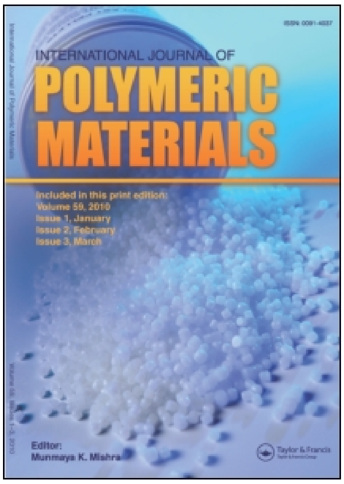

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Synthesis and Properties of Unsaturated Epoxyfumarate Resin Containing Bromine

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One-step procedure synthesis of epoxyfumarate resin is presented. The resin is formed by the addition of *in statu anscendi* acidic propyl maleate to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether with simultaneous isomerization of maleate bonds to fumarate ones. The properties of the resin before and after curing are studied. Its thermal and chemical resistance associated with the presence of bromine atoms suggests special applications.

Keywords: Unsaturated epoxyfumarate resin; synthesis conditions; bromine; properties of the resin

INTRODUCTION

Unsaturated polyester resins are among the most widely used thermosetting materials due to their low cost and to the advantages they offer such as light weight and resonably good mechanical properties [1]. They are employed in the fabrication of a broad range of products such as structural parts of automobiles, building materials, coating materials, engineering plastics *etc.* Thus, studies on developing polyesters into flame retardant materials have practical significance [2–4]. A number of chloro-, bromo-, nitrogen, or phosphorus-containing compounds as well as metal hydroxides were studied as

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fire retardants. Because of low prices, reduced flammability of the resin is often achieved by an introduction of halogen atoms into the resin chains. Agrawal *et al.* [5] studied the influence of halogen contence on fire retardancy of the resins obtained from maleic and phthalic anhydrides and ethylene and propylene glycols. They observed correlation between the concentration of halogen in the resin skeleton and its flame-retardancy and also influence on the resin thermal resistance.

In some applications not only flame retardant resins are especially useful but also chemically resistant. The latter are formed by the addition of acrylic or methacrylic acids or acidic esters of maleic acid to epoxy resins [6–8]. The addition processes can be carried out in the one- and two-step procedures. During these syntheses isomerization of maleate bonds to fumarate ones takes place. Fumarate bonds (*trans*) are responsible for better thermomechanical properties and chemical resistance.

In our previous paper we present two-step synthesis of unsaturated epoxyfumarate resin by adding acidic ester of maleic acid to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether. In our present studies we discuss the synthesis of unsaturated epoxyfumarate resin obtained by the addition of *in statu nascendi* acidic maleate ester to mentioned earlier epoxycompound. In the synthesis of acidic maleate ester *n*-propanol was used. Properties of the resin before curing and after crosslinking are determined.

EXPERIMENTAL

Materials

Maleic anhydride was from Nitrogen Works, Kędzierzyn-Koźle (Kędzierzyn-Koźle, Poland), while *n*-propanol, styrene, hydroquinone, and cobalt naphthenate (1% solution in styrene) were from POCh (Gliwice, Poland). Piperidine was purchased in Merck (Darmstadt, Germany) and Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) 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 [7, 9].

One-step Synthesis of Epoxyfumarate Resin

The mixture of 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether, *n*-propanol, and maleic anhydride was heated gradually at each of the temperatures: 120, 130, . . . , 170°C for 1 h, while stirring. Reaction was carried out in the presence of hydroquinone as an inhibitor and piperidine catalyzing the transformation of maleate groups to fumarate ones. 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 11.7 mg KOH/g was dissolved in styrene, giving 60% solution (Tab. I).

NMR Characterization

^{1}H-NMR spectra were recorded at 20°C on a NMR Model BS 567A (Tesla, Czechoslovakia) spectrometer operating at the ^{1}H resonance frequency of 100 MHz. Chemical shifts were referenced to tetramethyl silane serving as an internal standard. The convolution difference resolution enhencement method was used to improve the spectral resolution and, consequently, the accuracy of integration of peak position determination. First resin sample for ^{1}H-NMR analysis was taken up at 120°C, before adding piperidine. Next the examined resin samples were taken up at 150°C and 170°C.

Curing Procedure

The obtained unsaturated resin was crosslinked using 2.5% of Luperox and the mixture containing 0.4% cobalt naphthenate and

TABLE I Synthesis recipe

Substrate	(*g*)
1,1-Di(3,5-dibromophenyl)-cyclohexane diglycidyl ether	200.00
Maleic anhydride	55.00
n-Propanol	34.00
Piperidine	1.45
Hydroquinone	0.12
Styrene	187.00

1.2% of the adduct of *p*-toluidine with Epidian 5. The resin was preliminarily cured at room temperature for 16 h and then postcured at 80°C for 4 h.

Thermomechanical Properties of the Resin

The obtained unsaturated resin was characterized in a noncrosslinked state, during curing, and after crosslinking. In a noncrosslinked state density (PN-86/C-89082/03), viscosity (PN-86/C-89082/04) and the acid value (PN-87/C-89082/15) were measured. The gelation time and peak exotherm temperature of the resin were determined in a temperature-controlled bath (25°C) according to Polish Standard PN-75/C-89082. After crosslinking, the following were examined: 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), heat resistance by the Martens method (PN-90/C-89025), and thermal stability by use of MOM derivatograph (Budapest, Hungary) at a heating rate of 5°C/min in a range from 20°C to 1,000°C in the air. The initial decomposition temperature was determined from the course of the TG curve.

Chemical Resistance of the Resin

To study the resistance of resin to corrosion, the plates of the resin were immersed in 25% H_2SO_4, 5% NaOH, saturated solution of NaCl, and distilled water. Experiments were carried out at room temperature according to PN-81/C-89032.

RESULTS AND DISCUSSION

The reaction between 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether, maleic acid and *n*-propanol is presented in Figure 1. As the studies of Boutevin *et al.* [6] indicate that in the reaction of epoxy resins with carboxylic compounds, besides esterification, several side reactions may occur, our experiments were made carefully. 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

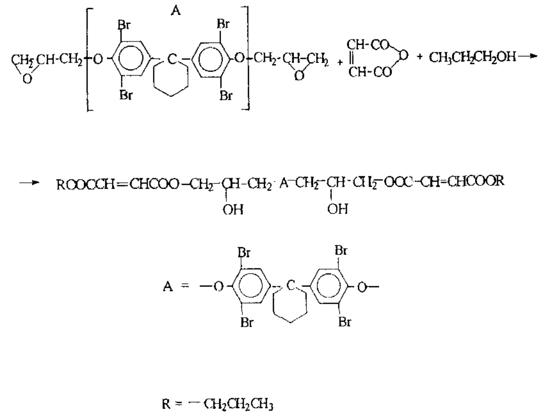

FIGURE 1 Synthesis of unsaturated epoxyfumarate resin.

method of Curtis *et al.* [10] using the areas of the signals due to fumarate (~6.9 ppm) and maleate (~6.4 ppm) olefinic protons. The results from NMR analysis (Fig. 2) indicate that isomerization of maleate bonds to fumarate ones take place. It is visible that transformation ran gradually. These results are similar to those obtained for the resin synthesized in the two-step procedure [7].

The properties of the resin before and after curing are summarized in Tables II and III. From these data one can see that the obtained unsaturated epoxyfumarate polyester is a liquid of high viscosity and softening temperature 62°C. Thermomechanical properties of the resin are similar to those obtained previously. Only derivatographic data indicate that decomposition starts at higher temperature (Fig. 3).

The results of chemical resistance studies are presented in Figure 4. The figure shows the relative mass change of the resin after keeping it in different corrosive solvents. In all solvents studied insignificant mass growth is visible. The greatest mass change is observed in water and 5% NaOH. Absorptions of 25% H_2SO_4 and saturated NaCl are similar.

The results presented here indicate that unsaturated epoxyfumarate resin can be obtained in simple on-step procedure synthesis. Its thermomechanical properties and chemical resistance suggest special applications.

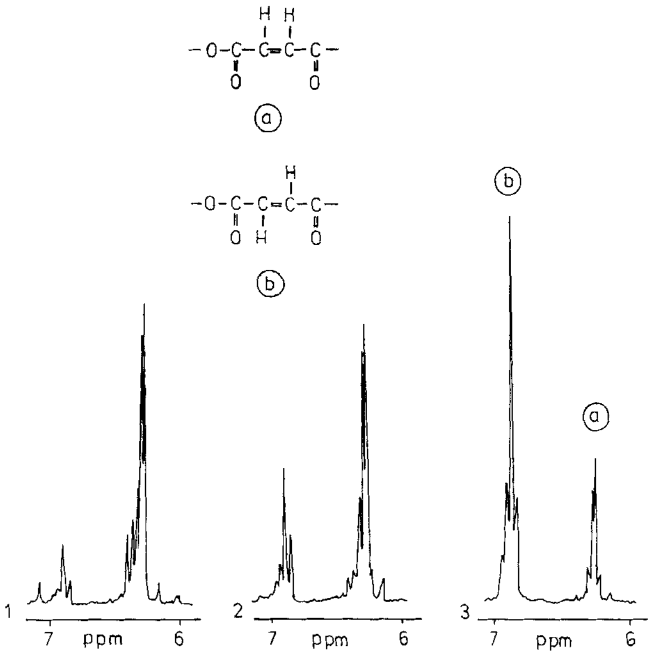

FIGURE 2 ^{1}H-NMR spectra of the resin samples: (1) taken up at 120°C (before adding piperidine); (2) 150°C; and (3) 170°C. Maleate bonds: $\delta = 6.4$ ppm (a); fumarate bonds: $\delta = 6.9$ ppm (b).

TABLE II Properties of the resin before curing

Properties	*Value*
Density (g/cm^3)	1.218
Viscosity at 25°C (MPa s)	160
Acid value (mg KOH/g)	8.0
Gelation time (min)	38
Peak exotherm temperature (°C)	114

TABLE III Thermomechanical properties of the resin after crosslinking

Properties	
Thermal resistance according to Martens (°C)	66
Impact strength according to Charpy (kJ/m^2)	2.9
Ball indentation hardness (MPa)	112.9
Flexural strength (MPa)	82.6
Tensile strength (MPa)	31.6
Initial mass loss temperature (°C)	135
Initial decomposition temperature (°C)	325

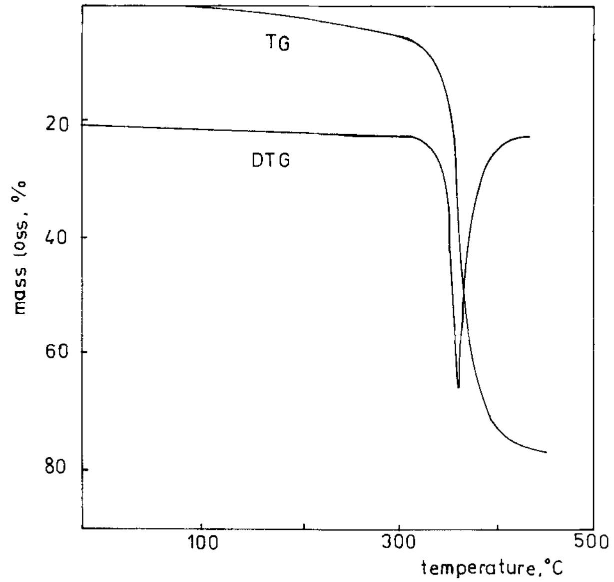

FIGURE 3 Derivatographic analysis of the unsaturated epoxyfumarate resin.

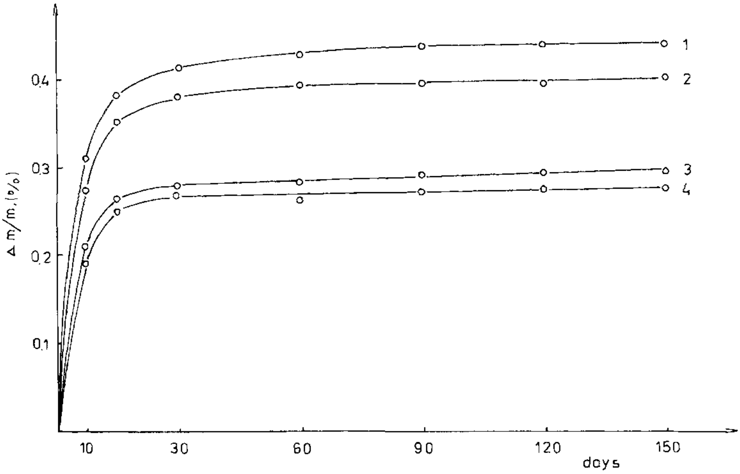

FIGURE 4 Relative mass change (Δm, %) of the resin studied at room temperature. Curves: 1 = distilled water; 2 = 5% NaOH; 3 = saturated solution of NaCl; 4 = H_2SO_4.

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