Polymer Bulletin 4, 479-485 (1981)

Polymer Bulletin

The Influence of Bridge Groups Nature in Diepoxy Compounds on Kinetics of Curing Process by Diamines and on Physical and Mechanical Properties of Forming Polymers

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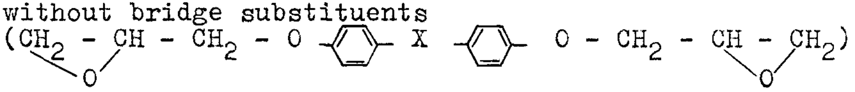
Summary

In the present work the initial monomer reactivity in curing reaction of epoxy compounds by aromatic diamines has been investigated. Also physical and mechanical properties of cured polumers of diglycidyl ethers 4,4’-bisaromatic compounds with bridge groups have been examined.

Introduction

The investigations of the kinetics and mechanism of the formation of epoxy polymers from diepoxides and diamines were intensively carried out in the past years (Arutyunyan et al. 1974, Arutyunyan et al. 1976, Enikolopyan 1977, Rozenberg 1975, Vedenyapina et al. 1976). There a number of works (Litvinenko et al.1957a, Litvinenko 1957b, Litvinenko 1962, Parker et al. 1961), which deal with the structure and reactivity of aromatic amines, but data concerning the reactivity of epoxy compounds are practically missing.

In the present paper some results are presented concerning the reactivity of epoxy compounds with and without bridge substituents



(where x is O, CH_2, S, SO_2, CO) in reactions with aromatic diamines : 2,6-diaminopyridine (DAP) and m-phenylenediamine (m-PhDA), Also physical and mechanical properties of the polymers formed are discussed.

Experimental

Diglycidyl ethers with bridge substituents were purified by reprecipitation from toluene solution by heptane. The agreement between experimentally measured and theoretically calculated concentrations of epoxy groups proved the purity of monomers. DAP and m-PhDA were purified by the method described in the paper (Efremova et al. 1979).

The kinetic was investigated by the calorimetric

0170-0839/81/0004/0479/$01.40

method using the isothermal microcalorimeter of the Calvet type (constructed made in the Institute of Chemical Physics, USSR Academy of Sciences) in the temperature range 80-120°C. Physical and mechanical characteristics were determined by the "Instron-1122". Glass-transition temperatures were determined both by calorimetric and thermomechanical methods.

Results and Discussion

Kinetic curves at different initial amine concentrations are shown in Fig. 1.

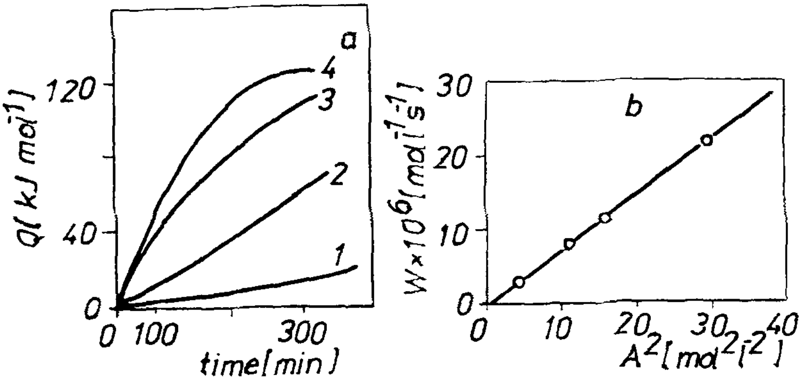


Figure 1. Kinetic curves a) and their anamorphosis b) of the curing process of diglycidyl ether 4,4'-diphenyl oxide by diaminopyridine at 100°C.
Epoxy groups concentration: 2.2 mol/1; amine: 1 - 1.1; 2 - 2.2; 3 - 3.33; 4 - 4.44 mol.1^{-1}.

The experiments were carried out at constant concentration of epoxy groups (2 mol/1) and amine concentration varying from 0.5 to 6 mol/1. The quadratic dependence of the reaction rate (W) on the amine concentration (A) shows that the latter acts both as electrophilic and nucleophilic agent (Efremova et al. 1979).

The determonation of noncatalytic (in the absence of proton-donor additives of any kind rate constants was carried out by the method described recently (Efremova et al. 1979). The values of these noncatalytic rate constants of the curing reaction of the investigated diglycidyl èthers with bridge sustituents at different temperatures are presented in Table 1. As one can see from the table 1, the kinetic parameters of the curing process of epoxy bridge compounds with both investigated amines are similar.

TABLE 1
Noncatalytic Rate Constants of the Curing Processes of Epoxy Compounds with Aromatic Diamines

	DAP				m-PhDA			
	$k_1 x 10^7$ $L^2 mol^{-2} s^{-1}$			E kJ•mol^{-1}	$k_2 x 10^6$ $L^2 mol^{-2} s^{-1}$			E kJ•mol^{-1}
T°C / x	80	100	120		80	100	120	
O	1.4	7.5	23.4	79.13	1.7	6.0	20.0	71.18
S	2.0	10.0	22.4	63.64	2.0	8.2	14.0	58.61
without	1.5	7.4	25.0	83.7	2.2	8.4	23.0	76.62
CH_2	1.3	8.5	20.0	81.64	2.0	7.1	21.4	68.24
SO_2	3.3	11.0	42.0	80.39	3.7	15.0	66.0	76.62
CO	2.1	6.4	30.0	74.52	2.6	8. 0	25.1	66.15
N=N	-	9.9	-	-	-	-	-	-

The comparison of the reactivity of the investigated epoxy compounds was made by the Hammet equation

$$lg(K/K_0)=\sigma\rho$$

where K and K_0 are the reaction rate constants for the substituted and unsubstituted compound; σ is the characteristic of the electronic nature of substituent and ρ the constant of a reaction serie.

Phenylglycidyl ether (PhGE) was taken as the reference unsubstituted compound.

In Fig.2 the Hammet correlation of the investigated compounds is presented. The small ρ value indicates a weak sensitivity of the reaction center to the nature of the bridge groups.

This conclusion is not surprising, because in diglycidyl ethers the reaction center (epoxy ring) is separated from the benzene ring (and substituents connected with it) by the low-conducting oxymethylene bridge.

The obtained data mean that the curing regime of different bisphenol diglycidyl ethers with the identical amine hardener can be the same in the first approximation.

Figure 3 presents the σ-ε diagram for the investigated samples.

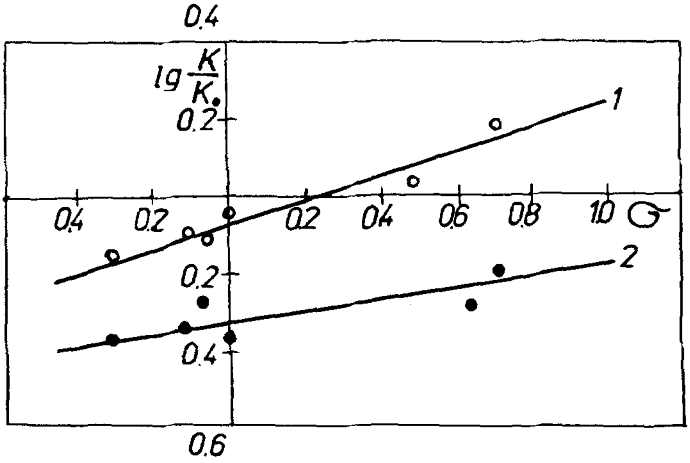


Figure 2. The correlation of the rate constants of epoxy compounds curing reaction by diaminopyridine (1) at 100°C and by m-phenylenediamine at 80°C (2) with the Hammet constants.

As one can see from the figure the polymers on the base of diglycidyl ethers 5-6 (Fig.3) are failed fraily, while the polymers on the base of diglycidyl ethers 1,3,4 are distorted with the yielding area.

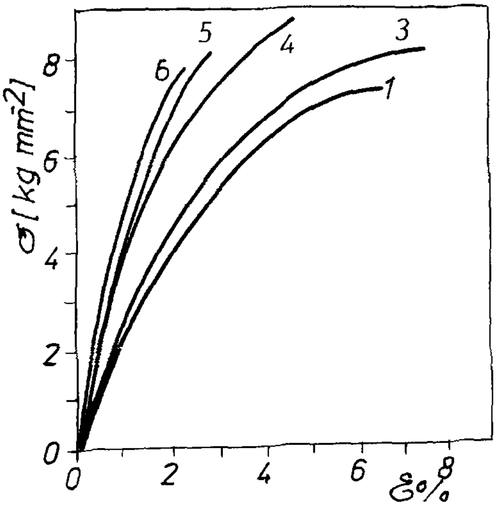


Figure 3. The σ-ε diagram of compounds on the base of diglycidyl ether. 1 - 4,4'-diphenyloxide; 3 - 4,4'-diphenylmethane; 4-4,4'-benzophenone; 5 - 4,4'-diphenyl; 5 - 4,4'-diphenylsulfone.

In Table 2 the data concerning the physical and mechanical properties in glassy and high-elasticity states are presented for a number of compositions on the base diglycidyl ethers if diphenyls with bridge substituents, cured by 2,6-diaminopyridine and m-phenylenediamine. As one can see, the change in the bridge groups nature weakly influence the strength of these polymers both in the glassy and high-elasticity states (test temperature T_g +40°C).

TABLE 2
Physical and Mechanical Properties of Polymers on the base of Diglycidyl Ethers 4,4'-bisaromatic Compounds with Bridge Substituents

Diglycidyl ethers of 4,4'-diphenyl with bridges	Glassy state			High-elasticity state		
	σ kg/mm^2	ε %	E kg/mm^2	σ kg/mm^2	ε %	E kg/mm^2
1.- O -	8.2	9.0	220	0.21	14.0	1.5
2.- S -	7.7	5.5	234	0.19	8.0	2.5
3.-CH_2-	8.8	4.9	215	0.14	9.1	1.45
4.-CO -	9.3	5.2	360	0.18	20.7	2.0
5. without	7.3	2.7	500	0.32	65.0	2.4
6.-SO_2-	7.7	1.8	510	-	-	-

The decrease in the flexibility of polymer that determined by the barrier of internal rotation of bridge group, leads to the increase in Young's modolus of polymers (E) and to the decrease in the limit deformation (Bessonov et al. 1974).

Great difference are observed in the values of the coefficient of molecular packing (K_{20}) for the polymers with and without bridge groups. Data on the kinetics of water sorption (Fig.4) show that polymers on the basis of diglycidyl ether of diphenyl have an anomalous high density.

As far as one can see from Figure 4 both current and maximum rates of water sorption of diglycidyl ether of diphenyl two times less than the polymer with flexible bridge groups (O, S, CH_2). In Table 3 the calculated and experimental values of the glass tran-

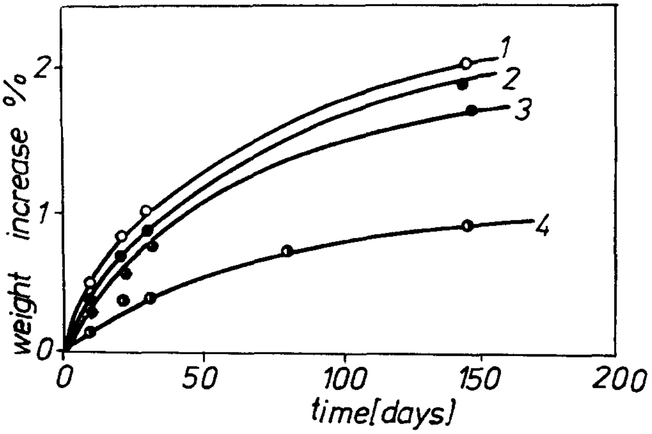


Figure 4. Kinetics of water sorption by epoxy polymers on the base of diglycidyl ether.
1 - 4,4'-diphenylmethane; 2 - 4,4'-diphenyloxide; 3 - diphenyl sulfide; 4 - 4,4'-diphenyl.

sition temperatures for polymers obtained by curing of DAP and m-PhDA are presented. The calculated glass transition temperatures were determined by the method of the additivity of the group contributions.

TABLE 3
Glass Transition Temperature and **Molecular** Packing og Investigated Polymers with curing agents DAP and m-PhDA

Diglycidyl ethers of 4,4'-diphenyls with bridges	DAP	m-PhDA	
	T_g °C calc/exp	T_g °C calc/exp	k_{20}
- O -	153/120	135/137	0.715
- S -	157/135	139/128	0.715
$-CH_2-$	151/110	134/135	0.712
-CO -	162/147	-	0.713
without	165/170	-	0.738
$-SO_2-$	204/147	-	-

Lower values of experimental glass transition temperatures of polymers cured by DAP are connected odviously, with polymerization process (Kushch et al. 1979).

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Received September 28, 198o
Revised November 13, 198o and March 16, 1981
Accepted March 23, 1981