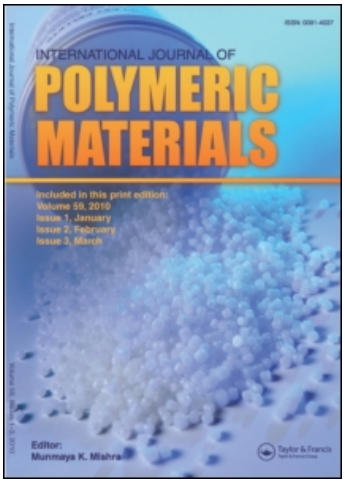

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One- and Two-step Syntheses of Unsaturated Epoxyfumarate Resins Containing Bromine

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One- and Two-step Syntheses of Unsaturated Epoxyfumarate Resins Containing Bromine

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Syntheses and properties of epoxyfumarate resins obtained by the addition of acidic butyl maleate to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether are presented. The resins were synthesized in the one and two-step procedures. In the two-step procedure, acidic butyl maleate was synthesized separately and then used for the addition reaction with epoxycompound. 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 are compared.

Keywords: Unsaturated epoxyfumarate resins; one- and two-step syntheses; bromine

INTRODUCTION

Owing to a wide range of properties, the unsaturated polyester resins have found various applications, nowadays. They are used in fiber-reinforced composites, in production of chemically resistant building elements or some things of reduced flammability.

In preparation of unsaturated polyester resins of reduced flammability a number of chloro-, bromo- nitrogen, or phosphorus-containing compounds as well as metal hydroxides as fire retardants are used. The most effective are halogen containing compounds. Among them those

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containing bromine are the most active [1, 2]. It is stated that above 15% of bromine in the resins make them self-extinguishing, while those of lower halogen concentration have reduced-flammable properties and create lower toxic smokes. These resins are synthesized from maleic anhydride, propylene glycol, glycidyl ethers, and tetrabromophthalic acid or anhydride [3].

Chemically resistant resins are formed by the addition of acrylic or methacrylic acids or acidic ester of maleic acid to epoxy resins [4–6]. The addition process can be carried out in the one- or two-step procedures.

In our previous paper, we present syntheses of unsaturated epoxy-fumarate resins by adding acidic ester of maleic acid to 1,1-di(3, 5-dibromophenyl)-cyclohexane diglycidyl ether with simultaneous isomerization of maleate groups to fumarate ones [7, 8]. Acidic ethyl maleate was added to the earlier mentioned epoxycompound in the two-step synthesis. Then the synthesis was simplified and acidic propyl maleate (formed during the synthesis process) was added to 1,1-di(3,5-dibromophenyl)cyclohexane diglycidyl ether in the one-step procedure.

In our present paper, we discuss the properties of the epoxyfumarate resins obtained both in the one- and two-step procedures. In these syntheses 1,1-di(3,5-dibromophenyl)cyclohexane diglycidyl ether and acidic butyl maleate were used.

EXPERIMENTAL

Materials

Maleic anhydride was from Nitrogen Works, Kędzierzyn-Koźle (Kędzierzyn-Koźle, Poland), while styrene, hydroquinone, and cobalt naphthenate (1% solution in styrene) were from POCh (Gliwice, Poland). *n*-Butanol was purchased in Aldrich-Chemie (Steinheim, Germany), piperidine in Merck (Darmstadt, Germany), and Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phalate) in "Luperox" (Gunzburg, Germany). 1,1-Di(3,5-dibromophenyl)-cyclohexane diglycidyl ether and the adduct of *p*-toluidine and Epidian 5 (10% solution in styrene) came from our laboratory [9].

Synthesis of Epoxyfumarate Resins

Unsaturated epoxyfumarate resins were synthesized in the one- and two-step procedures [7, 8]. In the two-step procedure, acidic butyl maleate was synthesized separately. To obtain this compound, maleic anhydride and *n*-butyl alcohol were heated for 4 h at 80°C while stirring. The obtained raw compound of the acidic value 332 mg KOH/g was then added to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether, in the temperature gradient. The mixture containing 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether, acidic butyl maleate, hydroquinone as an inhibitor, and piperidine catalyzing the transformation of maleate groups to fumarate ones was heated gradually at each of the temperatures: 120, 130, ... 170°C for 1 h. The reaction was controlled by the change of the acid value and ^{1}H-NMR analysis. When the reaction of addition was finished, the obtained unsaturated epoxyfumarate ester of the acid value of 11 – 13 mg KOH/g was dissolved in styrene, giving 60% solution (Tab. I, resin no. I). In the one-step procedure, the step of the synthesis of acidic butyl maleate as a separate compound was omitted. In this method, all chemicals were mixed and heated gradually at each of the temperatures: 120, 130, ... 170°C for 1 h. The reaction was controlled as mentioned above (Tab. I, resin no. II).

NMR Characterization

^{1}H-NMR spectra were recorded at 20°C temperature on a NMR Model 567 A (Tesla, Czechoslovakia) spectrometer operating at the

TABLE I Synthesis recipe

Substrate (*g*)	*Resin number*	
	I	II
1,1-Di(3,5-dibromophenyl)-cyclohexane diglycidyl ether	100.00	100.00
Maleic anhydride	27.20	–
n-Butanol	21.00	–
Acidic butyl maleate	–	45.90
Piperidine	0.74	0.73
Hydroquinone	0.06	0.06
Styrene	99.30	97.70

^{1}H resonance frequency of 100 MHz. Chemical shifts were referred to tetramethyl silane serving as an internal standard. The first sample of the resin was taken at 120°C, next the examined samples were taken at 140 and 170°C.

Curing Procedure

The obtained unsaturated resins were crosslinked using 2% of Luperox and the mixture containing 0.4% cobalt naphthenate and 1.2% of the adduct of *p*-toluidine with Epidian 5. 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 standard PN-81/C-89032.

RESULTS AND DISCUSSION

As our previous results indicated that unsaturated epoxyfumarate resins can be prepared in the one- and two-step syntheses, the new resin formed by the addition of acidic butyl maleate to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether, was synthesized using these two methods (Fig. 1).

Development of the reaction was monitored by ^{1}H-NMR. The contents of *trans* isomers were determined from ^{1}H-NMR spectra according to the method of Curtis *et al.* [10] using the areas of the signals due to fumarate ($\sim$ 6.9 ppm) and maleate ($\sim$ 6.4 ppm) olefinic protons.

The results from NMR analysis (Fig. 2) indicate that isomerization of maleate bonds to fumarate ones responsible for better thermomechanical properties of the resin take place [11]. For both syntheses the process runs gradually but this transformation is more effective for the resin obtained in the two-step procedure synthesis.

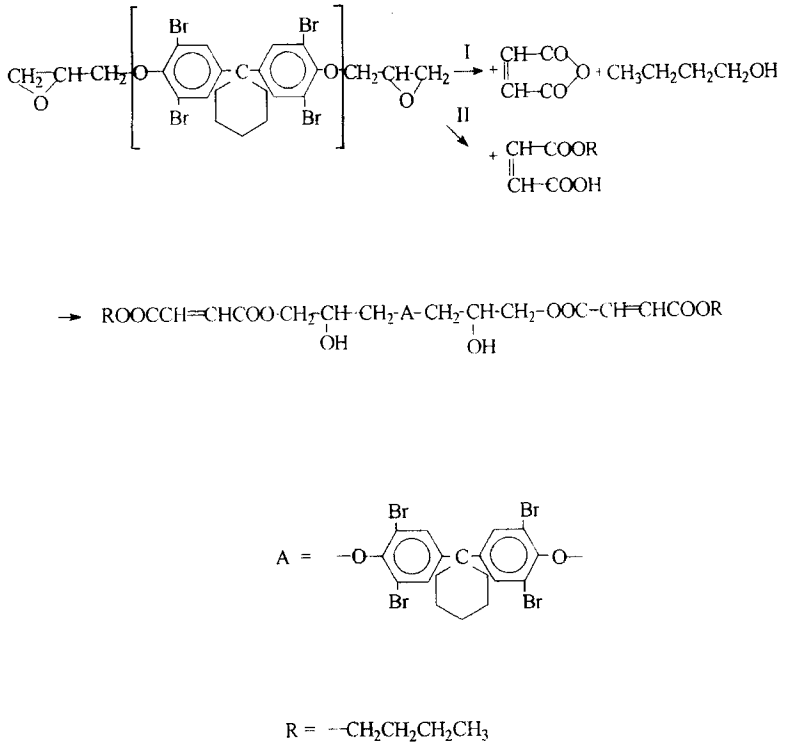

FIGURE 1 Synthesis of unsaturated epoxyfumarate resins; I = one-step procedure; II = two-step procedure.

The properties of the studied resins before and after curing are summarized in Tables II and III. From these data one can see that the properties of the resins are similar. Only exothermic peak of the resin obtained in the two-step procedure is insignificantly smaller. Thermomechanical properties determined for the resins after curing are also very similar. The deflection temperatures measured by the Martens method are rather high. They exceed 70°C. Only hardness of the resins indicate some differences. Its value is higher for the resin obtained in the two-step procedure synthesis.

The results from chemical resistance studies are also similar. For both resins insignificant mass change is observed after maintaining them in different corrosive environments. The greatest mass growth is

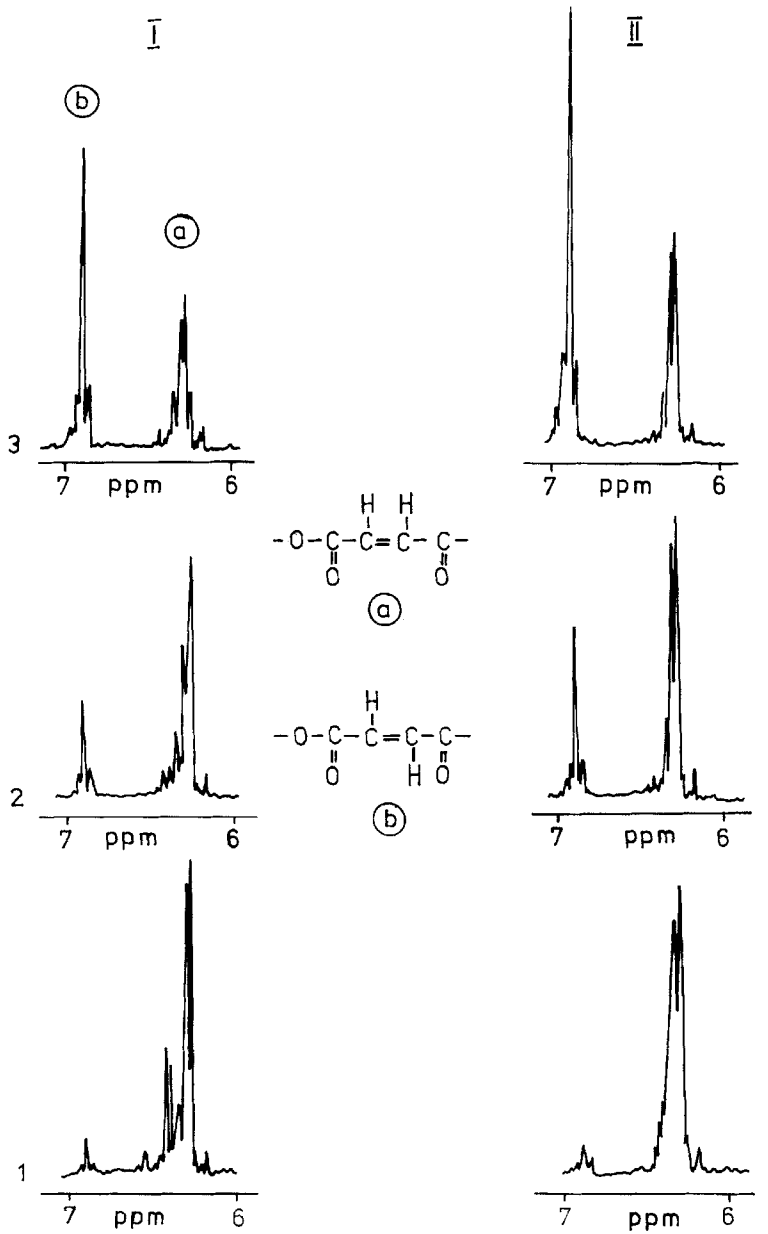

FIGURE 2 ^{1}H-NMR spectra of the resin samples: (1) taken up at 120°C; (2) 140°C; and (3) 170°C; Maleate bonds: $\delta = 6.4$ ppm (a); fumarate bonds: $\delta = 6.9$ ppm (b); Numbering as in Figure 1.

TABLE II Properties of the resins before curing

Properties	*Resin number*	
	I	II
Density (g/cm^3)	1.23	1.22
Viscosity at 25°C (MPa s)	103	104
Acid value (mg KOH/g)	10.6	9.8
Gelation time (min)	30	32
Peak exotherm temperature (°C)	56	46

TABLE III Thermomechanical properties of the resins before crosslinking

Properties	*Resin number*	
	I	II
Thermal resistance according to Martens (°C)	73.5	71.5
Impact strength according to Charpy (kJ/m^2)	2.8	3.1
Ball indentation hardness (MPa)	125.3	138.0
Flexural strength (MPa)	50.7	56.4
Tensile strength (MPa)	30.0	27.2
Initial mass loss temperature (°C)	100	100
Initial decomposition temperature (°C)	325	325

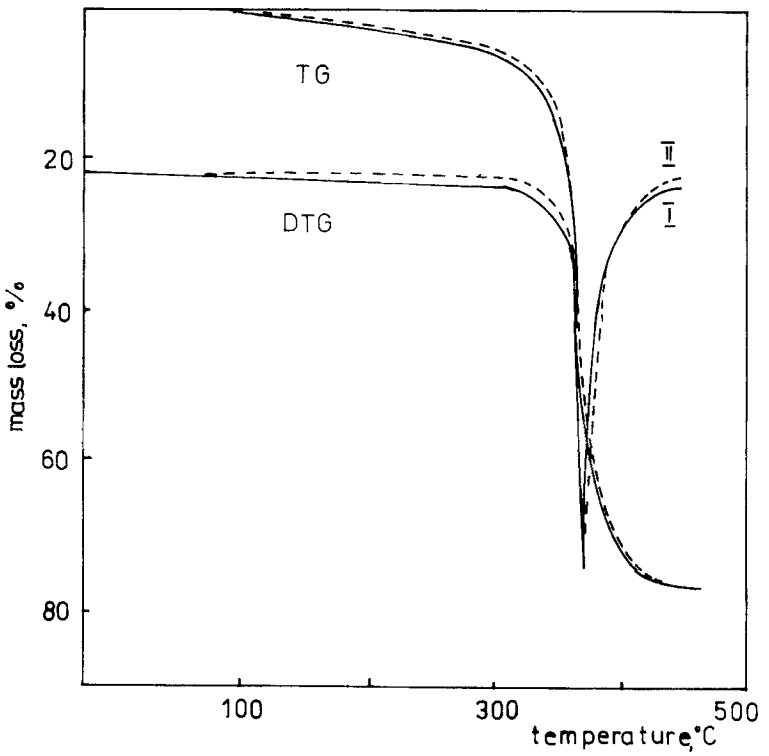

FIGURE 3 Derivatographic analysis of the unsaturated epoxyfumarate resins; Numbering as in Figure 1.

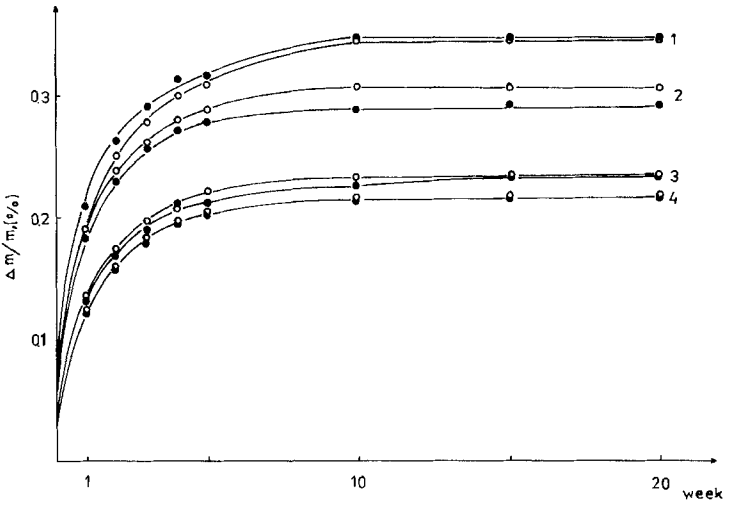

FIGURE 4 Relative mass change (Δm, %) of the resins studied at room temperature; Curves: 1 = distilled water; 2 = 5% NaOH; 3 = saturated solution of NaCl; 4 = 25% H_2SO_4.

observed in distilled water while the smallest in 25% H_2SO_4. These changes are especially visible in the first 10 weeks of experiment.

The results presented here indicate that unsaturated epoxyfumarate resins can be obtained in the one- and two-step procedure syntheses. For both resins isomerization of maleate bonds to fumarate ones take place. Other properties are practically the same.

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