Synthesis of Unsaturated Epoxyfumarate and Epoxymaleate Resins

TADEUSZ MATYNIA, JERZY KSIĘŻOPOLSKI

Faculty of Chemistry, MCS University, pl. Marii Curie-Sklodowskiej 3, 20-031 Lublin, Poland

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ABSTRACT: Synthesis and properties of epoxyfumarate and epoxymaleate resins obtained by the addition of acidic benzyl maleate to the commercially available epoxy resin are presented. The resins were synthesized in one- and two-step procedures. In the two-step procedure, acidic benzyl maleate was synthesized separately and then used for the addition reaction with epoxy resin, Epidian 5. In the one-step procedure, acidic ester was formed during the synthesis process. Properties of the resins in a noncrosslinked state, during curing, and after crosslinking were compared. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1815–1820, 1999

Key words: unsaturated epoxyfumarate resins; unsaturated epoxymaleate resins; one- and two-step syntheses; properties of the resins; isomarization

INTRODUCTION

Unsaturated polyester resins are well known as commercially available polymeric materials with numerous applications. They are obtained by the polycondensation of unsaturated and saturated acids or anhydrides with diols. The resulting linear polyester is dissolved in styrene, and the solution is processed into a rigid crosslinked thermoset in a free radical copolymerization between styrene and the double bonds in the polymer chain.^{1–3}

The most important parameters affecting the properties of unsaturated polyesters include chemical composition and the degree of *cis-trans* isomerism occurring during polycondensation. 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 the *trans* isomer in copolymerization with vinyl monomers.⁴⁻⁶ According to Delahave et al.⁷ it is diffi-

cult to obtain 100% transformation. Moreover, depending upon the processing conditions, some residual monomers can remain after the cure. The residual unsaturation could be a source for oxidation and degradation, which can limit the durability of the industrial product. This is the reason the state of the final product; that is, the transformation rate, should be controlled.

Chemical composition of the resins influences their mechanical, thermal, and chemical resistance.^{8,9} To improve properties of the resins, different modifications of the synthesis procedure were undertaken. An interesting result of these studies are epoxyfumarates—the resins that share advantages of unsaturated polyesters and epoxy resins.^{10–14} These are formed by the addition of acrylic or methacrylic acids or acidic esters of maleic or fumaric acids to epoxy resins.

In our previous article, we studied the preparation of epoxyfumarate resins obtained in oneand two-step procedures.¹⁴ The resins were synthesized by addition of acidic cyclohexanol maleate to the epoxy resin with simultaneous isomerization of maleate groups to fumarate ones. Now, we discuss synthesis and properties of epoxyfumarate and epoxymaleate resins obtained by the

Correspondence to: T. Matynia.

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Substrate			Resin 1	Number							
	1	2	3	4	5	6					
Epidian 5	28.2820	25.9250	28.4680	26.0980	26.0525	26.2270					
Benzyl alcohol	16.5185	15.1410	_	_	15.2150						
Maleic anhydride	14.7070	13.4810	_	_	13.5480						
Acidic benzyl maleate			31.0350	28.4460		28.5875					
Styrene	40.0	45.0	40.0	45.0	45.0	45.0					
2,4,6-Tri(dimethylamino)phenol	0.1920	0.1762	0.1935	0.1773	0.1770	0.1780					
Piperidine	0.2930	0.2693	0.2960	0.2712							
Hydroquinone	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075					

Table I Synthesis Recipe

addition of acidic ester of maleic acid to the commercially available epoxy resin. In our present studies of the synthesis of acidic ester, benzyl alcohol is used. As previously, the resins were synthesized in one- and two-step procedures. The properties of unsaturated resins before and after crosslinking are determined.

EXPERIMENTAL

Materials

Maleic anhydride was purchased in Zakłady Azotowe (Nitrogen Works, Kdzierzyn-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, benzyl alcohol, hydroquinone, and cobalt naphthenate (1% Co in styrene) were from POCh (Gliwice, Poland). Luperox (50% solution of methylethylketone peroxide in dimethyl phthalate) was from Luperox (Gunzburg, Germany), and piperidine was from Merck (Darmstadt, Germany). Aromatic amine adduct (*p*-toluidine and epidian 5) was from our laboratory.¹⁵

Synthesis of Epoxyfumarate Resins

As previously, unsaturated epoxyfumarate resins were synthesized in one- and two-step proce-



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



Figure 2 ¹H-NMR spectra of resin no. 1 (I) and 3 (II) heated at 120°C (1), 150°C (2), and 170°C (3): (a) maleate bonds: $\delta = 6.4$ ppm; (b) fumarate bonds: $\delta = 6.9$ ppm.

dures.¹⁴ In the two-step procedure, acidic benzyl maleate was synthesized separately. To obtain this compound, maleic anhydride (294 g) and benzyl alcohol (331 g) were heated for 4 h at 80°C while stirring. The obtained raw compound of the acidic value 282.5 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 addition were heated gradually at: 80, 90, 100, 110, and 120°C for 1 h. At 120°C, piperidine catalyzing transformation of maleate groups to fumarate ones was added. Reaction was continued at: 120, 130, 140, 150, 160, and 170°C for 1 h. The reaction was controlled by change of the acid value and ¹H-NMR analysis. When the reaction of addition was finished, the obtained unsaturated ester was dissolved in styrene, giving 60 and 55% solutions.

In the one-step procedure, the step of the synthesis of acidic benzyl maleate as a separate compound was omitted. In this method, all chemicals were mixed and heated gradually at: 80, 90, ..., 170°C for 1 h. The reaction was controlled as described above. The obtained compound was dissolved in styrene to get 60 and 55% solutions. 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 ones. In these studies only one 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. The convolution difference resolution en-



Figure 3 ¹H-NMR spectra of the resin no. 5 (I) and 6 (II); the conditions are as in Figure 1.

Properties		Resin Number						
	1	2	3	4	5	6		
Density (g/cm ³)	1.09	1.08	1.09	1.08	1.08	1.07		
Viscosity (MPa s^{-1})	346	161	362	222	143	151		
Acid value (mg KOH/g)	15.4	14.4	12.5	11.3	10.1	10.5		
Gelation time (min)	8.0	8.5	7.0	8.0	18.0	18.0		
Peak exotherm temperature (°C)	149	147	150	148	48	44		

Table II	Properties	of the	Resins	Before	and After	Curing
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hancement method was used to improve the spectral resolution, and, consequently, the accuracy of integration of peak position determination.

The first sample of the resins was taken at 120° C (in the case of epoxyfumarate resins, it was before adding piperidine to the reaction). Next, the examined resin samples were taken at 150 and 170° C.

Curing Procedure

The obtained unsaturated resins were crosslinked using 2.5% of Luperox, the mixture of cobalt naphthenate, and the adduct of *p*-toluidine with the epoxy resin. Similar gelation times were achieved when 0.4% of cobalt naphthenate and 1.2% of *p*-toluidine adduct were used for curing the resins obtained in the one-step procedure and 0.2% of cobalt naphthenate and 0.6% of amine adduct for the two-step procedure resins. The resins were preliminarily cured at room temperature for 16 h and then postcured at 80°C for 4 h.

Thermomechanical Properties of the Resins

The obtained unsaturated resins were characterized in a noncrosslinked state, during curing, and after crosslinking. Their properties were determined according to the Polish standards, as described earlier.¹⁴

Chemical Resistance of the Resins

To study the resistance of resins 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 the resins mass in time were studied.

RESULTS AND DISCUSSION

Our previous results indicate that unsaturated epoxyfumarate resins can be prepared both in the one- and two-step procedures. Properties of the obtained resins were almost the same. Now we try to determine if the change of alcohol in acidic maleate ester gives similar results. This time we carry out the synthesis not only in the one- and two-step procedures, but also with and without piperidine responsible for isomerization of maleate bonds to fumarate ones. Development of the

Table III Thermomechanical Properties of the C	Cured Resins
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Properties			Resin I	Number					
	1	2	3	4	5	6			
Initial decomposition temperature (°C)	260	260	260	260	200	200			
Thermal resistance according to Martens (°C)	76	75	78	76	48	53			
Impact strength according to Charpy (kJ/m ²)	1.99	2.34	3.55	3.97	2.16	3.84			
Ball indentation hardness (MPa)	117.6	120.0	117.1	118.1	130.08	129.8			
Tensile strength (MPa)	48.79	55.18	50.04	52.97	68.18	67.04			
Flexural strength (MPa)	99.68	100.03	94.78	100.44	72.94	69.81			



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

reactions was monitored by ¹H-NMR. NMR spectrum of acidic benzyl maleate is presented in Figure 1. On the spectrum, maleate bonds at 6.4 ppm are clearly visible. In Figure 2, fragments of NMR spectra obtained under the same conditions (120, 150, and 170°C) for the resins prepared in the presence of piperidine in the one- and two-step procedures are presented. For both resins, isomerization of maleate bonds to fumarate takes place. The contents of *trans* isomers were determined from ¹H-NMR spectra, according to the method of Curtis et al.,¹⁶ using the areas of the signals attributable to fumarate (~ 6.9 ppm) and maleate (~ 6.4 ppm) olefinic protons. The data indicate that most transformation occurs above 150°C. These results differ from those obtained for epoxyfumarate resins formed from the epoxy resin and acidic cyclohexanol maleate.¹⁴ Then, isomerization ran gradually.

In Figure 3 analogical fragments of NMR spectra for the resins obtained in the one- and twostep procedures, without piperidine, are pre-



Figure 5 Relative mass change of the resins studied at 50°C; numbering is as in Figure 4.

sented. On these spectra, maleate bonds are clearly visible. Their intensity did not change while heating. This means that without piperidine, isomerization of maleate bonds to fumarate ones does not occur. Even heating at the temperatures of $160-170^{\circ}$ C has an insignificant influence on the transformation efficiency.

The properties of the studied resins before and after curing are summarized in Tables II and III. From these data, we can see that before curing, the properties of the epoxyfumarate resins prepared in the one- and two-step procedures are similar. Unsaturated epoxymaleate resins are significantly less reactive. Their gelation times are c. twice longer than those for analogical epoxyfumarate resins. Their exothermic peaks are also very small, as compared to those for the resins obtained in the presence of piperidine.

Thermomechanical properties of epoxyfumarate resins differ from those for epoxymaleate. The deflection temperatures measured by the Martens method are significantly higher for the epoxyfumarate resins independent of the synthesis procedure. However, these values are smaller than those for the resins of acidic cyclohexanol maleate and epoxy resin.¹⁴ The epoxyfumarate resins are characterized by higher values of flexural strength, and their tensile strength values are smaller than those for the epoxymaleate resins. Only the hardness of both epoxyfumarate and epoxymaleate resins is similar.

The results of chemical resistance studies for the epoxyfumarate resins obtained in the oneand two-step procedures are presented in Figures 4 and 5. These figures show the relative mass change of the studied resins. As supposed, all the studied resins absorb solvents. The smallest mass growth of resins is observed in 20% NaOH both at room temperature and at 50°C. The greatest increase exceeding 2% is visible in toluene at room temperature. At 50°C, destruction of the resins obtained in the one- and two-step procedures after 7 days occurred. The results presented here indicate that unsaturated epoxyfumarate resins from the epoxy resin and acidic benzyl maleate can be obtained both in the one- and two-step procedures. For these resins, isomerization of maleate bonds to fumarate ones occurs at high temperatures. As comparing to epoxyfumarate resins of epoxy resin and acidic cyclohexanol, maleate thermomechanical properties of currently studied resins are different.

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