Curing of epoxy resins with dicyandiamide: NMR and IR investigation of isolated main products

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Summary

The mechanism of the epoxy resin curing with dicyandiamide was studied using the model phenyl glycidyl ether. Some reaction products were isolated by HPLC and characterized by FTIR and Carbon-13 NMR spectroscopy. Examples are given to illustrate the presence of linear and cyclic structures with or without nitrile functions in the complex reaction mixture.

Introduction

The complex mechanism of the dicyandiamide (DCDA) cure of epoxy resins has been discussed in a series of papers (1-14). In (15) a summary of suggested reaction pathways is given. However, a lot of ambiguities exist taking into consideration the published difference in results and their interpretations. Furthermore, the analytical investigations were hampered due to the insolubility of the DCDA and the inherent inhomogeneity of the epoxy cure using DCDA. Thus, we used phenyl glycidyl ether (PGE) as monofunctional epoxy compound, DCDA, imidazole as accelerator and DMF as solvent in order to obtain more information on the curing mechanism.

The first reaction step should be the addition of the glycidyl ether to the NH_2-group of the DCDA. Furthermore, the etherification of the hydroxyl groups formed in the first step was described in the literature (2-15). 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. Different suggestions exist for reactions leading to cyclic products. ZAHIR (2), PASCAULT et al. (3,4), GILBERT et al. (5,6) and PFITZMANN et al. (12-16) supposed cycles with various oxazoline or oxazolidine structures.

The aim of this paper is to represent our investigation of products separated by preparative HPLC. These products were characterized by FTIR and Carbon-13 spectroscopy to study the main reaction course. Taking into account the progress of reaction and the chromatographic behaviour some structures will be presented.

Experimental

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

The reactions of a PGE-DCDA-DMF = 3:1:3 mixture at 140 °C for 1 hour and of a PGE-DCDA-imidazole = 8:1:0.04 mixture at 110 °C for 1 hour were carried out in a thermostated three necked flask equipped with a thermometer, magnetic stirrer and reflux condenser.

Preparative HPLC was run with apparatus from KNAUER (Wissenschaftliche Geräte KG);

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column: 250 * 16 mm with LiChrosorb RP-18, 5 µm; eluent: acetonitrile-water 30:70 to 100:0 linear (Fig. 1a) or 15:85 to 85:15 linear + 100:0 nonlinear + 100:0 isocratic (Fig. 1b); flow: 18 ml/min; detection: UV 254 nm; sample: 500 µl of a 20 % solution in acetonitrile.

Carbon-13 NMR spectra were obtained on a BRUKER MSL 200 and on a VARIAN Gemini 300 spectrometer (frequency: 50.32 and 75.43 MHz) using DMSO-d_6 as solvent and HMDS as standard. Depending on the sample the number of scans was extended up to 30, 000.

FTIR spectra were recorded with a NICOLET 205 and an IRF-180/SM 1420 spectrometer from solutions in chloroform or as KBr pellets (32 scans, resolution: 4 cm^{-1}).

MS spectra were recorded according to ref. (20).

Results and discussion

Fractions named Px were separated from an imidazole accelerated reaction mixture in order to demonstrate the formation of linear epoxide-amide addition products in the first reaction steps at lower temperatures and at a certain level of conversion (Fig. 1a). More than 20 peaks were found in DCDA-PGE-DMF reaction mixtures using analytical HPLC (11). 10 fractions (called Mx) were chosen for running the preparative HPLC with differently expanded gradients (Fig. 1b). The complete assignment of the NMR data succeeded only for some fractions.

The chemical shift of the four different aromatic carbon atoms appear at about 159, 130, 120 and 115 ppm similar to the initial PGE. Double peaks, shoulders or a number of separated signals especially for the carbon atoms at 160 - 158 ppm and at 121 - 119 ppm demonstrate the presence of various chemical neighbours located in the aliphatic part of the molecules. Strongly structured aromatic regions give reason to suppose a high degree of rearrangements inside the aliphatic chains or the initial DCDA structure. Particularly instructive in the characterization of the isolated products are the chemical shifts of the aliphatic carbons between 40 and 80 ppm.

The peak with the highest downfield shift into the 78 - 76 ppm region was detected as a >CH- group formed by etherification or a >CH-group of an oxazoline formed by cyclization (15).

Most of the peaks are located between 72 and 66 ppm. Our data for PGE-DCDA-DMF reaction mixtures, published for the first time in (12), gave not only the attribution for the initial compounds and the aromatic carbon atoms but also for some possibly different aliphatic carbon atoms located in the 70 ppm region.
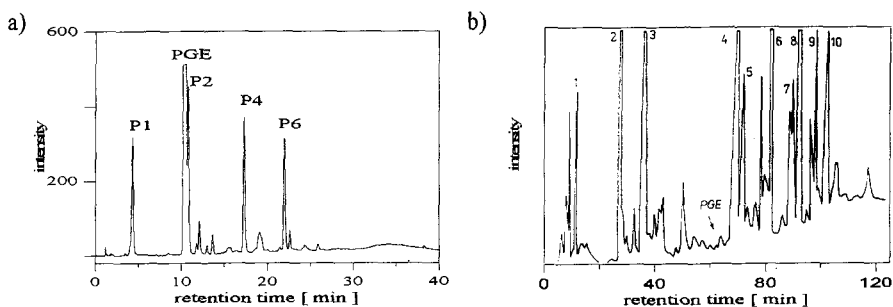

Fig. 1: HPLC chromatograms with the attribution for the separated fractions:
a) PGE-DCDA-imidazole = 8:1:0.04 at 110 °C and 35 % epoxy conversion (Px)
b) PGE-DCDA-DMF = 3:1:3 at 140 °C and nearly 100 % epoxy conversion (Mx)

They belong to linear epoxy-amide addition products formed in the first reaction step that was described by a number of authors, to the etherification of secondary hydroxyl groups and also to some proposed cyclic compounds:

- the different -O-CH$_2$-groups next to the phenyl rest
- the -CH(OH)-group in secondary alcohols and
- the -CH$_2$-O-group of an aliphatic ether linkage mostly between 72 and 71 ppm

The -NH-CH$_2$-groups are located in the 45 ppm region. In (12) the peak at 49.2 ppm next to the initial epoxy peak at 50.4 ppm was assigned as secondary amide investigating samples of a complete and highly viscous reaction mixture. No we are in the position to evaluate our experiments and NMR data reported in (12) by more detailed measurements.

Corresponding to their chromatographic behaviour, the FTIR results, the MS data (mole peaks and typical fragments (20)) and their simple NMR spectra (high purity, 3 aliphatic carbon atoms, see Fig. 2), the products P1 and P2 were identified as the first two linear amide-epoxide-addition products. P2 has been already reported by PASCAULT et al. as 3:1 product with ether structure (fraction B in (3) or in our summary (15)). However, the only 3 aliphatic carbons found are a sure analytical evidence for a symmetrical compound. The products possess their -NH-CH$_2$- peaks at 44.5 and 45.3 ppm, respectively. Unfortunately, these peaks were covered by the epoxy signal at 44.3 ppm in (12). The nitrile function (118 ppm and 2180 cm^{-1}) and the >C=N-group (about 161 ppm) are unambiguously visible. 118.8 ppm for the nitrile function and 163.4 ppm for the >C=N-group were found in a spectrum of the initial DCDA (12). P1 (MS mole peak at 234 g/mole) contains a small part of about 10 % of a second product (Fig. 5) identified as PGE glycol (see our chromatographic studies (11)) with a mole peak at 168 g/mole.
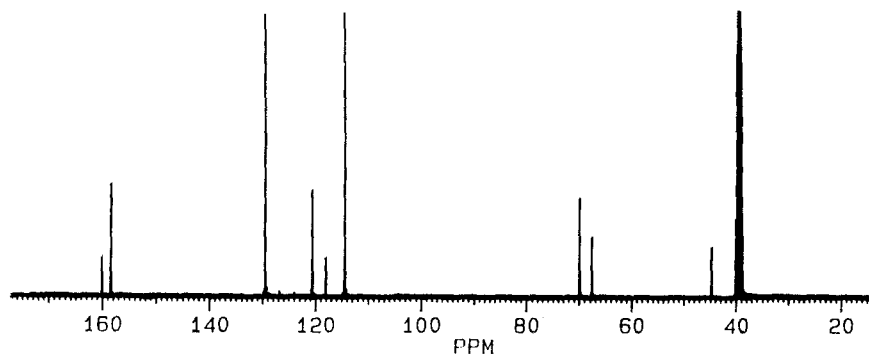

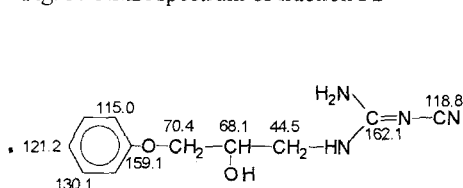Fig. 2: NMR spectrum of fraction P2

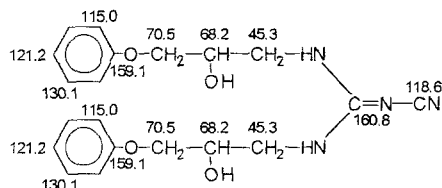Fig. 3: Assignment for fraction P1

Fig. 4: Assignment for fraction P2

115.0

70.5   70.0   63.3

121.0 〈◯〉-O-CH₂-CH-CH₂-OH
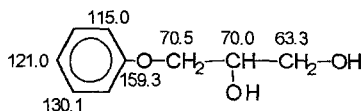   159.3

130.1   OH

Fig. 5: Main component of fraction M2 (PGE glycol)

M2 possessing under similar chromatographic conditions the same retention time as P1 is a mixture of two products. However, with increasing temperature and epoxy conversion the composition was changed. The separated fraction consists of PGE glycol as main component (Fig. 5) and a product with a peak at 78.9 ppm (>CH- of an oxazoline ?) and a >C=N- (or >C=O) function at 161.1 ppm as well as IR bands in the 1670 cm^{-1} region that is typical for oxazolines. But no nitrile group was found. Moreover, the small 1740 cm^{-1} band could be the >C=O of a third component. This demonstrates the difficult problems concerning the interpretation of the analytical data obtained for this complex reaction system. At least 3 products were eluated and detected as one HPLC peak. In addition, the composition of this fraction depends on the temperature on the phase behaviour and on the conversion.

The most important structure elements to distinguish among the formed products are the >N-CH₂- and the -NH-CH₂-groups. A lot of different peaks were found between 45 and 65 ppm standing for secondary and tertiary amides or ureas and cyclic products such as oxazolines and oxazolidine-2-ones. Some oxazolines were measured as model compounds showing their carbon atom of the >N-CH₂-group between 55 and 54 ppm. GILBERT et al. assigned a peak at 51.8 ppm to this group (6).

In accordance with the results published by GILBERT (6), fraction M6 should have a cyclic oxazolidine structure with intact nitrile function shifted to 115.1 ppm and 2204 cm^{-1}, respectively. The presence of split signals with differences of tenths of ppm for some peaks shown in Fig. 6 is still an unsolved problem.

69.6   66.4   48.9   69.8   67.0   46.8
69.7   66.3   49.2   162.4   115.1   69.9   66.8   47.0   157.5

Ph-O-CH₂-CH-CH₂-N-C=N-C≡N   Ph-O-CH₂-CH-CH₂-N-C=O

       OH   47.8 CH₂ O   OH   45.9 CH₂ O

       Ph-O-CH₂-CH   Ph-O-CH₂-CH
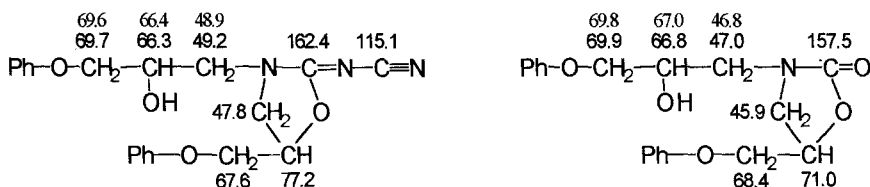   67.6   77.2   68.4   71.0

Fig. 6: Assignment for fraction M6 (left: oxazolidine, right: oxazolidin-2-one)

The spectrum of M6 shows 6 further aliphatic carbon atoms of a 2 : 1 product in a lower quantity (max. 20 %) with the same characteristic double peaks as the main component. The difference in the chemical shifts depends on the distance from the >C=N-CN unit. Thus, the >CH- peak appears at 71.0 ppm. Furthermore, the fractions M2, M6 and P4 show weak >C=O bands at 1740 cm^{-1}. Oxazolidin-2-ones having their IR signals in this region are imaginable products. It was shown by GILBERT (6) and in (16) that the formed oxazolidines could be hydrolyzed. This reaction occurs during the curing process. Both products have a similar chromatographic behaviour (neighbour peaks (6)). It is already known that traces of carbonyl compounds are visible in IR caused by the high extinction while often no adequate NMR peak could be found. Moreover, we are not able to completely exclude the partial hydrolysis of the collected fraction containing more than 50 % water and an oxazolidine after its separation. Thus, we suggest an oxazolidin-2-one as second component of fraction M6 (Fig. 6).
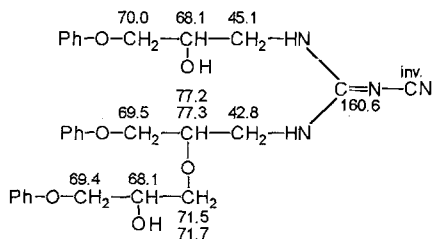
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   70.0   68.1  45.1
Ph–O–CH₂—CH—CH₂—HN
              |           \
             OH            \      inv.
                           C=N—CN
   77.2                   /160.6
   69.5   77.3  42.8     /
Ph–O–CH₂—CH—CH₂—HN
              |
   69.4  68.1 O
Ph–O–CH₂—CH—CH₂
          |    71.5
         OH    71.7
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Fig. 7: Proposed chemical structure
and chemical shifts of P4

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                                        N=\    NH₂
   70.6    67.7   43.6              N—\      \
Ph–O–CH₂—CH—CH₂—HN——\    N          165.6 to
              |                \   //         166.3 for
             OH                N—              >C=N—
                                    \
                                     NH₂
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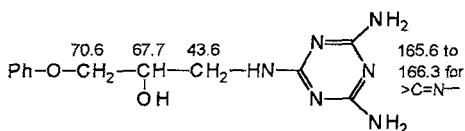
Fig. 8: Proposed chemical structure and
chemical shifts of M3

Fraction P4 was identified as 3:1 linear addition product (Fig. 7) possessing for ether linkages typical NMR peaks at 77.3 and 77.2 ppm (>CH-) as well as two peaks at 71.7 and 71.5 ppm (-CH₂-). The low concentrated -CN (quarternary carbon atom, long relaxation time) could only be found in the IR spectrum. However, the molecular weight was determined using MS (mole peak of 534 g/mole) demonstrating a further evidence for the proposed structure of a 3:1 product. A second component shows peaks at 78.9 and at 159.5 ppm. It seems to be a cyclic oxazoline or a tautomeric oxazolidine with a structure not clearly definable, but similar to the second part of M2 with 2 PGE-units difference.

A further series of products were found in the fractions M1, M3, M4 and M8 (see Fig. 1b). The characteristic split peaks near 166 ppm are probably caused by substituted melamine structures that were also proposed by GRENIER-LOUSTALOT (10). The peak assignment of the aliphatic part is still not completely clear. However, typical signals were observed at 43.6 ppm, near 68 and 70 ppm. All the fractions contain more than one product, and the determination of the molecular weight was not successful.

M3 consists of two products. We suppose the 1:1 addition product of PGE and melamine shown in Fig. 8. The second part correspond to the spectroscopic data of P1. This product could be separated from M2 using a flat and long gradient.

M4 is also a mixture of two or more linear and/or cyclic components with two peaks for the >C=N- unit (163.8 and 163.9 ppm). However, the -CN group is very weak in the NMR spectrum. Split aromatic signals and a lot of different aliphatic carbon atoms including three various >CH₂-N< signals were found at 43.6, 46.0 and 46.1 as well as 50.9 and 51.1 ppm. A small part should be an unsymmetrical linear 2:1 addition product with an ether structure at 76 and 71 ppm (Fig. 9) or a melamine product with ether structure. Thus, the difference between the products of this series (M1, M3, M4 and M8) is one PGE-unit.

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                     H₂N
                        \          118.5
             46.1       C=N—CN
   69.7   76   46.0    /163.9
Ph–O–CH₂—CH—CH₂—HN     163.8
              |
   69.4  68.4 O
Ph–O–CH₂—CH—CH₂
          |
         OH  71
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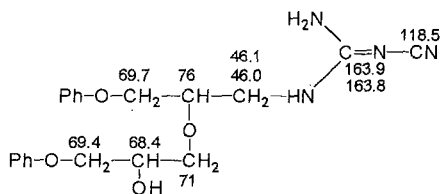
Fig. 9: Proposed chemical structure and
chemical shifts of one part of M4

Table 1: IR bands of separated fractions (* oxazo = oxazolidin-2-one)

Peak No. M x	-CN linear ν in cm^{-1}	-CN cycl. ν in cm^{-1}	oxazo * ν in cm^{-1}	amide I ν in cm^{-1}	amide II ν in cm^{-1}	amide II ν in cm^{-1}
2	-	-	1740	1676	-	1576
3	2176	-	-	-	1640	1572
4	2180	-	-	-	1640	-
5	2180	-	1760	1700	1640	1534
6	-	2204	1734	-	1640	-
7	2180	-	1734	1676	1640	1572
8	-	-	-	-	1632	1544
9	-	-	-	1700	1640	1572

NMR spectra were run for the fractions M8, M9, M10 and P6. Complex mixtures, low concentrations and a great number of NMR-peaks prevent a detailed discussion. Thus, the detection for 3 or more (up to 8 signals in the case of M8) different aromatic rings or more than 30 peaks in the aliphatic region were found. Some IR-data are given in Table 1. The NMR-spectra correspond to the possible product formation reported in (15). An example of a further product type was found in fraction M9 possessing three groups of three peaks near 68, 66 and 57 ppm. No -CN and no >C=N- function were detected.

The collected products were dried carefully. However, it was not possible to eliminate all traces of water. This fact is a problem for the discussion of >NH and -NH$_2$ groups in the 3600 - 3100 cm^{-1} region of an IR-spectra. The most important regions for the interpretation are the nitrile region at about 2200 cm^{-1} and the carbonyl region between 1800 and 1600 cm^{-1}. Taking into consideration the data taken from the literature (Table 2) and results obtained with prepared model compounds or the Carbon-13 NMR investigations, some wavelengths could be attributed to defined structure units (Table 1). The positions of the found IR bands are summarized in Table 1. It is remarkable that a number of different bands in the carbonyl region should indicate a various series of products possessing differently bound >C=N- or >C=O functions.

Table 2: IR bands in the carbonyl region of DCDA - epoxide reaction systems taken from the literature

wavelength in cm^{-1}	author	ref.
1700	SAUNDERS	(1)
1736, 1700, 1660	ZAHIR	(2)
1740, 1680 -1650	PASCAULT	(3,4)
1774, 1758, 1722, 1700, 1650 -1640, 1560	GILBERT	(5,6)
1740, 1680, 1645	GRENIER-LOUSTALOT	(10)
1725 -1700	EYERER	(17)
1738, 1683	ZEPPENFELD	(18)
1760, 1748, 1690, 1650, 1570	DAVIDSON	(19)

Conclusion

Our model investigation give rise to distinguish among different series of products formed in DCDA-epoxy-reactions. The characterization of some products is given in this paper concerning our recent NMR, IR and MS studies. Evidences for proposed structures and the corresponding reaction course reported in (15) are useful to understand the complex chemical nature of the epoxy cure with DCDA more completely. This knowledge is the crucial point to influence successfully the prepreg formation and curing technology which is important in electronic industries.

Acknowledgement

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