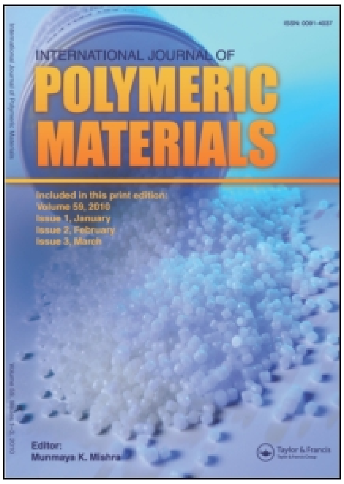

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Synthesis of Unsaturated Polyester Resin Containing Bromine

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Synthesis of unsaturated epoxyfumarate resin by adding acid ester of maleic acid to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether with simultaneous isomerization of maleate groups into fumarate ones is presented. The properties of the resin in a non cross-linked state, during curing and after cross-linking are studied. To evaluate its usefulness as a constructional resin its thermomechanical properties and chemical resistance are examined. The obtained results and the fact that the resin contains bromine in its chemical structure suggest that the resin may be applied for the production of elements characterized by reduced flammability.

Keywords: Unsaturated polyesters; epoxyfumarate resin; bromine; synthesis; properties

INTRODUCTION

Studies on the synthesis and properties of unsaturated resins characterized by high chemical and thermal resistance are the subject of many papers [1-4]. The most important parameters affecting the properties of unsaturated polyesters include chemical composition and the degree of cis-trans isomerism taking place during polycondensation of maleic anhydride with diols. It is known that the presence of condensed ring systems in the polymer chain improved both chemical and thermal properties [5-7]. Blocking the terminal groups with phenyl isocyanate [8] and modification of unsaturated epoxyfumarate resin with tolylene diisocyanate [9] affect their chemical resistance. These chemically resistant resins possess self-extinguishing properties which are useful for some applications. Similar properties indicate unsaturated polyester resins of propoxylated tetrabromo-bisphenol A as well as epoxyacrylic resins of tetrabro-bisphenolA [10]. Diglycidyl ether resins obtained by condensation of cycloaliphatic diphenols with epichlorohydrin belong to the same group. These resins can be applied as components for different compositions [11].

In this paper we present the synthesis of unsaturated epoxyfumarate resin by adding acid ester of maleic acid to 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether with the simultaneous isomerization of maleate groups to fumarate ones. The properties of both uncured resin and after cross-linking are presented.

EXPERIMENTAL

Materials

Maleic anhydride was from Zaklady Azotowe (Nitrogen Works, Kędzierzyn-Koźle (Kędzierzyn-Koźle, Poland). Toluene, ethyl acetate, isopropyl alcohol, cyclohexanone, styrene, bromine, sodium hydroxide, hydroquinone and N, N-dimethylaniline were from POCh (Gliwice, Poland) while ethyl alcohol 99.8% from TZPS "Polmos" (Lublin, Poland). Epichlorohydrin was brought in VEP Jenapharm (Jena, Germany) while phenol and piperidine in Merck (Darmstadt, Germany). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) was from "Luperox" (Gunzburg, Germany). Cobalt salt of monobutyl maleate was produced in our laboratory [12].

Synthesis of Unsaturated Epoxyfumarate Resin

The initial material was 1,1-di(4-hydroxyphenyl)-cyclohexane [2], which subjected to the reaction of bromine in the methanol medium, was transformed into 1,1-di-(4-hydroxy-3,5-dibromophenyl)-cyclohexane [13]. This bromine compound of m.p. of 142–143°C condensed in the medium of isopropanol with epichlorohydrin using sodium hydroxide formed diglycidyl ether. The raw product [14] was purified from the ethyl acetate and methanol mixture (1:1;V/V) by means of crystallization and characterized by the elemental analysis and epoxide equivalence. The analysis for $C_{24}H_{24}Br_4O_4$ (695.8). Calculated: 41.2% C; 3.5% H; epoxide equivalence 0.28 eq/100g. Obtained 41.3% C; 3.6% H and epoxide equivalence equal to 0.28 eq/100g.

In the next step 1,1-di-(4-hydroxy-3,5-dibromophenyl)-cyclohexane of m. p. 116–117°C was subjected to the addition reaction with acidic ester of maleic acid whose the acid value was equal to 382.7 mg KOH/1g. The addition process was carried out at 125–170°C with hydroquinone (0.04%) as an inhibitor and piperidine (0.5%) catalyzing the addition reaction and the maleate-fumarate transformation. The reaction was controlled by the change of the acid value and H NMR analysis of the samples taken up after 1, 4 and 7 hrs. When the reaction of addition was finished, obtained unsaturated epoxyfumarate ester of the acid value equal to 15.2 mg KOH/g and the bromine content 23.14% was dissolved in styrene giving 60% solution.

N.M.R. Characterization

H NMR spectra were recorded at 20°C on a NMR Model BS 567A (Tesla, Czechoslovakia) spectrometer operating at the ^1H resonance frequency of 100 Mhz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. The convolution difference resolution enhancement method was used to improve the spectral resolution and consequently the accuracy of integration and peak position determination.

Curing Procedure

The obtained unsaturated resin was cross-linked using a typical curing system containing 1.6% of Luperox and 0.64% of 1% solution of cobalt monobutyl maleate. The resin was preliminarily cured at room temperature for 16 h and then post-cured at 80°C for 4 h.

Thermomechanical Properties of the Resin

The obtained unsaturated resin was characterized in a non cross-linked state during curing and after cross-linking. In a non cross-linked state and during curing the softening temperature by means of the, "ring and ball" method (PN-73/C-0402), viscosity (PN-86/C-89082/04), the acid value and gelation time (PN-87/C-89082/15), were determined. After cross-linking there were examined: flexural strength (PN-68/C-89027), tensile strength (PN-81/C-89034) determined by means of FP-10 ("Fritz-Heckert", Germany) durability machine, impact strength by the Charpy method (PN-81/C-89029), hardness HK (PN-84/C-89030), heat resistance by the Martens method (PN-90/C-89025) and thermal stability by use of MOM derivatograph (Budapest, Hungary).

Chemical Resistance of the Resins

To study the resin resistance to corrosion the following solutions were used: 25% H_2SO_4, 5% NaOH, saturated solution of NaCl and distilled water. Experiments were carried out at room temperature and at a boiling point of 5% NaOH solution according to PN-81/C-89032 and PN-81/C-89067.

RESULTS AND DISCUSSION

The reaction between 1,1-di(3,5-dibromophenyl)-cyclohexane diglycidyl ether and acid ester of maleic acid leading to unsaturated resin is presented in Figure 1. The results from H NMR analysis confirm the assumed structure of the resin. Isomerization of maleate bonds to fumarate ones after 1 h, 4 and 7 hrs are presented in Figure 2. These data are in agreement with the findings of Vancso-Szmercsanyi *et al.* [15] and Curtis *et al.* [16] who suggest that the most isomerism takes place at the early stage of polycondensation. The overall content of transisomers was determined from the spectra according to the method described by Curtis *et al.* [16] and Grobelny [17], using the areas of the signals due to fumarate (~ 6.9 ppm) and maleate (6.4 ppm) olefinic protons.

Epoxyfumarate unsaturated polyester resin is a liquid of high viscosity and softening temperature 53°C. This compound copolymerizes readily with styrene in the presence of typical curing systems. The properties of the obtained cured product are summarized in Tables I and II. From these data one can see that thermomechanical properties of the resin are rather typical. The deflection temperature

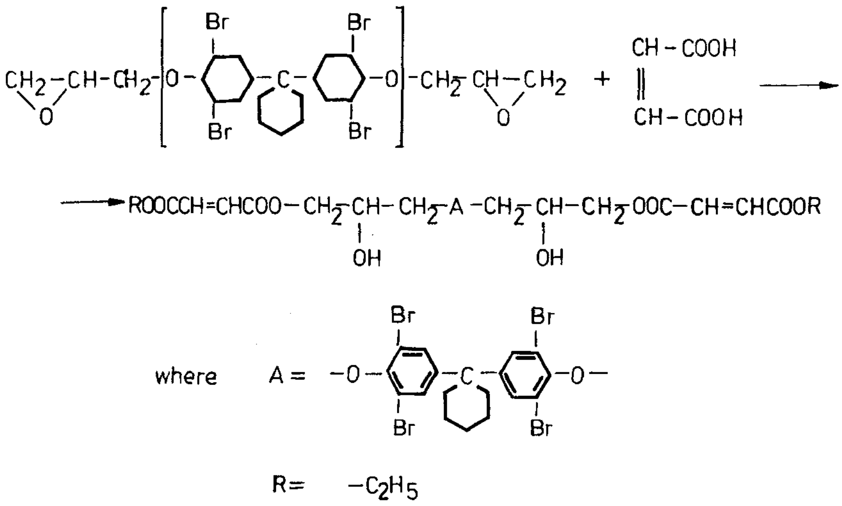

FIGURE 1 Synthesis of unsaturated epoxyfumarate resin.

TABLE I Properties of the resin in a non cross-linked state and during curing

Properties	*Value*
Viscosity at 25°C (MPa.s)	801.0
Acid value (mg KOH/g)	15.2
Gelation time at **20**°**C** (min.)	35
Softening temperature (°C)	53

TABLE II Thermomechanical properties of the resin after cross-linking

Properties	*Value*
Thermal resistance according to Martens (°C)	69
Impact strength according to Charpy (kJ/m^2)	2.8
Hardness HK (MPa)	124.7
Flexural strength (MPa)	100.3
Tensile strength (MPa)	23.5
Initial mass loss temperature (°C)	95
Initial decomposition temperature (°C)	280

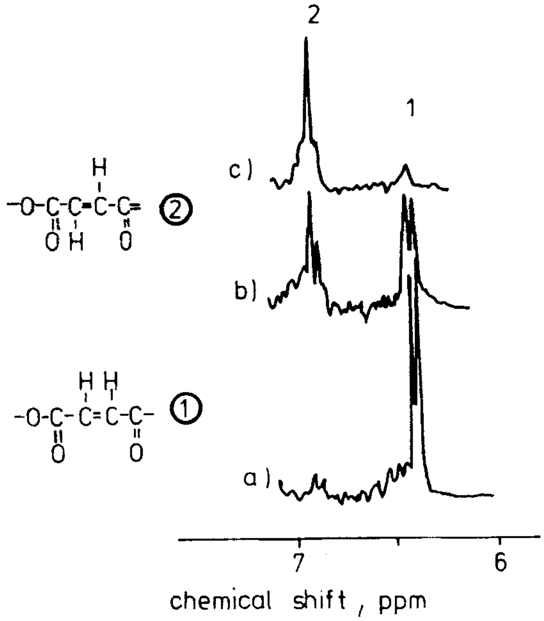

FIGURE 2 H NMR spectra of the studied resin after a) 1h b), 4 hrs and c) 7 hrs Maleate bonds $\delta = 6.4$ ppm; fumarate bonds $\delta = 6.9$ ppm. Integral for the maleate bonds band after 1 h 95.94; after 4 hrs 64.12; after 7 hrs 0. Integral for the fumarate bonds after 1 h 0; after 4 hrs 35.09; and after 7 hrs 156.32.

measured by the Martens method is not high. It is equal to 69°C. On the other hand, the resin is rather thermally resistant. Derivatographic analysis indicates that decomposition of the copolymer starts at 280°C (Fig. 3). The resin is also resistant to corrosive effect of 5% NaOH at room temperature (Fig. 4). Small loss of the resin mass is caused by 25% H_2SO_4 and saturated solution of NaCl. At a boiling point of 5% NaOH the changes of the mass are significant after 60 hours (Fig. 5).

The above properties and the fact that the resin contains bromine in its chemical structure suggest that it can be applied for the production of chemically resistant elements characterized by the reduced flammability.

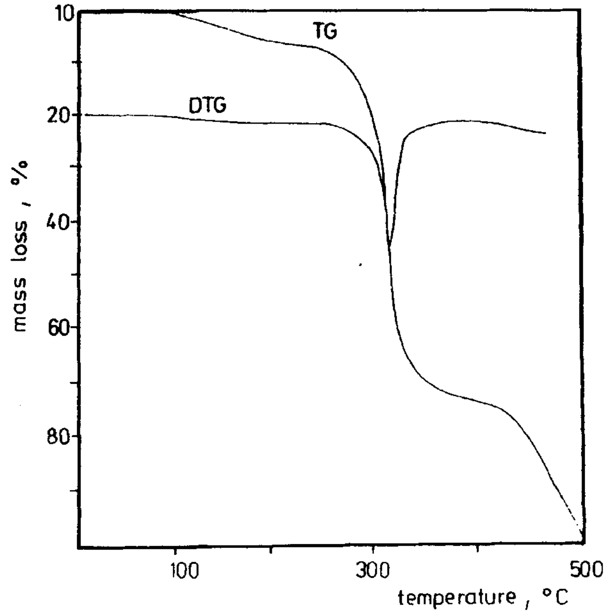

FIGURE 3 Derivatographic analysis of the unsaturated polyester resin.

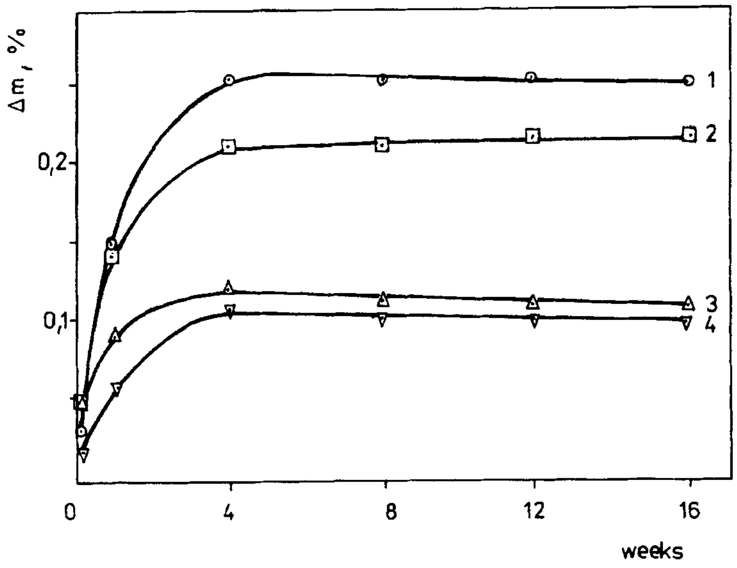

FIGURE 4 Relative mass change (Δm, %) of the resin studied at room temperature Curves: 1 = distilled water; 2 = 5% NaOH; 3 = 25% H_2SO_4; 4 = saturated solution of NaCl.

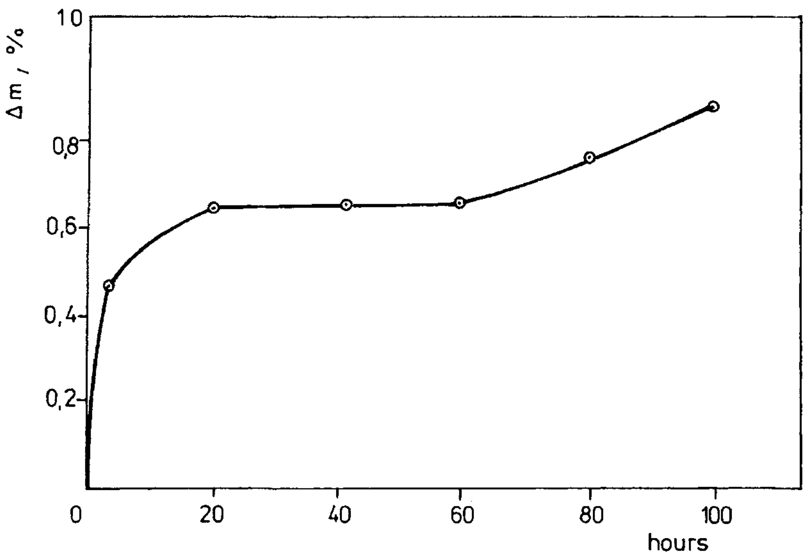

FIGURE 5 Relative mass change (Δm, %) of the resin at a boiling point of 5% NaOH.

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