New urethane multiblock-copolymers obtained using naphthalene diisocyanate

V Yu Senichev, M A Makarova, A I Slobodinyuk, E V Pogoreltsev and M V Kulakova

Institute of Technical Chemistry of Ural branch of Russian Academy of Sciences, 3 Akad. Korolev Street, Perm, 614013, Russia

E-mail: senichev85@yandex.ru

Abstract. Multiblock-copolymers were synthesized on the base oligoethers, oligoesters, naphthalene diisocyanate, and butanediol. The thermal, thermomechanical, and physico-mechanical properties of obtained copolymers with a variable composition of soft and hard segments were investigated. The relationship between the structure and properties of a new type of multiblock-copolymers was established. New materials can find application in various conditions of mechanical loading.

1. Introduction

The polymer chains of the majority of polyurethanes are composed of alternating soft and hard segments. The chemical structure of the soft segments is determined by the oligomers used. Hard segments are formed as a result of the reaction of a diisocyanate with a low molecular weight diol [1-3].

The difference in polarity of the soft and hard segments leads to their microphase separation with the formation of a soft and hard micro-dispersed phase, which plays the role of a reinforcing filler and nodes of a specific physical network in the elastomer [4]. The properties of polyurethanes are regulated by changing the chemical structure, molecular weight, polarity of the soft segments, concentration and structure of hard segments. Thus, a lot of materials with various properties have been obtained, which are used in various industries and medicine [1,5].

The ultimate physical and mechanical properties of elastomers (tensile strength and critical strain) are important criterions for the ability of a material to withstand applied loads and deformations.

The most widely studied polyurethane elastomers are the ones synthesized using toluene diisocyanate and diphenylmethane diisocyanate. At the same time, similar materials based on naphthalene diisocyanate (NDI) were studied to a much lesser extent. New objects of research are of significant interest from the standpoint of identifying the patterns and behavior of urethane-containing elastomers with a complex structure of polymer chains.

This report presents the results of a study of the physic-mechanical and other most important properties of block-copolymers containing different polyester, and polyether soft segments and hard segments, forming during a reaction between the molecules of butanediol and diisocyanate. In the synthesis of these polyurethanes, 1,5-naphthalene diisocyanate was used.
2. Experimental section

2.1 Materials
Initial components for the synthesis were 1,5-naphthalene diisocyanate (NDI) from BASF (Germany), oligotetramethylene oxide diol (OTMO) from BASF ($Mn = 1000 \text{ g} \cdot \text{mol}^{-1}$ for OTMO-1000 and $Mn = 1400 \text{ g} \cdot \text{mol}^{-1}$ for OTMO-1400), 1,4-butane diol (BD) from Sigma Aldrich (Belgium) as a chain extender. Oligoesterdiols OMA-2100 (polycondensation product of adipic acid, ethylene glycol, and 1,4-butane diol, $Mn = 2000 \text{ g} \cdot \text{mol}^{-1}$), and OMA-1950 (polycondensation product of adipic acid and ethylene glycol, $Mn = 1838 \text{ g} \cdot \text{mol}^{-1}$) were manufactured by the VEST company (Kazan, Russia).

The synthesis was carried out in two stages with the preliminary manufacture of prepolymers based on NDI and oligoethers (oligoesters). The prepolymers were prepared by the reaction of oligomer diols with diisocyanate (NCO/OH = 2.2) while maintaining the temperature of the reaction mixture $60-70 \, ^\circ\text{C}$. Afterwards these prepolymers were cured by mixes based on BD and the starting oligoesters (oligoesters) used to synthesize the corresponding prepolymer.

The process of synthesis of prepolymers and obtaining samples of crosslinked polyurethanes was described in detail in Ref. [6]. Four series of elastomers were synthesized: P-1000 on the base of OTMO-1000; P-1400 on the base of OTMO-1400; P6 on the base of OMA-1950; P6-BA on the base of OMA-2100. The composition of investigated samples for all the series is shown in table 1. Before testing, the samples were kept for at least 15 days at room temperature.

Table 1. The composition of the samples in molar fractions

| Prepolymer | BD | Oligomer diol |
|------------|----|-------------|
| 1.1        | 1.0| 0           |
| 1.1        | 0.67| 0.33       |
| 1.1        | 0.33| 0.67       |
| 1.1        | 0   | 1.0         |

2.2 Methods
The glass transition temperature of the soft phase was determined by the differential scanning calorimetry (DSC) method using a DSC 822e calorimeter (Mettler Toledo, USA) at a scanning rate of 0.08 K s$^{-1}$. FTIR spectra of surfaces of samples were registered using an attenuated total reflectance (ATR) installation A 225/Q (Platinum ATR diamonds F) with a diamond crystal of single reflectance. Mechanical tests of samples were performed using an Instron 3365 universal testing machine (Instron, United Kingdom). Tensile strength of the samples ($\sigma_p$), relative critical strain values ($\varepsilon$) were determined at a stretching rate of 500 mm min$^{-1}$. The engineer modulus ($E_{100}$) was determined at a relative strain of $\varepsilon=100\%$.

3. Results and discussion
It was found that curing of polyurethanes based on NDI and oligoethers was associated with catastrophic changes in values of critical strain and tensile strength which in our opinion were linked with forming complex supramolecular structures. The formation of these structures can negatively affect the deformability of the cured elastomers. This effect is especially pronounced for samples synthesized based on Polyfurite 1000 (P-1000 series). When using butane diol as an only hardener, a structure with poor deformability is formed almost immediately after curing ($\varepsilon=70\%$). Further exposure of the samples for a month increases this parameter. However, a clear process of the deformability loss during storage is clearly visible for samples with a smaller content of butane diol in the hardening mixes. The initial high values of tensile strains (806÷969%) decrease by $3\div4.5$ times, exerting a corresponding negative effect on the strength value (figure 1).

The described effect was less pronounced for samples of the P-1400 series. Nevertheless, a decrease in the value of critical strains during exposure was observed for almost all the studied samples. The final value of the strength of the samples of P-1000 series after 30 days of exposure was reached at 22.7 MPa
with a strain of 438% and an $E_{100}$ value of 13.5 MPa. For similar samples of the P-1400 series, the maximum strength was reached at 23.8 MPa with a strain of 448% and an $E_{100}$ value of 12.2 MPa, which shows a fundamentally close result. Thus, the same negative effect of the formation of supramolecular structures was manifested in the both cases. This effect prevents an appearance of strain high values during loading.

Figure 1. Dependence of tensile strength (1, 2), engineer modulus (3, 4) and critical strain (5,6) for samples of the P-1000 series on the molar fraction of butanediol $x_2$ and the exposure time of the samples.

A manifestation of the described effect was reflected in a change in the mobility of polymer chains too. It was found that a decrease in the butanediol fraction in the curing mixture lead to increase in the glass transition temperature for samples of both series based on oligoethers. This phenomenon is systematic, the difference in the glass transition temperatures of samples cured with pure butanediol and pure oligoether reaches 4°C for the P-1400 series (from -71 to -67 °C) and 6°C for the P-1000 series (from -68°C to -62°C). This effect could be attributed to the partial crystallization of the studied polyethers; however, crystallization was observed for the P-1000 series only on a sample cured with pure polyether without butanediol. A similar picture was observed for the samples of the P-1400 series. Generally, the thermal effect of crystallization did not exceed 8-10 J/g, which corresponded to several percent of crystallized material in the samples.

In contrast to compositions based on oligoethers, similar materials based on oligoesters (P6 and P6-BA series) did not show the effect of decrease in $\varepsilon$ value almost at all. The glass transition temperature of the samples was practically unchanged regardless of the composition of the curing mixture and was equal to -33 °C for the P6 series and -40 °C for the P6-BA one. For these both series of elastomers, the level of critical strains does not fall below 600%, regardless of the exposure time or the ratio of components during curing (figure 2).

A small decrease in the value of critical strains during exposure, which is characteristic of almost all investigated elastomers, is compensated by a noticeable increase in strength, being higher than the corresponding increase in the $E_{100}$ value. A higher level of strength is achieved for the P6-BA series (46.5 MPa) with a value of $E_{100} = 4.4$ MPa, the maximum strength value is 38.5 MPa for the P6 series, and the correspondent $E_{100}$ value is 8.7 MPa (figure 3). The almost ideal ratio of strength and $E_{100}$ (10:1) for a sample of the P6 series cured with pure butanediol shows that conditions for the formation of supramolecular structures providing high deformability and, accordingly, strength are provided for the oligoester-NDI-butanediol systems. The small partial crystallization observed for all compositions based on oligoesters apparently played some positive role in this process.
Figure 2. The dependence of the relative critical strain on the molar fraction of butanediol in the hardening mix of samples of the series: P6 (a) and P6-BA (b) and the exposure time of the samples.

It was interestingly, that the studied materials based on oligoesters cured with mixtures of butanediol and oligoesters demonstrated high strength characteristics combined with relatively low Shore A hardness. For example, the composition of the P6 series cured with a mixture of oligoester and butanediol at a molar ratio of the latter 0.67: 0.33 showed a strength of 35 MPa with a critical strain of 860% and a hardness of 62 Shore A units. This strength value exceeds this parameter for analogues based on toluene diisocyanate by about 40%.

Figure 3. Dependence of tensile strength (1, 2), and engineer modulus (3, 4) of P6 samples (a) and P6-BA ones (b) on the molar fraction of butanediol in the hardening mix.

In our opinion, the processes of phase separation play the main role in the described effects; they are reflected in the correspondent spectra of the obtained samples.

So, one can observe a regular decrease in the intensity of the absorption band at 1733 cm$^{-1}$ with an increase in the content of butanediol in the curing mixture on the spectra of samples of the P-1000 series (figure 4). This band is characteristic of vibrations of the free C=O group. In a similar way, the intensity of band at 1713 cm$^{-1}$ changes too, and this band can be attributed to vibrations of the bounded C = O groups in disordered regions of the polymer [7]. On the other hand, the intensity of the band at 1692 cm$^{-1}$ (vibrations of the bounded C=O groups in ordered regions) naturally increased; however, the maximum intensity of this band was observed for the sample with the content of butanediol $x_2 = 0.67$ in the curing mixture. This behavior of the MATR spectra of the obtained polyurethanes indicates that, as the content
of butanediol in the curing mixture increases, the process of phase separation intensifies with an increase in the fraction of ordered regions, despite individual effects of a non-systematic nature (mutual arrangement of curves 3 and 4).

Figure 4. MATR spectra of the P-1000 series samples with different fraction of butanediol $x_2$ in the mix with Polyfurite-1000: $x_2 = 0$ (1), 0.33 (2), 0.67 (3), 1.0 (4).

4. Conclusions
The results of our studies illustrate the possibility of constructing segmented polyurethanes based on naphthalene diisocyanate with high ultimate physical and mechanical properties. The combination of high strength properties of the new multiblock-copolymers, and improved processability can be useful in various applications.

Acknowledgments
The study was performed using equipment CCU “Investigation of materials and matter” PFIC UrB RAN, and the state budget fond within the framework of the state assignment for “ITC UrB RAN” (the state budget theme AAAA-A18-11802290056-8).

References
[1] Yilgör I, Yilgör E and Wilkes G L 2015 Critical parameters in designing segmented polyurethanes and their effect on morphology and properties: A comprehensive review Polymer 58 1-36
[2] Oprea S 2010 Synthesis and properties of new polyurethane elastomers: influence of hard segment structure Polimery 55(2) 111-17
[3] Jiang L, Ren Z, Zhao W, Liu W, Liu H and Zhu C 2018 Synthesis and structure/properties characterizations of four polyurethane model hard segments Royal Society open science 5(7) 180536
[4] Christenson E M, Anderson J M, Hiltner A and Baer E 2005 Relationship between nanoscale deformation processes and elastic behavior of polyurethane elastomers Polymer 46(25) 11744-54
[5] Lamba N K et al 1998 Polyurethanes in biomedical applications (Boca Raton: CRC Press)
[6] Tereshatov V V, Slobodinynuk A I, Makarova M A, Vnutskikh Zh A, Pinchuk A V and Senichev V Yu 2016 Characteristics of polyether urethanes with mixed soft segments, prepared by two- and three-step procedures Russian Journal of Applied Chemistry 89(5) 943-8
[7] Coleman M M, Lee K H, Skrovaneck D J and Painter P C 1986 Hydrogen bonding in polymers. Infrared temperature studies of a simple polyurethane Macromolecules 19(8) 2149-57