

Effects of reactive diluents in curing of epoxies as revealed by model reactions

F. Domaratius, S. Walther, and M. Fedtke*

Technische Hochschule "Carl Schorlemmer" Leuna-Merseburg, DDR-4200 Merseburg, German Democratic Republic

Summary

The tertiary amine induced oligomerization of diglycidyl ether of bisphenol A (DGEBA) containing epoxide-based diluents as well as the model reaction with phenyl glycidyl ether (PGE) itself were investigated. The oligomer products obtained were separated by HPLC. The structure of these oligomers was elucidated by spectroscopic methods. Reactive diluents such as phenyl glycidyl ether and cyclohexyl glycidyl ether (CHGE) influence the cure time and the network formation of the final crosslinked product.

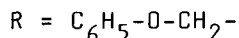
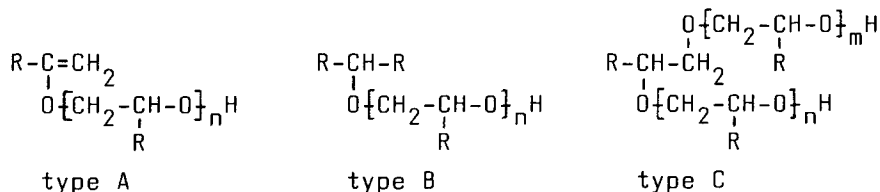
Introduction

The curing of epoxy resins with various hardeners is of great technical importance. Usually commercial low- and mediummolecular epoxy resins contain diluents to reduce their initial viscosity. These diluents can be divided into three groups: (A) non-reactive, (B) reactive, containing epoxides and (C) reactive, containing functional groups other than epoxides (1).

We examined the influence of epoxide containing diluents on the oligomerization reaction of glycidyl ethers with tertiary amines as accelerators. The mechanisms of the homopolymerization with tertiary amines have been studied in length in many laboratories (2-7). We recently published a review of these mechanisms (8).

The end groups of the oligomers formed depend on the different possibilities of the amine-epoxide interactions. The oligomers investigated are shown in Scheme 1. The mechanisms leading to these oligomers have already been published (8).

Scheme 1 : Types of phenyl glycidyl ether oligomers



*To whom offprint requests should be sent

The present paper deals with the cooligomerization of PGE and DGEBA with monofunctional glycidyl ether as epoxide containing reactive diluent using dimethylbenzylamine (DMBA) as accelerator.

Experimental

2,2-Bis[4-(2,3-epoxypropoxy)phenyl]propane (DGEBA): Epilox A17-00 (VEB Leuna-Werke "Walter Ulbricht", GDR) was purified by crystallization from an acetone-methanole-mixture; m.p. 42 °C. PGE (1-phenoxy-2,3-epoxypropane) was prepared according to ref.(9); b.p. 96-98 °C / 0.4 kPa. CHGE (1-cyclohexyl-2,3-epoxypropane) was prepared according to ref.(10); b.p. 83-88 °C / 0.5 kPa. DMBA was dried with potassium hydroxide pellets, purified with phenyl isocyanate and distilled under reduced pressure; b.p. 55-56 °C / 1.2 kPa.

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

The epoxy content was determined by a direct method with HBr in acetic acid; initiator was crystal violet (11). HPLC was carried out with a KNAUER-apparatus (Dr.-Ing. H. Knauer Wissenschaftliche Geräte KG, FRG); column: 250x4 mm, LiChrosorb RP-18 (5 µm) for analytical scale and 250x16 mm LiChroprep RP-18 (5-20 µm) for preparative scale; eluent acetonitrile-water (gradient mode); detection: UV λ /nm = 254. ¹H-NMR-spectroscopy was performed with a HX-90R instrument from BRUKER.

Gelation times were determined by a method according to Gough and Smith (12) using an instrument that we ourselves had constructed.

Results and Discussion

Reaction of phenyl glycidyl ether with cyclohexyl glycidyl ether catalyzed by dimethylbenzylamine

The simultaneous oligomerization of PGE and CHGE was used for the kinetic measurement. Fig. 1 shows the conversion curves of epoxide for different molar ratios of the reactants. The consumption of epoxide depends on the ratio of the epoxide components. With a gradual increase in concentration of CHGE we found a decrease in the reaction rate.

The decrease of both epoxide monomers was determined by gaschromatography. At equimolar ratio (PGE:CHGE=1) the rate of PGE consumption is about five times higher than that of CHGE.

For further characterization of the reaction course, it appeared to be necessary to use high performance liquid chromatography (HPLC) as an analytical method. Using PGE as epoxy component, the homologous oligomeric compounds could be detected with an UV-detector. Fig. 2 illustrates a typical chromatogram of the simultaneous formation of different types of oligomers (n_{A_i} , x_i). The products n_{A_i} are the well-known type A oligomers with a double bond at the chain end (7). Homooligomers of CHGE could not be analyzed under these analytical conditions.

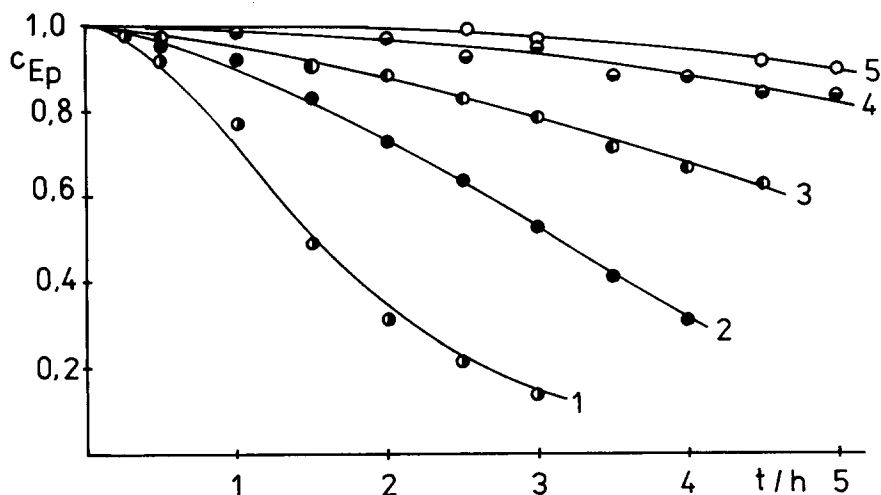


Fig. 1: Epoxide conversions in the PGE/CHGE system
(temperature: 100 °C; DMBA: 10 mole %)
1 = 1 : 0; 2 = 0.7 : 0.3; 3 = 0.5 : 0.5;
4 = 0.3 : 0.7; 5 = 0 : 1

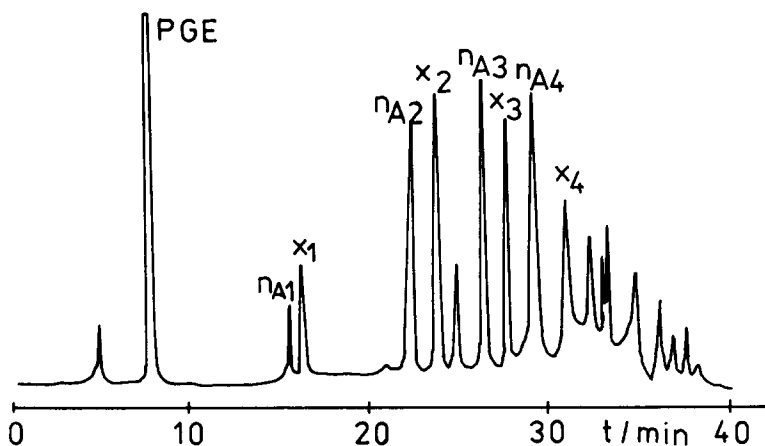
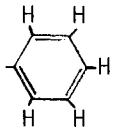
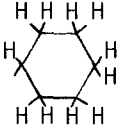


Fig. 2: HPLC of reaction products in the PGE/CHGE/DMBA system;
molar ratio: 0.5:0.5:0.1; temperature: 80 °C; epoxide
conversion: 60 %; eluent: CH₃CN/H₂O, changing from
vol. ratio 30:70 to 100:0 in 30 min at flow rate of
1.7 ml/min
n_{Ai} - type A oligomers
x_i - cooligomers

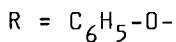
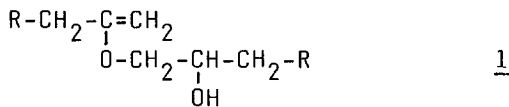
According to these results we classify the unknown oligomers (x_i) as cooligomers of PGE and CHGE. To identify the structure of the oligomer range (n_{A1}, x₁, x₂) we separated by preparative HPLC. The substances obtained were analyzed by

Table 1: $^1\text{H-NMR}$ -spectra of compounds n_{A1} , x_1 , x_2

Functional groups	Chemical shift (in ppm)	Intensity					
		n_{A1}		x_1		x_2	
		Number of protons	found	Number of protons	found	Number of protons	found
	6.8...7.4	10	10.5	5	5.5	10	10.5
-CH-; -CH ₂ -	3.4...4.2	7	8.4	7	6.6	12	11.9
-OH	3.2	1	0.9	1	1.1	1	1.2
>C=CH ₂	4.4	2	1.9	2	1.9	2	2.1
	1.0...1.7	-	-	11	11.0	11	9.5

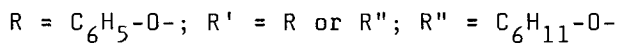
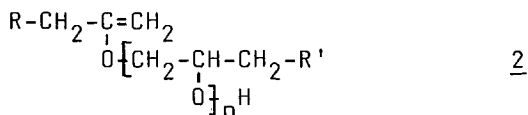
spectroscopic methods. Table 1 shows the results of $^1\text{H-NMR}$ -spectroscopy.

The signals of compound n_{A1} are in agreement with structure 1 and can be assigned as follows:



This formula confirmed the structure of the type A oligomers with a double bond at the chain end postulated in previous papers (4-8).

An analogous structure is proposed for compounds x_1 and x_2 :



Compound x_1 may have been formed from 1 mole PGE and 1 mole CHGE ($n = 1$). The formation of the compound x_2 can be explained from x_1 and PGE or from n_{A1} and CHGE ($n = 2$). However, the formation of the latter proves the effect of CHGE as comonomer for the model reaction of glycidyl ethers with tertiary amines.

Reaction of diglycidyl ether of bisphenol A with mono-functional glycidyl ethers induced by dimethylbenzylamine

The crosslinking DGEBA accelerated by DMBA was investigated using CHGE and PGE as reactive diluents. Information about the cure of DGEBA was obtained by gelation time analysis. The data generated are shown in Table 2. A significant increase in gelation time and hence a decrease in

Table 2 : Gelation times of DGEBA-systems accelerated with DMBA (5 mole%); temperatures 90 °C

system	ratio	gel time (min)
DGEBA		93
DGEBA : PGE	0.7 : 0.3	118
DGEBA : PGE	0.5 : 0.5	152
DGEBA : CHGE	0.7 : 0.3	183
DGEBA : CHGE	0.5 : 0.5	353

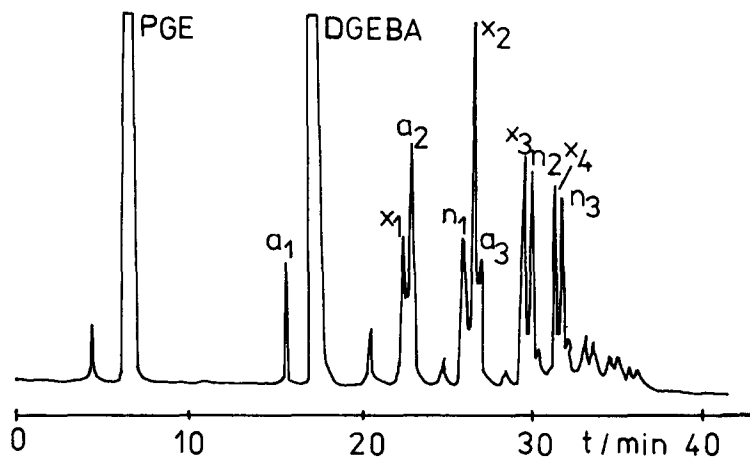


Fig. 3: HPLC of reaction products in the DGEBA/PGE/DMBA system molar ratio: 0.5:0.5:0.1; temperature: 80 °C; epoxide conversion: 30 %; HPLC conditions see Fig. 2

a_i - oligomers from DGEBA/DMBA

n_i - oligomers from PGE/DMBA

x_i - cooligomers

curing rate was caused by the addition of an epoxy-reactive diluent, e.g. PGE, CHGE.

The course of the reaction between DGEBA and a diluent (PGE, CHGE) catalyzed by DMBA can be analyzed by HPLC where the epoxide conversion is not higher than 35%. Fig. 3 illustrates the effect of PGE as epoxide containing diluent under this condition.

A chromatographic comparison with the products of DGEBA/DMBA (a.) and PGE/DMBA (n.) was carried out to determine the oligomer structure of the primary products. It is shown in Fig. 3 that a third group of oligomers (x_i) was formed. We classify these products as cooligomers from DGEBA and PGE accelerated with DMBA. With CHGE as diluent similar chromatograms were obtained and determined as cooligomers from DGEBA and CHGE. The amount of cooligomers from DGEBA and CHGE is less than with PGE as diluent. The values in Table 2 can be interpreted in this way. PGE is a more reactive diluent than CHGE. CHGE acts more as a non-reactive than as a reactive diluent.

For practical cure of epoxy resin system it is possible that diluent play not only an important role in variation of cure time. In the same way reactive diluents influence the formation of the resulting network.

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