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PROPERTIES PREDICTION OF LINEAR BLOCK-POLYURETHANES BASED ON THE MIXTURES OF SIMPLE OLIGOETHERS

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Abstract:
Polyurethanes are materials usable in wide spectrum of applications. This article is aimed at the properties tailoring of selected polymers by an alteration in initial materials. To achieve that goal, we proposed form the polyurethane matrix by mixing materials that have a different ratio of the initial components. Mathematical model has been developed that describes relationship of structure and strength, deformation, rheological and tribotechnical characteristics of linear block-polyurethanes based on oligoether blends. Oligoethers blend samples were obtained by injection moulding on an automatic thermoplastication machine with varying proportions of the starting components over the whole concentration range. A significant change of properties over the whole concentration range was observed and compositions with unique combination of characteristics have been determined. Obtained dependencies allow to predict the composition of the binary mixture with a tailored level of strength, deformation, rheological and tribotechnical characteristics. The obtained results are fully consistent with the practical experience of processing and exploitation of initial polyurethanes.

Key words: *linear block-polyurethane, oligoether, physico-mechanical characteristics, melt flow characteristics, melt flow, wear intensity, material quality indicator*

INTRODUCTION

Wide application of polymeric materials based on polyurethanes is due to the unique combination of high strength properties and elasticity, oil and gas resistance, strike and vibration resistance [1, 2].

The relevance of modern technologies [6, 7, 8, 9] is primarily determined by ecological factors – polyurethanes of block structure (block-polyurethanes) provide a unique set of properties and, at the same time, they are also suitable for recycling, are recycled by waste-free technology on high-speed automated equipment, including 3D prototyping methods [17, 18]. In addition, block-polyurethanes based on oligoethers have increased hydrolytic resistance, frost resistance, more resistant to microorganisms, and therefore are of particular interest.

Therefore, the relationship study of linear block-polyurethanes (BPU) based on mixtures of oligoethers structure with strength, deformation, rheological and tribotechnical characteristics, mathematical prediction of their behavior in different operating conditions, taking into account the quality indicators of the material, is of great practical importance for use in industry [3, 4, 14, 16].

It was found that main characteristics that determine the properties of linear block-polyurethanes are their molecular weight and the concentration of rigid segments in a macromolecule [11, 13, 19, 20]. It is possible to obtain materials with preset exploitation characteristics by adjusting these parameters at the stage of synthesis. However, this approach is time-consuming and costs a lot in industrial conditions [5, 15, 21]. Therefore, now the main way of obtaining binary mixtures based on block-polyurethanes is the mechanical mixing of the initial polymers in the melt. It is proposed to form the polyurethane matrix by mixing materials that have a different ratio of the initial components.

LITERATURE REVIEW

Recently, effort focused on developing and improvements of advanced materials with properties tailored for various applications is closely connected with multifactorial analysis of its preparation, processing and characterization of properties during life-time.

Berladir et al [3] and Panda et al [16] studied physical and chemical principles of the technology of formation of polymer composite materials. Anisimov [1], Dyadyura et al [6] and Bakirova & Galeeva [2] reported on the properties of thermoplastic polyurethanes based on the various mixtures of oligoethers. Murcinkova & Krenicky [12] applied altered composite microstructures for damping of production machines and manipulator devices, Todic et al.

[20] and Krenicky [10] implemented multifactorial monitoring methods for evaluation of complex material characteristics. Durdan et al. [5] implemented various annealing procedures to alter material properties, Piechocki et al. [19] controlled properties of oligoethers by using radiation, Macala et al. [11] and Pandova et al. [18] reported on ways of reduction of harmful substances.

Jurko et al. [6, 7, 8] studied mechanical deformation of materials during processing and operation, Valicek et al [21] developed method of the deformation evaluation. Cacko & Krenicky [4] and Panda et al. [13, 14, 15, 17] analyzed thermal and tribotechnical characteristics of mechanically exposed parts in order to determine their operating status and durability.

METHODOLOGY OF RESEARCH

As initial materials it was chosen BPU based on oligoether oligooxytetramethyleneglycol (OOTMG) with molecular weight about 1000, 1,4-butanediol (BD) and 4,4'-diphenylmethanediisocyanate (MDI) with different contents of rigid blocks P_c (%): BPU OOTMG$_{1000}$ (37) and BPU OOTMG$_{1000}$ (48) (the value of P_c is given in brackets). The basic physico-mechanical characteristics of the output BPU are shown in Table 1.

Table 1
Physical and mechanical properties of starting block-polyurethanes

Property	BPU OOTMG$_{1000}$ (37)	BPU OOTMG$_{1000}$ (48)
Density, kg/m^3	1080	1110
Shore A hardness number, conventional units	87.2	92
Tensile strength, f_t, MPa	22	31
Elastic modulus, E, MPa	60	15
Elongation at rupture, ε_r, %	650	700

Various binary mixtures of polyether-based BPU were produced at the pressure of 80 to 100 MPa and the temperature of 463 K through mechanical blending of the starting materials in the melt using automatic thermoplastication machines.

The physical and mechanical properties of the BPU mixtures were evaluated by means of Instron TT-DM-4, universal machine, using standard methods. The hardness of involved materials was studied using IIRT-M device at the load of 0.216 MPa and the temperature of 463 K.

The BPU tribotechnical characteristics were estimated using “disk – I-sample” scheme on a disk-type frictional machine at the speed of V = 0.4 m/s and load of ρ = 0.2 MPa [1]. The results of the study were computer-processed using Mathcad 7.0 pro program.

RESULTS OF RESEARCH

Figure 1 depicts the main physical and mechanical properties (tensile strength f_t, elastic modulus E_p, elongation at rupture ε_r of the starting BPU at various temperatures (223 to 353°K).

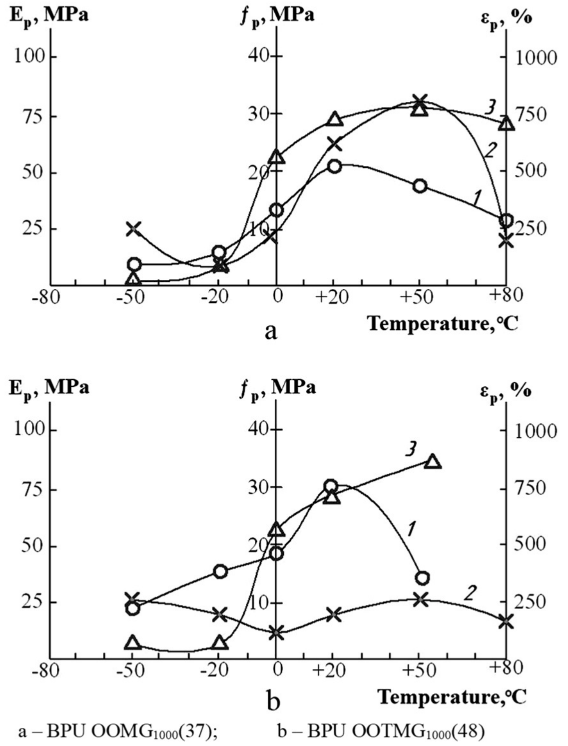

Fig. 1 Physico-mechanical characteristics of initial polyurethanes based on oligoethers (conditional tensile strength f_p (1), elastic modulus at tensile E_p (2), relative elongation at rupture ε_p (3)) at different temperatures

The behavior of the raw materials at low (negative) temperatures is due primarily to the glass transition temperature of the elastic segments microphase, which is in the range from -30°C to -20°C. With decreasing temperature rigid segments of block type limits the mobility of the elastic phase, that’s why in this temperature range low values of strength and deformation characteristics are observed [11].

At the positive region of temperatures in the range from +20°C to +50°C a maximum of values of strength and deformation characteristics is observed. At this temperature interval heating of the crystalline regions of the microphase of elastic segments occurs. The obtained results are fully consistent with the practical experience of processing and exploitation of initial polyurethanes [1, 3, 9].

PROPERTIES OF LINEAR BLOCK-POLYURETHANES BASED ON MIXTURES OF OLIGOETHERS

Oligoethers blend samples were obtained by injection moulding on an automatic thermoplastication machine with varying proportions of the starting components over the whole concentration range.

Considering the physical and mechanical characteristics of the starting BPU (Table 1), one might note almost near values of density, hardness, tensile strength, and elongation. An essential (4-fold) difference was only demonstrated by elastic modulus**.**

The character of physico-mechanical, rheological and tribotechnical characteristics change of binary mixtures of these polyurethanes is given in Table 2. Thus, at content of BPU OOTMG$_{1000}$ (48) in the mixture up to 40 mass %, there is a rapid increase in the values of conditional strength at tensile and modulus of elasticity in approximately 1,5 times. The maximum values of the wear intensity are noted in the same area. The binary mixture of this composition practically does not flow at a loading of 21.2 N and a temperature of 190°C.

Table 2
Properties BPU OOTMG$_{1000}$(37) i BPU OOTMG$_{1000}$(48) and their mixtures

Indicator	Experiment 1	2	3	4	5
Composition, mass %					
BPU OOTMG$_{1000}$ (37)	100.0	80.0	60.0	30.0	–
BPU OOTMG$_{1000}$ (48)	–	20.0	40.0	70.0	100.0
Properties					
Conditional tensile strength (**f_p**), MPa	22.5	30.3	34.1	32.1	31.3
Elastic modulus at tensile (**E_p**), MPa	60	82	100	25	15
Relative elongation at rupture (**ε_p**), %	650	625	620	625	700
Temperature of melt (**T**), °C	195±5	195±5	195±5	200±5	205±5
Indicator of melt fluidity 190 °C (**IMF**), g/10 min	0.5	0.5	0.5	2.0	>20.0
Wear intensity (while friction without lubrication: P=0.1 MPa, V=0.2 m/s) (**$I \cdot 10^4$**), g/kg	40	54	41	21	4
Coefficient of friction (**f**)	0.17	0.17	0.30	0.28	0.22

In the case of further growth of BPU fraction based on BPU OOTMG1000 (48) in the mixture from 40 to 100 mass %, there is an insignificant decrease in the values of conditional tensile strength and a rapid (almost 7 times) decrease in the elastic modulus. At the same time, the mixture exhibits a sufficiently high fluidity during heating, and the intensity of wearing monotonously decreases.

Stability or insignificant changes throughout the concentration range of such characteristics as hardness, friction coefficient and relative elongation at rupture should be noted. The stability of these characteristics indicates satisfactory compatibility of the investigated mixtures.

Thus, the analysis of the structure-property relationship (Table 2, Experiment 1.5) shows that increase of hard-phase content in the BPU molecule from 37% to 48% leads to the conditional strength at stretching 30% increase and 10 times wear resistance increase.

We can also observe the effect of strength characteristics increase for a mixture of BPU based on oligoethers, and these patterns already take place on one of the components content of 20 mass. % (Table 2, Experiment 2-4). The maximum values of strength characteristics, while the conservation of deformation, rheological and tribotechnical characteristics are at a satisfactory level, are shown by mixture based on the BPU OOTMG$_{1000}$ (37) + BPU OOTMG$_{1000}$ (48) at a ratio of 60:40.

Graphic representation of this dependencies is visually understandable, but inaccurate. Therefore, the mathematical representation of the above dependences in the form of a linear algebraic equations system is developed.

The described system is a set of functions of one argument – concentration of BPU OOTMG$_{1000}$ (48), denoted by the letter P. After approximation of each individual dependence, we obtain a set of regression equations that describe interconnection between all parameters.

For approximation of each individual dependence, the "linfit" function of the application MathCad is used. For each individual function the most appropriate degree of polynomial can vary depending on the complexity of the function behavior. If possible, polynomials of lower degrees are used. The approximating functions of another type (not polynomial) usage is not appropriate in this case, because additional restrictions of solving method occur.

After all dependencies approximation, following system of linear algebraic equations is obtained:

$$f_p\ (P) = 21.754 + 0.637P - 0.011P^2 + 5.1 \cdot 10^{-5} \cdot P^3$$

$$E_p\ (P) = 63.916 - 4.397P + 0.495P^2 - 0.014 \cdot P^3 + 1.561 \cdot 10^{-4} \cdot P^4 - 5.792 \cdot 10^{-7} \cdot P^5$$

$$\varepsilon_p\ (P) = 652.953 - 3.067P + 0.116P^2 - 1.825 \cdot 10^{-3} \cdot P^3 + 1.02 \cdot 10^{-5} \cdot P^4$$

$$T\ (P) = 194.91 + 0.097P - 7.609 \cdot 10^{-3} \cdot P^2 + 1.674 \cdot 10^{-4} \cdot P^3 - 9.088 \cdot 10^{-7} \cdot P^4$$

$$IMF\ (P) = 0.538 - 0.042P + 3.655 \cdot 10^{-3} \cdot P^2 - 1.014 \cdot 10^{-4} \cdot P^3 + 8.848 \cdot 10^{-7} \cdot P^4$$

$$I(P) = 37.869 + 2.222P - 0.092P^2 + 1.153 \cdot 10^{-3} \cdot P^3 - 4.904 \cdot 10^{-6} \cdot P^4$$

$$f(P) = 0.171 - 1.786 \cdot 10^{-3} \cdot P + 2.697 \cdot 10^{-4} \cdot P^2 - 4.688 \cdot 10^{-6} \cdot P^3 + 2.261 \cdot 10^{-8} \cdot P^4$$

The obtained system of equations can be used both to determine the characteristics of the material, produced at a given concentration of BPU OOTMG$_{1000}$ (48) and to obtain a material with preset properties, calculating the concentration of BPU OOTMG$_{1000}$ (48) for the specified values of the required characteristic.

CONCLUSIONS

Properties of BPU mixtures based on oligoethers with different content of the rigid phase are characterized by a significant increase (in a few times) of strength, deformation and tribotechnical characteristics. Improvement of properties, in our opinion, is achieved due to satisfactory combination of initial materials.

The rational level of characteristics is shown by mixtures of BPU based on oligoethers BPU OOTMG$_{1000}$ (37) and BPU OOTMG$_{1000}$ (48) is at a mass ratio of components 60:40 mass. %;

Obtained dependencies allow to predict the composition of the binary mixture with an optimal level of strength, deformation, rheological and tribotechnical characteristics.

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