

Preparation and Properties of Cured Diallyl Phthalate Resin Modified with Dimeric Acid Polyamide Derivatives

Keiko Ohtsuka,¹ Hajime Kimura,¹ Akihiro Matsumoto,¹ Masanori Saito,² Koji Yamano²

¹Osaka Municipal Technical Research Institute, Joto-ku, Osaka, 536-8553, Japan

²Harima Chemicals, Inc., 671-4, Mizuashi, Noguchi-cho, Kakogawa, Hyogo, 675-0019, Japan

Received 22 February 2011; accepted 4 January 2012

DOI 10.1002/app.36749

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The allyl ester of dimeric acid polyamide, a compound which has a flexible unit in the main chain and reacts with the diallyl phthalate (DAP) resin to have an allyl group, was synthesized by the reaction of dimeric acid polyamide with allyl glycidyl ether. The allyl ester of dimeric acid polyamide was blended with DAP resin to improve the adhesive properties to metal. These blends were cured with dicumyl peroxide. By modification with allyl ester of dimeric acid polyamide, the T-peel adhesive strength to copper improved. This result is due to the increase in flexibility generated by introducing the unit of dimeric acid polyamide and subsequent increase in interfacial adhesive strength due to the amide bond being located in the surface of the copper plate. On the other hand, the

lap-shear adhesive strength did not improve significantly because of the decrease in rigidity. On increasing concentration of allyl ester of dimeric acid polyamide, the glass-transition temperature slightly decreased, but there was little decrease of the thermal decomposition temperature. From scanning electron microscope observations, it was found that the DAP resin modified with allyl ester of dimeric acid polyamide formed a microphase-separated structure consisting of small dimeric acid polyamide particles dispersed in the DAP resin matrix. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: diallyl phthalate resin; dimeric acid polyamide; allyl ester; adhesive property; polar group

INTRODUCTION

Diallyl phthalate (DAP) resins, which are highly crosslinked thermosetting resins, are used as thermosetting reinforced plastics, molding compounds, and electronic devices requiring 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 usage of DAP resins is limited because of their poor adhesive properties to various metals.

There are a few approaches to the improvement of 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 foil on the DAP resin increased through blending with epoxy resin; however, the heat resistance of the DAP resin that was blended with epoxy resin decreased markedly. In our previous article,^{12,13} we reported that an epoxy resin and a vinyl ester resin that contained hydroxymethyl group had excellent

adhesive properties to metal because a hydrogen bonding was 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 an increasing concentration of hydroxymethyl group. Moreover, it was found that the lap-shear adhesive strength of the DAP resin modified with allyl ester compounds having hydroxyl group increased compared with that of DAP resin.¹⁴ And Kishi et al.¹⁵ reported that the lap-shear adhesive strength to metal of the epoxy resin having polar group increased with increasing the interfacial interaction between metal and epoxy resin.

On the other hand, the dimeric acid polyamide synthesized by the condensation reaction of dimeric acid with amine, is widely used in the field of adhesive and coating, because of excellent flexibility and adhesive property. In this study, allyl ester of dimeric acid polyamide was synthesized by the reaction of dimeric acid polyamide with allyl glycidyl ether. DAP resin was modified with allyl ester of dimeric acid polyamide to improve the adhesive property to metal. The T-peel adhesive strength and the lap-shear adhesive strength were measured to evaluate the adhesive properties of the modified DAP resin. To examine the influence that amide bond give adhesion strength, the surface of the copper plate which peeled after measuring the lap-shear

Correspondence to: K. Ohtsuka (ohtsuka@omtri.or.jp).

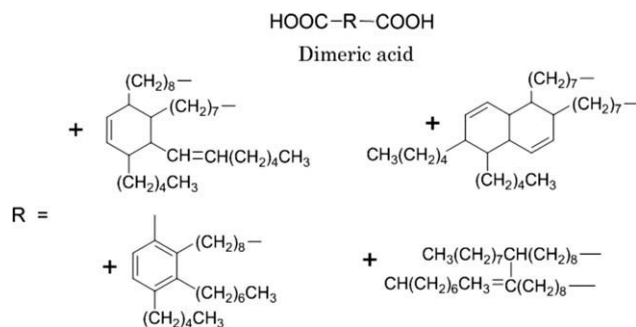


Figure 1 Structure of dimeric acid.

adhesive strength test was analyzed by using FTIR. Moreover, the thermal property and morphology of the cured modified DAP resin were examined.

EXPERIMENTAL

Materials

Reagent-grade *m*-xylylenediamine, diethylenetriamine, methacrylic acid, and allyl glycidyl ether were purchased from Nacalai Tesque (Kyoto, Japan) and used without further purification. Dicumyl peroxide (PERCUMYL[®] D) as a catalyst was supplied by NOF Corporation (Tokyo, Japan). DAP monomer (DAISO DAP[®] Monomer) and DAP prepolymer (DAISO DAP[®] A; M_n , 6000, M_w , 41,600; iodine value, 55) were supplied by DAISO Co. (Osaka, Japan). Dimeric acid (HARIDIMER 200) was supplied by Harima Chemicals (Osaka, Japan). Dimeric acid is the dicarboxylic acid that the carbon number is 36 and is a mixture that contains aliphatic compounds, monocyclic compounds, and polycyclic compounds by about 15, 70, and 15%, respectively. The chemical structures of dimeric acid are shown in Figure 1.

Synthesis of allyl ester of dimeric acid polyamide

The synthesis pathway for allyl ester of dimeric acid polyamide is shown in Figure 2. The allyl ester of dimeric acid polyamide was synthesized by the reac-

tion of dimeric acid polyamide with allyl glycidyl ether. It was a compound which has an allyl group on the structure end and an amide bond in the main chain.

Synthesis of allyl ester of dimeric acid polyamide using *m*-xylylenediamine

Dimeric acid (58 g) and *m*-xylylenediamine (27.2 g) were added to a three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. This solution was reacted for 4 h at 200°C under nitrogen atmosphere. From the reaction mixture, water of by-product was removed by distillation under reduced pressure. A transparent, brown viscous fluid of dimeric acid polyamide was obtained.

Next, dimeric acid polyamide (81.6 g) was added to a three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and thermometer. Allyl glycidyl ether (22.8 g) was dropped into this solution for 2 h at 80°C, and then reacted for 4 h at 200°C under nitrogen atmosphere. A transparent, brown viscous fluid of allyl ester of dimeric acid polyamide (amine value, 105) was obtained. The allyl ester of dimeric acid polyamide synthesized by using *m*-xylylenediamine as a primary amine is abbreviated as APA1. The chemical structure of APA1 was confirmed by FTIR with a Nicolet 6700 (Thermo Fisher Scientific K.K., Tokyo, Japan). FTIR spectra of APA1 and dimeric acid polyamide which is a starting material of APA1 are shown in Figure 3. In the FTIR spectrum of APA1, we can see peak at 999 cm^{-1} representing the characteristic band of allyl group (C=C stretching), and ether broad peaks (C—O—C asymmetric stretching) of attached to allyl group can be observed at 1088 cm^{-1} .

Synthesis of allyl ester of dimeric acid polyamide using diethylenetriamine

Allyl ester of dimeric acid polyamide was synthesized by the method similar to APA1 by using

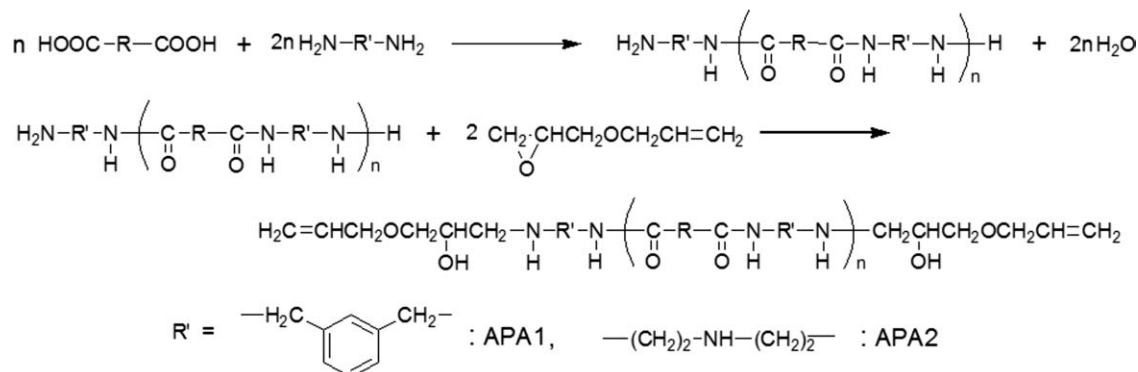


Figure 2 Reaction scheme of allyl ether of dimeric acid polyamide.

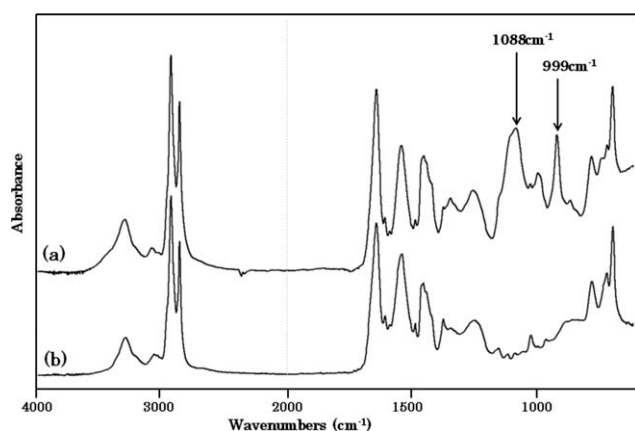


Figure 3 FTIR spectra of APA1 (a) and dimeric acid polyamide (b).

diethylenetriamine, dimeric acid, and allyl glycidyl ether. A transparent, brown viscous fluid of allyl ester of dimeric acid polyamide (amine value, 227) was obtained. The allyl ester of dimeric acid polyamide synthesized by using diethylenetriamine as a primary amine is abbreviated as APA2. The chemical structure of APA2 was confirmed by FTIR.

Synthesis of allyl ester of polyamide using methacrylic acid and *m*-xylylenediamine

APA3 as a reference of APA1, 2 was synthesized. The structure of APA3 is shown in Figure 4. APA3 was synthesized by the method similar to APA1 by using methacrylic acid, *m*-xylylenediamine, and allyl glycidyl ether. A transparent, viscous fluid of allyl ester of methacrylic acid polyamide (amine value, 297) was obtained. The chemical structure of APA3 was confirmed by FTIR.

Measurements of the cured modified DAP resin

The T-peel adhesive strength and the lap-shear adhesive strength were measured to evaluate the adhesive properties of the modified DAP resin. The T-peel adhesive strength was measured with an Instron-type universal testing machine AL-50 (Minebea Co., Nagano, Japan) at a crosshead speed of 100 mm/min, according to JIS K 6854. Copper (oxygen-free) plate was used as a substrate. Copper plate was degreased with acetone, soaked in 25 wt % HNO₃ solution for 30 s, and then washed with distilled water; this was followed by drying before

curing. APA1–3 were blended with the DAP resin (5 : 5 wt % mixture of DAP monomer and DAP prepolymer) at various weight ratios, respectively. As a catalyst, 1.5 wt % of dicumyl peroxide of the total weight of the DAP resin was mixed into each blend. The mixture was applied to copper plate. 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.

The lap-shear adhesive strength was measured with an Instron-type universal testing machine at a crosshead speed of 5 mm/min, according to JIS K 6850. The test pieces were made by the method similar to those of the T-peel adhesive strength. The chemical composition analysis in the interfacial destruction part of the surface of copper plate after the lap-shear adhesive strength test was evaluated by FTIR using ATR method.

Heat resistance of the cured modified DAP resins was estimated by the glass-transition temperature from dynamic mechanical analysis and by the thermal decomposition temperature from thermogravimetric analysis. The test pieces were made as follows: The mixture of the modified DAP resin was made by the method similar to the test pieces of the T-peel adhesive strength. 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, and 1 h at 180°C.

Dynamic mechanical analysis was measured in three-point bending mode at 1 Hz with a heating rate of 2°C/min on a SII NanoTechnology (Chiba, Japan), DMS-110. The α dissipation of the loss tangent curve was taken to estimate the glass-transition temperature.¹⁶

The crosslinking density, $\rho(E')$, can be calculated using the equation of state for rubbery elasticity¹⁷;

$$\rho(E') = E' / (3\phi RT)$$

where ϕ is the front factor, T is the absolute temperature, R is the gas constant, and E' is the storage modulus of the sample at temperature T . This equation is applicable to polymer networks that have a rubbery plateau region.¹⁸ In this study, crosslinking density of the samples were calculated at the glass-transition temperature plus 30°C according to this equation,¹⁹ and assuming ϕ is equal to 1.²⁰

Thermogravimetric analysis was carried out at a heating rate of 10°C/min under a nitrogen atmosphere with a SII NanoTechnology, TG/DTA 220.

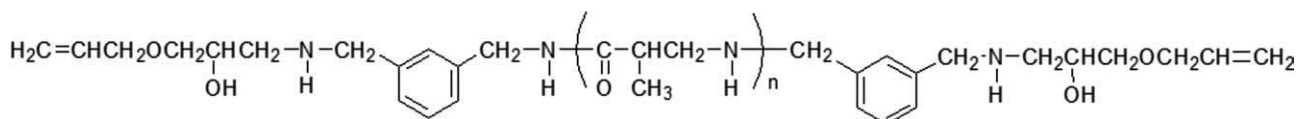


Figure 4 Structure of APA3.

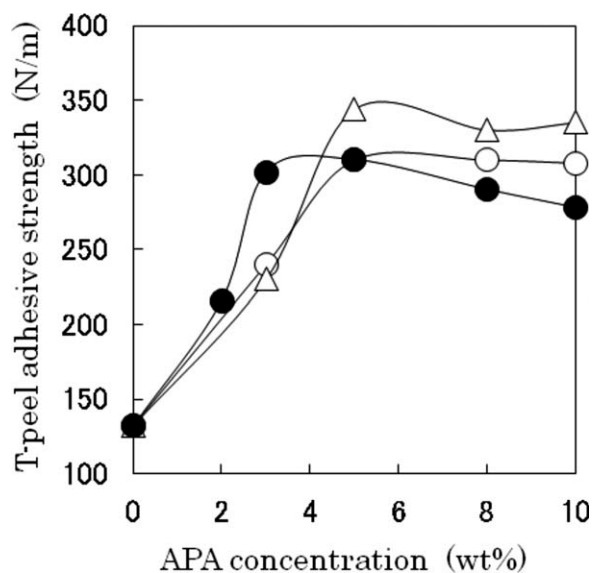


Figure 5 T-peel adhesive strength of DAP resin modified with APA depending on APA concentration: substrate, copper; ○, APA1; △, APA2; ●, APA3.

The thermal decomposition temperature was determined to be the temperature at which 10% weight loss was observed.

Morphologies of the cured modified DAP resin

Morphologies of the fracture surface of the cured modified DAP resins were observed by a scanning electron microscope (SEM) (JSM-5800, JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Adhesive properties of the modified DAP resin

The T-peel adhesive strength and the lap-shear adhesive strength of the modified DAP resins are shown in Figures 5 and 6, respectively. In Figure 5, the T-peel adhesive strength increased by modification with APA1–3. With the addition of 5 wt % of APA2, the T-peel adhesive strength was about 2.6 times larger than that of DAP resin. When <3 wt % concentration of APA1–3, the T-peel adhesive strength of the DAP resin modified with APA3 became larger than those of modified with APA1, 2. And when the concentration of 3 wt % or more of APA1–3, the T-peel adhesive strength of modified with APA3 became smaller than those of APA1, 2. In Figure 6, the lap-shear adhesive strength increased by the addition of up to 5 wt % of APA1, 2 and decreased thereafter. On the other hand, the lap-shear adhesive strength increased by modification with APA3. With the addition of 3 wt % of APA3, the lap-shear adhesive strength was about 1.8 times larger than that of DAP resin.

Generally, if the adhesive is flexible, the stress was added to the junction adhesive and substrate can be relaxed. As a result, the T-peel adhesive strength increases. On the other hand, the lap-shear adhesive strength is increased with increasing of rigidity of adhesive.²¹ Therefore, adhesive strength results are considered as follows: when the increasing the concentration of APA1, 2 which has long chain hydrocarbon group, the flexibility of the modified DAP resin increased. As a result, the T-peel adhesive strength increased and the lap-shear adhesive strength decreased; while, when APA3 was blended to DAP resin, the T-peel adhesive strength and the lap-shear adhesive strength increased. This result is considered to be due to the influence of the amide bond of APA3. Next, to examine the localization of the amide bond in DAP resin modified with APA1–3, the chemical composition analysis in the interfacial destruction part of the surface of copper plate after the lap-shear adhesive strength test was evaluated by FTIR using ATR method. The bulk cured modified DAP resin was used as a reference. One example of the result of FTIR measurement is shown in Figure 7. From the FTIR measurement result, it was examined whether the amide bond existing in the modified DAP resin was located in the surface of the copper plate. Figure 8 shows the absorbance ratio of the absorption of $-\text{NH}$ stretching vibration at 3432 cm^{-1} based on the absorption of $-\text{CH}$ stretching vibration at 2854 cm^{-1} . In all systems, $-\text{NH}/-\text{CH}$ absorbance ratios of the interface of the modified DAP resin and copper surface showed a value bigger than those of the bulk cured modified DAP resin. Furthermore, $-\text{NH}/-\text{CH}$ absorbance

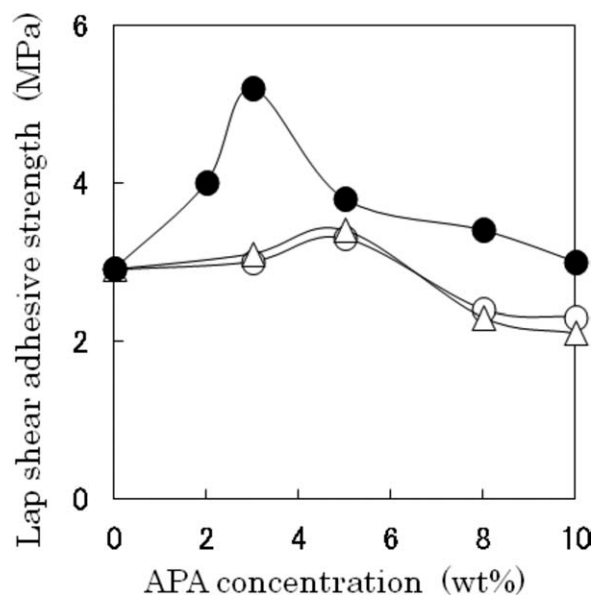


Figure 6 Lap-shear adhesive strength of DAP resin modified with APA depending on APA concentration: substrate, copper; ○, APA1; △, APA2; ●, APA3.

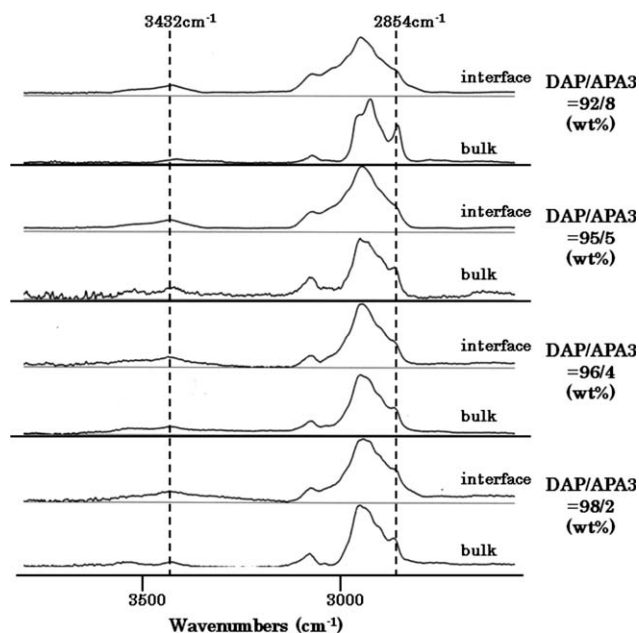


Figure 7 FTIR spectra of DAP resin modified with APA3.

ratios of DAP resin modified with APA3 were bigger than those of modified with APA1, 2. Therefore, it is considered that the amide bond in DAP resin modified with APA3 is located in the surface of copper plate, compared with those of modified with APA1, 2. These results found that: when blended with short chain length APA1 to DAP resin, the T-peel adhesive strength was increased, due to the improved the interfacial adhesive strength, despite the small effect of the increased flexibility. In addition, the increase in the lap-shear adhesive strength

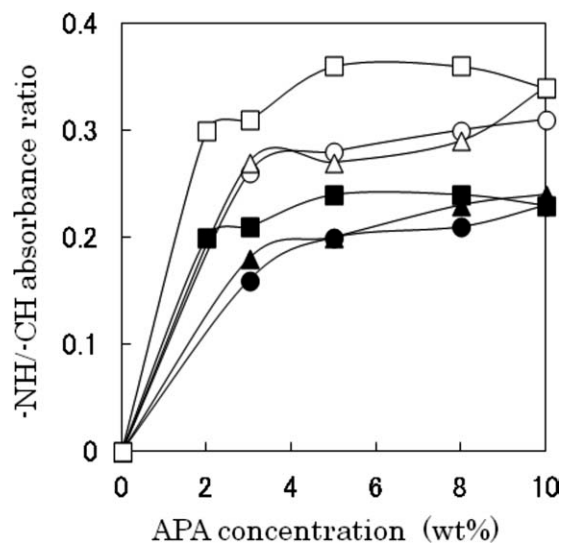


Figure 8 $-NH/-CH$ absorbance ratio of the interface of DAP resin modified with APA and copper surface depending on APA concentration: interface: \circ , APA1; \triangle , APA2; \square , APA3; bulk: \bullet , APA1; \blacktriangle , APA2, \blacksquare , APA3.

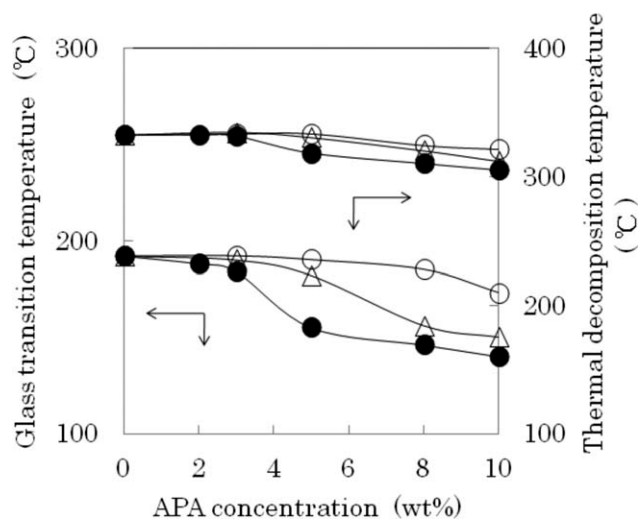


Figure 9 Glass transition temperature and thermal decomposition temperature of DAP resin modified with APA depending on APA concentration: \circ , APA1; \triangle , APA2; \bullet , APA3.

of DAP resin modified with APA3 is considered to be due that the decrease of rigidity was small and the interfacial adhesive strength increased.

Heat resistance of the cured modified DAP resin

The glass-transition temperature and thermal decomposition temperature of the cured modified DAP resin are shown in Figure 9. The glass-transition temperature decreased with increasing concentration of APA1–3. To examine these results, the crosslinking density is calculated. The results are shown in Table I. The crosslinking density of the modified DAP resin was smaller than those of DAP resin, and decreased with increasing concentration of APA1–3. Therefore, the decrease in the glass transition temperature of the modified DAP resin is considered to be due to the decrease in crosslinking density. On the other hand, there was a little decrease of the thermal decomposition temperature by an increase of the concentration of APA1–3.

Morphologies of the cured modified DAP resin

Figure 10 shows the SEM of the fracture surface of the cured modified DAP resin. In the case of the DAP resin modified with APA1, 2, a microphase-separated structure consisting of small particles dispersed in the DAP resin matrix could be observed. On the other hand, the fracture surface was one-phase in blending of APA3. These results are considered as follows: APA1, 2 are easy to cohere because of including a lot of amide bond that is the polar group. As a result, dimeric acid polyamide unit of APA1, 2 separated and formed domain, although

TABLE I
Crosslinking Density of DAP Resin Modified with APA1-3

DAP/APA (weight ratio)	Crosslinking density (mol/m ³)
DAP	6.35×10^3
DAP/APA1 = 95/5	4.91×10^3
DAP/APA1 = 92/8	2.97×10^3
DAP/APA2 = 95/5	4.89×10^3
DAP/APA2 = 92/8	2.47×10^3
DAP/APA3 = 95/5	3.35×10^3
DAP/APA3 = 92/8	2.45×10^3

DAP resin and APA1, 2 having allyl group were copolymerized. While, compared with APA1, 2, a chain length of APA3 was short and the number of amide bonds of APA3 was small. Therefore, DAP resin modified with APA3 formed one-phase structure.

CONCLUSIONS

A DAP resin was modified with allyl ester of dimeric acid polyamide (APA1, 2) to improve the adhesive properties to metal. By modification with APA1, 2, the T-peel adhesive strength to copper improved. This result is due to the increase in flexibility generated by introducing the unit of dimeric acid polyamide and increased interfacial adhesive strength due to the amide bond being located in the

surface of the copper plate. On the other hand, the lap-shear adhesive strength did not improve significantly, because of the decrease in rigidity. In addition, APA3 that the main chain was short was blended to DAP resin, the T-peel adhesive strength and the lap-shear adhesive strength increased. From the chemical composition analysis in the interfacial destruction part of the surface of copper plate after the lap-shear adhesive strength test by FTIR measurement, these results were considered as follows: the amide bond existing in the modified DAP resin was located in the surface of the copper plate, as a result, copper surface and the amide bond that is polar group formed interfacial interaction. To summarize the above results, improvement of adhesive properties of the DAP resin modified with APA1-3 is considered to be due to increased flexibility and increased interfacial interaction to metal surface by the amide bond.

The thermal decomposition temperature of the modified DAP resin was little decreased with an increasing concentration of APA1-3. But the glass-transition temperature slightly decreased with an increasing concentration of APA1-3, because of the decrease in the crosslinking density.

From SEM observation, it was found that the DAP resin modified with APA1, 2 formed a microphase-separated structure consisting of small dimeric acid polyamide particles dispersed in the DAP resin matrix.

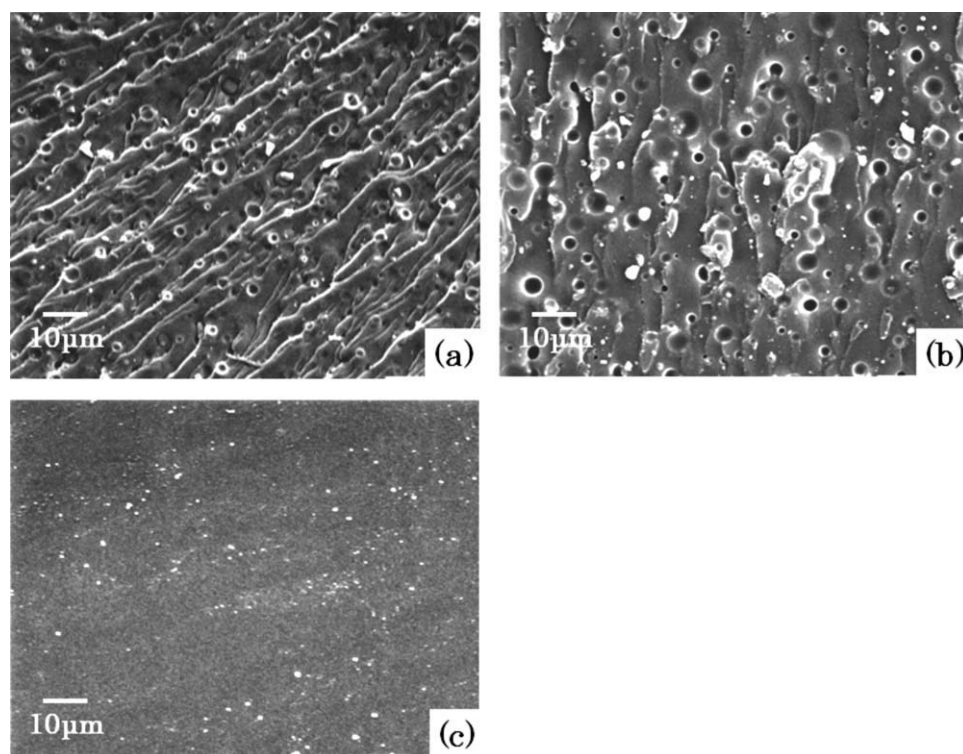


Figure 10 SEMs of surface of DAP resin modified with 10 wt % of APA: (a) APA1, (b) APA2, and (c) APA3.

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