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Volodymyr Anisimov

PROPERTIES OF THERMOPLASTIC POLYURETHANES BASED ON THE MIXTURES OF SIMPLE OLIGOETHERS

DVNZ «Ukrainian State Chemical Technology University»
8, Gagarina Ave., 49005 Dnipropetrovsk, Ukraine

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Abstract. The interrelation between structures and strength, deformation, rheological, and tribotechnical characteristics of thermoplastic polyurethanes based on oligoether blends has been studied. A notable change of properties over the whole concentration range was observed. The best compositions have been found.

Keywords: thermoplastic polyurethane, oligoether, physico-mechanical properties, melt flow characteristics.

1. Introduction

Production of polyurethanes with a set of required properties is still a burning problem in spite of the seemingly great number of polymers available [1, 2]. Polyurethanes are a widely used class of polymers that can be applied for production of any commercially valuable polymeric material from glues to engineering plastics including elastomers and thermoplastics. Such capabilities are mainly based on the peculiarities of their chemical structure determined by the structure of initial components used in polyurethane production [3-5].

Thermoplastic polyurethanes (TPU), which entered the world market in the early 1960s, have now become universally recognized. They are characterized by high strength and elasticity, oil and grease resistance, good impact strength and resistance to vibrations [6]. Besides, oligoether-based thermoplastic polyurethanes demonstrate hydrolytic stability, low temperature flexibility, high microbial resistance, and hence are of special interest.

Molecular weight and hard segments ratio were formerly considered the main characteristics that determine the TPU properties [7-10]. By adjusting these parameters at the stage of synthesis it is possible to produce various materials with preset performance characteristics. This approach, however, is time-consuming and costly under industrial conditions. At present, the main way of producing composite materials based on thermoplastic polyurethanes is mechanical blending of components in the melt.

The study suggests the formation of polyurethane matrix by blending materials of different chemical compositions, i.e. producing mechanical mixtures using the principle of interpenetrating networks (IPN).

2. Experimental

Thermoplastic polyurethanes based on oligoethers (polyethers) synthesized at OAO “Polymersintez” (Vladimir, Russian Federation) were chosen as the object of investigation. They were of special interest because of their enhanced hydrolytic stability, low temperature flexibility, and higher microbial resistance.

In compliance with the recommendations [7-10], the TPU selected had the ratio of hard segments in the macromolecule φ_h = 30 to 50 wt % and the molecular weight with internal viscosity $[\eta]$ = 0.8 to 1.0 dl/g. Those were industrial TPU based on polyoxytetramethylene glycol (PTMG) ether with the molecular weight of 1000, 1,4-butanediol (BD) and 4,4’-diphenyldiisocianate (MDI): ViturTM-0333-90 and ViturTM-0533-95 [6]. The main physical and mechanical properties of the starting TPU are shown in Table 1.

Table 1

Physical and mechanical properties of starting thermoplastic polyurethanes

Property	Vitur TM-0333-90	Vitur TM-0533-95
Density, kg/m^3	1080	1110
Shore A hardness number, arbitrary 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 TPU 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 TPU mixtures were evaluated by means of Instron TT-DM-4 universal machine using standard methodics. The hardness of the materials involved was studied using IIRT-M device at the load of 0.216 MPa and the temperature of 463 K.

The TPU tribotechnical characteristics were assessed using "disk – I-sample" scheme on a disk-type frictional machine at the speed of $V = 0.4$ m/s and specific load of $\rho = 0.2$ MPa [11].

The results of the study were computer-processed using Mathcad 7.0 pro program.

3. Results and Discussion

Fig. 1 shows the main physical and mechanical properties (tensile strength f_t , elastic modulus E, elongation at rupture ε_r of the starting TPU at various temperatures (223 to 353 K)

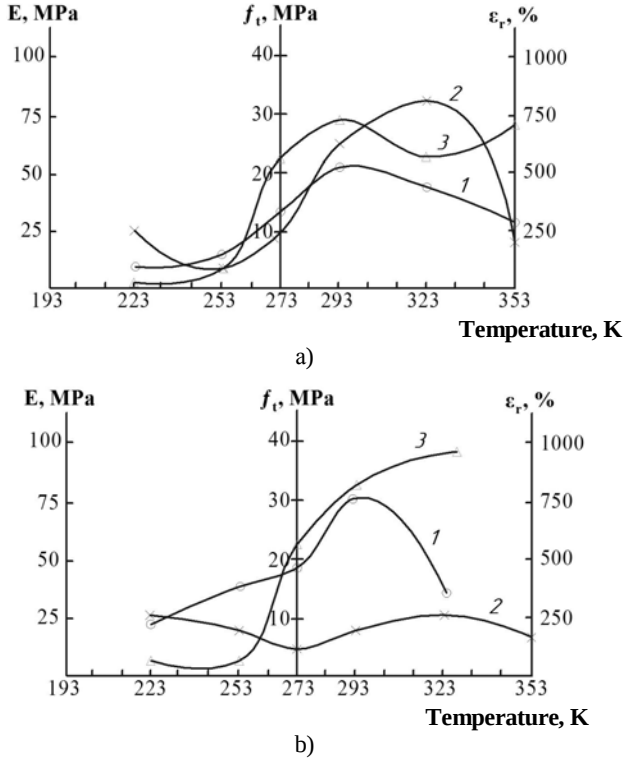

Fig. 1. Physical and mechanical properties of the starting oligoether-based polyurethanes (tensile strength f_t , elastic modulus E, elongation at rupture ε_r of the starting TPU at various temperatures: Vitur TM-0333-90 (a) and Vitur TM-0533-95 (b)

The behavior of the starting materials at low (negative) temperatures was conditioned primarily by the vitrification temperature of the soft segment microphase, which ranged from 253 to 243 K. As the temperature decreased hard-block-like segments started to limit the movability of the flexible phase. That is why worse strength and deformation characteristics were observed in this area.

Maximum values of strength and deformation characteristics were observed over the positive range of temperatures (293 to 323 K). It was within this temperature interval that crystalline areas of soft segment microphases melted down [4, 5]. The results fully agreed with the practical experience of processing and application of the starting polyurethanes.

3.1. Properties of Thermoplastic Polyurethanes Based on Polyether Blends

Polyether 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 TPU (Table 1), one might note practically the same values of density, hardness, tensile strength, and elongation. An essential (4-fold) difference was only demonstrated by elastic modulus**.**

A different pattern of changes in physical, mechanical, rheological, and tribotechnical properties was observed in binary blends of the above polyurethanes. Thus, a slight addition of Vitur TM-0533-95 to a blend (up to 20 parts by weight) resulted in a sharp decrease of tensile strength values (more than two-time), and of elastic modulus (more than twentyfold). No wonder that the highest wear rate values is observed in this area. The binary blend of this composition did not practically flow at the load of 0.261 MPa and the temperature of 463 K (Fig. 2).

Further addition of TPU based on Vitur TM-0533-95 up to 40 wt % resulted in a sharp increase of strength values (tensile strength – over 4-time increase; elastic modulus – more than 30-time increase). At the same time, the blend demonstrated sufficient melt flow characteristics, while wear-out rate tended to its minimum (Fig. 2).

The further increase of the proportion of TPU based on Vitur TM-0533-95 in a blend from 40 to 100 wt % caused a small decrease in tensile strength values and a rapid decrease (nearly to one seventh of its value) in elastic modulus (Fig. 2)**.**

It should be noted that such characteristics as hardness, friction coefficient and elongation at rupture

were stable or only slightly changed over the whole concentration range. The stability of these properties confirms a good compatibility of the blends (Fig. 2).

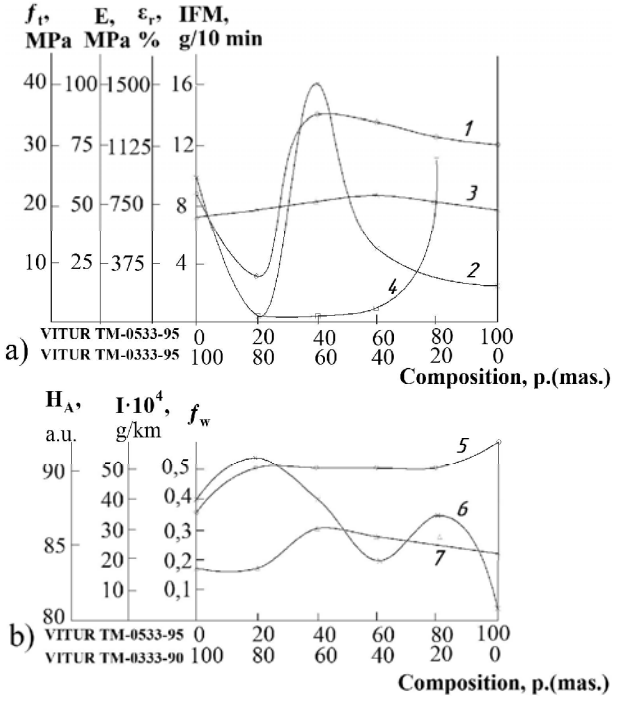

Fig. 2. Dependencies of conventional strength at elongation f_t (1); elastic modulus E (2); conditional elongation at break ε_r (3); indication of fluidity of melt IFM (4); shore hardness (5); intensity of wearing I (6) and coefficient of friction f_w (7) for mixtures of thermoplastic polyurethanes, based on simple oligoether upon its composition

Thus, from the point of view of strength, deformation and tribotechnical characteristics, TPU blends based on the two starting components: Vitur TM-0333-90 and Vitur TM-0533-95 in the ratio of 60 to 40 wt % respectively, demonstrate the optimum values.

4. Conclusions

1. When blended, thermoplastic polyurethanes based on oligoethers Vitur TM-0333-90 and Vitur TM-0533-95 demonstrate considerable (several fold) changes in the values of strength, deformation and tribotechnical characteristics. The enhanced properties, in our opinion, are the result of good compatibility of the starting materials.

2. Optimum characteristics are demonstrated by TPU blends when the ratio of the starting components Vitur TM-0333-90 and Vitur TM-0533-95 is 60 to 40 wt % respectively.

3. The study shows an easy way of producing binary blends with preset characteristics under the conditions of any plastics processing enterprise. These results allow using the obtained products under the best conditions for every particular case.

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ВЛАСТИВОСТІ ТЕРМОПЛАСТИЧНИХ ПОЛІУРЕТАНІВ НА ОСНОВІ СУМІШЕЙ ПРОСТИХ ОЛІГОЕТЕРІВ

Анотація. *Розглянуто взаємозв'язок будови із міцнісними, деформаційними, реологічними і триботехнічними характеристиками поліуретанових термопластів на основі сумішей простих олігоетерів. Встановлено суттєву зміну властивостей у всьому концентраційному діапазоні та визначено оптимальний склад композицій.*

Ключові слова: *термопластичний поліуретан, простий олігоетер, фізико-механічні характеристики, плинність розплаву.*