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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Synthesis and Curing of Epoxy–Anhydride Polymers Modified with an Oxirane of the Tetrahydroquinoline Series

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Abstract—Epoxy–anhydride polymers were prepared from diphenylolpropane diglycidyl ether and isomethyltetrahydrophthalic anhydride in the presence of a chemical modifier, oxirane of the tetrahydroquinoline series. The kinetics of the reaction of the modifier with the anhydride and the curing kinetics of the polymeric compound containing the modifier were studied. The thermal properties and water absorption of the polymers after their curing and structure formation were determined.

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Thanks to a favorable combination of physicomechanical, adhesion, and insulation properties, polymeric materials based on epoxy binders are widely used in spacecraft engineering, in aircraft, machine, and ship building, in radio electronics, in building, and in homes [1]. One of the drawbacks of many epoxy materials is low water resistance. They absorb up to 8–10% water, which impairs their heat resistance [2, 3].

One of possible ways to enhance the water resistance of polymers is introduction into their structure of hydrophobic chemical modifiers that do not cause phase segregation of the system in the course of the synthesis, do not give rise to thermodynamic and aggregative instability of the system [4, 5], and do not deteriorate the physicomechanical and thermal properties of the material under the action of elevated temperatures and strains. It was shown [5] that the water resistance of epoxy–anhydride polymers is enhanced by their modification with polyfluoroalkyl glycidyl ethers in the course of curing.

In this study we prepared epoxy–anhydride polymers modified with an oxirane of the tetrahydroquinoline series, containing fluorine atoms in the molecule, and examined the properties of the products.

EXPERIMENTAL

We used vinylimidazole produced by Alfa Aesar (Lancaster). The melting point of the oxirane (OTQ) was determined with a PTP device. Thin-layer chromatography was performed with Sorbfil silica gel plates. The chromatograms were visualized under UV light. The IR spectrum was recorded with a Bruker IFS 66ps Fourier spectrometer (mull in mineral oil); the ¹H and ¹³C NMR spectra, with a Varian Mercury+300 spectrometer (300 and 75 MHz), solvent CDCl₃, internal references HMDS and residual solvent signal (CHCl₃, ¹³C NMR, δ = 77.0 ppm); and the mass spectrum, with an Agilent 6890N device equipped with an MSD 5975B mass detector. Elemental analysis was performed with a Leco CHNS 9321P device.

1,2-Epoxy-8-fluoro-4-phenyl-5-trifluoroacetyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinoline (OTQ, mixture of diastereomers) was synthesized by epoxidation of the corresponding olefin with *m*-chloroperoxybenzoic acid (MCPBA), following the procedure described in [6]:



To a solution of 0.5 g (1.30 mmol) 8-fluoro-4phenyl-5-trifluoroacetyl-3a,4,5,9b-tetrahydro-3Hcyclopenta[c]quinoline (synthesized by the method described in [7]) in 10 ml of dichloromethane, prepared at 0°C, we added dropwise with stirring a cooled solution of 0.95 g (5.5 mmol) of m-chloroperoxybenzoic acid in 10 ml of dichloromethane. The mixture was stirred for 1 h at 10°C and for 6 h at room temperature, until the starting compound fully disappeared (TLC monitoring). The reaction mixture was washed with a 10% Na₂SO₃ solution $(3 \times 20 \text{ ml})$ to decompose excess per acid) and then with a 5% Na₂CO₃ solution. The crude epoxide obtained after drying over sodium sulfate and distillation of the solvent was subjected to chromatography on a silica gel column (eluent hexane-ethyl acetate, 1 : 1), followed by recrystallization from ethanol. Yield 0.40 g (78%), colorless crystals, mp 152–154°C, $R_{\rm f}$ 0.61 (Sorbfil plates, hexane-ethyl acetate, 1 : 1). ¹H NMR spectra, δ, ppm (CDCl₃): 0.99 m (1H, H_{ax}C³), 1.63 m $(1H, H_{eq}C^3)$, 3.21 m $(1H, HC^{3a})$, 3.40 m $(2H, HC^1)$ and HC²), 3.99 d (1H, HC⁴, J = 2.4 Hz), 5.95 d (1H, HC⁹b, J = 10.8 Hz), 6.79 m (2H, H_{arom}), 7.04 m (1H, H_{arom}), 7.14–7.30 m (5H, $H_{arom}).$ ^{13}C NMR spectrum, $\delta_C,$ ppm (CDCl₃): 29.83, 38.71, 56.44, 57.08, 57.62, 113.35, 113.67, 114.20, 11450, 118.32, 127.59, 127.80, 128.45, 131.71, 135.48, 137.92, 155.82, 156.31, 159.84, 163.14. Mass spectrum: m/z 377 (M⁺). Found, %: C 63.65, H

4.01, N 3.71. $C_{20}H_{15}NO_2F_4$. Calculated, %: C 63.33, H 3.09, N 3.72.

As a system for modification, we chose an epoxy binder based on diphenylolpropane diglycidyl ether (ED-20) and a curing agent, isomethyltetrahydrophthalic anhydride (IMTHPA), in combination with the reaction catalyst, 2,4,6-tris(dimethylaminomethyl)phenol. The kinetics of the reaction of IMTHPA with the modifier was studied by DSC with a DSC 822^e calorimeter (Mettler Toledo, Switzerland). The reaction was performed in the dynamic mode in the temperature interval 20–300°C at a heating rate of 5 deg min⁻¹. In the thermograms we recorded the reaction onset temperature T_0 and the reaction maximum temperature T_{max} . From the DSC results, we calculated the thermal effect of the reaction. The results of studying the reaction are given in Table 1. For comparison, we present the kinetic parameters for the reaction of IMTHPA with phenyl glycidyl ether (PGE). The modifier of the quinoline series reacts with IMTHPA in the temperature interval 122-166°C with a small thermal effect (42 J g^{-1}) to form esters. The compound of simpler structure, PGE, reacts with IMTHPA only in the presence of an active catalyst, vinylimidazole (1 wt %).

Curing of the epoxy–anhydride compound in the presence of 10 wt % modifier in the temperature interval found for the reaction of IMTHPA with the modifier yields a network polymer. The structure of the node of its chemical network is shown in the scheme.

The physicomechanical characteristics of the polymer specimens prepared in the form of blades (nominal tensile strength σ , relative critical deformation ϵ) were determined at $25 \pm 2^{\circ}$ C and extension velocity of 0.056 s⁻¹ with an Instron 3565 tensile-testing machine (the United Kingdom) in accordance with GOST (State



Scheme.

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Modifier	Catalyst	T _o	T _{max}		
		°C		Q, J g '	
OTQ	No catalyst	122	166	42	
PGE	Vinylimidazole	100	150	410	

Table 1. Kinetic parameters of the reaction of IMTHPA with the modifiers

 Table 2. Physicomechanical properties and moisture absorption of cured epoxy polymers modified with oxirane of the tetrahydroquinoline series

Modifier	σ, MPa	ε, %	T _g , ℃	Moisture absorption, %, in 24 h
OTQ	67	12	104	0.138
PGE	59	10	86	0.456
No modifier	53	9	99	0.260
DEG-1	63	11	84	0.352

 Table 3. Results of thermal gravimetric analysis of the polymers

Modifier	Temp indicate	Residue at 650°C,		
	5	10	50	wt %
OTQ	310	340	400	19
No modifier	307	322	370	14

Standard) 270–75. The glass transition point $T_{\rm g}$ was determined by thermomechanical analysis with a UIP-70 device. Analysis was performed in the temperature interval 20–250°C at a scanning rate of 0.08 deg s⁻¹. The water absorption was determined from the specimen weight gain in cold water. The results are given in Table 2.

We found that OTQ positively affects the formation of the polymeric matrix of the binder. The cured polymers exhibit high physicomechanical characteristics, not inferior to those of the polymers prepared without modifiers and in the presence of PGE and DEG-1 (aliphatic epoxy resin). At the same time, introduction of the oxirane of the tetrahydroquinoline series into the compound made it more hydrophobic and, correspondingly, reduced the moisture absorption by the polymers by a factor of approximately 2.

It seemed necessary to evaluate the heat resistance of the polymers whose moisture content was reduced by introducing a fluorinated modifier. The thermal oxidative stability of the polymers was studied with a Q-1500D derivatograph (MOM, Hungary). Programmed heating of the samples (100 mg) was performed at a rate of 20 deg min⁻¹ to 1000°C in air. As reference we used calcined aluminum oxide. The sensitivity was as follows: DTA 500 μ V and DTG 2.5 mV. The results of thermal gravimetric analysis of the polymers, characterizing the thermal oxidative degradation, are given in Table 3.

Our results show that the heat resistance of the polymers modified with fluorinated OTQ is high, with 50% weight loss observed at 400°C and 75–80% weight loss, at 650°C.

It should be noted that, with respect to the heat resistance in the temperature range 300–400°C, the modified polymers are similar to the polymers without modifiers. At the temperature increased to 650°C, the polymer with the modifier is more heat-resistant. This is apparently due to the fact that the polymer modified with OTQ has higher cross-linking density and, correspondingly, higher tensile strength (Table 2) and higher heat resistance.

CONCLUSIONS

(1) An oxirane of the tetrahydroquinoline series was synthesized. Its structure was confirmed by the ¹H and ¹³C NMR data.

(2) The temperature interval and thermal effects of the reactions of oxiranes with isomethyltetrahydrophthalic anhydride were determined.

(3) Introduction of the oxirane into the epoxy compounds as structural modifier enhances the moisture resistance by a factor of approximately 2 and allows preparation of the polymers with high levels of physicomechanical properties and heat resistance.

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