

Some Aspects of Monuron-Accelerated Dicyandiamide Cure of Epoxy Resins

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Synopsis

The synergistic effect of dicyandiamide and certain trisubstituted ureas in the curing of epoxy resin is shown by differential scanning calorimetry and exotherm profiles. When 3-(*p*-chlorophenyl)-1,1-dimethylurea (Monuron) was reacted with dicyandiamide, we could isolate dimethylamine and a derivative of dicyandiamide. The role of these products in epoxy resin curing is speculated.

INTRODUCTION

Dicyandiamide has been used for several years to cure epoxy resins. The mechanism of the dicyandiamide-glycidyl ether reaction is not clearly understood. This type of curing requires a temperature of at least 150°C, with good cures obtained at 175°C. Many of the new modified epoxy resin adhesives employ dicyandiamide with accelerator to obtain good cures and adhesion when cured between 100° and 120°C.

Others have suggested a possible mechanism for the tertiary amine acceleration of the dicyandiamide curing of epoxy resins.¹ A recent patent² also reveals the use of trisubstituted ureas as dicyandiamide accelerators. One substituted urea that is available commercially is 3-(*p*-chlorophenyl)-1,1-dimethylurea (Monuron, registered trade mark of E. I. du Pont de Nemours & Co.).

However, to our knowledge no one has explained how substituted ureas can act as accelerators in dicyandiamide-epoxy resin cures. This paper attempts to shed some light on the cure mechanism of such systems.

RESULTS AND DISCUSSION

The effectiveness of 3-(*p*-chlorophenyl)-1, 1-dimethylurea (Monuron) as an accelerator in dicyandiamide-epoxy resin cure is easily shown by differential scanning calorimetry (DSC) thermograms or by exotherm profile curves. DSC curves were obtained from a du Pont 900 differential thermal analyzer with a heating rate of 10°C per minute. Figure 1 reveals that epoxy resin (DER 332) starts to react with dicyandiamide at 170°C. This is followed by two exothermic peaks at 200° and 211°C.

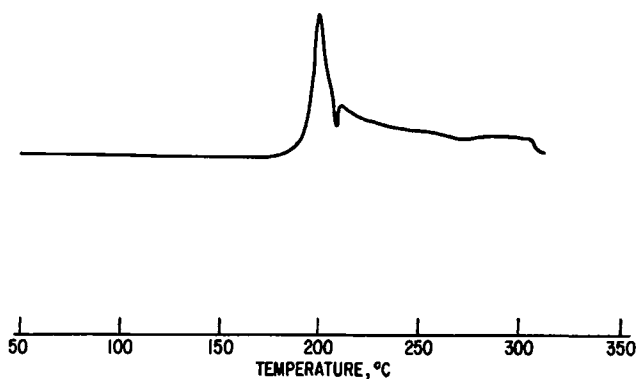


Fig. 1. DSC curve for the reaction between dicyandiamide (10 phr) and epoxy resin (DER 332). Sample size 3.00 mg.

On the other hand, the reaction between 3-(*p*-chlorophenyl)-1,1-dimethylurea and epoxy resin (DER 332) shows only a slight exotherm at 160°C, as shown in Figure 2.

The synergistic effect between 3-(*p*-chlorophenyl)-1,1-dimethylurea and dicyandiamide is shown in Figure 3. Crosslinking starts at 135°C, which is lower than with either of the two previous reactions.

Interestingly, 3-(*p*-chlorophenyl)-1,1-dimethylurea by itself shows no endotherm below 150°C (Fig. 4). The sharp endotherm at 175°C corresponds to its melting point, and the irregularly shaped endotherm in the 200°–230°C region is presumably due to dissociation of the urea into dimethylamine and *p*-chlorophenyl isocyanate.

Dicyandiamide by itself also has a high endotherm, 210°C. It is followed by an exotherm which may be due to decomposition (Fig. 5). Likewise DER 332 (epoxy resin) by itself shows no sign of reaction below 225°C (Fig. 6).

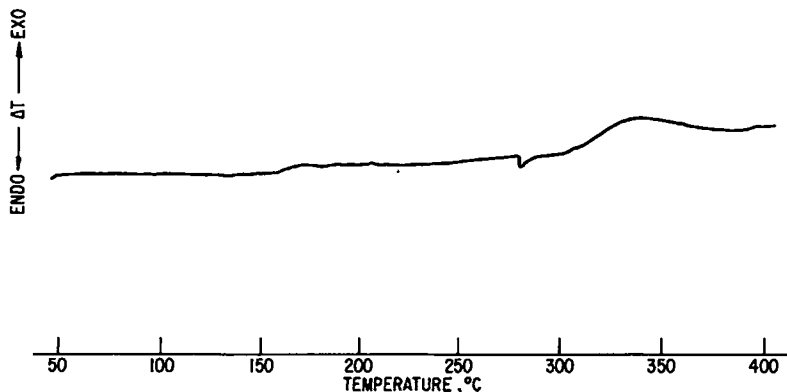


Fig. 2. DSC curve for the reaction between 3-(*p*-Chlorophenyl)-1,1-dimethylurea (3 phr) and epoxy resin (DER 332). Sample size 3.08 mg.

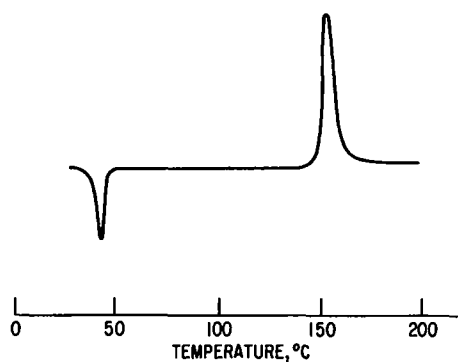


Fig. 3. DSC curve for crosslinking epoxy resin (DER 332) in the presence of dicyandiamide (10 phr) and 3-(*p*-chlorophenyl)-1,1-dimethylurea (3 phr). Sample size 2.79 mg.

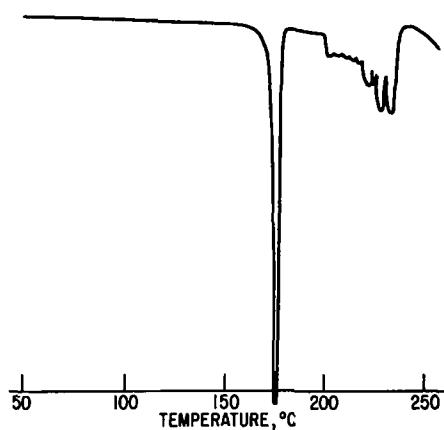


Fig. 4. DSC curve of 3-(*p*-chlorophenyl)-1,1-dimethylurea (rate of heating, 10°C per min; ΔT scale, 0.2°C/in.).

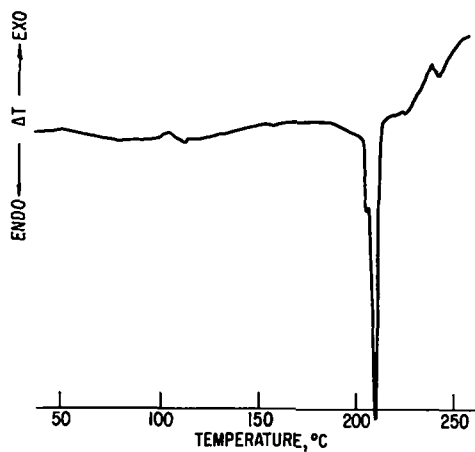


Fig. 5. DSC curve for dicyandiamide.

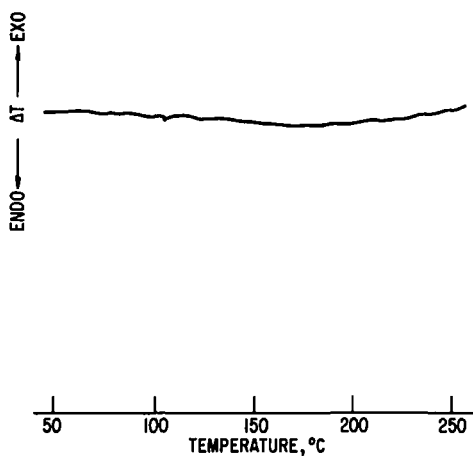


Fig. 6. DSC curve of DER 332.

The synergistic effect between dicyandiamide and 3-(*p*-chlorophenyl)-1,1-dimethylurea in epoxy resin curing may be shown more dramatically by running exotherm profiles. Thus, 4 g of each component are placed in a test tube which is immersed in a constant-temperature (120°C) bath. A thermocouple probe is inserted into the sample and the temperature is recorded versus time. The results are shown in Figure 7. The mixture of

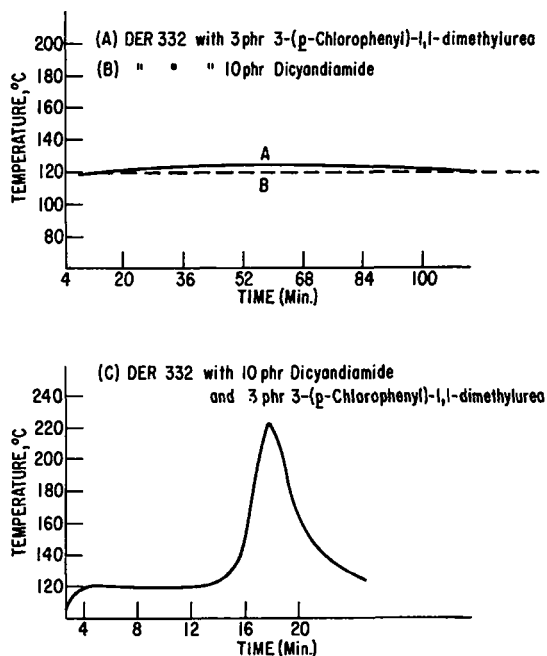


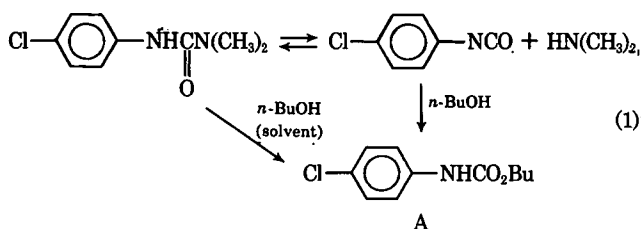
Fig. 7. Exotherm profile.

DER 332 and 3-(*p*-chlorophenyl)-1,1-dimethylurea (line A) has a slight exotherm after 18 to 20 min at 120°C. The sample becomes clear amber and remains a fluid at 120°C even after 60 min. The DER 332 dicyandiamide mixture shows no exotherm or physical change at 120°C after 2 hr.

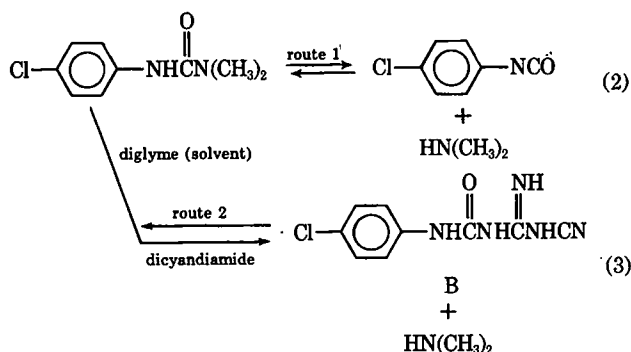
The combination of epoxy resin, dicyandiamide, and 3-(*p*-chlorophenyl)-1,1-dimethylurea begins to exotherm after 8 to 10 min. The 4-g sample foams, and the exotherm peaks at approximately 220°C after 16 to 18 min. The peak exotherms and time to exotherm can vary slightly with successive experiments. This is probably controlled by the effectiveness of the mixing operation since both dicyandiamide and 3-(*p*-chlorophenyl)-1,1-dimethylurea are powders.

It is quite evident from these data that the combination of accelerator and dicyandiamide with epoxy resins is faster curing at 120°C than either system by itself. We also show that 3-(*p*-chlorophenyl)-1,1-dimethylurea dissociates into dimethylamine and *p*-chlorophenyl isocyanate and that this reaction is facilitated by dicyandiamide.

If Monuron is in equilibrium with *p*-chlorophenyl isocyanate and dimethylamine, then one should be able to isolate dimethylamine as well as *p*-chlorophenyl isocyanate. Indeed, we isolated 11% of dimethylamine as the hydrochloride and 7% of *p*-chlorophenyl isocyanate as *p*-chlorophenyl *n*-butylcarbamate (A): The relatively low yields prompted us to

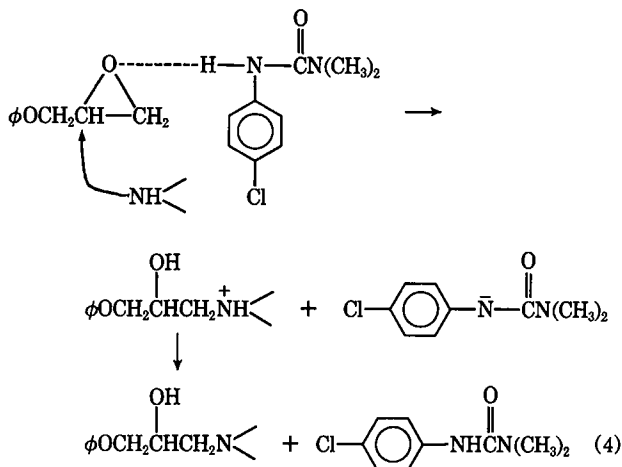


question whether the carbamate A is produced by direct nucleophilic attack of the oxygen atom of *n*-butyl alcohol on the carbonyl carbon atom of Monuron or by the reaction *p*-chlorophenyl isocyanate with *n*-butyl alcohol. With the hope of clarifying this point we studied the decomposition of Monuron with and without dicyandiamide. If dicyandiamide acts as a nucleophile and participates in the process of releasing dimethylamine from Monuron, one would expect to get more dimethylamine in the presence of dicyandiamide. We isolated 5.6% of dimethylamine in the presence of dicyandiamide and only 0.8% in the absence of dicyandiamide (the yields are based on Monuron used). Diglyme was used as the solvent. Also, we isolated 1-cyano-3-(*p*-chlorocarbanilino)guanidine (B) in 35.5% yield in the former case. If the establishments of equilibrium in both routes one and two are very slow and the rate determining step is the forward reaction in route 2, then the amount of dimethylamine formed should not exceed the equimolar amount of compound B:

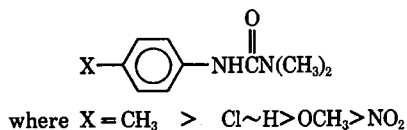


The dimethylamine so released will attack the oxirane group of epoxy resins and cure the resin through the mechanism which Saunders et al. proposed.¹ However, it is premature to conclude that dimethylamine released from Monuron is the sole active species which catalyzes epoxy resin cures in the presence of Monuron and dicyandiamide. Other alternatives have been considered:

a. Monuron may act as an acid, as illustrated in reaction (4):



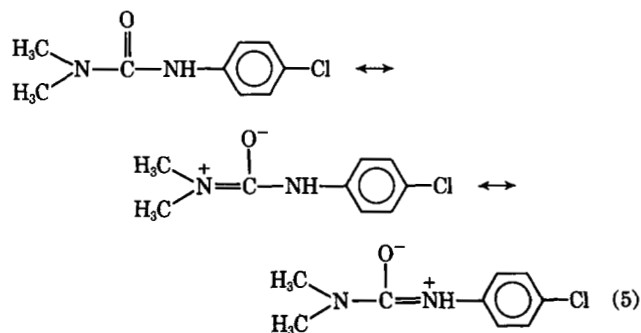
If it does, one would expect 3-*p*-nitrophenyl-1, 1-dimethylurea to be more reactive than Monuron. However, according to published data², 3-*p*-nitrophenyl-1, 1-dimethylurea is less active. The reactivity of 1-aryl-3, 3-dimethylureas decreases in the order shown in the presence of dicyandiamide:



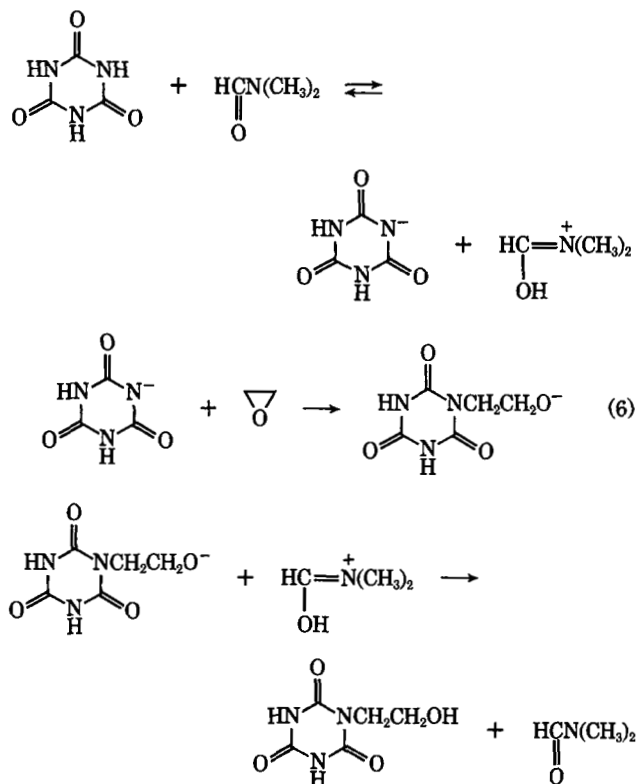
b. If Monuron acts as a nucleophile, then it is obvious that the sulfur analog should be more reactive than Monuron. Although we failed to

synthesize 3-*p*-chlorophenyl-1, 1-dimethylthiourea, we were able to compare the gel time of an epoxy resin accelerated either by Monuron or 3-phenyl-1, 1-dimethylthiourea. There was no appreciable difference.

c. Monuron could act as a base:



The case where an amide acts as a base is not unprecedented. For example, cyanuric acid reacts with ethylene oxide in the presence of DMF or dimethylacetamide:



A major drawback of this mechanism lies in the fact that the concept of base cannot explain why there is an outstanding steric effect. For example, 2,4-toluene diisocyanate blocked by dimethylamine is an excellent accelerator, whereas the one blocked by diethylamine is poor.²

In short, we believe the in situ formation of dimethylamine from Monuron and the participation of dicyandiamide in this process are important factors to be considered in explaining the mechanism of the Monuron-accelerated dicyandiamide cure of epoxy resins.

EXPERIMENTAL

Isolation of Dimethylamine Hydrochloride and *p*-Chlorophenyl *n*-Butylcarbamate

In a 500-ml three-necked flask, equipped with a condenser, two traps, and a dropping funnel, 250 ml *n*-butyl alcohol is placed and heated to reflux. To the stirred *n*-butyl alcohol is added 21.5 g Monuron. Nitrogen is bubbled in. After heating 3 1/2 hr, the resulting slurry is cooled to room temperature and filtered, recovering 8.8 g Monuron. The filtrate is concentrated by a stream of nitrogen. The semisolid left is digested with two 200-ml portions of hot hexane. The insoluble solid is an additional 5.7 g of Monuron. The hexane extracts are concentrated, leaving 1.6 g *p*-chlorophenyl *n*-butylcarbamate (mp 70–72°C, from hexane). The structure is confirmed by IR and NMR spectra. Concentration of the material in the first trap left 0.9 g dimethylamine hydrochloride (hygroscopic). Its structure is further confirmed by comparison of the IR spectrum with that of an authentic sample.

Isolation of 1-Cyano-3-(*p*-chlorocarbanilino)guanidine

In a 500-ml three-necked flask is placed 200 ml bis(2-methoxyethyl) ether and heated to 112°C. To this stirred solvent are added 12.8 g (0.064 mole) 3-(*p*-chlorophenyl)-1, 1-dimethylurea and 47.2 g (0.56 mole) dicyandiamide. The reaction is maintained at 112–118°C. After 3 1/2 hr, an exothermic reaction takes place, and the slurry becomes a light brown solution at 163°C. Heating is terminated at this point. When the pot temperature reaches 119°C, after 10 min a slurry is formed again. The resulting slurry is further cooled and stirred for 3 1/2 hr, and filtered to remove 16.2 g unreacted dicyandiamide. The filtrate is concentrated by removing the solvent at reduced pressure, leaving 18.0 g of grey solid. Only DMF-insoluble solid (5.4 g, 35.5% yield) is the desired product. It does not melt up to 300°C and is insoluble in common organic solvents. The IR (carbonyl band at 1690 cm⁻¹) and mass spectra of this product are in harmony with the open chain product. The molecular weight by mass spectroscopy is 237, which agrees with the title compound.

References

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2. A. C. Nawakowski, A. M. Schiller, and S. S.-N. Wang, U.S. Pat. 3,386,955 (1968); to American Cyanamic, Co., U.S. Pat. 3,386,966 (1968).

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