The relationship between abrasive wear behavior and chemical structure of polyurethane urea elastomers

V Yu Senichev and E V Pogoreltsev
Institute of Technical Chemistry of Ural branch of Russian Academy of Sciences, 3 Akad. Korolev Street, Perm, 614013, Russia
E-mail pogorelcev1995@gmail.com

Abstract. The relationship between abrasive wear and the chemical structure of molded polyurethane urea elastomers based on polyethers and polyesters was investigated. The regularities of the influence of the hard blocks content in the polymer chain on the abrasive resistance of the studied elastomers in a wide range of their hardness values were revealed.

1. Introduction
Cast elastomers based on polyurethane and polyurethane ureas are widely used in engineering due to the high level of strength and exploitation characteristics [1-2]. Especially these materials stand out for their wear resistance, much higher comparing with one for widely used rubbers [3].

Several mechanisms of abrasive wear of elastomers were proposed, each of which became predominant in one or another variant of mechanical action [4–6]. However, it is generally accepted that the determining factors affecting abrasive wear behavior of elastomers are their elastic and strength characteristics. For example, abrasive wear of rubber, caused by the separation of micro-particles of a material as a result of mechanical destruction, is associated with rubber’s modulus and conditions of propagation of micro-cracks in the material relating to its ultimate strain ability [7].

It is known that almost all cast polyurethanes and polyurethane ureas used in the industry have a two-phase structure, where the hard phase domains playing the role of an active filler being evenly distributed in an elastic matrix [1]. This phase is a set of domains of hard segments that are separated from a soft matrix due to the phase separation, as a result of the large difference in polarity of the hard polymer segments and the soft ones. The presence of these domains plays a major role in reducing the effect of crack propagation in elastomers based on polyurethanes and polyurethane ureas during mechanical destruction [8]. It should be noted that the dependence of the critical strain on the hard phase content is not pronounced [4], which makes it possible to mark the Young modulus value as the main factor affecting the wear resistance of segmented elastomers. This value is tightly associated with the Shore A hardness being a useful technical characteristic. The Shore A hardness is easy to determine under manufacturing conditions.

One can find some published data linking the magnitude of the abrasive resistance of thermoplastic polyurethanes with their chemical structure and the content of hard segments [4, 9]. However, similar data for polyurethane ureas are scattered in nature and refer, as a rule, to individual commercial materials, which makes it impossible to optimize the chemical structure of these polymers in the direction of increasing their wear resistance.
The target of this work is to study the relationship between abrasive resistance and chemical structure of elastic polyether urethane ureas and polyester urethane ureas as well.

2. Materials
Two series of samples of segmented polyurethane ureas based on oligoethers (PPL) and oligoesters (SPL) were investigated. Oligobutylene oxide diol with a molecular weight of 1000 (Polyfurite 1000 trademark), oligoethylene-butylene glycol adipate with a molecular weight of 2000 (Polyester P6-BA trademark), 2,4-toluene diisocyanate (TDI), methylene-o-bis-chloroaniline (MOCA trade mark) were used as precursors.

The moisture in oligodiols was removed before the synthesis at 80°C under stirring for 8 h under a vacuum of ~ 0.2 kPa. The synthesis of samples was performed as a two-step process. At the first stage, prepolymers with terminal NCO-groups were synthesized using TDI: SKU-PFL based on Polyfurite 1000, and SKU-7L based on P6-BA. The prepolymers were produced with reaction temperature being kept at 60–70°C under stirring.

The NCO/OH molar ratio 2.06 was kept in the both cases excluding the synthesis of the prepolymer for the SPL-1 sample. The above mentioned synthesis was performed using the NCO/OH molar ratio equal to 2.2.

In the second stage, the prepolymers were cured with mixtures of the initial oligodiols and the MOCA chain extender in accordance with the ratios given in tables 1, 2. The molar NCO/(OH + NH₂) ratio during all curing reactions was kept equal to 1.03. Curing was provided within 48 hours under 90°C.

| Sample | SKU-PFL, molar contents | Polyfurite 1000, molar contents | MOCA, molar contents | C_Hs (%) | Shore A hardness | ε_k, % |
|--------|--------------------------|---------------------------------|---------------------|----------|-----------------|-------|
| PPL-1  | 1.03                     | 0                               | 1.0                 | 37.5     | 97              | 386   |
| PPL-2  | 1.03                     | 0.15                            | 0.85                | 33.3     | 96              | 440   |
| PPL-3  | 1.03                     | 0.3                             | 0.7                 | 28.6     | 94              | 443   |
| PPL-4  | 1.03                     | 0.4                             | 0.6                 | 25.2     | 91              | 478   |
| PPL-5  | 1.03                     | 0.5                             | 0.5                 | 21.7     | 86              | 527   |
| PPL-6  | 1.03                     | 0.4                             | 0.4                 | 17.9     | 82              | 528   |
| PPL-7  | 1.03                     | 0.3                             | 0.3                 | 13.9     | 76              | 600   |
| PPL-8  | 1.03                     | 0.2                             | 0.2                 | 9.6      | 61              | 621   |
| PPL-9  | 1.03                     | 1.0                             | 0                   | 1.2      | 55              | 771   |

| Sample | SKU-7L, molar contents | P6-BA, molar contents | MOCA, molar contents | C_Hs (%) | Shore A hardness | ε_k, % |
|--------|------------------------|-----------------------|---------------------|----------|-----------------|-------|
| SPL-1  | 1.1                    | 0                     | 1.0                 | 27.1     | 89              | 648   |
| SPL-2  | 1.1                    | 0                     | 1.0                 | 23.0     | 87              | 650   |
| SPL-3  | 1.1                    | 0.15                  | 0.85                | 20.1     | 85              | 643   |
| SPL-4  | 1.1                    | 0.3                   | 0.7                 | 16.9     | 82              | 678   |
| SPL-5  | 1.1                    | 0.5                   | 0.5                 | 12.5     | 72              | 707   |
| SPL-6  | 1.1                    | 0.6                   | 0.4                 | 10.2     | 65              | 705   |
| SPL-7  | 1.1                    | 0.7                   | 0.3                 | 7.8      | 62              | 764   |
| SPL-8  | 1.1                    | 0.85                  | 0.15                | 4.0      | 58              | 835   |
| SPL-9  | 1.1                    | 1.0                   | 0                   | 1.1      | 55              | 950   |

3. Methods
Mechanical tests were conducted at 25°C using an Instron 3365 universal stretching machine according to GOST 270-75 (Russian state standard) or ASTM D 412, DIN 53 504. The engineer strength ε_k of the
samples (maximum stress calculated for initial cross-sectional area samples), the relative critical strain value $\varepsilon_k$ were determined at a constant strain rate $0.28\,s^{-1}$ (500 mm/min). Shore A hardness testing was carried out using a TIR-2033 hardness meter in accordance to GOST 263–75 (ASTM D 2240-86 and ISO 868). Abrasive wear was determined using the GT-7012-D abrasive tester according to GOST 23509-79 (ISO 4649-85). The C_{HS} mass content of hard segments in the polymer chain was calculated according to [4] with an unconditional assignment of MOCA fragments and neighboring TDI fragments to this value.

4. Discussion

The calculation of the hard segments content in the synthesized samples allowed us to compare the dependencies of the Shore A hardness (tables 1, 2), strength and critical deformation (figure 1) on the above mentioned value, as well as the correspondent dependence of the abrasive wear (figure 2). A fairly clear picture was observed for the dependence of the Shore A hardness, this value increases monotonously with increasing content of hard segments in the polymer chain ($C_{HC}$). The plots of strength versus $C_{HC}$ are characterized by the presence of a certain limited strength in the region of relatively high $C_{HC}$ values. One can know that strength is an integral characteristic, depending both on the modulus (reflecting the slope of the stress-strain curve) and on the magnitude of the critical strains. Really, changes in the modulus and critical strain values depending on the content of hard segments are of a multidirectional nature, which is a potential cause of the extremes appearance in the $\sigma_k$ versus $C_{HC}$ plots. Indeed, the hard phase becomes a matrix at the phase inversion point ($C_{HC}\approx50\%$). In this case elastic segments are distributed in the hard matrix; one can see a sharp decrease in the strain ability. In the framework of the experiments, it was not possible to obtain the mentioned extremes due to a sharp decrease in the pot life of compositions for cases when MOCA was used as an only hardener, especially for prepolymer synthesized with a large excess of NCO groups.

The described effects influence directly the relationship between the abrasive wear and the content of hard segments (figure 3).

One can see in figure 2, that an increase in the content of hard segments causes a consistent decrease in the degree of volumetric wear, excluding small areas of high $C_{HC}$ values. Such a relationship is directly consistent with the corresponding dependence of strength (figure 1). With a further increase in the $C_{HC}$ value, the abrasive resistance should decrease sharply, because polymer’s properties should approaching to the same of hard plastics [10].

The obtained results differ from the data given in the paper of Anisimov et al. [4], where the degree of abrasive wear of polyurethanes increases with an increase in the content of hard segments. This distinction can be explained by another mechanism of material destruction under conditions of gas abrasive wear.

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![Figure 1. Tensile strength and critical strain versus hard segments content dependences (solid lines and dotted ones correspondingly) for PPL samples (○,●) and SPL ones (◇,♦).](image-url)
Another important conclusion that can be made from the analysis of the obtained data is related with the relative abrasive resistance of polyurethane ureas based on polyesters comparing with ones based on polyethers. Polyurethane ureas based on polyester with medium and low hard segments content, possess the less abrasive wear. This effect, in our opinion, is due to the higher cohesive energy of polyesters compared with polyethers.

![Figure 2](image2.png)  
**Figure 2.** Volumetric wear of samples versus hard segments content dependence for PPL samples (○) and SPL ones (●).

![Figure 3](image3.png)  
**Figure 3.** Volumetric wear of samples versus Shore A hardness for PPL samples (○) and SPL ones (●).

Also it was interesting to trace the correlation of volumetric wear with the hardness of the material, which was presented in figure 3. One can see that the wear resistance with the same hardness has the higher level for polyurethane ureas based on polyester within the Shore A hardness diapason 50-85. However, polyurethane ureas based on polyethers have the better wear resistance at a hardness level higher than 85 Shore A, which explains the high prevalence of these materials in industry.

5. Conclusion
The obtained dependences of the abrasive wear of the studied elastomers on the content of hard segments in them show that the wear value consistently decreases as the mentioned content increases up to a certain critical value. This value depends probably on the degree of approach of the considered two-phase systems to the inversion point. With a further increase in the concentration of hard segments, a constant or an increase in the amount of wear can be observed, which can be associated with a change in the mechanism of interaction of abrasive particles with elastomers in the direction of wear of the hard plastics.

Polyurethane urea elastomers based on polyesters possess greater abrasion resistance in a wide range of hardness (55-85 Shore A), which can be explained by a large interchain interaction in more polar polymers based on polyesters.

Acknowledgments The study was supported within the framework of the state budget theme AAAA-A18-118022290056-8.

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