JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 2707–2714 (1965)

Base Catalysts for the Cure of Epoxy Resins

ALLAN E. SHERR and ALEX A. KRUPNIK, *Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut*

Synopsis

Tetramethylguanidine and heptamethylisobiguanide have been shown to be catalysts for the cure of epoxy resins. The reagents were effective when used in very small concentrations. Their reactivity is postulated to be a result of their several accessible tertiary amine nitrogen atoms, high base strength, and good solvent powers.

Introduction

Organic bases are well known as catalysts and/or curing agents for epoxy polymers. Among the many such compounds in common use are diethylenetriamine, triethylenetetramine, diethylaminopropylamine, dicyandiamide, and *m*-phenylenediamine.[1,2]

In the course of some work with tetramethylguanidine (TMG) and heptamethylisobiguanide (HEPTA) it became of interest to investigate briefly their reactions with epoxy resins.

Both compounds are liquids of very high base strength[3] and are excellent solvents for a wide variety of materials. Some properties of the compounds are given in Table I.

Catalytic Quantities

Two of the nitrogen atoms of TMG can be considered to be tertiary, while the third nitrogen can be considered to be secondary. All five of the nitrogen atoms in HEPTA may be considered to be tertiary in nature.

An approximate calculation of the amount of base needed as a catalyst for curing epoxy resins can be made as follows.[4]

For tetramethylguanidine:

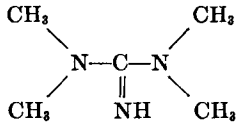
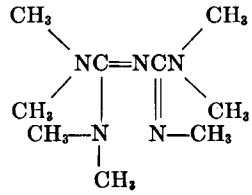
$$\text{phr} = 100(MW)/\text{EQ}\ [1(N_t) + H_a]$$

For heptamethylisobiguanide:

$$\text{phr} = 100(MW)/\text{EQ}\ (3N_t)$$

where phr is the amount of base in parts per hundred parts of resin, MW is the molecular weight of the base, EQ is the epoxide equivalent of the resin (grams of resin containing 1 g.-equiv. of epoxide), N_t is the number of

TABLE I
Properties of TMG and HEPTA

	Tetramethylguanidine	Heptamethylisobiguanide
Abbreviation	TMG	HEPTA
Formula		
Molecular weight (theory)	115.18	199.29
Boiling point, °C.	160	124/5 mm.
Freezing point, °C.	<−50	22
Specific gravity, g./ml.	0.91 (25°C.)	0.98 (30°C.)
Refractive index, n_D^{25}	1.4667	1.5118
pK_a	14.1	17.1

tertiary amine nitrogens in the base, and H_a is the number of active amine hydrogens per molecule of base.

For example, if an epoxy resin (Epon 828, Shell Chemical Corp.) which has an EQ of about 200 is cured with TMG, the amount of base needed would be:

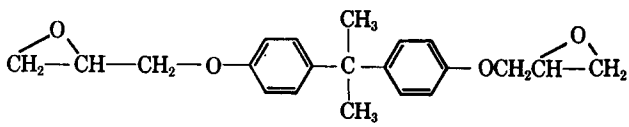
$$115\ (100)/[200\ (2+1)] = 17.5 \text{ phr of TMG}$$

For HEPTA, the amount of base needed would be:

$$199.3\ (100)/200\ (3 \times 5) = 6.6 \text{ phr}$$

Experimental Results

Epon 828 epoxy resin was used in the initial evaluation of the two curing agents. The resin consists essentially of the diglycidyl ether of bisphenol A



and has a molecular weight of 350–400.

Castings 6 × 6 × 1/8 in. were made between two glass plates. To make a casting, a 100-g. portion of epoxy resin (Epon 828) was heated to 50°C. in a beaker and the required amount of catalyst was added with stirring. The warm epoxy solution was poured between the glass plates. In some castings, 75 g. of epoxy resin was used with a proportionate reduction in the amount of catalyst. The results are summarized in Table II.

TABLE II
Summary of Results for Epon 828 Epoxy Resin + TMG or HEPTA

Sample	Modifier	Concentration Phr	Concentration Moles	Cure cycle	Flexural modulus, psi × 10^{-6}	Flexural strength, psi	Rockwell hardness, M	Deflection temperature under load, °C.	Dielectric constant[a]	Dissipation factor[a]
A	Curing agent D	12	—	4¼ hr/94°C.	0.44	16,200	76	68	3.50	0.0051
1	TMG	7	0.06	4¼ hr./94°C.	0.48	18,800	80	82	3.53	0.0044
2	TMG	2	0.017	4¼ hr./94°C.	0.47	19,900	88	95	3.62	0.0038
3	TMG	1	0.008	20 hr./100°C.	0.47	19,500	79	95	3.78	0.0033
4	TMG	0.5	0.004	20 hr./100°C. 2 hr./150°C.	0.51	19,500	87	70	3.72	0.001
5	TMG	0.1	0.0008	20 hr./100°C. 24 hr./150°C.	Did not cure					
6	HEPTA	7	0.035	4¼ hr./94°C.	0.47	18,600	84	81	3.54	0.0048
7	HEPTA	2	0.01	4¼ hr./94°C.	0.50	20,200	88	82	3.61	0.0034
8	HEPTA	1	0.005	20 hr./100°C.	0.49	19,300	78	91	3.74	0.009
9	HEPTA	0.5	0.0025	20 hr./100°C.	0.56	20,100	91	50	3.75	0.0003
10	HEPTA	0.1	0.0005	20 hr./100°C. 24 hr./150°C.	Did not cure					

[a] At 60 cycles/sec.

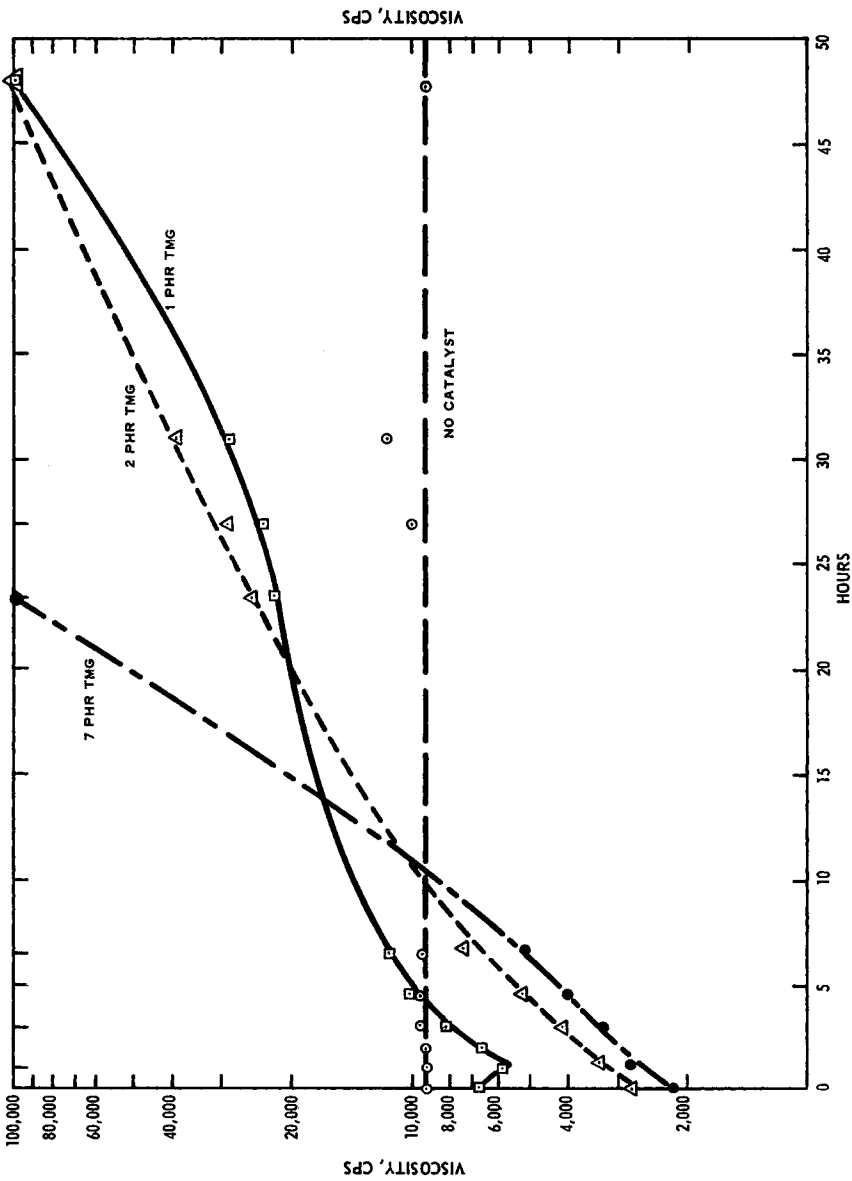


Fig. 1. Viscosities of epoxy resin–TMG solutions.

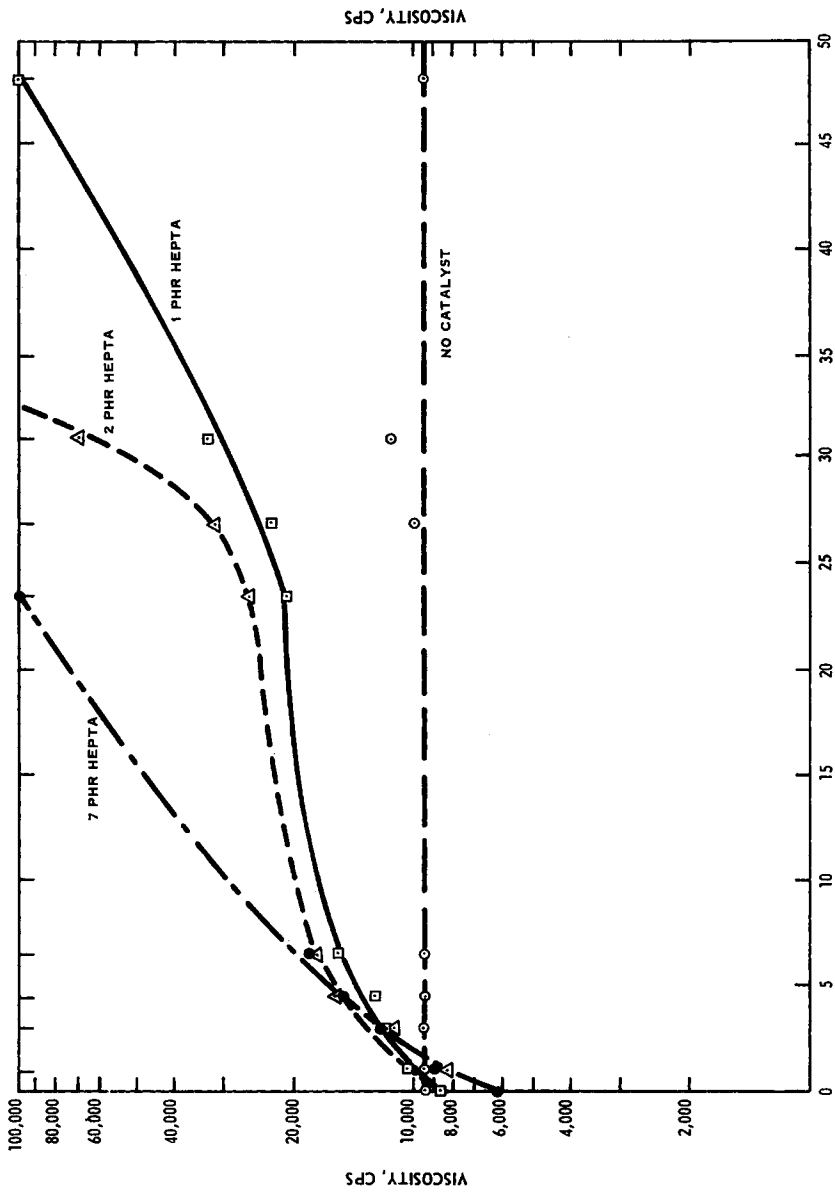


Fig. 2. Viscosities of epoxy resin–HEPTA solutions.

Both TMG and HEPTA were agents for the cure of the epoxy resin as shown in Table II. In both cases, it would appear that 2 phr was the optimum concentration to be used at 94°C. to obtain the maximum physical properties of the resin. However, under proper conditions as little as 0.5 phr of catalyst was effective.

In a separate experiment to test the effect of increased temperature on the cure of epoxy resin, it was found that 45–60 min. at 160°C. was sufficient to give a cured resin when 1 or 2 phr of TMG was used as the catalyst.

The heat distortion temperatures of the castings were raised by use of TMG or HEPTA (Table II). Both flexural strength and modulus were raised when the epoxy resin was cured with small quantities of either of the two catalysts.

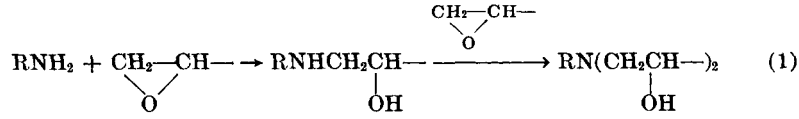
To evaluate the pot life of the mixtures, the composition was put in a 4-oz. glass bottle and Brookfield viscosity measured with time (Figs. 1 and 2) at room temperature. Mixtures of catalyst and epoxy resin appear to have a pot life of at least 6 1/2 hr. at room temperature.

HEPTA gave a mixture with much shorter pot life as can be seen by comparing the rate of viscosity increase when 2 or 7 phr of each material was used.

Discussion

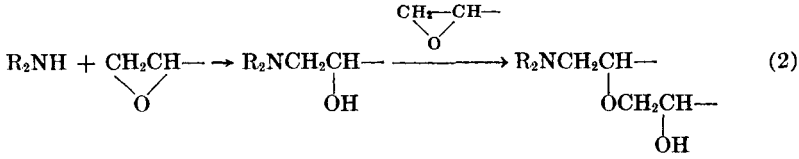
Both tetramethylguanidine and heptamethylisobiguanide were more active as curing agents than was predicted empirically. Since such a small quantity of curing agent was used, it is interesting to speculate on the mechanism of the reaction.

Primary amines react with epoxies as shown in eq. (1).



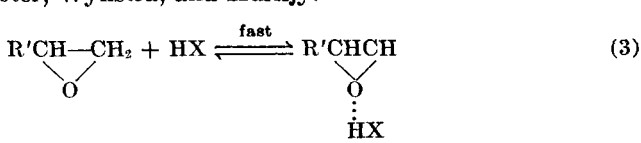
(1)

Secondary amines can react to form a tertiary amine and ethers as shown in eq. (2).

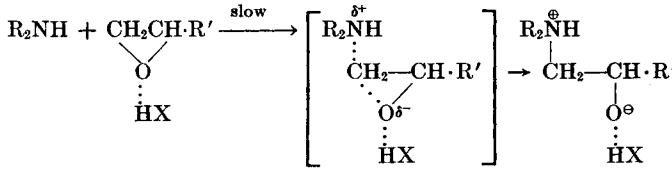


(2)

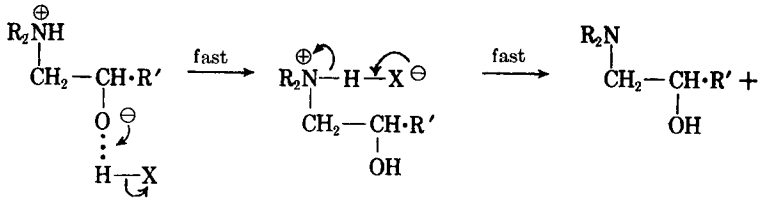
Smith[5] presents a mechanism for curing epoxide compounds as shown in reaction sequence of eqs. (3–5). He suggests that the reaction proceeds by a rate-controlling step rather than a concerted termolecular mechanism as proposed by Shecter, Wynstra, and Kurkjy.[6]



(3)

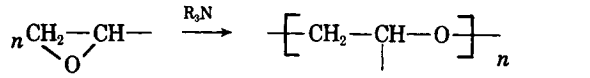


(4)



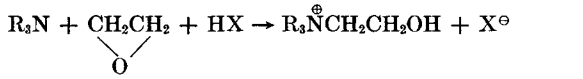
(5)

Tertiary amines are catalytic in action, as described in eq. (6).[7]



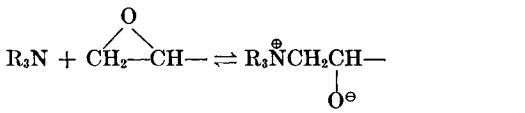
(6)

Considerable discussion has been presented regarding the exact mechanism of the reaction of tertiary amines with epoxides. Eastham and co-workers believe the reaction is as shown in eq. (7).[8,9]

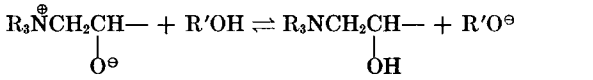


(7)

Shecter, et al.[5,10] postulate that tertiary amines initiate by addition to the epoxide, followed by reaction with alcohol as shown in eqs. (8) and (9)



(8)

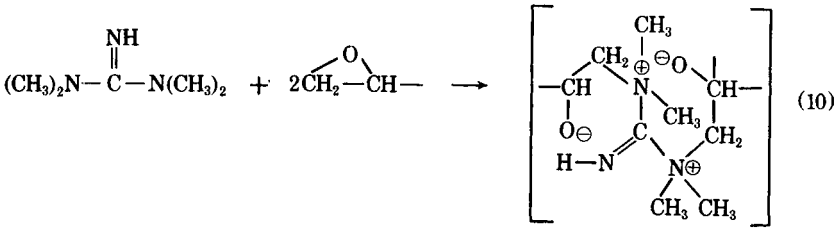


(9)

These authors[10] found a steric effect with the tertiary amines. The less hindered the amine, the more active it was as a catalyst.

Tetramethylguanidine and HEPTA both are most likely catalysts rather than curing agents for the epoxy polymerizations. The data in Table II indicate that both agents were effective in very low molar concentrations. The high activities can be attributed to the presence of several tertiary amine nitrogens which are not too sterically hindered, as well as to the high base strength of both reagents with their concomitant high solvent powers.

Thus, the reactions probably proceed by one of the paths shown in eqs. (6–9). In addition, with TMG, there undoubtedly is a contribution from the secondary amine through reaction paths (2) and (3–5). For example, a possible reaction intermediate could be that shown in eq. (10).



(10)

The assistance of C. Wikstrand and F. Graves in determination of the physical properties of the castings is gratefully acknowledged.

References

1. Skeist, I., and G. R. Somerville, *Epoxy Resins*, Reinhold, New York, 1958.
2. Harper, C. A., *Electronic Packaging with Resins*, McGraw-Hill, New York, 1961.
3. Flynn, K. G., and D. R. Nenortas, *J. Org. Chem.*, **28**, 3527 (1963).
4. Jones and Dabney Co. Technical Data Bulletin, *Epoxy Resins for Coatings*, November 30, 1958, p. 16.
5. Smith, I. T., *Polymer*, **2**, 95 (1961).
6. Shecter, L., J. Wynstra, and R. P. Kurkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).
7. Spitzer, W. C., *Off. Dig. Federation Soc. Paint Technol.*, **36**, No. 475, 52 (Sept. 1964).
8. Eastham, A. M., B. De B. Darwent, and P. E. Beaubien, *Can. J. Chem.*, **29**, 575 (1951).
9. Eastham, A. M., and B. De B. Darwent, *Can. J. Chem.*, **29**, 585 (1951).
10. Shecter, L., and J. Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).

Résumé

On montre que la tétraméthyl guanidine et l'heptaméthylisobiguanide sont des catalyseurs pour le traitemnt des résines époxy. Les réactifs sont actifs quand ils sont employés en très faibles concentrations. On admet que leur réactivité est le résultat de leurs multiples atomes d'azote amine tertiaire accessibles, de leur basicité élevée et de leur bon pouvoir dissolvant.

Zusammenfassung

Tetramethylguanidin und Heptamethylisobuiguanidin sind Katalysatoren für die Hartung von Epoxyharzen. Sie sind bei Verwendung in sehr kleiner Konzentration wirksam. Es wird angenommen, dass ihre Reaktivität durch die zuganglichen tertiären Aminstickstoffatome, durch die hohe Basenstärke und das gute Lösungsvermögen bedingt ist.

Received January 13, 1965
Revised March 3, 1965