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## EVALUATION OF INFLUENCE OF THE ADDITION NANOFILLERS ON THE MECHANICAL AND THERMAL PROPERTIES TERPOLYMERS ESTER-ETHER-AMIDE

## OCENA WPŁYWU DODATKU NANONAPEŁNIACZY NA WŁAŚCIWOŚCI MECHANICZNE I TERMICZNE TERPOLIMERÓW ESTROWO-ETEROWO-AMIDOWYCH

The results of studies of mechanical and thermal properties of synthesized elastomeric nanocomposites have been presented. An elastomeric multiblock terpoly(ester-b-ether-b-amide)s as polymeric matrix and nanoparticles SiO<sub>2</sub> i TiO<sub>2</sub> used as fillers. It was shown that the introduction of multiblock thermoplastic elastomer matrix of SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles allows to obtain nanocomposite materials with improved mechanical properties compared to the terpolymer before modification. An increase in glass transition temperature, which has a positive effect for the processing of terpolymers.

*Keywords:* thermoplastic elastomers, nanocomposites, mechanical properties

Zbadano właściwości mechaniczne i termiczne syntezowanych nanokompozytów elastomerowych. Osnowę polimerową stanowił elastomer multiblokowy terpoli(estro-etero-amidowy), w roli napełniacza zaś zastosowano nanometryczny SiO<sub>2</sub> i TiO<sub>2</sub>. Wykazano, że wprowadzenie do matrycy multiblokowego elastomeru termoplastycznego nanocząstek SiO<sub>2</sub> i TiO<sub>2</sub> pozwala na otrzymanie materiału nanokompozytowego o polepszonych właściwościach mechanicznych w porównaniu z wyjściowym terpolimerem. Stwierdzono wzrost temperatury zeszklenia, co ma korzystny wpływ na przetwórstwo terpolimerów.

### 1. Introduction

Polymer nanocomposites are used in a variety of industries as products for the electronics, construction as well as for medicine. There are known nanocomposites with thermoplastic matrices, duroplastic or elastomer. The use of different nanofillers allows modeling properties of materials in the direction of obtaining the best possible interaction with the matrix, and which translates into the properties of the final product [1].

The aim of this study was to obtain and examine the properties of polymer nanocomposites, where matrix was multiblock thermoplastic elastomer – terpoly(ester-b-ether-b-amide)s – (BS-b-PTMO-b-PA12)<sub>n</sub> – consisting of an oligoester hard segment BS and oligoamide hard segment PA12. Soft segment was oligo(4,4'-oxydiphenylene)tetramethylene diol (PTMO). Nanometric SiO<sub>2</sub> and TiO<sub>2</sub> as a reinforcing phase were used.

### 2. Materials and methods

Multiblock terpolymers, terpoly(ester-b-ether-b-amide) – (BS-b-PTMO-b-PA12)<sub>n</sub> – with oligoamide – oligo(4,4'-oxydiphenylene)tetramethylene diol (PTMO) – soft block and oligo(butylene se-

bacate) were obtained. As oligoester hard block (BS) was used prepared by esterification reaction of sebacic acid (SA) with 1,4-butanediol (BD-1,4). Synthesis of the terpolymer described in the publications [2-5].

Mechanical and thermal study were terpolymer –(BS-b-PTMO-b-PA12)<sub>n</sub>– does not contain nanoparticles, as well as received on the basis of nanocomposites with SiO<sub>2</sub> and TiO<sub>2</sub>. Nanocomposites containing 0.2 wt % SiO<sub>2</sub> (Aerosil®805, Evonik Degussa) or TiO<sub>2</sub> (Aeroxide®P25, Evonik Degussa) as the corresponding terpolymer prepared without the addition of nanoparticles by in-situ polycondensation of maintaining the same parameters of synthesis. Before the process nanofiller is dispersed in the liquid monomer by means of ultrasound (sonicator Hilscher, Germany), with a frequency of 24 kHz, the amplitude of the cycle 70% in 30 min.

The limiting viscosity number ([ $\eta$ ], LVN) of the poly[ether-block-ester-block-amide] terpolymers in phenol-trichloroethylene (50:50%vol.) was determined by an Ubbelohde viscometer IIA at 30°C.

Hardness (H) measurements were performed on a Shore D apparatus (Zwick, type 3100) according to standard PN-ISO 868.

The quasi-static tensile data were collected at room temperature with an Instron TM-M tensile tester equipped with

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Composition and selected properties of the terpolymers

Lp	Composition [mol]				DP <sub>BS</sub>	addition	[ $\eta$ ] dl/g	H ShD	E MPa	$\sigma$ MPa	$\epsilon$ MPa
	PTMO	PA12	KS	1,4-BD							
1	2	1	5	9	4	-	0,37	34	7,5 $\pm$ 0,7	7 $\pm$ 0,2	280 $\pm$ 8,5
2	2	1	5	9	4	0,2% wag SiO <sub>2</sub>	0,75	38	18 $\pm$ 1,4	9,5 $\pm$ 0,8	250 $\pm$ 34,5
3	2	1	5	9	4	0,2% wag TiO <sub>2</sub>	0,92	40,5	25 $\pm$ 1,2	12,5 $\pm$ 0,4	238 $\pm$ 54,3

\*/ notations were explained in experimental part

a 500 N load cell employing a crosshead speed of 100 mm/min to standard PN-EN-ISO 527-1:1998. The starting clamp distance was 25 mm. The obtained results were averaged from 6 specimens with cross section of 0.5 $\times$ 4 mm.

The differential calorimetric method were recorded on a TA Instruments (DSC Q100) apparatus. The samples were examined in a triple cycle (heating-cooling-heating) in the temperature range from -100 $^{\circ}$ C to +250 $^{\circ}$ C. The heating and cooling rates were 10 $^{\circ}$ C min<sup>-1</sup>.

The dynamical mechanical analysis (DMA) were performed on a DMA Q-800 modulus (TA-Instruments) in the temperature range from -100 to +125 $^{\circ}$ C at 35 Hz. The storage modulus E', loss modulus E'', and loss tangent tan $\delta$  were determined.

### 3. Results and Discussion

The basic physical and chemical properties of the terpolymer -(BS-b-PTMO-b-PA12)<sub>n</sub>- before and after the modification of SiO<sub>2</sub> and TiO<sub>2</sub> are shown in Table 1. Terpolymers after modification of nanofillers are characterized by an increase in both hardness and limiting viscosity numbers.

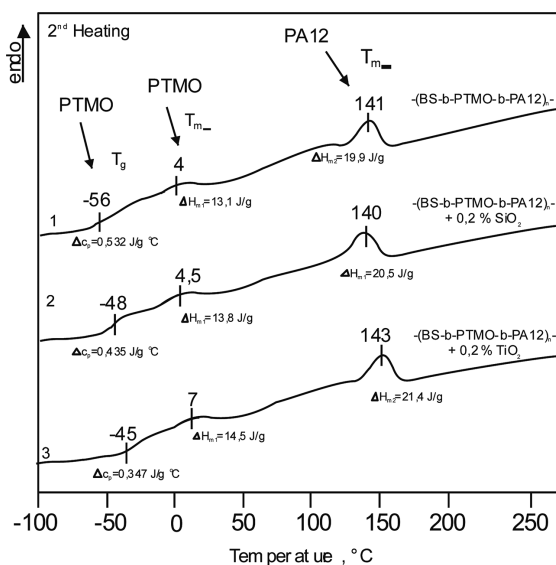


Fig. 1. DSC 2<sup>nd</sup> heating thermograms of the -(BS-b-PTMO-b-PA12)<sub>n</sub>- terpolymers before and after modification of SiO<sub>2</sub> i TiO<sub>2</sub>

For the identification of temperature phase transition of terpolymer and nanocomposites obtained with SiO<sub>2</sub> and TiO<sub>2</sub> tests were carried out by the DSC method. Figure 1 shows the results of the second heating of the polymers.

The terpolymer and the resulting nanocomposites are characterized by low-temperature glass transition ( $T_g$ ) attributed to soft segments phase derived from PTMO. The glass transition temperature range after modification of nanofillers moves to higher temperatures suggesting the placement of nanoparticles in the amorphous phase of the soft segment. In case of application of nanometric TiO<sub>2</sub> increase of the glass transition temperature is higher than when SiO<sub>2</sub> for modification of material were used. For terpolymers containing nanoparticles there were no significant changes in the crystalline phase derived from both the segments soft PTMO and hard PA12.

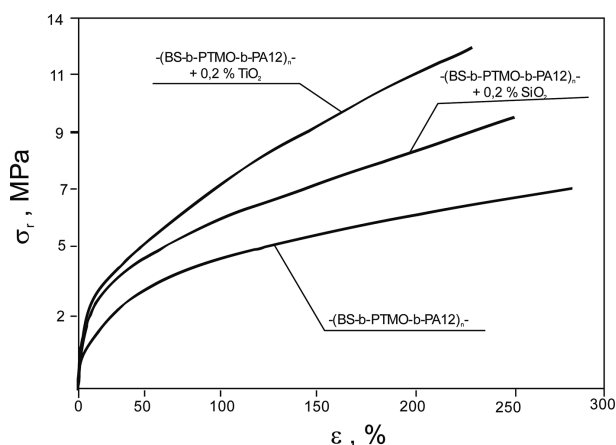


Fig. 2. Stress-strain curves for investigated -(BS-b-PTMO-b-PA12)<sub>n</sub>- terpolymers before and after modification of SiO<sub>2</sub> i TiO<sub>2</sub>

On Figure 2 are presented stress-strain curves, while Table 1 shows the results of measurements of the mechanical properties for the -(BS-b-PTMO-b-PA12)<sub>n</sub>- before and after the modification of SiO<sub>2</sub> and TiO<sub>2</sub>. Nanocomposites are characterized by an increase of the module and tensile strength, and a slight decrease of elongation at break was observed. TiO<sub>2</sub> modified terpolymer is characterized by a higher tensile strength values than the terpolymer modified by SiO<sub>2</sub>. These results indicate that the addition of nanofiller positively influences to improve the mechanical properties, acting at the same time reinforcement for multiblock terpolymer matrix.

Spectra of storage modulus  $E'$  of terpolymers  $-(BS-b-PTMO-b-PA12)_n-$  (Fig. 3) characterize different temperature ranges where values of  $E'$  change with the change after modification of  $SiO_2$  and  $TiO_2$ .

In the temperature range from  $-100^\circ C$  to  $-50^\circ C$  functions  $E' = f(T)$  have a flat course, the modulus does not change and  $-(BS-b-PTMO-b-PA12)_n-$  is in the glassy state.

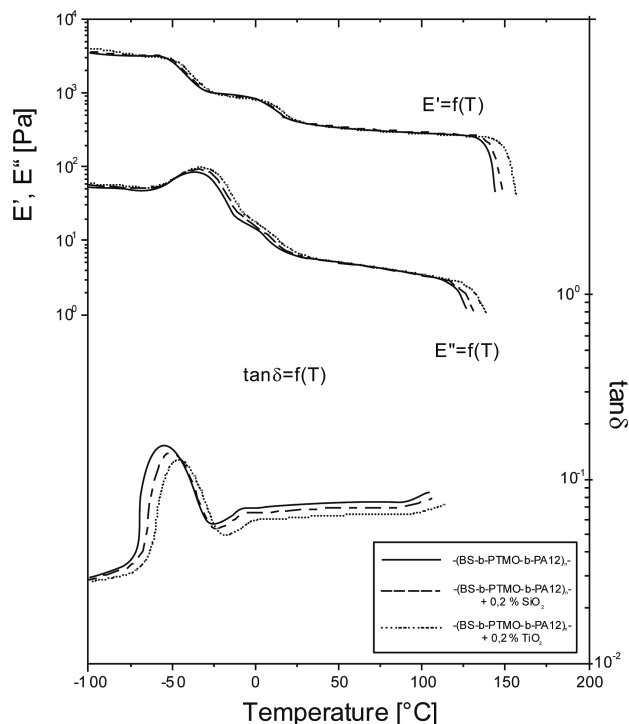


Fig. 3. The storage modulus  $E'$ , the loss modulus  $E''$ , and the loss tangent  $\tan \delta$  of  $-(BS-b-PTMO-b-PA12)_n-$  terpolymers before and after modification of  $SiO_2$  i  $TiO_2$  versus temperature

In the interval from  $-50^\circ C$  to  $-25^\circ C$  modulus occur decreases and in the macromolecules there is viscoelastic relaxation processes connected with the glass transition of amorphous phase of the PTMO soft block. This interval moves towards higher temperatures after modification  $SiO_2$  and  $TiO_2$ . The third temperature range is a 'flexibility plateau', the modulus in this interval is constant. The fourth region observed in the temperature range  $0^\circ C$  to  $25^\circ C$  is characterized by a further slight decrease of the modulus associated with the melting of the crystalline phase transformation of the PTMO soft block.

For the terpolymer after modification  $TiO_2$  melting transition of the PTMO is observed in higher temperatures compared to the  $SiO_2$ , which was confirmed in the DSC studies.

In the temperature range of  $80^\circ C$  to  $130^\circ C$  terpolymers achieve the predominance of viscous on elastic properties, and their storage modulus is rapidly declining.

Inflection on the curves related to this decrease determine temperature of polymer softening, and therefore also the upper temperature range of applicability decreasing after modification of nanofillers. On the curves  $E' = f(T)$  and  $\tan \delta = f(T)$   $-(BS-b-PTMO-b-PA12)_n-$ , there is a maximum of  $\alpha$  relaxation associated with glass transition temperature of PTMO overlapping with the results of DSC.

#### 4. Conclusion

The addition of a thermoplastic elastomer multiblock structure of  $SiO_2$  and  $TiO_2$  nanoparticles, allowing to obtain a nanocomposite material with improved mechanical properties in comparison with the initial terpolymer. Even a small amount of nanoparticles (0.2%). Increases the glass transition temperature, resulting in to improve the physicochemical properties of  $-(BS-b-PTMO-b-PA12)_n$  terpolymers.

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