Evaluation of the Suitability of Selected Aliphatic Polyester Blends for Biodegradable Fibrous Materials with Improved Elasticity

Abstract
Poly (lactic acid) (PLA) blends with biodegradable aliphatic polyester of butylene glycol and succinic- and adipic acids (Bionolle) were studied with respect to their usefulness for the preparation of fibrous materials with biodegradability and improved elasticity. The miscibility of PLA/Bionolle blends was investigated by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The spinnability of blends was also tested. For the evaluation of the mechanical properties of the blends, testing monofilaments were prepared. The Young’s modulus and elastic recovery of monofilaments were determined. It was found that Bionolle forms with PLA heterogeneous blends. The addition of Bionolle to PLA improves the elasticity of the blends obtained.

Key words: aliphatic polyester, poly(lactic acid), polymer blend, biodegradable fibrous material.

Introduction
For over 30 years development works have been conducted in the field of biodegradable synthetic thermoplastic polymers. Well-known thermoplastic polymers that undergo complete biodegradation under natural conditions are aliphatic polyester composed of various monomers like glycolic acid, lactic acid, butyric acid, and caprolacton [1, 2]. Polymers and copolymers made of such monomers have been used for a long time in the manufacture of medical devices like implants and sutures. Recently, in the search for useful biodegradable resin, attention has been given to polymers based on raw materials from natural renewable resources, not from fossil. The most attractive appears to be poly(lactic acid) (PLA) derived from 100% renewable sources [3]. This polymer can be synthesised from lactic acid produced mainly by fermentation using starch contained in agricultural products like corn or cereals.

Previously, due to lack of availability and cost of manufacture, most initial uses of PLA were limited to biomedical applications. Over the past few years, large-scale operations for the economic production of PLA polymer have been developed [4, 5]. The leader in the production of PLA is a company from the USA called Cargill Dow Polymers (presently NatureWorks LLC), which offers many types of this polymer under the trade name Nature Works Polylactide Resin. Different types are recommended for injection molding, extrusion, thermoforming and melt spinning. Presently, PLA could reasonably substitute conventional polymers. PLA is the most promising candidate among the biodegradably degradable materials, especially in the case of disposable or short term products like plastic packaging (films, bottles) as well as for textile materials eg. fibres and non-woven for medicine and agriculture. However, some mechanical properties, such as the low deformation at break, hardness, rigidity and fragility limit its application.

Considerable efforts have been made to improve the properties of PLA so as to compete with low-cost and flexible commodity polymers. Therefore several modifications have been proposed, such as copolymerisation, plasticisation and polymer blending [6 - 8]. Polymer blending is regarded as a useful and economical way to produce new materials with a variety of properties. Blends of PLA with various non-biodegradable and biodegradable polymers have been investigated [9]. PLA was found to be miscible with natural poly(3-hydroxybutyrate), synthetic atactic poly(3-hydroxybutyrate), poly(methyl methacrylate), and poly(vinyl phenol) [10, 11]. In the case of polymers such as poly(butadiene-co-acrylonitrile, poly(vinyl alcohol), poly(butylene adipate-co-tereflatelate, and poly(ethylene succinate) the immiscibility has been proved, but it does not limit the practical application of such blends. Some heterogenous blends of PLA with other polymer are characterised by a better crystallisation rate and improved flexibility [12, 13].

The aim of this work was to evaluate the suitability of PLA blends with a biodegradable aliphatic polyester use in deferent contents to form fibrous materials, such as monofilaments, films and melt blown non-woven.

Biodegradable fibrous materials with improved elasticity in relation to PLA materials were expected as a result of this study.

Presently, PLA is used for the manufacture of some textile raw materials, including spun bonded and melt-blown non-woven [14 - 16]. The suitability of aliphatic polyester of butylene glycol, succinic and adipic acids (Bionolle type 3001 made by Showa Denko) for the forming of fibres and melt-blown non-woven was found in previous works [17, 18]. Biodegradable polymer Bionolle 3001 displays...
a crystallisation capacity. The glass transition temperature of the material is notable below ambient temperature, therefore textiles made from the polymer are elastic and flexible [19].

Therefore the Bionolle 3001 polymer was selected as a component of blends with PLA.

Materials and investigation methods

Polymers

- PLA NCP0005, supplied by Wei Mon Industry Ltd, Taiwan, poly(lactic acid), specific gravity = 1.21 g/cm³ (ASTM D729), Melt Flow Index, (MFI) = 10 - 30 g/10 min (190 °C, ASTM 1238),

- Bionolle, made by Showa Highpolymer Co. Ltd., a trade product of type 3001, aliphatic polyester of butylene glycol, succinic and adipic acids, specific gravity = 1.23 g/cm³ (ASTM D729), MFI = 0.8 - 1.8 g/10 min (190 °C, ASTM 1238)

The producer does not inform of the percentage content of the individual acids in the polymer composition.

Preparation of polymer blends

The polymers were pre-dried in a rotary dryer: PLA at 80 °C for 10 hours, Bionolle at 60 °C for 16 hours, vacuum < 1 mm Hg.

Granulate blends were prepared from the dried polymers according to the assumed PLA/Bionolle composition:
- 90%wt / 10%wt;
- 70%wt / 30%wt;
- 50%wt / 50%wt,

In the trials no compatibilising agents were used, which are substances that do not degrade in a natural environment and cannot, therefore, be used with biodegradable polymers.

The blends were melted and mixed in a twin extruder (screw dia D = 25 mm, L/D = 30) at 190 °C, at a screw speed of 110 r.p.m and regranulated using a regranulating line.

The polymer blends were dried in a shelf dryer for 24 hours at 75 °C in a vacuum of 80 mm Hg.

Forming monofilament samples for testing

Monofilament samples were formed on a weight plasticator with the use of a spinneret of D = 0.5 mm, at a temperature adopted for each of the polymers on the basis of MFI measurements.

Drawing was conducted in a water bath at 60 °C, with maximum drawing ratios selected for each of the monofilaments within the range of 2.7 - 3.7.

Test methods

The melt flow index (MFI) of polymers was measured using a plastometer according to method A, in accordance with Standard ASTM D1238 (with a spinneret of D = 2 mm, at a temperature of 190 °C), and method B developed at IBWC/ for fibre-forming polymers (using a spinneret hole of 0.5 mm, within a temperature range of 170 °C to 280 °C).

Differential scanning calorimetry (DSC) measurements were performed on a Diamond Perkin-Elmer Co. instrument in a nitrogen atmosphere. Samples of 7 ± 10 mg in weight were analysed in the following cycle: heating → cooling → second heating within a temperature range of -60 °C to +190 °C and heating speed of 20 °C/min. Temperatures and enthalpies of the phase transitions were determined using a Pyris calculate program. The specific enthalpies per component of the PLA/Bionolle blends were found from the following equation:

$$\Delta H_A = \Delta H / X_A$$ in J/g

where:
- \(\Delta H_A\) - enthalpy for component A,
- \(\Delta H\) - measured enthalpy,
- \(X_A\) - a part by weight of the component A in the blend.

The carbon content in the polymers was measured by means of a Euro EA 3000 elementary analyser, Euro Vector SpA; 21144 Milan.

The physical-mechanical properties of the testing monofilaments were measured using Instron 5540 tensile tester, according to the following Polish-ISO standards:
- Tenacity: PN-EN ISO 2062:1997
- Elongation at break: PN-EN ISO 2062:1997
- Young’s modulus: from the breaking curves (computer programme)
- Elastic recovery at elongation limit 20%; PN-84/P-04667

The monofilament and granulate cross-sections of the polymer blends were inspected and photos were taken using a scanning electron microscope of the type QUANTA 200, FEI.

Results

PLA blends with a biodegradable aliphatic polyester of butylene glycol, succinic, and adipic acids were studied with re-

Figure 1. DSC curves for the PLA/Bionolle blends: a) first heating, b) cooling, c) second heating.

Figure 2. The specific melting enthalpies of PLA and Bionolle components in the blends with different PLA content found from the curve of the: a) first heating, b) second heating.
istic for the adequate single component of PLA and Bionolle. This means that the blends analysed are characterised by heterogeneity, and the individual components may influence each other’s kinetic crystallisation.

The specific melting enthalpies of PLA and Bionolle components in the PLA/Bionolle blends versus the PLA content in the blends are shown in Figure 2.

In particular it may be concluded that Bionolle, as a homopolymer (T_g = -41.5 °C; T_m = 96.7 °C), displays good kinetic ability for thermal crystallisation in contrast to PLA (T_g = 64.1 °C; T_m = 168.7 °C), which after melting in first heating, remains in an amorphous state during cooling and second heating. The Bionolle component is characterised by lower crystallinity than Bionolle homopolymer. The crystallinity increases with a growing percentage of this component in the PLABionolle blend but significantly improves its crystallinity during technological processing. This phenomenon is noticeable when we compare the melting enthalpies found during the first and second heating.

The PLA component occurs in an almost amorphous state after cooling from the melt but reaches a similar amount of the crystalline phase during cold crystallization in the second heating. This can result not only from thermal treatment but also from mutual influences between components in the blends. The glass transition temperatures of components in the second heating are visibly lower in the blends than in homopolymers. This is presented in Figure 3.

In particular, it may be concluded that the observed thermal behaviour of PLA and Bionolle components in the blends can lead to significant differences in their crystallinity, depending on the technological parameters of processing.

Estimation of carbon content in the polymer blends

Table 1 presents results of the MFI tests of PLA, Bionolle and their blends, performed according to method B, that was adopted in IBWCh for fibre-forming polymers (method B). Testing the outflow of polymer through a 0.5 mm spinneret allows to evaluate, with high probability, the possibility of forming fibres from such polymers as well as to pre-select conditions for the spinning.

In Figure 5 the results of the MFI tests of PLA, Bionolle and their blends, performed according to method B, are compared. In the case of PLA/Bionolle blends, the MFI values are close to those of PLA. It can be assumed that the processing of the blends may be performed at thermal conditions using pure PLA.

There is good accordance between the analyzed and calculated carbon content, which may be regarded as confirmation of a good blending of the polymer components.

Estimation of rheology properties of the polymer blends

Figure 4 presents MFI values for both the PLA and Bionolle components as well for the polymer blends.

MFI’s were also measured at conditions adopted in IBWCh for fibre-forming polymers (method B). Testing the outflow of polymer through a 0.5 mm spinneret allows to evaluate, with high probability, the possibility of forming fibres from such polymers as well as to pre-select conditions for the spinning.

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Estimation of spinnability and evaluation of the properties of monofilaments from polymer blends

Monofilaments were extruded at temperatures adopted on the basis of MFI measurements. For each system a temperature was selected at which the MFI (method B) amounted to 0.5 g/10 min. All polymer blends showed good spinnability. An even stream of polymer from the spinneret could be observed. The monofilaments were drawn at maximum possible draw ratios. In the case of the PLA/Bionolle monofilament, the drawing ability clearly increases with a rise in the Bionolle content of the blend. The correlations are shown in Figure 6.

Physico-mechanical properties of the test monofilaments are shown in Table 2. Figures 7 and 8 present the correlations between the composition of PLA/Bionolle and the two parameters which characterise elasticity and flexibility: elastic recovery ER20% and Young’s modulus.

The ER20% values, amounting to 40%, are the lowest of the monofilaments of PLA with the highest Young’s modulus, being at 305 cN/tex. The addition of Bionolle improves the elasticity and flexibility of the monofilaments.

SEM investigation of the polymer blends

The monofilament and granulate cross-sections of the PLA/Bionolle polymer blends were inspected under an electron microscope at a magnification in the range of 500x – 4000x. Figures 9.a – 9.d present SEM photos of the granulates and monofilament tested.

The microscopic inspection confirmed the heterogeneous character of the polymer blends.

For all cases a phase separation can be seen. However, the polymer dispersion in the blends differs depending upon the type of polymer and composition.

In the PLA/Bionolle 90/10 and 70/30 blends, the average size of dispersed polymer particles does not exceed 4 μm. In the PLA/Bionolle 50/50 blend, the interphase surfaces are not so distinct. It may suggest that a phase inversion occurs with equalised component concentration.

The forming of non-woven by melt-blowing was performed as introductory trials. The non-woven was formed directly from the melt using an experimental melt-blowing stand at the Central Institute for Labour Protection, Lodz, Poland (Polish name: Centralny Instytut Ochrony Pracy- CIOP, Łódź). It was found that the PLA/Bionolle blends show satisfactory spinnability during melt-blowing.

The assessment of the physical-mechanical properties of melt blown non-woven made from PLA/Bionolle blends and their biodegradation ability will be the subject of further studies.

The results of these experimental investigations will be published in the foreseeable future.

The biodegradation tests carried out to now have shown that melt-blown non-woven made of PLA/Bionolle polymer blends undergo biodegradation faster than those made of pure PLA and Bionolle polymers. The increased speed of

Table 2. Physical-mechanical properties of the testing monofilaments.

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<th>Parameter</th>
<th>Testing monofilaments sample</th>
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<td></td>
<td>PLA</td>
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<tr>
<td>Draw ratio</td>
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<tr>
<td>Linear density</td>
<td>dtex</td>
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<td>CV%</td>
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<td>Breaking force</td>
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<td>CV%</td>
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<td>Tenacity</td>
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<td>Elongation</td>
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<td>Young’s modulus</td>
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<td>Elastic recovery ER20%</td>
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biodegradation in the case of non-woven made of heterogeneous polymer blends is justified in view of the much more developed inner surface and the surface separation of the two components [20].

Reassumption

PLA blends with a biodegradable aliphatic polyester of butylene glycol, succinic and adipic acids, (Bionolle Type 3001 made by Showa Highpolymer Co. Ltd.), prepared with a proportion of PLA/Bionolle of 90/10, 70/30 and 50/50%wt., were studied with respect to their usefulness for the preparation of melt-spun fibrous materials like monofilaments and non-woven with biodegradability and improved elasticity.

Based on the investigation results, it may be concluded that Bionolle with PLA forms heterogeneous blends. The addition of Bionolle to PLA improves the elasticity of the blends obtained. In the trials no compatibilising agents were used, which are substances that do not degrade in a natural environment and therefore cannot be used with biodegradable polymers.

PLA/Bionolle blends show satisfactory spinnability in melt-processing. Considering all the results of the investigations, it may be concluded that blends of PLA and flexible, biodegradable aliphatic polyester, Bionolle in particular, are promising materials for fibrous products, such as monofilaments and melt blown non-woven with improved elasticity and high biodegradation ability.

Acknowledgment

These investigations were carried out within the research project “New polymers for melt blown non-woven” sponsored by the Taiwan Textile Research Institute (TTRI). The project was conducted according to the agreement signed between the Institute of Biopolymers and Chemical Fibres, Lodz, Poland and the Taiwan Textile Research Institute, Taipei, Taiwan in June 2007.

We would like to thank Dr Chen Heng-yi from the Technical Textiles Section of the Department of Product Development of TTRI for the PLA polymer sample. We would also like to thank the research team from the Technical Textiles Section of the Department of Product Development at TTRI for all comments and useful discussions. We would also like to acknowledge the kind assistance of Mr. Howard Lo from the Functional Modification Section of the Department of Product Development at TTRI.

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Received 17.06.2008 Reviewed 23.08.2008