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# Curing of epoxy resins with dicyandiamide

## Model investigations with substituted dicyandiamides

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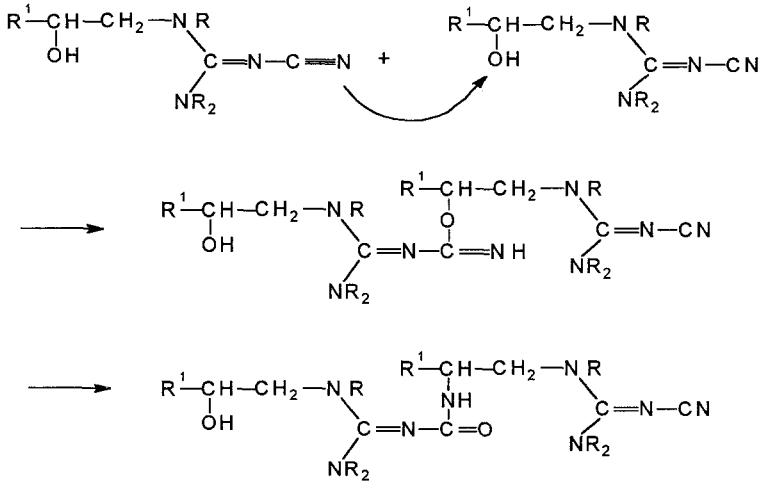
Summary

The mechanism of the epoxy resin curing with dicyandiamide was studied using the model phenyl glycidyl ether and different substituted dicyandiamides. Some reaction products were isolated by HPLC and characterized by FTIR and Carbon-13 NMR spectroscopy. A reaction pathway is proposed discussing the formation of cyclic structures, carbonyl groups and oligomerization products of the glycidyl ether.

## Introduction

Dicyandiamide (DCDA) is widely used as a latent curing agent in heat cured epoxy resins. The mechanism of the reaction of DCDA with epoxies has been investigated extensively during the last decade (1-16). A various number of reaction pathways and structures of the reaction products were suggested. The first reaction step is the addition of the glycidyl ether to the $NH_2$-group of the DCDA. Normally, only a small part of tertiary amides was found (5-7). Furthermore, the etherification of the hydroxyl groups formed in the first step was described.

SAUNDERS et al. (1) proposed a reaction between CN- and OH-groups with the formation of guanyl ureas for reaction temperatures higher than 100 °C.



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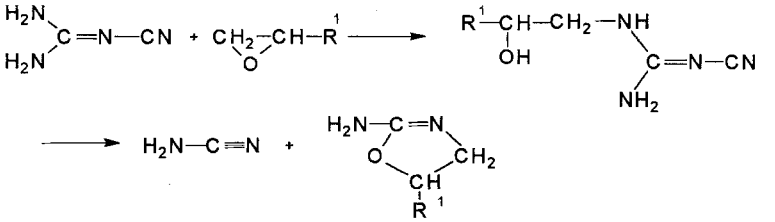
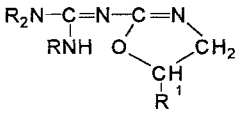
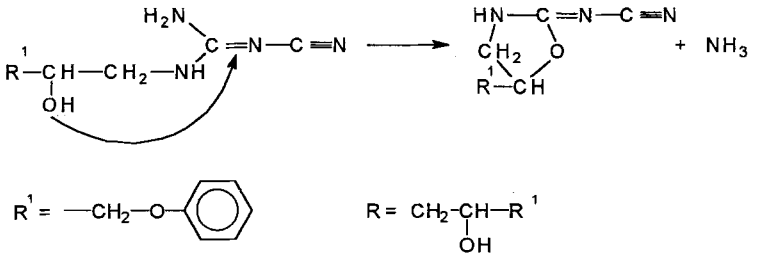
Different suggestions exist for reactions leading to cyclic products. ZAHIR (3) assumed an oxazoline structure that was produced in a reaction with the formation of cyanamide.



PASCAULT et al. (5,6) and PFITZMANN et al. (7) supposed the following cycle with an oxazoline structure.



GILBERT et al. (8,9) described a cyclization with the separation of ammonia.



The low solubility of DCDA in glycidyl ethers gives rise to experimental and analytical problems. Thus, we used phenyl glycidyl ether (PGE) as monofunctional epoxy compound and N,N'-diphenyl dicyandiamide (DPhDCDA) and N,N-dimethyl-N'-phenyl dicyandiamide (DMePhDCDA) as substituted DCDA in order to obtain more information on the curing mechanism. Some products were separated by HPLC and investigated by FTIR and Carbon-13 NMR to follow the main reaction course.

## Experimental

PGE (Fluka) was distilled (b.p. 96 - 98 °C / 0,4 kPa) before utilization.

Starting with N,N'-diphenyl thiourea the diphenyl carbodiimide was prepared using HgO for the desulphuration. The carbodiimide and cyanamide were reacted in ether to obtain the N,N'-diphenyl dicyanidamide. The product was recrystallized from ethanol (17-19), Fp: 195-196 °C.

Phenyl thioisocyanate was reacted with dimethyl amine to produce the N-phenyl-N',N'-dimethyl thiourea. The thiourea was refluxed with an excess of lead cyanamide in ethanol for three hours. The precipitate, N-phenyl-N',N'-dimethyl dicyanidamide, was recrystallized from

ethanol, Fp: 178 - 180 °C.

The reactions were carried out at 120 °C 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 (20).

HPLC samples were run with apparatus from KNAUER (Wissenschaftliche Geräte KG); column: 250 * 4 mm (preparative: 250 * 32 mm) with LiChrosorb RP-18, 5 µm (LiChrospher RP-18, 5 µm); eluent: acetonitrile-water 30 : 70 to 100 : 0 linear; flow: 1.8 ml/min (24 ml/min); detection: UV 265 nm; samples: 10 µl of a 5 % (700 µl of a 50 %) solution in acetonitrile.

Carbon-13 NMR spectra were obtained on a BRUKER MSL 300 spectrometer (frequency: 75.43 MHz) using DMSO-$d_6$ or acetonitrile-$d_3$ as solvents and HMDS as standard.

FTIR spectra were recorded with a NICOLET 205 spectrometer from a solution in chloroform or as film (32 scans, resolution: 4 $cm^{-1}$).

## Results and discussion

The reactions of PGE with the substituted DCDA were carried out with and without the solvent DMF that was used for extensive studies with the unsubstituted DCDA (7,14-16). By titration it was shown that the epoxy consumption in the presence of the trisubstituted (DMePhDCDA) is much higher than in the case of the disubstituted DPhDCDA. This observation is in contradiction with the knowledge of the unsubstituted DCDA. It was published by PASCAULT et al. (5,6) and PFITZMANN et al. (7) that only a small part of fully substituted tertiary amides could be found in a PGE-DCDA reaction mixture at epoxy conversions near 100 %.

However, the FTIR investigations demonstrate a similar reaction behaviour for the substituted DCDA systems. That includes the decreasing of the nitrile band at 2180 $cm^{-1}$ and the corresponding increasing of a > C = N- band at 1690 $cm^{-1}$. Furthermore, absorptions were registrated at 1640 $cm^{-1}$ and 1750 $cm^{-1}$. Figure 1 and 2 show typical FTIR spectra of the reaction mixtures PGE : DPhDCDA and PGE : DMePhDCDA.

The reaction course was followed by analytical HPLC. In Figure 3 and 4 two chromatograms of substituted DCDA-PGE systems are represented. They demonstrate a less complex nature of the reaction mixtures as it is known for DCDA systems (7,14). In order to obtain more information on the chemical structure the main products (peak 5,6,7 in Fig. 3 and 5,6,7,9 in Fig. 4) were separated by preparative HPLC.

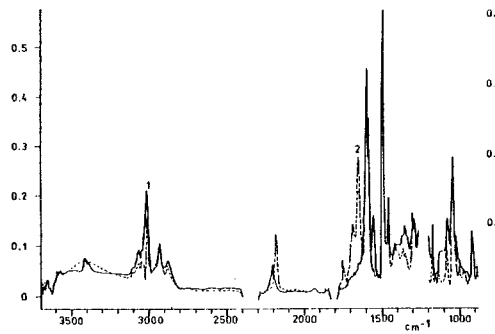



Fig. 1: FTIR spectra of the reaction mixture PGE-DPhDCDA = 6:1 at 120 °C
1: t = 0 min, 2: t = 480 min

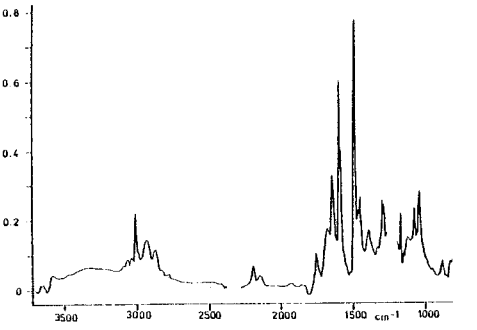



Fig. 2: FTIR spectra of the reaction mixture PGE-DMePhDCDA = 6:1 at 120 °C
t = 60 min

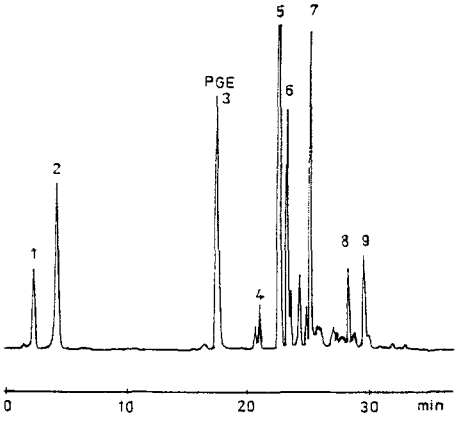



Fig. 3: HPLC of the reaction mixture PGE-DMePhDCDA = 6:1 at 120 °C t = 60 min

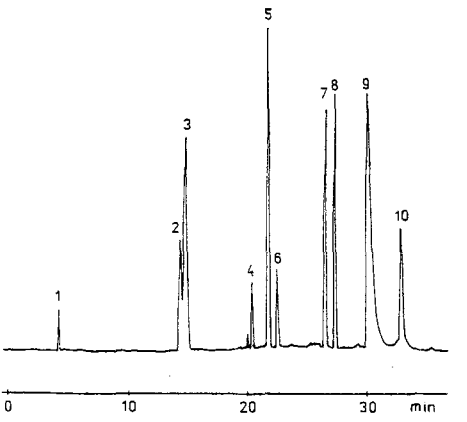
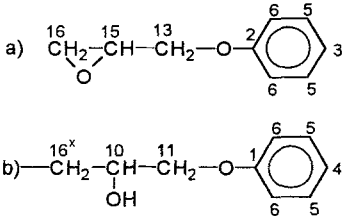
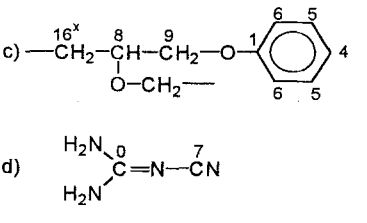


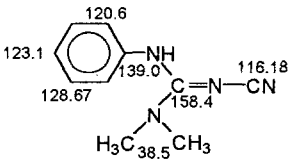

Fig. 4: HPLC of the reaction mixture PGE-DPhDCDA = 6:1 at 120 °C t = 480 min




x = * ... glycol x = ' ... sec. amide x = " ... tert. amide

| C-Atom | 0 | 1 | 2 | 5 | 3 | 4 | 7 | 6 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| ppm | 163.4 | 159.5 | 159.2 | 130.1 | 121.5 | 121.2 | 118.8 | 115.6 | 75.2 |
| | | | | | | | | | |
| C-Atom | 11 | 10 | 13 | 9 | 16" | 16* | 15 | 16' | 16 |
| ppm | 71.1 | 70.8 | 69.7 | 69.1 | 64.7 | 63.0 | 50.4 | 49.2 | 44.3 |



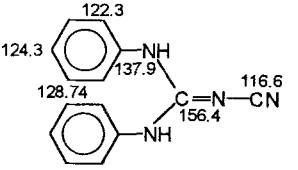
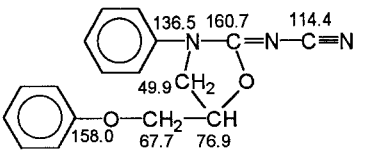



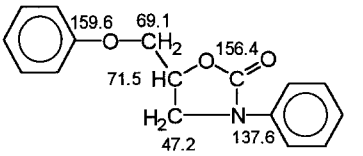

Fig. 5: Assignment and chemical shift for the Carbon-13 NMR measurements

The NMR data were assigned taking into account the chemical shifts of signals observed in PGE-DCDA systems (7) and the signals of the pure initial compounds given in Fig. 5.

Product No. 5




Product No. 6




Product No. 7

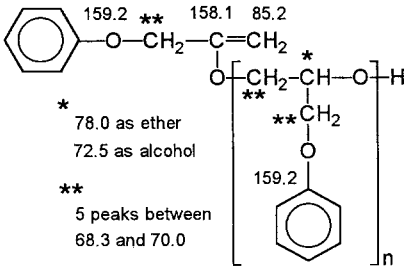
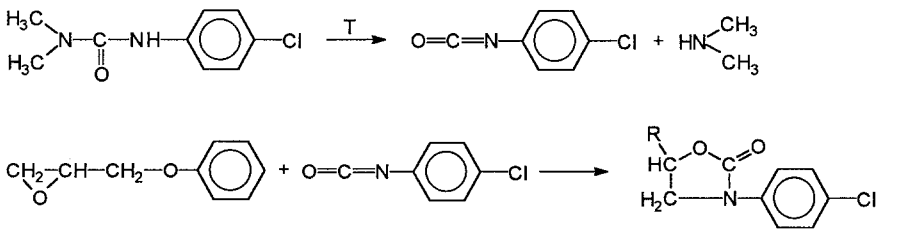



Fig. 6: Stucture of the isolated products

Furthermore, the NMR studies confirm the information obtained by HPLC. The products No. 5, 6 and 7 in Fig. 3 and 4 could be characterized to be the same for the both substituted DCDA. No signal for the methyl group of the substituted DCDA was found, either for product No. 5 or for product No. 7 or 9. Moreover, no signal (high field shift) was detected for a N-phenyl or other nitrogen containing groups in the case of product No. 7. The investigation by FTIR and Carbon-13 NMR allowed us to propose some structures of the separated products in Fig. 6.

Unfortunately, it was not possible to obtain the product No. 6 in a purity and quantity sufficient enough for the exact interpretation of the NMR spectrum. However, product No. 5 shows after its hydrolysis the same IR absorption at 1757 $cm^{-1}$ typical for oxazolidine-2-ones. The identical spectrum was recorded for the product formed in the reaction between PGE and phenylisocyanate according to ref. (21). Thus, it can be assumed that product No. 6 possesses the oxazolidine-2-one structure given in Fig. 6.

Summarizing these results, three different types of products were characterized, respectively, as an oxazoline, an oligomer of the type A and an oxazolidine-2-one. Taking into consideration the formation of these products we propose a reaction mechanism similar to the well known reaction pathway published for urea derivates such as Monuron and Diuron used as accelerators for the epoxy resin curing with DCDA (12,22).



The trisubstituted DMePhDCDA split into a carbodiimide and dimethyl amine (Eq. 1). The dimethyl amine or its addition product with PGE (tert. amino alcohol) are typical accelerators for the oligomerization of glycidyl ethers (Eq. 6) extensively described by FEDTKE (23). Main products using this accelerator type are known as A-oligomers possessing a endstanding double bond found as product No. 7 with n = 2.

The carbodiimide is able to react with epoxies forming oxazoline cycles (Eq. 4). Such a reaction is known for the tautomeric cyanamide. Thus, the same reaction course was proposed for DCDA glycidyl ether reactions discussing a tautomeric carbodiimide form of the DCDA favoured at higher temperatures (7).

The oxazolidine-2-one is formed by hydrolysis (Eq. 5) with the water available in the system. In Fig. 7 the proposed reaction course is summarized. The initial step for both of the substituted DCDA is their decomposition into a carbodiimide and an amine (Eq. 1-3). Two different possibilities were found for the decomposition of DPhDCDA (Eq. 2,3). The same products obtained in the case of DMePhDCDA were formed for the splitting into the nitrile phenyl carbodiimide. Additional products could be observed in the case of the decomposition into the diphenyl carbodiimide (Eq. 3). However, the disubstituted DPhDCDA is less reactive than the trisubstituted DMePhDCDA.

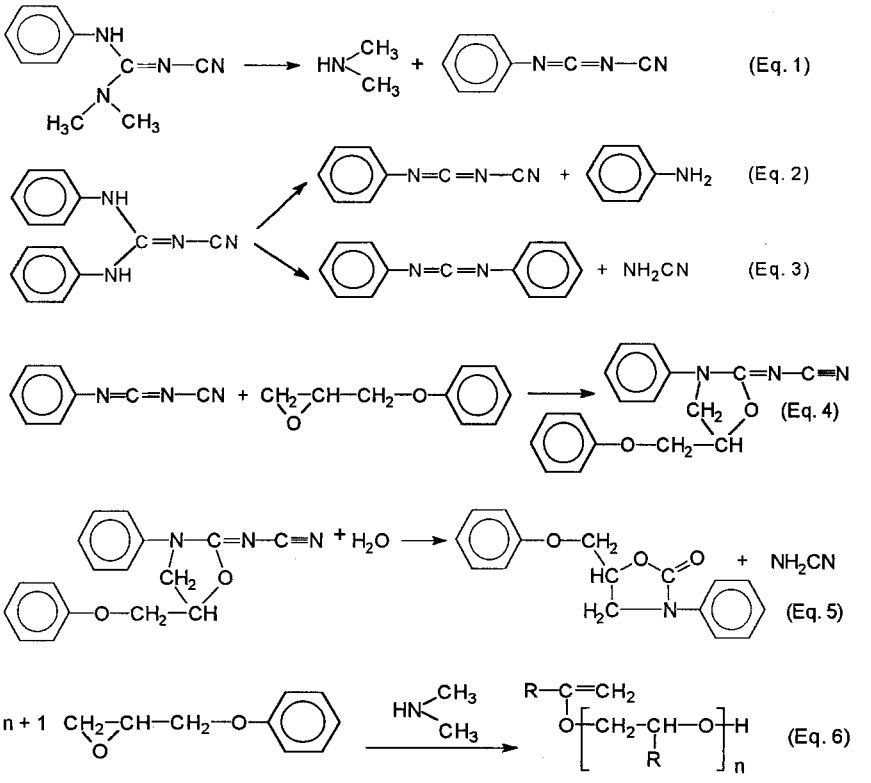



Fig. 7: Proposed reaction pathway for reaction mixtures containing PGE and a substituted DCDA

Taking into consideration these results the suggested reaction pathway for the tautomeric carbodiimide form of the DCDA is more comprehensible (7). More information concerning the stability of alkylated DCDA as products formed in DCDA - glycidyl ether reactions is needed for a better understanding of the complex curing mechanism using this hardener.

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