Abrasive resistance of polyetherurethane ureas

V Yu Senichev and E V Pogoreltsev

Federal State Budgetary Institution of Science Perm Federal Research Center, Ural Branch of the Russian Academy of Sciences, 3, ul. Akademika Koroleva, Perm, 614068, Russia

E-mail e.v.pogoreltsev@yandex.ru

Abstract. The relationship between the structure of the polymer chains and the abrasion resistance of segmented polyurethane ureas based on polyoxymethylene oligoether was studied. Experimental data were obtained for systems with the hard segments content above 39%. It was found that the function of the volumetric wear of polyurethane-urea samples on the content of hard segments had an extremum; at high contents of these segments (more than 35%), a further increase in this content lead to a deterioration in the abrasion resistance. The reasons for this effect can be associated with a sharp deterioration in the strength and strain properties of the studied elastomers when additional amounts of diisocyanate are introduced into the system, which can lead to the formation of excessive interchain bonds.

1. Introduction

Segmented polyurethane ureas (SPUU), which are used as structural and composite materials, are block-copolymers with alternating soft polyester or polyether segments and hard urethane ones. It is known that urethane-containing elastomers can have both a single-phase amorphous structure and a two-phase one. In the last case, a hard (high modulus) phase is formed during the curing process as a result of phase separation of more polar hard segments and less polar soft segments [1-3]. Polyurethane materials with different properties can be obtained using different raw materials, varying chemical composition or using different production methods and further processing. Functional properties of polyurethane materials can be varied quite simply by choosing components, adjusting the composition and production conditions [3].

Abrasive wear is a form of mechanical wear of a material as a result of cutting or abrasion of solids or hard particles. This wear has a particularly strong effect on the performance of rubber products based on conventional rubbers [4-5]. It is known that polyurethanes are highly resistant to abrasion compared to rubbers, plastics or even metals and therefore are widely used in products where high abrasion resistance is required, for example: sieves, collars, gaskets, seals. However, increasing the requirements for the durability of these products poses the problem of further increasing the abrasion resistance of polyurethane-type materials [2].

Unfortunately, the available data on the influence of the content of hard blocks (segments) in polyurethanes on their abrasion resistance are ambiguous [6-8]. In particular, the problem of the relationship between abrasive wear and material hardness in the region of high values of Shore A hardness was not studied.
The purpose of this work is to study the effect of the hard segments content on the physical and mechanical properties and abrasion resistance of polyurethane ureas of various structures in a wide diapason of the hardness level.

2. Materials and methods

The synthesis of segmented polyurethane urea samples was carried out in two stages in compliance with the same procedures and conditions described earlier [9]. At the first stage of the synthesis, the reaction was carried out to obtain a prepolymer (oligomer with terminal isocyanate groups) from a diisocyanate and the oligomeric diol Polyfurite-1000 (with a molar ratio of NCO:OH = 2.06, respectively). At the second stage, the prepolymer was cured with curing mixtures based on the original oligomer and a chain extender (diamine). A schematic representation of the synthesis reaction and the curing process of SPUU is shown in figure 1.

![Figure 1. The scheme for synthesis of the segmented polyurethane ureas.](image)

Polyoxytetramethylenediol (Polyfurite-1000) with a molecular weight of 1000 was used as the basis for the soft segments. 2,4-toluene diisocyanate (TDI) was used as a diisocyanate, and 4,4'-methylenebis-(2-Chloroaniline), MOCA, was used as a chain extender (hardening agent). Mixtures of prepolymer and initial diisocyanate were prepared for the synthesis of samples with a high content of hard segments. This allowed us to obtain for the first time experimental data for such systems with the content of hard segments above 39%. The chemical structures and molecular weights (M_w) are presented in table 1.

| Name                                                      | M_w  | Function     | Chemical structure                              |
|-----------------------------------------------------------|------|--------------|-------------------------------------------------|
| Polyoxytetramethylene diol (Polyfurite-1000)              | ~1000| oligoether   | HO(CH₂-CH₂-CH₂-CH₂-O)ₙ-H                         |
| 2,4-Toluene diisocyanate (TDI)                            | 174  | diisocyanate | ![diisocyanate structure](image)                 |
| 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA)         | 267  | diamine      | ![diamine structure](image)                      |
The samples were cured at a temperature of 80 ± 2 °C for three days in slot-type metal molds. The molar fractions of the components and the calculated content of hard segments in the structure of polymer chains of the obtained samples are shown in table 2. The calculation of the hard segments content (HS) was carried out in accordance with [10].

Table 2. The molar ratios of the components and the content of hard segments in the samples.

| Sample | Prepolymer (Polyfurite-1000) | TDI | MOCA | HS, % |
|--------|------------------------------|-----|-------|-------|
| 1      | 1.03                         | 1.0 | –     | –     | 0     |
| 2      | 1.03                         | 0.9 | –     | 0.1   | 6.4   |
| 3      | 1.03                         | 0.6 | –     | 0.4   | 19.2  |
| 4      | 1.03                         | 0.4 | –     | 0.6   | 26.4  |
| 5      | 1.03                         | 0.1 | –     | 0.9   | 35.8  |
| 6      | 1.03                         | –   | –     | 1.0   | 38.6  |
| 7      | 1.0                          | –   | 0.06  | 1.03  | 39.6  |
| 8      | 1.0                          | –   | 0.12  | 1.09  | 40.6  |
| 9      | 1.0                          | –   | 0.18  | 1.15  | 41.6  |

Tensile strength $\sigma_k$, relative critical strain $\varepsilon_k$ were determined using an universal testing machine INSTRON 3365 in accordance with the Russian standard GOST 270-75. Abrasive wear, expressed as abrasion volume loss $V$, was determined on a GT-7012-D abrasive tester according to the Russian standard GOST 23509-79 / ISO 4649-85.

3. Results and its discussion

Figure 2 shows the dependence of the tensile strength and critical strain of materials on the content of hard segments of the obtained samples of polyurethane-urea materials.

![Figure 2. Dependences of tensile strength (●) and critical strain (○) of samples on the hard segments content.](image)

The dependence of strength of the investigated elastomers on the content of hard segments is characterized by the presence of a certain maximum value of strength in the region of relatively high values of the hard segments content. The main part of diapason of the hard segments content can be characterized by the increase in the strength value according increase in the mentioned content. Starting from a certain threshold value of the concentration of hard segments, the strength begins to decrease. This effect can be explained by an integral nature of the strength. This value depends both on the modulus and on critical strain values.

One can see that the dependences of the modulus and critical strains on the content of hard segments have different directions, which is a potential reason for the appearance of extrema on the curves of the
dependences $\sigma$ versus HS content. An increase in the content of hard segments is accompanied usually by an increase in hardness due to an increase in the fraction of the resulting hard phase, which, with a slight decrease in the deformability of the sample, leads to an increase in the strength. Hard segments in the polymer chain of block copolymers form hard blocks that can be considered as a kind of reinforcing fillers increasing the modulus of the material and, in the common case, strength. However, at a certain filling degree, depending on the structure of these blocks, the steric factor begins to play, when the degree of freedom of elastic segments of polymer chains begins to drop sharply, reducing the deformability of the material as a whole. In this case, an increase in the content of hard segments leads to the sharply decrease in the deformability of polymer chains. In the extreme case, the material can pass the inversion point when the polymer system goes from an elastic matrix filled with the dispersed hard filler to the form of a hard matrix with elastic inclusions. According to the authors, this behavior of the mentioned function is associated with the formation of additional interchain bonds in the system upon the introduction of a monomeric diisocyanate due to the reaction of isocyanate groups with NH groups in the urethane and urea fragments of the polymer chains.

Figure 3 shows the plot of the function volumetric wear versus the content of hard segments for the obtained samples.

An increase in the share of hard segments in the SPUU causes a consistent decrease in the degree of volumetric wear until the critical HS values are reached, where the factor of deterioration of the strain and strength characteristics begins to play a role. As a result, the function the volumetric wear versus the content of hard segments acquired an extreme character: an increase in the content of HS for the studied polyurethane ureas above the found critical value (35%) leads to a deterioration in their wear resistance.

4. Conclusion
It was found that the function the volumetric wear of polyurethane-urea samples versus the content of hard segments has an extreme character with a minimum at the mentioned content close to 35%. The further increase in this parameter in the field of values more than 35% leads to a deterioration in the abrasion resistance.

Acknowledgments
The study was performed using the equipment of the Center for Shared Use “Studies of Materials and Substance”, Perm Federal Research Center, Ural Branch, Russian Academy of Sciences, and budget funds within the framework of the project “Chemical products in Subsoil Use” of the Perm Scientific and Educational Center “Rational Subsoil Use”.

Figure 3. Dependence of the abrasion volume loss of samples on the hard segments content.
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] Prisacariu C 2011 Polyurethane elastomers: from morphology to mechanical aspects (New York: Springer Science & Business Media) p 280
[3] Sonnenschein M F 2014 Polyurethanes: science, technology, markets, and trends (New York: John Wiley & Sons) p 432
[4] Myshkin N K and Petrokovets M I 2007 Friction, lubrication, wear. Physical foundations and technical applications of tribology (Moscow: FIZMATLIT) p 368
[5] Popov V L Contact mechanics and physics of friction. From nanotribology to earthquake dynamics (Moscow: FIZMATLIT) p 352
[6] Beck R A and Truss R W 1998 Effect of chemical structure on the wear behaviour of polyurethane-urea elastomers Wear 218(2) 145-52
[7] Kwiatkowski K and Nachman M 2017 The abrasive wear resistance of the segmented linear polyurethane elastomers based on a variety of polyols as soft segments Polymers 9(12) 705(1-13)
[8] Anisimov V N, Semenets A A, Letunovskii M P and Strakhov V V 2002 Effect of rigid blocks on the mechanical characteristics and abrasive resistance of polyurethanes Materials Science 38(1) 95-8
[9] Senichev V Y and Pogoreltsev E V 2019 The relationship between abrasive wear behavior and chemical structure of polyurethane urea elastomers J. of Phys.: Conf. Ser. 1399 044006 1-6
[10] Petrović Zoran S 1991 Polyurethane elastomers Progr. in Polym. Scien. 16(5) 695-836