

Synthesis and Modification of Epoxy-Based Divinyl Ester Resin

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ABSTRACT: Syntheses of epoxy-based divinyl ester resin and its modification with toluene diisocyanate (TDI) are presented. The resin was obtained from commercially available epoxy resin Epidian 5 and methacrylic acid during graduated heating. Three different resin solutions were obtained by adding 45, 50, and 55% of styrene; then, each solution was modified with TDI at room temperature. Properties of the resins before and after modification were studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2062–2067, 2001

Key words: vinyl ester resin; styrene copolymers; modification with toluene diisocyanate; TDI; thermomechanical properties

INTRODUCTION

The vinyl ester resin family includes different kinds of materials which have a common feature of a bisphenol-A epoxy group or a urethane group in their structure.¹ Epoxy-based divinyl ester resins were developed to incorporate the generally superior cast resin properties of epoxies with the ease of fiber reinforcement processing during the conventional fabrication routes of composite materials.^{2–4} These resins also possess some advantageous characteristics including toughness, improved elongation, good chemical resistance, and better wetting and bonding to glass reinforcements. Similar to unsaturated polyester resins, they have excellent reactivity due to the terminal vinyl groups that can be cured by copolymerization with vinyl monomers, usually styrene or methyl methacrylate.⁵ Hydroxyl functional groups present in the divinyl ester resin chains can be used for chemical modifications or additional curing. These resins seem to be very at-

tractive because they share advantages of epoxides and polyesters.^{6–10}

In this article, we used hydroxyl functional groups in the chemical structure of epoxy-based divinyl ester resin for modification with TDI. Similar studies were carried out for typical unsaturated polyester resins.¹¹ The obtained results indicated that the addition of toluene diisocyanate (TDI) should not be larger than 1%, because, for higher concentrations, the resins exhibit thixotropic properties. In our present studies, we changed the concentration of TDI in the range 0.1–1.0%. Properties of the resin were determined for the three styrene solutions: 45, 50, and 55%.

EXPERIMENTAL

Materials

Epoxy resin Epidian 5 (resin based on bisphenol A) and 2,4,6-tri(dimethylamino)phenol came from the Organika–Sarżyna Chemical Plant (New Sarżyna, Poland). Methacrylic acid and *N,N*-dimethyl-*p*-toluidine were from Fluka AG (Buchs, Switzer-

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Table I Synthesis Recipe

Substrate	Resin No.		
	I	II	III
Epidian 5	38.00	34.54	30.74
Methacrylic acid	16.83	15.30	14.10
2,4,6-Tri(dimethyl- amino)phenol	0.16	0.15	0.15
Styrene	45.00	50.00	55.00
Hydroquinone	0.0074	0.0074	0.0080

land). Styrene, hydroquinone, and cobalt octoate (1% Co in styrene) were from POCh (Gliwice, Poland) while TDI came from the Chemical Plant "Organika-Zachem" (Bydgoszcz, Poland). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) was from Luperox (Günzburg, Germany).

Synthesis of Divinyl Ester Resin

To the epoxy resin Epidian 5 heated to 50–60°C, there were added methacrylic acid, hydroquinone as an inhibitor, and 2,4,6-tri(dimethylamino)phenol, catalyzing the reaction of addition. The mixture was heated gradually at 60, 70, 80, 90, 100, 110, and 120°C for 1 h while stirring. The conversion was monitored by the titration of residual acid groups with an alcoholic KOH solution and by FTIR spectroscopy performed on the samples

Table II Numbering of the Resins After Modification with TDI

Resin No.	Concentration of Styrene	Concentration of TDI
1	45.0	—
2	45.0	0.1
3	45.0	0.2
4	45.0	0.5
5	45.0	1.0
6	50.0	0.1
7	50.0	0.2
8	50.0	0.5
9	50.0	1.0
10	55.0	0.1
11	55.0	0.2
12	55.0	0.5
13	55.0	1.0

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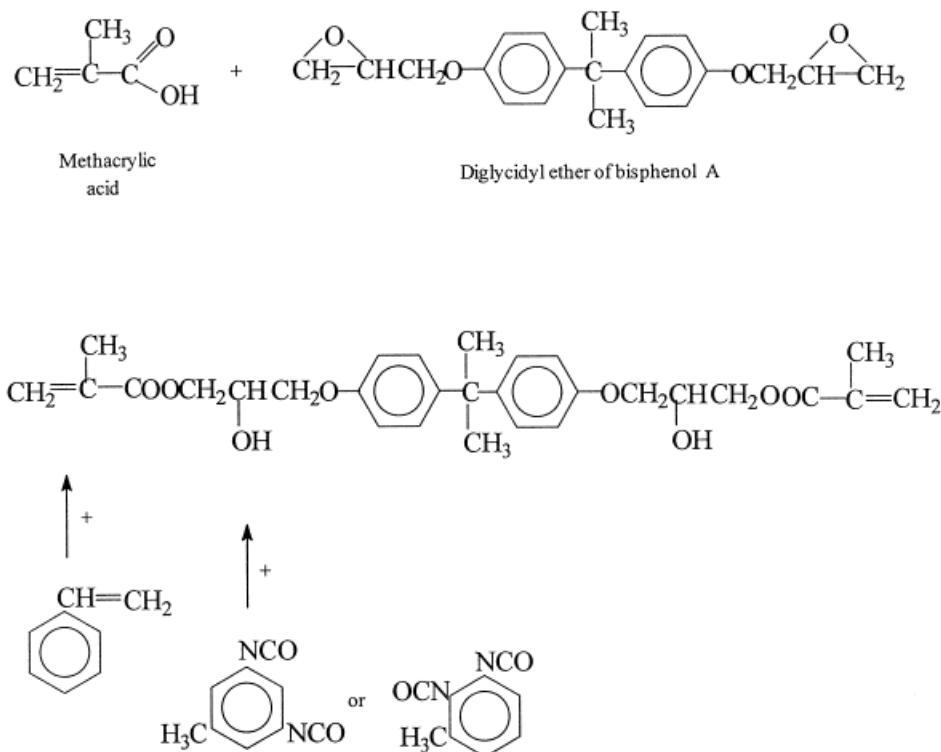


Figure 1 Scheme of the synthesis of divinyl ester resin and its crosslinking with styrene and TDI.

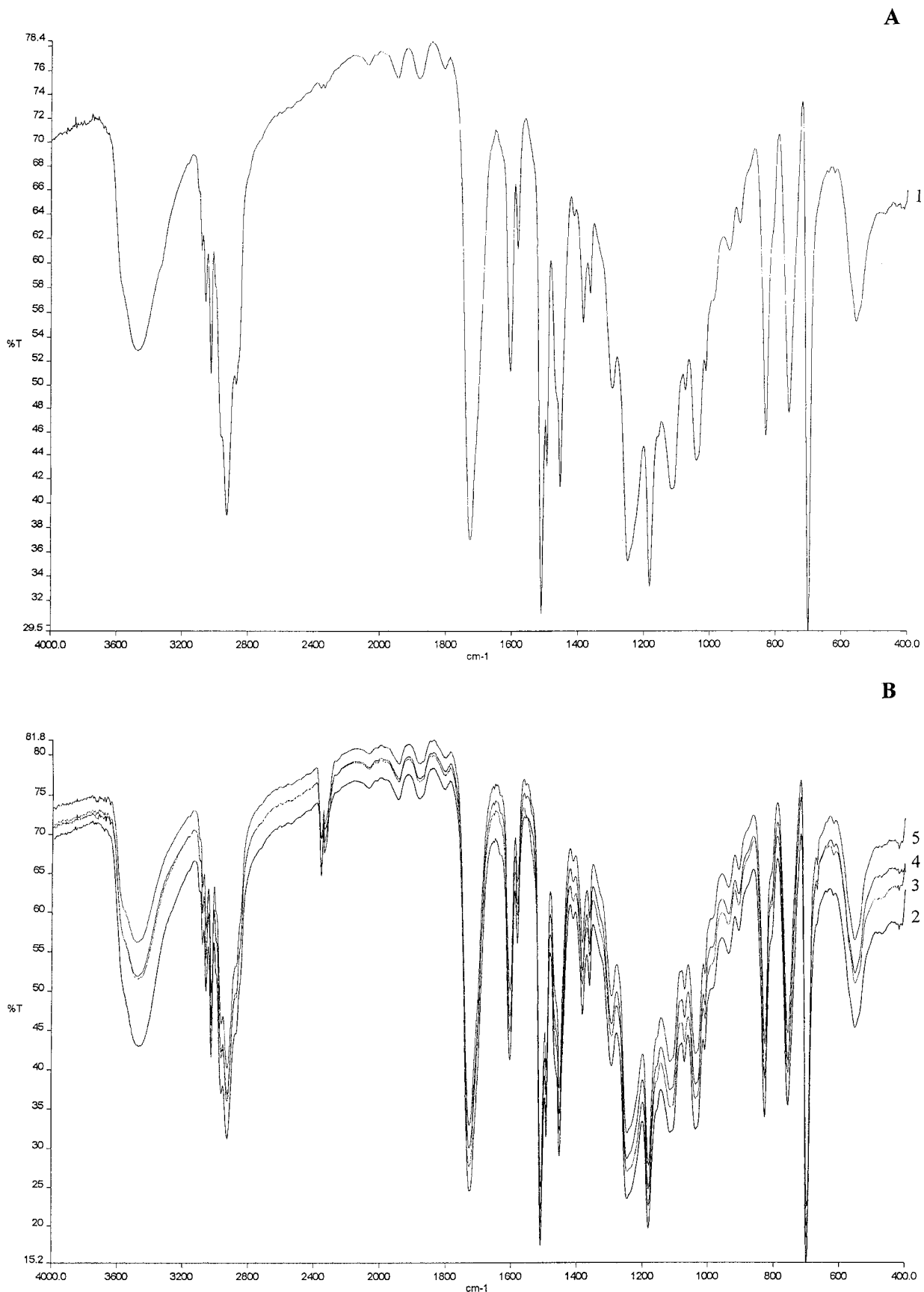


Figure 2 FTIR spectra of the (A) parent and (B) modified resins. Numbering of the resins as in Table II.

Table III Properties of the Resins in a Noncured State

Resin No.	Density (g/cm ³)	Viscosity (cP)	Acid Value (mg KOH/g)	Gelation Time (min)	Peak Exotherm Temperature (°C)	Stability at 60°C (days)
1	1.04	38.0	5.3	48	197	1
2	1.05	51.2	9.1	17	170	1.5
3	1.04	52.5	10.4	15	168	1.5
4	1.04	53.1	9.3	13	163	1.5
5	1.04	56.4	9.9	13	162	1.5
6	1.03	45.6	8.1	23	156	8.5
7	1.03	46.8	7.1	20	155	8.5
8	1.03	47.6	7.4	18	152	8.5
9	1.03	48.2	7.0	17	149	8.5
10	1.02	36.4	4.6	32	141	9.0
11	1.02	37.6	5.2	26	138	9.0
12	1.02	38.6	4.9	21	133	9.0
13	1.02	39.8	4.9	20	133	9.0

taken at different reaction times. When the addition reaction was finished, the divinyl ester obtained was cooled to 80°C and dissolved in styrene, giving 45, 50, and 55% solutions (Table I).

Modification of Divinyl Ester Resin with TDI

Each styrene solution of divinyl ester resin was modified by the addition of 0.1, 0.2, 0.5, and 1.0% of TDI. The ratios of NCO/OH were the following: 0.60; 0.30; 0.10, and 0.05. The reaction with TDI was carried out at room temperature.¹² In this way, 12 solutions were obtained (Table II).

Curing Procedure

The obtained resins were crosslinked at 25°C using 2% of Luperox, 1% of cobalt octoate, and 0.1% *N,N*-dimethyl-*p*-toluidine.

Thermomechanical Properties of the Resins

The resins were characterized in a noncrosslinked state during curing and after crosslinking. In the noncrosslinked state, the density (PN-86/C-89082/03), viscosity (PN-86/C-89082/04), acid value (PN-87/C-89082/15), and stability at 60°C (PN-86/C-89082/09) were measured. The gelation

Table IV Properties of the Cured Resins

Resin No.	Thermal Resistance According to Martens (°C)	Glass Transition Temperature T_g (°C)	Impact Strength According to Charpy (kJ/m ²)	Ball Indentation Hardness (MPa)	Tensile Strength (MPa)	Flexural Strength (MPa)
1	—	101.3	—	128.8	—	113.00
2	94	138.2	2.46	140.0	82.01	138.12
3	96	139.0	2.50	145.3	85.27	122.24
4	99	140.9	2.63	149.4	88.96	109.88
5	102.5	142.5	2.85	150.8	92.11	108.33
6	96.5	—	3.83	151.6	81.23	130.10
7	99	—	4.41	153.3	82.45	127.52
8	101	—	7.39	152.4	84.45	121.25
9	104	—	8.40	153.2	92.03	120.00
10	96	—	3.61	145.5	67.48	118.12
11	97	—	4.13	147.8	72.34	113.43
12	99	—	4.84	149.8	79.00	104.88
13	102	—	5.39	147.7	83.91	103.35

times and peak exotherm temperatures of the resins were determined in a temperature-controlled bath (25°C) according to the Polish Standard PN-75/C-89082. After crosslinking, we examined the impact strength according to the Charpy method (PN-81/C-89029), heat resistance by the Martens method (PN-90/C-89025), ball indentation hardness (PN-84/C-89030), tensile strength (PN-81/C-89034), and flexural strength (PN-89/C-89027). IR spectra for the parent and modified samples of the resins were made on a Perkin–Elmer 1700 FTIR spectrometer using KBr pellets. The mass of the modified resin samples was always the same.

The glass transition temperatures, T_g , were determined using a differential scanning calorimeter Netzsch DSC 200 (Netzsch, Germany). The conditions were as follows: sample weight ~4 mg, nitrogen atmosphere, and sealed aluminum pans. As a reference, an empty aluminum pan was used. The resins were heated in a scanning mode from 20 to 300°C at a rate of 10 K/min. T_g values were taken from the second DSC run.

RESULTS AND DISCUSSION

Figure 1 shows a scheme of the synthesis of divinyl ester resin and its crosslinking with styrene and TDI. FTIR spectra of the parent resin and four modified ones by TDI are presented in Figure 2. In the spectrum of the divinyl ester resin, the high-intensity band at 3300–3600 cm^{-1} , corresponding to hydroxyl groups is visible. The bands at 950 and 856 cm^{-1} , typical for epoxy groups, are not present.¹³ In the spectrum of the modified resins, the increase of the TDI concentration caused the decrease of the intensity of the bands for the hydroxyl groups. Unfortunately, the bands at 3340–3420 cm^{-1} , typical for the NH vibration in urethane linkages, are hidden. Broad bands at 2270 cm^{-1} (—NCO) are not visible.¹⁴

Properties of the resins obtained are presented in Table III. From these data, one can see that viscosity depends on two parameters: the concentration of styrene and the amount of TDI. With increase of the styrene concentration, viscosity decreases while increase of the TDI concentration causes a reversible phenomenon. An increase of the TDI concentration has an important influence on the resin gelation times. It should be noted

that gelation times for the modified resins are significantly shorter than that for the parent resin.

As expected, the addition of TDI caused a reduction of the peak exotherm temperature.¹¹ At the same time, the stability of the modified resins is better than that of the nonmodified resin. Additionally, the resins with greater styrene concentration are more stable over time.

Table IV presents the properties of the resins after crosslinking. From these data, one can see that, with an increase of TDI concentration, thermal resistance of the resins regularly increases. Glass transition temperatures are significantly higher than that for the parent one. With increase of the TDI concentration, a regular increase of T_g values is observed. All the resins studied are characterized by high-impact resistance. Also, tensile strengths have unexpectedly high values. Contrary to our previous results for unsaturated polyester resins,¹¹ modification of divinyl ester resins with TDI does not affect their hardness. Hardness values for all samples of the resins studied are very similar. Flexural strengths for the modified resins are smaller than that for the nonmodified one. With increase of the TDI concentration, their values decrease insignificantly. It should be stressed that the values of flexural strength for all the studied resins are generally high.

The results presented here indicate that epoxy-based divinyl ester resins can be easily modified with diisocyanates. A low concentration of TDI does not affect the resins' viscosity. On the other hand, the stabilities of the modified resins are significantly better. Modification also has an influence on the resin thermomechanical properties. The values of the glass transition temperatures and thermal resistance, according to the Martens method, are higher for the modified resins, by ~40°C, than are those for the parent epoxy-based divinyl ester resin.

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