The Synergistic Effect of Dicyandiamide and Resorcinol in the Curing of Epoxy Resins

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ABSTRACT: The synergistic effect of dicyandiamide (Dicy) and phenolic substances was studied, with resorcinol as a model compound. It was found that when Dicy and resorcinol are used jointly, the curing temperature of epoxy resin can be significantly lowered. FTIR and DSC data were used to illustrate the mechanism of the synergism. The addition of the phenolic hydroxyl group to epoxide was facilitated by Dicy, which favors the formation of phenoxy anions. The reaction of Dicy with epoxide was facilitated by resorcinol, which can exert "electrophilic assistance" for the addition of the amino group to epoxide. The presence of resorcinol also favors the addition of the hydroxyl group to the cyano group. The thermal and mechanical properties of the epoxy resins cured with Dicy/resorcinol or Dicy/phloroglucinol were studied. J Appl Polym Sci 89: 1869–1874, 2003

Key words: resorcinol; dicyandiamide; epoxy resin; synergistic effect; mechanical properties

INTRODUCTION

Dicyandiamide (Dicy) is widely used as a latent curing agent for epoxy resins. It is barely soluble in epoxy resins at room temperature such that resin formulations can be stored for long periods. As the temperature is increased, Dicy dissolves in the resin and the curing takes place. In the process of curing, various reaction pathways are possible.[1–4] The chemical reactions and the network structure of the cured resin, in turn, depend strongly on the temperature regime and the accelerator, which is used for lowering the curing temperature.

Phenolic oligomers such as Novolac are of importance in the formulation of epoxy molding compounds and epoxy adhesives. Epoxy resin systems cured with phenolic oligomers exhibit good physical properties and good thermal resistance.

When phenolic oligomers were used in combination with dicyandiamide for curing epoxy resins, we found a synergistic effect between the two curing agents. The curing temperature and the gel time can be reduced remarkably when both curing agents are present. In this study we report the synergistic effect of Dicy and phenolic oligomers, with resorcinol as a model compound. FTIR and DSC data are used to illustrate the mechanism of the synergism.

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EXPERIMENTAL

Materials

The epoxy resin used in this study was diglycidyl ether of bisphenol F (**Scheme 1**), Epikote 862 (Epon862) from Shell Co. (USA) (epoxy equivalent weight 165 g/mol). Dicyandiamide (Shanghai Reagents Factory, China) was analytically pure. It was pulverized to pass through a 200-mesh sieve. Resorcinol was from Beijing Chemical Factory, and was recrystallized before use. Phloroglucinol was used as received from Beijing Chemical Reagents Co. (China).

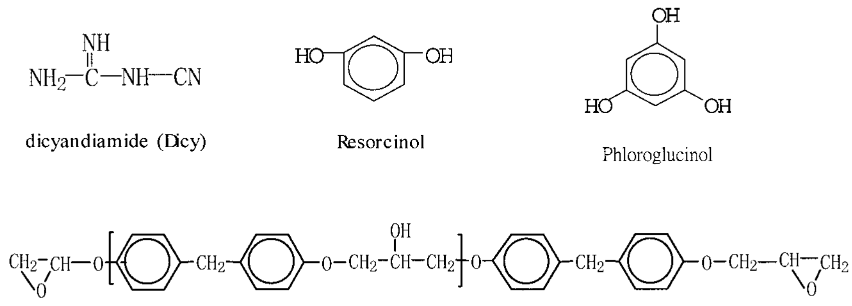
Characterization

FTIR spectroscopy

Infrared spectra were taken on a Perkin–Elmer Model 2000 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Samples were coated on KBr plates. The spectra were recorded in the range of 4000–400 cm^{-1}. Epoxy conversion is given by $X_{FTIR} = 1 - A_{(t)}/A_{(0)}$, where $A_{(0)}$ and $A_{(t)}$ are the ratio of the epoxy peak area to the phenyl peak area at the beginning and at time *t*.

DSC analysis

The curing process was studied by DSC analysis, using a Mettler Toledo 822e apparatus. Scans were run from room temperature to 300°C at a heating rate of 10°C/min under a nitrogen flow.



Scheme 1 Diglycidyl ether of bisphenol F (Epon862).

Mechanical properties

Tensile properties were determined according to the standard GB/T 2568-1995. The gauge dimension of dumbbell-shape specimens was $4 \times 10 \times 50$ mm^3, and the loading rate was 10 mm/min. Flexural tests were conducted according to the standard GB/T 2570-1995. The dimension of specimens was $4 \times 6 \times 55$ mm, the span of supports was 36 mm, and the loading rate was 2 mm/min. An Instron 1122 universal tester was used for the mechanical tests.

RESULTS AND DISCUSSION

The synergistic effect between resorcinol and dicyandiamide

The reactions of the epoxy resin with Dicy or with resorcinol need high temperatures. In the DSC thermogram for the curing of Epon862 with Dicy, the exothermic peak is located at 195°C, and the first peak for the reaction between Epon862 and resorcinol is at 226°C. When both curing agents are present, the peak temperatures are substantially reduced (see Figs. 1 and 2).

As shown by thermogram (3) of Figure 1, glycol is much less effective than resorcinol in lowering the reaction temperature of Dicy, although glycol has the same degree of functionality as that of resorcinol.

In Figure 3 the exothermic peak temperature in the DSC thermograms is plotted against the molar percentage of the phenolic hydrogen in the Dicy–resorcinol curing system and the Dicy–phloroglucinol curing system. The synergistic effect in the curing of the epoxy resin is indicated by the valley in the diagram, which extends from about 30 to 99 mol % of the phenolic reactive hydrogen proportion.

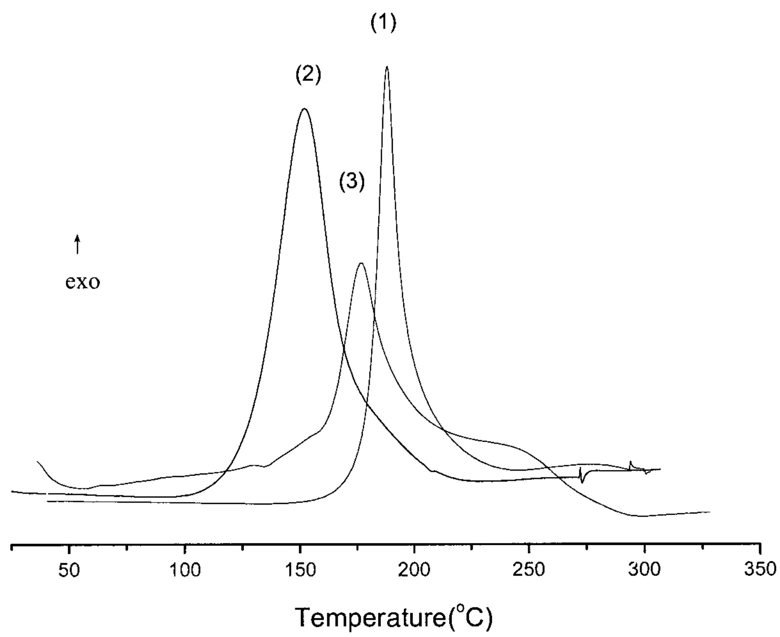


Figure 1 DSC thermograms for (1) Epon862–Dicy. The molar ratio of the epoxy group to the NH group in Dicy was 1 : 1; (2) Epon862–Dicy–resorcinol. The molar ratio of the epoxy group to the NH group in Dicy and the OH group in resorcinol was 1 : 0.5 : 0.5; and (3) Epon862–Dicy–glycol. The molar ratio of the epoxy group to the NH group in Dicy and the OH group in glycol was 1 : 0.5 : 0.5.

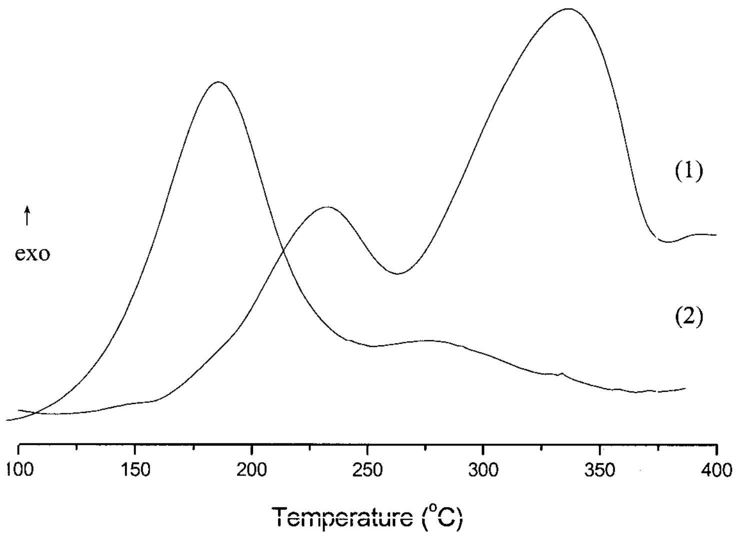


Figure 2 DSC thermograms for (1) Epon862–resorcinol. The molar ratio of the epoxy group to the OH group in resorcinol was 1 : 1; and (2) Epon862–Dicy–resorcinol. The molar ratio of the epoxy group to the NH group in Dicy and the OH group in resorcinol was 1 : 0.1 : 0.9.

It is seen that a small amount of Dicy (1 mol %) is enough to lower the reaction temperature between Epon862 resin and resorcinol. However, the effectiveness of resorcinol for lowering the reaction temperature between Dicy and the epoxy resin was insignificant at low molar levels. The accelerating effect becomes significant on condition that the proportion of reactive hydrogen of resorcinol exceeds 30 mol %.

Curing of the epoxy resin by Dicy–resorcinol is effected through addition of phenol groups to epoxy groups, and the amino groups to epoxy groups. The former reaction, accelerated by Dicy, quickly consumes resorcinol. Consequently, a large proportion of resorcinol is needed to accelerate the reaction of Dicy to any significant degree.

It is seen in Figure 3 that the change of exothermic peak temperature in DSC thermograms with the ratio of phenolic hydrogen to the reactive hydrogen in Dicy is similar for both the Dicy–resorcinol and the Dicy–phloroglucinol curing systems, although the reduction in peak temperatures is slightly less for the latter system. The difference may be accounted for by a higher crosslink density formed in the Dicy–phloroglucinol system.

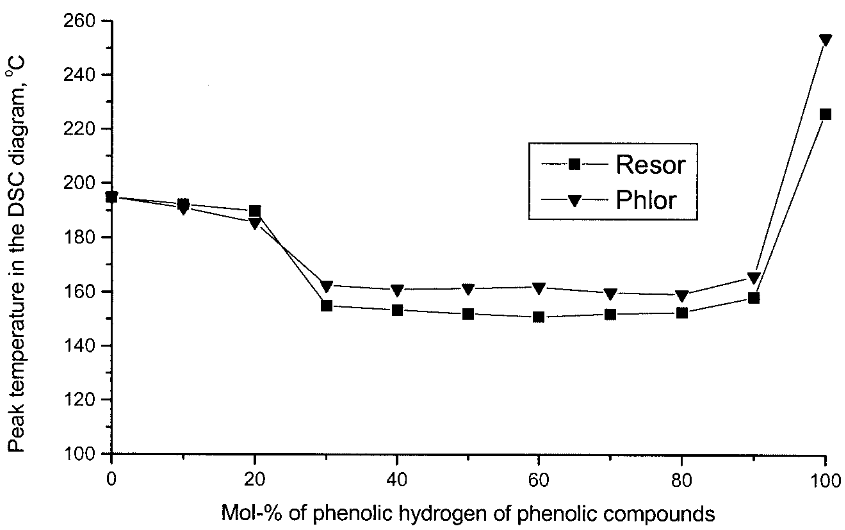
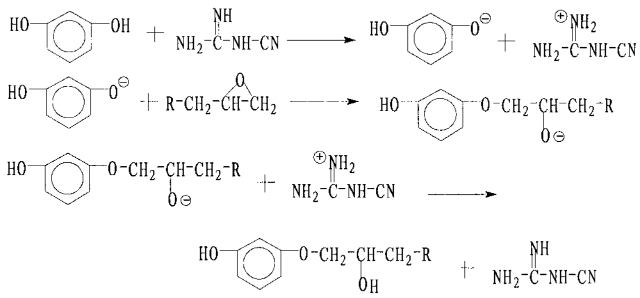
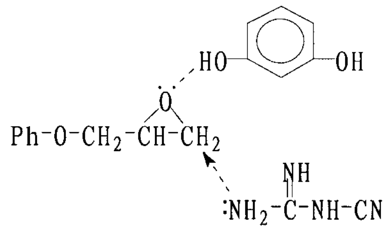


Figure 3 Change of the exothermal peak temperature with the molar percentage of the reactive hydrogen of resorcinol in the dicyandiamide–resorcinol curing system and the dicyandiamide–phloroglucinol system. The molar ratio of the epoxy group to the sum of phenolic hydrogen and amino hydrogen of Dicy was 1 : 1.



Scheme 2 Addition of resorcinol to epoxide catalyzed by Dicy.



Scheme 4 Electrophilic "assistance" for the addition of amine to epoxide.

Reaction of resorcinol with epoxide

Addition of resorcinol to the epoxide proceeds through the nucleophilic attack of the phenoxy anion to the epoxy group. Alkaline substances facilitate phenoxy anion formation. They are thus able to catalyze the reaction.

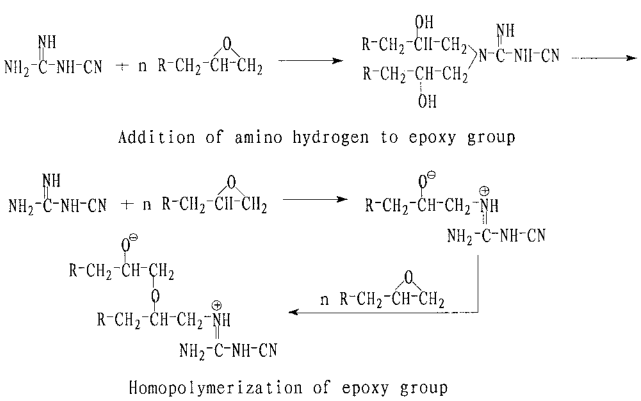
The reaction of resorcinol with epoxide catalyzed by Dicy is illustrated in **Scheme 2**. It is well known that guanidine is a very strong organic base. Although the basicity is reduced by substitution with a cyano group, cyan guanidine (i.e., dicyandiamide) is still quite a strong base. A proton of resorcinol is abstracted by Dicy to form a phenoxy anion. The latter attacks the epoxy group to complete the addition.

Therefore, Dicy is an effective catalyst for the cure of epoxy resin with phenolic oligomers. Curing of epoxy resins can be accomplished at 170°C when 1 phr Dicy is incorporated.

Reaction of Dicy with epoxide

The curing mechanism of epoxy resin with Dicy has been extensively studied, and various possible reaction pathways and products have been proposed.[1–4]

In the initial stage, the addition of amine hydrogens to the epoxy group is in competition with epoxy homopolymerization (**Scheme 3**).



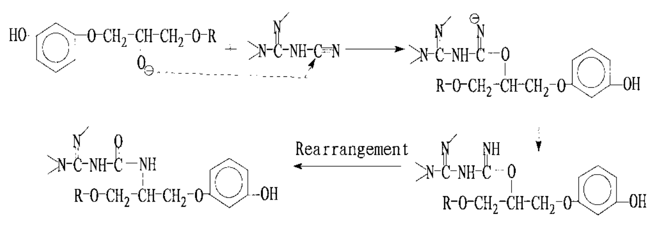
Scheme 3 Reactions in the cure of epoxy resin with Dicy.

There are both physical and chemical grounds for acceleration of the reaction of Dicy with epoxide in the presence of resorcinol. Physically, resorcinol can improve the solubility of Dicy in the epoxy resin, and thus facilitate the reaction. It was found that the epoxy–Dicy–resorcinol system turned transparent in 0.5 h at 80°C, whereas the epoxy–Dicy system remained opaque after 1.5 h. The chemical ground may be more important: resorcinol can promote the amine addition to epoxide by "electrophilic assistance,"[5] as shown in **Scheme 4**.

The catalytic effect of aliphatic alcohols, such as glycol, was insignificant, as shown in Figure 1. It suggests that the acidity of the hydroxyl group is essential to the "electrophilic assistance" for the addition of Dicy to epoxide. Resorcinol is effective because of its acidity.

In the later stage of the curing of epoxy resin with Dicy, the addition of hydroxyl groups to cyano groups and rearrangement of the reaction product become significant (**Scheme 5**).[2,6] A high temperature favors the rearrangement to form guanylurea derivatives. The addition to cyano groups promotes intramolecular cyclization or intermolecular crosslinking.

In IR spectra, the appearance of the 1640 and 1740 cm^{-1} bands indicates the formation of guanylurea derivatives[2] (Fig. 4). It is interesting to point out that resorcinol significantly facilitates the formation of guanylurea. The data for the conversion of epoxy group at the moment when the 1740 cm^{-1} band became visible (the absorbance reached 0.15) are summarized in Table I. In the Epon862–Dicy system, the 1740 cm^{-1} band became visible when 73% of the epoxy group was consumed. By comparison, only 52% of



Scheme 5 Addition to cyano group and rearrangement of the product.

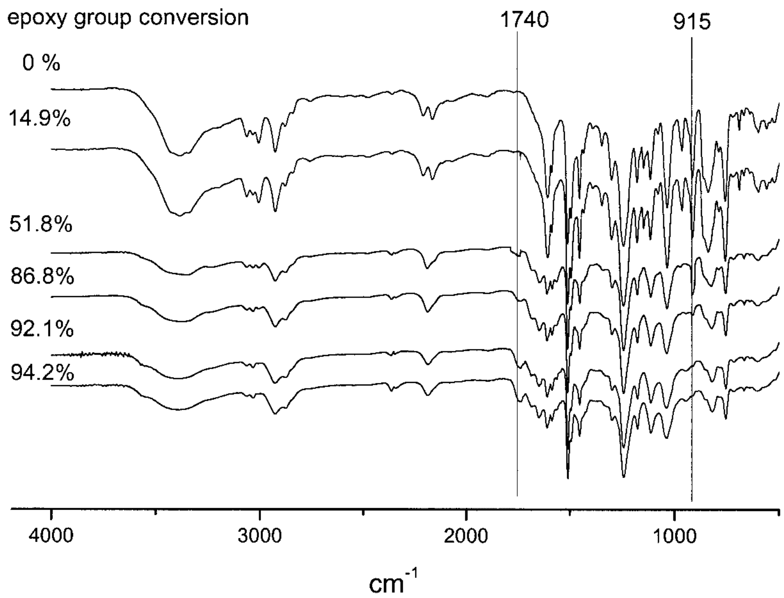


Figure 4 Change of IR spectrum in the course of curing for an Epon862–Dicy–resorcinol system. The molar ratio of the reactive hydrogen of resorcinol to that of Dicy was 3 : 7 at 150°C.

the epoxy group was used in the Epon862–Dicy–resorcinol system (molar ratio of the epoxy group : OH : NH = 1 : 0.3 : 0.7) as the 1740 cm^{-1} band became visible, where the conversion of the epoxy group was calculated according to the intensity of the 915 cm^{-1} band. The early appearance of guanylurea derivatives additionally suggests that the curing with Dicy was accelerated by resorcinol through facilitating the reaction of cyano groups.

Network structure and the glass-transition temperature

The network structure of the cured resin depends on the composition of the system. Because resorcinol is a bifunctional compound, it reacts with Epon862 to form linear polymers. Therefore, cured resins of low glass-transition temperature (T_g) were obtained when resorcinol was the main component, along with a minor amount of Dicy to catalyze the addition.

When resorcinol is included in the network of epoxy resin and Dicy, the crosslinking density will be lowered. On the other hand, resorcinol facilitates the addition of hydroxyl groups to cyano groups, as discussed above. Therefore, the reduction in crosslinking density will be compensated to some extent [curve (1) in Fig. 5]. When the phenolic hydroxyl group of resorcinol constituted 30 mol % of the total reactive hydrogen, a reduction in the T_g for about 10°C was found. The cost is acceptable for reducing the curing temperature.

Phloroglucinol is a trifunctional phenolic compound. Therefore, when phloroglucinol was used in combination with Dicy for curing the epoxy resin, the crosslinking density of network was influenced to a lesser degree. As shown by curve (2) of Figure 5, the T_g of the cured resin was not changed significantly by incorporation of phloroglucinol.

Mechanical properties of cured resins

Good mechanical properties of the cured epoxy resin can be achieved when the proportion of Dicy–resorcinol or Dicy–phloroglucinol curing systems is properly adopted. It is seen in Table II that for the Dicy–resorcinol curing system, as the proportion of resorcinol hydroxyl group increased from 30 to 60 mol %,

TABLE I
Effect of the Molar Ratio of Epoxy Group : OH : NH on the Appearance of the 1740 cm^{-1} Band in the IR Spectrum for the Epon862–Dicy–Resorcinol System[a]

Molar ratio of epoxide : OH : NH	1.0 : 0 : 1.0	1.0 : 0.1 : 0.9	1.0 : 0.2 : 0.8	1.0 : 0.3 : 0.7	1.0 : 0.4 : 0.6
Conversion of epoxy group (%)	73	58	55	52	53

[a] Reaction temperature: 150°C.

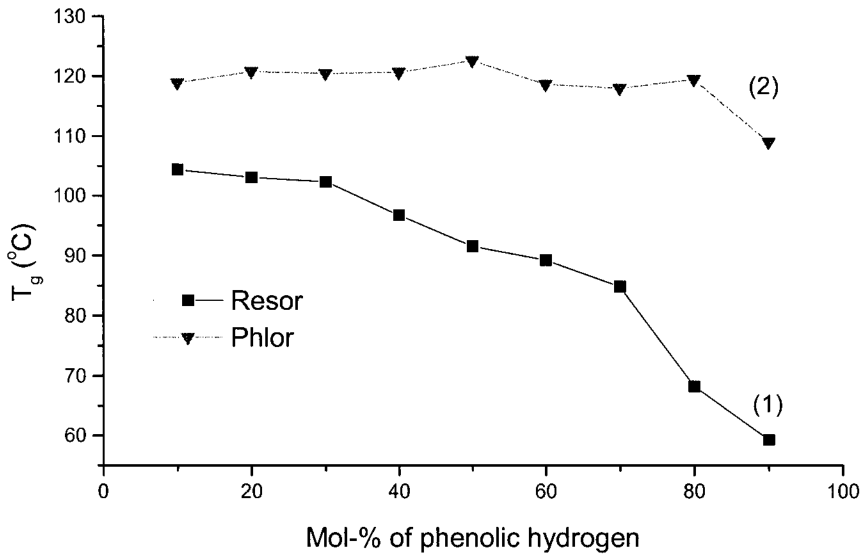


Figure 5 T_g of the cured resin versus molar percentage of phenolic hydrogen in the curing agent systems: (1) Epon862–Dicy–resorcinol and (2) Epon862–dicyandiamide–phloroglucinol. Curing conditions: 150°C, 1 h; and 170°C, 1 h.

the strength and the modulus of the cured resin decreased, whereas the elongation at break improved consistently. This trend is attributed to the reduction of crosslinking density with the increased proportion of resorcinol.

For the Dicy–phloroglucinol curing system, however, the properties of the cured resin are less sensitive to the ratio of the two substances. Good strength and modulus, and high elongation to break were achieved at high proportions of phloroglucinol, as shown by the data given in Table II. It is suggested again that crosslinking density of the cured resin is only slightly dependent on the proportion of Dicy to phloroglucinol.

TABLE II
Mechanical Properties of Epoxy Resins Cured with Dicy–Resorcinol or Dicy–Phloroglucinol[a]

Molar ratio of epoxide : OH : NH[b]	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
1 : 0 : 1	158.2	3.18	63.1	5.8
1 : 0.3 : 0.7 (Di)	150.3	3.04	67.0	6.5
1 : 0.4 : 0.6 (Di)	138.4	3.01	59.6	6.8
1 : 0.6 : 0.4 (Di)	137.4	2.98	50.8	8.9
1 : 0.6 : 0.4(Tri)	154.6	3.17	61.7	6.1
1 : 0.5 : 0.5(Tri)	154.5	3.09	61.5	6.4

[a] Curing regime: 100°C/1 hr + 150°C/1 hr + 170°C/1 hr.
[b] "Di" and "Tri" stand for resorcinol and phloroglucinol, respectively.

CONCLUSIONS

Both the curing of epoxy resin with Dicy and the curing of epoxy resin with resorcinol require a high temperature. When Dicy and resorcinol are used jointly, the curing temperature can be greatly reduced. The addition of the phenolic hydroxyl group to epoxide is facilitated by Dicy, which favors the formation of phenoxy anions. The reaction of Dicy with epoxide is facilitated by resorcinol, which can exert an "electrophilic assistance" for the addition of amino group to epoxide. The presence of resorcinol also favors the addition of the hydroxyl group to the cyano group. The crosslinking density of the epoxy network is dependent on the composition of the curing agent system. When trifunctional phloroglucinol is used in combination with Dicy, cured resins of good mechanical properties and high T_g can be obtained.

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