

Synthesis and Properties of Unsaturated Epoxyfumarate Resins

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ABSTRACT: Synthesis and properties of epoxyfumarate and epoxymaleate resins obtained by the addition of acidic ester of maleic acid to the commercially available resin, Epidian 5, is presented. In acidic ester preparation, *n*-hexanol was used. The resins were synthesized in one- and two-step procedures. In the two-step procedure, acidic hexyl maleate was synthesized separately and then used for the addition reaction with epoxy resin. In the one-step synthesis, acidic ester was formed during the synthesis process. Properties of the obtained resins were compared. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3077–3084, 2000

Key words: unsaturated polyester resins; epoxyfumarates; epoxymaleates; isomerization of maleate bonds to fumarate ones; properties of the resins

INTRODUCTION

Unsaturated polyesters are some of the most important matrix resins for composite application. They possess a wide range of properties and are used in marine, automobile, construction, sport, and furniture fields.^{1–3}

Unfortunately, these resins contain maleate or phthalate ester groups, which are characterized by a relatively high sensitivity to hydrolysis compared, for instance, to vinyl esters containing methacrylic esters.^{4–6} The latter are formed by the addition of acrylic or methacrylic acids or acidic esters of maleic or fumaric acids to epoxy resins and share advantages of unsaturated polyesters and epoxide resins. The most important features of these resins are chemically resistant epoxy backbone and terminal unsaturated vinyl groups that can be easily cured by copolymerization with vinyl monomers^{7–13} in analogy with the unsaturated polyesters.

Continuing the previous studies, we synthesized the resins by the addition of acidic maleate ester to the epoxy resin and copolymerized them with styrene. Properties of the obtained epoxy-maleate resins were compared with those for epoxyfumarate. The latter were obtained in the same way, but during the synthesis, isomerization of maleate groups to fumarate ones was carried out. Both epoxyfumarates and epoxymaleates were synthesized in one- and two-step procedures. Acidic maleate ester used in these studies was obtained from maleic anhydride and *n*-hexanol. In our previous studies, we used cyclohexanol and benzyl alcohol representing cycloaliphatic and aromatic alcohols.^{5,6} As we try to establish an influence of chemical structure of alcohol on the properties of the resins, we use aliphatic alcohol of similar carbon atoms number in our experiments. Our previous results indicated that the properties of the resin from epoxy resin and acidic cyclohexanol maleate are different from those for epoxy resin and acidic maleate ester of benzyl alcohol. On the other hand, thermomechanical properties of the resins obtained in the one- and two-step procedures are very similar.

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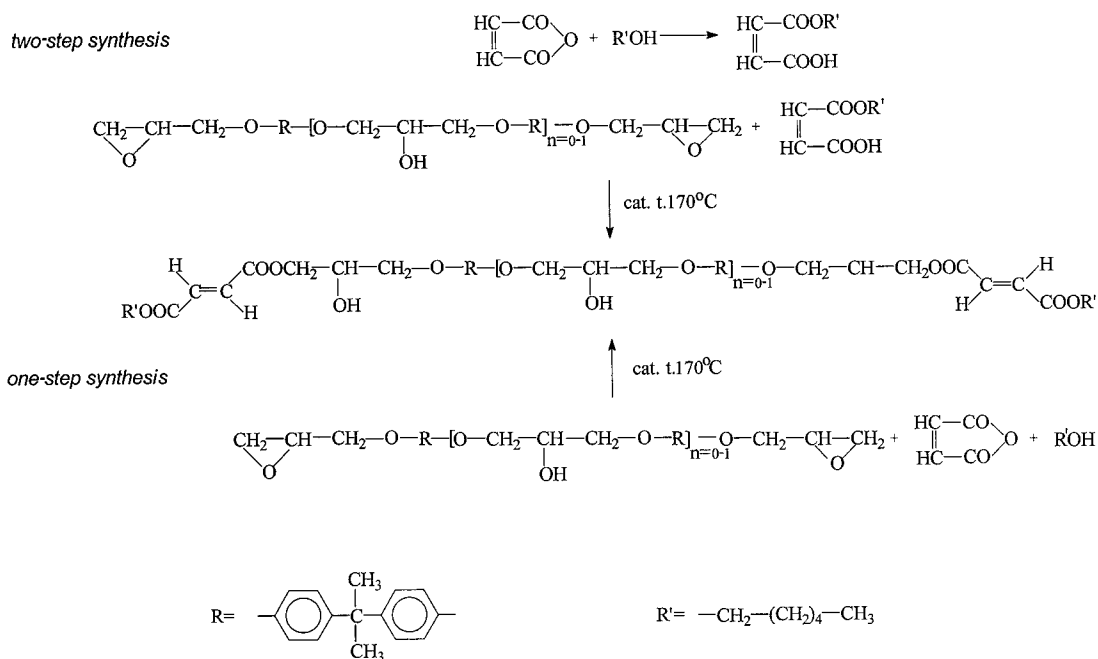


Figure 1 One- and two-step syntheses of the studied epoxyfumarate resins.

EXPERIMENTAL

Materials

Maleic anhydride was purchased in Zakłady Azotowe (Nitrogen Works, Kędzierzyn-Koźle, Poland). Epidian 5-epoxide resin based on Bisphenol A and 2,4,6-tri(dimethylamino)phenol came from the Organika-Sarzyna Chemical Plant (New Sarzyna, Poland). Styrene, hydroquinone, and cobalt octoate (1% Co in styrene) were from POCh (Gliwice, Poland). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) was from Luperox (Günzburg, Germany), whereas *n*-hexanol and piperidine were bought from Merck (Darmstadt, Germany). Aromatic amine adduct (*p*-toluidine and Epidian 5) came from our laboratory.¹⁴

Synthesis of Epoxymaleate Resins

As previously, epoxymaleate resins were synthesized in the one- and two-step procedures (Fig. 1). In the two-step procedure, acidic ester of maleic acid was synthesized separately. To obtain this compound, maleic anhydride and *n*-hexanol were heated at 80–85°C until the acid value achieved the value of 282 mg KOH/g (theoretical value is 280 mg KOH/g). Identification of this compound was made by the ¹H nuclear magnetic resonance

(¹H-NMR) analysis (Fig. 2). The obtained raw acidic hexyl maleate was then added to Epidian 5 in the temperature gradient. The mixture containing Epidian 5, acidic hexyl maleate, hydroquinone as an inhibitor, and 2,4,6-tri(dimethylamino)phenol catalyzing addition was heated gradually at each of the temperatures 80, 90, 100, and 110°C for 1 h. Next, the temperature was increased to 120°C, and piperidine, which catalyzed the transformation of maleate groups to fumarate ones, was added. The reaction was continued at each of the temperatures 120, 130, . . . , 170°C for 1 h. A detailed recipe used in this study is given in Table I.

The reaction was controlled by the change of the acid value and ¹H-NMR analysis. When the reaction of addition was finished, the obtained ester was dissolved in styrene, giving 60, 55, and 50 wt % solutions.

In the one-step procedure, the step of the synthesis of acidic hexyl maleate as a separate compound was missed. In this method, all chemicals were mixed and heated gradually at each of the temperatures 80, 90, . . . , and 170°C for 1 h. The reaction was controlled, as mentioned above. As previously described, the obtained compound was dissolved in styrene giving 60, 55, and 50 wt % solutions.

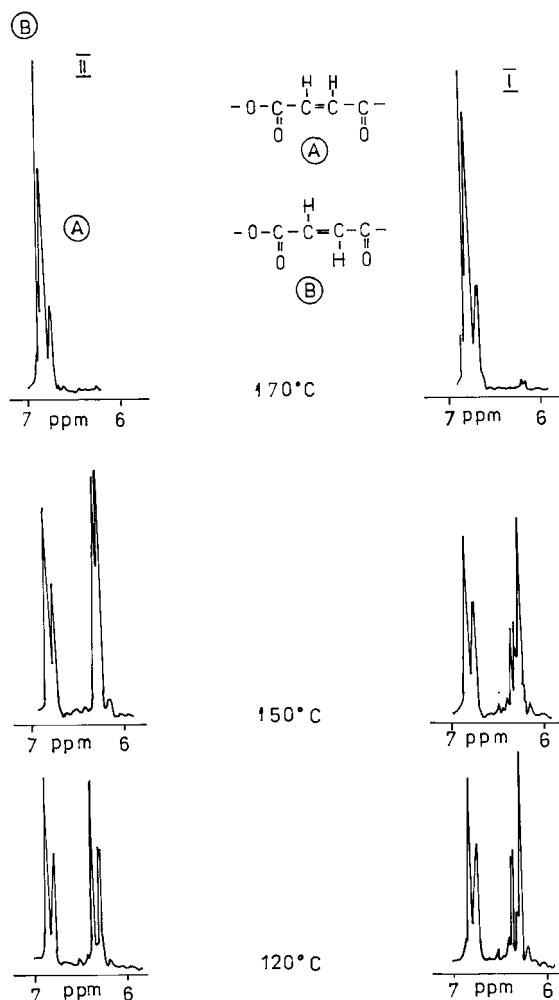


Figure 3 $^1\text{H-NMR}$ spectra of the epoxyfumarate resins obtained in the (I) one- and (II) two-step syntheses. (a) Maleate bonds: $\delta = 6.4$ ppm; (b) fumarate bonds: $\delta = 6.9$ ppm. Peak integrated areas of the maleate protons for the resin I at 120, 150, and 170°C are 55.09, 32.92, and 1.00, respectively. Peak integrated areas of the fumarate protons at 120, 150, 170°C are 48.76, 72.30, and 111.08. Peak integrated areas of the maleate protons for the resin II at the same temperatures are 42.60, 69.04, and 0.00, whereas integrated areas of the fumarate proton peaks are 45.10, 45.72, and 102.00.

enced to tetramethyl silane serving as an internal standard. The convolution difference resolution enhancement method was used to improve the spectral resolution and, consequently, the accuracy of integration of peak position determination. For all resins, the first samples for $^1\text{H-NMR}$ analysis were taken up at 120°C (in the case of unsaturated epoxyfumarate resins, it was before the addition of piperidine). Next samples were examined at 150 and 170°C.

Curing Procedure

The obtained unsaturated resins were crosslinked by using 2.5% of Luperox and the mixture containing 0.2% of cobalt octoate and 1.2% of the adduct of *p*-toluidine with epoxy resin.^{5,6}

Properties of Unsaturated Resins

Properties of the resins in a noncrosslinked state such as density, viscosity, and acid value were determined in the way published earlier.^{5,6}

Thermomechanical Properties of the Resins

The gelation times and peak exotherm temperatures of the resins were determined in a temper-

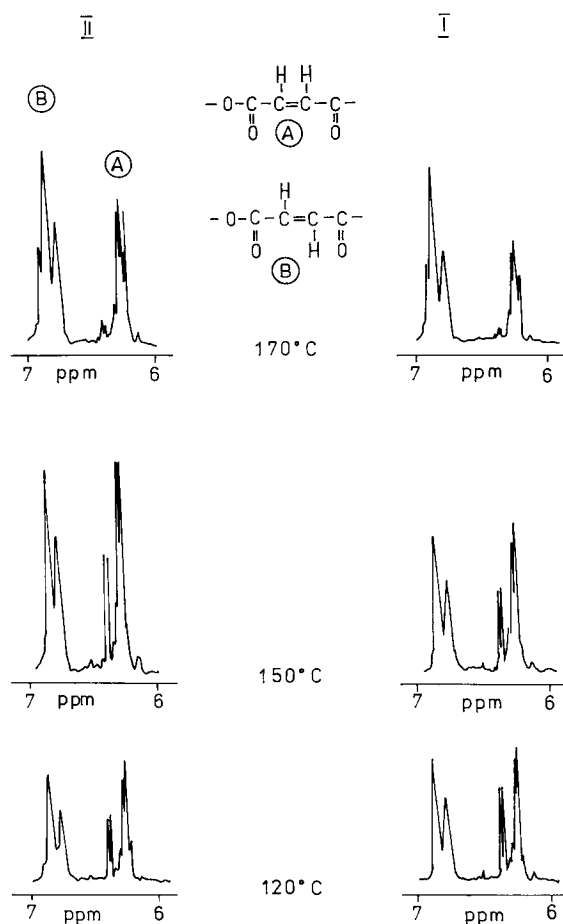


Figure 4 $^1\text{H-NMR}$ spectra of the epoxyfemaleate resins obtained in the (I) one- and (II) two-step syntheses. Peak integrated areas of the maleate protons for the resin I at 120, 150, and 170°C are 52.22, 56.07, and 39.58, whereas those of fumarate protons are 59.52, 62.00, and 67.54. Peak integrated areas of the maleate protons for the resin II at the same temperatures are 42.76, 50.50, and 57.32, whereas those of fumarate protons are 50.93, 60.08, and 55.38, respectively. Other meanings are as in Figure 3.

Table II Properties of the Resins Before and During Curing

Properties	Resin Number							
	1	2	3	4	5	6	7	8
Density (g/cm ³)	1.04	1.04	1.03	1.03	1.02	1.02	1.04	1.04
Viscosity (cP)	184	163	130	130	116	113	151	155
Acid value (mg KOH/g)	15.6	12.2	14.1	11.1	13.3	9.8	16.9	15.1
Gelation time (min)	14	11	11	11	10	9	25	25
Peak exotherm temperature (°C)	84	114	76	97	86	96	37	37

ature-controlled bath (25°C) according to Polish Standard PN-75/C-89082.

The calorimetric measurements were performed on a differential scanning calorimeter Netzsch DSC 200 (Netzsch, Germany). The conditions were as follows: sample weight ~ 4 mg, nitrogen atmosphere, sealed aluminum pans. An empty aluminum pan was used as a reference. The resins were cured in a scanning mode from 20 up to 400°C at 10 K/min heating rate. T_g values were taken from the second DSC run.

Heat resistance according to Martens method was determined by use of Polish Standard PN-90/C-89025.

Thermal stability of the resins was determined by using a MOM derivatograph (Budapest, Hungary). The heating rate was 5°C/min in the air. The initial decomposition temperatures were determined from the course of the TG curves.

Mechanical properties were performed according to the Polish Standards: flexural strength (PN-89/C-89027); tensile strength (PN-81/C-89034); ball indentation hardness (PN-84/C-89030); impact strength by the Charpy method (PN-81/C-89029).

Chemical Resistance of the Resins

To study the resin resistance to corrosion, the plates of the resins were immersed in tap water, 20% NaOH, 20% HNO₃, and toluene.

Experiments were carried out at room temperature and at 50°C according to PN-81/C-89067. Changes of mass of the resin samples in time were determined.

RESULTS AND DISCUSSION

In the papers of this series,^{5,6} we studied the role of transformation of maleate groups to fumarate

Table III Thermomechanical Properties of the Cured Resins

Properties	Resin Number							
	1	2	3	4	5	6	7	8
Initial decomposition temperature (°C)	250	240	—	—	—	—	200	200
Glass transition temperature (°C)	69.6	67.2	—	—	—	—	—	—
Thermal resistance according to Martens (°C)	56.5	55.6	58.5	58.0	59.2	59.0	30.3	28.3
Flexural strength (MPa)	76.4	75.4	77.8	72.9	—	—	45.8	47.0
Tensile strength (MPa)	64.9	56.9	67.9	61.3	—	—	43.6	31.8
Ball indentation hardness (MPa)	101.8	95.8	105.0	102.3	106.9	108.1	88.1	87.8
Impact strength according to Charpy (kJ/m ²)	3.5	3.0	1.9	2.3	1.8	1.7	4.2	4.0

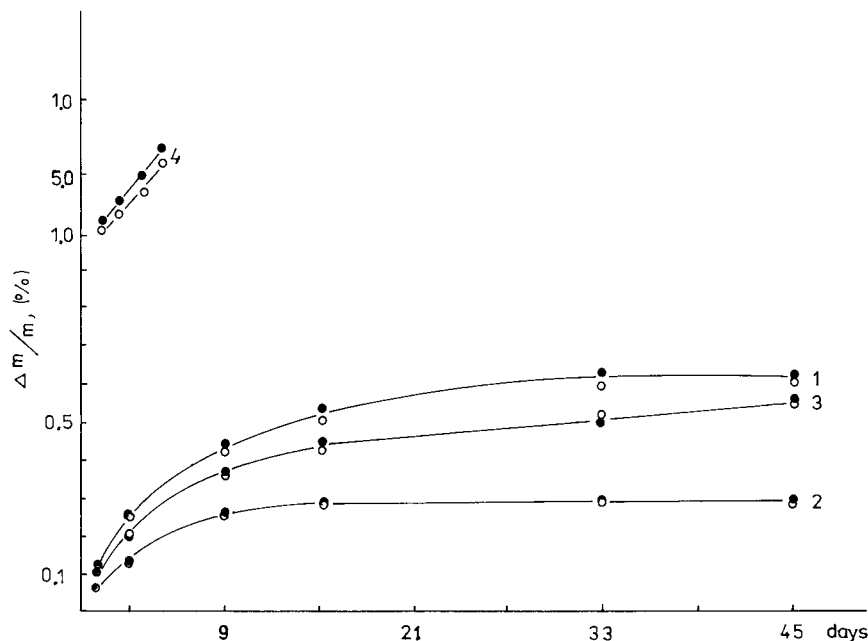


Figure 5 Relative mass change ($\Delta m/m$, %) of the epoxyfumarate resins at room temperature; (●), resin no. 1; (○), resin no. 2. Curves are as follows: (1) tap water; (2) 20% NaOH; (3) 20% HNO₃; and (4) toluene.

ones for some new resins. We also investigated an influence of chemical structure of an alcohol used for the synthesis of acidic maleate ester, which was added to epoxy compound. We established that the resins obtained from acidic benzyl maleate had better thermomechanical properties than those from acidic cyclohexanol maleate. To complete these studies, we synthesized the resins with the use of acidic maleate of *n*-hexanol.

As previously, reactions were monitored by ¹H-NMR analyses. In Figure 2, ¹H-NMR spectrum of acidic *n*-hexyl maleate is presented. Signals at 6.4 and 4.1 ppm confirm the chemical structure of acidic *n*-hexyl maleate.¹⁵ Fragments of ¹H-NMR spectra showing development of the addition reaction of the above mentioned acidic ester to epoxy resin Epidian 5 are visible in Figures 3 and 4. Figure 3 presents the spectra for epoxyfumarate

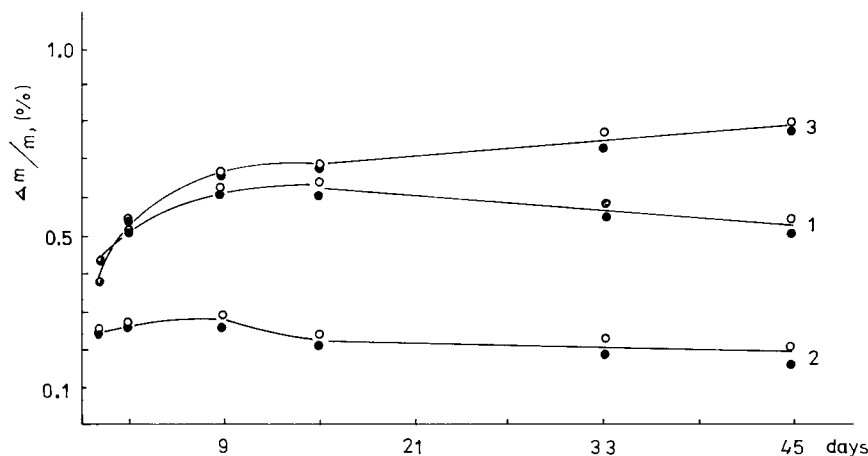


Figure 6 Relative mass change of the resins studied at 50°C; numbering is as in Figure 4.

resins obtained in the one- and two-step synthesis, whereas Figure 4 presents those for epoxy-maleate resins. The contents of *trans* isomers were determined by the method of Curtis et al.¹⁶ by using the areas of the signals due to fumarate (~ 6.9 ppm) and maleate (~ 6.4 ppm) olefinic protons. From these data one can see that in the presence of piperidine transformation of maleate groups to fumarate run gradually. This effect is independent of the synthesis method. When the reaction of addition is carried out without piperidine, isomerization does not take place. Even heating up to 170°C has insignificant influence on this process. The same effect is visible for the resins obtained in the one- and two-step procedure syntheses. These results are different from those obtained for epoxyfumarate resins formed from the epoxy resin and acidic maleate of benzyl alcohol.⁶

Properties of the resins are summarized in Table II. From these data one can see that significant differences are visible for epoxyfumarate and epoxy-maleate resins. Generally, unsaturated maleate resins are less reactive. Also, thermomechanical properties of the latter differ from those for epoxyfumarate (Table III). Thermal resistance of epoxyfumarate resins is significantly better. Independently of the synthesis method, their initial decomposition temperatures are ca. 50°C higher than those for epoxy-maleates. For this reason glass transition temperatures (T_g) were determined only for epoxyfumarates. The obtained values are rather high. Epoxyfumarate resins are also characterized by higher values of flexural and tensile strength. Their hardness is insignificantly greater. Only values of impact strength according to Charpy for fumarate resins are lower than those for unsaturated epoxy-maleates. As expected, the properties of the resins obtained in the one- and two-step procedures do not differ.

The results of chemical resistance studies for the epoxyfumarate resins obtained in the one- and two-step procedures are presented in Figures 5 and 6. These figures show the relative mass change of the studied resins. The course of the curves is nearly the same as those for the resins studied previously. The greatest mass increase is observed in toluene. In this solvent at 50°C, destruction of the resin samples takes place after a few hours. Inorganic solvents have rather small influence on the resins mass. This means that the resins are chemically resistant toward acid-base media.¹⁷

The results presented here indicate that for the resins from the epoxy resin and acidic hexyl maleate isomerization of maleate bonds to fumarate ones takes place at higher temperatures than those for the resins of epoxy resin and acidic benzyl maleate.⁶ Their thermomechanical properties are similar to those for the resins of epoxy resins and acidic cyclohexanol maleate.⁵ This means that the chemical structure of alcohol used for the synthesis of acidic maleate ester have important influence on the properties of the final product.

CONCLUSION

Eight unsaturated polyester resins from epoxy resin and acidic hexyl maleate are presented. The resins were synthesized both in the one- and two-step procedures. To obtain epoxyfumarate resins, isomerization of maleate (*cis*) to fumarate (*trans*) groups was carried out. This transformation is desirable because fumarate has greater reactivity and results in higher tensile and flexural strengths and better chemical resistance than maleate when cured. The obtained results indicate that isomerization *cis-trans* for currently studied resins takes place at higher temperatures than that for the resins of epoxy resin and acidic benzyl maleate, whereas their properties after curing are similar to those for the resins of epoxy resin and acidic maleate ester of cyclohexanol.

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