The effect of hard segments structure on the functional properties of polyurethane elastomers based on oligoesterurethane epoxides

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Abstract. A series of polyurethane elastomers based on polyester urethane epoxy oligomers and cycloaliphatic diamines was synthesized. The relationship of the physico-mechanical properties of these elastomers with the structure of their polymer chain was studied. It was established that various options for increasing the strength of the final elastomers can be implemented, depending on the type of initial oligoesters and diamines. They may be associated with an increase in the degree of microphase separation between hard and soft polymer segments, and with partial crystallization of soft segments as well.

1. Introduction
Polyurethanes based on epoxyurethane oligomers occupy special position among polyurethane elastomers. This fact can be explained by a high content of urethane groups, and by the presence of hydroxyl groups in the chain formed during the curing reactions as well. Compositions based on such materials due to their good strength and adhesive characteristics can be used as the basis for adhesives and casting compounds for various purposes [1-3]. The most widespread among epoxyurethane oligomers are oligomers based on oligoethers [1-8]. But data on similar materials synthesized based on oligoesters are extremely rare, although it is known that such products should be of great interest for the development of biocompatible materials [9]. The aim of this work is to study a series of polyurethane elastomers on the base of epoxyurethane oligomers based on various oligoesters.

2. Materials and methods
We used the following components for the synthesis of elastomers: 2,4-toluene diisocyanate (TDI), 2,3-epoxy-1 propanol (glycidol) and oligoesters PDA-800, OMA-1950 and OMA-2100. These oligoesters are based on 1,4-butandiol, ethylene glycol, adipic acid (OMA-2100); ethylene glycol, and adipic acid (OMA-1950); diethylene glycol, and adipic acid (PDA-800). A molecular weight of these oligomers was equal to 2000, 1838 and 800 respectively. The functionality of all these oligomers is strictly equal to 2, which is important for subsequent syntheses. The synthesis of epoxyurethane oligomers on the above mentioned oligoesters, TDI and glycidol was carried out according to the conditions described in [5].
The characteristics of the synthesized intermediate oligodiisocyanates and epoxyurethane oligomers based on them are given in Table 1. The synthesized oligomers were used to obtain cured samples of the EsEx series for the study of physico-mechanical and other functional properties. As a hardener, two cycloaliphatic amines, liquid at room temperature, were used: 3-aminomethyl-3,5,5-trimethylcyclohexylamine (IFDA) and aminoethylpiperazine (AED).

| Sample  | Used precursors | diamine | Content of free functional groups in oligomer, % | isocyanate (in oligo diisocyanates) | epoxy (in epoxyurethane oligomers) |
|---------|----------------|---------|-----------------------------------------------|-------------------------------------|-----------------------------------|
|         | PDA-800        | IFDA    |                                               | calculated | experimental | calculated | experimental |
| EsEx-1  | PDA-800        | IFDA    | 7.51                                          | 7.28 | 6.52 | 6.55 |
| EsEx-2  | PDA-800        | AED     | 7.51                                          | 7.28 | 6.52 | 6.55 |
| EsEx-3  | OMA-1950       | IFDA    | 3.95                                          | 3.62 | 3.82 | 3.42 |
| EsEx-4  | OMA-1950       | AED     | 3.95                                          | 3.62 | 3.82 | 3.42 |
| EsEx-5  | OMA-2100       | IFDA    | 3.70                                          | 4.06 | 3.88 | 3.68 |
| EsEx-6  | OMA-2100       | AED     | 3.70                                          | 4.06 | 3.88 | 3.68 |

Two model compounds TDGA-1 and TDGA-2 were additionally synthesized to improve analyzing FTIR- spectra of the obtained samples. They were prepared using TDI, glycidol, and two above mentioned diamines, in accordance with the known procedure [10]; the difference being that in the first stage the ratio of amine to isocyanate was taken 2 to 1, and in the second stage the synthesized compound reacted with a two-fold excess of glycidol.

The glass transition temperature was determined by differential scanning calorimetry (DSC) using Mettler Toledo DSC 822e calorimeter at a scan rate of 0.08 deg.s⁻¹. The FTIR-spectra of the cured samples were recorded on a Bruker IFS-66/S FTIR-Fourier spectrometer at a resolution of 1 cm⁻¹. The spectral curves were normalized using the band at 1600 cm⁻¹, which is characteristic of the C – C stretching vibrations of the aryl ring. 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.

3. Discussion
An important feature of the class of polyurethanes is the factor of microphase separation between hard and soft segments. A microdispersed hard phase formed during curing plays the role of a reinforcing filler of an elastic matrix, consisting mainly of soft segments. Polyurethanes with a high content of hard phase have not only the high strength properties and wear resistance, but also good deformation characteristics determined by the elastic matrix of soft segments [11]. Hard segments in urethane-containing polymers form due to the presence of characteristic fragments in the polymer chains introduced by diisocyanates and low molecular weight chain extenders. There are diols for polyurethanes and diamines for polyurethane ureas.

Terminal epoxy groups of epoxyurethane oligomers form specific hard urethane segments containing hydroxyl groups upon curing (scheme 1). The study of the features of these segments for polyurethanes based on the mentioned oligomers was limited by materials based on oligoethers [3-8].
Scheme 1. Structure of polyurethane based on TDI, glycidol, and diamine.

The development of new materials based on epoxyurethane oligomers is often associated with the need to ensure a wide temperature range of high elasticity, which is associated with the level of the glassing transition temperature of the elastic matrix. The second important task is to ensure maximum strength properties. The solution of these problems is made taking into account the analysis of the structure of the considered polymers.

Figure 1. DSC thermograms of elastomers samples for EsEx series: EsEx-1 (1), EsEx-2 (2), EsEx-3 (3), EsEx-4 (4), EsEx-1 (5), EsEx-1 (5), EsEx-6 (6).

An analysis of DSC thermograms of EsEx samples (figure 1) shows that their glassing transition temperature $T_g$ is practically independent of the type of the used curing agent, i.e. it does not depend on the type of the formed hard segments. This temperature is determined mainly by the type of the used oligoester. So, it is 0°C for EsEx-1 and EsEx-2 samples based on PDA-800, it is 26-27°C for EsEx-3 and EsEx-4 samples based on OMA-1950, and it is 38°C for EsEx-5 and EsEx-6 samples based on OMA-2100. It was shown earlier that polyurethane elastomers synthesized on the base of OMA-1950 oligoester were capable to partial crystallization, which could be a positive factor contributing to an increase in the strength of elastomers [12]. Crystallization was recognized for sample cured using aminoethylpiperazine (curve 6 in figure 1). But any crystallization of the soft phase was practically absent for samples cured by isophorone diamine. In our opinion, this is due to steric difficulties associated with a more cumbersome structure of hard segments formed from isophorone diamine. A more detailed analysis of the structure of the obtained samples can be given using the corresponding FTIR-spectra. The assignment of characteristic absorption bands was performed using the spectra of model compounds TDGA-1 and TDGA-2 synthesized without the use of oligoesters. The structure of these compounds consists almost exclusively of hard segments. The structural formulas of these segments HS-1 and HS-2 are given in schemes 2,3.
Scheme 2. Structure of HS-1 segments in TDGA-1 based on TDI, glycidol, and AED.

Figure 2 shows fragments of the FTIR- spectra of the synthesized model compounds. One can see two characteristic intense absorption bands in this figure that can be attributed to self-associates of urethane-containing hard segments: the band at 1646 cm$^{-1}$ assigned to HS-1 segments, and the one at 1712 cm$^{-1}$ assigned to HS-2 segments [13]. It should be noted an appearance of the absorption band at 1612 cm$^{-1}$ in the FTIR-spectrum of TDGA-2, which is attributed to vibrations of the benzene ring with some substituents. It is characteristic of urethane-containing elastomers synthesized with use of TDI [14].

Scheme 3. Structure of HS-2 segments in TDGA-2 based on TDI, glycidol, and IPDA.

Figure 2. Fragments of FTIR- spectra for TDGA-1 (1), and TDGA-2 (2).

Figure 3. Fragments of FTIR- spectra for elastomer samples with HS-2 segments: EsEx-1 (1), EsEx-3 (2), and EsEx-5 (3).
Generally, it is necessary to distinguish several characteristic absorption bands for polyurethanes based on oligoesters in the region of carbonyl stretching vibrations:

1) absorption band of free carbonyl (1731-1735 cm\(^{-1}\)); 2) absorption bands of the bonded carbonyl for the urethane-containing hard segments, bonded with the urethane group of the hard segments (self-associates of urethane-containing hard segments); these bands correspond to the same ones for model systems characterizing the presence of a separate phase of hard domains based on the HS-1 and HS-2 segments (1712 cm\(^{-1}\), 1646 cm\(^{-1}\)); 3) absorption band of carbonyl of the hard segment, hydrogen bonded to oxygen of the ester group, which corresponds to the hard urethane-containing segments dissolved in the elastic phase of the polymer (1708-1722 cm\(^{-1}\)).

An analysis of the FTIR spectra of elastomers containing HS-2 segments (figure 3) shows that all samples are characterized by the appearance of a rather intense absorption band of C=O at 1712 cm\(^{-1}\) in the region of stretching vibrations of the C=O group, which proves the formation of the separate phase based on urethane-containing hard segments.

![Figure 4](image)

**Figure 4.** Fragments of FTIR spectra for samples with HS-1 segments in a broad diapason (a), and in a narrowed one (b): EsEx-2 (1), EsEx-4 (2), and EsEx-6 (3).

Elastomers containing HS-1 hard segments also showed the band that was found in the spectrum of the model compound (at 1646 cm\(^{-1}\)), however, this band (with some shifting to 1644 cm\(^{-1}\)) was characteristic only for EsEx-2 samples, as well as EsEx-4. There is no such band in the spectrum of the EsEx-6 sample, which indicates that there are no a special phase of hard segments in this case.

![Figure 5](image)

**Figure 5.** Stress versus strain dependence for EsEx samples with HS-1 segments (a), and HS-2 ones (b): EsEx-1 (1), EsEx-2 (2), EsEx-3 (3), EsEx-4 (4), EsEx-5 (5), and EsEx-6 (6).
The degree of microphase separation between soft blocks and hard ones in a urethane-containing polymers can be appreciated according to the intensity of absorption bands of self-associates of hard segments [16].

Table 2. Physico-mechanical properties of EsEx samples.

| Sample     | Hard segment | Tensile strength, MPa | Engineer modulus, MPa | Failure strain, % |
|------------|--------------|-----------------------|-----------------------|------------------|
| EsEx-1     | HS-2         | 25.25                 | 9.23                  | 261              |
| EsEx-2     | HS-1         | 4.09                  | 1.27                  | 645              |
| EsEx-3     | HS-2         | 5.33                  | 1.23                  | 325              |
| EsEx-4     | HS-1         | 8.19                  | 6.07                  | 248              |
| EsEx-5     | HS-2         | 5.26                  | 1.68                  | 285              |
| EsEx-6     | HS-1         | 1.94                  | 0.21                  | 428              |

Figures 2-3 show that the intensity of the absorption bands of self-associates of urethane-hydroxyl hard segments is much higher for systems based on HS-2 segments. Therefore, the degree of microphase separation is higher in elastomers whose molecules contain HS-2 segments, than that of analogues containing HS-1 ones. This is reflected in the higher physical and mechanical characteristics (table 2) and the corresponding stress versus strain dependences (figure 5).

4. Conclusions

- A series of polyurethane elastomers based on oligoester urethane epoxides with different hard segments was synthesized. It was shown that a higher degree of microphase separation is realized in the final elastomers in the case of using isophorone diamine with PDA-800, and OMA-2100 oligoesters. This degree of microphase separation relates with the maximum strength for non-crystallizing elastomers.
- The higher strength is realized for polyurethane elastomers based on OMA-1950 oligoester at a relatively low degree of microphase separation when aminoethyl piperazine is used as a curing agent. The presence of segments in the polymer chain introduced by the mentioned agent leads to the increased degree of interchain interaction. This effect determines the mechanism of strengthening of the elastomers through the partial crystallization of the elastic chains of the soft matrix.

Acknowledgments
This work was financially supported by the Russian Academy of Sciences (project 19-43-590005 r_a).

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