Polymer Bulletin 27, 557–564 (1992)

Polymer Bulletin

Curing of epoxy resins by dicyandiamide

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Summary

The reaction course, the final structure and the thermal behaviour of dicyandiamide cured epoxy resins were studied by HPLC, Carbon-13 NMR (liquid and solid state), IR, gel time determination, DSC and evolved gas analysis. N,N-dimethylbenzylamine, imidazole and Monuron were applied as three different accelerator types. Dimethylformamide was used as solvent to obtain homogeneous reaction mixtures. Two reaction pathways depending on tautomeric dicyandiamide structures are suggested explaining the reaction mechanism.

Introduction

The low solubility of dicyandiamide (Dicy) in epoxy resins and its high melting point are an advantage for the high stability of Dicy-epoxy systems. In contrary, the handling and analysis of such heterogeneous systems can not be done without a number of problems. Most experimental studies have been concerned with heterogeneous systems (1 - 10), where repeatedly complications arise in the interpretation of the results. The aim of this paper is to compare heterogeneous and homogeneous Dicy-epoxy systems by using diemthylformamide (DMF) as the solvent. Diglycidyl ether of bisphenol-A (DGEBA) was used as epoxy compound. Dimethylbenzylamine (DMBA), imidazole and Monuron (N-4-chlorophenyl, N',N'-dimethyl urea) were applied as accelerator. The reaction behaviour was studied by ^{13}C-NMR, IR, HPLC, gel time determination, DSC and evolved gas analysis.

Experimental

Dicy, imidazole and Monuron 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 ^{o}C / 1.2 kPa). DMF was purified according to ref. (11). DGEBA was purified by recrystallisation from a methanol-acetone mixture (m.p. 42 - 43 ^{o}C).

Gel times were determined according to ref. (12). Carbon-13 NMR spectra were recorded on a Bruker HX 90-R at 22.635 MHz using d_6-DMSO as solvent (liquid state). Solid state spectra were obtained on a Bruker MSL 200 operating at 50.32 MHz and using CP-MAS technique (sample rotation 5 kHz). For more information relating calculation methods see ref. (13) IR spectra were recorded with different instruments (SPECORD M80 (Carl Zeiss Jena), BOMEM MICHELSON-100, PERKIN ELMER 580 B) using KBr discs or capillary techniques. DSC samples were run on a PERKIN

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ELMER DSC 7 with a heating rate of 10 K / min. Evolved gas analysis was made on a gas chromatograph using a FID (see ref. 14). HPLC was run on a KNAUER apparatus using RP technique and an acetonitrile-water mixture as eluent (see ref. 15).

The mole ratio epoxide/amide (e/a) was calculated taking into account the number of functional groups (for DGEBA 2, for Dicy 4) according to ref. (7). The concentration of the accelerator was applied to the epoxy groups.

Results and Discussion

First chromatographic and kinetic studies of heterogeneous systems have already shown the difficulties in preparing or analysing the samples. Insoluble products had been formed in the early stage of these reaction systems (15). After that, the samples became completely insoluble in the nonpolar HPLC eluent acetonitrile very quickly. The period of that procedure and the gel time are given for accelerated systems in Tab. 1. In opposition reactions in an unaccelerated Dicy-epoxy system are only known at temperatures higher than 140 °C (7). Thus, no product formation could be detected on the adequate unaccelerated systems in our study using HPLC.

Table 1
Gel times tg and the related times t to get in acetonitrile completely insoluble products of DGEBA - Dicy systems accelerated with 1 mole% DMBA (e/a = 1.25)

T in °C	t in min	t_G in min
80	60 - 80	71
100	20 - 30	36
120	5 - 10	17

In order to obtain more information relating to the heterogeneous behaviour of these systems a number of samples were cured under different conditions which are summarized in Tab. 2. Still after heating and mixing the insoluble, cristalline Dicy was clearly visible. High viscouse mixtures were obtained after curing cycles. This result was not expected relating to the corresponding measured gel points. Only two samples (No. 1a and 2a) hardened giving a typical compact epoxy resin.

Table 2
Curing conditions of heterogeneous DGEBA-Dicy-DMBA systems

No.	mole ratio DGEBA : Dicy	e/a	mole % DMBA	curing cycle
1	2 : 1	1	3	a, b, c
2	4 : 1	2	3	a, b, c
3	2 : 1	1	1	a, b, c
4	4 : 1	2	1	a, b, c

a 180 min at 160 °C
b 180 min at 120 °C + 120 min at 160 °C
c 360 min at 120 °C + 120 min at 160 °C

Sedimentation of Dicy was observed on closer consideration of the curing process. The greatest part of the insoluble Dicy went down to the bottom depending on particle size in the liquid epoxy resin melt. Thus, inclusions of cristalline Dicy are visible in the lower part of these mixtures. Above that region a very slow reaction took place without Dicy. That behaviour is typical for DMBA initiated epoxide oligomerisation (8) leading only under special conditions to a completely cured resin (see Tab. 2).

In reality, no unambiguous analytical evidence was found for the presence of Dicy by spectroscopic methods in the cured samples (see Fig. 1). No signal was indicated for the nitrile group in the 2200 cm^{-1} range of an IR spectrum. Furthermore, only typical oligomerisation product structures such as ether-bonds and hydroxyl groups were visible in these spectra including an incomplete epoxy conversion.

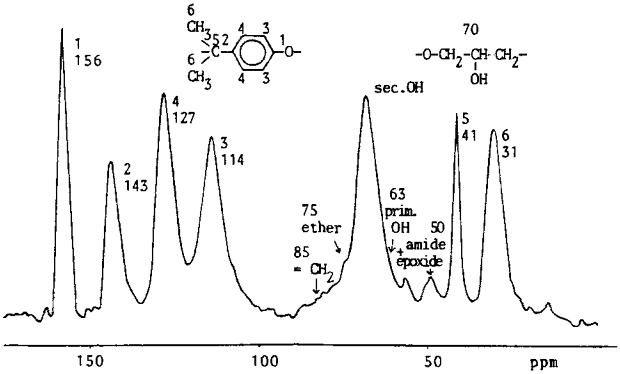


Fig. 1 ^{13}C-NMR-spectrum of a DGEBA-Dicy-DMBA-system (solid state)
T = 160 °C t = 180 min sample 1a

In summary, it is shown that procedures and analytics of heterogeneous Dicy-epoxy systems possess a complex nature. Sedimentation and diffusion controlled reactions give rise to the major problem for the use of Dicy in technical application.

A homogeneous system can be obtained using the polar solvent DMF. The reaction course was followed by HPLC measurements, since the samples have been completely soluble in acetonitrile up to a high epoxy conversion (15). But, these reaction mixtures with the content of about 66 wt.% DMF are not able to build up high cured networks. In order to approach technical conditions the proved standard system with a constant mole ratio of Dicy : DMF = 1 : 6 was used by utilization of a 16.1 wt.% solution of Dicy in DMF for all of the following reactions with DGEBA.

Samples were investigated by HPLC, IR and ^{13}C-NMR. Coordination and calculation of NMR data are extensively described in a previous paper (13). The epoxide conversion was obtained from the epoxy band at 916 cm^{-1} in an IR spectrum. Furthermore, the nitrile absorption was followed near 2190 cm^{-1} (see Fig. 2).

Using DMF as solvent, control calculations were carried out to check the quality of undisturbed internal standards. The obvious data are given and related to other results in Tab. 3.

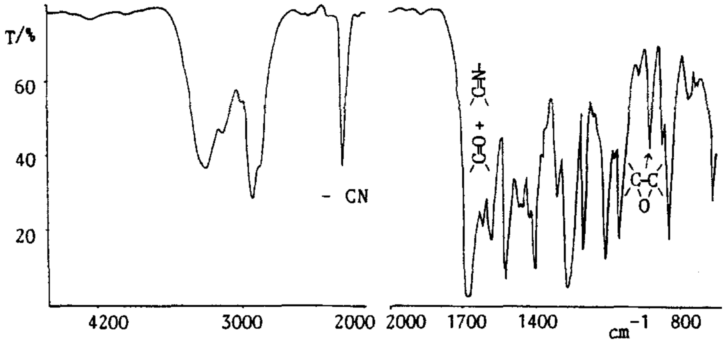
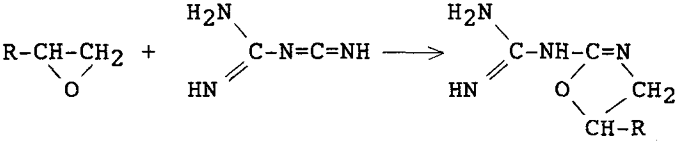


Fig. 2 IR-spectrum (cappilary) of a DGEBA-Dicy-DMF-system (e/a = 1.25)
T = 120 °C t = 40 min U_{NMR} = 36 %

Table 3
Consumption of functional groups in % determined by IR (capillary) and other methods
a) DGEBA : Dicy : DMF = 2.5 : 1 : 6, T = 120 °C
b) DGEBA : Dicy : DMF = 1 : 1 : 6, T = 120 °C
* insoluble parts

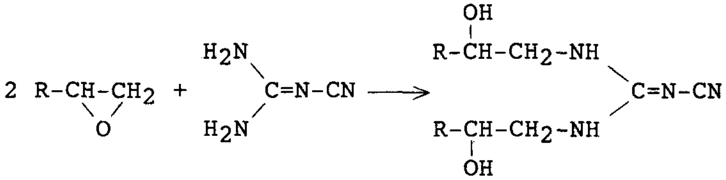
Method	signal/standard at cm^{-1} / at cm^{-1}	function	reaction time in min			
part a			20	30	40	
IR	916 / 1180	epoxy	18	34	43	
IR	916 / 1500	epoxy	13	29	46	
IR	2188 / 1180	- CN	6	17	29	
IR	2188 / 1500	- CN	7	11	32	
NMR	carbon - 13	epoxy	17	-	36	
HPLC	DGEBA / 254 nm	epoxy	10	37	56*	
part b			20	40	60	150
IR	916 / 836	epoxy	10	40	95	98
IR	916 / 662	epoxy	14	36	94	97
IR	916 / 2932	epoxy	-	41	94	98
IR	2188 / 2932	- CN	4	0	12	23
NMR	carbon - 13	epoxy	19	29	99	100
HPLC	DGEBA / 254 nm	epoxy	12	53*	93*	100*

Taking into account the similar reactivity all of the epoxy groups, the DGEBA conversion from HPLC conforms with the total epoxy consumption. It is remarkable that the nitrile function participates in reactions at such low temperatures. The nitrile group consumption stopped at a level of about 20 up to 30 %. Similar results have already been reported for homogeneous systems (16, 17). Thus, the band of the nitrile absorption could be found in all of the fully cured samples. These results point to a direct reaction between Dicy and an epoxy group forming oxazoline derivatives in accordance with Eq. (1).



Eq. (1)

A tautomeric Dicy with carbodiimide structure has been suggested to explain this cycloaddition and other reactions forming C=O and C=N-groups (18). So far, no satisfactory proposal has existed to interpret the high activity of the Dicy's nitrile function. The limited consumption of nitrile groups could be connected with amide-substituted Dicy-epoxy products formed in Eq. (2) that are not able to the formation of a tautomeric carbodiimide structure.



Eq. (2)

The gel point determination is a further method to get information about the curing behaviour and its dependence on reaction conditions. A number of experiments was carried out varying the mole ratio epoxide-amide e/a, the accelerator and the temperature in a wide range (14). The gel time dependence on temperature is shown in an ARRHENIUS plot (Fig. 3). Calculated activation energies beeing valid up to 140 °C are summarized in Tab. 4. Above that temperature a turning of the curve is visible. The point of that changing was determined as 143 °C by 5 K temperature steps. Resulting activation energy decreases dramatically from about 70 to 25 kJ/mol. It was observed that the turning is independent on mole ratio e/a or accelerator. A possible explaination has been given as two overlaped different reaction types (see Eq. (1) and (2)) depending on tautomerization of Dicy (18).

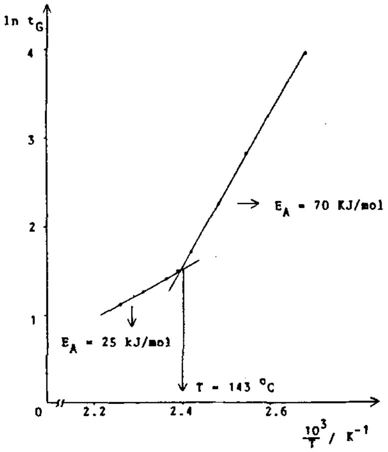


Fig. 3
ARRHENIUS plot of the general temperature dependency of gel times in the DGEBA-Dicy-DMF-system

Table 4
ARRHENIUS activation energy E_A in KJ/mol of DGEBA-Dicy-DMF-systems under different reaction conditions calculated from gel time-temperature dependence

	1 mole % DMBA	without DMBA
e/a = 1	66	70
e/a = 2	74	75

In order to obtain more information relating to the network structure spectroscopical investigations were carried out on fully at 120 up to 150 °C cured samples (Tab. 5). No analytical evidence for a great difference in the chemical structure could be detected (13), though three different accelerator types have been used. However, that result confirms very well with our model reaction study (18).

Table 5
Reaction conditions for cured samples of DGEBA-Dicy-DMF-accelerator systems

series	e/a	T in °C	t cure in min	wt. % DMF
IV	2	120	180	23
IX	2	150	90	23
XIV	1.25	140	120	32

Each series contains 4 samples with different accelerators:
1 - 1 mole % DMBA
2 - 1 mole % imidazole
3 - 2 mole % Monuron
4 - without

DMF was found in all of the samples indicated by IR and ^{13}C-NMR (13). The cure in the presence of a solvent can cause the physical insertion of the solvent into the network structure.

Table 6
Glass transition temperature and DMF-content of cured samples according Table 5

Sample	Tg in °C	wt. % DMF gravimetrically	wt. % DMF gas analysis
IV/1	52	16	17
IV/2	50	14	12
IV/3	42	17	19
IV/4	54	17	16
IX/1	48	15	13
IX/2	52	10	12
IX/3	49	12	15
IX/4	54	12	13

Thus, the resulting glass transition temperature Tg was determined by DSC. They are very low (see Tab. 6 and 7) relating to these, which have been reported for heterogeneous systems with about 130 °C (7). It was also shown by DSC that a slow evaporation of DMF occures by heating above its boiling point of 153 °C. The content of DMF in the network was determined by gravimetrical experiments and evolved gas analysis. A good correlation between a low Tg and a high content of DMF is demonstrated in Tab. 6 and 7.

Table 7
Dependence of glass transition temperature and DMF content on post curing

Sample	Tg in °C	120 min 180 °C mass defect	Tg in °C	240 min 220 °C mass defect	Tg in °C
XIV/1	25	18 %	66	25 %	115
XIV/2	20	22 %	75	26 %	113
XIV/3	25	19 %	68	25 %	113
XIV/4	29	17 %	67	26 %	116

The effect of a reflexibilizer is clearly to be seen. Its content was influenced by the composition of starting materials. A certain fraction of the solvent evaporated during the cure process. This part depends on the cure cycle, especially on temperature (see Tab. 5 and 6). But, there is no strong dependence on the used accelerator type.

The evolved gas analysis showed the content of volatile substances and the thermal stability of the cured resins (see Fig. 4). Thus, the DMF evaporated in a wide temperature range above its boiling point. Other volatile substances such as monomers or oligomers like in other systems (14) could not be detected. The rapid thermal degradation started at temperatures about 375 °C.

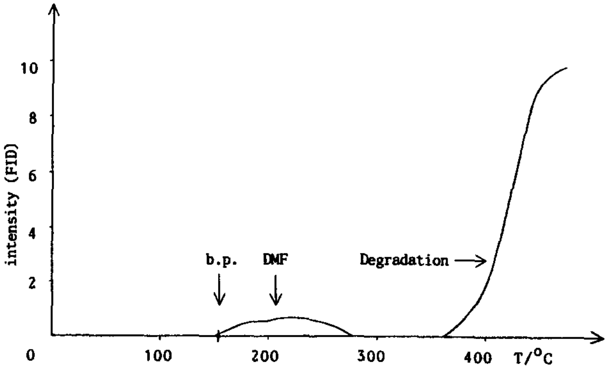


Fig. 4 Typical curve for an evolved gas analysis of a DGEBA-Dicy-DMF-system (schematic)

Basing on these data a post cure process can be selected. The examples given in Tab. 7 show an increase of the glass transition temperature Tg. Post cured samples beeing nearly free of DMF achieved a Tg range of 110 - 120 °C. That is lower, but similar to epoxy resins cured with Dicy in the absence of a solvent (7). Perhaps, a part of the DMF is so heavily enclosed that the evaporation is connected with degradation. The relative low mass defect (see Tab. 7) relating to about 32 wt.% DMF in the beginning of reaction points to that possibility.

However, the studies showed no important differences of the accelerator activity. The resulting networks possess the same chemical structure including similar temperature behaviour. In summary it can be said that the proposed mechanism obtained by model investigations (18) is transferable to DGEBA-Dicy-DMF systems. Thus, a survey of the literature reported including our studies of the reaction mechanisms will be given in (19).

Acknowledgement

The authors have to thank K. G. Häusler and K. F. Arndt discussing evolved gas analysis and DSC measurements. We are gratefully indepted the Bundesminister für Forschung und Technologie (Project 03 M 40545) and the Fonds der Chemischen Industrie for financial support.

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Accepted October 28, 1991 C