Curing of Epoxy Resins with Amines
Gelation of Polyepoxides Derived from Diglycidylaniline

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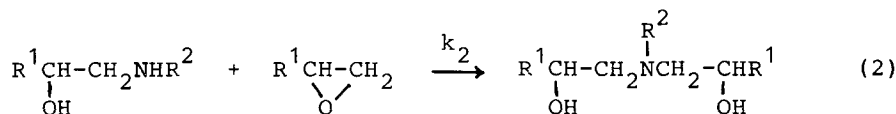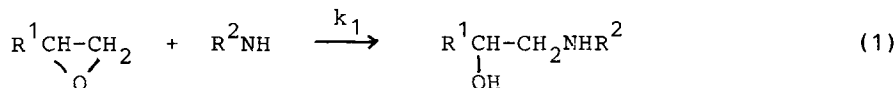[2] Research Institute of Synthetic Resins and Lacquers, Pardubice, Czechoslovakia

Summary

Using determination of the critical molar ratio of functional groups necessary for gel formation with amino groups in excess, network formation was investigated in the reaction of diglycidyl ether of Bisphenol A (DGEBA) and nitrogen-containing epoxy resins - diglycidylaniline and N,N,N´,N´-tetraglycidyl-4,4´-diaminodiphenylmethane with aromatic or aliphatic amines. It was found that in the case of nitrogen-containing epoxides the crosslinking is accompanied by pronounced cyclization, unlike in systems with DGEBA. Gelation depends on the relative reactivity of the primary and secondary hydrogen atom of the amino group. In the case of nitrogen-containing polyepoxides, the dependence of reactivities of adjacent glycidyl groups is also operative.

Introduction

Epoxy resins used for high-performance composites with high heat resistance are usually polyfunctional. Most often, N,N,N´,N´-tetraglycidyl-4,4´-diaminodiphenylmethane - TGDDM is used

TGDDM
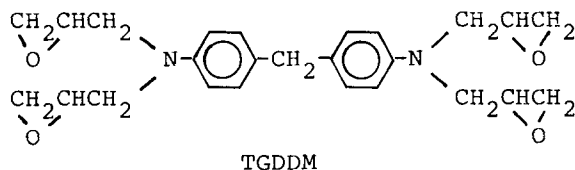
The primary amine group is added to the epoxy group in two stages

$$R^1CH\!-\!CH_2 \; + \; R^2NH \xrightarrow{\;k_1\;} R^1CH\!-\!CH_2NHR^2 \tag{1}$$

$$R^1CH\!-\!CH_2NHR^2 \; + \; R^1CH\!-\!CH_2 \xrightarrow{\;k_2\;} R^1CH\!-\!CH_2NCH_2\!-\!CHR^1 \tag{2}$$

With the epoxide in excess, etherification may take place via a reaction between the epoxy and hydroxyl group. In the absence of etherification an important parameter, which determines the network structure, becomes the ratio of rate constants, $k_2/k_1 = \rho$. With polyepoxides having independent reactivities of the epoxy groups, such as, e.g., bis(epoxy-2,3-propoxy)-4-phenyl-2,2-propane (diglycidyl ether of Bisphenol A - DGEBA) the value of ρ determines the critical molar ratio between the amino and epoxy groups, $r_c = 2[NH_2]_0/[E]_0$, where $[NH_2]_0$ and $[E]_0$ are the initial molar concentrations of amino and epoxy groups, respectively. The ratio r_c is also affected by the functionality of polyepoxide and polyamine (an independent reactivity of amino groups is assumed), and by cyclization, if it does occur. In the case of DGEBA the tendency towards cyclization is very weak (1,2), especially if aromatic diamines are used. The effect of cyclization on r_c may be eliminated by determining r_c as a function of dilution, followed by extrapolation to a hypothetical state of infinite concentration of groups (cf., e.g., (3)).

In TGDDM and its bifunctional analog N,N-diglycidyl-aniline (DGA),

$$\langle \bigcirc \rangle - N \underset{CH_2CHCH_2}{\overset{CH_2CHCH_2}{\diagdown}}$$

DGA
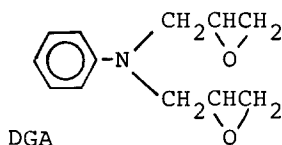
however, the glycidyl groups are relatively close to each other, which (a) may affect their reactivity, (b) raises the probability of cyclization (4-6).

In this study we used the critical molar ratio of functional groups in characterizing the relative reactivity of functional groups and the extent of cyclization in DGA and TGDDM compared with DGEBA.

Experimental

Diglycidylaniline (DGA) contained 9.75 mmol epoxy groups/g (theory 9.76 mmol/g); according to liquid chromatography, it was 100%. Its synthesis has been described in a preceding paper (7). N,N,N´,N´-Tetraglycidyl-4,4´-diaminodiphenylmethane (TGDDM) was prepared in two stages, similarly to DGA: In the first stage, chlorohydrine was prepared from 4,4´-diamino-diphenylmethane, and was dehydrochlorinated in the second stage by the following procedure: A solution of 285 g of N,N,N´,N´-tetra-(2-hydroxy-3-chloropropyl)-4,4´-diaminodiphenylmethane (m.p. 138-139°C) in 210 g of methylisobutyl ketone was heated to 50°C, and 280 g of a 50% aqueous NaOH solution was added with stirring within one hour. The mixture was stirred at 50°C for 8 h, the reaction product NaCl was dissolved in 200 ml water, and the organic phase was washed three times with 100 g of a 5% NaCl solution. After the solvent had been distilled off at pressure 1330 Pa and temperature had been raised up to 140°C, 200 g of liquid was obtained, with the content of epoxy

groups 9.16 mmol/g, chlorine content 0.28%, M_n (VPO) = 440 and viscosity 70 Pa.s at 25°C. The content of epoxy groups was determined using the addition of HCl in pyridine and back titration of HCl in excess. From GPC and liquid chromatography measurements, an approximate composition of the resin was estimated as 91.7% TGDDM, 8.0% TGDDM dimer and 0.3% chloro-hydrine. Bisphenol A diglycidyl ether (DGEBA) contained 5.62 mmol epoxy groups per g (theory 5.88 mmol/g).

Diaminodiphenylmethane (DDM) (99.5% - gas chromatography) was recrystallized from toluene; the purity of octamethylene diamine (OMDA) was 99.3% (titration). Triethyleneglycoldimethyl ether (TEGDME) (Fluka) was used as obtained (98% - gas chromatography).

Experimental techniques

The reaction of epoxides with amine in excess proceeded in bulk or in the presence of a diluent, TEGDME (20-60%) 2-7 days at 130-140°C up to the full conversion of epoxy groups. A series of samples with various ratios of functional groups, r, was prepared. The critical molar ratio, r_c, was determined as an interval between the last sample containing gel and the first sample in which the gel was not formed any more. The samples were prepared in ampoules, the inner surface of which was hydrophobized with dimethyldichlorosilane. Dimethylsulf-oxide at 80°C was used for the solubility check.

By using liquid chromatography and model systems DGEBA-N-methylaniline (NMA) and DGA-NMA, it was verified that with amine in excess no etherification takes place under the experimental conditions used.

Results and Discussion

Cyclization

Fig.1 shows the dependence of the critical molar ratio of functional groups on dilution (1/C), where C is the initial molar concentration of functional groups. The slope of this dependence characterizes the tendency to cyclization (3). It can be seen that in systems DGEBA-DDM and DGEBA-OMDA no cycli-zation takes place, because r_c is independent of dilution. The DGEBA-DDM system is very stiff, which impedes cyclization; also, it can be seen that the more flexible DGEBA-OMDA does not react intramolecularly either.

On the contrary, in the case of DGA and TGDDM the decrease in the critical ratio with dilution of the reaction mixture suggests the distinct role played by the intramolecular reac-tion. Cyclization is possible in the transformation of the monoadduct (a) by an intramolecular reaction of the secondary amino group (4,5), or (b) by a reaction between the OH group and the adjacent epoxy group (6).
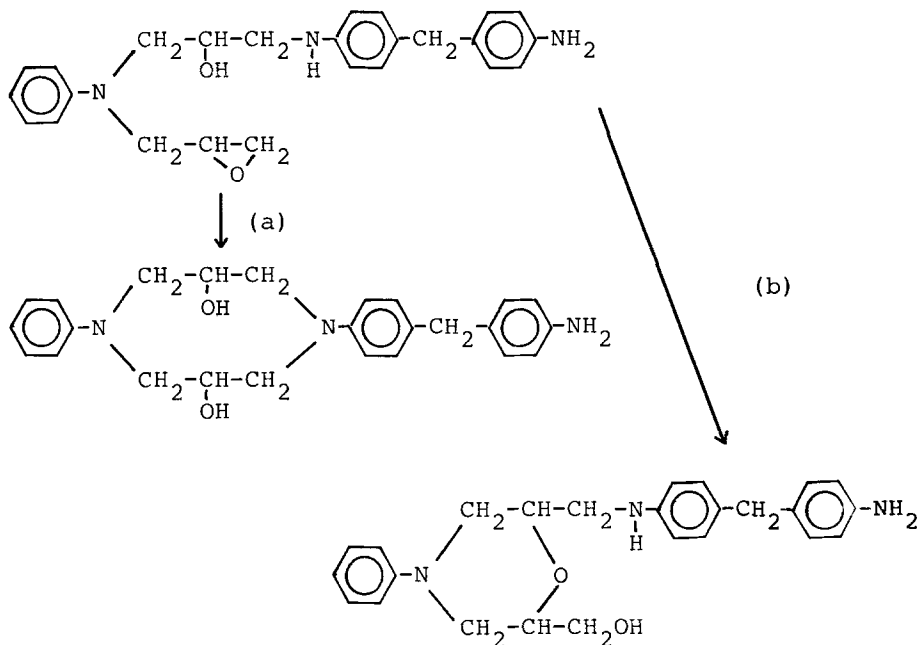
This reduces the effective functionality, and r_c decreases. The higher cyclization in the case of DGA—OMDA is probably due to the higher flexibility of the aliphatic amine.

Strong cyclization takes place particularly in TGDDM. The shape of the dependence may be affected by association with the solvent, because in the TGDDM-DDM system the curvature is less pronounced in the solution in dioxan than in TEGDME (Fig.1).

Under the given experimental conditions (amino groups in excess) reaction (b) is unlikely, because for the system DGA-NMA it has been proved by NMR analysis that the reaction gives rise to noncyclic stereoisomers only (7).

Relative reactivity of amino and epoxy groups

The effect of cyclization may be eliminated by extra-polating the r_c vs. 1/C dependence to infinite concentration of groups $(1/C \rightarrow 0)$, but extrapolated $(r_c)_{ext}$ values (Table 1) are lower than those corresponding to the independent reactivity of epoxy groups, amino groups and hydrogen atoms in primary and secondary amino groups ($\rho = 1/2$ cf.(8)). In the case of systems containing DGEBA with independent epoxy groups such decrease is given by the lower reactivity of hydrogen in secondary amino groups compared with hydrogen atoms in primary groups (negative substitution effect, $\rho < 1/2$); Equations (1) and (2) are applicable. The ρ - values calculated from experimental data $(r_c)_{ext}$ by using the theory of branching processes (9) lie within the range of values determined earlier for similar systems and by employing other methods (8). Fig.2 shows the theoretical dependences of
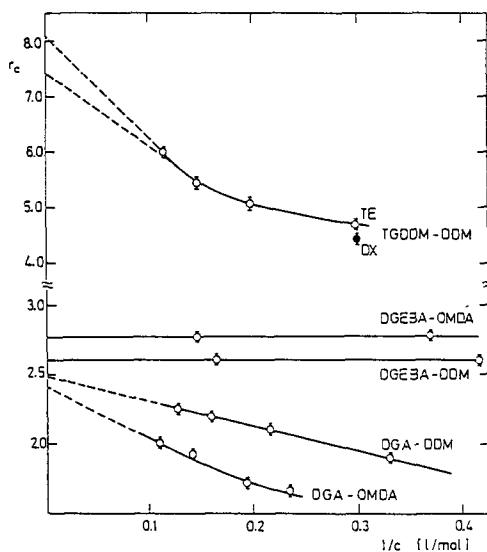
r_c on ρ.

Fig.1 Dependence of critical molar ratios ($r_c = 2[NH_2]_0/[E]_0$) on dilution of the reaction mixture epoxide-amine. DX, TEGDME - reaction in dioxane or in triethylene glycol dimethyl ether

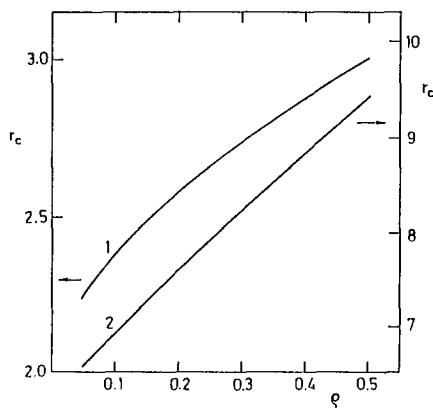Fig.2 Theoretical dependences of the critical ratio r_c the ratio of rate constants ρ of the reaction between secondary and primary amino group 1 - system di-epoxide-diamine 2 - TGDDM-diamine (functionality distribution of TGDDM: 91.7% monomer, 8% dimer, 0.3% chlorohydrine of TGDDM).
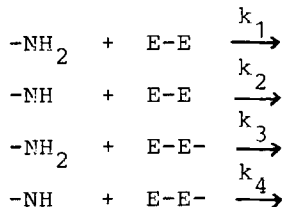
Table 1

Critical molar ratios of functional groups, r_C, and ratios of the rate constants, ρ, for the reaction of the secondary and primary amino group with epoxide

	$(r_C)_{ext}$	ρ
DGEBA-DDM	2.61	0.22
DGEBA-OMDA	2.77	0.32
	$(r_C)_{ext}$	ρ/ρ_{DGEBA}
DGA-DDM	2.48	0.68
DGA-OMDA	2.41	0.37
TGDDM-DDM	7.4 - 8.0	0.8 - 1.2

Curing temperature T=130-140°C, $(r_C)_{ext}$ is the r_C value extrapolated to $1/C \rightarrow 0$, where C is the initial concentration of functional groups.

Another situation arises with nitrogen-containing poly-epoxides, where the pair of glycidyl groups on the nitrogen atom can be regarded as dependent with respect to reactivity. Equations (1) and (2) do not adequately reflect the reaction course any more, and the following steps are to be considered (schematically)

$$-NH_2 + E\text{-}E \xrightarrow{k_1}$$
$$-NH + E\text{-}E \xrightarrow{k_2}$$
$$-NH_2 + E\text{-}E\text{-} \xrightarrow{k_3}$$
$$-NH + E\text{-}E\text{-} \xrightarrow{k_4}$$

(where -E is the unreacted and -E- is the reacted epoxy group), which means that the critical ratio is determined by three rate constant ratios, i.e.- k_2/k_1, k_3/k_1 and k_4/k_1, instead of one as with DGEBA. In the case of additivity of the activation energies, when the reactivities of the primary and secondary amino group with a reference epoxy group are characterized by the constants k_{A1} and k_{A2}, and the reactivities of the unreacted and one reacted diepoxide with a reference amino group are characterized by the constants k_{E1}, k_{E2}, two ratios, $k_{A2}/k_{A1} = \rho$, (as before), and $k_{E2}/k_{E1} = \sigma$ are sufficient. Then, $k_1 \propto k_{A1}k_{E1}$, $k_2 \propto k_{A2}k_{E1}$, $k_3 \propto k_{A1}k_{E2}$, $k_4 \propto k_{A2}k_{E2}$; $k_2/k_1 = \rho$, $k_3/k_1 = \sigma$, $k_4/k_1 = \rho\sigma$.

Thus, a single measurement of the critical ratio is by no means sufficient for characterizing the reactivities. If, however, the additivity assumption is satisfied and ρ is known, it is possible to calculate σ by rearranging the relation for the gel point which follows from the theory of branching processes (9).

The assumed additivity may be checked by measuring the critical ratios for a series of amines characterized by various ρ values. In this information, the influence on the reactivity of epoxy groups has been characterized by a hypothetical reflection of all reactivity changes in the ρ value and by examining the ratio, R, for the nitrogen polyepoxide and DGEBA ($R = \rho/\rho_{DGEBA}$). In order to determine ρ in TGDDM, the calculation procedure (9) was extended to include the tetrafunctional epoxide, taking into account functionality distribution (cf.Experimental). The $(r_c)_{ext}$ in the case of TGDDM may be subjected to a considerable error due to the curved r_c vs. $1/C$ dependence and to the ambiguity of extrapolation (Fig.1). Also, already small deviations in the determination of the functionality distribution have a distinct effect on ρ. It can be seen in Table 1 that the ratio R for the given amine in the case of DGA is lower than unity. This confirms the dependence of the reactivity of epoxy groups in DGA. Assuming additivity, this would mean that the reactivity of the epoxy group in the nitrogen diepoxide decreases after the second epoxy group has reacted.

Conclusion

The results suggest that in the curing og DGA or TGDDM having sterically close epoxy groups, both cyclization and the dependence of reactivities of adjacent epoxy groups are operative. Cyclization is most probably contributed mainly by the formation of an eight-membered ring in an intramolecular reaction within the monoadduct DGA-amine.

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