

Unsaturated Ester Resins

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ABSTRACT: Vinyl ester resins (VERs) are often described as a cross between unsaturated polyester resins and epoxy resins. VERs offer an upgrade to epoxy resins, and they tend to be selected when chemical and temperature resistance is required. This research was aimed at developing the synthesis of unsaturated ester resins (UERs), which are similar to VERs. UERs were synthesized by the addition of dihydrodicyclopentadienyl hydrogen maleate to the terminal epoxy groups in low-molecular-weight bisphenol A/epichlorohy-

drin epoxy resins. The effect of urethanization of UERs on the properties of the crosslinked polymer was also investigated. As crosslinking monomers, styrene and glycol dimethacrylates were used. The following properties of cured UERs were determined: the heat deflection temperature, alkali resistance, and the mechanical strength. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2627–2631, 2006

Key words: polyesters; crosslinking; curing of polymers

INTRODUCTION

Vinyl ester resins (VERs) are addition products of methacrylic acid to epoxy groups in epoxy resins, mainly in epoxy resins made of bisphenol A (BPA) and epichlorohydrin (ECH; Scheme 1). The so-called epoxy acrylic resins or VERs are used as solutions in styrene. The curing of VERs is carried out in the same way as that of unsaturated polyester resins (UPRs), that is, by the radical copolymerization of the unsaturated methacrylate units with styrene. VERs differ from typical polyesters in having only terminal unsaturation, pendant hydroxyl groups, and no carboxyl or hydroxyl end groups, so they exhibit after curing high chemical resistance, particularly alkali resistance.^{1,2} VERs owe their high mechanical strength to the terminal position of polymerizable double bonds. Generally, almost all properties of VERs (and cost) are intermediate between those of polyester resins and epoxy resins.

A similar structure was achieved when alkyl hydrogen maleates were added to terminal epoxy groups in low-molecular-weight BPA/ECH epoxy resins³ (Scheme 2). The alkyl group (e.g., cyclohexyl or benzyl) influenced the properties of the cured resins.^{4,5}

Our idea is that dihydrodicyclopentadienyl hydrogen maleate can be reacted with the terminal epoxy groups in the BPA/ECH epoxy resin to form an un-

saturated ester resin (UER; Scheme 3). Chromium(II) acetate has been used, having been proven to be the most effective carboxyl/epoxy catalyst.^{5,6} Because the maleate (cis) ester group exhibits lower reactivity in copolymerization with styrene than the fumarate (trans) ester group, the maleate has been isomerized to fumarate in the presence of a morpholine catalyst.⁷

We assumed that the advantages of dicyclopentadiene (DCPD)-modified UERs would be connected to the effect of the DCPD units on the mechanical and thermal properties as well as the chemical resistance. We expected that the compatibility with styrene would be increased and the oxygen inhibition would be counteracted because of the allylic group in the cyclopentene ring of DCPD. To differentiate UPRs and VERs from the novel resins, they are called UERs.

In a former publication,⁸ the urethanization of VERs through the reaction of toluene diisocyanate with hydroxyl groups in VERs is described. The same approach applied to UERs is the subject of this article.

The effect of a partial replacement of styrene in UERs with ethylene glycol dimethacrylate (EGDMA) or triethylene glycol dimethacrylate (TEGDMA) on the properties of the cured resins was also investigated.

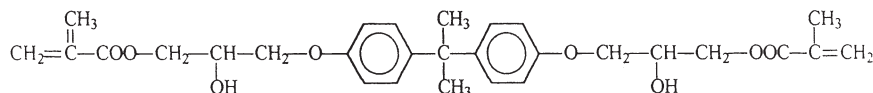
EXPERIMENTAL

Reagents

We used the following: low-molecular-weight BPA/ECH epoxy resin Epidian 6 (Chemical Works Organika-Sarzyna, Nowa Sarzyna, Poland; epoxy number = 0.522 mol/100 g); maleic anhydride (MA; Nitrogen Works Kędzierzyn, Kędzierzyn-Koźle, Po-

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Scheme 1 VER.

land); DCPD (94%; Shell Chemical Co.); styrene (inhibited with 0.006% hydroquinone; Chemical Works Dwory, Oświęcim, Poland); isophorone diisocyanate (IPDI; Vestanat, Hüls, Germany); polymeric 4,4'-methylenebis(phenylisocyanate) (MDI) (PMDI; Voranate M220, Dow Chemical Co., Midland, MI); butanol, allyl alcohol, benzyl alcohol, and morpholine (Aldrich, Milwaukee, WI); chromium(III) acetate and benzyl dimethyl amine (Aldrich); and EGDMA (Bisomer) and TEGMA (Bisomer, International Specialty Chemicals, Southampton, England). All syntheses were carried out under an inert gas (CO_2) atmosphere.

Synthesis of UERs

A mixture of MA (407.6 g, 4.16 mol) and water (75.0 g, 4.16 mol) was heated at 80°C , and then DCPD (392.0 g, 2.97 mol) was added dropwise at such a rate that the temperature of the reaction mixture was below 150°C . Then, the reaction mixture was heated at 145°C until the formation of dihydrodicyclopentadienyl hydrogen maleate was complete (3 h). The epoxy resin (891.1 g, 5.12 mol of epoxy groups) with chromium(III) acetate (0.56 g) was then added to the reaction mixture at 145°C . After the addition of the epoxy resin was complete, morpholine (2.0 g) was added. The reaction mixture was heated for an additional 4 h at 145°C . The reaction of the epoxy resin with the hydrogen maleate was considered complete when the acid number was less than 30 mg of KOH/g. The unreacted COOH groups could be bonded with a stoichiometric amount of Cardura E10 (Shell Chemical Co., Belgium) (ca. 10 g; Fig. 1).

Urethanization of UERs

The urethanization consisted of the reaction of isocyanates with OH groups in UERs. It was performed in a

solution in styrene at the ambient temperature. The stoichiometric OH/NCO ratio was used. The number of OH groups in the UER was calculated under the assumption that it corresponded to the number of epoxide groups reacted with the hydrogen maleate.

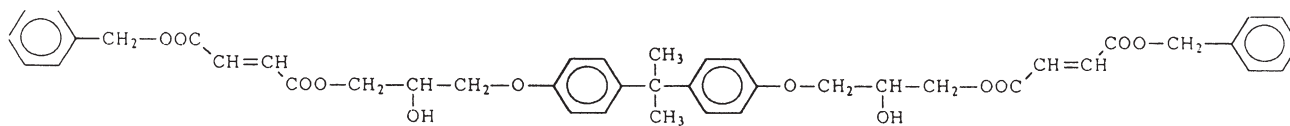
The amount of isocyanate was 6.25 or 12.5% of the stoichiometric amount (mol of NCO/100 mol of OH groups in the UER). At a higher isocyanate content, a high viscosity of the resin was obtained, or premature gelation occurred.

The urethanization was carried out with 6.25 or 12.5 mol of IPDI or PMDI/100 mol of OH groups in the UER, which corresponded to 8.74 or 17.48 g of IPDI or 10.85 or 21.69 g of PMDI/kg of UER. The amount of 12.5 mol of IPDI was too high: the increase in the viscosity was so high that the cast profiles could not be poured.

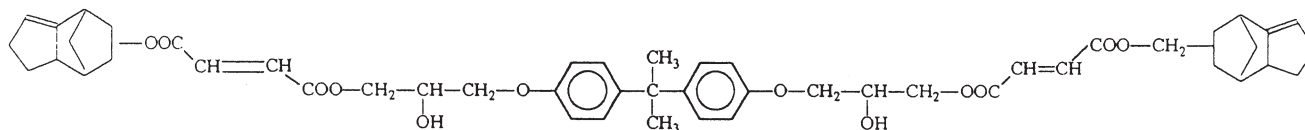
The urethanization was followed on the basis of the viscosity measurements. Complete urethanization at the ambient temperature was reached after 3–4 days.

Curing of UERs

UERs were cured by radical copolymerization with styrene: 50 wt % styrene was applied to the tested UERs. The cast profiles were used for the determination of the mechanical and thermal properties [heat deflection temperature (HDT)]. Apart from the HDT, the effect of the structural modifications of UERs on the chemical resistance was investigated. The chemical resistance of cured UPR was evaluated on the basis of the weight increase after 14 h of immersion in aqueous solutions of 10% KOH, 5% HNO_3 , and 25% H_2SO_4 at 65°C (Table I).



Scheme 2 Epoxy fumarate resin.



Scheme 3 UER.

TABLE I
Chemical Resistance of Cured UERs

	Crosslinking monomer	
	50% styrene	45% styrene and 5% EGDMA
Weight increase after 7 days of immersion at 65°C (%)		
In 10% KOH	0.16	0.14
In 5% HNO ₃	0.30	0.26
In 25% H ₂ SO ₄	0.18	0.15
Weight increase after 1 month of immersion at 65°C (%)		
In 10% KOH	0.35	0.32
In 5% HNO ₃	0.52	0.48
In 25% H ₂ SO ₄	0.32	0.32

RESULTS AND DISCUSSION

UERs tend to gel over the course of the synthesis. This gelation can be avoided if an alcohol is used to partially replace DCPD. Thus, terminal alkyl groups (methyl, butyl, benzyl, and allyl) were built in (Table II). Those groups adversely affected the HDT value: the highest HDT values were reached when no additional substituents were incorporated.

Styrene exhibits limited miscibility with UERs. To avoid phase separation and to enhance the compati-

bility of the monomer-free resin with styrene, EGDMA and TEGDMA were used. The effects of the dimethacrylates on selected properties of UERs are presented in Table III. A partial replacement of styrene with EGDMA resulted in a decrease in the gain in weight after the immersion. Both methacrylates had a significant effect on HDT, particularly EGDMA. The characteristics of the cured resin with 45 wt % styrene and 5 wt % EGDMA were improved in comparison with those of UER containing 50 wt % styrene (Table IV).

The urethanization of UERs affected the HDT and alkali resistance of the cured UERs (Table V). Moreover, the effect of the partial replacement of DCPD with methanol or benzyl alcohol in the urethanized UERs was investigated. The urethanization resulted in an increase in the HDT values and in an enhancement of the alkali resistance of cured UERs, consisting of a decrease in the weight rise after long-term immersion in 10% aqueous KOH at 65°C. The highest HDT value of UERs urethanized with IPDI was as much as 64–68°C, and it was accompanied by alkali resistance of 0.6% in comparison with 6.7% absorption in 10% KOH in the case of nonurethanized cast profiles. The alkali resistance data for the UERs with DCPD partially replaced by benzyl groups amounted to 3.6% (uretha-

TABLE II
Effects of the Terminal Groups in UERs on Some Properties of UERs

	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8
MA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
H ₂ O	1.05	1.0	0.875	0.92	0.92	0.92	0.875	0.92
DCPD	1.05	1.0	0.92	1.05	0.92	1.05	0.92	1.05
Methanol	—	—	0.125	0.125	—	—	—	—
1-Butanol	—	—	—	—	0.125	—	—	—
Benzyl alcohol	—	—	—	—	—	0.125	0.125	—
Allyl alcohol	—	—	—	—	—	—	—	0.125
Epoxy resin	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
HDT (°C)	60	64	59	53	52	46	58	55
Alkali resistance	10.0	6.7	5.7	10.7	8.7	4.7	11.6	9.6

TABLE III
Effects of Glycol Dimethacrylates on Selected Properties of UERs

	D-0	D-1	D-2	D-3	D-4	D-5	D-6
Styrene	45.0	45.83	41.67	33.33	45.83	41.67	33.33
EGDMA	—	4.17	8.33	16.67	—	—	—
TEGDMA	—	—	—	—	4.17	8.33	16.67
Monomers (styrene + EGDMA/TEGDMA)	45.0	50.0	50.0	50.0	50.0	50.0	50.0
Viscosity at 23°C (mPa s)	1656	390	406	470	415	480	545
Exotherm temperature peak (°C) ^a	44	39	43	84	37	43	56
Time to reach the exotherm peak (min) ^a	68	132	142	112	130	133	128
HDT (°C)	64	71	72	73	66	68	67
Alkali resistance ^b	6.7	1.8	1.6	1.5	—	—	—

^a Butanone peroxide (50%; 2 phr) and cobalt naphthenate solution (1% Co; 0.4 phr).

^b Weight increase after 14 days (%) in 10% aqueous KOH at 65°C.

TABLE IV
Mechanical and Thermal Properties of Cured UERs

	UER, 50% styrene, nonurethanized	UER, 45% styrene, 5% EGDMA, nonurethanized	UER, urethanized with IPDI
Static flexural strength (MPa)	84	85	87
Static flexural deflection (mm)	4.6	4.8	4.7
Flexural modulus (MPa)	3370	3440	3550
Static compression strength (MPa)	109	106	121
Ball indentation hardness (MPa)	153	159	153
Impact strength (kJ/m ²)	1.3	1.8	—
Elongation at break (%)	3.8	4.2	—
Heat deformation temperature (Martens; °C)	60	57	—
HDT (°C)	68	62	61
Glass-transition temperature (°C)	83	87	—

TABLE V
Effect of Urethanization with Diisocyanates (DICs) on Some Properties of UERs

No.	U-01	U-11	U-21	U-31	U-41	U-02	U-12	U-22	U-32	U-42	U-03	U-13	U-23	U-33	U-43	U-04	U-14	U-24	U-34	U-44	
MA			1.0					1.0					1.0						1.0		
H ₂ O			1.0					1.5					0.875						0.875		
DICPD			1.0					1.5					0.92						0.92		
Methanol			—					—					0.125						—		
Benzyl alcohol			—					—					—						0.125		
Epoxy resin			0.5					0.5					0.5						0.5		
No DIC	+					+					+					+					
PMDI																					
6.25		+						+				+						+			
12.5			+						+				+							+	
IPDI																					
6.25					+					+					+						+
12.5						+					+					+					+
HDT (°C)	64	67	—	68	68	60	64	64	63	64	59	63	—	62	64	58	62	—	60	63	
Alkali resistance ^a	6.7	3.3	—	1.4	0.6	10.0	5.1	5.1	6.2	4.2	5.7	3.7	—	5.1	5.2	11.6	5.0	—	6.2	3.6	

^a Weight increase after 14 days (%) in 10% aqueous KOH at 65°C.

TABLE VI
Comparison of the Syntheses and Properties of UERs with Benzyl Dimethyl Amine (BDMA) and Chromium (III) Acetate as the Catalysts

Properties	Catalyst	
	BDMA (0.07 wt %)	Chromium(III) acetate (0.008 wt %)
Synthesis		
Maleic acid DICPD addition product (acid value)	218.5	218.5
Addition of the epoxy resin (min)	42	45
Hydroxyl value after the completion of the addition of the epoxy resin	83.3	33.6
Hydroxyl value over the course of heating at 130°C		
After 0.5 h	60.4	8.4
After 1 h	46.9	4.8
After 1.5 h	39.9	End of the reaction
After 2 h	34.3	
After 2.5 h	31.9	
After 3 h	29.8	
Product		
Softening point of the UER (°C)	78	74
Viscosity of the UER at 23°C (MPa s) ^a	302	183
HDT (°C)	66	67

^a 45.83% styrene + 4.17% TEGDMA in the UER.

nized) in comparison with 11.6% (nonurethanized) absorption in 10% KOH.

CONCLUSIONS

UERS, similar to VERs and epoxy fumarate resins, were synthesized by the addition of dihydrodicyclopentadienyl hydrogen maleate followed by the cis-trans isomerization of the double bonds and were cured by radical copolymerization with styrene. The effect of the structure modification on HDT was investigated. A partial replacement of styrene with EGDMA or TEGDMA and the urethanization of OH groups resulted in an increase in HDT. A considerable decrease in the weight gain after immersion in aqueous alkali at 65°C was found for the UERS with EGDMA. Urethanization enhanced the alkali resistance to some extent, too. The urethanization of UPR with IPDI had a positive effect on some mechanical

strength properties. Moreover, the increase in HDT was accompanied by an improvement of the alkali resistance.

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