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A low-temperature fast curing latent catalyst microencapsulated in a porous resin structure

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ABSTRACT

Low-temperature, fast curing latent catalysts for epoxides were prepared by microencapsulation of aluminum complexes through interfacial and radical polymerization. The resulting resin microcapsules were thermally responsive. Moreover, because the inside of the capsule had a porous structure, a highly active aluminum complex could be forced into the capsule by solvent penetration. The differential scanning calorimetric curve of the encapsulated complex showed an exothermic peak at 100 °C or less. In addition, after a mixture of bisphenol A epoxy resin, the curing catalyst, and triphenyl silanol was stored for 5000 h at 30 °C, the viscosity was only 1.6 times greater than the viscosity just after blending.

1. Introduction

Epoxy resin adhesive is easy to handle and has excellent electrical characteristics, and is therefore widely used for electronic part mountings such as multi-layer wiring boards, semiconductor packages, mobile computers, and portable information terminals. In recent years, the reduction in weight and the miniaturization of electronic parts means that the packing density is higher [1]. Adhesives that cure fast at low temperatures are required because excessive heat cannot be applied to the adherend and peripheral components. Furthermore, flame retardant adhesives with lower concentrations of ionic impurities are also desirable.

In 1981, Hayase and coworkers reported a catalyst for initiating epoxy polymerization that was suitable for electronics [2,3]. This catalytic initiator is composed of an aluminum complex and an active silicon compound that forms a Brønsted acid, which induces fast curing of epoxy resin at low temperatures [2–4]. Aluminum complexes are the most suitable for this system because their epoxide polymerization rate is faster than the rate for other organometallic complexes [5]. Moreover, a composite catalyst containing aluminum complexes is appropriate for electronics, which require adhesives to be electrically insulating. The aluminum complex does not function as an ionic impurity in cured resin, unlike conventional Lewis acid cationic initiators [6]. However, because the acid species generated from the aluminum complexes are very active, it is necessary to increase the shelf life of the epoxy resin using a latent initiator.

Murai et al. used phenolic derivatives, which were not active at ambient temperature, in aluminum complex latent initiators in a composite catalyst system. The phenolic moieties generated by the thermal decomposition of the derivatives at 150 °C showed sufficient catalytic activity to initialize epoxy polymerization [7]. Aluminum complexes containing long-chain alkyl groups have also been used, although the solubility in the epoxide was reduced [8]. However, these methods have the drawback of slow curing times. A further latent method is physically separating the catalytic aluminum complex and silicon compound. Microencapsulation of one of the components using interfacial polymerization is a suitable separation method [9–11].

Microcapsules are small spherical containers that are several hundred of nanometers to several hundred micrometers in diameter. They contain solid or liquid materials in an organic or inorganic thin film. Microencapsulation enables sustained release control, powderization of volatile and liquid materials, and the isolation of highly active materials, and has been used in various fields [12–14].

In this work, we have successfully prepared microcapsules containing an aluminum complex by interfacial polymerization of isocyanate. The polymer capsule was a thermally responsive poly(urea-urethane) resin in which the intramolecular hydrogen bonds break when the resin is heated above the glass transition temperature. Breaking the hydrogen bonds reduces the density and increases the permeability of the polymer capsule wall. This allows the epoxy monomer to enter the capsule and come into contact with the catalyst [15]. No aluminum complex derivatives were required for our approach; therefore, the original catalytic activity of the aluminum complex-silicon compound system was retained. We also evaluated the microencapsulated materials as latent epoxy curing catalysts with a view to shelf life extension.

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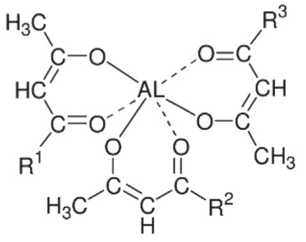
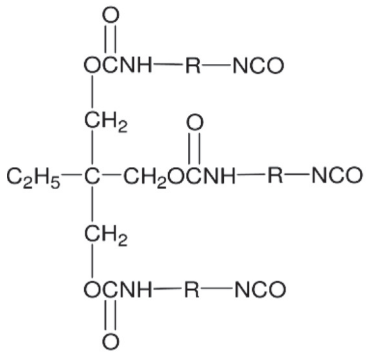
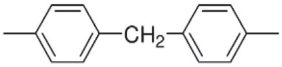
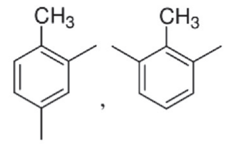
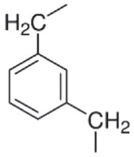
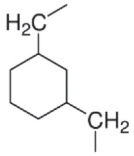
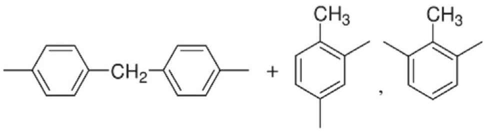
2. Experimental

2.1. Materials

An aqueous solution of the surfactant, sodium *n*-dodecylbenzenesulfonate, SDS (Newrex R, NOF Corp., Japan); dispersion stabilizer, polyvinyl alcohol, PVA (PVA-205, Kuraray Co. Ltd., Japan); the silane coupling agent, 3-glycidoxypropyltrimethoxysilane, 3GPTMS (Silquest A-187 silane, Momentive Performance Materials Japan LLC., USA); the cycloaliphatic epoxy compound, 3′,4′-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, EMEC (CEL2021P, Daicel Co., Japan); 1,6-hexanediol diacrylate, HDDA (LIGHT ACRYLATE 1.6HX-A, Kyoeisha Chemical Co. Ltd., Japan); trimethylolpropane triacrylate, TMPA (LIGHT ACRYLATE TMP-A, Kyoeisha Chemical Co. Ltd., Japan); and glycidyl ether epoxy resin, bisphenol A epoxy resin, BER (EP828, Mitsubishi Chemical Co., Japan) were commercially available and were used without further purification. Divinylbenzene (Merck Co. Ltd., Germany) was washed with 1 N NaOH

Table 1
Chemical structures of aluminum complexes and DI/TMPs.

	$R^1, R^2 = -OC_2H_5$, $R^3 = -CH_3$	ALC-1
	$R^1, R^2, R^3 = -OC_2H_5$	ALC-2
	R= 	MDI/TMP
	R= 	TDI/TMP
	R= 	XDI/TMP
	R= 	H6XDI/TMP
	R= 	(MDI+TDI)/TMP

Trifunctional isocyanate compounds were obtained by reacting 1 mol of trimethylolpropane with 3 mol of diisocyanate compound.

In the formula of trifunctional isocyanate, the substituent R is the moiety of the diisocyanate molecule excluding the isocyanate group.

MDI: methylenediphenyl-4,4'-diisocyanate.

TDI: toluene-2,4-diisocyanate, toluene-2,6-diisocyanate.

XDI: *m*-xylylene diisocyanate.

H6XDI: hexahydro-*m*-xylylene diisocyanate.

(MDI+TDI)/TMP was obtained by reacting 1 mol of trimethylolpropane with 1.5 mol of TDI and MDI.

and deionized water to remove polymerization inhibitors before use. Radical polymerization initiator dilauroyl peroxide (PEROYL L, NOF Co., Japan) and triphenylsilanol, TPS (Tokyo Chemical Industry Co. Ltd., Japan) were purified by recrystallization. Table 1 summarizes the chemical structures of the aluminum complexes (ALC) and trifunctional isocyanates used in this study. Bis(ethylacetoacetato)(2,4-pentanedionato)aluminum, ALC-1 (Kawaken Fine Chemicals Co. Ltd., Japan); and tris(ethylacetoacetato)aluminum, ALC-2 (Kawaken Fine Chemicals Co. Ltd., Japan) were commercially available and used after recrystallization or distillation. The reaction products of diisocyanates and trimethylolpropane, DI/TMPs (MDI/TMP, TDI/TMP, XDI/TMP, H6XDI/TMP and (MDI+TDI)/TMP), were commercially available (Mitsui Chemicals Co. Ltd., Japan) and used after distillation. Diisocyanate reactants were methylenediphenyl-4,4'-diisocyanate (MDI), toluene diisocyanate (TDI), *m*-xylylene diisocyanate (XDI), hexahydro-*m*-xylylene diisocyanate (H6XDI), and the mixture of MDI and TDI (MDI+TDI), respectively (the structures are shown in Table 1). Ethyl acetate and cyclohexane were dried over CaH_2 and distilled before use. Distilled water was supplied from a water distillation system (RFS533PA, Toyo Seisakusho Kaisha, Ltd., Japan).

2.2. Preparation of thermo-responsive microcapsules by interfacial polymerization

A solution of DI/TMP (11 g) and ALC-1 (11 g) dissolved in ethyl acetate (39 g) was added to an aqueous solution (842 g) of 0.48 wt% PVA and 0.006 wt% SDS and then emulsified by using a homogenizer (Ultra-Turrax T-25, IKA, Germany) stirring at 11,000 rpm for 10 min in a glass cylindrical reactor. The interfacial polymerization was carried out at 60 °C for 12 h under a nitrogen atmosphere. After the reaction was complete, the solution was left to cool to room temperature and the microcapsules were collected by filtration and dried at room temperature. The microcapsule aggregates were broken up with a jet mill (AO-JET MILL, Seishin Enterprise Co. Ltd., Japan). The five types of thermo-responsive microcapsule (TRM) obtained using this procedure were named IP-TRM-1 to 5.

2.3. Preparation of thermo-responsive composite resin microcapsules by interfacial and radical polymerization

A solution of MDI/TMP (70 g), radical polymerizable monomer (divinylbenzene, 1,6-hexanediol diacrylate or trimethylolpropane triacrylate, 30 g), dilauroyl peroxide (0.3 g), and ALC-1 (100 g) in ethyl acetate (168 g) was added to an aqueous solution (842 g) of 0.48 wt% PVA and 0.006 wt% SDS and then emulsified by using the homogenizer stirring at 10,000 rpm for 5 min in a glass cylindrical reactor. The interfacial and radical polymerization was carried out at 80 °C for 6 h under a nitrogen atmosphere. After the reaction was complete, the microcapsules were collected by the procedure described in the previous section. The three types of TRMs obtained by this process were named RP-TRM-1 to 3.

2.4. Microcapsule penetration of highly active ALC

ALC was dissolved in ethyl acetate under the conditions listed in Table 2. The solution (300 g) and RP-TRM-1 (30 g) prepared by interfacial and radical polymerization were stirred at 200 rpm in a glass cylindrical reactor at 30 °C for 6 h under a nitrogen atmosphere. The suspension was filtered and washed with cyclohexane. The microcapsules were collected and dried at 60 °C for 4 h in a vacuum oven and the aggregates were broken up by jet milling. The two types of TRMs obtained from this penetration process using P-A and P-B (see Table 2), were named RP-TRM-1-A and B, respectively.

Table 2
Conditions for the solvent penetration of microcapsules with ALC.

Penetration process	P-A	P-B
Ingredient	Weight (g)	
ALC-1	113	38
ALC-2	0	75
Ethyl acetate	187	187
RP-TRM-1	30	30

ALC-1: bis(ethylacetoacetato)(2,4-pentanedionato)aluminum.
ALC-2: tris(ethylacetoacetato)aluminum.
RP-TRM: radical polymerization thermo-responsive microcapsules.

Table 3
Conditions for evaluating the curing characteristics of latent microencapsulated catalysts.

No.	C-1	C-2
Ingredient	Weight (g)	
EMEC	90	–
BER	–	80
3GPTMS	8	–
TPS	–	8
TRM	2	4

EMEC: 3′,4′-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate.
BER: bisphenol A epoxy resin.
3GPTMS: 3-glycidoxypropyltrimethoxysilane.
TPS: triphenylsilanol.
TRM: thermo-responsive microcapsules.

2.5. Morphological analysis

The morphologies of the microcapsules containing ALC were observed using a scanning electron microscope (SEM; JSM-6510A, Nippon Electronics Co. Ltd., Japan). The cross-sectional structure of the microcapsules was observed using a field emission scanning electron microscope (FE-SEM; FE-SEM S-4700, Hitachi High-Technologies Co., Japan) by cutting the microcapsules with a microtome knife and an Al distribution image was obtained by energy dispersive X-ray analysis (EDS; EMAX-7000, Horiba, Ltd., Japan).

2.6. Curing characteristics of microencapsulated latent curing catalysts

The curing characteristics of the TRMs were evaluated. Using conditions C-1 (Table 3), TRM, 3GPTMS, and EMEC were mixed using a planetary centrifugal mixer (AR-250, Thinky Corp., Japan). Using conditions C-2 (Table 3), TPS was dissolved in BER and heated at 80 °C for 2 h before use, and then mixed with TRM. This thermosetting composite was subjected to thermal analysis in a nitrogen atmosphere using a differential scanning calorimeter (DSC; EXSTAR DSC6200, Seiko Instruments Inc., Japan).

2.7. Determination of the amount of ALC in TRMs

The weight ratio of the aluminum complex in TRM was determined by thermogravimetric differential thermal analysis (TG/DTA; EXSTAR TG/DTA6200, Seiko Instruments Inc.) in a nitrogen atmosphere. The temperature range was 30–350 °C and the heating rate was 10 °C/min. The weight ratio of the aluminum complex was obtained from the TG data for TRMs with and without ALC. The TRM ALC content was also determined by liquid chromatography–mass spectrometry (LC/MS; ACQUITY UPLC SQD, Waters Co., USA). The measurement was performed by adjusting the amount of TRMs to 0.05 wt% in acetonitrile.

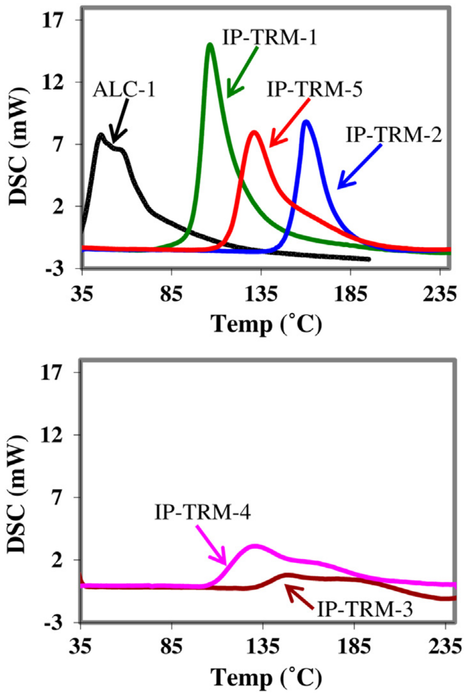


Fig. 1. DSC curves for cycloaliphatic epoxy compound curing with several microcapsule latent catalysts.

2.8. *Particle size distribution of TRM*

The particle size distribution of the TRM was determined using a laser diffraction scattering analyzer (MT3300EX2, Nikkiso Co. Ltd., Japan).

2.9. *Shelf life of TRM in the epoxy resin*

The shelf life of the TRM catalyst in the epoxy resin was evaluated. The TRM (5 g) and a mixture of TPS (15 g) and BER (80 g) were mixed. The time course of the liquid viscosity at 30 °C was measured with a viscometer (BH2, Toki Sangyo Co. Ltd., Japan).

3. Results and discussion

3.1. *Microencapsulation of the aluminum complex by interfacial polymerization*

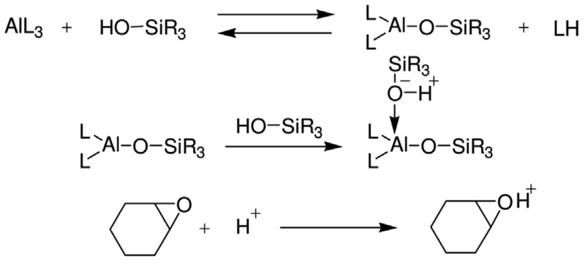
The aluminum complex was microencapsulated by interfacial polymerization using a variety of DI/TMPs (Table 1). The curing characteristics of this capsule aluminum complex evaluated by DSC are shown in Fig. 1 and Table 4. An EMEC containing a cyclohexene oxide ring was used (C-1 in Table 3). This cyclohexene oxide is an α,β-disubstituted epoxide [16], and it is excellent for cationic polymerization compared with the representative terminal epoxide, glycidyl ether. Therefore, when the unencapsulated aluminum complex is added directly to the epoxy compound with a silane coupling agent, heat is immediately generated by the exothermic epoxy curing. Fig. 1 shows that the exothermic reaction begins as soon as the aluminum complex is added. The proposed mechanism of the initiation of cationic polymerization by composite catalysts consisting of silanols and aluminum complexes is shown in Scheme 1 [17].

The active species is a Brønsted acid produced by silanols and aluminum complexes. When a silane coupling agent is used, the silanols, which are generated by hydrolysis, react. Because the Brønsted acid generated from silanols and aluminum complexes is very active, it is difficult to handle the mixture when the catalyst is added directly to the epoxy compounds. However, when the aluminum complex is encapsulated by isocyanate interfacial polymerization, the activation temperature should be dependent on the glass transition temperature of the poly(urea-urethane) resin that forms the capsule wall [15]. Therefore, the isocyanate structure and the polymerization conditions are important. The results in Table 4 and Fig. 1 show that the exothermic onset temperature is dependent on the structure of the DI/TMP [18]. MDI/TMP and TDI/TMP showed good exothermic epoxy curing reactions, and MDI/TMP had the lowest onset temperature. (MDI+TDI)/TMP (IP-TRM-5 in Fig. 1) showed an intermediate exothermic peak temperature between TDI/TMP and MDI/TMP. However, the effect of factors such as the core agent and solvent must be considered, because these will affect the plasticity of capsule wall [19]. In addition, in this research, high boiling point solvents, such as alkyl naphthalene and alkyl biphenyls, which are used for poly(urea-urethane) microcapsules [20,21], were not used to dissolve the isocyanate and aluminum complex because of the possible effect of residual solvent. Thus, ethyl acetate was used because of its low-boiling point and high polarity, and pores were formed in the capsules by solvent volatilization during the polymerization. Therefore, a porous polymer matrix that did not contain a solvent was formed instead of a core-shell structure containing a high-boiling point solvent. The cross-sectional FE-SEM images and schematic diagram of multicore-shell type microcapsule (IP-TRM-1) are shown in Fig. 2. Fig. 2B and C are magnified images of 2A. In this study, the structure of the prepared microcapsules is similar to that in Fig. 2. Moreover, the EDS Al map in Fig. 3 shows that the aluminum complex was dispersed in the capsule.

Table 4
Characterization of epoxy curing for microcapsule latent catalysts.

TRM	Isocyanate	Exothermic onset temperature (°C)	Exothermic peak temperature (°C)	Total heat value (J/g)
ALC-1	–	Simultaneously with a measurement start	46	–
IP-TRM-1	MDI/TMP	75	106	−508
IP-TRM-2	TDI/TMP	136	160	−256
IP-TRM-3	XDI/TMP	124	148	−100
IP-TRM-4	H6XDI/TMP	101	131	−211
IP-TRM-5	(MDI+TDI)/TMP	103	131	−374

Measurement temperature range was 30–300 °C and the heating rate was 5 °C/min. TRM: thermo-responsive microcapsules.



Scheme 1. Proposed mechanism of the initiation of cationic polymerization.

3.2. *Composite resin microcapsules formed by interfacial and radical polymerization*

As shown in the previous section, MDI/TMP resin is suitable for the microencapsulation of the aluminum complex. However, the

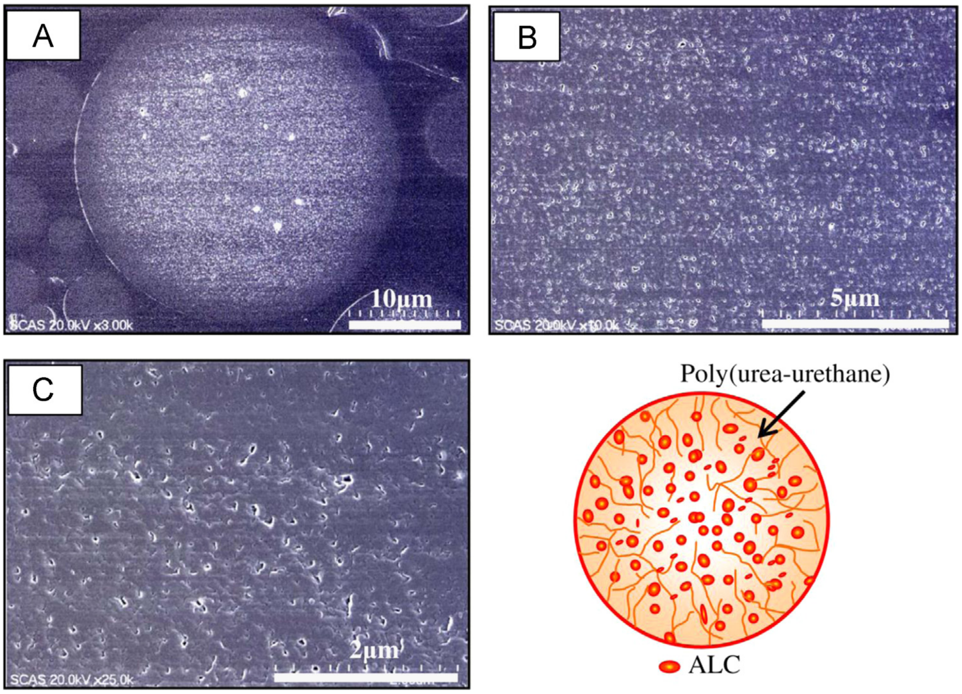


Fig. 2. Cross-sectional FE-SEM images and schematic diagrams of an IP-TRM-1 microcapsule.

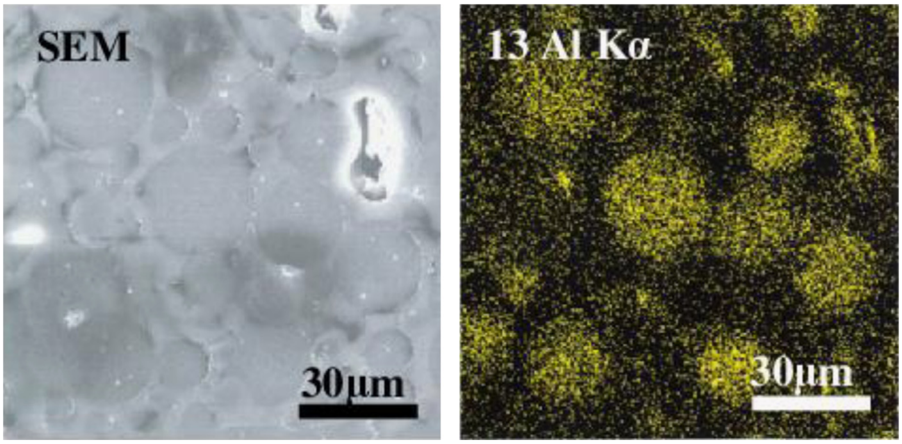


Fig. 3. SEM-EDS Al map of the cross section of an IP-TRM-1 microcapsule.

cycloaliphatic epoxy compound, EMEC, only has limited uses [22]. For TRM, the widely used glycidyl ether epoxy resin, BER, is more suitable. For this system, TPS was used instead of 3GPTMS as the silanol compound because 3GPTMS cannot cure BER. In BER, there is no steric hindrance at the back of an oxirane ring as there is in the cyclohexene oxide ring in EMEC [16]. Therefore, when a silanol compound with a small steric hindrance, such as a silane coupling agent is used, the Brønsted acidity of silanols and aluminum complexes is removed by the SN2 reaction of the silanolate anion. This is why sterically bulky silanol compounds are necessary. The composition of this system is shown in Table 3, C-2. Furthermore, a radical polymerizable monomer and initiator were added to this system to reduce the exothermic peak temperature. In this case, two kinds of polymers from DI/TMP and radical polymerizable monomer were formed and those will form microcapsule matrix and wall. The DSC results for divinylbenzene or acrylic monomers are shown in Table 5 and Fig. 4. The DSC exothermic peak appeared at a lower temperature when a radical polymerization monomer was added.

Next, the weight ratio of the aluminum complex in the microcapsules was evaluated from the TG/DTA data of RP-TRM-1 and the capsule prepared under the same conditions without the aluminum complex (RP-TRM-1#). The results are shown in Table 6 and Fig. 5. From the TG result of RP-TRM-1#, the weight loss up to 260 °C was attributed to residual monomer and solvent evaporation. At higher temperatures, the weight loss is dramatic, because of the decomposition of the polymer capsule wall. In contrast, the TG curve of RP-TRM-1 shows that the weight loss is higher than that of RP-TRM-1#. It was assumed that the weight loss included the vaporization of the ALC and a value of 260 °C was used to calculate the ratio of ALC-1 in the RP-TRM-1 capsules as about 18%. Also, quantitative analysis of the aluminum complex in the capsule was carried out by LC/MS. This showed that the amount of ALC-1 in RP-TRM-1 capsules was about 3%. Therefore, the aluminum complex in the capsules did not retain the initial structure because of the reaction with water during emulsification and polymerization.

3.3. Microcapsule penetration of the highly active aluminum complex

To retain the original activity of the aluminum complex, the solvent penetration of the ALC into the capsule was examined. Because the inside of the microcapsules are porous structures,

Table 5
Characterization of epoxy curing for microcapsule latent catalysts.

TRM	Radical polymerizable monomer	Exothermic onset temperature (°C)	Exothermic peak temperature (°C)	Total heat value (J/g)
IP-TRM-1	–	97	133	−271
RP-TRM-1	Divinylbenzene	99	124	−285
RP-TRM-2	HDDA	77	109	−307
RP-TRM-3	TMPA	94	116	−305

Measurement temperature range was 30–250 °C and the heating rate was 10 °C/min.
HDDA: 1,6-hexanediol diacrylate.
TMPA: trimethylolpropane triacrylate.

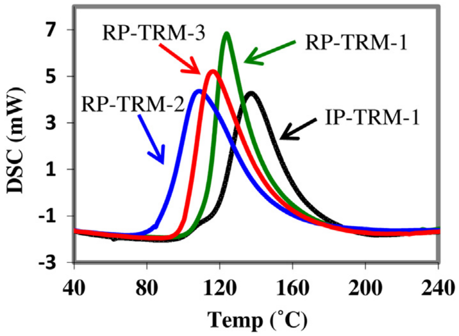


Fig. 4. DSC curves for glycidyl ether epoxy resin cured with several microcapsule latent catalysts.

Table 6
TG weight loss up to 260 °C and ALC weight ratio in TRM.

TRM	Weight loss (mg)	ALC weight ratio in TRM (%)
RP-TRM-1#	0.3	0.0
RP-TRM-1	1.2	17.9

Measurement temperature range was 30–350 °C and the heating rate was 10 °C/min.
Sample weight was 5 mg.

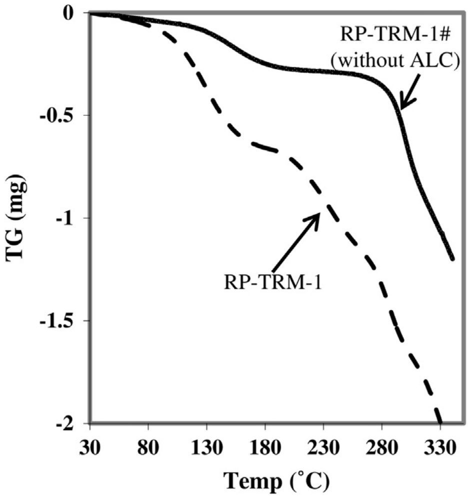


Fig. 5. TG curves of TRMs.

Table 7
Mean volume diameter of RP-TRM-1.

Solvent for immersion	MV after immersion (μm)	MV after drying (μm)
Cyclohexane	2.6	2.6
Ethyl acetate	3.0	2.6

MV: mean volume diameter.
MV value of RP-TRM-1 before immersion is 2.6 μm.

some solvents can penetrate and swell the capsules. The mean volume diameters of the microcapsules (RP-TRM-1) treated with cyclohexane and ethyl acetate are shown in Table 7. Fig. 6 shows the particle size distribution immediately after immersion in ethyl acetate for 4 h at 30 °C and then after vacuum drying for 4 h at 30 °C. When immersed in cyclohexane, which is a nonpolar solvent, the mean volume diameter did not change. However, immersion in ethyl acetate swelled the capsule and increased the particle size, because ethyl acetate is a polar solvent. In addition, removing the solvent by drying returned the capsules to their initial diameter.

Therefore, the aluminum complex was introduced to the capsules using ethyl acetate. A schematic of the solvent penetration process is shown in Fig. 7. First, microcapsules are dispersed in an ethyl acetate solution of the ALC, and the active complex penetrates the capsule wall. After filtration, washing with cyclohexane, drying, and jet milling, highly active capsules were obtained. RP-TRM-1 was treated with the P-A and P-B mixtures (shown in

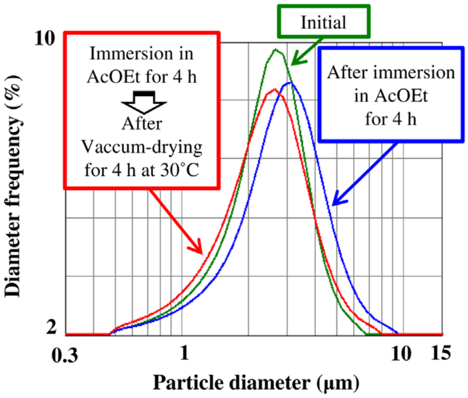


Fig. 6. Particle size distribution curves for RP-TRM-1 microcapsules.

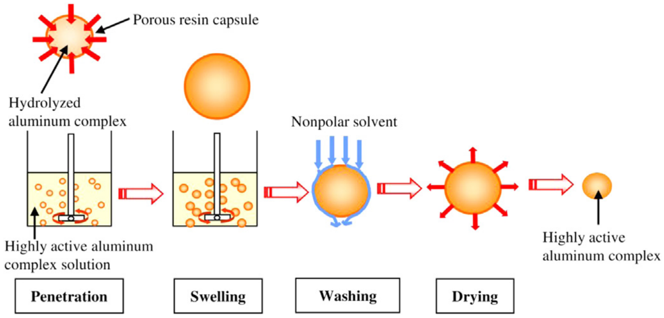


Fig. 7. Solvent penetration of the highly active ALC.

Table 8
Characterization of epoxy curing for microcapsule latent catalysts.

TRM	Penetration process[a]	Exothermic onset temperature (°C)	Exothermic peak temperature (°C)	Total heat value (J/g)
PR-TRM-1	Without treatment	99	124	−285
RR-TRM-1-A	Treatment	70	96	−380
RP-TRM-1-B	Treatment	77	100	−375

Measurement temperature range was 30–250 °C and the heating rate was 10 °C/min.

[a] Recipes: See Table 2.

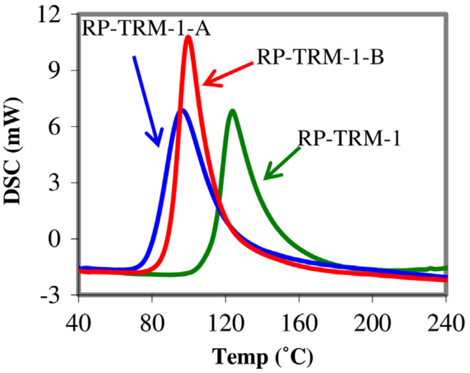


Fig. 8. DSC curves for glycidyl ether epoxy resin cured with several microcapsule latent catalysts.

Table 9
TG weight loss up to 260 °C and ALC weight ratio in TRM.

TRM	Weight loss (mg)	ALC weight ratio in TRM (%)
RP-TRM-1-A#	0.2	0.0
RP-TRM-1-A	1.4	24.0

Measurement temperature range was 30–350 °C and the heating rate was 10 °C/min.
Sample weight was 5 mg.

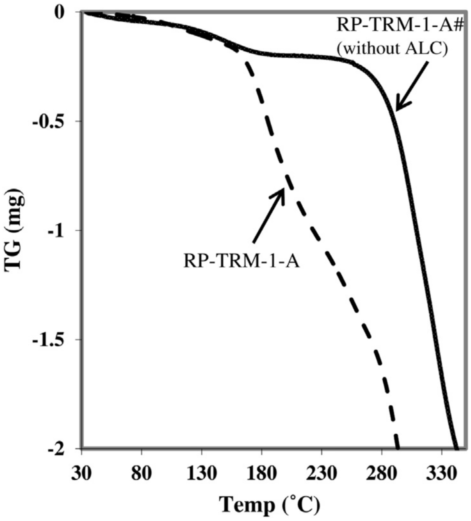


Fig. 9. TG curves of TRMs.

Table 2) to produce microcapsule samples RP-TRM-1-A and B. These samples were used to evaluate the curing characteristics by DSC (conditions C-2, Table 3). The results are shown in Table 8 and Fig. 8. For comparison, the data for RP-TRM-1 (also shown in Table 5 and Fig. 4) are included. As shown in Table 8, the exothermic peak temperatures for both RP-TRM-1-A and B were reduced by more than 20 °C. This is because of the high concentration of active ALC.

Subsequently, TG measurements were carried out for RP-TRM-1-A and RP-TRM-1-A#, which was treated by using the same process but without ALC. The TG results are shown in Table 9 and Fig. 9. The ALC ratio by weight in the RP-TRM-1-A catalyst was about 24%, and was about 6% higher than RP-TRM-1. Moreover, quantitative analysis of microencapsulated ALC by LC/MS showed that the ALC-1 content of RP-TRM-1-A capsules was about 16%, which was a difference of about 13% compared with that before solvent penetration (RP-TRM-1). In addition, the RP-TRM-1-B catalyst using ALC-1 and 2 in the penetration process (Table 1) showed an exothermic onset temperature of 77 °C, which was 7 °C higher than that of the RP-TRM-1-A catalyst, and also had a very sharp exothermic peak. The SEM images of the RP-TRM-1-B catalyst are shown in Fig. 10. Fig. 10B is a magnified image of 10A. The catalyst microcapsules are individual spheres, and no aggregates are visible. Thus, the RP-TRM-1-B catalyst is more suitable for practical use.

To evaluate the shelf life of the final composite of RP-TRM-1-B, BER, and TPS, the liquid viscosity of samples stored at 30 °C was measured (Fig. 11). The maximum increase in the viscosity after 1 week was 10% compared with the initial value. Moreover, the increase after 5000 h storage was also about 60%, demonstrating the outstanding latency.

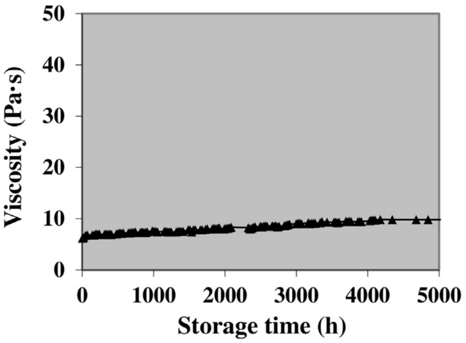


Fig. 11. Shelf life evaluation of the epoxy resin containing TRM (RP-TRM-1-B) at 30 °C.

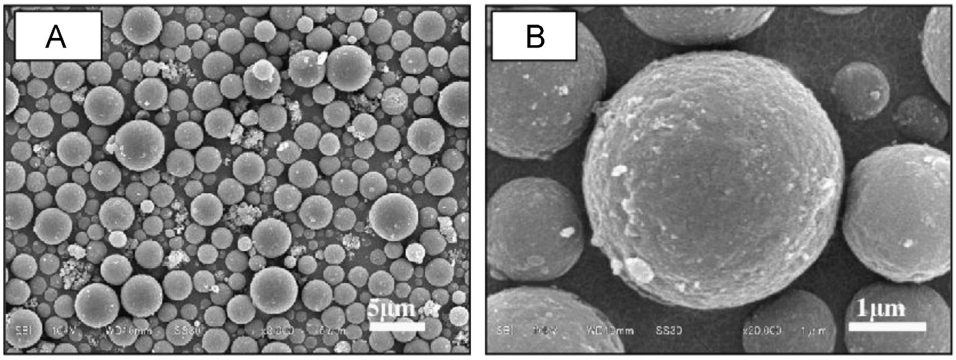


Fig. 10. SEM images of the microcapsules (RP-TRM-1-B).

4. Conclusion

We investigated the microencapsulation of an aluminum complex to separate it from the silicon compound. The DSC measurements of the encapsulated aluminum complexes composed of epoxy and silicon compounds, TG and LC/MS analysis of the microencapsulated aluminum complex, and evaluation of the shelf life of a one-liquid system adhesive show that a suitable trifunctional isocyanate was identified for fabricating an encapsulated aluminum complex. Moreover, we obtained a low-temperature, fast curing thermo-sensitive latent catalyst by using the penetration process of the highly active aluminum complex into the capsule. Furthermore, the resulting one-liquid epoxy resin adhesive system has a long shelf life.

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