

Aminimide as Hardener/Curing Promotor for One Part Epoxy Resin Composition

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Synopsis

Three kinds of aminimide compounds were examined as latent hardeners/promotors for epoxy resins. Since aminimides are thermolyzed to generate tertiary amine and isocyanate, the compounds are useful as polymerization initiators for the epoxy group as well as promotors for epoxy-acid anhydride reaction. The pot life was over 30 days at 40°C for a formulated one-part epoxy resin system. In comparison with epoxy resins cured with conventional hardeners, several interesting characteristics of the mechanical and electrical properties were observed. In particular, the epoxy resins cured by aminimides exhibited high tensile strength and high impact strength, which make them excellent curing agents for adhesive applications. The reasons for these unique properties are discussed.

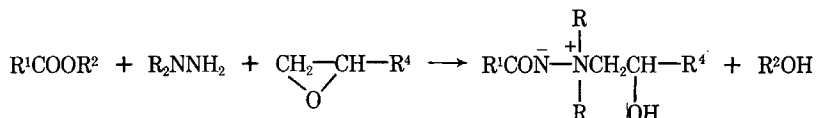
INTRODUCTION

The market for epoxy resin composition is expanding in the fields of adhesives, paints, coatings, molding resins, matrix for composite material, and so forth. Various curing agents and promotors have been used to meet different required performances and working conditions. The general procedure is to mix an epoxy resin with curing agents and/or promotors such as amines, Lewis acids, acid anhydrides, and others immediately before use. The pot life of formulated epoxy compositions ranges from a few minutes to several days depending upon the kinds of curing agent/promotor.

It is certainly more desirable to develop one-part formulations which can be cured simply by heating. Research efforts have been dedicated to the development of latent promotors such as substituted imidazoles, organic acid dihydrazides, or boron trifluoride amine salts.^{1,2} For example, a pot life between 2 and 20 days with imidazoles is still shorter than that required for one-part epoxy resin formulation. Boron trifluoride amine salts provide much longer pot lives, for example, exceeding 6 months for the monoethanolamine salt. Easy hydrolysis of these amine salts by atmospheric moisture is, however, a shortcoming.

Several years ago we found that aminimide compounds could be excellent curing agents which were activated only at elevated temperatures and that the mechanical properties of the cured epoxy resin exhibited a number of interesting characteristics.³⁻¹⁰ Aminimide is a family of ylides consisting of the $\equiv\text{N}^+ - \text{N}^-$ structure. Sulfonyl aminimides have been known for many years,¹¹ whereas carbonyl aminimides were first reported in 1959.¹² The chemistry of

this class of compounds has developed rapidly, and an easy synthetic procedure shown below was established¹³⁻¹⁴:



The application of the aminimide compounds in the polymer industry has been extensively investigated by the research group at Ashland Chemical Co.,¹⁵⁻¹⁷ focussing on their characteristics of generating isocyanate by thermal decomposition. In particular, polymeric aminimides synthesized by polymerization and copolymerization of *N,N,N*-trimethylamine-*N'*-methacrylimide generate isocyanate side groups by heating so that thermal curing is possible.¹⁸ The ylides structure of aminimide endorses strongly hydrophilic properties to the polymers and the uses as emulsifier and water-soluble polymer have been proposed¹⁹⁻²¹

These applications stem from the natures of the ylide as a polar group and a precursor of the isocyanate group. We were interested in the tertiary amine liberated together with the isocyanate. Tertiary amines are known to be catalysts for epoxide polymerization, and, consequently, aminimides are expected to function as latent curing agents for the epoxy compositions which are curable above the decomposition temperature of aminimides.

In this article, we will describe the use of aminimides as epoxy resin hardener and promoters for the epoxy-acid anhydride or dicyandiamide compositions.

EXPERIMENTAL SECTION

Materials

Aminimide compounds: The synthetic procedure was essentially the same as the reported methods.^{22,23} A representative example of synthesis is shown below.

N,N-Dimethyl-*N*-(2-hydroxy-3-allyloxypropyl)amine-*N'*-lactoidimide: 60.1 g of 1,1-dimethylhydrazine was added dropwise to a solution of ethyl lactate (118.1 g), allyl glycidyl ether (114.1 g), and isopropyl alcohol (78.6 g) over a 2-h period below 10°C. The mixture was stirred for 5 h below 20°C and for another 7 h below 50°C. The unreacted raw materials and the solvent were distilled off *in vacuo* to give the final product.

Yield: 213.0 g (86.5%), viscous liquid, purity: 99.17%. The purity was determined by means of nonaqueous volumetric titration.²⁴ IR (KBr): 1590 cm⁻¹ (>C=O). Epoxy resins and the curing agents other than aminimides were used as supplied.

Pot Life of Epoxy Resin Composition

Epoxy resin (Epon resin 828) containing aminimide (10 phr) was kept at 40°C. Pot life was defined as the time required to increase the viscosity by a factor of 10 from the initial value. Viscosity was determined by a Brookfield viscometer.

Gelation Time

Epoxy resin composition was heated in a test tube equipped with a rotating glass rod with a temperature-controlled oil bath. Gelation time defined as the time when the glass rod was no longer movable.

Curing of Epoxy Resin

The mixture of Epon resin 828 and an aminimide was degassed under vacuum and poured into a mold. After curing for 5 h at 120°C, the resin was taken out of the mold and post-cured at 180°C for 8 h. When solid epoxy resin (Epon resin 1001) was used in combination with acid anhydride and aminimide, all components were ground and mixed in the form of powder. Test specimens were prepared from the powdered composition by compression molding at 150°C for 3 min, and post-cured at 180°C for 1 h.

Measurement of Mechanical and Electrical Properties

Deflection temperature was measured according to the procedure described in ASTM D 648-56.

Flexural strength was measured by an Instron type tester at 20°C with a crosshead speed of 5 mm/min. Flexural strength measurement and Izod impact test were conducted according to the procedure of JIS 6911.

All electrical properties were measured according to the procedure of JIS 6911 at 20°C.

RESULTS AND DISCUSSION

Properties of Aminimide Compounds

Among a number of aminimides which we have synthesized the following three compounds given in Table I were chosen for detailed investigation after primary screening. The criteria for choosing these compounds were feasibility of large scale production, ease of handling, stability of epoxy resin composition, and curing ability.

These compounds are obtained as crystals or viscous oil and soluble in most polar solvents. The toxicity level is very low as shown by large LD₅₀ values tested for mouse. Human skin is not irritated by these compounds as evidenced by a patch test on the arm. Furthermore, handling of aminimides as a component of epoxy resin formulation is easier than conventional epoxy resin hardeners.

When aminimides are mixed with Epon resin 828, the composition are very stable at room temperature as shown in Table II. The viscosity increase at 40°C is very slow as shown in Figure 1 whereas the gelation is rapid at elevated temperatures.

Properties of Epoxy Resin Compositions Cured with Aminimides

These one-part epoxy compositions will find use in various fields common to conventional epoxy resins. As a part of market feasibility study, mechanical as well as electrical properties of the present one-part epoxy resins are compared

TABLE I
Properties of Aminimide Compounds

Name	Structure	Appearance	Solubility in ^a							Toxicity LD ₅₀ (mouse)
			1	2	3	4	5	6	7	
YPH-103	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CO}-\text{N}^--\text{N}^+-\text{CH}_2-\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array}$	white crystal mp 144–146°C	⊙	○	×	×	⊙	⊙	⊙	>6.0
YPH-201	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCO}-\text{N}^--\text{N}^+-\text{CH}_2\text{CHCH}_2-\text{O}-\text{CH}_2\text{CH}=\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{CH}_3 \quad \text{OH} \end{array}$	viscous liquid <i>n</i> _D ²⁰ : 1.4828	⊙	⊙	⊙	×	⊙	⊙	⊙	>13.3
YPH-208	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CO}-\text{N}^--\text{N}^+-\text{CH}_2\text{CHCH}_2-\text{O}-\text{CH}_2\text{CH}=\text{CH}_2 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array}$	viscous liquid <i>n</i> _D ²⁰ : 1.4871	⊙	⊙	⊙	⊙	⊙	⊙	⊙	>12.7

^a (1) H₂O; (2) *n*-BuOH; (3) MEK; (4) xylene; (5) cellosolve; (6) DMF; (7) DMSO; ⊙ freely soluble; ○ soluble; × insoluble.

TABLE II
Pot Life and Gelation Time of Epon 828 Containing Aminimide (10 phr)

YPH	Pot-life (days)	Gelation time (min)		
		185°C	155°C	125°C
103	30	25	60	180
201	50	15	20	30
208	30	25	60	120

with those by conventional formulations in Table III. These reference compositions are for conventional one-part or semi-one-part use. Except for Ref. 3, the pot life is very short. Although the deformation temperature of Ref. 3 is high, the resin is brittle as shown by small values of flexural strength and Izod impact strength relative to those for composition 1 and 2. Mechanical properties of Refs. 1 and 2 are also much inferior. Hard but tough properties are characteristics of the present compositions. High flexural strength and high impact strength

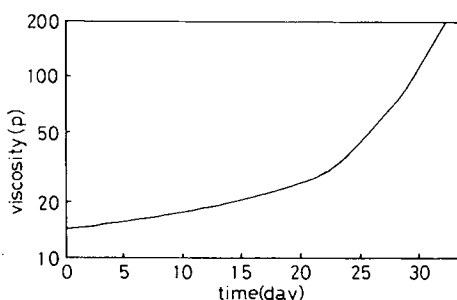


Fig. 1. Viscosity increase of Epon 828 added with YPH 208 (8 phr) at 40°C.

TABLE III
Mechanical and Electrical Properties of One-Part Epoxy Resin Compositions

Item	Composition 1 ^a	Composition 2 ^b	Ref. 1 ^{c,f}	Ref. 2 ^{d,f}	Ref. 3 ^{e,f}
Heat deformation temp (°C)	84	92	80	141	170
Mechanical properties					
Flexural strength (kg/cm ²)	1412	1240	1012	1096	1160
Izod impact strength (kg-cm/cm ²)	6.0	8.9	1.9	—	3.5
Electrical properties					
Volume resistivity (Ω-cm) × 10 ⁻¹⁵	2.0	—	1.0	10	10
Dielectric constant (1 kHz)	4.5	—	3.5	3.7	3.7
tan δ(1 kHz)	0.0377	—	0.003	0.004	0.008

^a Epon 828 (100 parts) and YPH-208 (8.0 parts) are cured at 120°C for 5 h, and then at 180°C for 8 h.

^b Epon 828 (100 parts) and YPH-201 (6.0 parts) are cured at 110°C for 3 h, and then at 150°C for 8 h.

^c Epon 828 (100 parts) and trisdimethylaminomethylphenyl-2-ethylhexoic acid salt (10 parts) are cured at 80°C for 2 h.

^d Epon 828 (100 parts) and 2-ethyl-4-methylimidazole (4 parts) are cured at 60°C for 2 h.

^e Epon 828 (100 parts) and BF₃-monoethanolamine (3 parts) are cured at 120°C for 4 h, and then at 200°C for 4 h.

^f The pot life of Refs. 1-3 are 7 h at 23°C, 20 h at 30°C, and 6 months at 23°C, respectively.

cannot be rivaled by curing of Epon resin 828 by ordinary amines such as triethylenetetramine.

These properties are favorable for the applications to adhesives as shown in Table IV. In some cases, the aluminum test plates (thickness 1.0 mm, width 10 mm, adhesion area 1 cm²) broke before fracture of the adhesive layer. The strong adhesion would be attributed to the toughness of the present epoxy compositions. The slow curing controlled by thermolysis rate of aminimide at the curing temperature much above the glass transition temperature of cured resin would afford strain relaxation during curing, which increases the adhesivity.

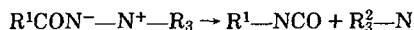
Use of Aminimides as Promotor for Epoxy-Acid Anhydride Compositions

The aminimides could also act as promotor for epoxy-acid anhydride compositions while the aminimides do not influence the pot life of the resin mixture at room temperature. As presented in Table V, curing is reasonably fast in the presence of aminimide whereas curing does not occur in its absence. Although heating for 2 min at 150°C is sufficient to cure the resin for compositions A and B, the mechanical properties are further improved by post-curing at 180°C. When benzyldimethylamine was used as promotor instead of aminimide, the elastic modulus is lower for the reference.

Consequently, the use of aminimide is doubly favorable since both life time extension and performance improvement are effected.

Proposed Functions of Aminimide Compounds

Excellent performance of aminimides either as hardener or as promotor in one-part epoxy compositions indicates that the compounds interact with epoxide groups after thermal decomposition to tertiary amines. The decomposition mechanism has been well documented as follows^{25,26}:



Tertiary amines are active initiators of ring-opening polymerization of epoxide

TABLE IV
Adhesivity of Various Epoxy Compositions

Hardener or catalyst (phr)		Curing conditions		Adhesivity (kg/cm ²)	
		Temp (°C)	Time (h)	Al—Al ^a	Fe—Fe ^b
YPH-103	(6)	155	5	118	197
	(8)	185	1.5	240	
YPH-208	(8)	155	5.0	236	
Epicure Z	(20)	110	1.5	97	
	(20)	170	1.5	111	
BF ₃ -MEA ^c	(5)	130 + 150	2 + 2	51	no adhesion

^a Aluminum test pieces (thickness 2.0 mm, width 10 mm, adhesion area 1 cm²) were immersed in phosphoric acid/*n*-BuOH/*iso*-PrOH/water mixture (1:4:3:1) for 10 min, washed with aqueous acetone, and dried in air.

^b Iron test pieces (thickness 1 mm, width 10 mm, adhesion area 1 cm²) were burnished with a sandpaper, washed with acetone, and dried in air.

^c MEA: mono(ethanolamine).

TABLE V
Mechanical and Electrical Properties of Epoxy-Acid Anhydride Compositions

Item	Compositions ^a			Reference ^b BDMA
	A	B	C	
Heat deformation temp (°C)	98	142	127	128
Mechanical properties				
Bending strength (kg/cm ²)	866	908	1272	1274
Modulus of elasticity (kg/cm ²) × 10 ⁻³	104	104	35	27
Tensile strength (kg/cm ²)	529	643	—	—
Izod impact strength (kg/cm ²)	1.2	1.1	2.0	2.1
Electrical properties				
Volume resistivity (Ω-cm) × 10 ⁻¹⁵	1.7	3.9	170	20
Dielectric constant (1 MHz)	4.0	4.1	2.3	3.2
tan δ (1 MHz)	0.013	—	0.012	—
Arc resistance time (s)	187	187	125	134
Water absorption				
Room temp (%)	0.05	0.06	0.11	—
Boiling water absorption (%)	0.59	0.15	—	—

^a Formulation and curing condition:

Epon 1001	100 parts	} Composition A:	150°C × 2 min	
pyromellitic anhydride	17 parts		} Composition B:	150°C × 2 min
YPH-208	2.0 parts			+ 180°C × 1 h
Epon 828	100 parts	} Composition C:	90°C × 2 h	
hexahydrophthalic anhydride	80 parts		} Reference:	100°C × 2 h
YPH-208	1.0 parts			+ 150°C × 8 h

^b Formulation and curing condition:

Epon 828	100 parts	} Reference:	100°C × 2 h	
hexahydrophthalic anhydride	80 parts		} Reference:	100°C × 2 h
BDMA (benzyl dimethylamine)	1.0 parts			+ 150°C × 4 h

as well as promoters for the reaction between epoxide and acid anhydride. The role of aminimides as latent hardener/promotor of epoxy resin is well understood.

The mechanical properties of cured resins presented in Tables III and IV are, however, different from those of conventional epoxy resin cured with small molecular amines. The hard and tough resin may be a result of slow curing at elevated temperature. When free amines are used, the curing starts at a low temperature so that the strain generated during curing cannot be sufficiently relaxed. In the present system, the curing temperature is 70°C higher than the T_g of cured resin, and, furthermore, the curing reaction is moderated by the limited rate of tertiary amine generation. We do not think, however, that the physical property characteristics can be attributed only to strain relaxation. The isocyanate fragments simultaneously generated with the tertiary amines would participate in the curing process. There are good possibilities of reactions of isocyanate with hydroxyl groups to form urethane bondings. This might be a reason for obtaining nonbrittle epoxy resin having high elastic modulus.

Research projects are now under way to clarify the functions of this unique class of hardener/promotor using monofunctional epoxides as model compounds.

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