Structure and properties of elastomers with hard segments and crystallizing soft segments suitable for the Arctic and the Far North

Alexei Slobodinyuk¹, Dmitriy Kiselkov and Daria Slobodinyuk
Institute of Technical Chemistry, Branch of the Perm Federal Research Center, Ural Branch, Russian Academy of Sciences, 614013, Perm, Russia

¹E-mail: slobodinyuk.aleksey.ktn@mail.ru

Abstract. The physicomechanical and structural characteristics of several elastomers based on terminal epoxy oligomers synthesized from oligotetramethylene oxide diol, various diisocyanates and oligotetramethylene oxide diamine were studied. Additionally, two model compositions of urethane containing elastomers with hard segments were synthesized to reveal the peculiarities of the organization of the supramolecular structure. It was found that the use of 2,4-toluene diisocyanate allows to obtain elastomers with a higher degree of microphase separation and, accordingly, a lower glass transition temperature. It was shown that regardless of the type of diisocyanate used in the synthesis, the elastomer contains crystalline phase. New materials can be used as compounds, adhesives and sealants for various purposes with the possibility of using them under extreme conditions of the Arctic and the Far North.

1. Introduction
Elastic materials with urethane hydroxyl hard segments, synthesized from epoxyurethane oligomers, are used in various fields of technology: in sealing of electrical products, industrial equipment for load-bearing and enclosing structures of buildings, as inserts to reduce vibration from ventilation systems, for bonding items suitable for high mechanical, shock and vibration loads [1-6].

The most famous synthesis of epoxyurethane oligomers is two-stage, with the formation of an intermediate product - oligodiisocyanate. At the second stage, the oligodiisocyanate is chemically modified by a compound with functional epoxy and hydroxyl groups - glycidol. Compounds with terminal amine, carboxyl, anhydride groups are used as hardeners for epoxyurethane oligomers [7-8].

Elastomers from epoxyurethane oligomers consist of alternating soft and hard segments, the difference in polarity of which causes phase separation with the formation of a separate phase – hard segment domains that play the role of a reinforcing filler and nodes of a specific physical network [9]. Hydrogen bonds stabilize the domain structure.

The use of various polyesters in the synthesis of oligodiisocyanates makes it possible to regulate the structure of the soft segment. The rigid segment structure allows the selection of isocyanate, epoxy alcohol and chain extender used in the synthesis of the polymer to be regulated.

For reliable operation in the Arctic and the Far North, materials are required that retain elastic properties at extreme cold temperatures. Such materials include compositions based on oligodientetraurethane epoxides [10], the glass transition temperature of which is -78 °C. Moreover,
this type of materials is characterized by a sufficiently low strength - no more than 5 MPa and consequently low adhesive strength [10].

In work [11] a new method to increase the strength characteristics was introduces. It was proposed to use oligotetramethylene oxide tetraurethane diepoxide as an epoxyurethane oligomer, when cured by low molecular weight hardeners (isophorone diamine, aminoethylpiperazine). It is proposed to use an oligomeric linear hardener with a molecular weight of more than 1000 amu. in order to create conditions for the crystallization of the polymer.

2. Materials and methods

The epoxyurethane oligomer was synthesized using two step method through an intermediate product - oligodiisocyanate. Oligodiisocyanate was synthesized from polyether - oligotetramethylene oxide diol (polyfurite) with a mass fraction of hydroxyl groups of 1.69 % and 2 diisocyanates: 2,4-toluene diisocyanate (TDI) or isophorone diisocyanate (figure 1). The molar ratio between the NCO groups of the diisocyanate and the OH groups of the polyether was 2.05.

Synthesis epoxyurethane oligomers produced according to the method [12] of the scheme:

![Figure 1. Synthesis of epoxyurethane oligomers.](image)

The above oligomers were cured oligotetramethylene oxide diamine (OTMODA), with a mass fraction of amine groups of 3.18 wt% was used as a hardener.

The completeness of the conversion of epoxy groups was determined by FTIR spectroscopy by the disappearance of the absorption band at 910 cm\(^{-1}\) [13].

The glass transition temperature T\(_g\) of the cured samples was determined by differential scanning calorimetry (DSC) using METTLER TOLEDO DSC 822e calorimeter at a scan rate of 5 °C/min.

The FTIR spectra of the cured samples were recorded on a Bruker Vertex 80V FTIR spectrometer with 64 scans at 2 cm\(^{-1}\) resolution. For convenience of comparison, the spectral curves were normalized to the band at 1600 cm\(^{-1}\), that corresponds to the stretching vibrations of the C - C aryl ring.

3. Results

Table 1 shows the theoretical and experimentally determined values of free isocyanate groups in the oligodiisocyanate and free epoxy groups in the epoxyurethane oligomer.

| Table 1. Characteristics of epoxyurethane oligomers and intermediate synthesis products. |
|---|---|---|
| Used ether | Used | Content of free functional groups in oligomer, % |

2
### 4. Discussions

An important feature of urethane-containing elastomers is the microphase separation factor due to the difference between hard and soft segments with the formation of nanodispersed filler - domains of hard segments, which plays the role of a reinforcing filler. With an increase in the content of such a filler, the deformation-strength characteristics and wear resistance of the cured polymers increase. The degree of microphase separation of soft and hard segments in elastomers based on epoxyurethane oligomers is lower than in polyurethanes / polyurethane ureas. The principal molecular structure of elastomers based on epoxyurethane oligomers is shown in figure 2.

![Molecular structure of elastomers from epoxyurethane oligomers.](image)

Meanwhile the use of a low-molecular-weight chain extender (R1 in figure 2) causes a high segmental mobility of the hard segment. When an oligomeric diamine is used, the molecular weight of the hard segment increases and thus steric hindrances appear for the phase organization of the segment structure. On the other hand, the linear structure of the diamine should favor the appearance of the crystalline phase of the polymer. Thus, two opposite factors are superimposed on the value of the strength characteristics: a decrease in the degree of microphase separation should lower the strength value, and the appearance of a crystalline phase should in contrast increase the strength value.

Different methods are used to determine the degree of microphase separation, including FTIR spectroscopy. The degree of microphase separation in polyurethane-ureas synthesized from 2,4-toluene diisocyanate and 3,3'-dichloro-4,4'-diaminodiphenylmethane is determined by the absorption band at 1640 cm\(^{-1}\). Polyurethanes synthesized from 1,4-butanediol and diphenylmethane diisocyanate is determined by the absorption band at 1702 cm\(^{-1}\). Some shift of absorption band depends on the type of initial component that build the hard segments. For polyurethane-ureas, the absorption band of self-associates of had segments made of isophorone diisocyanate shifts by 20 cm\(^{-1}\) up to 1660 cm\(^{-1}\).

To analyze the FTIR spectra of the obtained samples, model compounds DA-1 and DA-2 were additionally prepared that contained two types of urethane hydroxyl segments based on TDI, glycidol and OTMODA, as well as IPDI, glycidol and OTMODA, respectively. According to the synthesis method [14] at the first step the ratio of amine to isocyanate was taken 2 to 1, and at the second stage the synthesized compound reacted with a twofold excess of glycidol.
When using low molecular weight chain extenders in the synthesis of models for determining the wave number by FTIR spectroscopy of hydrogen bonds between NH and C = O groups of hard segments and thus phase separation in the elastomer, there is one band in the region of carbonyl stretching vibrations absorption (when 2,4-toluene diisocyanate is used, two more bands appear at 1600 cm\(^{-1}\), 1612 cm\(^{-1}\)). In this study, the chain extender is an oligomeric diamine. Therefore, when analyzing the FTIR spectra of the synthesized model compounds, it is necessary to take into account the fact that due to the polyester component of the diamine used in the synthesis, the FTIR spectrum in the region of carbonyl stretching vibrations should show several absorption bands characterizing the hydrogen bonds between the oxygen group of the PTMO polyester and the NH group 1695 - 1700 cm\(^{-1}\), as well as free carbonyl groups 1730-1732 cm\(^{-1}\) in the case of 2,4-toluene diisocyanate, 1721 cm\(^{-1}\) in the case of isophorone diisocyanate. The types of hydrogen bonds in the synthesized elastomers are schematically shown in figure 5.

**Figure 3.** Model DA-1.

**Figure 4.** Model DA-2.

**Figure 5.** Types of hydrogen bonds in synthesized elastomers.
In FTIR spectra of the model synthesized from 2,4-toluene diisocyanate absorption bands appear: at 1600 cm\(^{-1}\), characteristic of the stretching vibrations of the C - C aryl ring, 1732 cm\(^{-1}\), as well as a peak at 1660 cm\(^{-1}\) characterizing phase separation (figure 6). For the model from isophorone diisocyanate, two absorption bands appear - at 1721 cm\(^{-1}\), and at 1631 cm\(^{-1}\) characterizing phase separation. It should be noted that the FTIR spectrum of model DA-2 lacks an absorption band at 1698-1700 cm\(^{-1}\), which is associated with steric hindrances of hydrogen bonding due to the bulky structure of isophorone diisocyanate.

Analysis of the FTIR spectra of the synthesized elastomers shows that microphase separation appears only on the sample synthesized from 2,4-toluene diisocyanate - an absorption band at 1660 cm\(^{-1}\) (figure 7).

The absorption band at 1612 cm\(^{-1}\) attributed to the vibrations of the benzene ring with some substituents is typical for urethane-containing elastomers synthesized from TDI [15]. For the elastomer synthesized from isophorone diisocyanate there are only two absorption bands at 1721 cm\(^{-1}\) and 1698 cm\(^{-1}\) which can be attributed to interchain interaction (figure 7).

Figure 8 shows DSC curve of synthesized elastomers. The elastomer from isophorone diisocyanate has a higher glass transition temperature due to absence of microphase separation and the presence of interchain interaction. Both elastomers contain crystalline phase.
5. Conclusions
Two epoxyurethane elastomers from oligotetramethyldenedioxidiol with a molecular weight of 2000, 2
types of diisocyanate, glycidol, and an aliphatic diamine - oligotetramethylene oxide diamine were
synthesized. It was found that, regardless of the type of diisocyanate used in the synthesis of the
epoxyurethane oligomer, elastomers contain a crystalline phase. It has been proven that the use of 2,4-
toluene diisocyanate, in contrast to isophorone diisocyanate, promotes phase organization with the
formation of a separate hard segments, which leads to a lower glass transition temperature of the
elastomer which makes it possible to use these elastomers in conditions of the Arctic and the Far
North.

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References
[1] Chen D S, Ma C C M, Hsia H C, Wang W N and Lin S R 1994 J. Appl. Polym. Sci. 51(7) 1199-
206
[2] Hsia H C, Ma C C M, Li M S, Li Y S and Chen D S 1994 J. Appl. Polym. Sci. 52(8) 1137-51
[3] Yeganeh H, Mehdipour-Ataei S and Ghaffari M 2008 High Perform. Polym. 20(2) 126-45
[4] Pavlova M, Draganova M and Kabaivanov V 1988 Polym. Commun. 29(3) 80-2
[5] Chuvilina L F2007Patent 2291176 RU
[6] Sidorov O I, Milekhin Yu M, Matveev A A, Poisova T P, Bykova K A and Sadchikov N V 2012Klei. Germet. Tekhnol. 9 15-21
[7] Chen W H, Chen P C, Wang S C, Yeh J T, Huang C Y and Chen K N 2009 J. Polym. Res. 16 601-30
[8] Madhavan K and Reddy B S R 2006J. Polym. Scie. Part A: Polym. Chem.44(9) 2980-9
[9] Hsia H C, Ma C C M and Chen D S1994 Macromol. Mater. Eng. 220(1) 133-149
[10] Fedoseev M S, Tereshatov V V and Derzhavinskaya L F 2010 Russ. J. Appl. Chem. 83(8) 1367-
71
[11] Senichev V Y, Slobodinyuk, A I, SlobodinyukD G, Savchuk A V, KulakovaM V, Oshchepkova
T E and Dolinskaya R M2020 Russ. J. Appl. Chem.93(8) 1172-8
[12] Slobodinyuk A, Strelnikov V, Kiselkov D and Slobodinyuk D 2021 Zeitschrift für
Naturforschung B. 1-5
[13] Socrates G 2001 *Infrared and Raman characteristic group frequencies: tables and charts* (ChichesterNew York : John Wiley & Sons) 349
[14] Zhang S, Ren Z, He S, Zhu Y and Zhu C 2007 *Spectrochim. Acta, Part A* 66(1) 188-93
[15] Kothandaraman H and Nasar A S 1993 *Polymer* 34(3) 610-5