

Epoxy resin curing by dicyandiamide using model compounds

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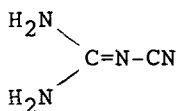
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Summary

The reaction behaviour of different accelerated homogeneous epoxy-dicyandiamide systems was studied using phenyl glycidyl ether as a model and as solvent *N,N*-dimethylformamide. *N,N*-dimethylbenzylamine, imidazole, 2-methylimidazole were applied as accelerators. The reaction course was followed by HPLC and ¹³C-NMR measurements. A reaction mechanism involving a tautomerisation of dicyandiamide depending on temperature is suggested.

Introduction

The cyano substituted guanidine, dicyandiamide (Dicy),



is widely used as a latent curing agent in heat cured epoxy resins for laminates and prepreg fabrication. It is nearly insoluble in liquid glycidyl ethers, but soluble in high polar solvents such as water, alcohols, glycol ethers, ketones or dimethylformamide. Normally a solvent or mixtures of solvents are necessary in technical epoxy resin formulations. Furthermore, some different types of accelerators (tertiary amines, imidazoles, substituted ureas) were used in the curing process.

Although the cure mechanism and the formed network structures of dicyandiamide cured epoxy resin systems have been investigated extensively (1 - 10), no analytical evidence for a predominant reaction course has been presented. The mechanism of an epoxy system based on Dicy is largely dependent on the accelerator, the reaction temperature, the ratio of epoxy/amide and the solvent used.

More information relating to the cure behaviour of this hardener would be useful for understanding and influencing the curing process in technical applications.

Therefore, the aim of this paper is to explain effects of the reaction conditions in homogeneous Dicy-epoxy systems using dimethylformamide (DMF) as a solvent. The model reaction of phenyl glycidyl ether (PGE) with Dicy was studied in the presence of different accelerators (dimethylbenzylamine - DMBA, imidazole - Im and 2-methylimidazole - MeIm) by HPLC and ¹³C-NMR measurements.

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Experimental

PGE was prepared according to ref. (11) (b.p. 96 - 98 °C / 0,4 kPa). Dicy, imidazole and 2-methylimidazole were commercially available and were used without further purification. DMBA was dried with KOH pellets, purified with phenyl isocyanate and distilled under reduced pressure (b.p. 55 - 56 °C / 1.2 kPa). DMF was purified according to ref. (12).

The reactions were carried out in a thermostated three necked flask equipped with a thermometer, magnetic stirrer and reflux condenser.

Epoxyde values were determined by a titrimetric method according to Durbetaki (13).

HPLC samples were run with apparatus from KNAUER (Wissenschaftliche Geräte KG); column: 180 x 3.2 mm with LiChrosorb RP-18, 5 µm; eluent: acetonitrile-water 30 : 70 to 100 : 0 linear; flow: 1.8 ml/min; detection: UV 254 nm; Dicy and DMF are eluted as unretained components at 254 nm; samples: 5 % solution in acetonitrile.

¹³C-NMR spectra were obtained on a Bruker HX90R spectrometer operating at a frequency of 22.635 MHz using d₆-DMSO as solvent.

The mole ratio epoxyde/amide (e/a) was calculated taking into account the number of functional groups (for PGE 1, for Dicy 4) according to ref. (6). The accelerator concentration was applied to the epoxy groups.

Results and Discussion

In a previous paper chromatographic investigations of heterogeneous and homogeneous Dicy-epoxy systems have already been reported by us (14). The advantages for handling and analysis preparing homogeneous reaction mixtures using DMF as solvent were demonstrated. A different reaction course to diffusion controlled heterogeneous systems was detected by HPLC measurements. In order to determine the effect of accelerators a series of reactions was carried out in a temperature range from 80 up to 140 °C. The reaction conditions are summarized in Table 1. Product development was followed by HPLC, and epoxy conversion was controlled using a titration method.

Table 1
Reaction conditions of the kinetic investigation reported in Fig. 1; mole ratio PGE : Dicy : DMF = 4 : 1 : 6

No.	T in °C	accelerator	marking in Fig.1 / 4
1	80	DMBA	o
2	100	DMBA	+
3	100	Im	●
4	100	MeIm	x
5	120	without	+
6	120	DMBA	●
7	120	Im	+
8	120	MeIm	o
9	140	without	x / +
10	140	DMBA	o / o
11	140	Im	x / ●
12	140	MeIm	+ / x

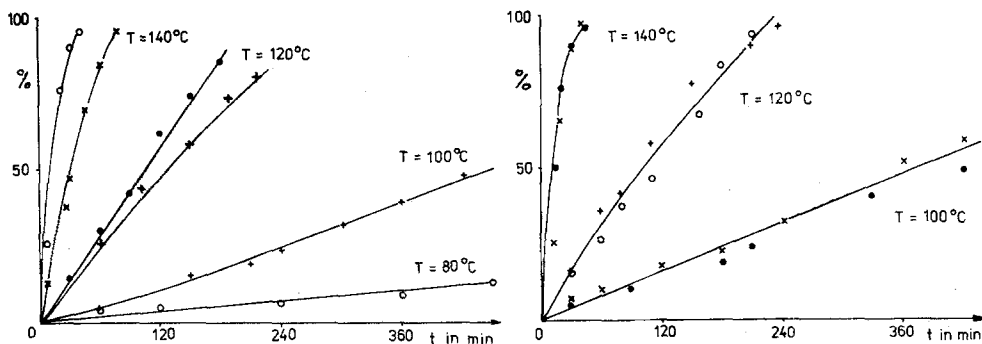


Fig. 1 Epoxide conversion versus time of different accelerated PGE-Dicy-DMF systems depending on temperature (samples see Table 1)

The kinetic course of the reaction is given in Figure 1. Reaction rates in accelerated systems are about two times higher than in systems without accelerator. No differences exist in the catalytic activity of these various accelerator types. In addition, the systems without accelerator reacted relative rapidly referring to the inactivity of solvent free heterogeneous samples up to 140 °C (6, 14). The reaction rate is strongly influenced by the temperature. Activation energies of about 85 kJ/mol were determined for all of the accelerators including the unaccelerated system.

A typical chromatogram of a reaction mixture contains more than 20 peaks. The main products were followed by the integrated peak area. Mostly, about 90 % of peak area based on 10 up to 20 main products (see Fig. 2).

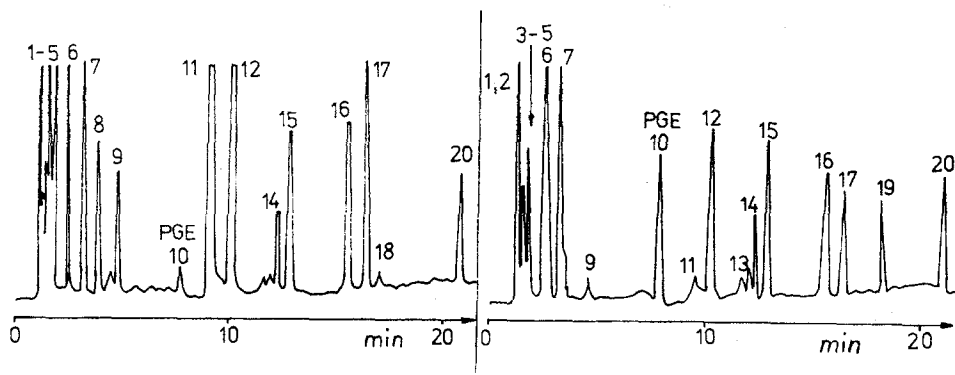


Fig. 2 Chromatogram of the reaction mixture containing PGE : Dicy = 3 : 1 in 30 wt.% DMF at 120 °C
 a) reaction time = 5 h; epoxide conversion > 95 %; without DMBA
 b) reaction time = 1,5 h; epoxide conversion = 95 %; with 2 mole % DMBA

The peak formation is independent on the accelerator used. The content of nonpolar species increased at 120 °C and with epoxy excess. A full conversion of Dicy is only achieved in the presence of epoxy excess for e/a > 1. That is a typical case for the formation of great molecules with etherbonds.

PGE oligomers of type A (see (8, 14)) were found in systems containing a high concentration of DMBA and an excess of epoxy compound. The PGE glycole (1-phenoxy-propane-2,3-diol) was detected in all samples in a low quantity resulting of the reaction of PGE with water. Another typical PGE product formed without Dicy, 1,3-diphenoxypropanol-2, was observed by HPLC too. A summary describing the reaction mechanism leading to glycidyl ether oligomers by tertiary amine initiated anionic epoxy ring opening is given in (8). However, the content of all these oligomers does not reach more than 5 to 10 % peak area under conditions, which are used in practice.

In order to obtain more information about the main reaction course ¹³C-NMR investigations were carried out. The chemical shift of PGE and Dicy carbon atoms is listed in Scheme 1. Similar model compounds were measured to determine the structure of the unknown products. The regions of secondary hydroxyl groups and etherbonds formed in well known epoxy reactions were described in (15). Thus, the new signals in ¹³C-NMR spectra of product mixtures were assigned in the following manner (Scheme 1).

Epoxy conversion and the content of typical new structure units were calculated from relative intensities using an internal standard. The aromatic carbon atoms 5 and 6 show a constant chemical shift during the reaction. Few experimental NMR data are listed and compared with results obtained by HPLC and titration (see Table 2) to check the force of expression.

Table 2

Epoxy consumption determined by different methods for model reactions at 140 °C (reactions 9 - 12 according Table 1)

method	epoxy consumption of reaction											
	9			10			11			12		
¹³ C-NMR	51	74	94	16	44	77	70	93	94	62	77	92
HPLC	55	77	87	-	-	-	60	87	100	56	71	85
Titration	38	71	86	16	43	69	76	91	100	50	76	91

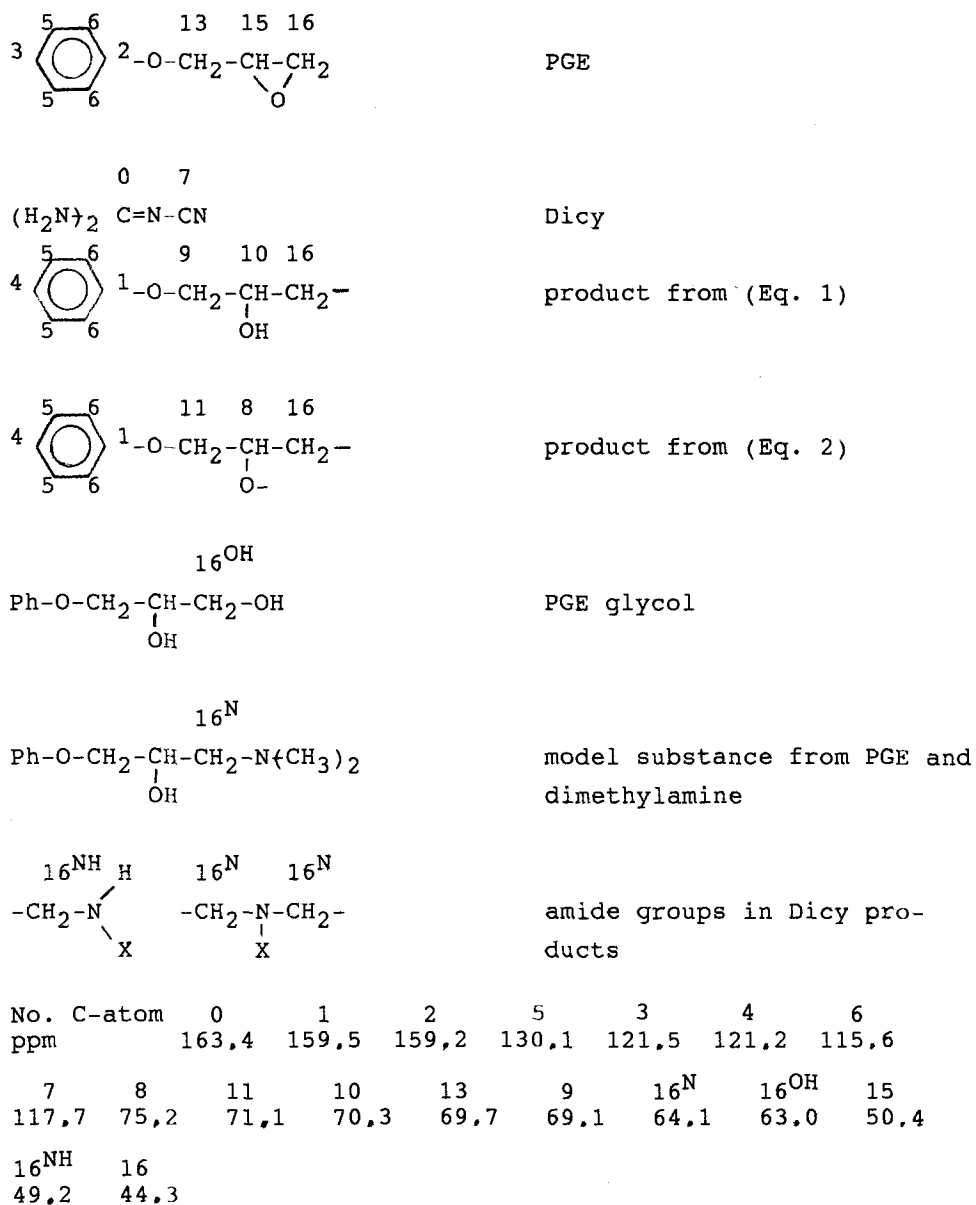
Based on the NMR data the relations for development of secondary hydroxyl groups and etherbonds versus epoxy conversion were determined (Figure 3). It is shown that both main reactions

- epoxy-amide-addition (Eq. 1)

- etherification of secondary OH groups (Eq. 2)

at 120 °C with DMBA and without an accelerator proceed with the same mechanism. The reaction progress is illustrated by a single curve in each case of the both main reactions independently on accelerator.

Scheme 1



Signal 16^{OH} was found in a quantity of 2 to 5 % for all reaction conditions. The represented content of primary hydroxyl groups (PGE glycol) corresponds to results obtained by HPLC analysis. The signal 16^{N} for tertiary amides at 64 p.p.m. appears in a similar low intensity. Epoxy carbon 15 and the secondary amide peak 16^{NH} in the 50 p.p.m. range were not separated sharply enough for certain calculations.

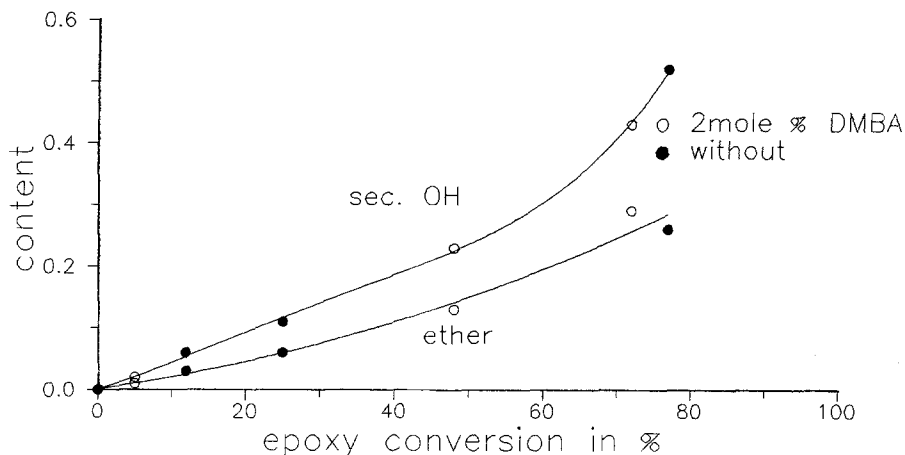


Figure 3 Content of structure units in PGE-Dicy-DMF (4:1:6) reaction mixtures at 120 °C by ^{13}C -NMR data

The situation is more complex in systems reacted at 140 °C. Figure 4 shows for the epoxy amide addition forming secondary OH groups an independence on the accelerator type too. On the other hand, a small difference in etherification is reported by a lower content of ether bonds in the DMBA accelerated system (Figure 4).

A decrease of activity with increasing temperatures from 120 °C also was described for reactions of epoxy compounds with diols in the presence of DMBA (16). Furthermore, an intensity loss of the aliphatic carbon signals during the reaction was calculated. The peaks of these main reactions found at 120 °C formed later than the epoxy conversion calculated has been suggested.

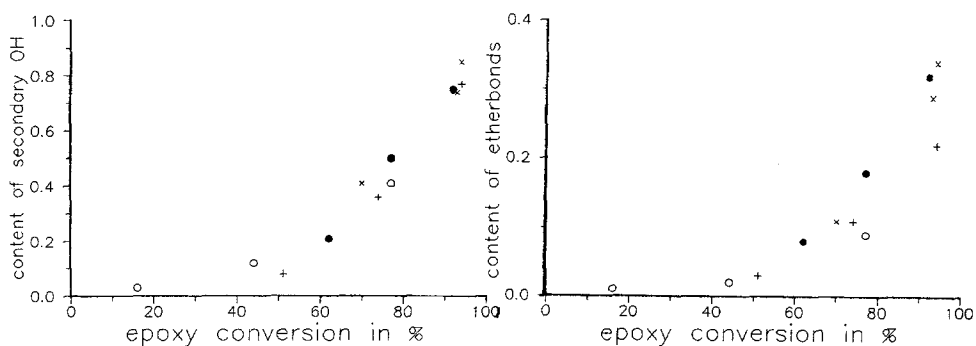
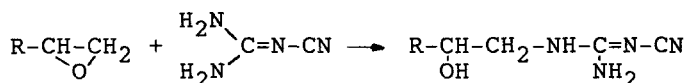
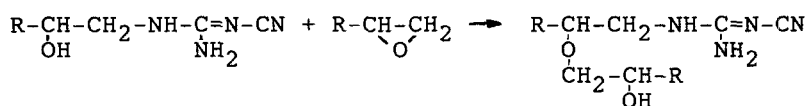


Figure 4 Content of structure units in PGE-Dicy-DMF reaction mixtures by ^{13}C -NMR data
mole ratio PGE : Dicy : DMF = 4 : 1 : 6; e/a = 1;
T = 140 °C (samples 9 - 12 acc. Table 1)

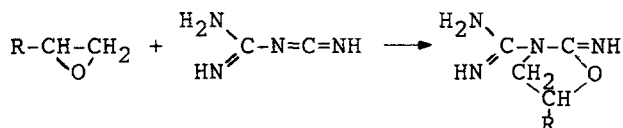
Scheme 2



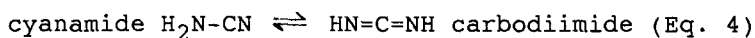
epoxy-amide addition (Eq. 1)



etherification (Eq. 2)



cycloaddition to oxazolidines (Eq. 3)



Other results concerning with NMR and IR measurements on diglycidyl ether - Dicy systems showed a loss of the nitrile function, and in opposition a relative increase in the $>\text{C}=\text{N}$ -function followed by reactions forming other $>\text{C}=\text{N}$ - or $>\text{C}=\text{O}$ groups (17 - 19). Having taken into account the literature about heterogeneous systems (6, 10) we suggest a third main reaction. A direct cyclisation leads to substituted oxazoline derivatives (Eq. 3). This cyclic compound is probably more rigid than the aliphatic chains or the aromatic endgroups. Thus, a condition for a high resolution ^{13}C -NMR spectra, the isotropical movement all of carbon atoms, is not realized for these cycles.

However, a change in cure mechanism was observed by gel point determination. Two different lines extrapolated in an ARRHENIUS plot intersect in the temperature range from 140 to 145 °C. The point of intersection is independent on the mol ratio epoxy-amide and the accelerator applied (17).

Thus, we are able to propose the following mechanism with reference to our studies on chromatographic separated fractions of Dicy-epoxy products (19) and the results about cyanamide-epoxy reactions by ZAHIR (4).

The amide form of Dicy (may be as two tautomeric structures (18)) reacts in the same way as amines. The first step is the amide-epoxy addition (Eq. 1). Secondly, the etherification of secondary OH groups formed in (Eq. 1) proceeds to linear products possessing an intact nitrile group (Eq. 2). On the other hand, with increasing temperature a third main reaction plays a more important role. Similar to cyanamide (4), a tautomeric carbodiimide structure can be postulated forming by cycloaddition with epoxies an oxazoline or its tautomeric oxazolidine structures (Eq. 3).

Such a reaction was described for diphenyl carbodiimide-phenyl glycidyl ether systems (20). Furthermore, a number of reactions of the tautomeric cyanamide is well known.

Thus, the carbodiimide tautomer of Dicy can react with alcohols to form isoureas, with water to ureas and urethanes or with itself to melamine products. All these compounds possess $>C=O$ or $>C=N$ -groups. Such bands were found in the 1800 - 1600 cm^{-1} region of IR spectra, but mostly, the interpretations have been contradictorily.

The course of the main reaction is summarized in Scheme 2. A number of other intra- and intermolecular reactions according to the peaks of Fig. 2 have not been elucidated yet. More investigation relating to the curing reactions, the ratio of the resulting rate constants and their dependence on the temperature in order to describe the complex nature of epoxy resin curing using Dicy more carefully are in progress.

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