Macromol. Symp. 2006, 239, 209–216 DOI: 10.1002/masy.200650727

Physical Properties of the Biodegradable Polymer Compositions Containing Natural Polyesters and their Synthetic Analogues

Piotr Dacko, Marek Kowalczuk, Henryk Janeczek, Michal Sobota*

Summary: The thermal, mechanical and thermo-mechanical properties of polymer compositions, containing synthetic biodegradable polymers i.e. polylacide (PLA) and aliphatic-aromatic copolyester (BTA), natural biopolyester n-PHB and its synthetic atactic analog (a-PHB) were investigated. Thermal properties of the polymer compositions were studied by means of DSC . The compositions of various polymer weight ratio were tested. Compositions containing BTA and n-PHB create polyphase systems, what was confirmed by DSC. In this case the two Tg and two Tm values were observed. Polymer compositions containing PLA and BTA showed different behaviours. At the BTA content up to 30 weight % only one Tg and one Tm were indicated. At the increase of the BTA content to 50% weight and above, the two Tg, and two Tm were observed. Mixtures of BTA with n-PHB, PLA and with a-PHB show considerably greater values of the strain (ε) in comparison with initial polymers (n-PHB, PLA). It was found that in contrary to mixtures containing PLA, at the BTA content in the mixture with n-PHB above 50% of weights increases not only the strain, but also the stress at break (σ). Strong increase of the ε value in PLA/a-PHB mixtures with the content of a-PHB above 30% of weights were observed.

Keywords: biodegradable polymers; blends; mechanical properties; thermal properties; mechanical properties

Introduction

The well-known natural and synthetic biodegradable polymers not always satisfy the technological and application requirements what along with a high price of biopolymers is a hindrance for their wider use. However, profitable properties of biodegradable polymer materials may be achieved by the chemical or physical modification of plain polymer components, their reactive processing and by preparation of polymer blends or composites. Now, most attention turns on such biodegradable polymers as biopolyesters like poly[(R)-3-hydroxybutyrate] (n-PHB), copolymer of 3-hydroxybutyrate with 3-hydroxyvalerate (PHBV) or 3-hydroxyhexanoate (Nodax^{TM}), their synthetic analogues and also polylactide (PLA) produced from renewable raw materials.[1]

The high degree of crystallinity of natural n-PHB its brittleness, small unit elongation and the melting-point only 10°C lower than the temperature of its thermal degradation considerably makes the industrial processing difficult. Also the brittleness of PLA and possible degradation at processing temperature (about 200°C) needs suitable modification.[2] Aliphatic-aromatic polyester (BTA) produced by BASF under trade name Ecoflex$^{®1}$ Possesses perfect mechanical and processing properties and its biodegradation properties may be tuned by blending or addition of special additives.

The use of a synthetic analogue of natural n-PHB i.e. atactic poly[(R,S)-3-hydroxybutyrate] (a-PHB) gives large possibilities of

Centre of Polymer Chemistry, Polish Academy of Sciences, 34 M. Curie-Sklodowska Street, 41-819 Zabrze, Poland
E-mail: pdacko@cchp-pan.zabrze.pl

the biodegradable polymers modification.[3] It was found, that this polymer undergoes total degradation in the natural environment (compost, sea water)[4], and water-soluble degradation products undergo bioassimilation in the presence of chosen bacterial strains.[5] The presence of a-PHB in mixtures with natural polyesters lowers the degree of crystallinity and positively influences on their mechanical and thermal properties.[6,7]

The aim of the present work was to study the thermal and mechanical properties of polymer compositions, containing synthetic biodegradable polymers, PLA, BTA, natural n-PHB and its synthetic atactic analog a-PHB.

Experimental

Materials

Natural poly[(R)-3-hydroxybutyrate] (n-PHB), was used as received from BIOMER. Synthetic biodegradable aliphatic-aromatic copolyester (BTA) was used as kindly received from BASF. Polylactide (PLA) was used as received from GALACTIC. Atactic poly[(R,S)-3-hydroxybutyrate] (a-PHB) was synthesized by anionic polymerization of β-butyrolactone and characterized as described in.[8]

Preparation of Polymer Blends

Samples of n-PHB/BTA and PLA/BTA granulate were obtained by the triple melt extrusion of plain polymer mixtures (see Table 1).

After each melt extrusion the product was granulated and again melt extruded. The specially constructed laboratory single-screw extruder (diameter of screw - 12 mm, lengths – 240 mm) and the laboratory granulator (ZMP-TW, Gliwice, Poland) were used for sample preparation.

Samples of PLA/a-PHB mixture were prepared by dissolution of initial polymers in chloroform (10% solution). The polymer films were obtained by casting of prepared solutions on a glass plates. The received films were first dried at room temperature during 72 hours and finally dried under vacuum at 40°C during 96 hours.

Characterisation Techniques

Size Exclusion Chromatography (SEC)

Molecular weights of the investigated materials was determined by size exclusion chromatography (SEC). The experiments were carried out using a Spectra Physics 8800 solvent delivery system at the temperature of 308K. A differential refractometer Shodex SE61 was used as detector. Chloroform was used as the eluent and Polystyrene (PS) samples of narrow polydispersity as standards.

Differential Scanning Calorimetry (DSC)

Thermal characteristics of the investigated materials (sample weight of *ca.* 20 mg, heating rate of $20C \cdot min^{-1}$) were determined by differential scanning calorimetry (DSC) on Du Pont 9900 apparatus using sealed aluminium pans under nitrogen atmosphere (flow rate of *ca.* $30\ ml \cdot min^{-1}$) in the temperature range of -80 – $+200$°C, using the standards to the calibration with the highest purity (Indium and Gallium).

Wide Angle X-Ray Scattering (WAXS)

X-ray diffraction patterns were recorded on a wide-angle TUR M62 diffractometer

Table 1.
Extruding temperatures of the polymer compositions in particular extruder warm zones.

Composition (weight ratio)	Warm zones, °C			
	1	2	3	4
n-PHB/BTA (50/50)	100	180	135	130
n-PHB/BTA (30/70)	90	180	135	110
n-PHB/BTA (20/80)	85	180	135	100
PLA/BTA (70/30)	140	180	170	155
PLA/BTA (50/50)	120	180	160	125
PLA/BTA (30/70)	110	180	150	115

working in typical Bragg geometry with CuK_{α}, $\lambda = 0{,}154$ nm and nickel filter.

Mechanical Properties of the Materials

Mechanical properties of the investigated materials were determined using the Instron Model 4204 tensile tester at 20 mm/min tensile speed. Samples of n-PHB/BTA and PLA/BTA as a monofilaments with 1.35 mm diameter were obtained by extrusion moulding (see Preparation of polymer blends). Polymer compositions of PLA/a-PHB were prepared as a films with 10 mm width and 0.15 mm thick. In both cases distance between the grips was 100 mm.

Thermo-Mechanical Properties of the Materials

Thermo-mechanical properties of the investigated materials were determined using Höppler consistometer, loading of the samples was 30 kg/cm^2, while heating rate was 3°C/min Samples for thermo-mechanical tests were prepared by the precipitation of the 5% chloroform solution of initial polymers in hexane and then were dried as described above. The tablets for tests were formed from the obtained material in special forms (13 mm diameter and 10 mm height) under the pressure of 150 atm.

Results and Discussion

Properties of the Plain Polymers

The molecular weights, polydispersity, thermal (Tm, Tg) and mechanical (ε, σ, E) properties as well as crystal phase content for the plain polymers are summarized in Table 2.

The DSC curves recorded with repeated heating-cooling cycles allowed the evaluation of Tg values of the initial polymers in the range −23°C – +61°C (see Table 2). It is obvious that they depend on the structure of the polymers. As is seen from the dates presented in Table 2 in opposite to PLA and n-PHB, the BTA exhibited two glass transition temperature with ranges of vitrification with maximum at −23°C and 61°C, which should be connected with the glass transition temperature of the area created by flexible aliphatic and rigid aromatic blocks, respectively.

For all plain polymers the endotherms of melting were also observed. In the case of n-PHB, PLA and BTA this is due to the presence of the crystalline phase, as confirmed X-ray studies (Fig. 1a).

The endotherm of melting for a-PHB is connected probably with the small ordering of particles, however the value of enthalpy ΔH is very small (see Table 2).

Properties of the Polymer Compositions

DSC data and preliminary mechanical tests (Fig. 2) allowed selection of the temperature conditions for processing of investigated compositions.

The obtained thermo-mechanical data show, that the increase of the BTA content in mixtures with PLA shifts the transition temperature into viscous flow state to lower temperatures, restricting also temperature range of the rubber like state. For mixtures of n-PHB with BTA the rubberlike state is

Table 2.
Molecular weights, polydispersity coefficients, thermal and mechanical properties and crystal phase content for the plain polymers: n-PHB, PLA, BTA and a-PHB.

Code	Mn	Mw/Mn	Tg [°C]	Tm [°C]	ΔH [J/g]	Xc [%]	σ [MPa]	ε [%]	E [MPa]
n-PHB	200000	2.5	21.0	180.8	71.80	55.30*	29.00	4.50	2500
BTA	34000	2.1	−22.8 +60.8	135.0	17.23	33.50	30.30	1650.0	100
PLA	58000	1.9	55.9	173.9	47.43	50.96**	45.00	14.00	1900
a-PHB	6000	1.2	0.1	60.25	4.75		nm	nm	nm

* $\Delta H(100\%)$ n-PHB = 130J/g.[9]
**$\Delta H(100\%)$ PLA = 93 J/g.[10]
nm-not measured.

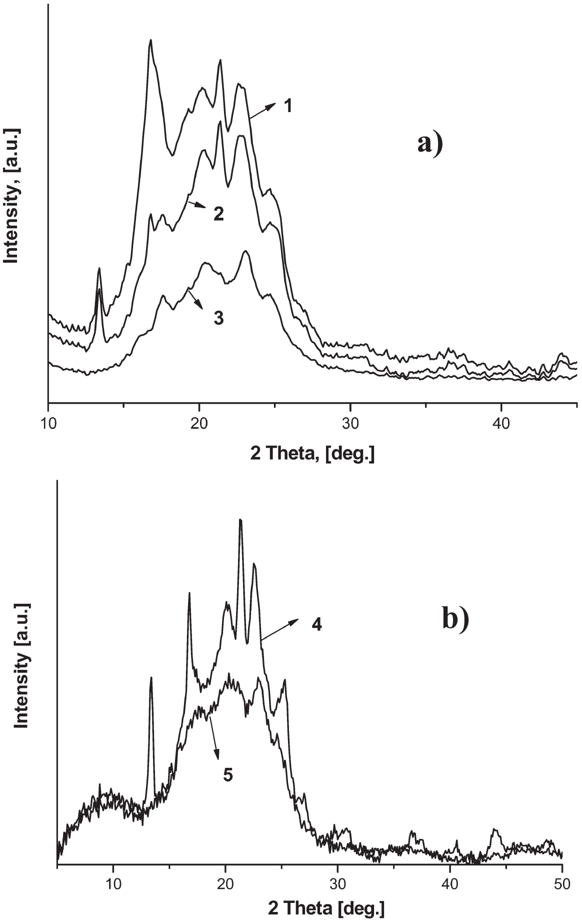

Figure 1.
X-ray diffraction profiles of the plain polymers: **1:** n-PHB, **2:** PLA, **3:** BTA (a) and of the n-PHB/BTA (50/50% weight) - **4** and PLA/BTA (50/50% weight) - **5** (b) polymer compositions.

less expressive and its temperature range is considerably narrower. While for pure n-PHB, in chosen research conditions, temperatures appears between 160°C–170°C. Similarly as in case of PLA/BTA mixture with the increase of the BTA content, this temperature range shifts to lower temperatures. Extrusion temperatures in each zones of extruder are summarized in the Table 1. In the plasticizing zone (zones 2, 3) temperatures were near or a little higher from the melting point of n-PHB and PLA. Temperatures in the extrusion head zone were near or a little lower from the viscous-liquid state temperature of the suitable mixtures.

Thermal Properties of the Biodegradable Polymer Compositions

The changes of a polymer properties during processing may be expected. They can influence on manufacturing parameters and mechanical properties of a polymer. Therefore, the additional DSC studies of the prepared polymer compositions were performed (Table 3).

It was found, that compositions containing BTA and n-PHB create polyphase systems, what confirms two glass transition temperatures (Tg1, Tg2), and two melting-points (Tm). The glass transition temperature in the negative area of temperatures (Tg1) is a little lower from the glass

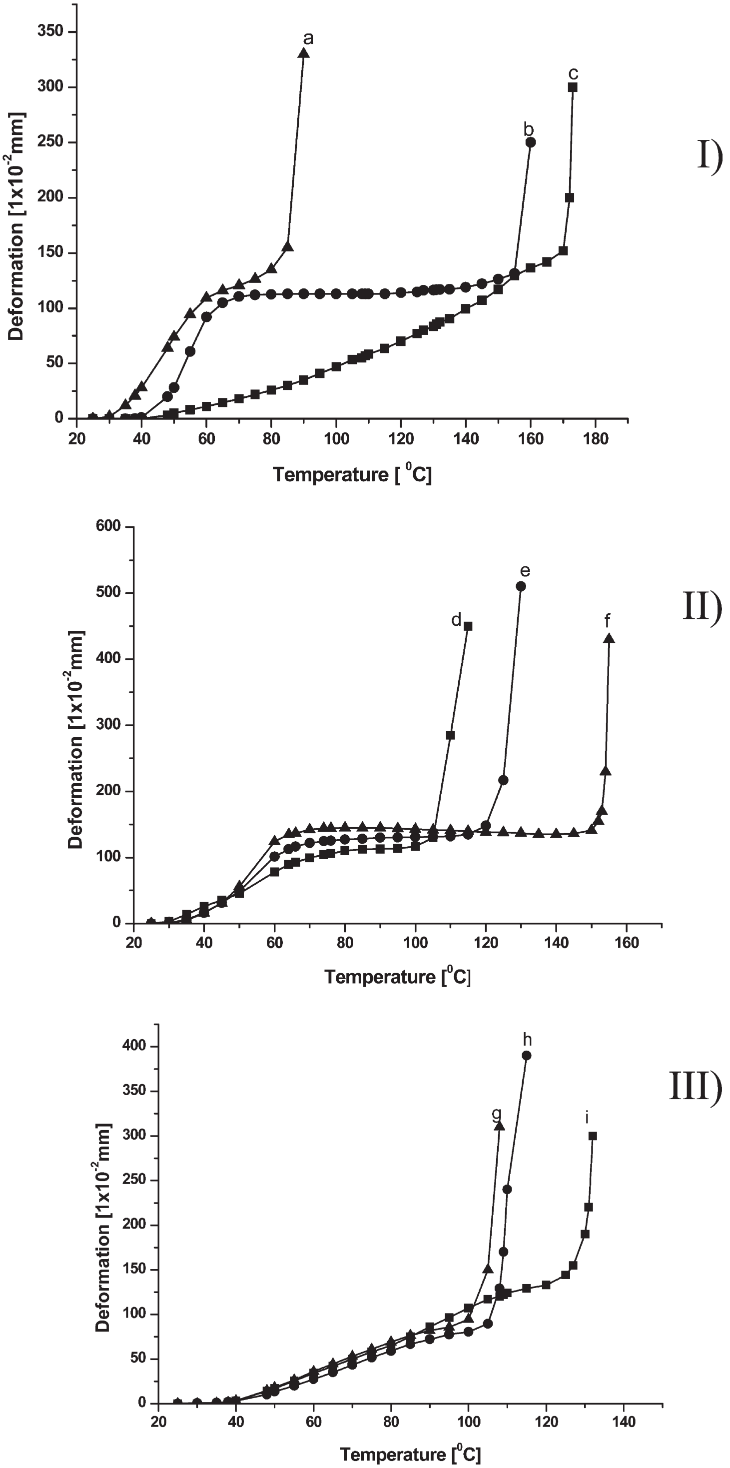

Figure 2.

Thermo-mechanical curves of the plain polymers and respective compositions: **a:** BTA, **b:** PLA, **c:** n-PHB (I); **d:** PLA/BTA (30/70% weight), **e:** PLA/BTA (50/50% weight), **f:** PLA/BTA (70/30% weight) (II); **g:** n-PHB/BTA (20/80% weight), **h:** n-PHB/BTA (30/70% weight), **i:** n-PHB/BTA (50/50% weight) (III).

Table 3.
Thermal properties of the biodegradable polymer compositions.

Composition	Weight ratio	Tg1 [°C]	Tg2 [°C]	Tm1 [°C]	Tm2 [°C]	ΔH1 [J/g]	ΔH2 [J/g]
n-PHB/BTA	50/50	−26.30	47.40	147.40	183.00	1.70	16.40
	30/70	−28.55	46.70	127.70	176.40	7.55	19.20
	20/80	−30.40	46.10	125.70	179.80	12.65	7.40
PLA/BTA	70/30	54.30	nd	178.70	nd	23.05	nd
	50/50	40.30	53.90	121.20	174.30	5.73	16.80
	30/70	44.80	57.20	125.40	173.50	4.60	7.60
PLA/a-PHB	80/20	−5.40	55.10	173.20	nd	39.00	nd
	70/30	−1.89	55.20	169.30	nd	38.90	nd
	50/50	−1.27	66.10	163.10	nd	26.10	nd

nd-not detected.

transition temperature of BTA flexible segments and shifts slightly to negative temperatures with the increase of the BTA content. While the glass transition temperature in the positive temperatures area (Tg2) is a superposition of both glass transition temperatures of areas formed by BTA stiff segments and of n-PHB glass transition temperature. Values of Tg2 lie above the glass transition temperature of n-PHB and below the glass transition temperature of BTA stiff segments. This testifies about the presence in amorphous areas of two phases formed by n-PHB and BTA with mutually penetrating chains. Two melting points of examined systems testify about the presence of two different crystal structures. About the presence of the crystalline phase testify X-ray diffraction patterns presented on Fig. 1b.

On the other hand it should be emphasized that polymer compositions containing PLA and BTA showed different behaviours. At the BTA content up to 30% weight the mixture exhibits one Tg and one Tm, what can testify about the comparatively good miscibility of components and the creation of homogeneous structure. At the increase of the BTA content to 50% weight and above, the two Tg, and two Tm are observed. Tg in the negative range of temperatures disappears, and values of Tg1 and Tg2 are lower than Tg for PLA and Tg2 for BTA.

The presence of so many transition temperatures testifies about this that n-PHB/BTA and PLA/BTA mixtures with a content of BTA above 30% weight are systems having complicated supramolecular structure.

Clearly two-phase polymer systems create foils obtained from PLA/a-PHB mixtures, received by the evaporation of the common solvent. This confirms two glass transition temperatures from which Tg1 appears at negative temperatures, slightly lower than Tg of a-PHB, and Tg2 is close to Tg of PLA.

The compositions of PLA/a-PHB show only the one Tm close to Tm of PLA, what

Table 4.
Mechanical properties of the biodegradable polymer materials.

Composition	Weight ratio	σ [Mpa]	ε [%]	E [Mpa]
n-PHB/BTA	50/50	10.5	115.8	131.8
	30/70	11.6	565.4	98.6
	20/80	20.0	1406.0	100.2
PLA/BTA	70/30	46.0	830.0	1052.0
	50/50	37.0	880.5	663.0
	30/70	22.0	957.0	313.0
PLA/a-PHB	80/20	21.0	19.0	1098.0
	70/30	14.5	20.0	1172.0
	50/50	12.0	69.5	664.0

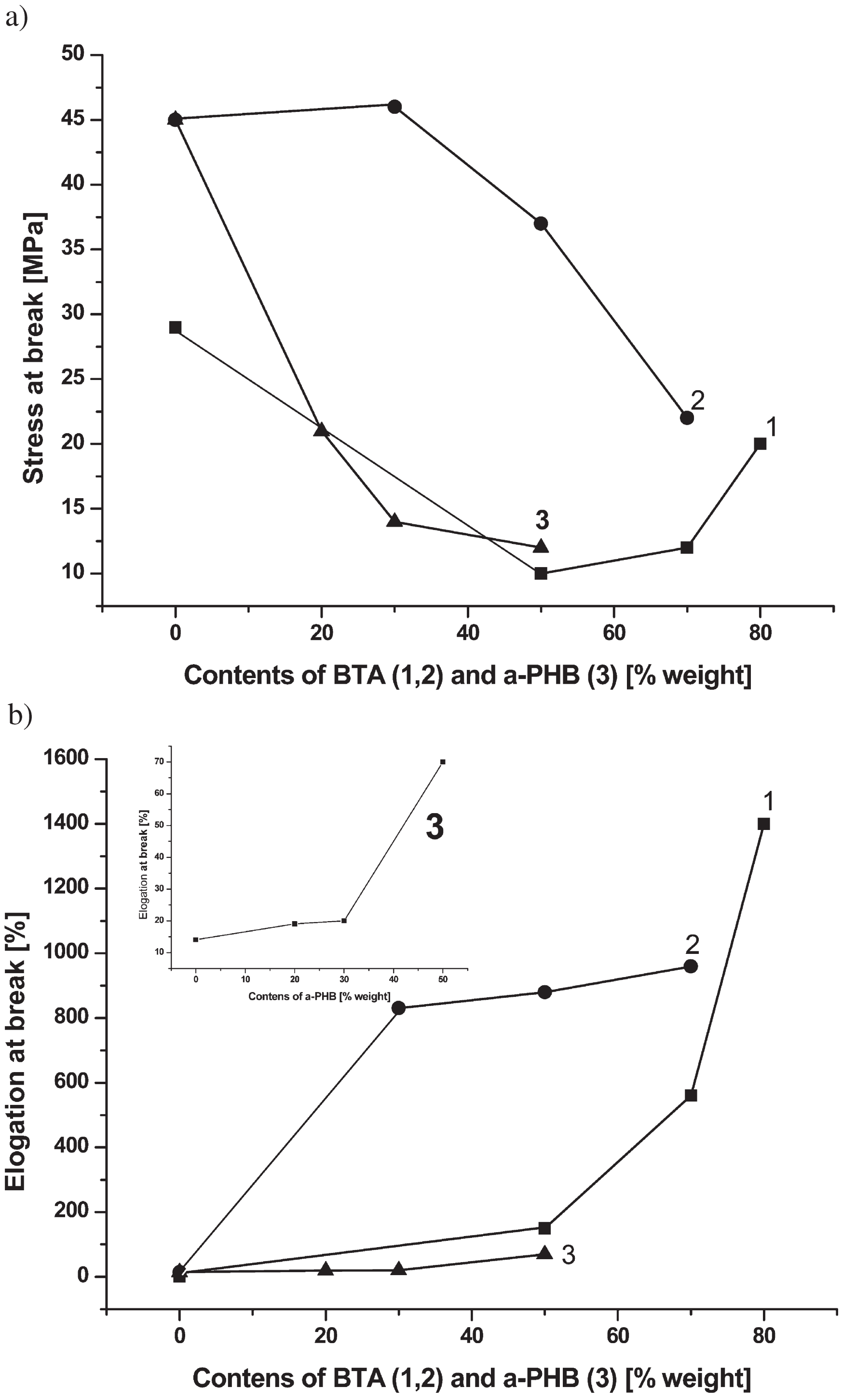

Figure 3.
Mechanical properties of the polymer compositions (a- stress at break, b-elongation at break). **1:** n-PHB/BTA, **2:** PLA/BTA, **3:** PLA/a-PHB.

is in contrary to previous sets. Thus the amorphous phase of these mixtures consists first from separated areas of a-PHB and PLA, and the crystalline phase consists of crystalline areas of PLA.[11]

Mechanical Properties of the Biodegradable Polymer Composition

The mechanical properties of the biodegradable polymer compositions were depicted in Table 4 and Fig. 3.

Fig. 3a shows dependences of stress at break (σ) and Fig. 3b shows the strain (ε) of investigated biodegradable polymer compositions.

The content of BTA in the mixture with n-PHB up to 50% weights decreases 'σ' values from 29 MPa to 10 MPa. Increasing of BTA content to 70% and 80% increases 'σ' values to 12 MPa and 20 MPa, respectively.

The introduction of BTA to PLA slightly increases the value 'σ' to 46 MPa. This value decreases to 22 MPa when the BTA content is equal to 70% weights.

The substantial decrease of the strain 'σ' is observed after introduction of synthetic a-PHB to PLA, to the content 30% of weights (45 MPa and 14 MPa, respectively). The increase of a-PHB content to 50% of weights decreases slightly the 'σ' value (to 12 MPa).

It could be expected, that mixtures of BTA with n-PHB and PLA and with a-PHB will show considerably greater values of the strain (ε) in comparison with plain polymers (n-PHB, PLA). It was found that in contrary to mixtures containing PLA, at the BTA content in the mixture with n-PHB above 50% of weights increases not only the strain, but also the stress at break (σ). Strongly increases the ε value in mixtures of PLA/a-PHB with the content of a-PHB above 30% of weights (Fig. 3b). In mixtures of PLA/BTA the essential increase of the ε value is observed at the content of BTA up to 30% of weights and then this increase is already less visible.

Conclusions

The presented results demonstrate, that synthetic biodegradable BTA polyester and synthetic atactic poly[R, S)-3-hydroxybutyrate] (a-PHB) can be efficiently used as modifiers of the properties of natural biodegradable polyester poly[(R)-3-hydroxybutyrate] (n-PHB) and of polylactide (PLA) derived from renewable raw materials. The compositions studied are characterized with high values of the strain (ε) and with satisfactory values of the stress at break (σ). They can be processed by extrusion, extrusion blow molding and the respective films may be obtained from melt and solution.

Acknowledgements: The research was supported by State Committee of Scientific Research grants: EUREKA 3064, Ministry of Scientific Research and Information Technology (PBZ-KBN-070/T09/2001/7) and Polish State Committee of Scientific Research (4T08E 05124).

[1] Steinbüchel A. Ed. *Biopolymers* vol. 4 Polyesters III Aplications and commercial product Doi Y, Steinbüchel A. Ed. Wiley-VCH, **2001**.
[2] Duda A, Penczek S.*Polimery* **2003**; *48*, 16.
[3] Jedlinski Z, Kowalczuk M, Kurcok P, Adamus G, Matuszowicz A, Sikorska W.*Macromolecules* **1996**, *29*, 3773.
[4] Rutkowska M, Krasowska K, Hejmowska A, Kowalczuk M.*Biorelated Polymers. Sustainable Polymer: Science and Technology*, Edited by Chiellini E, Kluver Academic/Plenum Publishers, New York, **2001**, 313.
[5] Focarete ML, Scandola M, Jendrossek D, Adamus G, Sikorska W, Kowalczuk M.*Macromolecules* **1999**, *32*, 4814.
[6] El-Taweel SH, Höhne GWH, Mansour AA, Stoll B, Seliger H.*Polymer* **2004**, *45*, 983.
[7] Abe H, Matsubara I, Doi Y.*Macromolecules* **1995**, *28*, 844.
[8] Kurcok P, Śmiga M, Jedlinski Z.*J.Polym. Sci.Polym Chem.* **2002**, *40*, 2184.
[9] Kamiya N, Sakurai M, Inoue Y, Chujo R, Doi Y;*Macromolecules* **1991**, *24*, 2178.
[10] Fischer EW, Sterzel HJ, Wegner G.*Kolloid Z.Z. Polym* **1973**, *251*, 980.
[11] Focarete M.L., Scandola M., Dobrzynski P, Kowalczuk M.*Macromolecules* **2002**, *35*, 8472.