Synthesis of Unsaturated Epoxyfumarate Resins

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ABSTRACT: One- and two-step procedure syntheses of epoxyfumarate resins are presented. In the two-step procedure, acidic ester of maleic acid was synthesized separately and then used for the addition reaction with epoxy resin, Epidian 5. In the one-step procedure, synthesis acidic ester was formed during the synthesis process. Properties of the resins obtained in the one- and two-step procedures, in a noncrosslinked state during curing and after crosslinking, were compared. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1423–1429, 1998

Key words: unsaturated epoxyfumarate resins; synthesis conditions; comparison of two methods of the synthesis; properties of the resins

INTRODUCTION

Unsaturated polyester resins are well known as commercially available polymeric materials with numerous applications. The most important structural parameters affecting the properties of unsaturated polyesters include chemical composition and the degree of *cis-trans* isomerism taking place during polycondensation. The *cis-trans* isomerism received much attention in the literature, owing to the considerable practical consequences of this process. In fact, the presence of fumarate unsaturation sites plays a key role in determining the physical and chemical properties of the final crosslinked polyesters, owing to a higher reactivity of the *trans* isomer in copolymerization with vinyl monomers.[1–7] The chemical composition of the resins has influence on their mechanical properties and thermal resistance. It is known that the presence of considered ring systems in the polymer chain improved both chemical and thermal properties.[8–10] Aromatic copolyesters of excellent thermal and chemical stabilities belong to the same group.

An interesting group of chemically resistant resins are epoxyfumarates. These are formed by the addition of acrylic or methacrylic acids or acidic esters of maleic or fumaric acids to epoxy resins.[11–15] Epoxyfumarates share advantages of unsaturated polyesters and epoxide resins. The aim of this article is the synthesis of epoxyfumarate resins by adding acidic ester of maleic acid to commercially available epoxy resin Epidian 5 with simultaneous isomerization of maleate groups to fumarate ones. The resins were synthesized in one- and two-step procedures. The properties of unsaturated resins before and after crosslinking were determined. In acidic ester preparation, cyclohexanol was used. In our future studies, we plan to investigate the influence of chemical structure of different alcohols on the properties of epoxyfumarate resins.

EXPERIMENTAL

Materials

Maleic anhydride was purchased in Zakłady Azotowe (Nitrogen Works, Kędzierzyn-Koźle, Poland). Epidian 5 (the resin based on Bisphenol A) and 2,4,6-tri(dimethylamino)phenol came from the Organika-Sarzyna chemical plant (New Sarzyna, Poland). Styrene, cyclohexanol, hydroquinone, and cobalt naphthenate (1% Co in styrene) were from POCh
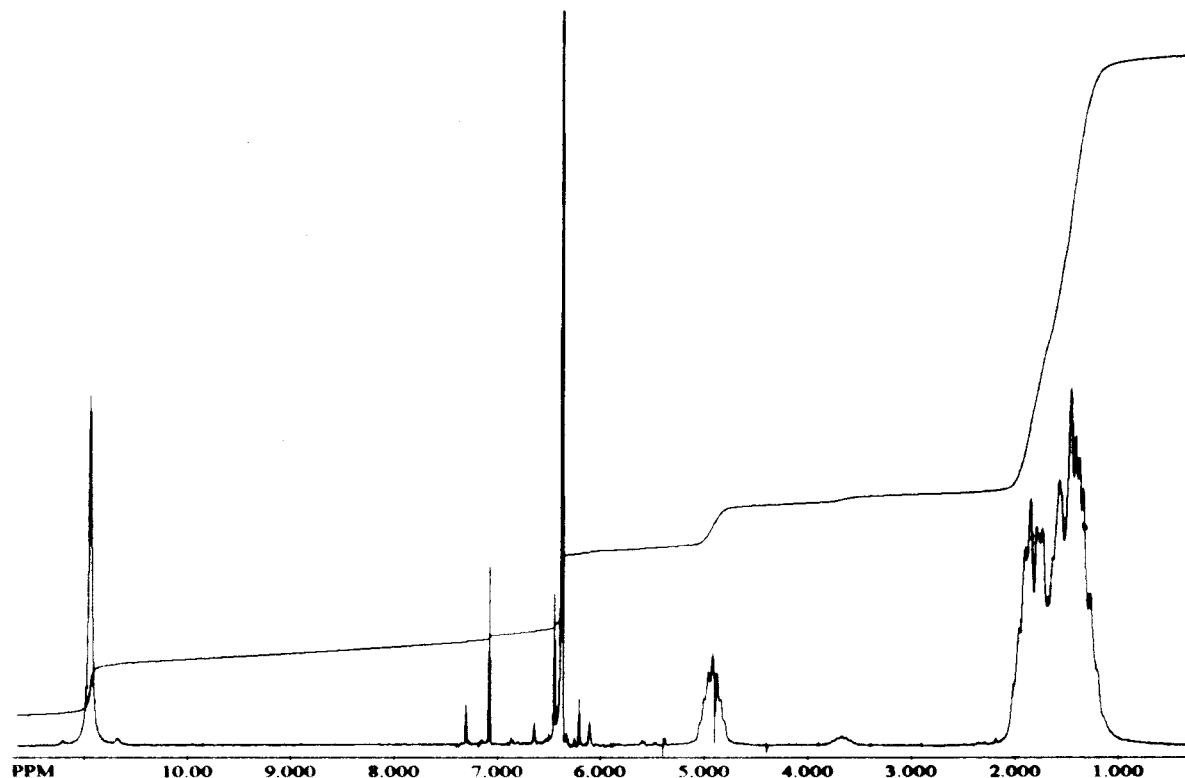

Figure 1   ¹H-NMR spectrum of acidic cyclohexanol maleate.

(Gliwice, Poland). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) was from Luperox (Gunzburg, Germany), while piperidine was bought in Merck (Darmstadt, Germany). Aromatic amine adduct (*p*-toluidine and Epidian 5) came from our laboratory.[16]

Synthesis of Epoxyfumarate Resins

Unsaturated epoxyfumarate resins were synthesized in two- and one-step procedures. In the two-step procedure, acidic ester of maleic acid was synthesized separately. To obtain this compound, maleic anhydride and cyclohexanol were heated for 4 h at 80°C while stirring. Identification of this compound was made by ¹H nuclear magnetic resonance (¹H-NMR) analysis (Fig. 1). The obtained raw acidic cyclohexanol maleate 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 each of the temperatures of 80, 90, 100, and 110°C for 1 h. Next, the

Table I   Synthesis Recipe

Substrate (g)	Resin Number			
	1	2	3	4
Epidian 5	29.10	26.64	29.72	27.29
Cyclohexanol	—	—	14.63	13.40
Maleic anhydride	—	—	15.20	13.90
Acidic cyclohexanol maleate	30.46	27.95	—	—
Styrene	40	45	40	45
2,4,6-Tri(dimethylamino)phenol	0.149	0.136	0.149	0.136
Piperidine	0.298	0.273	0.298	0.273
Hydroquinone	0.0075	0.0075	0.0075	0.0075

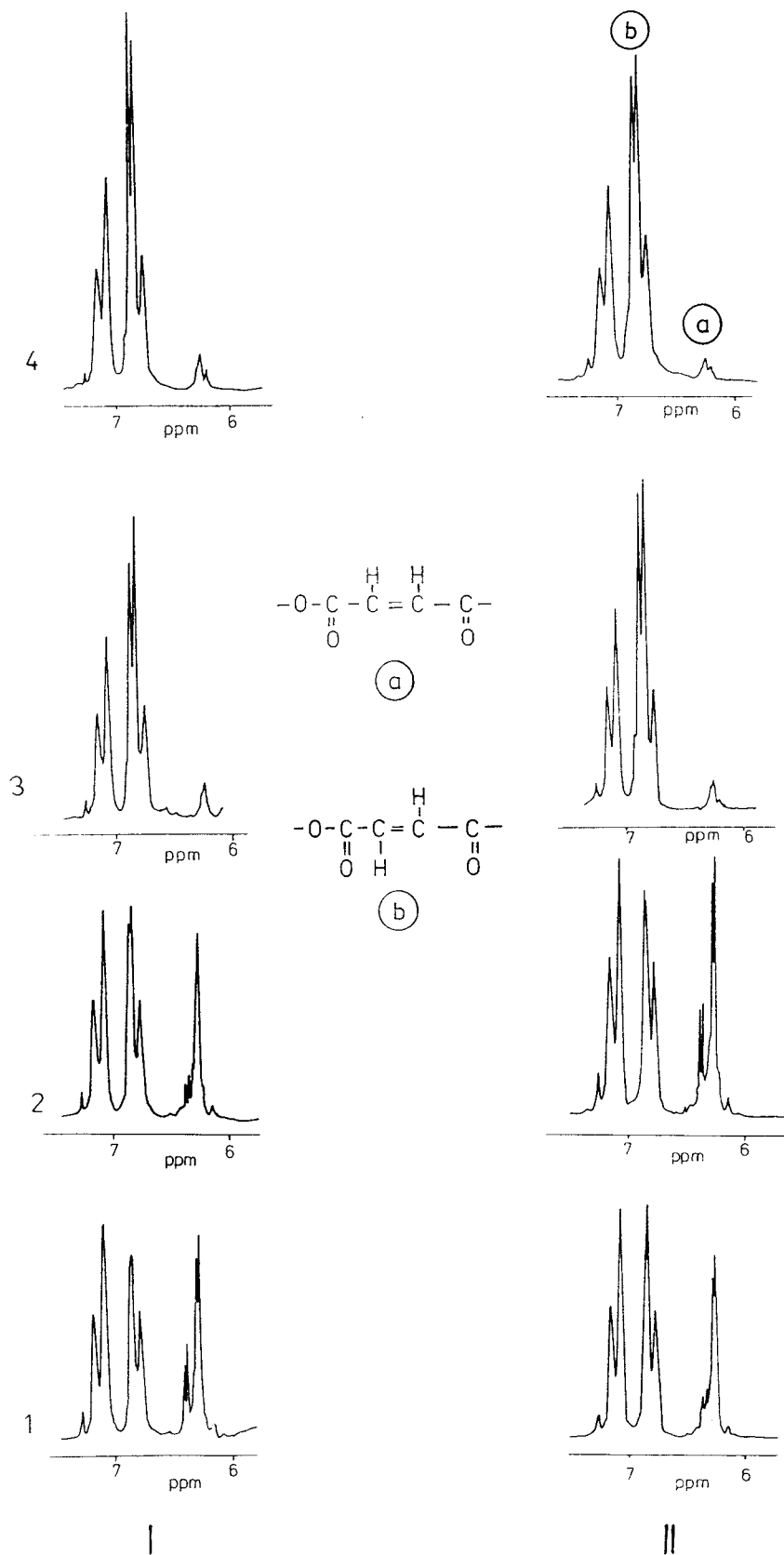**Figure 2** ¹H-NMR spectra of resin no. 1 (I) and resin no. 3 (II) before (1) adding piperidine, and after (2) 1, (3) 4, and (4) 7 h. (a) Maleate bonds: δ = 6.4 ppm. (b) Fumarate bonds: δ = 6.9 ppm.

Table II   Properties of the Resins Before and During Curing

| | Resin Number | | | |
Properties	1	2	3	4
Density (g/cm^3)	1.05	1.04	1.05	1.04
Viscosity (MPa s^{-1})	506	194	516	254
Acid value (mg KOH/g)	13.3	12.6	13.8	13.3
Gelation time (min)	21	12	20	14
Peak exotherm temperature (°C)	125	118	110	113

temperature was increased to 120°C, and piperidine, which catalyzed the transformation of maleate groups to fumarate ones, was added. Reaction was continued at each of the temperatures of 120, 130, 140, 150, 160, 165, and 170°C for 1 h. A detailed recipe used in this study is given in Table I.

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 approximately 12–14 mg KOH/g was dissolved in styrene, giving 60 and 55% solutions.

In the one-step procedure, the step of the synthesis of acidic ester of maleic acid as a separate compound was missed. In this method, all chemicals were mixed and heated gradually at each of the temperatures of 80, 90, . . . , 160, 165, and 170°C for 1 h. The reaction was controlled, as mentioned above. As previously described, the obtained compound was dissolved in styrene to get 60 and 55% solutions.

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 enhancement 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 before adding piperidine. Next, samples were examined after 1, 4, and 7 h after adding it to the reaction mixture.

Curing Procedure

The obtained unsaturated resins were crosslinked using 2% of Luperox and the mixture of cobalt naphthenate and the adduct of p-toluidine with epoxy resin. Similar gelation times were achieved when 0.4% of cobalt naphthenate and 1.2% of toluidine adduct were used for curing the resins obtained in the one-step procedure and 0.2% of cobalt naphthenate and 0.6% of aromatic amine accelerator 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. In a noncrosslinked state den-

Table III   Thermomechanical Properties of the Cured Resins

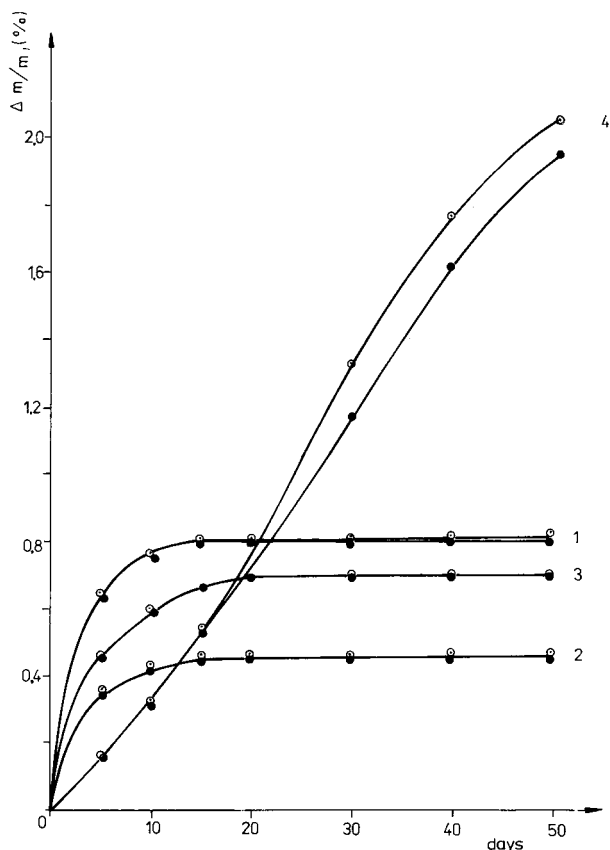| | Resin Number | | | |
Properties	1	2	3	4
Initial decomposition temperature (°C)	180	180	160	160
Thermal resistance according to Martens (°C)	82.5	80.5	79	80
Impact strength according to Charpy (kJ/m^2)	3.6	4.5	2.7	2.8
Ball indentation hardness (MPa)	119.5	107.8	111.1	117.2
Tensile strength (MPa)	44.8	31.5	38.1	39.1
Flexural strength (MPa)	70.4	72.6	84.2	75.8

Figure 3 Relative mass change ($\Delta m/m$, %) of the resins studied at room temperature: resins (■) no. 1 and (□) no. 3. Curves are as follows: (1) tap water, (2) 20% NaOH, (3) 20% HNO$_3$, and (4) toluene.

sity (PN-86/C-89082/03), viscosity (PN-86/C-89082/04) and the acid value (PN-87/C-89082/15) were measured. The gelation times and peak exotherm temperatures of the resins 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) determined by means of a FP-10 (Fritz-Heckert, Germany) durability machine, 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 to 1000°C in the air. The initial decomposition temperature was determined from the course of the TG curve.

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% HNO$_3$, and toluene. Experiments were carried out at room temperature and at 50°C according to PN-81/C-89067. Changes of the resins properties in time were determined.

RESULTS AND DISCUSSION

Studies of Boutevin et al.[14] indicate that in the reaction of epoxy resins with carboxylic compounds, besides esterification, several side reactions may occur. Taking this into account, our experiments with the synthesis of epoxyfumarate resins in the one-step procedure were carefully made. Development of the reaction was monitored by ^{1}H-NMR. NMR spectra obtained in the same conditions for the resins prepared in the one- and two-step procedures are shown in Figure 2. For both resins, the spectra are similar. Isomerization of maleate bonds to fumarate ones is visible. The contents of *trans* isomers were determined from ^{1}H-NMR spectra according to the method of Curtis et al.,[2] using the areas of the signals due to fumarate ($\sim$ 6.9 ppm) and maleate ($\sim$ 6.4 ppm)
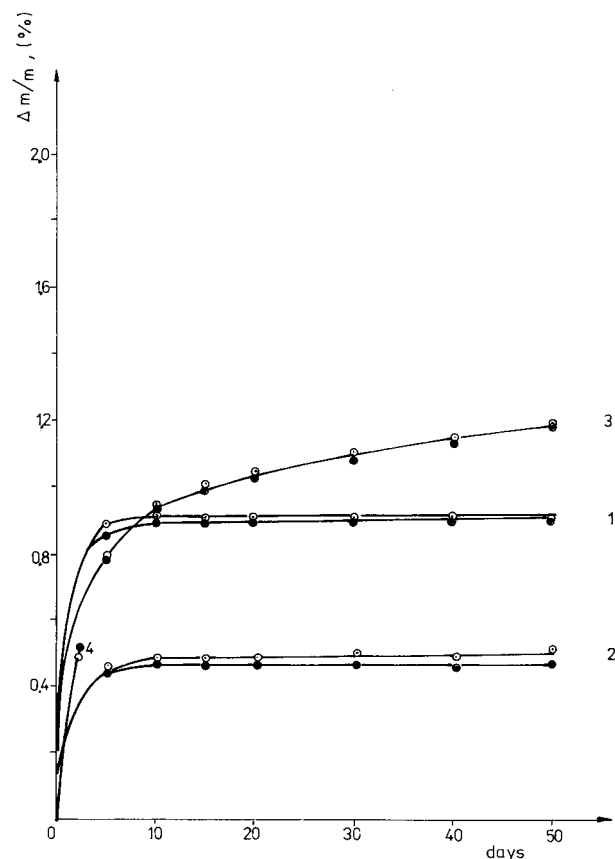

Figure 4 Relative mass change of the resins studied at 50°C. Numbering is as in Figure 3.
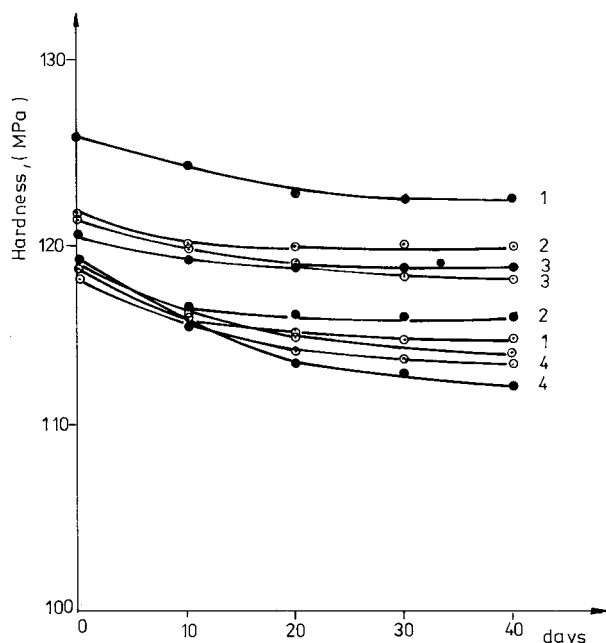
Figure 5   Changes of the resins hardness as a function of time. Conditions and numbering are as in Figure 3.

olefinic protons. The data suggest that the most transformations take place below 150°C. At the end of experiment, the degree of isomerism exceeds 90% for both resins.

Properties of the resins obtained in one- and two-step procedures after curing are summarized in Tables II and III. From these data, one can see that, before curing, properties of the resins of the same concentrations are similar. 65% solutions of the resins indicate only insignificant differences. Among 60% solutions, resin no. 1 gives the highest exothermic peak. Thermomechanical properties of the resins determined after curing are also very similar. The deflection temperatures measured by the Martens method are rather high. For all resins, these are close to 80°C. Their hardnesses are also not different. Besides flexural strength, other mechanical properties of the resins obtained in the two-step procedure are insignificantly better. For example, they have higher values of impact strength. Of the studied resins, no. 1 obtained in the two-step procedure indicates especially high tensile strength.

The results of chemical resistance studies are presented in Figures 3–7. These figures present relative mass change of the studied resins and changes of their hardness, tensile strength, and flexural strength after keeping them in different environments (water, acid, base, and organic solvent). The obtained results indicate that 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 higher temperatures, this determination was impossible because destruction of the resin samples took place after 2 days. Hardness of the samples determined by ball indentation technique does not change. Only insignificant decrease of the values are observed for sample no. 1 (obtained in the two-step synthesis) after 20 days in toluene. Tensile strength decreases in water, increases insignificantly in NaOH and toluene, and changes irregularly in HNO_3 solutions. In all the studied solutions, sample no. 1 is resistant to breaking even after 40 days.

As the resins obtained in the one-step procedure were characterized by higher flexural strengths, changes of these properties were also measured after keeping the resins in different solvents. Of the studied solvents, flexural strengths increase only in toluene. It is especially visible after 40 days when its value is similar to that for the one-step procedure resin. In NaOH and HNO_3 solutions, flexural strength decreases. Tap water has rather small influence on its values. This
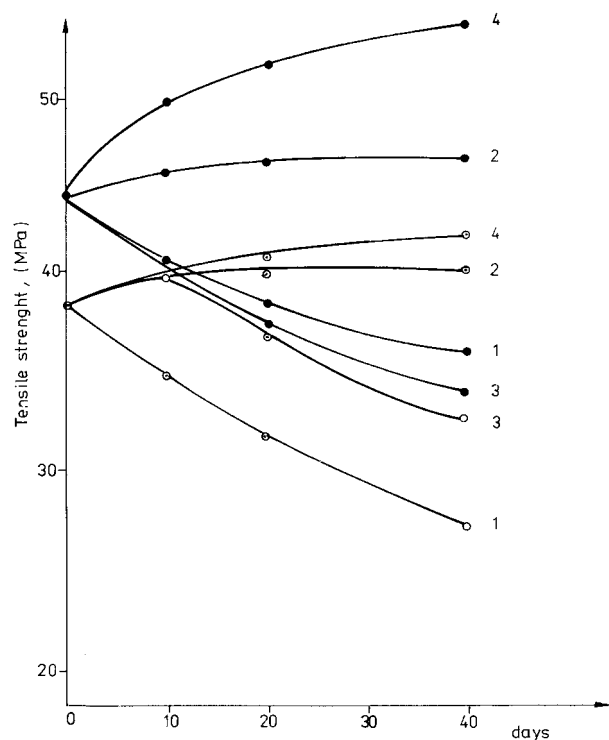

Figure 6   Changes of the resins tensile strength as a function of time. Conditions and numbering are as in Figure 3.
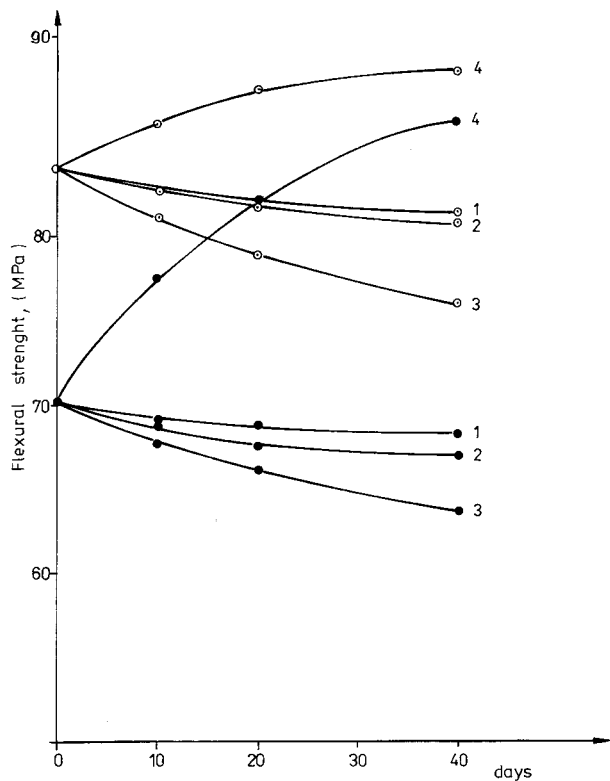
Figure 7 Changes of the resins flexural strength as a function of time. Conditions and numbering are as in Figure 3.

means that in organic solvents epoxyfumarate resins become more flexible.

The results presented here indicate that unsaturated polyester resins derived from epoxyfumarates can be prepared both in one- and two-step procedures. The one-step procedure, which is eas-

ier, makes the synthesis of the resins with good thermomechanical properties possible.

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