

RELAXATION PROCESSES IN POLY (ESTER-*b*-AMIDE) THERMOPLASTIC ELASTOMER CONTAINING POLY(BUTYLENE SEBACATE) SEGMENTS

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Abstract. A poly(ester-*block*-amide) multiblock copolymers containing an aliphatic ester: poly(butylene sebacate), which plays role of a soft block and polyamide PA12 as a hard or rigid block, were synthesized in some different compositions during three-step process. An investigation of their physical properties by such experimental techniques as DSC, DMTA, and DETA (dielectric spectroscopy) were performed to recognize of phase structure of these materials. There was find that this structure becomes more complex in samples with high soft phase contents (above 40 wt.%), which reflects mostly onto dielectric spectra of these materials.

1. INTRODUCTION

Problems with pollution of environment caused the search of such a materials which are either easy to recycle or susceptible to degradation itself. Newly synthesized in our laboratory poly(ester-*block*-amide) (PEA) containing an aliphatic ester: poly(butylene sebacate) (which is a biodegradable compound [1]) should to fulfill the above second condition. A polyamide PA12 plays the role of a hard or rigid block, while the above mentioned butylene sebacate as a soft block has been used.

The main aim of this work was to recognize the basic properties and phase structure of the mate-

rial and to examine how the content of soft (W_s) and hard segments (W_h), i.e. the W_s/W_h ratio reflects onto the phase structure and relaxation properties of this copolymer. There was also interesting to compare this polymer with other poly(ester-*block*-amide)s which were investigated previously in our laboratories. In the last ones, the ester and amide blocks play just opposite role than in the new material presented here [2].

The applied experimental techniques were: calorimetric (DSC), mechanical analysis (DMTA), and dielectric spectroscopy (DETA). Copolymers with W_s within 20 to 70 wt.% were prepared adequate to each experiment condition.

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2. SYNTHESIS AND FORMULA OF POLYMERS

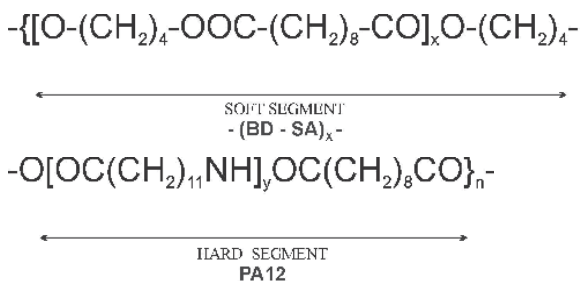
Materials

The following materials were used to synthesize multiblock copolymers: 1,4-butanediol (1,4-BD, BASF), dodecano-12-lactam (lauro lactam, Aldrich Chemie), sebacic acid (Aldrich Chemie).

Synthesis

Poly(ester-*block*-amide)s were obtained in a three-step process: oligoamide preparation, esterification, and polycondensation in the melt. All the reactions were carried out in a pressurized autoclaves.

The condensed formula of the final product can be expressed as below:



where: PA12 – polilauro lactam, m.w. 2000, DP polymerisation degree of PA12, $y \approx 10$; SA – residue of sebacic acid; BD – residue of 1,4-butanediol; x – degree of polymerisation of the poly(butylene sebacate) changed from 1.7 to 17.9

As a result of these processes, a number of copolymers with different ratio W_s/W_h , (i.e. soft segment content to hard segment one), has been obtained and used to preparation of the samples with respect to the experimental techniques requirement. Details of the synthesis are previously described in [3].

3. PREPARATION OF THE SAMPLES

The polymers samples studied by DSC, DMTA, and DETA methods were prepared by pressing under pressure 25 MPa. In this method, the temperature was maintained 5 °C higher than melt temperature of every polymer. The form of samples was prepared adequately to requirements of used methods. The samples for DETA method were covered by aluminium electrodes (the thickness of samples were 0.01 mm). The sample designation and some characteristic temperatures are presented in Table 1.

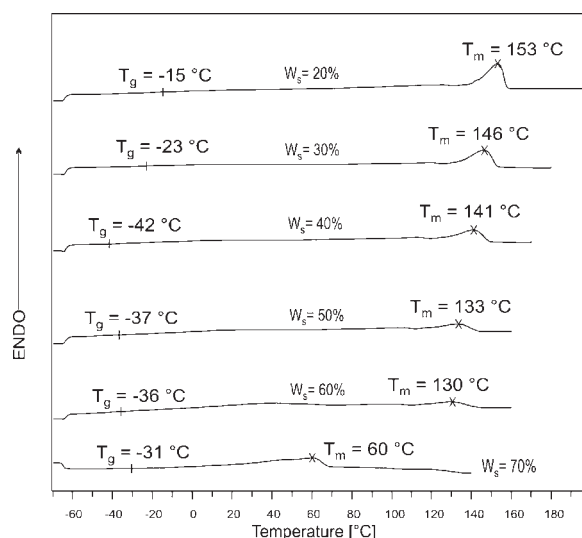


Fig. 1. Scheme of DSC- plots of the poly(ester-*b*-amide)s with different soft segment contents (W_s).

4. INVESTIGATION (DSC, DMTA, DETA)

Differential scanning calorimetry (DSC) measurements were performed using the Mettler Toledo set, in the cycle of heating-cooling-heating, with the heating rate of 10 °C per minute and in the temperature range from -100 °C to +200 °C.

DMTA- measurements were performed using the DMTA Polymer Laboratories Mk-II set at the frequency of 1 Hz and the temperature rate 1 °C/min.

Dielectric spectroscopy measurements were done by means the Hewlett-Packard Impedance Analyser type HP 4192A connected with a nitrogen thermostate, within the frequency range 0.1 to 1000 kHz and temperatures -150 °C to 120 °C. Samples in a form of a thin, flat disc were equipped with aluminium electrodes. The measured value was the complex dielectric permittivity $\epsilon^* = \epsilon' - j\epsilon''$. More detail on this measurements are described previously [2].

5. RESULTS AND DISCUSSION

5.1. Results of the DSC investigation

The DSC thermograms obtained at 2nd heating scans of the poly(ester-*b*-amide)s are shown in Fig. 1. They expressed essential differences in their form. This

Table 1. The characteristic temperature points for some samples.

Sample No.	W_s [wt.%]	W_h [wt.%]	x	T_m DSC [K]	T_g DSC [K]	T_α DMTA [K]	T_0 DETA [K]
A20	20	80	1.7	426	258	275	279
A30	30	70	3.1	419	250	259	271
A40	40	60	4.9	414	231	252	266
A50	50	50	7.5	406	236	246	259
A60	60	40	11.4	403	237	244.4	247
A70	70	30	17.9	333	242	243.7	249

T_m – melting temperature from DSC data,

T_g – glass transition temperature from DSC data,

T_α – temperature of max. ($\tan \delta$) from DMTA at 35 Hz,

T_0 – extrapolated glass relaxation temperature from dielectric spectroscopy, x - polymerization degree of soft segment.

form come from different soft-to-hard segment ratio of the used samples. Only one low-temperature glass transition has been observed in each sample. This fact indicates that there is one homogeneous, amorphous phase [4]. The glass temperature T_g varies within: -42 °C and -15 °C for samples with different W_s . The dependence of T_g versus W_s is not monotonic and it reaches a minimum for $W_s = 40$ wt.%.

This fact could indicate that mutual miscibility of the soft and hard segments. This is most intensive at this soft phase content.

In this study T_m presents a high temperature melting point of the PA12 which enriches the hard phase. The decreasing values of T_m with increasing soft segment contents enhance a mutual parity miscibility of the two phases in the poly(ester-*b*-amide)s.

5.2. Results of DMTA study

Fig. 2 shows the results of dynamic mechanical thermal analysis: a storage modulus E' and loss tangent ($\tan \delta$) as a function of temperature. At low temperatures: $E'(T)$ of the PEA is high and thus, typical for the glassy state (Fig. 2A). As the temperature is increased, E' decreases slightly over the transition from the glassy to the rubber-like state, i.e. glass transition. In the high temperature region, a distinct drop of E' – value is observed which can

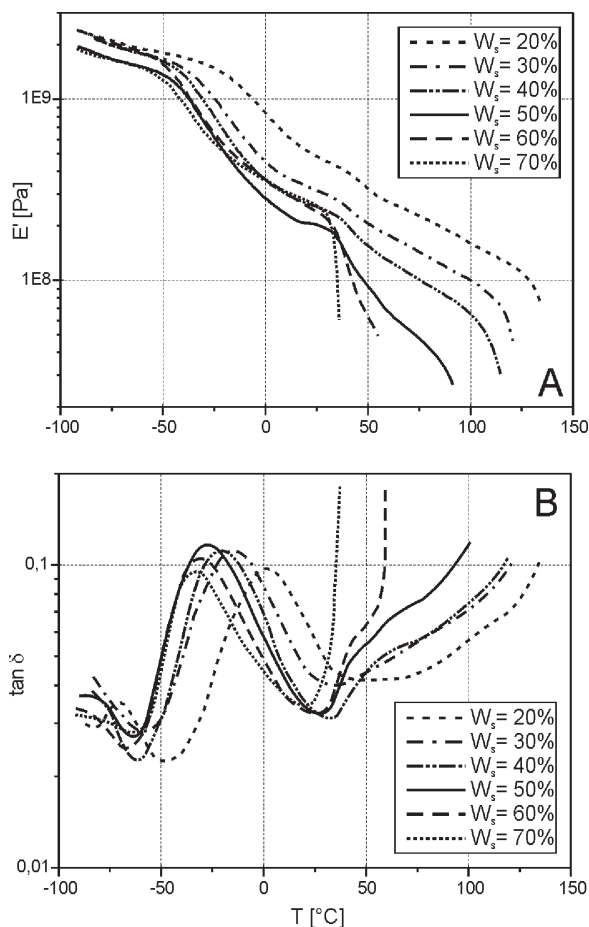


Fig. 2. DMTA- plots: storage elastic modul E' and the loss tangent $\tan(\delta) = E'/E''$ at 1 Hz of frequency for all samples of the poly(ester-*b*-amide) .

be related to a transition from the high-elasticity state to the plastic state of the PEA. The loss tangent ($\tan\delta$) run (Fig. 2B) shows one maximum at low temperatures which can be attributed to the high homogeneous, amorphous oligoester phase transition (i.e. relaxation process associated with the low-temperature glass transition).

5.3. Results of dielectric spectroscopy (DETA)

The dielectric spectroscopy have been used for segmental molecular dynamics study of PEA block copolymer. One of the spectra, in a form of the temperature dependences of the ϵ' and ϵ'' for the sample with maximal value of W_s , are presented in Figs. 3A and 3B.

For the samples with $W_s \geq 50$ wt.% the $\epsilon'(T)$ plots have unusual, two-step shape at all frequencies used during the measurements (Fig. 3A), while at lower W_s they show more simple, one-step runs. This fact has not an endorsement in the $\epsilon''(T)$ -plots; a high electric conductance (or eventually so-called MWS-effect [3]) covers up the high temperature region (Fig. 3B). In such case the data can to be transformed into a form of the *dielectric modulus* according to the equation:

$$M^* = \epsilon' / (\epsilon'^2 + \epsilon''^2) - j\epsilon'' / (\epsilon'^2 + \epsilon''^2) = M' - jM'' \quad (1)$$

where M' and M'' are not sensitive to conductance contribution [5]. In Fig. 3C, temperature dependence of the M'' for the same sample: A70, is presented. One can see a second peak appearance at the same temperature region that the second step in Fig. 3A. The origin and sense of this peak will be discussed later. Fig. 4. shows temperature dependence of dielectric loss ϵ'' for the all samples at one frequency of 10 kHz. the peak connected with α 1-relaxation shifts to lower values and temperatures with increasing of the soft segment contents W_s . The β -relaxation process looks to be almost independent of the copolymer composition.

5.4. Discussion

Basing on the above results, one can consider these materials as belonging to a group of thermoplastic elastomers which combine easily processability of thermoplasts with elastic properties of vulcanised rubber [6]. Below $W_s = 40$ wt.% they represent two-phase systems containing the soft- and hard phases. Such data as: minimum of T_g , second step of the $\epsilon'(T)$ -dependence, and a third peak on the M''

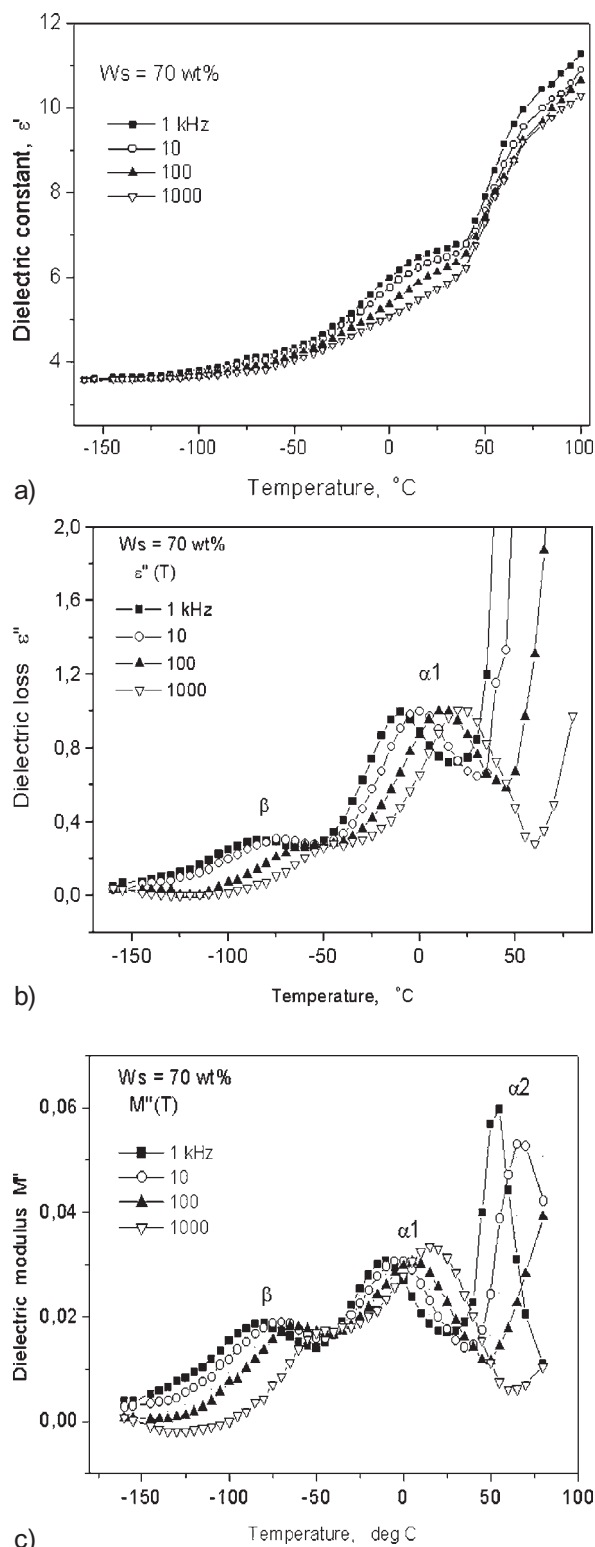


Fig. 3. A - Dielectric constant ϵ' , B - dielectric loss ϵ'' , and C dielectric modul M'' as a function of temperature at selected frequencies for the A₇₀ sample with soft phase contents $W_s = 70$ wt.%.

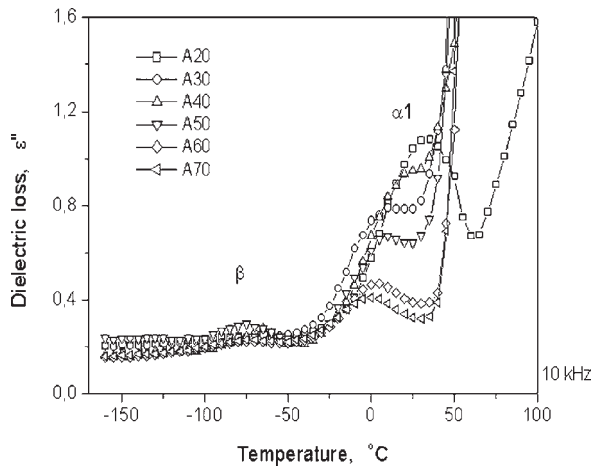


Fig. 4. Dielectric spectra in the *temperature domain* of the poly(ester-*b*-amide) samples at 10 kHz.

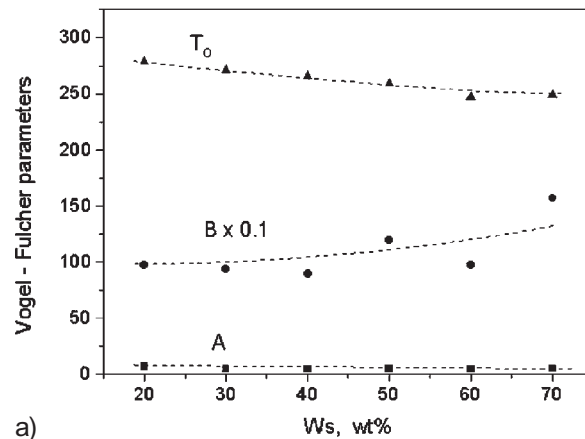
show that a third phase appears above this W_s -value. *Per analogiam* to another copolymers [7], this phase could be an interphase composed of amorphous part of the PA12 segment dissolved into the poly(butylene sebacate) soft phase. This new phase is highly electro-conducting one. Probably this conductance is not caused by the water molecules presence in these materials, because: a) it strongly depends on the W_s -value, b) the β -relaxation is very weak [8], and c) these samples were stored and measured in nitrogen atmosphere. It would be necessary to study this structure by different methods to understand better the physical reasons of this phenomenon.

5.5. Vogel-Fulcher analysis

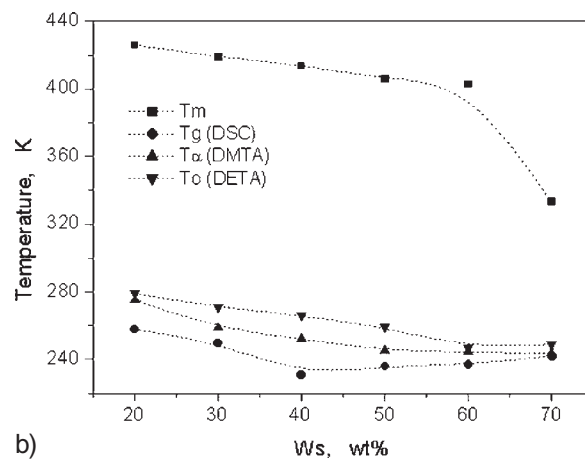
The α -type relaxation processes usually does not fulfil the Arrhenius law. Instead, the Vogel-Fulcher equation can be applied here. This one can be expressed as

$$\log(f_{max}) = A - B(T - T_0), \quad (2)$$

where: f_{max} is the frequency of maximal value of the ϵ'' , A and B are constants characteristic for the material, T is temperature in K and T_0 is the extrapolated (Vogel) glass temperature [9]. Using the data obtained for all samples and Eq. (2), the above mentioned parameters were estimated and presented as a function of the W_s in Fig. 5A. Fig. 5B contains, for comparison, four characteristic temperatures: T_m (DSC), T_g (DSC), T_a (DMTA), and T_0



a)



b)

Fig. 5. a) – Fitting parameters of the experimental results to the Eq. (2); b) – some characteristic temperatures of the samples.

(DETA) as a function of the sample composition (W_s). A nonlinear changes of all these dependences at high W_s are clearly seen (Table 1.).

6. CONCLUSION

A poly(ester-*block*-amide) multiblock copolymers containing an aliphatic ester: butylene sebacate, which plays role of a flexible block and polyamide PA12 as a rigid block, were synthesized in some different compositions during three-step process. The results of investigation by experimental DSC, DMTA, and DETA allow to classify these materials as a thermoplastic elastomers having multiphase structure. This structure becomes more complex in samples with high soft segment contents (above 40 wt.%), which reflects mostly onto dielectric spec-

tra. Further investigations of these materials will be continued.

ACKNOWLEDGEMENT

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