One-Pot Curing System of Epoxy Resin Imines Initiated with Water

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ABSTRACT: The curing and adhesive properties of one-component epoxy resins containing Epikote 828 and diimines, derived from *N,N′*-di(1-ethylpropylidene)-*m*-xylylenediamine, *N,N′*-di(1-ethylpropylidene)-1,3-diaminomethylcyclohexane (**2**), and *N,N′*-di(1,3-dimethylbutylidene)-*m*-xylylenediamine, which were used as water-initiated hardeners, were examined. Diethyl ketone-based imines with a lower electron density on the C═N carbon were efficiently hydrolyzed and showed curing activity. **2**, a novel diethyl ketone-based diimine, served as an efficient latent hardener of the epoxy resin. A paste of the epoxy resin with **2** showed good storage stability at room temperature and good adhesive properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 878–882, 2003

Key words: adhesives; resins; coatings

INTRODUCTION

Epoxy resins cured by the mixing of reactive resins and hardeners (initiators) are widely used in coatings, paintings, and adhesives, showing good mechanical strength and chemical resistance.[1] However, these two-component epoxy resins are sometimes incompletely cured, mainly because of insufficient mixing. It is desirable to develop one-component systems with latent hardeners that show no activity under normal conditions but do under external stimulation, such as heating and photoirradiation. We have developed many latent initiators, such as onium salts, amine imides, carboxylates, sulfonates, phosphonates, and phosphonium ylides,[2–4] that show catalytic activity by heating and photoirradiation. Thermally or photocurable one-component epoxy resins are very useful for line production, and atmospheric water is desirable as the stimulant used to achieve one-component epoxy resins for some purposes such as outdoor use. The candidates for water-stimulated latent hardeners are imines,[5] oxazolidines,[6] enamines,[7] and silylamines,[8] releasing amines as the initiating species. Of these compounds, easily synthesizable imines have attracted much attention, but only a few imines have been industrialized as hardeners so far. The main reason for this is their slower hydrolysis rate, which is inappropriate for practical use. This article deals with novel imines showing faster hydrolysis rates and the adhesive properties and storage stability of epoxy resins containing the imines as hardeners.

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EXPERIMENTAL

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL EX-400 (Tokyo, Japan) at 27°C, with tetramethylsilane as an internal standard in $CDCl_3$. IR spectra were recorded on a PerkinElmer Spectrum One (Yokohama, Japan). Mass spectra were recorded on a Shimadzu GCMS-QP5050A (Kyoto, Japan). The hydrolysis rates of the imines were evaluated by gas chromatography (GC) on a Yokogawa Denki HP 5890 series II instrument. Gelation and thin-film set times were measured with a Yasuda Seiki RCI drying-time tester (Osaka, Japan). The adhesive strength was measured with a Shimadzu Autograph AG-50kNG (Kyoto, Japan). The viscosity was measured with a Toki Sangyo RB-80-H (Tokyo, Japan).

Materials

Toluene was dried and distilled by the usual method and was stored over 4-Å molecular sieves before use. Diethyl ketone and methyl isobutyl ketone were obtained from Lancaster and Tokyo Kasei Kogyo Co. (Tokyo, Japan), respectively. Glycidyl phenyl ether (GPE) was obtained from Tokyo Kasei Kogyo. *m*-Xy-

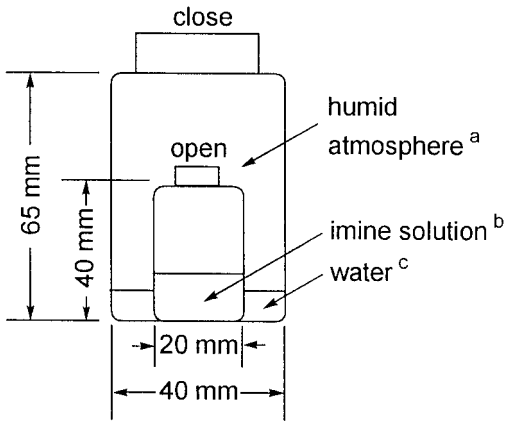


Figure 1 Hydrolysis conditions of the imines: (a) >99% RH, (b) 0.5 mol/L solution in benzene (5.0 mL), and (c) 5.0 mL.

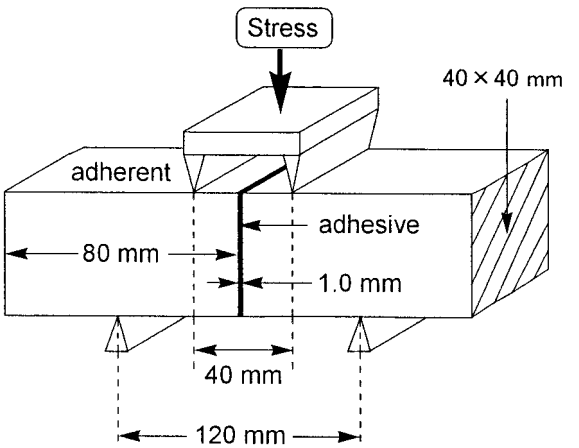


Figure 2 Schematic diagram of the bending test.

lylenediamine (MXDA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) were obtained from Mitsubishi Gas Chemical Co. (Tokyo, Japan). These ketones and amines were used as received. A bisphenol A-type epoxide oligomer (Epikote 828) was obtained from Japan Epoxy Co. (Tokyo, Japan). The fillers NS100, MS700, and RY200S were obtained from Shiraishi Calcium Co. (Amagasaki, Japan), Maruo Calcium Co. (Akashi, Japan), and Nihon Aerogel Co. (Tokyo, Japan), respectively. The dryer KBM403 (γ-glycidoxypropyltrimethoxysilane) was obtained from Shin-etsu Chemical Co. (Tokyo, Japan)

Synthesis of the imines

The imines were prepared by the refluxing of the corresponding amine (1 mol) and ketones (4 mol) for 3 days. After that, 1.5 equiv of phenylisocyanate was added to the reaction mixture, and the resulting mixture was heated at 40°C for 2 h to block the residual amino groups.

N,N′-di(1-ethylpropylidene)-*m*-xylylenediamine (1)

Yield: 255.1 g (93.8%). IR (KBr): 1663 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.03–1.15 (m, 12H), 2.33 (m, 8H), 4.56 (s, 4H), 7.16–7.28 (m, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 10.76, 24.11, 32.58, 53.94, 125.46, 126.60, 128.12, 140.59, 175.94. Mass spectrometry (*m/e*): 272 (M^+).

N,N′-di(1-ethylpropylidene)-1,3-diaminomethylcyclohexane (2)

Yield: 255.1 g (93.8%). IR (KBr): 1663 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.56–0.91 (m, 2H), 1.01–1.10 (m, 12H), 1.24–1.51 (m, 2H), 1.57–2.00 (m, 6H), 2.20 (m, 8H), 3.15 (m, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 10.76, 23.60, 31.51, 32.61, 39.10, 54.78, 57.29, 174.61. Mass spectrometry (*m/e*): 278 (M^+).

N,N′-di(1,3-dimethylbutylidene)-*m*-xylylenediamine (3)

Yield: 287.1 g (95.7%). IR (KBr): 1663 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.91–0.97 (m, 12H), 1.86–2.10 (m, 8H), 2.20 (m, 4H), 4.48 (s, 4H), 7.21–7.31 (m, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.75, 22.47, 26.51, 50.67, 55.05, 126.32, 127.64, 128.23, 140.51, 170.65. Mass spectrometry (*m/e*): 300 (M^+).

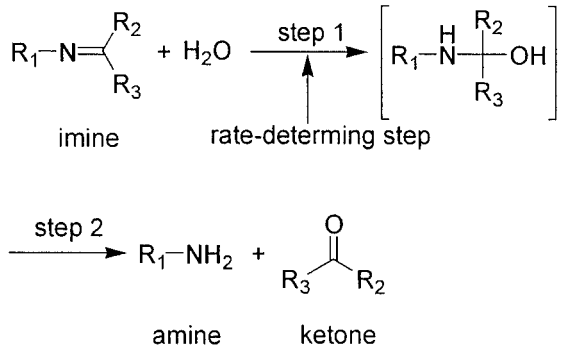
Formulation of the one-component epoxy resins with the fillers and imines

The one-component epoxy resins were compounded as follows. Epikote 828 (100 g) was mixed with cal-

TABLE I
Hydrolysis Rates and ^{13}C-NMR Chemical Shifts of C═N of Imines

Imine [R_1—(N═CR_2R_3)$_2$]				Hydrolysis rate[a]	^{13}C-NMR chemical shift of C═N[b]
No.	R_1	R_2	R_3	(M/day)	(ppm)
1	*m*-xylylene	Et	Et	0.89	175.94
2	1,3-Bismethyl-cyclohexyl	Et	Et	0.68	174.61
3	*m*-xylylene	Me	*i*-Bu	0.21	170.65

[a] Conditions: 0.5 mol/L solution in toluene at 23°C, which was placed under less than 99% RH.
[b] Measured in $CDCl_3$.



Scheme 1

cium carbonate [NS100 (120 g) and MS700 (60 g)] and silica [RY200S (7.5 g)] as fillers at 100°C under reduced pressure for 2 h with an Inoue Seisakusho PML-5L (Yokohama, Japan). After the mixture cooled to room temperature, an imine and KBM-403 (40 g), as a dryer, were added to the mixture, and the resulting resin was further kneaded for 1 h under an atmosphere of N_2.

Measurement of the hydrolysis rate of the imines

An imine solution in toluene (0.5 mol/L) was placed under a high-humidity condition [>99% relative humidity (RH)] at 23°C (Fig. 1). The hydrolysis of the imines was monitored by GC analysis with decane as a standard. The hydrolysis rate was estimated from the slope of the time–conversion plot.

Reaction of GPE with the amines

A solution of GPE (4.0 mmol) and an amine (1.0 mmol) in toluene (0.5 mL) was placed at 23°C. The reaction was monitored by GC analysis with decane as a standard.

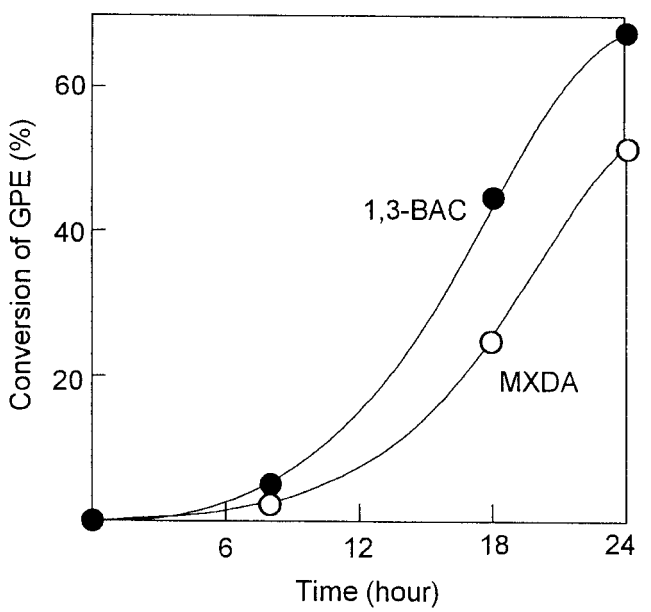


Figure 3 Time–conversion curves of GPE reacted with MXDA or 1,3-BAC (25 mol %) at 23°C.

TABLE II
Curing Time of One-Component Epoxy Resins

Adhesive[a]	Curing beginning time[b] (h)	Curing ending time[c] (h)
A_1	6.6	10.5
A_2	4.5	10.7
A_3	11.0	18.0

[a] Epikote 828 containing 50 mol % of 1 (A_1), 2 (A_2), or 3 (A_3), which was applied on a glass plate at 23°C. The applied thickness was 0.3 mm.
[b] The time when the formation of thin cured film was observed on the surface of the applied one-component epoxy resin.
[c] The time when curing had completely ended.

Evaluation of the curing properties

The curing properties were evaluated by the measurements of thin-film set times according to the normalized method (JIS A6024). The one-component epoxy resins were applied on a glass plate with a 0.3-mm thickness and stored at 23°C and 50% RH for 1 day, and then the curing time was measured.

Evaluation of the adhesive properties

The adhesive properties were evaluated by a bending test according to the normalized method (JIS A6024) at

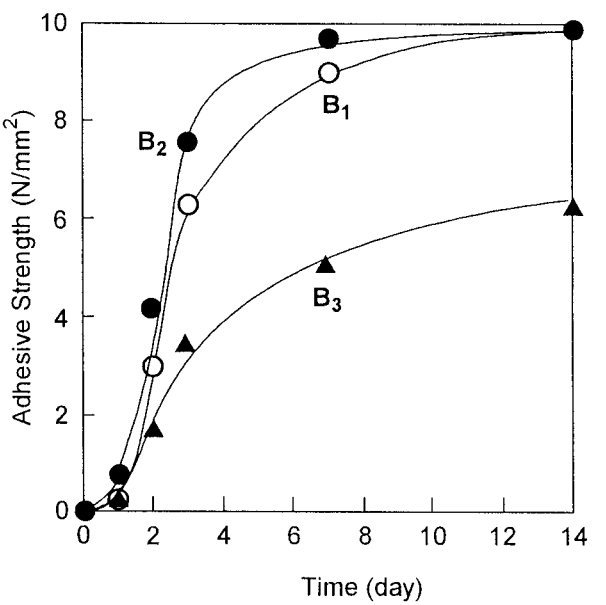


Figure 4 Adhesive strength of Epikote 828 containing **1**, **2**, or **3** (50 mol %), a filler, and a dryer at 23°C and 50% RH (adhesive thickness = 1.0 mm). The fillers NS100 (120 g), MS700 (60 g), and RY200S (7.5 g) were contained in Epikote 828 (100 g). The dryer KBM403 (40 g) was also contained in Epikote 828 (100 g).

TABLE III
Destruction Mode in the Four-Point Bending Test at 23°C and 50% RH

	Destruction mode of test piece[b]					
Adhesive[a]	1 day	2 days	3 days	4 days	7 days	14 days
B_1	N + C	C	C + M	C + M	M	M
B_2	N + C	C	C + M	M	M	M
B_3	N	N + C	C	C	C + M	M

[a] Epikote 828 (100 g) containing 50 mol % of 1 (B_1), 2 (B_2), or 3 (B_3); fillers [NS100 (80 g), MS700 (40 g), and RY200S (10 g)]; and dryer [KBM403 (40 g)].
[b] M-material destruction; C-condensation destruction; N-not cured.

23°C. Mortar, which was made of sand and cement, was used as an adherent with an applied area of 40×40 mm^2 (Fig. 2). The epoxy resin was applied to the adherent with a 1.0-mm thickness, the adherent surface frequently being rubbed with sand paper. The applied adherents were stored at 23 or 5°C and 50% RH for 14 days, and then the adhesive strength was measured.

Evaluation of the storage stability

A sample was stored in a glass bottle with a cap in an incubator at 40°C for a set time, and the viscosity was measured at 25°C.

RESULTS AND DISCUSSION

Hydrolysis of the imines

The imines were submitted to hydrolysis with water under a high-humidity condition at 20°C (>99% RH). Table I summarizes the hydrolysis rates of imines **1–3**, as determined from the slopes of the initial step of the time–conversion plots, along with the ^{13}C-NMR chemical shifts of the C═N carbon atoms. The order of the hydrolysis rates of the imines was **1** > **2** > **3**, which agreed with the order of the chemical shifts of the C═N carbon. It might be suggested that an imine with a lower electron density on the C═N carbon was hydrolyzed faster, presumably because water attack on the C═N group might be the rate-determining step in this reaction (Scheme 1).[9]

Reaction of GPE with the diamines

In epoxy-curing systems with imines as hardeners under humid conditions, epoxides react with amines generated by hydrolysis with water. Therefore, it is necessary to elucidate the reaction of epoxides with amines to develop efficient water-initiated hardeners for epoxy resins. In this work, we examined the reaction of GPE with MXDA or 1,3-BAC in toluene at 23°C. The epoxide–amine reaction was strongly influenced by the nucleophilicity of the amines.[10] 1,3-BAC was more reactive than MXDA (Fig. 3), probably because of the higher nucleophilicity.

Curing properties of the one-component epoxy resins

We examined the curing times of the one-component epoxy resins $\mathbf{A_1}$, $\mathbf{A_2}$, and $\mathbf{A_3}$ prepared from Epikote 828 and imines **1**, **2**, and **3**, respectively. The curing times of $\mathbf{A_1}$ and $\mathbf{A_2}$, containing diethyl ketone-based imines **1** and **2**, were shorter than those of $\mathbf{A_3}$, which contained methyl isobutyl ketone-based imine **3** (Table II), and this agreed with the hydrolysis experiments of the corresponding imines; however, $\mathbf{A_1}$ showed longer curing times than $\mathbf{A_2}$. In epoxy curing systems with imines as hardeners under humid conditions, epoxides directly react not with imines but with amines, which are generated by the hydrolysis of the imines. Therefore, it is necessary to consider both the hydrolysis rate of the imines and the reactivity of the amines. In this case, imine **1** showed a slightly faster hydrolysis rate (Table I) and lower reactivity than **2** (Fig. 3). Consequently, it is suggested that the curing rate of one-component epoxy resins depends

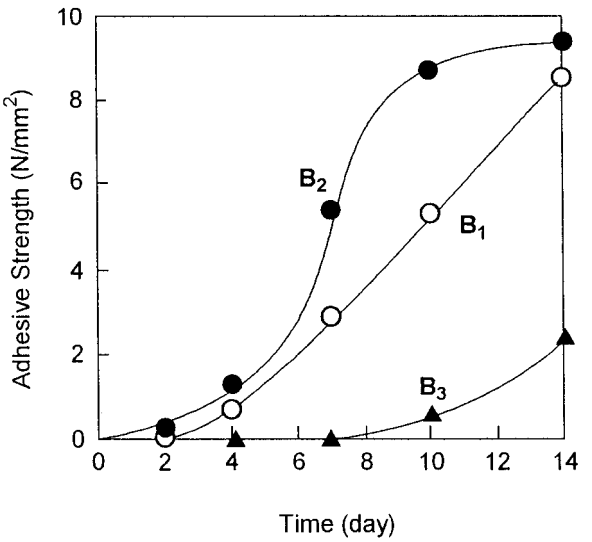


Figure 5 Adhesive strength of Epikote 828 containing **1**, **2**, or **3** (50 mol %), a filler, and a dryer at 5°C and 50% RH (adhesive thickness = 1.0 mm). The fillers NS100 (120 g), MS700 (60 g), and RY200S (7.5 g) were contained in Epikote 828 (100 g). The dryer KBM403 (40 g) was also contained in Epikote 828 (100 g).

TABLE IV
Destruction Mode in the Four-Point Bending Test at 5°C and 50% RH

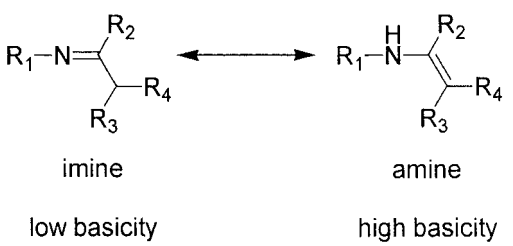
	Destruction mode of test piece[b]				
Adhesive[a]	2 days	4 days	7 days	10 days	14 days
B_1	N	N + C	C	M + C	M + C
B_2	N	C	M + C	M	M
B_3	N	N	N	N + C	C

[a] Epikote 828 (100 g) containing 50 mol % of 1 (B_1), 2 (B_2), or 3 (B_3); fillers [NS100 (80 g), MS700 (40 g), and RY200S (10 g)]; and dryer [KBM403 (40 g)].
[b] M-material destruction; C-condensation destruction; N-not cured.

more on the reactivity of the amines generated from the imines when the hydrolysis rates of the imines are close to one another.[11]

Adhesive properties of the one-component epoxy resins

The adhesive properties of the one-component epoxy resins $\mathbf{B_1}$, $\mathbf{B_2}$, and $\mathbf{B_3}$. which were prepared from Epikote 828, fillers, a dryer, and imines **1** and **2**, were evaluated by a four-point bending test at 23°C and 50% RH for 14 days (Fig. 4). The adhesive strength of the one-component epoxy resins increased in the order $\mathbf{B_2} \geq \mathbf{B_1} \gg \mathbf{B_3}$, which agreed with the order of the thin-film set experiments. $\mathbf{B_1}$ exhibited a destruction mode slightly different from that of $\mathbf{B_2}$ at 4 days (Table III). The mechanical strength of epoxy resins cured by diamines is higher than that of mortar, so the destruction of the adhesive part means incomplete curing. The difference in the destruction mode was more significant in the test at 5°C and 50% RH (Fig. 5 and Table IV), for which the curing rates were slower than those at 23°C (Table III); of course, the hydrolysis rate of the imines and the reactivity of the amines decreased at lower temperatures. The mortar adhered by $\mathbf{B_2}$ was destroyed at 10 days, but $\mathbf{B_1}$ was not done even at 14 days. It was concluded that imine **2** served as an active water-initiated hardener.



Scheme 2

TABLE V
Storage Stability of Epikote 828 Containing 50 mol % of 1 (B_1), 2 (B_2), or 3 (B_3); Filler[a] and Dryer[b]

	Viscosity (mPa/s)	
Adhesive	Before storage	After storage[c]
B_1	12,000	13,000 (108%)
B_2	11,800	12,000 (102%)
B_3	11,800	13,200 (112%)

[a] NS100 (120 g), MS700 (60 g), and RY200S (7.5 g) were contained in Epikote 828 (100 g).
[b] KBM403 (40 g) was contained in Epikote 828 (100 g).
[c] Storage at 25°C for 1 month.

Storage stability of the one-component epoxy resins

Although imines exhibit lower basicity than corresponding amines, they also exist as enamines, tautomers with larger basicity than imines (Scheme 2).[12] Therefore, a one-component epoxy resin with an imine as a hardener may possibly increase in viscosity during storage. Epikote 828 containing 50 mol % **1**, **2**, or **3**, a filler, and a dryer was kept at 40°C for 1 month so that the storage stability could be examined. The viscosity slightly increased during this period (Table V), but it would cause no problem for practical usage.

CONCLUSIONS

We developed novel diethyl ketone-based imines that efficiently underwent hydrolysis in comparison with methyl isobutyl-based ones commercially utilized as water-initiated hardeners for epoxy resins. One-component epoxy resins containing a diimine synthesized by diethyl ketone and 1,3-BAC were efficiently cured with a water initiator and showed good curing properties, adhesive properties, and storage stability.

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