

One-Component Epoxy Resin with Imine as Water-Initiated Latent Hardener: Improvement of the Mechanical and Adhesive Properties by the Addition of Methacrylate Copolymer

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Received 15 June 2004; accepted 17 November 2004

DOI 10.1002/app.21651

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of addition of methacrylate polymer into a one-component epoxy resin, containing Epikote 828 and diimine as a water-initiated hardener, was examined. Although the cured epoxy resin in the presence of methyl methacrylate–butyl acrylate (MMA–BA) copolymer was very brittle, the resin containing MMA–BA–[γ -(methacryloxy)propyl]trimethoxysilane (TMSMA) copolymer showed good mechanical and adhesive properties. The ad-

hesive strength of the cured epoxy resin containing MMA–BA–TMSMA copolymer was much higher than that without its polymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1943–1949, 2005

Keywords: imines; one-component epoxy resin; initiators; adhesives; mechanical properties

INTRODUCTION

Two-component epoxy resin, which can be cured by mixing reactive resin with hardeners (initiators), shows good mechanical strength and chemical resistance, and therefore it is widely used in coatings, paints, and adhesives.¹ However, several issues still remain with respect to practical usage of epoxy resins. First, is the occurrence of incomplete curing mainly as a result of insufficient mixing of curable and catalytic pastes. It is desirable to develop one-component systems using “latent initiators,” which show no activity under normal conditions but do by external stimuli such as heating and photoirradiation. Imines are useful as water-stimulated latent initiators for epoxy resin. Imines are hydrolyzed by atmospheric water to release the corresponding amines as the active species. We have recently reported that diethyl ketone–based imines show a faster hydrolysis rate than that of industrially used methyl ethyl ketone– and methyl isobutyl ketone–based imines, and one-component epoxy resin with the diethyl ketone–based imines shows good curing properties.^{2–4}

Another remaining issue is the brittleness of epoxy resins, although this difficulty can be overcome by use of amines and/or epoxy resin with soft segments such as flexible aliphatic and polyoxyalkylene groups. We previously elucidated the curing of one-component epoxy resin containing a bifunctional five-membered cyclic dithiocarbonate (DTC).⁵ DTC reacts with an amine to give the corresponding thiourethane compound with a thiol group.⁶ DTC-containing epoxy resin is tough compared with common epoxy resin because, presumably, the thiourethane moieties effectively provide flexibility for the amine–epoxy networked polymer. Another method for improvement of brittleness of epoxy resins is the addition of plasticizers or soft polymers such as rubber.^{7,8} A wide variety of acrylate and methacrylate polymers are obtainable, some of which with soft segments are expected to be used as additives to epoxy resin for the purpose mentioned above. This article describes the effect of addition of methacrylate polymers to a one-component epoxy resin on the mechanical and adhesive properties.

EXPERIMENTAL

Measurements

¹H- and ¹³C-NMR spectra were recorded on a JNM-LA-270 apparatus (JEOL, Tokyo, Japan) at 23°C, using

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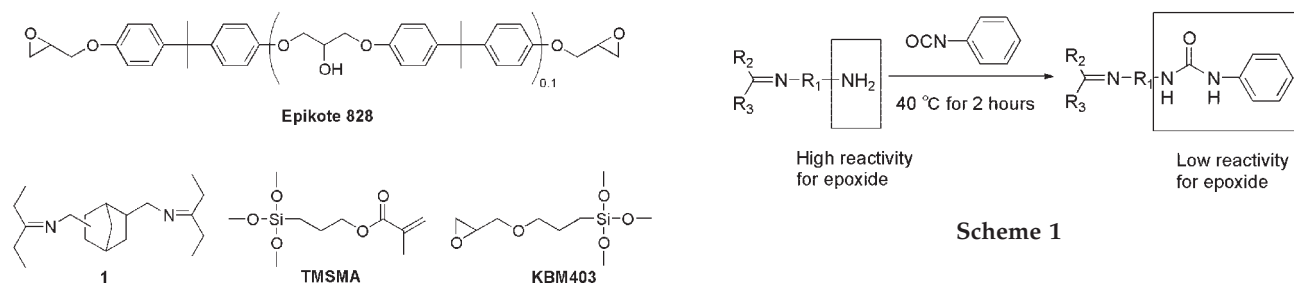


Figure 1 Structures of Epikote 828, imine **1**, TMSMA, and KBM403.

tetramethylsilane as an internal standard in CDCl_3 . IR spectra were recorded on a Perkin–Elmer Spectrum One (Perkin–Elmer Cetus Instruments, Norwalk, CT). Mass spectra were recorded using a GCMS-QP5050A instrument (Shimadzu, Kyoto, Japan). Number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography on a DP-8020 pump system (Tosoh Corp., Tokyo, Japan), equipped with a TDA model 300 detector (RI; Viscotek, Houston, TX) and consecutive polystyrene-gel columns (Tosoh TSK gels GMHXL, G4000XL, G3000XL, and G2500XL), using polystyrene samples as standards. Curing rates were measured with an RCI drying time tester (Yasuda Seiki, Japan). Adhesive and tensile strengths were measured with a Shimadzu Autograph AG-50kNG.

Materials

Diethyl ketone and phenyl isocyanate were obtained from Tokyo Kasei Kogyo Co. (Japan). 2,5-Bis(aminomethyl)bicyclo[2.2.1]heptane was obtained from Mitsui Chemical Co. (Chiba, Japan). [γ -(Methacryloxy)propyl]trimethoxysilane (TMSMA) and γ -gly-

cidoxypropyltrimethoxysilane (KBM403) were obtained from Shin-Etsu Chemical Co. (Tokyo, Japan). Bisphenol-A-type epoxy oligomer (Epikote 828) was obtained from Japan Epoxy Resin Co. (Tokyo). RY200S, a filler, was obtained from Nihon Keizai Aerogel Co. (Japan). The structures of the compounds are depicted in Figure 1. These reagents were used as received. Methyl methacrylate (MMA), butyl methacrylate (BMA), glycidyl methacrylate (GMA), ethyl acrylate (EA), and butyl acrylate (BA) were obtained from Tokyo Kasei Kogyo Co. and used after distillation. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Tokyo Kasei Kogyo Co. and used as received.

Synthesis of *N,N'*-di(1-ethylpropylidene)-bicyclo[2.2.1]heptanebis(methylamine) (**1**)

A solution of 2,5-bis(aminomethyl)bicyclo[2.2.1]heptane (154 g, 1 mol) and diethyl ketone (344 g, 4 mol) in hexane (500 mL) was heated with refluxing for 24 h. Water was removed during the reaction with a Dean–Stark trap. After that, hexane and residual diethyl ketone were distilled off from the mixture under reduced pressure to obtain the product. Phenyl isocyanate (3.6 g, 0.03 mol) was added to the product, and the resulting mixture was heated at 40°C for 2 h to block the residual amino groups

TABLE I
Copolymerization of Methacrylate Monomers^a

Run	Initial monomer concentration (<i>M</i>)				Yield ^b (%)	M_w^c (M_w/M_n^c)	Appearance ^d
	MMA	BA	GMA	TMSMA			
1	1.00	—	—	—	62.5	— ^e	Hazy
2	—	1.00	—	—	63.5	— ^e	Hazy
3	0.50	0.50	—	—	60.5	17,300 (1.35)	Hazy
4	0.40	0.50	0.10	—	61.9	— ^e	Hazy
5	0.45	0.50	—	0.05	60.2	— ^f	Hazy
6	0.40	0.50	—	0.10	58.8	— ^f	Transparent

^a Polymerized with AIBN (0.12M) in toluene at 60°C for 24 h.

^b Hexane-insoluble part.

^c Determined by GPC eluted with THF, polystyrene calibration.

^d A mixture of epoxy resin (Epikote 828: 100 g), imine **1** (40 g), and methacrylate copolymer (100 g). Curing condition: 23°C, humidity 50%RH for 7 days.

^e Not measured.

^f Insoluble in THF.

(Scheme 1). Yield: 94.5%. IR (KBr): 1662 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 1.03–1.14 (m, 16H), 1.42–1.55 (m, 2H), 1.76–1.89 (m, 2H), 2.19–2.30 (m, 10H), 3.06–3.37 (m, 4H). $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 21.35, 21.86, 34.19, 39.77, 43.19, 43.79, 46.56, 49.96, 50.47, 53.57, 54.39, 63.22, 172.84. Mass spectrum: m/e 290 (M^+).

Synthesis of methacrylate copolymers

Methacrylate monomers (total 20 mmol) and AIBN (0.39 g, 2.4 mmol) were dissolved in toluene (20 mL), and the resulting solution was heated at 60°C for 24 h under N_2 atmosphere. Then, the reaction mixture was poured into a large amount of hexane to precipitate a copolymer. It was rinsed with hexane and dried under vacuum for 24 h. The M_w and M_w/M_n of the polymers are summarized in Table I. The copolymerization ratio was determined by the integration ratio of the $^1\text{H-NMR}$ spectrum, as shown in Figure 2.

Formulation of one-component epoxy resin with acrylate polymer

Methacrylate monomers (total 1 mol) were polymerized with 12 mol % of AIBN in toluene (1 L) at 60°C for 24 h under N_2 atmosphere. Epikote 828 (100 g) and imine **1** (40 g) were added to this reaction mixture and the resulting solution was stirred for 30 min at room temperature. Then, unreacted methacrylate monomers and toluene were distilled off by evaporation (Fig. 3). If necessary, silica (RY200S, 10 g) and dryer (KBM403, 40 g) were added to the resin and further kneaded for 1 h under N_2 atmosphere.

Observation of SEM image

A plate of cured resin was folded and broken into two pieces. The destructive phase was observed by an

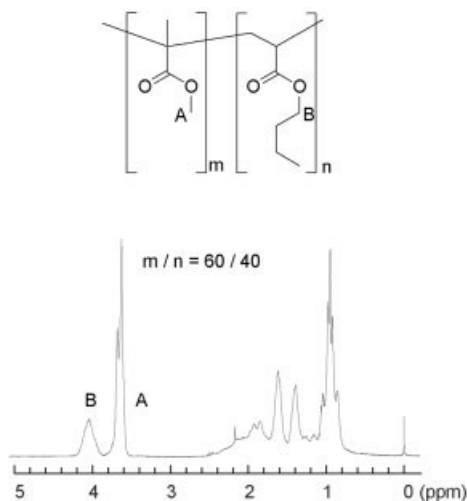


Figure 2 $^1\text{H-NMR}$ spectrum of a methacrylate copolymer measured in CDCl_3 at 27°C .

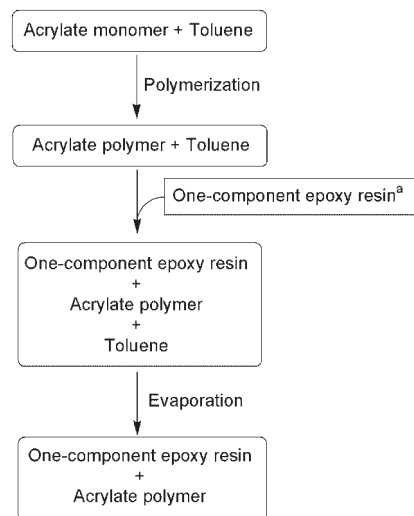


Figure 3 Flowchart of formulation of one-component epoxy resin with methacrylate copolymer.

S-3000N scanning electron microscope (Hitachi Science Systems, Osaka, Japan) with the accelerating voltage at 15 kV, under a pressure of 30 MPa, at 25°C .

Estimation of mechanical properties

Mechanical strength and elongation of a cured film were evaluated by tensile testing. The test pieces were made as follows. A one-component epoxy resin was applied onto a silicon film (1.0 mm thickness) and cured at 40°C and 90%RH (relative humidity) for 3 days. The resin was removed from the film by hand, and the reverse side was cured for 4 days under the same condition. After that, glass fiber-reinforced plastics were pasted onto the test pieces with two-component epoxy resin (Fig. 4).

Evaluation of curing properties

The curing rate was evaluated by a Yasuda Seiki RCI drying time tester (Fig. 5). The one-component epoxy resin was applied onto a glass plate (0.3 mm thickness) and stored at 23°C and 50%RH for 1 day, after which the curing time was measured.

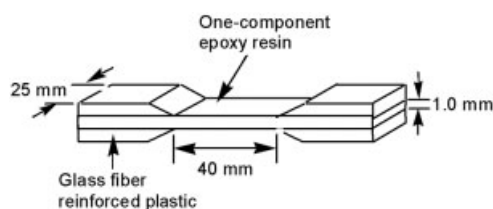


Figure 4 Test piece for a tensile strength test.

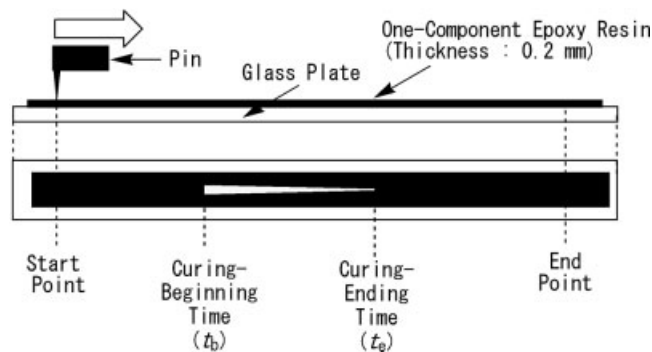


Figure 5 Schematic diagram of measurement of curing time.

Measurement of adhesive strength

Plastics or metals and wood were used as the adherent with the applied area of $25 \times 25 \text{ mm}^2$ (Fig. 6). The epoxy resin was applied on the adherent, after being washed with ethanol, and then dried. The applied adherents were stored at 23°C and 50%RH for 7 days, and then the adhesive strength was measured by lap-shear testing (test speed 5.0 mm/min).

RESULTS AND DISCUSSION

Curing of one-component epoxy resin in the presence of methacrylate copolymer

MMA, BA, GMA, and TMSMA were copolymerized with AIBN as an initiator in toluene (Table I). Considering the chain-transfer nature, toluene was used as a solvent to obtain the corresponding copolymers with relatively low molecular weights in the current study. High molecular weight polymers are inappropriate because it is difficult to prepare a homogeneous mixture of a highly viscous polymer solution and epoxy resin. After the solution of copoly(methacrylate) was added to a mixture of Epikote 828 as epoxy resin and imine 1 as a latent initiator, toluene was evaporated to obtain a modified one-component epoxy resin. The resultant mixture was transparent, although it became hazy and more brittle than that without acrylate polymer when it was cured by water in ambient air. Figure 7 shows the SEM image of a destructive phase of the cured resin. It was confirmed that the reason for opaqueness and brittleness of the resin modified with

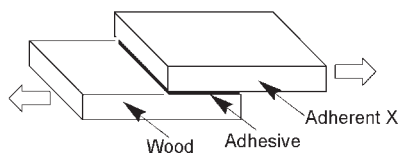


Figure 6 Schematic diagram of lap-shear test. Adhesive area: $25 \times 25 \text{ mm}^2$.

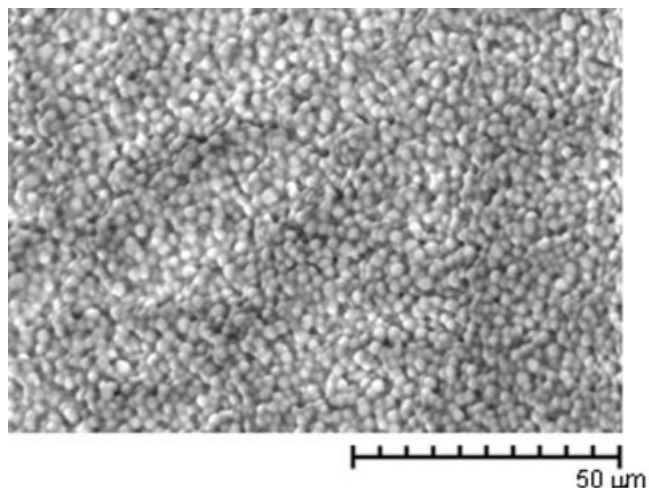


Figure 7 SEM images of destructive side of one-component epoxy resin with MMA-BA copolymer. A mixture of epoxy resin (Epikote 828: 100 g), MMA-BA copolymer (run 3 in Table I, 50 g), and imine 1 (40 g) was cured at 23°C and 50%RH for 7 days.

copoly(methacrylate) was the presence of spherical particles (diameter $2.5 \mu\text{m}$), probably formed by phase separation of epoxy resin and copoly(methacrylate). Commonly, cured epoxy resin is homogeneous at the nanometric scale,⁹ but there are some examples of heterogeneous amine-epoxy networks, such as epoxy resin cured with a diamine having poly(propylene oxide) chains, wherein the resin and amine are not sufficiently miscible to cause phase separation during the curing process.¹⁰ Another example is curing of epoxy resin consisting of two kinds of epoxy monomers with dicyanodiamide.¹¹ In the present study,

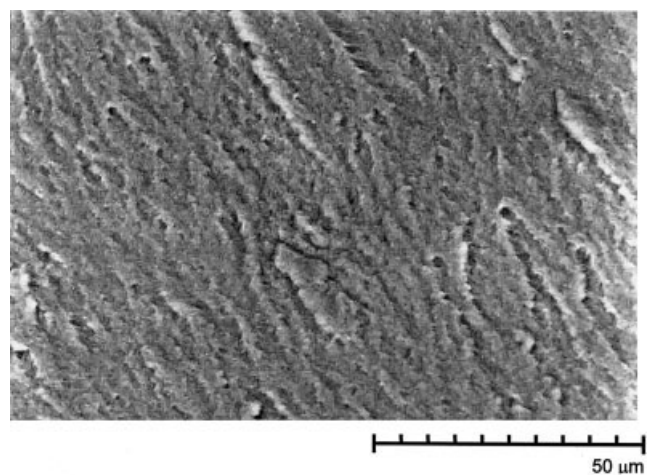


Figure 8 SEM image of one-component epoxy resin with MMA-BA-TMSMA copolymer. A mixture of epoxy resin (Epikote 828: 100 g), MMA-BA-TMSMA copolymer (run 6 in Table I, 50 g), and imine 1 (50 g) was cured at 23°C and 50%RH for 7 days.

TABLE II
Mechanical Properties of One-Component Epoxy Resin Modified with Methacrylate Copolymers^a

Run	Monomer unit ratio in the copolymer					Tensile strength (MPa)	Elongation (mm)
	MMA	BMA	EA	BA	TMSMA		
6	0.40	—	—	0.50	0.10	28.5	3.7
7	0.40	—	0.50	—	0.10	23.7	4.0
8	0.15	—	—	0.75	0.10	13.6	4.2
9	0.65	—	—	0.25	0.10	27.8	1.3
10	—	0.90	—	—	0.10	24.6	4.2
11	—	0.65	—	0.25	0.10	26.9	0.6
12	0.40	—	—	0.40	0.20	34.8	2.7
13	0.20	—	—	0.40	0.40	38.0	1.9
14	—	—	—	—	—	41.9	1.8

^a The mechanical properties were estimated by a Shimadzu Autograph AG-50kNG. Test speed: 5 mm/min. The resin was a mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), methacrylate copolymer (100 g), and 1 (50 g), and cured at 40°C and 90%RH for 7 days. The Methacrylate copolymers were obtained by polymerization with AIBN (12 mol %) in toluene (total initial monomer concentration: 1M) at 60°C for 24 h.

only Epikote 828 was used as epoxy resin, and the resin and imine **1** or amine (norbornandiamine, NBDA) released from the imine are completely miscible. It is therefore assumed that copoly(methacrylate)s are responsible for the phase separation as observed in Figure 7.

MMA-BA copolymer was not miscible with one-component epoxy resin, as described above, so we examined another polymer instead. The copolymer of TMSMA, MMA, and BA was synthesized, and the mixture of its copolymer and the epoxy resin was cured. When the TMSMA feed ratio was 10 mol %, the cured one-component epoxy resin was transparent (run 6 in Table I). The destructive phase of the test piece made from the resin exhibited no phase separation, which was confirmed by the SEM image, as shown in Figure 8. The resin containing GMA as a crosslinkable unit was hazy (run 4 in Table I). The glycidyl group of the GMA unit possibly reacts with an amine released from the imine, resulting in increased transparency; however, it was not operative in this case, presumably because the reaction rate of

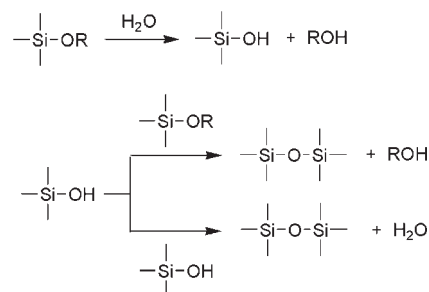
GMA unit with an amine is slower than the curing rate of epoxy resin.

The effect of the methacrylate monomer feed ratio on the mechanical strength of the cured resin is summarized in Table II. When the feed ratios of MMA and TMSMA were increased, the cured one-component epoxy resin became harder. The resin modified with MMA-BA-TMSMA copolymer of run 6 (the same sample as that in run 6 in Table I) achieved moderate flexibility. The elongation of the modified epoxy resin became twice as large as that of the nonmodified one, keeping the tensile strength when a half amount of MMA-BA-TMSMA copolymer was used to that of epoxy resin (Table III). It was confirmed that the addition of MMA-BA-TMSMA improved the toughness of the epoxy resin. The reason for this result may be explained as follows: the trimethoxysilyl group of TMSMA undergoes hydrolysis to transform into a hydroxysilyl group releasing methanol. Hydroxysilyl groups react with each other or react with methoxysilyl groups to form a siloxane linkage, resulting in crosslinking of the methacrylate copolymer (Scheme 2).¹² Consequently, an interpenetrating polymer network (IPN) may be formed in conjunction with

TABLE III
Mechanical Properties of One-Component Epoxy Resin Modified with MMA-BA-TMSMA Copolymer^a

Epoxy resin (g)	MMA-BA-TMSMA copolymer (g)	Tensile strength (MPa)	Elongation (mm)
100	100	28.5	3.7
100	50	41.7	3.6
100	—	41.9	1.8

^a The mechanical properties were estimated by a Shimadzu Autograph AG-50kNG. Test speed: 5 mm/min. The resin was a mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), MMA-BA-TMSMA copolymer (run 6 in Table I, 100 g), and **1** (50 g), and cured at 40°C and 90%RH for 7 days.



Scheme 2

TABLE IV
Curing Rate of One-Component Epoxy Resin^a

Additive	Curing-ending time (h)
MMA-BA-TMSMA copolymer ^b	4.5
MMA-BA copolymer ^c	20.0
None ^d	18.0

^a Cured at 5°C and 50%RH.

^b A mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g) dryer (KBM403: 40 g), MMA-BA-TMSMA copolymer (run 6 in Table I, 50 g), and 1 (50 g).

^c A mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), MMA-BA copolymer (run 3 in Table I, 50 g), and 1 (50 g).

^d A mixture of epoxy resin (Epikote 828: 100 g), imine 1 (50 g), silica (RY200S: 10 g), and dryer (KBM403: 40 g).

crosslinking of epoxy resin, which is effective in preventing phase separation of the poly(methacrylate) and epoxide. In fact, when MMA-BA-TMSMA copolymer was isolated by precipitation with hexane and dissolved in THF containing water (2%), solvent-insoluble products precipitated after 10 min. On the other hand, no precipitate formed when its copolymer was dissolved in dry THF. It was confirmed that MMA-BA-TMSMA copolymer crosslinked by hydrolysis of the methoxysilyl group of TMSMA.

Table IV summarizes the curing rates of the epoxy resin in the presence of MMA-BA-TMSMA and MMA-BA copolymers, together with data of the epoxy resin without modification. The epoxy resin containing MMA-BA-TMSMA copolymer cured much faster than that without it. It is assumed that the crosslinking reaction by the silyl group is faster than curing of epoxide. The crosslinking by the silyl group may effectively reduce the mobility of the

resin to prevent the phase separation of the epoxy resin and methacrylate copolymer (Fig. 9).

Adhesive property of cured one-component epoxy resin containing MMA-BA-TMSMA copolymer

The cured one-component epoxy resin containing MMA-BA-TMSMA copolymer was more tenacious with respect to its adhesive property than that without it. It can be expected that the adhesive strength of the modified resin for plastics and metals is also improved. Table IV summarizes the results of lap-shear testing of the epoxy resin modified with methacrylate polymer as the adhesive for wood with several plastics as the adherents. The adhesive strength was improved [except in poly(ethylene terephthalate)] by modification with methacrylate polymer, as expected. It is noteworthy that the breakage mode was dramatically improved by modification; that is, not the adhesive but the adherents were broken when modified epoxy resin was used as the adhesive in most cases. The adhesiveness of the epoxy resin modified with MMA-BA-TMSMA copolymer was also excellent when it was used with metals as the adherents, as summarized in Table V and VI. The hardness of adhesives primarily depends on adhesive strength. When the adhesive is hard, stress is concentrated at the adhesive-adherent interface, resulting in destruction at the interface. When the adhesive is moderately soft, stress is distributed throughout the entire adhesive and the adhesive strength increases. Too soft an adhesive is inappropriate because it causes a decrease of cohesion force, resulting in a decrease of adhesive strength. In the current study, a precise balance between the hardness attributed to the IPN structure and the softness attributed to methacrylate co-

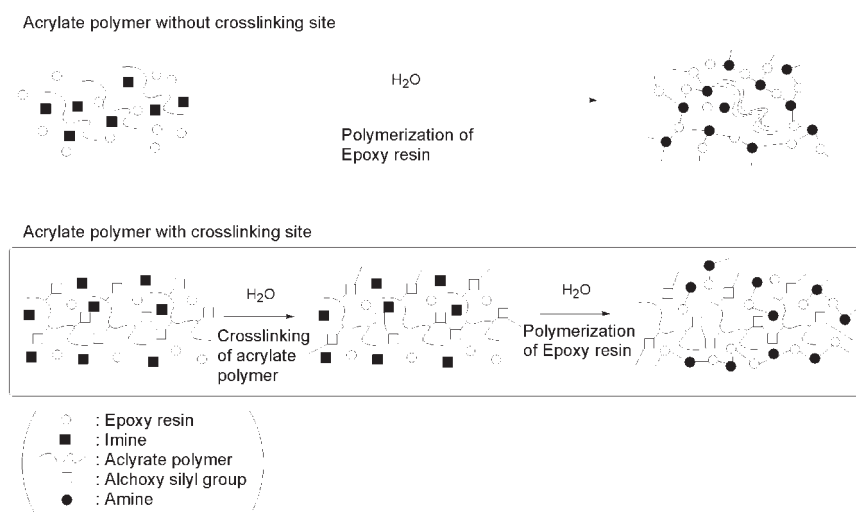


Figure 9 Polymerization of epoxy resin and crosslinking of methacrylate copolymer.

TABLE V
Adhesive Strength of One-Component Epoxy Resin Modified with MMA-BA-TMSMA Copolymer^a

Parameter	Additive	Adherent X (plastics) ^b					
		PS	PET	PVC	ABS	FRP	PC
Adhesive strength, MPa	MMA-BA-TMSMA copolymer	2.85 (MX)	3.35 (MX)	4.16 (MX)	3.98 (MX/C)	5.84 (MX/C)	1.77 (A/C)
Mode ^c	None ^d	2.52 (C/A)	3.54 (MX)	3.29 (MX/C)	2.68 (MX/C)	3.75 (C)	1.34 (A)

^a Adhesive strength was estimated by a Shimadzu Autograph AG-50kNG. Curing condition: 23°C and 50%RH for 7 days. Test speed: 5 mm/min. The method is shown in Figure 6. The resin was a mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), MMA-BA-TMSMA copolymer (run 6 in Table I, 50 g), and **1** (50 g).

^b PS, polystyrene; PET, poly(ethylene terephthalate); PVC, poly(vinyl chloride); ABS, acrylonitrile-butadiene-styrene copolymer; FRP, fiber-reinforced plastic; PC, polycarbonate.

^c MX, breakage of adherent X; C, breakage of cohesive; A, breakage of adhesive.

^d A mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), and **1** (50 g).

TABLE VI
Adhesive Strength of One-Component Epoxy Resin Modified with MMA-BA-TMSMA Copolymer^a

Parameter	Additive	Adherent X (metal)		
		Steel	Al ^b	Stainless
Adhesive strength, MPa	MMA-BA-TMSMA copolymer ^d	6.82 (MW/C)	4.69 (MW/C)	4.29 (MW/C)
Mode ^c	None ^e	3.73 (C)	3.05 (MW/C)	2.53 (MW/C)

^a Adhesive strength was estimated by a Shimadzu Autograph AG-50kNG. Curing condition: 23°C and 50%RH for 7 days and 40°C and 90%RH for 7 days. Test speed: 5 mm/min.

^b Al, aluminum.

^c MW, breakage of wood; C, breakage of cohesive.

^d A mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), MMA-BA-TMSMA copolymer (run 6 in Table I, 50 g), and **1** (50 g).

^e A mixture of epoxy resin (Epikote 828: 100 g), silica (RY200S: 10 g), dryer (KBM403: 40 g), and **1** (50 g).

polymer should be achieved by the modification of epoxy resin with MMA-BA-TMSMA copolymer.

CONCLUSIONS

In this article, we demonstrated that the addition of methacrylate copolymer to a one-component epoxy resin satisfactorily enhanced the adhesive properties. The epoxy resin modified with MMA-BA-TMSMA copolymer exhibited high adhesive strength for woods, plastics, and metals. By SEM analysis of the destructive phase and the reaction of MMA-BA-TMSMA copolymer with water, it was confirmed that the trimethylsiloxy group of TMSMA unit underwent a coupling reaction, resulting in crosslinking. It is likely that an IPN structure of polyepoxide and methacrylate copolymer was effectively formed to improve the adhesiveness.

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