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## Preparation and Properties of Frost-Resistant Room-Temperature-Curable Compounds Based on Oligoethertetraurethane Diepoxides of Various Chemical Structures

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**Abstract**—New polytetraurethane diepoxides were prepared from oligo(tetramethylene oxide)diols of various molecular masses, various diisocyanates, and glycidol. High-strength frost-resistant cold-curable elastic compounds were prepared on their basis. The use of aminoethylpiperazine as a curing agent allows the cured materials to be prepared in 24 h at room temperature. The elastomers based on isophorone diisocyanate exhibit higher mechanical and thermal characteristics than those based on 2,4-toluene diisocyanate, which is due to higher degree of microphase segregation of soft and hard blocks of elastomers based in isophorone diisocyanate.

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Owing to excellent adhesion to various materials and to good dielectric and physicochemical properties, epoxy–urethane oligomers (EUOs) in which the terminal epoxy groups are combined with urethane groups in the backbone are used as a base of various-purpose casting compounds and adhesives resistant to moisture and aggressive media [1–5].

However, despite satisfactory characteristics under common operation conditions, such materials do not meet requirements to stability of the characteristics under extreme conditions. For example, operation in the Arctic climate poses stringent requirements upon lower temperature limit of operation. The minimal temperature in the coldest month, January, can reach  $-60^{\circ}\text{C}$ , and in some cases even  $-70^{\circ}\text{C}$ .

The most frost-resistant polymer materials are compounds based on certain polytetraurethane epoxides (PUEs) [6] with the glass transition point of down to  $-76^{\circ}\text{C}$ . These are block copolymers consisting of alternating hard (HBs) and soft (SBs) blocks [7, 8]. The

most known polytetraurethane epoxides are synthesized from diene oligomers [9]. The difference in the polarity of hard and soft segments (blocks) in such polymers usually leads to their microphase segregation with the formation of hard domains acting as nanodispersed reinforcing filler and as cross-linking points of a specific physical network, which is important for ensuring high strength of the materials.

Amines, dicarboxylic acid anhydrides, and compounds with carboxy groups are used as PUE curing agents [7]. Curing is usually performed at temperatures no lower than  $+80^{\circ}\text{C}$ . A significant drawback of the known individually used materials is low strength (no higher than 5 MPa). The use of PUE blends with dianic epoxy resins often enhances the strength of the composites, but gives rise to problems with maintaining the other technical characteristics on the required level, especially at low temperatures [10]. Therefore, studies aimed at improving the physicochemical and technological properties of PUE-based materials are topical.

**Table 1.** PP composition

PP	Oligoetherdiol	Diisocyanate	Content of free isocyanate groups, %	
			theoretical	experimental
PP-1	Polyfurite (MM~1000)	TDI	6.29	6.40
PP-2	Polyfurite (MM~1400)	TDI	4.78	4.82
PP-3	Polyfurite (MM~2000)	TDI	3.48	3.25
PP-4	Polyfurite (MM~1000)	IPDI	5.86	5.89
PP-5	Polyfurite (MM~1400)	IPDI	4.52	4.55
PP-6	Polyfurite (MM~2000)	IPDI	3.34	3.15

Here we report the results of studying PUEs that are curable at room temperature and can operate in a wide temperature interval, down to  $-70^{\circ}\text{C}$ .

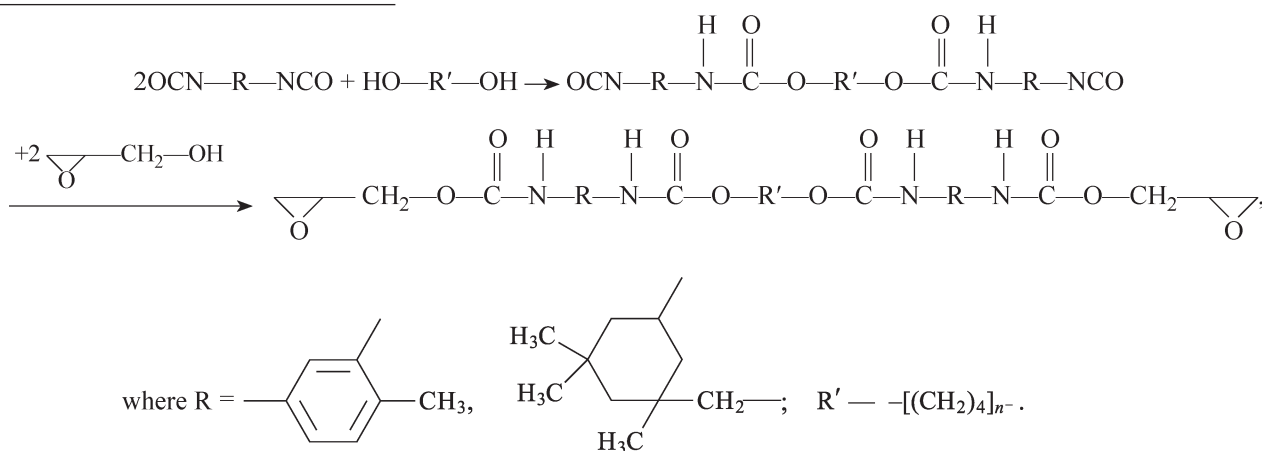
### EXPERIMENTAL

Experiments were performed with a series of tetraurethane diepoxide oligomers synthesized from urethane-containing prepolymers (PPs) with terminal functional isocyanate groups [oligo(tetramethylene oxide) diisocyanates] and glycidol. The PPs were prepared from oligo(tetramethylene oxide)diol (polyfurite) samples with molecular masses off 1000, 1400, and 2000 and 2,4-toluene diisocyanate (TDI) or isophorone diisocyanate (isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate).

The ratio of the NCO and OH groups in the PP synthesis was 2.03 : 1. Polyfurite was preliminarily dried with stirring at  $80^{\circ}\text{C}/1-2$  kPa. The prepolymer was prepared with a conventionally gastight laboratory mixer equipped with a heating jacket. After loading the components, the mixture was kept at  $60^{\circ}\text{C}$  for 1 h, heated to  $80^{\circ}\text{C}$ , and kept at this temperature with stirring for 6 h. In the case of using isophorone diisocyanate (IPDI), a catalyst, dibutyltin dilaurate, was added in an amount of 0.02 wt % relative to the reaction mixture. The reaction was performed until the content of isocyanate groups became constant (monitoring by back-titration according to ASTM D2572-080).

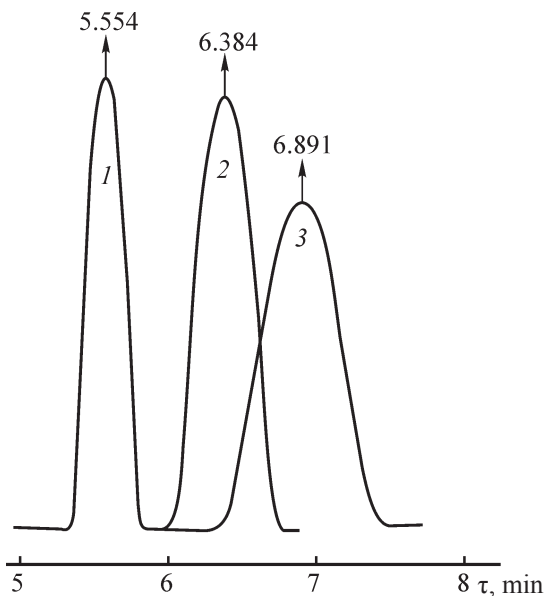
The properties of the synthesized PPs are given in Table 1.

The scheme of the EUO synthesis is shown below:

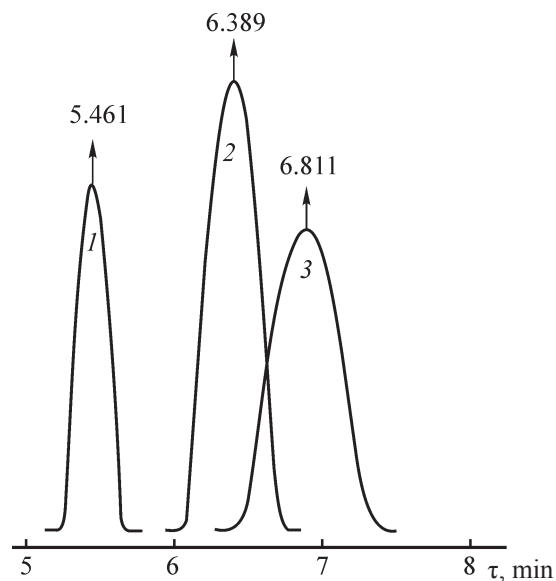


The molecular mass of the oligomers obtained was determined by gel permeation chromatography using an ULTIMATE 3000 chromatograph (Dionix Thermo Scientific) equipped with a RefractoMax 521 refractometric detector according to [11].

The synthesized oligomers were used for preparing cured samples to study the physicomechanical and other functional properties. A liquid cycloaliphatic amine, aminoethylpiperazine (AEP), was used as a curing agent. It contains simultaneously primary, secondary,



**Fig. 1.** Chromatograms of TDI-based EUO samples. ( $\tau$ ) Retention time; the same for Fig. 2. (1) EUO-3, (2) EUO-2, and (3) EUO-1; the same for Fig. 2.



**Fig. 2.** Chromatograms of IPDI-based EUO samples.

and tertiary nitrogen atoms. The EUO : amine molar ratio was 1 : 0.87.

EUO was stirred with AEP for 5 min in a vacuum (1–2 kPa) at  $25 \pm 1^\circ\text{C}$ . The resulting reaction mixture was cured for 24 h at  $25 \pm 1^\circ\text{C}$ . To determine the curing time, the conversion of epoxy groups was monitored in preliminary experiments by Fourier IR spectroscopy (disappearance of the absorption band at  $910\text{ cm}^{-1}$  [12, 13]). The softening point of the hard phase,  $T_n$ , of the segmented polyurethane was determined by thermomechanical analysis with a TMA/SDTA 841<sup>e</sup> device (Mettler Toledo) at a scanning rate of  $0.05\text{ deg s}^{-1}$  under a load of 0.015 MPa. The glass transition point  $T_g^s$  was determined by DSC with a DSC 822<sup>e</sup> differential scanning calorimeter (Mettler Toledo) at a scanning rate of  $0.08\text{ deg s}^{-1}$ .

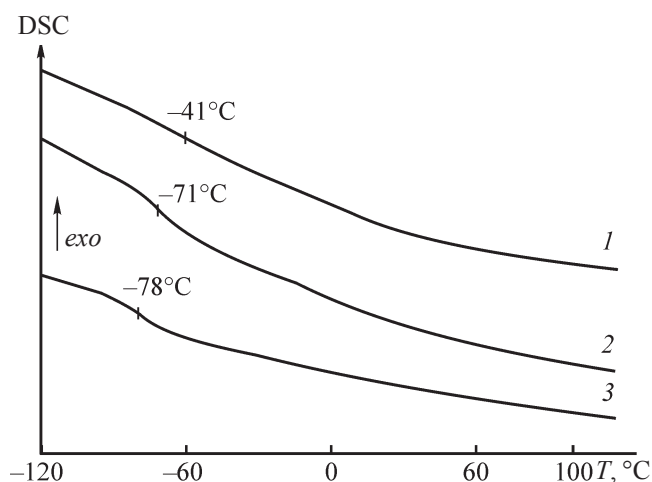
The IR spectra of the initial epoxy-containing oligomers were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  with an IFS-66/S Fourier IR spectrometer (Bruker) at a resolution of  $1\text{ cm}^{-1}$ . For the convenience of comparison, the spectra were normalized with respect to the band at  $2860\text{ cm}^{-1}$ , corresponding to symmetrical stretching vibrations of  $\text{CH}_2$  groups [13]. The IR spectra of the surface of the cured samples in the region of carbonyl stretching vibrations (total wavenumber interval  $\nu = 4000\text{--}400\text{ cm}^{-1}$ ) were recorded using an

A 225/Q ATR module (Platinum ATR Diamonds F) equipped with a diamond single reflection crystal.

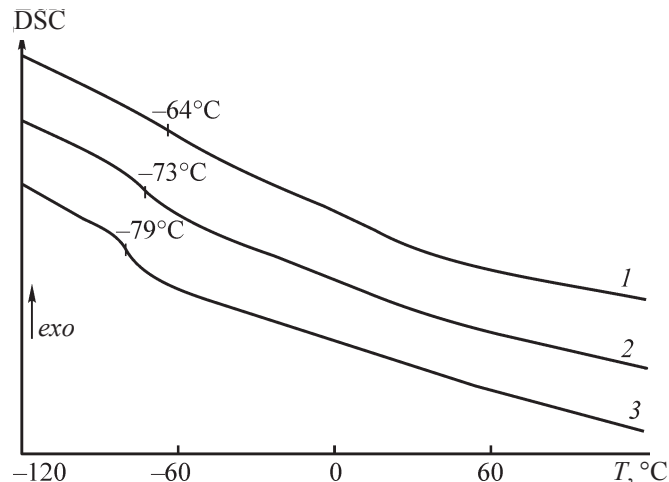
The network density in the cured samples was determined by the Cluff–Glading method [14]. Mechanical tests of the samples of the materials obtained were performed with an INSTRON 3365 universal testing machine at the strain rate  $\nu = 0.28\text{ s}^{-1}$  and  $25 \pm 1^\circ\text{C}$  in accordance with ISO 37–2013. We determined the nominal strength  $\sigma_k$  (maximal stress per initial cross section of the specimen), relative critical strain  $\varepsilon_k$  (%), conditional (engineer) elastic modulus  $E_{100}$  (stress at relative

**Table 2.** Composition and properties of EUOs

EUO	PP	Molecular mass	
		theoretical	experimental
EUO-1	PP-1	1479	1564
EUO-2	PP-2	1903	2033
EUO-3	PP-3	2556	2800
EUO-4	PP-4	1575	1638
EUO-5	PP-5	1999	2020
EUO-6	PP-6	2652	2886



**Fig. 3.** DSC thermograms of TDI-based PUE samples. (*T*) Temperature; the same for Fig. 4. (1) PUE-1, (2) PUE-2, and (3) PUE-3.



**Fig. 4.** DSC thermograms of IDPI-based PUE samples. (1) PUE-4, (2) PUE-5, and (3) PUE-6.

strain  $\varepsilon = 100\%$ ), and breaking stress (true strength)  $f_r = \sigma_k \lambda_k$ , where  $\lambda_k = (\varepsilon_k + 100)/100$ .

## RESULTS AND DISCUSSION

The composition and properties of EUOs are given in Table 2. The theoretical values of the molecular masses of the oligomers were estimated from those of the prepolymers taking into account the analytically determined content of free isocyanate groups and the

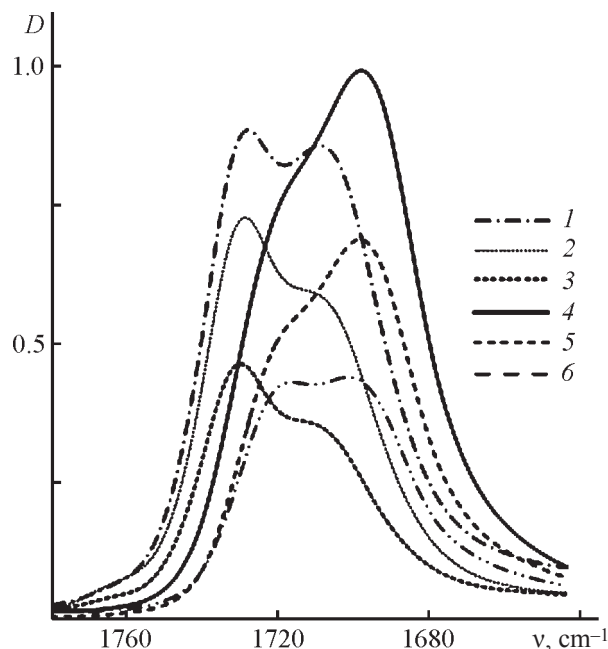
extension of the molecular chain of the oligomer by the glycidol moiety in the course of the synthesis.

In determination of the molecular mass of EUO samples based on TDI, the retention time was from 5.4 to 6.9 min (Figs. 1, 2). The accurate values are shown in the figures. The obtained values of the average EUO molecular mass agree with the theoretical values (Table 2). Small width of the peaks corresponds to narrow molecular-mass distribution of the oligomers [11].

**Table 3.** Physicomechanical characteristics of PUEs

PUE	EUO	<i>T</i> , °C <sup>a</sup>	$\sigma_k$ , MPa	$\varepsilon_k$ , %	$E_{100}$ , MPa	$f_r$ , MPa	$N_{dx}$ , kmol m <sup>-3</sup>	Shore hardness <i>A</i> , units	$T_b$ , °C
PUE-1	EUO-1	25	5.7	385	2.0	21.9	0.0784	74	137
		-70	68.6	2	—	1.4			
PUE-2	EUO-2	25	8.9	491	1.8	43.7	0.0683	70	143
		-70	48.5	7	—	3.4			
PUE-3	EUO-3	25	7.9	577	1.6	45.6	0.0640	65	157
		-70	71.7	8	—	5.7			
PUE-4	EUO-4	25	16.1	416	3.9	67.0	0.301	86	208
		-70	51.5	2	—	1.0			
PUE-5	EUO-5	25	15.1	475	2.8	71.7	0.196	80	217
		-70	54.5	11	—	6.0			
PUE-6	EUO-6	25	8.1	408	2.3	31.4	0.170	75	199
		-70	40.6	264	19.2	107.2			

<sup>a</sup> (*T*) Testing temperature.



**Fig. 5.** IR spectra of samples (1) PUE-1, (2) PUE-2, (3) PUE-3, (4) PUE-4, (5) PUE-5, and (6) PUE-6. (*D*) Optical density and (*ν*) wavenumber.

The DSC curves of the elastomers show that the glass transition point of PUEs regularly decreases from  $-64$  to  $-79^{\circ}\text{C}$  with an increase in the polyurethane molecular mass. In contrast to the polyurethane and polyurethaneurea elastomers [15], crystallization of soft polyether blocks does not take place, which positively influences the performance of the materials at negative temperatures. It should be noted that the glass transition point of the IPDI-based elastomers is somewhat lower than that of the TDI-based elastomers (Figs. 3, 4).

Analysis of the FTIR spectra in the region of carbonyl stretching vibrations ( $\nu = 1600\text{--}1760\text{ cm}^{-1}$ ) revealed important features of structural organization of the substances (Fig. 5).

The assignment of the absorption bands was based on the results of spectroscopic studies of structurally related polymers with urethane groups [4, 16, 17].

Variation of the intensity of the absorption bands in the range  $1600\text{--}1760\text{ cm}^{-1}$  in the spectra of PUEs based on TDI and IPDI is shown in Fig. 5. For the PUE based on TDI, a peak appears at  $1702\text{ cm}^{-1}$ . It belongs to the absorption of the carbonyl group hydrogen-bonded with the N–H group of the urethane–hydroxyl hard block (HB–HB bond). Also, a peak corresponding to free carbonyl of the urethane group appears at  $1730\text{ cm}^{-1}$ . It

should be noted that the peak at  $1702\text{ cm}^{-1}$  considerably exceeds in the intensity the peak at  $1730\text{ cm}^{-1}$ , which shows that the degree of the microphase segregation in the polymer is low. With an increase in the molecular mass of the soft polyether segment, the intensity of the absorption band at  $1702\text{ cm}^{-1}$  decreases, and that of the band at  $1730\text{ cm}^{-1}$  regularly increases, which indicates that the degree of the microphase segregation decreases with a decrease in the molecular mass of the polyether [4].

Opposite pattern is observed for the PUEs based on IPDI (PUE-4, PUE-5, PUE-6). Two absorption bands are clearly manifested: the band at  $1695\text{ cm}^{-1}$ , corresponding to carbonyl hydrogen-bonded with the N–H group of the hard urethane–hydroxyl block (HB–HB bond), and the band at  $1722\text{ cm}^{-1}$ , corresponding to the absorption of free carbonyl [18]. The band at  $1695\text{ cm}^{-1}$  prevails over the band at  $1722\text{ cm}^{-1}$ . Hence, the IPDI-based PUE samples are characterized by higher degree of microphase segregation than those based on TDI.

This, higher degree of microphase segregation is reached when using IPDI, which ensures a decrease in the glass transition point of the cured elastomer (Figs. 3, 4) and an increase in the hardness and nominal modulus (Table 3). Both the nominal and true strengths of PUE-5 are approximately 70% higher than those of PUE-2 (Table 3). It should be noted that the IPDI-based PUEs exhibit higher strain characteristics at  $-70^{\circ}\text{C}$ .

The TMA data show that the softening point of the hard phase of the IPDI-based PUE is appreciably higher than  $T_n$  of the TDI-based PUE, which may be caused by the formation of the more defective structure of the hard phase in the latter case.

## CONCLUSIONS

The polytetraurethane epoxides prepared using different diisocyanates significantly differ in the properties. The less defective structure of the hard phase and increased level of microphase segregation ensure better physicomechanical and thermomechanical properties of the materials prepared using isophorone diisocyanate, including the properties at low temperatures. High performance at low temperatures is a necessary condition in the development of materials intended for use under the extreme conditions of Far North and Arctic.

## ACKNOWLEDGMENTS

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