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ACCELERATION OF THE EPOXY RESIN-DICYANDIAMIDE CURE CYCLE BY TRISUBSTITUTED UREAS

BERNARD R. LaLIBERTE, ROBERT E. SACHER, and
JOSEPH BORNSTEIN
POLYMER RESEARCH DIVISION

June 1981

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ABSTRACT

The addition of accelerators such as Monuron, N-(4-chlorophenyl)-N',N'-dimethylurea, or Diuron, N-(3,4-dichlorophenyl)-N',N'-dimethylurea, to epoxy resin-dicyandiamide mixtures significantly decreases the hardening temperature of these systems. These trisubstituted urea accelerators are believed to serve mainly as a latent source of dimethylamine. This amine is believed to play a very important role in the cure cycle. One pathway to dimethylamine is a low-temperature cyclocondensation reaction between the trisubstituted urea and the epoxy functionality to form a 2-oxazolidone; this reaction partially hardens the resin. The significance of this source of dimethylamine in the overall mechanism of epoxy hardening was illustrated by differential scanning calorimetry. Several epoxy formulations were examined at various heating rates. Arrhenius plots of the data indicated that the slope of a two-component mixture consisting of resin and Monuron was approximately the same as that of a three-component system composed of resin, dicyandiamide, and Monuron. In contrast, the slope of a two-component resin-dicyandiamide system was found to be considerably larger. Thus the reaction of Monuron with the resin is an important factor that must be considered in any explanation of the acceleration of the hardening process of dicyandiamide-containing resins.

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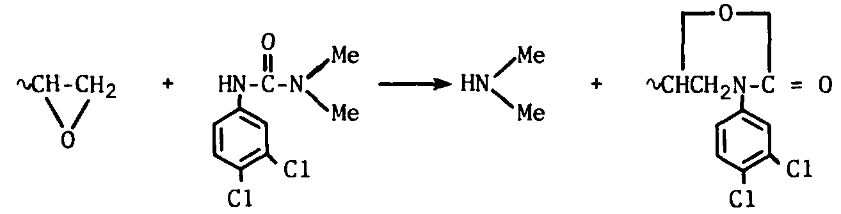
INTRODUCTION

Interest in the mechanism of the hardening of epoxy resin-dicyandiamide (Dicy)/ accelerator systems originated from a previous study* which had been conducted because the literature did not disclose the reason Diuron, N-(3,4-dichlorophenyl)-N',N'-dimethylurea, had the ability to lower the hardening temperature of tetraglycidyl methylene dianiline (TGMDA)-Dicy systems. The cure behavior of TGMDA-Dicy/Diuron mixtures composed of resin having various molecular weights was examined by differential scanning calorimetry (DSC) at a heating rate of 2°C/min. The cure temperatures of these systems were found to lie in a narrow range of 129° to 133°C. The TGMDA-Diuron reaction releases dimethylamine and subsequently it was found that a large variation in the composition of the resin system only slightly altered the hardening temperature. In fact, a TGMDA-Diuron reaction conducted in the thermal analyzer (DSC) at 2°C/min showed an exotherm at 129°C which is the same as that obtained in the presence of Dicy. This reaction mixture solidified on reaching room temperature. In contrast, the reaction of Dicy with pure TGMDA resin showed an exotherm at 170°C. These observations led us to believe that dimethylamine played a significant role in the cure cycle. Accordingly, attention was directed to the pathways leading to dimethylamine and these will be discussed.

Thickening occurs concomitantly with the evolution of dimethylamine in the TGMDA-Diuron reaction and in this process the accelerator was assumed to react with the epoxy groups of the resin. The isolation of a clean reaction product in such a complex polymeric mixture was not practical. Therefore, the reaction of Diuron with a simpler epoxy-containing compound, p-tert-butylphenyl glycidyl ether (PTBGE), was investigated by mass spectrometry (MS) in the hope of finding a reaction product that might be associated with the liberation of dimethylamine.† The MS examination did indeed indicate the presence of a 2-oxazolidone derivative whose formation suggested that dimethylamine must be a coproduct.



Similarly, the MS examination of the reaction mixture of Monuron, N-(4-chlorophenyl)-N',N'-dimethylamine, and PTBGE revealed a molecular ion ascribable to a 2-oxazolidone derivative. Evidence that the MS interpretations were correct was subsequently obtained by actually preparing substantial quantities of 2-oxazolidones and the accompanying dimethylamine by the reaction of phenyl glycidyl ether (PGE) with the above aryl ureas.‡

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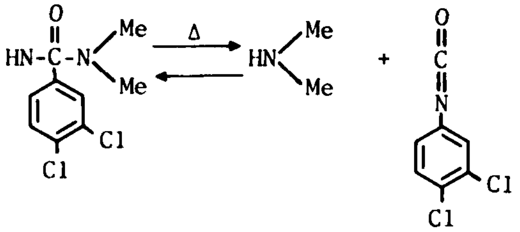
*LaLIBERTE, B. R., and BERGQUIST, P. R. *A Cure Study of Tetraglycidyl Methylene Dianiline System with Diuron and Dicyandiamide.* Army Materials and Mechanics Research Center, AMMRC TN 78-5, June 1978.

†LaLIBERTE, B. R. *The Reaction of Diuron with Epoxy Groups.* Army Materials and Mechanics Research Center, AMMRC TN 79-1, January 1979.

‡LaLIBERTE, B. R., and BORNSTEIN, J., manuscript in preparation.

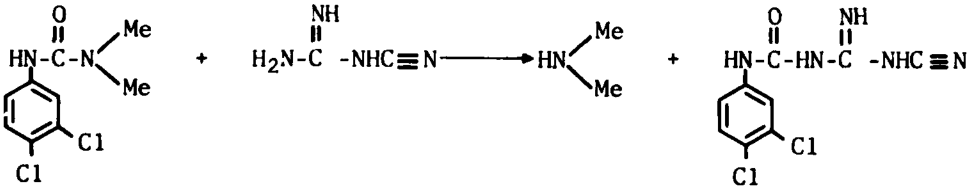
Another potential pathway to dimethylamine is the dissociation of the trisubstituted ureas to form an aryl isocyanate as shown with Diuron:



Due to the difference in the melting points of the urea accelerators we had suspected that Diuron (mp 154°C) might dissociate more readily than Monuron (mp 172°C). Examination of the decomposition of the aryl ureas by DSC and by thermogravimetric analysis (TGA) was hindered by the fact that sublimation competes with dissociation. However, we did infer from the TGA analyses that both Diuron and Monuron liberate the amine at about the same temperature. Thus, the TGA analyses did not seem to support our speculative view that dissociation was related to the melting point.

For this reason, each of the accelerators (0.1 g) was heated slowly in test tubes in an oil bath; evolution of the amine was monitored with moistened litmus paper. Both Diuron and Monuron were found to release minute quantities of dimethylamine at about 174°C. It is interesting that Nonuron, N-phenyl-N',N'-dimethylurea, (mp 134°C) begins to release amine at approximately 150°C. These experiments suggest that the dissociation temperature of the urea depends on the substitution pattern of the aromatic ring rather than on the melting point of the urea.

As a third possible source of dimethylamine we had considered a condensation reaction between the aryl urea and Dicy which would be expected to afford a linear guanidine derivative as shown:



DSC examination of an intimate mixture of Diuron and Dicy (1:4 mole ratio, respectively) failed to reveal a distinct exotherm and the same was true for a mixture of Monuron and Dicy. It should be pointed out that the failure to observe an exotherm is not necessarily an indication that a chemical reaction has not occurred. Subsequently, a literature search for the expected guanidine was conducted and this brought to light the investigation of Son and Weber.[1] They reported that Dicy and Monuron,

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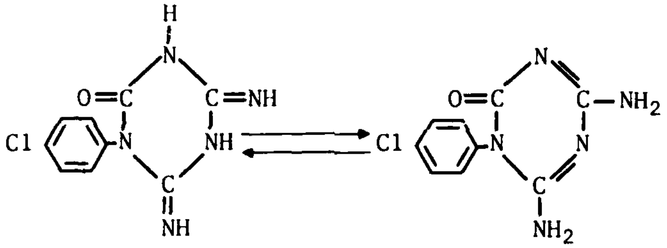
[1] SON, P., and WEBER, C. D. *Some Aspects of Monuron-Accelerated Dicyandiamide Cure of Epoxy Resins.* J. Applied Polymer Science, v. 17, 1973, p. 1305-1313.

upon heating in diglyme, afforded 1-cyano-3-(p-cholorcarbanilino)-guanidine in 35.5% yield along with dimethylamine in 5.6% yield. Their support for the guanidine structure was based on mass spectrometry, which gave the expected value of 237 for the molecular weight, and on infrared analysis, which showed a carbonyl band at 1690 cm^{-1}. Interestingly, they failed to report a peak in the infrared spectrum for the nitrile group which clearly is one of the salient features of their proposed structure. In addition, no elemental analysis was given for this substance which was described as not melting at 300°C. Prompted by these omissions, we repeated the reaction of Monuron with Dicy in diglyme. We found that at 120°C only small amounts of dimethylamine were evolved; analysis of the reaction mixture over a period of several hours revealed only unchanged Monuron and Dicy at this temperature. However, when the temperature of the reaction mixture was raised to 163°C, reflux ensued and copious volumes of the amine were evolved; after one hour the reaction was complete and a substantial amount of a light tan solid was isolated which, after purification (washing with methanol followed by recrystallization from boiling water), appeared from mass and infrared spectroscopy to be identical with the product isolated previously by Son and Weber.[1] Elemental analysis supported the guanidine structure reported by Son and Weber; however, infrared analysis indicated the nitrile function to be absent. For this reason we wish to assign tentatively the following isomeric cyclic structure to the product from the Monuron-Dicy reaction.



In this connection, it is noteworthy that fusion at 170°C of equimolar amounts of Monuron and Dicy affords the same cyclic compound and dimethylamine in quantitative yield.

RESULTS AND DISCUSSION

A mixture of Monuron and a colorless liquid epoxy resin (EPON 828) heated at 130°C quickly turned amber and became viscous. Small bubbles of amine gas could be observed. Upon cooling, the resulting viscous solution turned to a hard, solid mass. The infrared analysis of this reaction mixture yielded the characteristic carbonyl band[2] associated with 2-oxazolidones at 1745 cm^{-1}. In comparison, the neat resin heated to 130°C remained colorless and did not solidify upon cooling to room temperature. Another experiment was conducted in which the resin was treated with a small amount of a 2-oxazolidone and then heated to 130°C; this mixture also failed to solidify upon cooling. Noteworthy is the fact that the introduction of dimethylamine into the neat resin was found to harden the epoxy resin at room temperature. These experiments illustrate that the formation of the 2-oxazolidone ring in the resin medium has little significance to the hardening process outside of the fact that the cyclocondensation reaction is an important source of dimethylamine.

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2. SANDLER, S. R. *Preparation of Mono and Poly-2-Oxazolidones from 1,2-Epoxides and Isocyanates.* J. Polymer Science, A-1, v. 5, 1967, p. 1481-1485.

As previously mentioned, the Monuron-Dicy reaction liberates only trace amounts of dimethylamine at 120°C and, in contrast, DSC examination of a two-component EPON 828-Monuron mixture at the extremely slow heating rate of 0.5°C/min indicated the cyclocondensation reaction occurs in the proximity of 92°C. The introduction of Dicy to form a three-component EPON 828-Dicy/accelerator system displayed an exotherm at about the same temperature (94°C) as that of the two-component mixture. The heating of the three-component system was terminated at 130°C at which temperature the sample was found to be a solid mass. It should be pointed out that EPON 828 cannot be hardened by Dicy at 130°C within two hours. In this study, in order to investigate the activation of Dicy by dimethylamine, it was necessary to evaluate the resin-Dicy/accelerator and the resin-accelerator systems as two separate and distinct entities.

All mixtures were prepared with the diglycidyl ether of bisphenol-A (EPON 828) whose molecular weight was determined to be 350.6 on the basis of epoxy number. The first formulation was a three-component system consisting of 15 moles of resin, 4.0 moles of Dicy, and 1.0 mole of Monuron. The related two-component system was prepared with 15 moles of resin and 1.0 mole of Monuron. Also included in this study was a concentrated three-component system consisting of only 2.5 moles of the resin, 4.0 moles of Dicy, and 1.0 mole of Monuron. The curing agent combination of the concentrated system is 67%, whereas in the dilute three-component mixture it is 20% (on a molar basis).

The examination by DSC of these formulations was conducted at various heating rates and the resulting data treated according to the following expression:[3]

$$\log_{10} \text{Rate} = A/T + B$$

where:

Rate = heating rate (°C/min)
A = constant, related to activation energy
T = temperature (°K)
B = constant, related to the Arrhenius frequency factor.

The validity of the experiments depends on a linear relationship of the plot of the $\log_{10}$ rate versus the $1 \times 10^3/°K$ values. A computer program was used to analyze the data for reliability and from this data the graphs were obtained.

The equation for the activation energy (E_a) is:[4]

$$\text{Slope} = -E_a/2.303R$$

where R = the gas constant, 1.987 cal degree^{-1} mole^{-1}.

The slopes for the Monuron system, calculated from the thermal measurements of the three mixtures, were found to be:

Dilute (20%):	3510
Concentrated (67%):	4340
Monuron + Resin only:	3610

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3. CARPENTER, J. F. *Quality Control of Structural Nonmetallics.* Contract N00019-76-C-0138, manuscript prepared for the Naval Air System Command, Washington, D.C., June 1977, p. 15.
4. MARON, S. H., and PRUTTON, C. F. *Principles of Physical Chemistry.* Fourth Edition, MacMillan Company, New York, 1965, p. 572.

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Technical Report AMMRC TR 81-30, June 1981, 9 pp -
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It is especially noteworthy that the slope of the Monuron-resin mixture is nearly the same as that of the dilute three-component system.

This study was undertaken because of the belief that these two resin systems would have similar slopes and this has now been verified. It will be shown below that the resin-Dicy reaction has the largest slope. Consequently, these results are consistent with our earlier observations that the resin-accelerator reaction is responsible for the activation of Dicy. Since the concentrated three-component system has a slope larger than that of the corresponding dilute mixture, it would be expected that chemical reactions become more difficult to initiate as the availablity of epoxy groups is decreased.

The slopes of three systems containing Monuron are shown together. The formulation of the mixtures and reaction temperature at various heating rates are denoted by an experimental number; both are indicated in Table 1 and in Figure 1.

Table 1. THERMAL ANALYSIS RESULTS

		Moles of					
System	Experiment	Resin	Dicy	Accelerator	Rate (deg C/min)	Temp. (deg C)	
a. Monuron	1	15	4	1	0.5	94	
					2	121	
					5	139	
					10	145	
					20	171	
	2	2.5	4	1	1	108	
					2	116	
					5	133	
					10	145	
					20	155	
	3	15	0	1	1	109	
					2	131	
					5	143	
					10	157	
					20	172	
b. Diuron	4	15	4	1	1	108	
					2	119	
					5	137	
					10	145	
					20	165	
	5	2.5	4	1	1	105	
					2	117	
					5	131	
					10	144	
					20	159	
c. Nonuron	6	15	4	1	1	114	
					2	128	
					5	143	
					10	157	
					20	172	
	7	2.5	4	1	1	106	
					2	115	
					5	128	
					10	141	
					20	156	
d. Dicyandiamide	8	15	4	0	0.5	161	163
					1	176	173
					2	180	179
					5	190	188

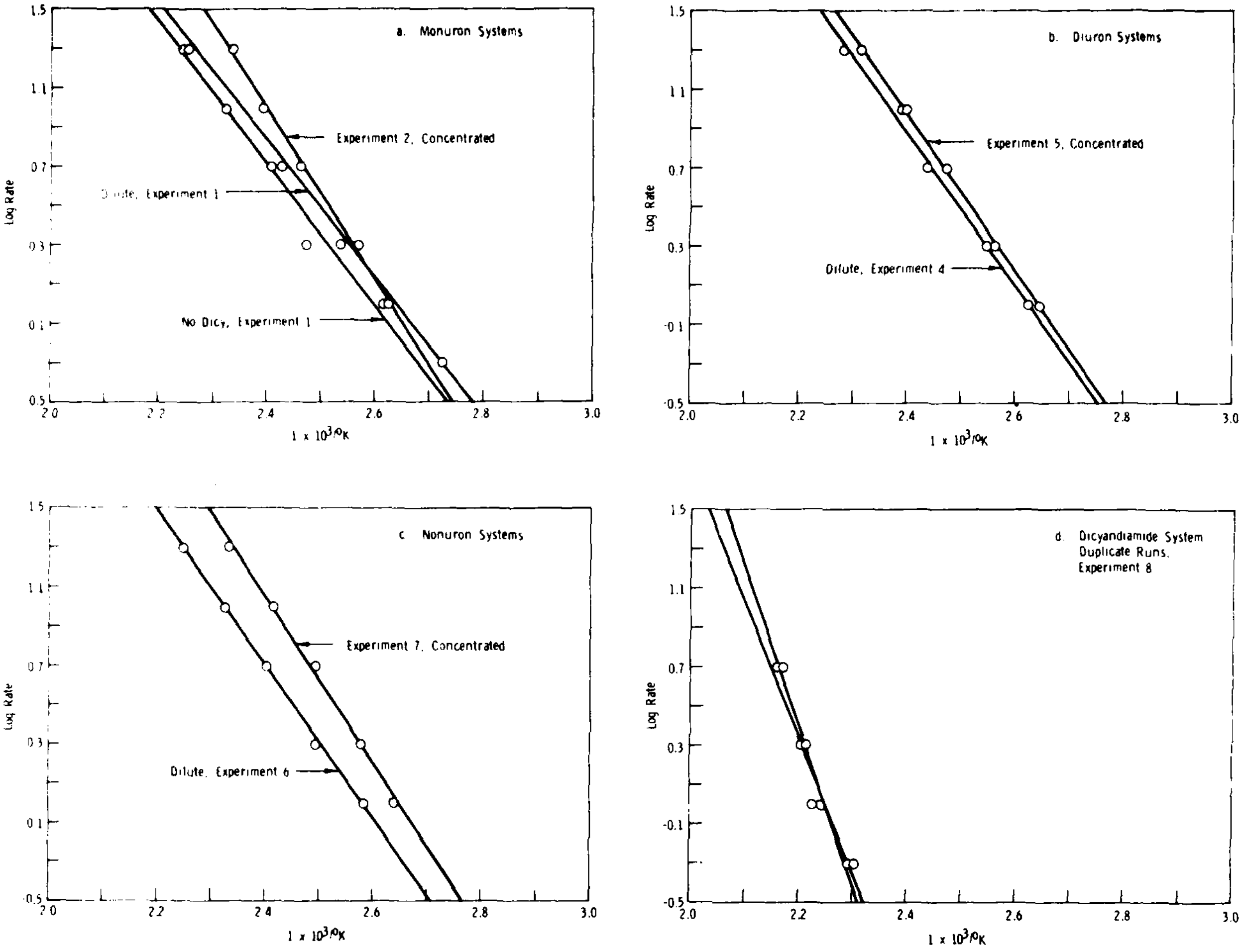

Figure 1. Thermal analysis results.

The slopes of the dilute and concentrated three-component systems of Diuron and Nonuron were found to be:

	Dilute (20%)	Concentrated (67%)
Diuron Systems	3910	4000
Nonuron Systems	3920	4240

All data points of Nonuron fall on a straight line, therefore the slope of these lines clearly illustrates the effect of concentration. In the case of Diuron, the data represents a magnification of the difficulties encountered in the preparation of homogenous mixtures. Prior to this study, we had become aware of the effects of high level concentration on reaction temperatures. Although concentration is of secondary importance, this factor was considered in this study because Son and Weber's[1] speculation concerning the source of dimethylamine was based on two components, the urea and Dicy, and failed to take into account systems in which epoxy resin was also present. Their interpretation of the DSC results is ambiguous as to the role of the resin-Monuron reaction. In connection to the synergistic effect between Monuron and Dicy the results of this particular study, "Mechanism of Monuron-Accelerated Dicyandiamide Cure of Epoxy Resins," will be published.

The final experiment conducted in this study was the examination of the two-component system prepared with 15 moles of resin and 4.0 moles of Dicy. Based on duplicate runs involving four different heating rates, the slope was found to lie between 7270 and 7890. Clearly, this system has the largest slope. Consequently, the magnitude of this slope illustrates that Dicy had indeed undergone activation in all three component systems used in this study.

In conclusion, the liberation of dimethylamine by the reaction of the trisubstituted ureas with the resin is an important factor that has to be taken into consideration in providing any explanation of the lowering of the cure temperature of dicyandiamide-containing resins.

EXPERIMENTAL

Differential scanning calorimetric experiments were conducted in open aluminum pans with a DuPont 990 thermal analyzer fitted with a 902 DSC plug-in module in a static atmosphere. The exothermic reaction temperatures were taken at the apex of the heating curves.

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