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Mechanical Properties of Hybrid Materials Based on Aliphatic Polyurethanes and Al_2O_3 Nanoparticles

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Abstract: *In this research, hybrid materials based on aliphatic polyurethanes and hydrophilic aluminum(III) oxide nanoparticles were synthesized. From an environmental point of view, synthesized hybrid materials represent significant engineering materials because the products of their thermal degradation are significantly less toxic compared to the products of thermal decomposition of polyurethane, for which production aromatic isocyanates are used. The presence of uniformly distributed Al_2O_3 nanoparticles in the sample containing 0.5 wt. % of inorganic filler influenced the additional formation of hydrogen bonds, as well as the improvement of the mechanical properties of the obtained polyurethane hybrid materials. Good mechanical properties, together with appropriate properties of thermal stability, allow the obtained hybrid materials based on aliphatic polyurethanes and Al_2O_3 inorganic filler to be used in the automotive industry (hydraulic seals, protective films), furniture and in the production of sports equipment.*

Keywords: *hybrid materials, aliphatic polyurethanes, Al_2O_3 nanoparticles, mechanical properties.*

1. INTRODUCTION

Hybrid polymer materials are attracting the attention of scientists worldwide due to many advanced properties compared to traditional composites. One of the most successful examples of this materials are composites obtained by incorporating the structural material into another substance, which represents a matrix, most often in the form of particles, fibers, lamellae or networks. Most of the resulting materials show improved mechanical properties. Today, this concept is intensively applied to obtain materials with exceptional mechanical properties that are used for various applications in numerous industrial branches.

Segmented polyurethanes and their nanocomposites, due to their exceptional application properties such as breaking strength, flexibility, chemical and abrasive resistance, are widely used in the automotive industry (hydraulic seals, protective films), furniture and in the production of sports equipment [1, 2].

From the environmental protection and sustainable development point of view, the appropriate choice of initial components is very important for the structuring of segmented polyurethanes and their nanocomposites. Thanks to their biostability and biocompatibility, they are used as "green" materials in the function of environmental protection [3, 4, 5].

Considering that thermoplastic polyurethane elastomers are multiphase and multicomponent materials (composed of heterogeneous blocks at the micro level), their thermal and mechanical properties are highly dependent on the degree of their phase separation. The presence of physical knots, instead of chemical ones, enables easier processing of polyurethane materials at high temperatures. The structure of the thermally reversible network of segmented polyurethanes provides them with elastomeric or apparently cross-linked properties. Thanks to the separation of phases, linear polyurethane elastomers have some properties of cross-linked elastomers, but unlike them, they can be processed by thermoplastic polymer processing procedures, so they are called thermoplastic elastomers [6, 7]. The modification of thermoplastic segmented polyurethanes based on polycarbonate diol with various nanoparticles and organic clays of a layered structure is the subject of numerous studies, with the aim of investigating the influence of the nanofillers addition on the structure and morphology of the obtained polyurethane nanocomposites, as well as improving their thermal and mechanical properties, thermal stability, and gas permeability [8]. The obtained polyurethane hybrid materials, due to the realized synergistic effect of nanofillers and a complex multi-component polyurethane system, showed improved thermal stability, dynamic-mechanical, as well as thermal and mechanical properties. It was determined that the addition of aluminum (III) oxide nanoparticles affects the increase in the degree of phase separation of soft and hard segments, as well as the improvement of mechanical properties [8 ,9, 10, 11]. The aim of this paper was to investigate the influence of the addition of different mass fractions of hydrophilic Al_2O_3 nanoparticles on the mechanical properties of thermoplastic polyurethane elastomers based on aliphatic non-toxic starting components, as well as the possibility of their application.

2. MATERIALS AND METHODS

All aliphatic components were used for the synthesis of multicomponent polyurethane systems. Hexamethylene diisocyanate (HMDI) (diisocyanate component) and 1,4-butane diol (chain extender) from the manufacturer Fluka were used as the building blocks of the hard segments, while the soft segments came from polycarbonate diol with a molar mass of about 100 g/mol (Asahi Kasei Corporation). The reaction to obtain polyurethane elastomers was catalyzed by a solution of dibutyl-tin-dilaurate, manufactured by Fluka. To obtain polyurethane hybrid materials, hydrophilic nanofillers of aluminum (III) oxide, produced by Evonik Industries, under the commercial name Alu C, were used. The particle size was 13 nm, and the specific surface area 100 m^2/g (data provided by the manufacturer).

Polyurethane nanocomposite elastomers (Table 1) with different content of hydrophilic Al_2O_3 nanoparticles (0.5, 1.0, 2.0 and 3.0 wt. %) were obtained in a one-step synthesis procedure (Figure 1). During the synthesis of segmented elastomers, the number of hydroxyl groups from the aliphatic polycarbonate diol and from the chain extender was equal ($R = [OH]_{diol}/[OH]_{BD} = 1$), and HMDI was added in excess $[NCO]/[OH] = 1.05$) [2]. Based on the mass of the initial components, the calculated share of hard segments of all samples was about 28 mass. %. In the first step, aluminum (III) oxide nanoparticles were added to a reaction flask with an aliphatic polycarbonate part, and after that, for the homogenization, mixing was carried out for 2 days. The chain extender, 1,4-butanediol, was added in a second step, after which stirring was applied for 2 h to achieve homogeneity of the mixture. The DBTDL catalyst solution (25%) was added to the reaction flask. After that, in the last step of the synthesis, the diisocyanate component was added. After 30 minutes of mixing (reaction between -NH and OH groups), the balloon with the reaction mixture was placed on the degassing system to remove any residual CO_2 bubbles. The prepared multicomponent mixture was poured using a microknife with a thickness of 350 μm onto polyethylene plates, in order to obtain polyurethane nanocomposites in the form of a film. Crosslinking of the reaction mixture lasted 26 h in a vacuum oven at 90 °C.

Table 1. *Sample name and composition of polyurethane thermoplastic materials based on polycarbonate diol, modified by the addition of different content of Al_2O_3 nanoparticles*

Sample name	Poly-carbonate diol	Al_2O_3 content [wt. %]	Hydrogen bonding index [%]
PU0	T5651	0	80.5
PU-0,5% AluC	T5651	0.5	83.5
PU-1,0% AluC	T5651	1	75.4
PU-2,0% AluC	T5651	2	65.6
PU-3,0% AluC	T5651	3	60.2

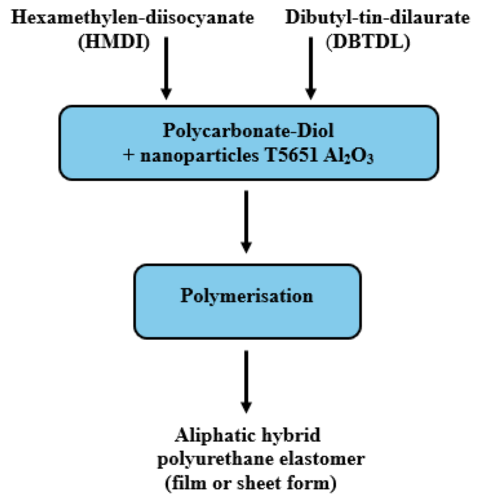

Figure 1. *Schematic representation of the one-step synthesis procedure of aliphatic hybrid polyurethane elastomer.*

A Nicolet Nexus 670 FTIR spectrometer was used to examine the chemical structure of nanocomposites based on aliphatic polyurethanes, the formation of new hydrogen bonds and the effect of the addition of nanoparticles on the separation of soft and hard domains. Absorptions were measured with a resolution of 2 cm^{-1}, in the infrared region in the range of wave numbers from 4000 to 500 cm^{-1}.

Stress-strain diagram was determined on an Instron model 6025 instrument, producer Instron Limited, England (constant speed, 10 mm/min, at room temperature). For testing the mechanical properties of aliphatic hybrid polyurethane elastomers, tubes size 25x4x1 mm, were used. As output data, the values of tensile strength σ, breaking elongation ε and Young's modulus of elasticity E were obtained.

3. RESULTS AND DISCUSSION

Data obtained after testing the mechanical properties of unmodified aliphatic polyurethane, as well as nanocomposite samples with 0.5; 1.0; 2.0 and 3.0 wt. %, of hydrophilic Al_2O_3 particles (values of tensile strength, maximum elongation and Young's modulus of elasticity) are shown in Table 2 and in Figure 2.

Table 2. *Mechanical properties of nanocomposites based on polyurethane and different content of hydrophilic nanoparticles Al_2O_3 (Alu C).*

Sample name	Tensile strength *σ* [MPa]	Modulus of elasticity *E* [MPa]	Maximum elongation A_{maks} [%]
PU-T5651-0,0	41.58	53.38	450
PU-T5651-0,5%AluC	50.11	54.28	462
PU-T5651-1,0%AluC	28.5	70.25	325
PU-T5651-2,0%AluC	12.94	19.28	275
PU-T5651-3,0%AluC	7.97	10.39	175

Based on the data shown in Table 2, it can be seen that the presence of a small amount of hydrophilic nanoparticles of aluminum(III) oxide (0.5 wt. %) affects the improvement of the values of mechanical properties, tensile strength (from 41.58 to 50.11 MPa), modulus of elasticity (from 53.38 to 54.28MPa) and maximum elongation (from 450 to 462%) of synthesized hybrid materials based on aliphatic polyurethanes and hydrophilic Al_2O_3 nanoparticles, compared to the pure sample, without the addition of filler nanoparticles.

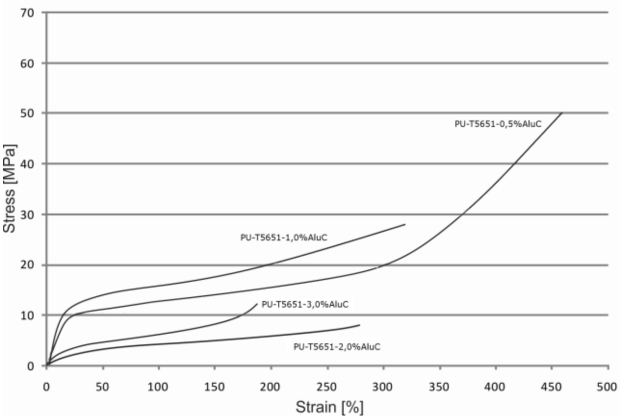

Figure 2. Stress/strain diagram for hybrid samples based on polyurethane and different content of hydrophilic *Al_2O_3* particles*.*

In all other samples (with a content of 1.0, 2.0 and 3.0 wt. % of hydrophilic Al_2O_3 nanoparticles) there was a drastic decrease in the value of the mechanical properties, which is in accordance with the results obtained for the hydrogen bonding index (Figure 3, Figure 4 and Table 1).

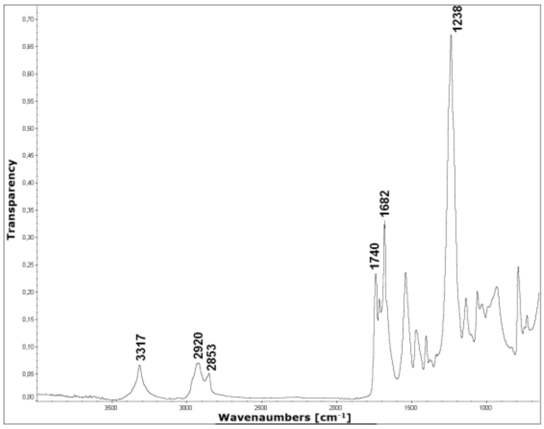

Figure 3. FTIR spectrum of polyurethane nanocomposite, obtained by using polycarbonate diol (T5651), with 0.5 wt. % of Al_2O_3 nanoparticles (Alu C).

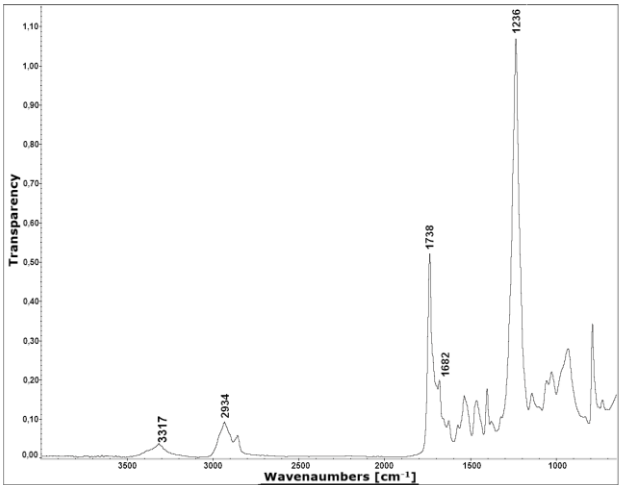

Figure 4. FT-IR spectrum of the polyurethane nanocomposite, obtained by using polycarbonate diol (T5651), with 3.0 wt. % of AluC nanoparticles.

4. CONCLUSION

In this research, hybrid materials based on aliphatic polyurethanes and small amounts of hydrophilic aluminum (III) oxide nanoparticles (0.5, 1.0, 2.0 and 3.0 wt.%) were synthesized. The best mechanical properties were determined for the hybrid material based on polyurethane with 0.5 wt. % Al_2O_3 (value of tensile strength - 50.11 MPa, Young's modulus of elasticity - 50.28 % and maximum elongation of 462%). The greatest decrease in breaking strength was observed in the polyurethane film with the highest proportion of Al_2O_3 nanoparticles (3.0 wt. %). A sample with 1.0 wt. % Al_2O_3 has the highest value of Young's modulus of elasticity - 70.25%, but significantly lower values of tensile strength (28.5 MPa) and elongation (325%) The obtained results of testing the mechanical properties of hybrid materials based on aliphatic polyurethanes and different proportions of Al_2O_3 nanoparticles are in accordance with the index values of hydrogen bonds. Good mechanical properties, together with appropriate properties of thermal stability, enable the application of these hybrid materials in the automotive industry (hydraulic seals, protective films), furniture and in the production of sports equipment.

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