

Synthesis and Characterization of the Epoxyfumarate Resins

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ABSTRACT: The synthesis and properties of the new epoxyfumarate and epoxymaleate resins obtained by the addition of acidic allyl maleate to the commercially available resin Epidian 5 are presented. The resins were synthesized in one- and two-step procedures and properties of the obtained resins are compared. It should be noted that the use of allyl alcohol in the synthesis of unsaturated resins has an advantageous influence on their properties. Glass-transition temperatures of the epoxyfumarate resins exceed 100°C, whereas those of epoxymaleates are higher than 70°C. The resins are also characterized by good chemical resistance. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 716–722, 2002; DOI 10.1002/app.10067

Key words: unsaturated polyester resins; epoxyfumarates; epoxymaleates; isomerization of maleate/fumarate bonds; thermomechanical properties; chemical resistance

INTRODUCTION

Unsaturated polyester resins find numerous applications in industry, space, and naval industries, especially in association with fibers in reinforced composite systems. They are inexpensive and can easily accommodate defined specifications by changing either the nature of the unsaturated polyester chain or the ratio of styrene/polyester amounts.¹

Unfortunately, unsaturated polyester resin materials may suffer from chemical degradations when they are exposed to atmospheric moisture or are in contact with water for a long time. This leads to a loss of mechanical resistance of the resin or laminate.

To improve the resin properties different modifications of the synthesis procedure were undertaken. An interesting result of these studies is epoxyfumarates, the resins that share advantages of unsaturated polyesters and epoxy res-

ins.^{2–5} These are formed by the addition of acrylic or methacrylic acids or acidic esters of maleic or fumaric acids to epoxy resins. Epoxyfumarates have an epoxy backbone structure with terminal unsaturated groups that can be cured by copolymerization with vinyl monomers, in analogy with the unsaturated polyesters.^{2,3} The presence of fumarate (*trans*) unsaturation sites plays an important role in determining the physical and chemical properties of the final product because of a higher reactivity of *trans*-isomer in copolymerization with vinyl monomers.^{4–6}

Compared with unsaturated polyester resins epoxyfumarates have some advantageous characteristics including excellent reactivity and good chemical and thermal resistances.

In our previous investigations we studied the preparation of epoxyfumarate resins in the one- and two-step procedures.^{6–8} Now we present the synthesis and properties of the new epoxyfumarate resins. These resins are characterized by a higher degree of crosslinking than that of other resins because they are synthesized by the addition of acidic allyl maleate to the epoxy resin and copolymerization with styrene.

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Table I Synthesis Recipe

| Substrate (g) | Resin Number | | | | | |
|--------------------------------|--------------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Epidian 5 | 32.47 | 32.59 | 29.76 | 29.85 | 32.65 | 32.76 |
| Allyl alcohol | 10.19 | — | 9.33 | — | 10.24 | — |
| Maleic anhydride | 16.83 | — | 15.44 | — | 16.92 | — |
| Acidic allyl maleate | — | 26.90 | — | 24.68 | — | 27.05 |
| Styrene | 40.00 | 40.00 | 45.00 | 45.00 | 40.00 | 40.00 |
| 2,4,6-Tri(dimethylamino)phenol | 0.177 | 0.177 | 0.163 | 0.163 | 0.177 | 0.178 |
| Piperidine | 0.325 | 0.326 | 0.300 | 0.300 | — | — |
| Hydroquinone | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 |

EXPERIMENTAL

Materials

Maleic anhydride was purchased in Zakłady Azotowe (Nitrogen Plant, Kędzierzyn-Koźle, Poland). Epoxy resin Epidian 5 (resin based on bisphenol A) and 2,4,6-tri(dimethylamino)phenol came from the Organika-Sarzyna Chemical Plant (New Sarzyna, Poland). Styrene was from the chemical firm Dwory S.A. (Oświęcim, Poland), whereas cobalt octenoate (1% Co in styrene), hydroquinone, and *N,N*-dimethylaniline (10% solution in styrene) were from POCh (Gliwice, Poland). Allyl alcohol and cumene hydroxyperoxide were from Fluka AG (Buchs, Switzerland). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) and piperidine were from Merck (Darmstadt, Germany).

Synthesis of Epoxyfumarate Resins

As previously described, unsaturated epoxyfumarate resins were synthesized in one- and two-step procedures.⁶⁻⁸ In the two-step procedure, acidic allyl maleate was synthesized separately. To obtain this compound, maleic anhydride (294 g) and allyl alcohol (118.5 g) were heated to 85°C. At this temperature an exothermic reaction was initiated and the temperature spontaneously increased to 95°C. After reducing it to 85°C, the mixture was maintained at this temperature for 4 h, with stirring. The obtained raw compound (acidic value 380 mg KOH/g) was then added to Epidian 5 in the temperature gradient. The mixture containing Epidian 5, acidic ester of maleic acid, hydroquinone as an inhibitor, and 2,4,6-tri(dimethylamino)phenol catalyzing reaction of addition, was heated for 2 h at 80°C, and gradually at: 90, 100,

110, and 120°C for 1 h. At 120°C, piperidine catalyzing transformation of maleate groups to fumarate groups was added. The reaction was continued at 120, 130, 140, 150, 160, and 170°C for 1 h. The reaction was controlled by changing the acid value and ¹H-NMR analysis. When the acid value of the compound was 29 mg KOH/g it was cooled to about 110°C and dissolved in styrene, giving 60 and 55 wt % solutions.

In the one-step procedure, the step of the synthesis of acidic allyl maleate as a separate compound was omitted. In this method, all chemicals were mixed and heated gradually in 10°C increments from 80 to 170°C for 1 h. The reaction was controlled as described above. The same styrene solutions were prepared. A detailed recipe used in this study is given in Table I.

Synthesis of Epoxymaleate Resins

Unsaturated epoxymaleate resins were prepared in the one- and two-step procedures without the addition of piperidine. Other synthesis conditions were the same as in the case of epoxyfumarate resins. In these studies only a 60 wt % styrene solution was prepared (Table I).

NMR Characterization

¹H-NMR spectra were recorded at 20°C on an NMR Model 567A (Tesla, Czechoslovakia) spectrometer operating at the ¹H resonance frequency of 100 MHz. Chemical shifts were referenced to tetramethyl silane serving as an internal standard.

Samples of unsaturated ester were taken at 100 and 120°C. In the case of epoxyfumarate resins, it was before adding piperidine to the reaction. The next ester sample was taken at 170°C.

Curing Procedure

The obtained unsaturated resins were crosslinked using 0.6% of Luperox, 0.4% cobalt octenoate, and a mixture of cumene hydroperoxide (2%) and 0.4% of styrene solution of *N,N*-dimethylaniline.

Properties of Unsaturated Resins

Properties of the resins in a noncrosslinked state such as density, viscosity, and acid value were determined according to previous studies.⁶⁻⁸ Gelation times were measured in a temperature-controlled bath (25°C) according to the Polish Standard PN-75/C-89082 and stabilities measured according to PN-86/C-89082/09.

Thermomechanical Properties of the Resins

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

Heat resistance according to Martens was determined by the use of Polish Standard PN-90/C-89025. The calorimetric measurements were performed on a differential scanning calorimeter Netzsch DSC 200 (Netzsch, Germany). The conditions were as follows: sample weight about 5 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.

Mechanical properties were determined according to the following Polish Standards:

- Flexural strength (PN-89/C-89027)
- Tensile strength (PN-81/C-89034)
- Ball indentation hardness (PN-84/C-8930)
- 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 xylene.

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

From our previous studies we draw the conclusion that the chemical structure of alcohol used in the synthesis of acidic maleate influences the properties of the final unsaturated epoxyfumarate resin. In our previous studies we used cyclohexanol, *n*-hexanol, and benzyl alcohol, representing cycloaliphatic, aliphatic, and aromatic alcohols, re-

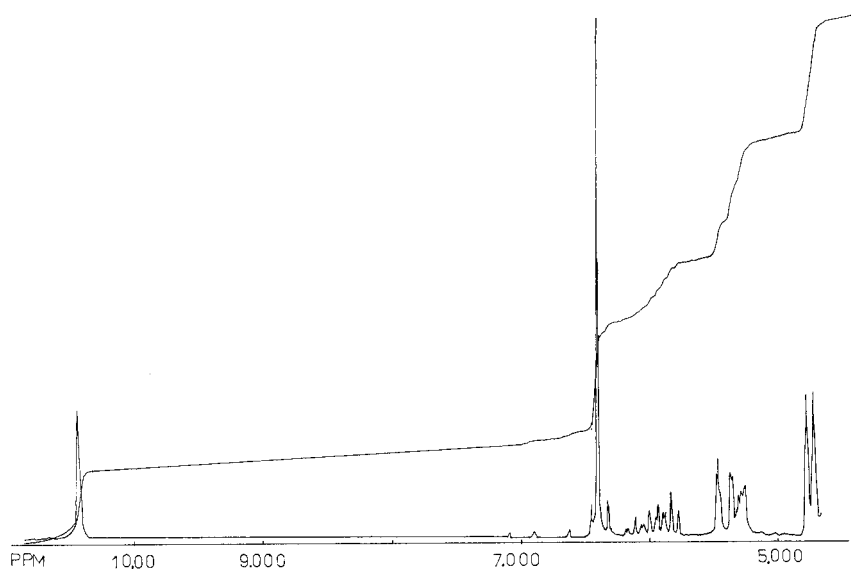


Figure 1 ¹H-NMR spectrum of acidic allyl maleate.

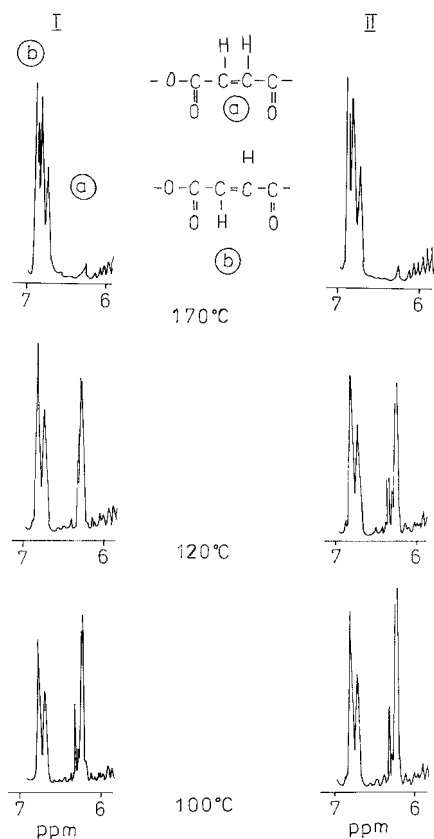


Figure 2 $^1\text{H-NMR}$ spectra of the epoxyfumarate resins obtained in the one- (I) and two-step (II) syntheses. Maleate bonds: $\delta = 6.4$ ppm (a); fumarate bonds: $\delta = 6.9$ ppm (b).

spectively. Here we use allyl alcohol for the synthesis of acidic maleate. We suspect that an additional unsaturated bond in the structure of unsaturated resin, contributed by acidic allyl maleate, can change its properties. As before, the syntheses of unsaturated resins are carried out not only in the one- and two-step procedures but also with and without piperidine, which is responsible for isomerization of maleate bonds to fumarate bonds. Development of the reactions was monitored by $^1\text{H-NMR}$. In Figure 1 the $^1\text{H-NMR}$ spectrum of acidic allyl maleate is presented. Signals at 6.4 ppm typical of maleate bonds, and at 5.1, 5.3, and 6.0 ppm (allyl group) confirm the chemical structure of the compound.⁹ Fragments of $^1\text{H-NMR}$ spectra showing development of the addition reaction of the above-mentioned acidic ester to epoxy resin Epidian 5 are visible in Figures 2 and 3. Figure 2 presents the spectra for epoxyfumarate resins obtained in the one- and two-step syntheses, whereas Figure 3 presents

those for epoxy-maleate resins. The contents of *trans*-isomers were determined by the method of Curtis et al.¹⁰ by using the areas of the signals assigned to fumarate (~ 6.9 ppm) and maleate (~ 6.4 ppm) olefinic protons. From the data presented in Figure 2 one can see that in the presence of piperidine, transformation of maleate groups to fumarate groups is over at the temperature of 170°C . This effect is independent of the synthesis method. In Figure 3 analogical fragments of NMR spectra for the resins obtained in the one- and two-step procedures, without piperidine, are presented. Intensities of maleate bonds presented in these spectra did not change while heating.

Properties of the studied resins before and after curing are summarized in Tables II and III. From these data one can see that significant differences are visible for epoxyfumarate and epoxy-maleate resins. Generally, unsaturated epoxy-

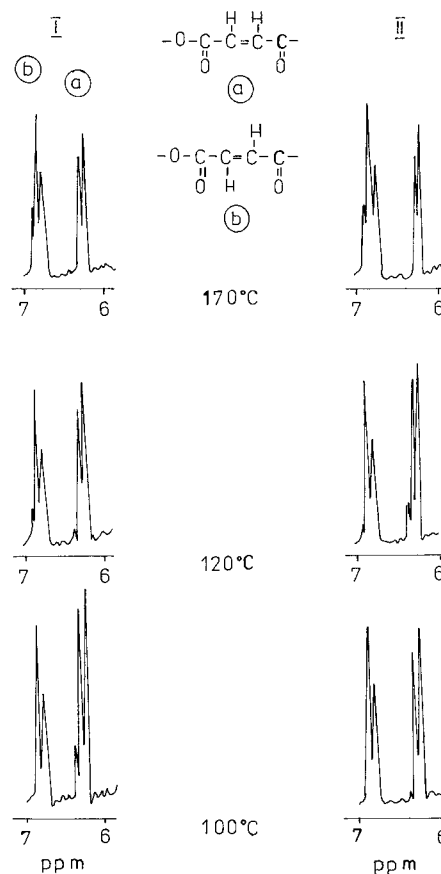


Figure 3 $^1\text{H-NMR}$ spectra of the epoxy-maleate resins obtained in the one- (I) and two-step (II) syntheses. Maleate bonds: $\delta = 6.4$ ppm (a); fumarate bonds: $\delta = 6.9$ ppm (b).

Table II Properties of the Resins Before and During Curing

| Property | Resin Number | | | | | |
|------------------------------|--------------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Density (g/cm ³) | 1.06 | 1.07 | 1.05 | 1.05 | 1.06 | 1.07 |
| Viscosity (cP) | 395 | 450 | 200 | 270 | 320 | 450 |
| Acid value (mg KOH/g) | 18.8 | 16.6 | 17.9 | 15.8 | 14.2 | 12.7 |
| Stability at 70°C (h) | 25 | 26 | 24 | 24 | 26 | 26 |
| Gelation time (min) | 49 | 58 | 30 | 31 | 90 | 100 |

maleate resins are less reactive. Surprisingly, the thermomechanical properties of the latter are not so poor. Glass-transition temperatures and thermal resistance measured by the Martens method are lower for epoxy-maleate resins but these values are relatively high. Thermal resistances according to Martens for these resins are close to 90°C, whereas those for epoxyfumarates exceed 100°C. Our previous studies indicate that use of saturated alcohols in the syntheses of unsaturated epoxyfumarates yielded resins of significantly smaller thermal resistances. For epoxyfumarates obtained from acidic cyclohexyl, benzyl, and *n*-hexyl maleates thermal resistances according to Martens did not exceed 80°C.⁶⁻⁸ Other properties of epoxy-maleate and epoxyfumarate resins are very similar. Even stabilities of the resins at 70°C are the same. Stability for 1 h at this temperature is equivalent to keeping the resin at room temperature for one day and night. The resins studied here are stable for not longer than about 1 month.

These results suggest that the use of allyl alcohol in the synthesis of acidic maleate ester completely changes the properties of the obtained resins. Undoubtedly, additional unsaturated bonds

take part in crosslinking of the resin, thus giving a more mechanically stable product.

The results of chemical resistance studies additionally confirm these observations. Figures 4 and 5 show the relative mass change of the epoxyfumarate resins synthesized in the one- and two-step procedures both at room temperature and at 50°C. Chemical resistances of the resins determined at room temperature are similar to those obtained previously. At room temperature the greatest mass growth of resins is observed in tap water. At 50°C the greatest increase is visible in xylene. It is important that the presently studied resins absorb xylene but their destruction does not take place. The smallest mass growth of the resins is observed in 20% NaOH.

CONCLUSIONS

The results presented here indicate that unsaturated epoxyfumarate resins from the epoxy resin and acidic allyl maleate can be obtained both in the one- and two-step procedures. Compared with the resins obtained from epoxy resin and acidic

Table III Thermomechanical Properties of the Cured Resins

| Property | Resin Number | | | | | |
|--|--------------|-------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Initial decomposition temperature (°C) | 70 | 70 | 80 | 70 | 70 | 70 |
| Glass-transition temperature (°C) | 110 | 110 | 105 | 108 | 75 | 77 |
| Thermal resistance according to Martens (°C) | 103 | 103 | 103.5 | 104 | 90 | 91 |
| Flexural strength (MPa) | 81.4 | 72.5 | 78.8 | 78.6 | 88.2 | 81.9 |
| Tensile strength (MPa) | 54.9 | 54.5 | 54.7 | 59.4 | 56.8 | 53.4 |
| Ball indentation hardness (MPa) | 127.4 | 133.0 | 131.6 | 133.1 | 133.4 | 136.2 |
| Impact strength according to Charpy (kJ/m ²) | 3.5 | 3.4 | 3.1 | 3.3 | 3.8 | 4.0 |

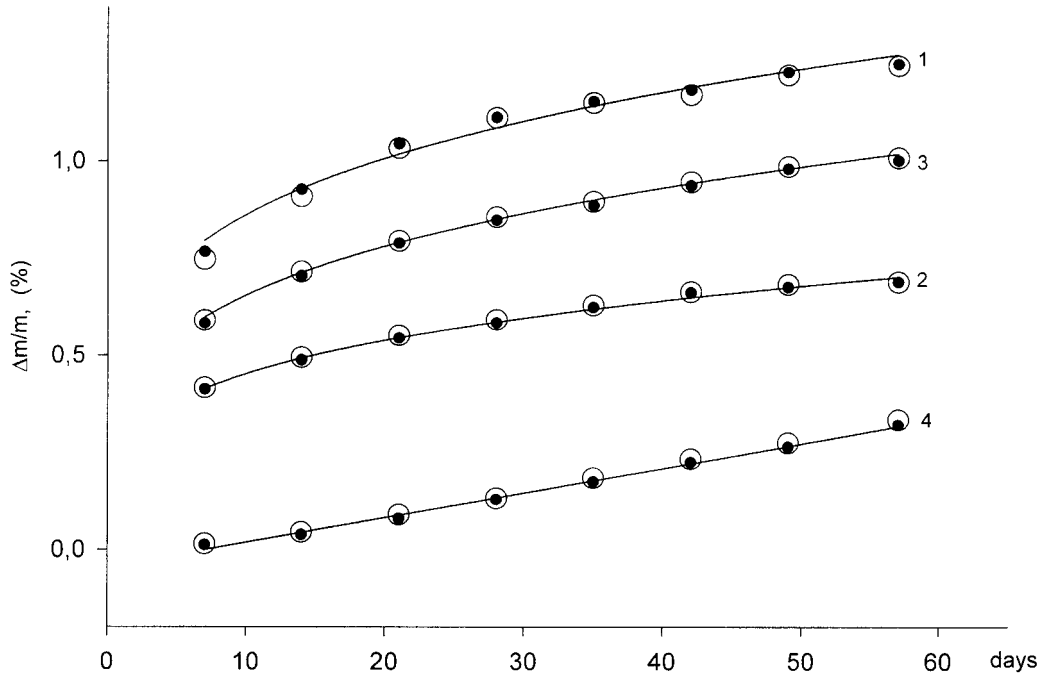


Figure 4 Relative mass change ($\Delta m/m$, %) of the epoxyfumarate resins at room temperature: Resin 1 (●); resin 2 (○). Curves are as follows: (1) tap water; (2) 20% NaOH; (3) 20% HNO₃; (4) xylene.

maleates of saturated alcohols (cyclohexanol, benzyl alcohol, *n*-hexanol), their thermomechanical properties are quite different. Additional unsat-

urated bonds are responsible for high crosslinking density of the final products. This means that the use of allyl alcohol in the synthesis of unsaturated

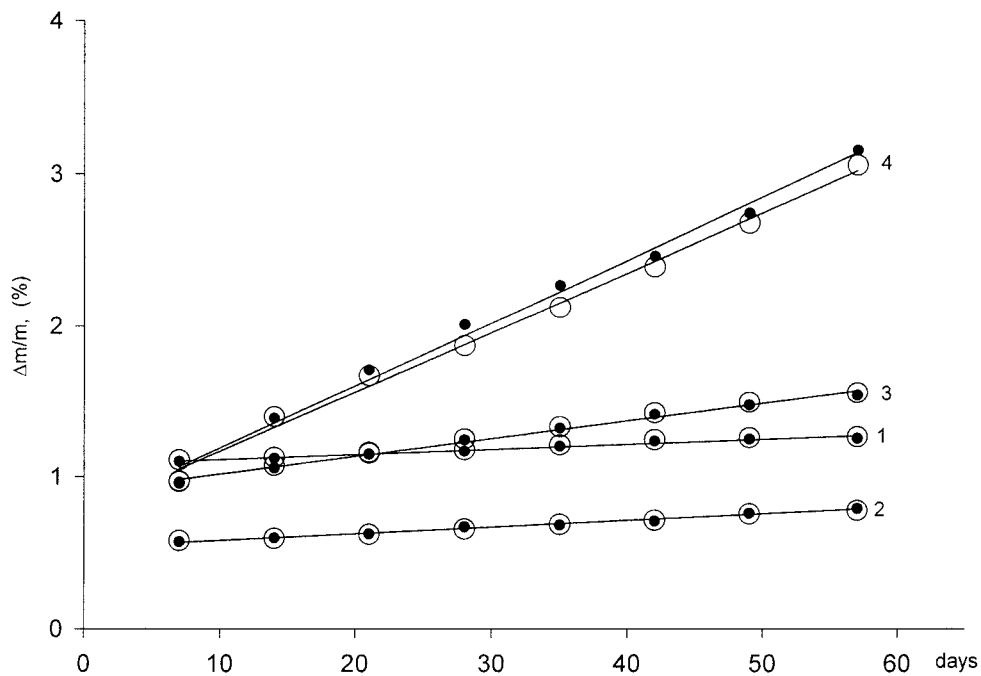


Figure 5 Relative mass change of the resins studied at 50°C. (The numbering is as in Fig. 4.)

polyester resins exerts an advantageous influence on their properties.

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