasing concentration of HDAP. The reason for this result is thought to be as follows: the distance between crosslinking points of the DAP resin modified with HDAP was longer than that of the DAP resin; as a result, the crosslinking density decreased, and then the glass-transition temperature was lowered.
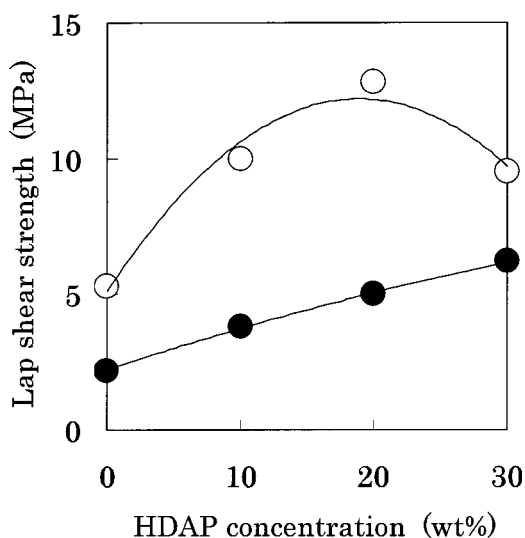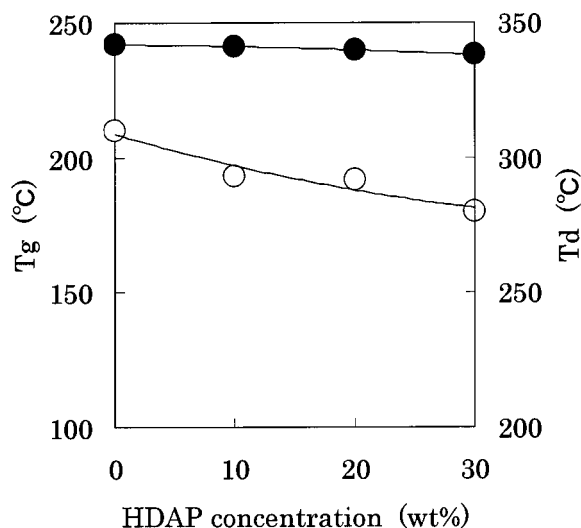
Figure 7 shows the flexural properties of the DAP resin modified with HDAP. The flexural strength of the modified DAP resin decreased a little with an increasing concentration of HDAP. On the other hand, the flexural modulus of the modified DAP resin increased with an increasing concentration of HDAP.

Table I shows the results for the electrical properties and water absorption. The volume resistivity and dielectric constant of the modified DAP resin in all the cured systems were almost the same as those of the DAP resin. Water absorption after boiling in
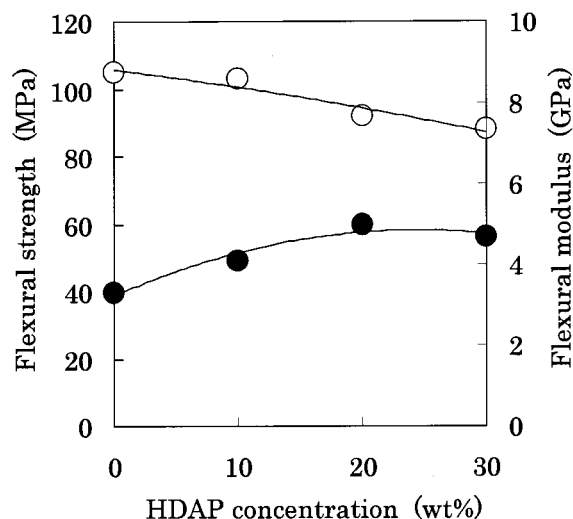

Figure 5 Lap shear strength of the DAP resin modified with HDAP versus the HDAP concentration: ($\bigcirc$) steel and ($\bullet$) copper.

Figure 7 Flexural strength and flexural modulus of the DAP resin modified with HDAP versus the HDAP concentration: ($\bigcirc$) flexural strength and ($\bullet$) flexural modulus.

TABLE I
Electrical Properties and Water Absorption of the DAP Resin Modified with HDAP

DAP/HDAP (weight ratio)	Volume resistivity (Ω cm)	Dielectric constant	Water absorption (%)
100/0	2.8×10^{16}	3.1	0.31
90/10	1.8×10^{16}	3.2	0.36
80/20	1.7×10^{16}	3.2	0.39
70/30	1.6×10^{16}	3.2	0.42

water for 1 h increased with an increasing concentration of HDAP. This result led to the conclusion that the secondary hydroxyl group of HDAP (used as a modifier) formed a hydrogen bond to water.

CONCLUSIONS

A DAP resin was modified with HDAP to improve the adhesive properties. The results showed that the lap shear strength to metal was increased by modification with HDAP. It was concluded that a secondary hydroxyl group of HDAP formed a hydrogen bond to a hydroxyl group of water existing on the metal surface. The thermal decomposition temperature of the modified DAP resin was almost the same as that of the DAP resin; on the other hand, the glass-transition temperature decreased with an increasing concentration of HDAP. In addition, the electrical properties of the modified DAP resin in all cured systems were almost the same as those of the DAP resin.

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