# Reactivity of Epoxy Resin in Dispersed Dicyandiamide System and Dynamic Viscoelasticity of the Resulting Product

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## Synopsis

A study was made on the curing reaction, leading to a cross-linked network, of bisphenol A diglycidyl either in a dispersed dicyandiamide (DICY) system containing benzyl dimethylamine accelerator and on the dynamic viscoelasticity of the resulting product as related to the DICY particle size (Ds), and compared with a dissolved DICY system. The curing reaction rate varied inversely with logarithmic Ds and directly with the total surface area of the DICY particles, and the finally attainable extent of reaction of the epoxide group decreased with increasing Ds. Activation energy ranged from 14 to 17 kcal/mole depending slightly on Ds. The dynamic viscoelasticity of the cured product was also affected greatly by Ds. Cured product from the system with a 3 μm DICY displayed only a primary transition peak around 180°C in plots of viscoelastic decrement as a function of temperature. With DICY of larger than 10 μm Ds, the number of transition peaks increased to two or three, with a primary peak, a secondary peak around 140°C, and a tertiary peak around 90°C. The relative height of the secondary or tertiary peak increased with increasing Ds. The reaction of the dissolved DICY system proceeded at much the same rate as the 25 μm Ds system, but yielded a cured product with viscoelasticity similar to that of the 3 μm Ds system.

## INTRODUCTION

This paper deals with the curing reaction of bisphenol A diglycidyl ether (BA type epoxy resin) containing dispersed particles of dicyandiamide (DICY) as curing agent and benzyl dimethylamine (BDMA) as accelerator, and the viscoelasticity of the resulting product, both as a function of the DICY particle size.

DICY remains stable and unreacted at room temperature for six months or more after its addition to epoxy resin, yet reacts rapidly with epoxy resin when heated to 140–180°C, to form a cured product with excellent mechanical and electrical properties. For this reason DICY is widely employed as a curing agent for printed circuit substrates, structural adhesives, and powder coatings.

In most of these applications DICY is first dissolved in polar solvents such as dimethyl formamide (DMF), as it is insoluble in epoxy resin at up to 180°C or, in the presence of an accelerator, at up to 140°C. For powder coatings and adhesives precluding the use of a solvent, however, DICY must be dispersed in the epoxy resin.

Various studies have been reported on the curing reaction and cured

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products obtained with such dispersed systems.[1,2] However, although the particle size may reasonably be assumed to influence both of these the only known report on this question is by Sacher,[3] who utilized differential scanning calorimetry (DSC) to compare the heat of curing reaction for DICY particle sizes classified as either under 125 μm or between 250 and 500 μm, and found both the rate constant and the order of the reaction to vary significantly with the particle size.

The present study was undertaken to further elucidate the effect of DICY particle size on the curing reaction and the cured product, with more finely classified DICY particle sizes and in comparison with a dissolved DICY system. It was promoted in part by the recent growing need for nonsolvent formulations of epoxy resins both for special applications and for cost reduction.

## EXPERIMENTAL

### Materials

Commercially available Asahi Chemical BA type epoxy resin, having an epoxide equivalent of 189 as measured by the HCl-KI method, was used without further purification. The resin is liquid and its viscosity was 14,000 cps at 25°C.

Commercially available DICY was rough-crushed and then jet-crushed to fine powder, which was sieved and classified into five size groups. The surface-average particle sizes (DS) of these groups, as determined from Stokes' diameter measured by centrifugal sedimentation with 3-heptanone as dispersant, were 3, 10, 22, 50, and 84 μm.

Commercially available BDMA as curing accelerator and DMF and ethyl cellosolve (EC) as solvent were all used without further purification.

## PREPARATION OF SAMPLES

Dispersed DICY systems were prepared by mixing 100 weight parts of BA type epoxy resin and 5.5 weight parts of DICY particles of size 3, 10, 22, 50, or 84 μm, kneading in mixed state at room temperature for about 30 min with a 3-roller kneader to obtain complete particle dispersion, and then adding 0.2 weight of BDMA. This formulation corresponds to 0.5 equivalent of DICY for each 1.0 equivalent of epoxy resin.

The dissolved DICY system was prepared by dissolving a portion of the above dispersed 84 μm DICY system in a solvent containing a 1:1 weight ratio of DMF and EC.

## MEASUREMENTS

### *Heat of Curing Reaction*

The heat generated during the progress of the curing reaction was measured with a Model DT-30 differential scanning calorimeter (DSC) from Shimazu Seisakusho, for samples of about 20 mg from each system. For the

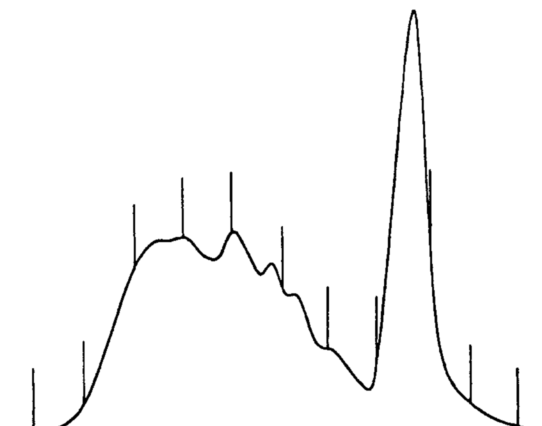

Fig. 1. GPC chart of the 3 μm dicy dispersed system, reacted for 4 minutes at 140°C.

dissolved system sample, the DSC measurement was made immediately after weighing, without evaporating the solvent. A sample of the 3 μm dispersed system which had previously been completely cured was submitted to DSC measurement under identical conditions, to establish the reference baseline. The total heat of reaction was determined from the area bounded by the DSC curve of the sample and the reference baseline.

### *Number-Average Molecular Weight*

The number-average molecular weight ($M_n$) before gelation was determined by gel permeation chromatography (GPC) with a Model HLC-830 from Shimazu Seisakusho and a series of four columns consisting of A-805 from Showa Denko and HGS-20, 15 and 10 from Shimazu Seisakusho. Each sample was dissolved in tetrahydrofuran to obtain a 1% solution. The flow rate of the carrier tetrahydrofuran was 0.9 mL/min. For example the GPC chart of 3 μm DICY dispersed system, reacted for 4 mins at 140°C is shown in Figure 1. $M_n$ was calculated by the equation $M_n = \Sigma H_i/\Sigma(H_i/M_i)$, where $H_i$ is the height of the effluent curve from the base line at 0.45 mL elution volume and $M_i$ the molecular weight corresponding to each elution volume, as determined from the calibration curve.

### *Concentration of Epoxide Group*

Cured product was crushed to powder, mixed with KBr, and tableted, and the epoxide group concentration was then determined by the base line method from absorption at 916 cm$^{-1}$ with antisymmetric stretching vibration of the epoxide group, with a model IR-430 infrared spectroscope from Shimazu Seisakusho.

### *Dynamic Viscoelasticity*

The dynamic viscoelasticity of cured product from each system was measured with a torsional braid analyzer (TBA) from Resca. About 20 mg of the sample was impregnated into a fiber glass torsional braid 1 mm in diameter

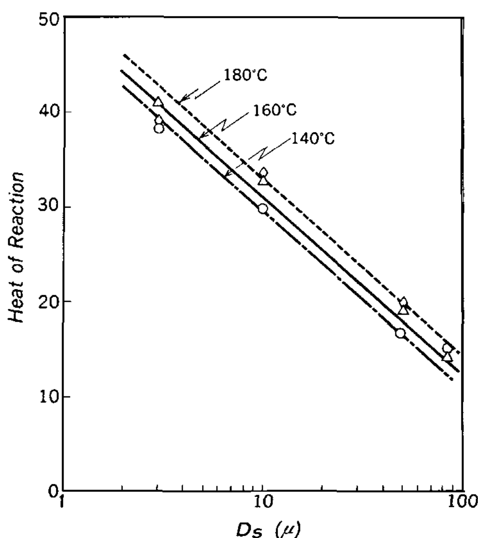


Fig. 2. Heat of reaction determined by DSC as a function of DS of DICY.

and 60 mm long. The impregnated braid was heated in a horizontal position at 170°C for 1 hr and then placed in the TBA. Logarithmic decrement (λ) was measured over the range of 25 to 250°C.

## RESULTS

The generation of heat during the curing reaction in each dispersed DICY system was measured isothermally at 140, 160, and 180°C, to obtain exothermal curves from which the maximum exothermal point and total heat of reaction were determined.

As shown in Figure 2 the total heat of reaction, which is an indicator of the extent of the reaction, decreased in nearly linear inverse proportion to logarithmic Ds and was relatively unaffected by the curing temperature. This indicates less complete curing reactions for systems with large DICY particle sizes. The direct relation between the total heat of reaction and the extent of the reaction is shown by Figure 3, which was obtained by IR spectroscopic analysis of the epoxide group in the product cured at 160°C.

The dissolved DICY system generated 25.1 cal/g at 160°C. Reference to Figure 2 shows this to correspond to the heat of reaction of a dispersed DICY system with Ds of approximately 25 μm, thus suggesting transformation of the dissolved DICY system from a homogeneous to a heterogeneous one in the course of the solvent evaporation.

Figure 4 shows curing reaction extent as a function $\int dH/H_0$ of curing time,[4,5] with $H_0$ as the total heat of reaction and $dH$ as the heat generated between curing times $t$ and $t + dt$. The maximum exothermal points are also indicated. The effect of Ds on the rate of reaction appears relatively small at 140 and 160°C, but it is quite noticeable at 180°C.

The rate constant at the maximum exothermal point, as determined from

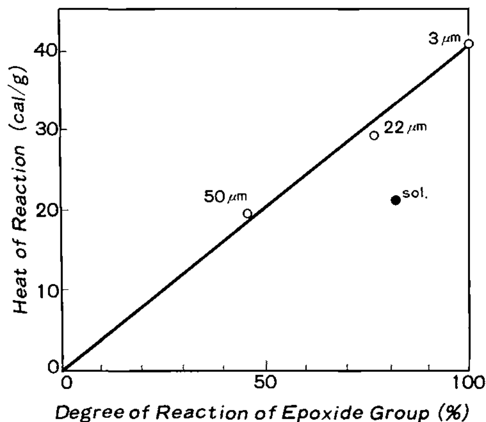


Fig. 3. Relation between extent of epoxide group reaction and heat of reaction at 160°C.

Figure 4 according to the method of Miyamoto et al.,[6] is shown as a function of Ds in Figure 5. The rate constant decreases linearly with increasing logarithmic Ds at all three curing temperatures, but exhibits steeper gradients at the higher curing temperatures.

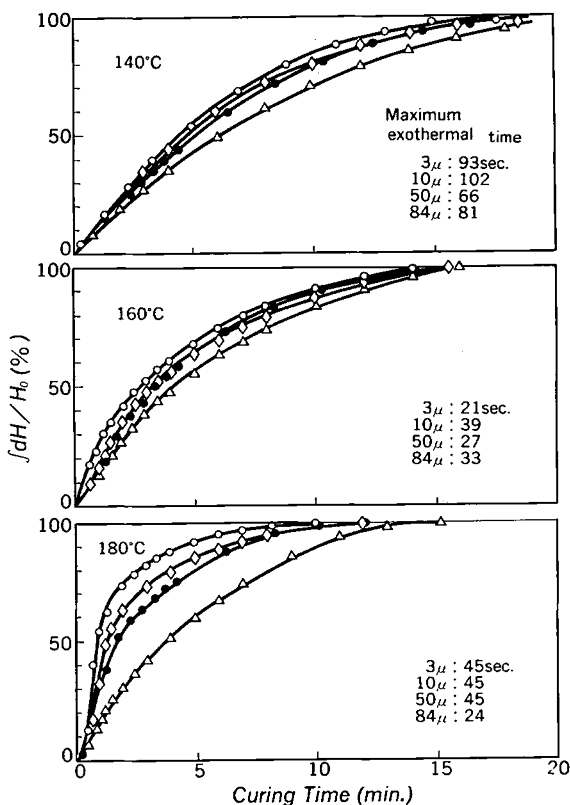


Fig. 4. Effect of Ds of DICY on rate of curing reaction. ○: 3 μm, ◇: 10 μm, ●: 50 μm, △: 84 μm.

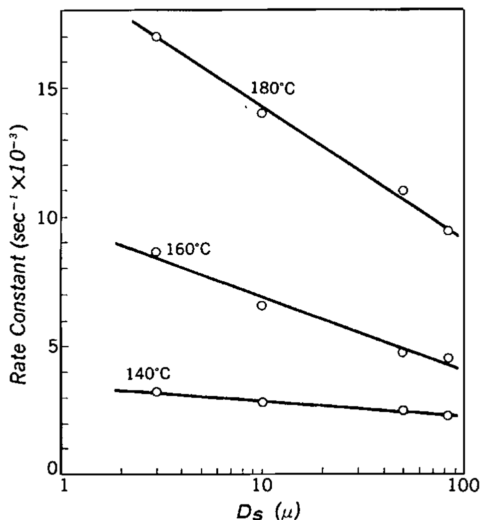


Fig. 5. Rate constant at maximum exothermal point as a function of Ds of DICY.

## INCREASE IN MOLECULAR WEIGHT

The $M_n$ increase can therefore be observed only in the early stage of the reaction. Figure 6 shows the increase in $M_n$, at 140°C, observed in dispersed DICY systems with Ds of 3 and 50 μm and in the dissolved DICY systems, as a function of curing time.

The course of the $M_n$ increase varied markedly with varying Ds. The system with Ds of 3 μm increased in Mn to gelation in a relatively short time, but the $M_n$ increase of the system with Ds of 50 μm proceeded at a

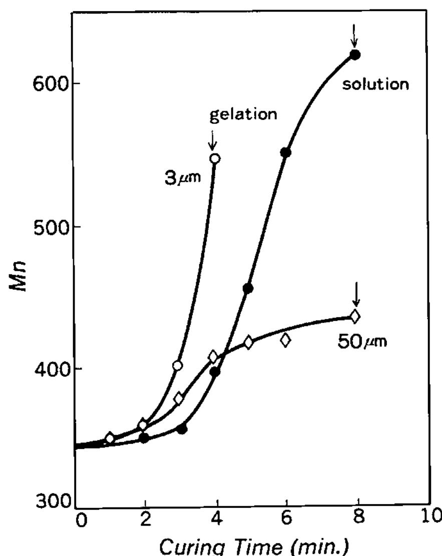


Fig. 6. Increase in Mn with curing time at 140°C.

slower rate and gelation occurred at a lower $M_n$ level. The dissolved DICY system proceeded in a manner similar to that of the 3 μm DICY dispersed system, but with a delayed onset in $M_n$ increase. This delay is presumably attributable to evaporation of the solvent. A separate evaporation test indicated a period of 3 mins at 140 C for a 65% solution system to become 100% solid.

## DYNAMIC VISCOELASTICITY OF CURED PRODUCT

The temperature dependence of λ in cured products from the dispersed DICY and dissolved DICY systems, as determined by TBA,[7] is shown in Figure 7. The dissolved system shows only one (primary) transition peak around 180°C, but the behavior of the dispersed systems varied greatly with Ds. With the 3 μm DICY systems only the primary peak was observed around 180°C, similar to that of the dissolved DICY system. In contrast, the 10 μm DICY system displayed both a primary peak and a secondary peak around 140°C. A tertiary peak was observed around 90°C in addition to the primary and the secondary peak with the 22 μm and 50 μm DICY system.

To allow clearer characterization of the peaks found by TBA and the related roles of the BDMA accelerator and DICY, DICY-free epoxy resin containing BDMA in a weight-part ratio of 100 to 10 was completely cured by 80°C for 2 hr and 180°C for 6 hr, and then subjected to TBA. The resulting plot of λ with temperature change displayed only one peak around 140°C, as shown in Figure 8. This indicates the secondary peaks of Figure 7 may be associated mainly with a BDMA-cured epoxy structure, and the primary and tertiary peaks with a DICY-cured epoxy structure in which the curing was accelerated by BMDA.

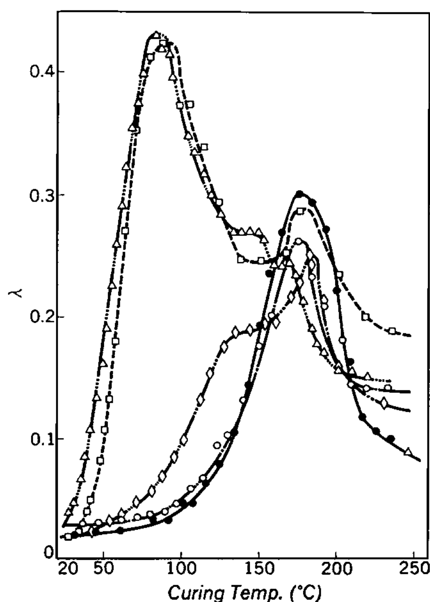


Fig. 7. Effect of Ds of DICY on dynamic viscoelasticity of cured epoxy resin. ○: 3 μm, ◇: 10 μm, △: 22 μm, □: 50 μm, ●: solution.

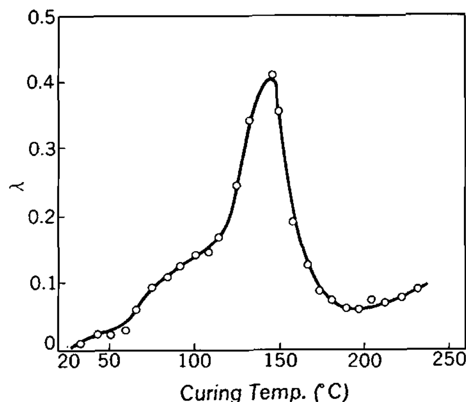


Fig. 8. Dynamic viscoelastic behavior of epoxy resin cured with BDMA only.

## DISCUSSION

The present study shows Ds to be a decisive factor in the curing reaction of the DICY dispersed BA type epoxy resin. The larger Ds was, the slower was the curing rate and the lower the finally attainable extent of reaction of the epoxide group. The curing rate was in part dependent on temperature, but also at a given constant temperature decreased inversely with logarithmic Ds. It has been reported that DICY first reacts with epoxy resin to form an intermediate product which then serves to assist in further dissolution of the remaining DICY.[8] It is therefore quite conceivable that in the dispersed DICY system this reaction occurs first at the DICY particle surfaces, thus forming an intermediate product layer, and that the DICY molecules then diffuse out through this layer to contribute to chain growth and crosslinking of the epoxy resin. It would then follow that the curing rate should be proportional to the surface area of the DICY particles.

Figure 9 shows Arrhenius plots of the curing reaction rate constants of

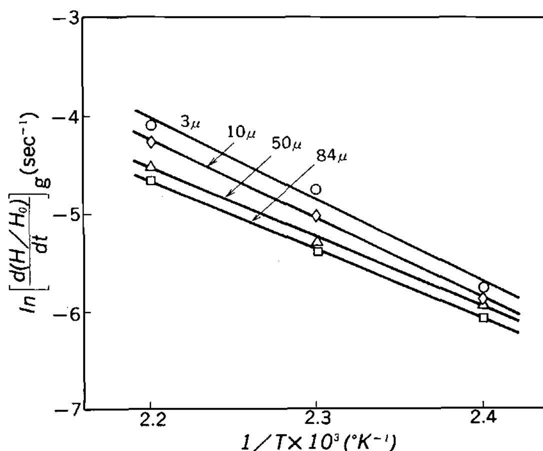


Fig. 9. Arrhenius plots for curing reaction of DICY dispersed epoxy resin.

Figure 5. The activation energy obtained from their gradients ranges from 14 to 17 kcal/mole, depending slightly on Ds. This is in accord with the 16 kcal/mole value reported by Kamon et al.[9]

The decrease in the finally attainable extent of reaction of the epoxide group and the heat of reaction with increasing Ds shown in Figures 2 and 3 may be logically explained by assuming that the curing reaction proceeds around the entire DICY particle before diffusion of the DICY molecules can be completed, and the shell thus formed retards further diffusion of the DICY molecules.

The dynamic viscoelasticity of the cured product was also affected by Ds to a remarkable degree. $\lambda$Curve for the dispersed DICY system of small Ds exhibited only one peak, in almost the same fashion as that of the dissolved DICY system. Systems with larger Ds yielded curves with primary, secondary, and tertiary peaks. The secondary peak may be attributable to the cured epoxy/BMDA structure, as shown in Figure 8, and the primary and tertiary peaks to the epoxy/DICY-cured structure. Increasing the Ds generally led to a lowering of the primary peak and a heightening of the secondary and tertiary peaks. This suggests that the primary peak is associated with a tightly cross-linked structure, and the tertiary peak with a loosely cross-linked structure resulting from insufficient DICY availability. The DICY insufficiency, which is believed to have resulted from a retarding of DICY molecule diffusion by a shell formation with a tightly cross-linked structure, thus may have caused a cured structure marked by loose cross-linking with DICY and a dominant crosslinking with BDMA.

Eyerer[10] and Kamon et al.[9] discuss the effect of DICY sedimentation for cured epoxy resins. Next we tried to clarify the effect. Tetrabrom bisphenol A (TBBA) was blended to BA epoxy resin as a way of controlling the blended resin's specific gravity to DICY's one (1.4 g/cm$^3$ at 25°C) for neglecting DICY sedimentation. Figure 10 shows dynamic viscoelastic behavior of cured epoxy-

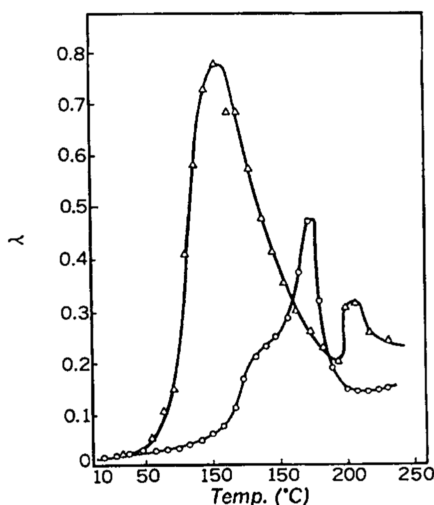


Fig. 10. Dynamic visco-elastic behavior of cured epoxy-TBBA resin the specific gravity of which is same as one of Dicy, ○: 3 μ; △: 50 μ.

TBBA resin with dispersed DICY by TBA. With 3 μm DICY system the primary peak was observed around 170°C, similar only to epoxy resin. 50-μm DICY system displayed both a primary peak and a secondary peak. Therefore, we believe the DICY sedimentation effect is able to neglect.

In regard to the dissolved DICY system, even though it might seem plausible to assume that system homogeneity is maintained as the curing reaction proceeds, the present study suggests that DICY precipitated during evaporation of the solvent and that the subsequent curing reaction proceeds in the same manner as in the dispersed system. In terms of curing rate, the particle size of the precipitated DICY corresponded to crushed DICY particles of about 25 μm, but in terms of viscoelasticity of cured product, to crushed particles of about 3 μm. No simple explanation was apparent for this difference.

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