Elastic compounds based on epoxy terminal oligomers synthesized on the basis of an oligoester

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Abstract. The physico-mechanical and structural characteristics of a series of elastomers based on epoxy terminal oligomers synthesized using a crystallizing oligoester were investigated. It was found that the use of isophorone diisocyanate allowed obtaining polymeric materials with a noticeable advantage both for the physical and mechanical characteristics, and for the temperature diapason of application as well. It was shown that the mentioned advantage of isophorone diisocyanate could be explained by the higher degree of microphase separation between soft and hard blocks in the polymeric matrix constructed using this component. New materials can be used as a base for compounds for various purposes.

1. Introduction

Urethane-containing polymeric materials (polyurethanes and polyurethane ureas) are used in various fields of industry and the construction industry [1-3]. The properties of such materials can be controlled within wide limits due to the use of oligomers of various chemical structure, diisocyanates, and low molecular mass chain extenders in the synthesis [1, 4]. The synthesis of polyurethanes and polyurethane ureas, as a rule, is carried out through the stage of obtaining oligodisocyanates-prepolymers obtained by the reaction between the starting macrodiols and diisocyanates. The second stage of the above mentioned synthesis is related with epoxidation to obtain epoxy terminal oligomers. The use of epoxy terminal oligomers allows to improve the adhesive characteristics of cured elastomers. Also, in contrast to oligodisocyanates, compositions based on epoxy terminal oligomers are insensitive to moisture, which is important for producing large-sized items. Compositions obtained on the basis of epoxy terminal oligomers are characterized by good dielectric properties and mechanical characteristics; they are used as adhesives and the basis of casting low-modulus compounds for various purposes. Elastomers based on epoxy terminal oligomers synthesized from polyethers (PEF-3A based on oligotetramethylene oxide diol, and PPG-3A based on oligopropylene oxide diol) were relatively widely studied [5-9]. At the same time, it is known that urethane-containing elastomers based on polyethers are characterized by the elevated abrasion resistance, which predetermines the prospects for their use in many technical applications.

The target of this work is investigation of the structure and properties of polyurethane elastomers based on epoxy terminal oligomers synthesized on the basis of OMA-1950 polyester.
2. Experimental part

2.1. Materials
Polyurethane elastomers were synthesized from polyester, diisocyanate and epoxy alcohol. OMA-1950 was used as a polyester, which is dual-functional and synthesized on the basis of 1,4-butanediol, ethylene glycol and adipic acid (1.85% of OH-groups), 2,4-toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), and 2,3-epoxy-1 propanol. The synthesis of epoxyurethane oligomers based on the above mentioned components was carried out in a two-stage method, according to the method described in [10]. The composition of the components of the synthesized oligodiisocyanates and epoxyterminal oligomers based on them are given in table 1. The synthesized oligomers were used to obtain cured samples of the RG-2020 series for the study of physical, mechanical and other functional properties.

Three liquid hardeners were used: 2 polyamide ones, PO-300 (amine number 290 mg KOH / g), L-20 (amine number 310 mg KOH / g) - the products of interaction of polymerized fatty acids from vegetable oils and polyamines, and also aliphatic amine hardener XT-488/4 (modified aliphatic amine with amine number 440 mg KOH /g). The samples were cured for 4 days at (90±1) °С. The curing time was previously established by monitoring the completeness of the conversion of epoxy groups by FTIR spectroscopy by the disappearance of the absorption band at 910 cm\(^{-1}\).

| Sample   | Diisocyanate | Hardener   |
|----------|--------------|------------|
| RG-2020 -1 | TDI          | L-20       |
| RG-2020 -2 | IPDI         | L-20       |
| RG-2020 -3 | TDI          | PO-300     |
| RG-2020 -4 | IPDI         | PO-300     |
| RG-2020 -5 | TDI          | XT-488/4   |
| RG-2020 -6 | IPDI         | XT-488/4   |

2.2. Methods
The glass transition temperature \(T_g\) was determined by the method of differential scanning calorimetry (DSC) on a DSC 822\(e\) calorimeter from METTLER TOLEDO at a scan rate of 0.08 deg/s. FTIR-spectra of the cured samples were recorded on a Bruker IFS-66 / S spectrometer at a resolution of 1 cm\(^{-1}\). For convenience of comparison, the spectral curves were normalized to the band at 2950 cm\(^{-1}\), characteristic of stretching vibrations of CH\(_2\) groups. Mechanical tests of samples of the obtained elastomers were carried out on a universal testing machine INSTRON 3365 at (25 ± 1) °C according to ISO 37-2013. A reliable measurement of the strain of the samples was provided with a video extensiometer. The strength \(\sigma_p\) (maximum stress calculated for the initial section of the sample) and the relative at break \(\varepsilon_p\) and the engineer modulus \(E_{100}\) (the stress calculated for the initial section of the sample at a 100% relative strain) were determined. The pull-off bonding strength \(\sigma_{pl}\) for the adhesive joints of the elastomer with steel (St3) was determined according to the Russian GOST 14760-69 on specimens with a polymer layer thickness of (2 ± 0.1) mm.

3. Discussion
Urethane-containing elastomers consist of alternating soft and hard blocks, the difference in polarity of which determines the phase organization with the formation of a nano-dispersed hard phase, which plays the role of a reinforcing filler. At the same time, a high degree of microphase separation leads to decrease in the glass transition temperature of cured composites by increasing the mobility of the soft phase.

The state of the phase organization of elastomers can be assessed by FTIR-spectroscopy. For elastomers synthesized on the basis of epoxy terminal oligomers, several reference bands were established: 1731-1735 cm\(^{-1}\), a band characterizing free carbonyl (absorption band of free carbonyl), 1645-1650 cm\(^{-1}\) – absorption bands of the bonded carbonyl for the urethane-containing hard segments,
bonded with the urethane group of the hard segments. One can judge the phase organization in the system using the difference in the intensities of these bands.

Figure 1 shows fragments of the FTIR-spectra of the synthesized elastomers. It can be seen that the samples synthesized on the basis of isophorone diisocyanate are characterized by a higher degree of microphase separation and, hence, a lower intensity of the absorption band which characterizes the free carbonyl. It should be noted that the FTIR-spectra of RG-2020-3 and RG-2020-5 samples in the 1800-1600 cm⁻¹ diapason are similar to ones for RG-2020-1. The ones of RG-2020-4, RG-2020-6 in the 1800-1600 cm⁻¹ are similar to the one for RG-2020-2. These factors should have a positive effect on the decrease in the glass transition temperature of elastomers synthesized on the basis of isophorone diisocyanate.

Figure 2 shows DSC-thermograms of the RG-2020 samples. Indeed, the glass transition temperature is in 1÷6°C lower for samples based on IPDI, than for analogs based on TDI (figure 2). It should be noted that the highest difference in glass transition temperature between samples synthesized on the basis of different diisocyanates is realized when using the amine hardener XT-488/4. Also, can see a melting peak at about 40 °C on the DSC-thermograms of samples RG-2020-3 and RG-2020-4. The peak area, and relatively the crystallinity degree, is higher for the sample synthesized on the basis of TDI, which is associated in our opinion with a lower degree of microphase separation in this elastomer.
Table 2. Physico-mechanical properties of the investigated samples.

| Sample     | σ_p, MPa | ε, %  | E_100, MPa | σ_pl, MPa |
|------------|---------|-------|------------|-----------|
| RG-2020 -1 | 5.88    | 202   | 4.66       | 5.7       |
| RG-2020 -2 | 4.82    | 151   | 4.49       | 3.1       |
| RG-2020 -3 | 10.64   | 212   | 7.38       | 9.6       |
| RG-2020 -4 | 7.22    | 231   | 3.65       | 7.1       |
| RG-2020 -5 | 2.67    | 142   | 2.01       | 2.7       |
| RG-2020 -6 | 8.66    | 261   | 2.92       | 8.5       |

Analysis of the physio-mechanical characteristics of synthesized elastomers (table 2, figure 3) shows that two samples have the highest strength properties: RG-2020-3 and RG-2020-6. The high properties of the first one are realized due to a high degree of crystallization, and the similar properties of the second one are realized due to a high degree of microphase separation between soft and hard blocks. It is worth noting that all synthesized compositions have good strain properties (the value of the relative at break is more than 150%).

Figure 3. Stress versus strain dependences for the RG-2020 samples.

4. Conclusions
A series of polyurethane elastomers was obtained on the base of epoxy terminal oligomers using OMA-1950 oligoester, two diisocyanates and three hardeners of amide and amine types. It was found that the use of isophorone diisocyanate allowed obtaining materials with a noticeable advantage in the physical and mechanical characteristics of elastomers, also the finite elastomers on the base of isophorone diisocyanate have the broader temperature diapason of application.

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