

Curing of epoxy resins with dicyandiamide

Reaction behaviour of glycidyl ethers

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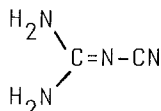
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Summary

The reaction behaviour of tertiary amine accelerated epoxy-dicyandiamide systems was studied using phenyl glycidyl ether and the diglycidyl ether of bisphenol A. N,N-dimethylbenzylamine was applied as accelerator. The solvent, N,N-dimethylformamide, was used to obtain homogeneous reaction mixtures. The influence of the solvent on the reaction was investigated. Depending on reaction conditions the formation of oligomerization products was followed by HPLC measurements.

Introduction

The cyano substituted guanidine, dicyandiamide (Dicy)



is a widely used latent curing agent for epoxy resins. Applications of such resins include, for example, laminates, prepregs, coatings and adhesives.

Extensive studies into the mechanism of curing epoxies with Dicy have already been carried out (1-9). However, no analytical evidence for a single predominant reaction has been presented. Rather, a number of possible reaction pathways and products have been proposed. The mechanism of an epoxy system based on Dicy is largely dependent on the accelerator, the reaction temperature and the ratio of epoxy/amine used. Therefore, the low solubility in liquid epoxy resins influences the application procedures.

HAGNAUER and DUNN (10) showed that only about 0.05 wt% Dicy is soluble at room temperature in a liquid Shell Chemical resin Epon 828, based on the diglycidyl ether of bisphenol A (DGEBA). The solubility increases to about 0.6 g Dicy in 100 g resin at 150 °C.

Normally, epoxy resin systems contain about 5% Dicy, and thus a solvent or mixture of solvents are necessary. More information relating to the solubility of Dicy in epoxy resin systems will be useful in order to better understand the curing behaviour of this hardener.

Therefore, the aim of this paper is to elucidate the effects of solvents and the influence of the accelerator used on the curing mechanism of the Dicy-epoxy system. DGEBA and

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phenyl glycidyl ether (PGE) were used as epoxy compounds and N,N-dimethylbenzylamine (DMBA) as accelerator. Analysis was carried out by HPLC.

Experimental

PGE was prepared according to ref.(11) (b.p. 96-98 °C / 0.4kPa). Technical DGEBA (Epilox A17-01; VEB Leuna-Werke G.D.R.) was purified by crystallization from an acetone-methanole-mixture (m.p. 42 °C). The Dicy was provided by the VEB Berlin-Chemie (G.D.R.). 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.

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

HPLC samples were run with apparatus from KNAUER (Wissenschaftliche Geräte KG, F.R.G.); column: 180x3.2 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.

The mole ratio epoxide/amine (e/a) was calculated taking into account the number of functional groups (for DGEBA 2, for Dicy 4) according to ref. (6,7). The DMBA concentration was applied to the epoxy groups.

Results and Discussion

Reaction of phenyl glycidyl ether with dicyandiamide

In order to obtain information about the reactions taking place during the curing of epoxies with Dicy in the presence of the accelerator DMBA, the products resulting from the tertiary amine-catalyzed oligomerization of PGE had to be taken into consideration. The influence of the accelerator was investigated at different temperatures up to 120 °C.

Figure 1a shows a chromatogram of the products built up during the reaction of PGE with 5 mole% DMBA at 100 °C. The main products are type A oligomers, one of three different oligomeric types described in (8). A typical distribution of these oligomers is illustrated in the chromatogram. The Dicy is nearly insoluble in this system. No reaction with PGE takes place in comparison to the faster oligomerization.

A chromatogram of the products obtained during the reaction of PGE with Dicy and 2 mole% DMBA as accelerator is represented in Fig.1b. Oligomeric products of PGE were not found using HPLC. The variation in the concentration of the accelerator plays an important role in the reaction course. The rate of oligomerization rapidly decreases with a decrease in the accelerator content. The reaction with 2 mole% DMBA at 100 °C gives rise to the formation of Dicy/PGE products only. Nearly the same products were received with 2 mole% DMBA at 120 °C. The peak areas calculated showed a small difference in

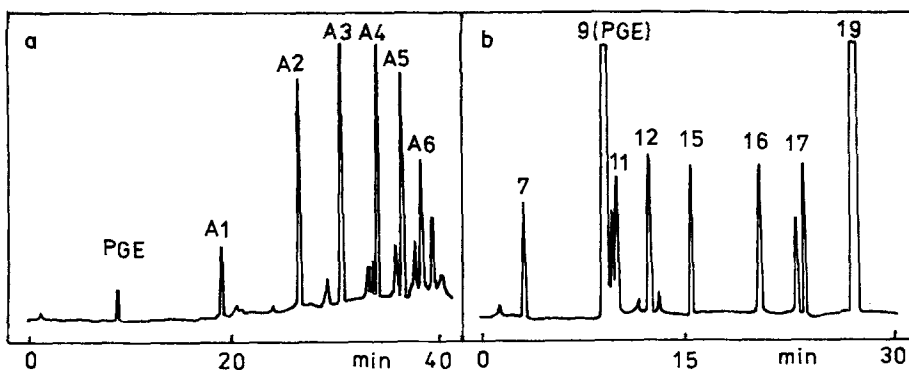
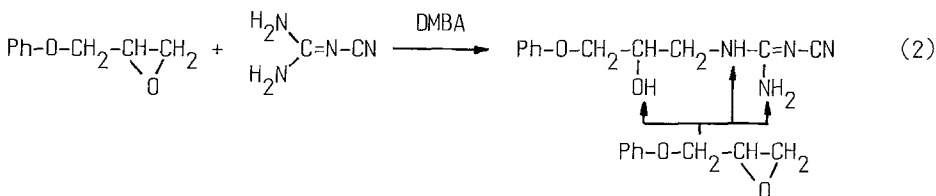
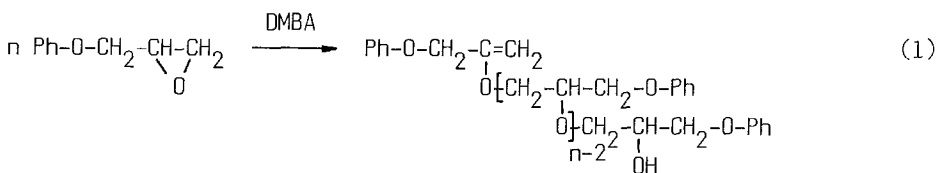


Fig. 1 Chromatogram of the reaction mixture containing PGE:Dicy = 5:1 at 95 °C;
 a) 5 mole% DMBA; reaction time = 2 h; epoxide conversion > 95%
 b) 2 mole% DMBA; reaction time = 15 h; epoxide conversion = 55%

quantity only. These results correspond with investigations by PASCAULT (6,7). When the Dicy/PGE system was heated without accelerator up to 120 °C no product formation could be detected by HPLC.

The accelerator considerably influences the mechanism and the reaction products of these heterogeneous systems. Depending on the amount of accelerator used, different types of products were found. A high content (5 mole%) of the accelerator leads to oligomeric hydroxy ethers initiated by anionic ring opening of the epoxide by tertiary amines (Eq. (1)). The formation of these products is favoured with a high content of accelerator and a high-ratio of epoxy/Dicy. Epoxy-Dicy reactions accelerated by a low content of DMBA (2 mole%) mainly form Dicy/PGE addition products. By adding one molecule Dicy to the glycidyl ether a substituted *N*-alkyl-cyanoguanidine is formed which undergoes further reactions



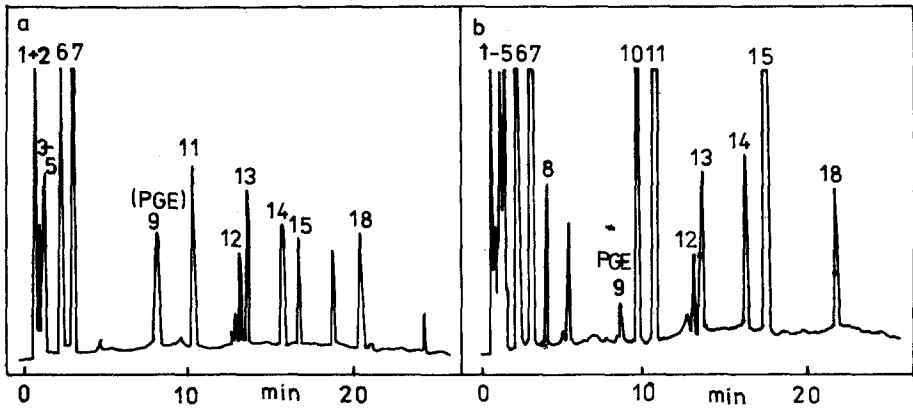


Fig. 2 Chromatogram of the reaction mixture containing PGE:Dicy = 3:1 in 30 wt.% DMF at 120 °C;
 a) 2 mole% DMBA; reaction time = 1.5 h; epoxide conversion = 95%
 b) without DMBA; reaction time = 5 h; epoxide conversion > 95%

with glycidyl ether (Eq. (2)).

A homogeneous system can be obtained using DMF. Figure 2a shows a chromatogram of the products obtained after a Dicy/PGE reaction accelerated by 2 mole% DMBA in DMF. Many products were separated by HPLC. Some peaks (No. 7, 10-12, 15) have already been recognised as reaction products in the absence of DMF. Taking into account the very low retention time, several products must possess a strong polarity. Oligomeric products, including the PGE-glycol (3-phenoxypropanediol-1,2), phenol, or 1,3-diphenoxypropanol-2 (intermediates of the oligomerization), were only obtained in a quantity of less than 10% of the peak area.

A very slow reaction was observed for PGE and DMF alone. The products are of the oligomeric type, but of no significance for a faster formation of Dicy products in a Dicy system.

In order to obtain more information relating to the solvent effect observed, reactions of PGE with Dicy in DMF were carried out without using an accelerator. The HPLC of the reaction mixture is shown in Fig. 2b. Strong polar compounds were also obtained. Compared to Fig. 2a, some different products are formed. In the absence of DMBA, a variation of some reactivities opposite the epoxy group takes place. This is also indicated by a small amount of unreacted phenol, identified as peak No. 8.

However, the number of oligomeric intermediates is very small in relation to the formation of Dicy products. Reactions in an unaccelerated epoxy-Dicy system are only known at temperatures higher than 140 °C (6,7). Our investigation demonstrated that reactions in an unaccelerated solvent system lead to the formation of many Dicy products.

Reaction of diglycidyl ether of bisphenol A with dicyandiamide

Unlike to the monofunctional system, it is difficult to separate all of the products of a diglycidyl ether reaction by an HPLC method. The solubility of the oligomerization products is limited by the non-polar eluent acetonitrile. Crosslinking occurs for epoxy conversions higher than 30-40 % and the products become insoluble. Figure 3a shows a chromatogram of the soluble oligomeric products obtained during the reaction of DGEBA with DMBA at 100 °C. The split main peak of DGEBA illustrates the p,p' and o,p' distribution of isomers. It can be clearly seen that the amine-initiated oligomeric products possess a non-polar character. Similar to the model system, the oligomers were detected as having a relatively high retention time.

The following chromatograms (Fig. 3b-4) obtained from reaction mixtures containing Dicy show significant differences. Fig. 3b illustrates a chromatogram of a DMBA-accelerated DGEBA-Dicy system in the absence of a solvent. This system was investigated at 80 °, 100 ° and 120 °C. It was not possible to dissolve completely the samples for HPLC analysis. Insoluble products had already been formed in the early stage of these heterogeneous reaction systems. However, the chromatogram indicates a high content of two product groups with polar character (No. 1,3). Only a small quantity of the homooligomers of the DGEBA were found.

In order to better understand solution effects, homogeneous reactions were carried out using DMF as solvent. The samples were completely soluble in acetonitrile up to a conversion of about 70-80% DGEBA. The reaction course was

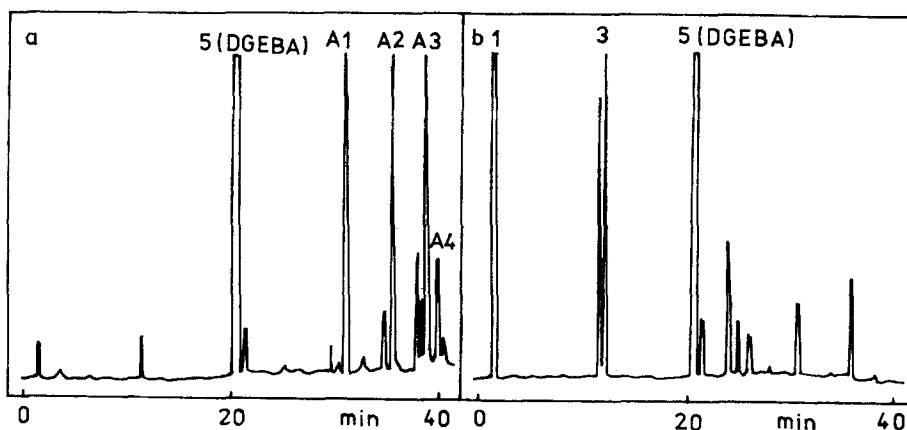


Fig. 3 Chromatogram of the reaction mixture containing
 a) DGEBA with 1 mole% DMBA at 120 °C; reaction time = 60 min;
 epoxide conversion: 21%
 b) Dicy and DGEBA; ratio e/a = 1.25 with 1 mole% DMBA at 100 °C;
 reaction time = 10 min (soluble part)

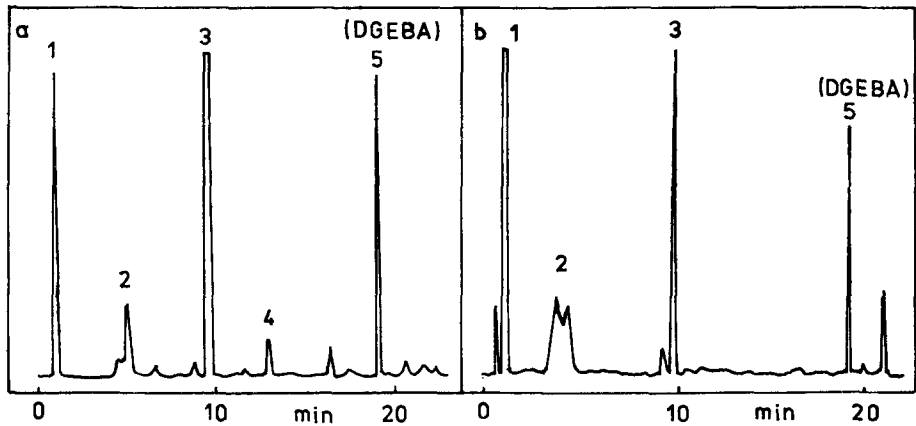


Fig. 4 Chromatogram of the reaction mixture containing Dicy and DGEBA; ratio e/a = 1.0 in 66 wt.% DMF at 100 °C;
 a) 1 mole% DMBA; reaction time = 45 min
 b) without DMBA; reaction time = 240 min

Table 1 Development of the relative concentration (peak area) of the main product groups depending on time and accelerator (according to Fig. 4).

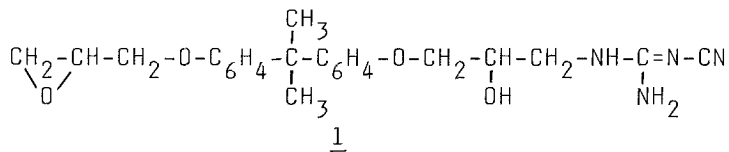
No. of peak	t_r range min	area in percent after reaction time					
		acc. Fig. 4a (+DMBA)			acc. Fig. 4b		
		t/min					
		15	30	45	60	120	240
		%					
1	1 - 2	5	19	21	17	34	33
2	4 - 5	-	-	10	-	-	15
3	9 - 10	3	20	28	2	7	30
4	11 - 12	-	-	4	-	-	-
5 (DGEBA)	18 - 19	89	46	20	79	55	11
Σ		97	85	83	98	96	89

observed using HPLC measurements. The chromatograms are shown in Figure 4.

According to these figures the resulting peak areas are listed in Table 1. Different products or product groups were formed successively depending on epoxy conversion versus time.

In all cases, a highly polar product (No. 1) was observed at the beginning of the reaction. The quantity of this product depends on the reaction time, the epoxy/amine ratio and on the presence of the accelerator. Some 50 to 80 % of the peak area was obtained in those samples to which a considerable excess of Dicy was added. Taking into account these facts, we put forward this product No. 1 as the first Dicy-DGEBA addition product. The chemical structure of this primary compound

contains different functional groups (1). The secondary or primary amine and the hydroxyl group are able to react with epoxide, the epoxy group with Dicy or the other functionalities listed.



Split or non-separated peaks demonstrate the complex nature of the secondary reaction steps (Fig. 4). Both temperature and accelerator shift the reactivities of the functional groups, which causes different product ratios. The situation is much more complex in accelerated systems (Fig. 4a) or at high temperatures. However, the same main products are formed at different temperatures ranging from 80 °C to 120 °C. The conversion rate of DGEBA is influenced by the presence of DMBA (Table 1). A considerable decrease of conversion was found at 80 °C in the absence of the accelerator. In this case, the reaction almost stopped after the formation of product 1.

Relative to the Dicy system, a very slow reaction gives rise to unknown products in an accelerated DGEBA-DMF system. A conversion of about 50% DGEBA was obtained after 8 hours. However, the same conversion was found after about only 15 min in the adequate Dicy system.

Summarizing, it can be said that similar behaviour to that of the model system based on phenyl glycidyl ether was observed. The accelerator DMBA and the reaction temperature influence the reaction course of a DGEBA-Dicy system. Furthermore, we were able to demonstrate that in an unaccelerated DGEBA-Dicy-solvent system reactions also take place at about 100 °C. Using HPLC, a method of analyzing the homogeneous reaction mixtures in a large range of epoxy conversions is shown. Further information relating to the initial reaction steps in the network formation process of a Dicy cured epoxy resin are useful in order to the better understand the technical important prepreg manufacturing. Thus, some preparatory chromatographic methods to separate products for spectroscopic analysis are now being investigated.

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