Mechanical properties and biodegradability of flax fiber-reinforced composite of polylactide and polycaprolactone

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Abstract: The aim of this work was to produce a composite based on the blend of polylactide and polycaprolactone and reinforced with flax fiber, intended for processing by injection molding, with improved mechanical and biodegradation properties as compared to neat polylactide (PLA) and polycaprolactone (PCL). The material was prepared by mixing PLA, PCL and flax fibers (about 5 mm long), extrusion and granulation with subsequent injection molding to obtain test samples. The composites differed in the content of PCL (0, 5, 10, 15 and 30 wt %) whereas the content of flax fibers was kept constant (20 wt %). The samples were characterized by means of scanning electron microscopy (SEM), tensile and impact strength measurements, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Biodegradation studies were carried out using proteinase K at laboratory conditions. It was found that a reduction of fiber lengths took place during the extrusion process and that addition of flax fibers to PLA/PCL blend resulted in an increase in elastic modulus and biodegradation rate. The composite impact strength was significantly improved at 30 wt % PCL fraction.

Keywords: polylactide, polycaprolactone, flax fibers, mechanical properties, biodegradation.

Właściwości mechaniczne i biodegradowalność wzmocnionego włóknami lnianymi kompozytu polilaktydu z polikaprolaktonem

Streszczenie: Celem badań było opracowanie kompozytu wzmocnionego włóknem lnianym na osnowie z mieszaniny polilaktyd/polikaprolakton, przeznaczonego do przetwórstwa metodą wtryskiwania, wykazującego lepsze właściwości mechaniczne oraz lepszą biodegradowalność niż niemodyfikowane polilaktyd (PLA) i polikaprolakton (PCL). Materiał przygotowano metodą wytłaczania. PLA, PCL oraz włókna lniane (o długości około 5 mm) mieszano, wytłaczano, granulowano, a następnie wtryskiwano w celu uzyskania próbek do badań. Kompozyty różniły się zawartością PCL (0, 5, 10, 15 lub 30 % mas.), natomiast udział procentowy włókien lnianych był stały (20 % mas.). Próbki badano metodami: skaningowej mikroskopii elektronowej (SEM), różnicowej kalorymetrii skaningowej (DSC) oraz dynamicznej analizy mechanicznej (DMA). Oceniano też ich wytrzymałość na jednoosiowe rozciąganie i udarność. Podatność na biodegradację badano w warunkach laboratoryjnych z zastosowaniem enzymu proteinazy K. Stwierdzono, że w procesie wytłaczania nastąpiła znaczna redukcja długości włókien lnianych, ich dodatek do mieszaniny PLA/PCL wpłynął na zwiększenie modułu sprężystości i szybkości biodegradacji, a udział 30 % mas. PCL wyraźnie poprawił udarność kompozytu.

Słowa kluczowe: polilaktyd, polikaprolakton, włókna lniane, właściwości mechaniczne, biodegradacja.

Polylactide (PLA) is one of the most important biodegradable thermoplastics in the emerging market of biopolymers [1]. Besides ecological aspects, wide industrial application of PLA results from its high elastic modulus and tensile strength, good optical and barrier properties, even as compared to petroleum-based polymers. However, low impact strength is generally considered as a disadvantage of this polymer [2].

In order to toughen PLA various modifications have been proposed [3, 4]. These include compounding with polycaprolactone (PCL) [5, 6]. Polycaprolactone is a hydrophobic, semicrystalline biodegradable polymer with unusual low melting point (50–64 °C), low Young's modulus (300–470 MPa) and high impact strength

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(28–38 kJ/m^2) [7, 8]. By mixing PLA with PCL, various biodegradable blends can be compounded compromising high elastic modulus and tensile strength of PLA with high impact strength of PCL. In general, modification of PLA by compounding with PCL lead to increase in impact strength whilst decreasing elastic modulus and tensile strength [9].

Some properties of PLA can also be improved by incorporation of natural fibers [10–12]. Natural fibers are characterized by low cost, high specific modulus, light weight, low energy consumption during production process, wide availability and biodegradability. They increase elastic modulus but often decrease impact strength of PLA [13–16].

In order to reduce brittleness of natural fiber-reinforced PLA various approaches have been used [17, 18]. Among them Goriparthi *et al*. proposed an application of PCL [19]. They used jute fiber mat placed in a stainless steel tray where the solvent of PLA/PCL was slowly evaporated. The so-formed prepregs were then pressed between the hot plates of a compression molding machine to form the samples. This method involves complex fiber pretreatment processing, therefore was time consuming and required special industrial equipment. Moreover, products with complex shapes cannot be manufactured by means of this method.

In this work 5 mm long flax fibers were applied in order to compound the samples by standard extrusion and injection molding industrial processing. The main objective of this work was to evaluate the effect of short flax fibers and polycaprolactone content on the mechanical and biodegradation properties of PLA. We expected to formulate biocomposites with improved mechanical properties and biodegradability as compared to neat PLA.

EXPERIMENTAL PART

Materials

The following materials were applied to prepare samples:

– polylactide (PLA), type 2002D (NatureWorks®, USA). Its density was 1.24 g/cm^3, melt flow rate 5 g/10 min (2.16 kg, 210 °C), and L-lactide content about 96.5 %;

– poly(ε-caprolactone) (PCL), type CAPA™ 6800 (Solvay Caprolactones, UK). Its density was 1.1 g/cm^3, melt flow rate 7.3 g/10 min (2.16 kg, 160 °C);

– flax fibers, originated from the harvest in the year 2014, Belgium (Kortrijk region). The length of the fibers was 5 ± 1 mm and their diameter was ranging from 15 to 25 μm as determined by SEM analysis. They were obtained by natural dew-retting and standard mechanical dressing.

Proteinase K from *Tritirachium album* (Blirt, Poland) was used for biodegradation treatment of studied samples.

Acetylacetonate, pure p.a. (Sigma Aldrich, Germany) was used to dissolve polymer matrix in order to reveal and estimate the length of the fibers.

Samples preparation

Before processing, PLA and flax fibers were dried at 60 °C for 24 h. Then, a master composite (batch) made of PLA and 35 wt % of short flax fibers was prepared by mixing and extruding in a co-rotating twin-screw extruder (type BTSK 20/40D, Bühler, Germany). This polymer batch was applied to produce the composite granulates with various content of PLA and PCL but at constant content of flax fibers (20 wt %). Reference samples of PLA/PCL blends without flax fibers were also prepared for comparative analysis. The detailed compositions and designations of the samples are presented in Table 1.

Table 1. Compositions and designations of samples

Sample	PCL, wt %	PLA, wt %	Fibers, wt %
A0	0	100	0
A1	5	95	0
A2	10	90	0
A3	15	85	0
A4	30	70	0
B0	0	80	20
B1	5	75	20
B2	10	70	20
B3	15	65	20
B4	30	50	20

The extrusion was performed maintaining the following temperatures of extruder zones: 180, 182, 184, 186 °C, and 185 °C of the extruder head. A three-channel die was used to form strands which were cooled by airflow and then in-line granulated by rotating knives. A throughput of extrusion process was evaluated to be 3 kg/h at 150 rpm screw rotation speed.

A special configuration of the screws was applied, intended to minimize the cutting of the fibers. It did not involve the elements returning and intensively mixing the polymer melt but they were replaced by the elements mainly transporting the melt. The applied elements of extruder screw configurations are presented in Fig. 1.

The obtained composite granulates were injection molded to produce the samples for impact, tensile and dynamic mechanical analysis (DMA) tests. It was performed using injection-molding machine type Tederic

Fig. 1. Elements of extruder screw configuration

TRX 80 ECO 60 (Tederic Machinery Manufacture, Taiwan) with the temperatures of barrel zones set to 170, 165, 165, 165 °C and the temperature of mold set to 35 °C.

In order to produce test samples for biodegradation analysis, granules were placed in a special compressing holder, attached to the DMA instrument and pressed to form thin films. The samples were compressed at 160 °C then cut into strips of film weighing from 15 to 17 mg.

Methods of testing

– Final length of the fibers was estimated based on scanning electron microscopy (SEM) of the samples treated with acetylacetone to dissolve polymer matrix and reveal the fibers. SEM images were recorded with a SU8010 scanning microscope (Hitachi, Japan) operating at an accelerating voltage of 5 kV and electron beam current intensity of 8–11 μA. The samples were covered with a 2 nm layer of gold before measurement.

– Thermal stability of flax fibers was evaluated using thermogravimeter Q 500 (TA Instruments, USA). The fibers were heated from 25 to 700 °C at the rate of 10 °C/min under nitrogen atmosphere.

– Determination of tensile strength and Young's modulus were performed using a tensile testing machine, type Instron 3367 (Instron, USA), according to the PN-EN ISO 527-1 standard. Impact strength tests were performed using a Charpy apparatus (ATS-FAAR, Italy), according to the PN-EN ISO 179-1 standard.

– Differential scanning calorimetry (DSC) measurements were conducted using Q 200 calorimeter (TA Instruments, USA) under nitrogen flow. About 4 mg samples cut off from polymer granules were placed on an aluminum pan for a measurement. The samples were quenched to 20 °C, heated to 200 °C at a rate of 5 °C/min, annealed at 200 °C for 3 min, cooled to 20 °C at a rate of 5 °C/min, and reheated to 200 °C at a rate of 5 °C/min.

– Dynamic mechanical analysis (DMA) was performed using DMA analyzer Q 800 (TA Instruments, USA). The bar-shaped injection molded samples were examined in a dual cantilever mode, at a constant frequency of 1 Hz and controlled amplitude of 15 μm, as a function of temperature ranging from -80 to 180 °C.

– The biodegradation was carried out for the samples in the form of films placed in test tubes with reaction mixtures containing 2 mg of proteinase K, 10 cm^3 of 0.1 M Tris-HCl buffer [Tris – tris(hydroxymethyl)aminomethane], and 2 mg of sodium azide, then the test tubes were placed in an incubator [20]. Enzymatic degradation took place at the constant temperature of 37 °C. After a specified periods of time (5, 13, 20, 27, and 35 days), the samples were withdrawn from the reaction mixture, washed in distilled water and dried at 40 °C in a moisture analyzer type MAX 50/1 (RADWAG, Poland) to a constant mass. Then the mass loss as a percentage was determined after each period of time using the formula:

$$\Delta m = \frac{m_s - m_f}{m_s} \cdot 100\% \qquad (1)$$

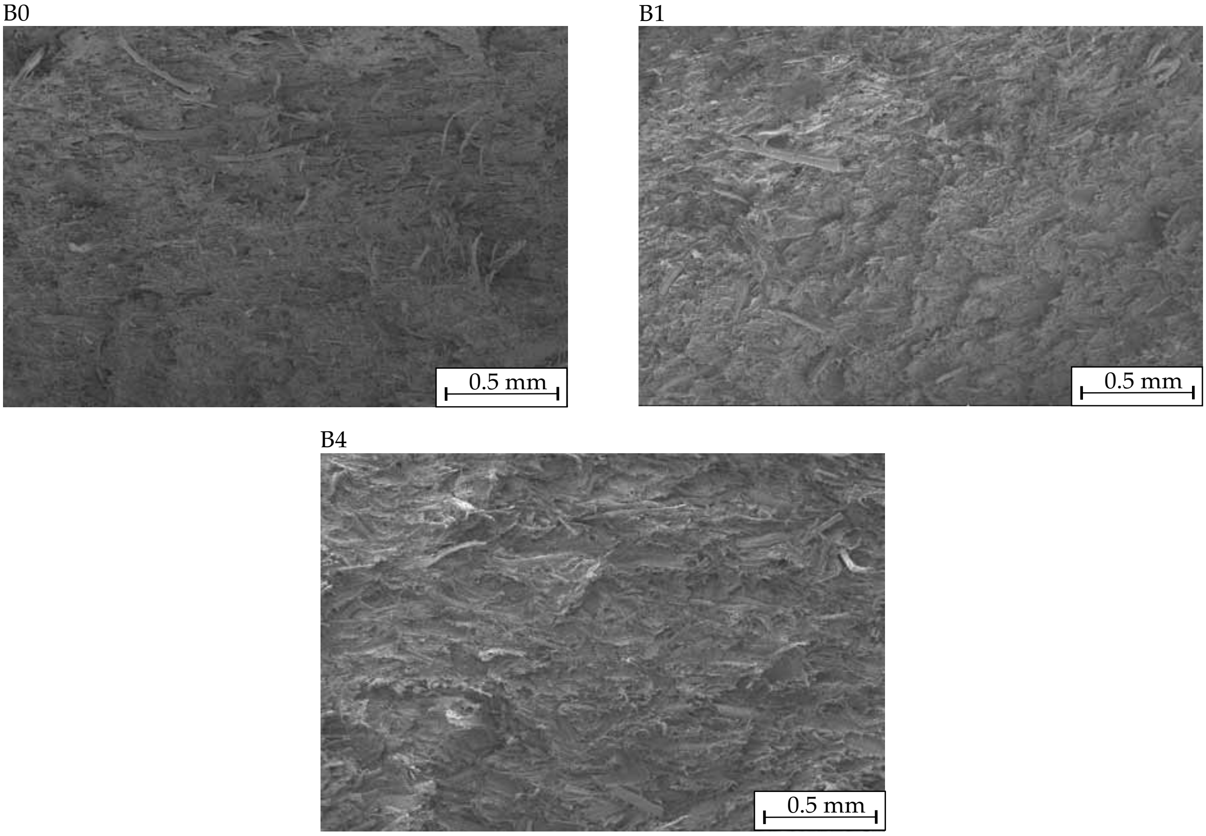

Fig. 2. SEM images of samples B0, B1 and B4 treated with acetylacetonate

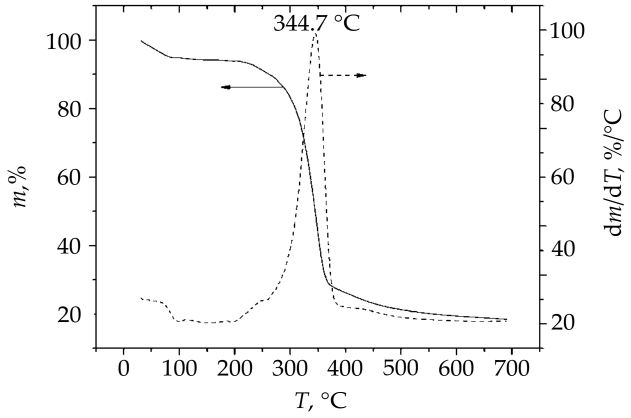

Fig. 3. Thermogravimetric curves for flax fibers

where: m_s – the initial mass of the test sample, and m_f – the mass of the sample after the specified period of incubation.

RESULTS AND DISCUSSION

It is well known that length of the fibers affect not only mechanical properties of the final fiber-reinforced composite but also the possible methods of industrial processing [21]. The elaborated biocomposite material was intended to be applied in injection molding products therefore short 5 mm flax fibers were used to prepare a granulate. During the twin-screw extrusion, the length of the fibers was decreased as an effect of shearing process. As follows from Fig. 2, demonstrating the dissolved polymer matrix, the final fiber length in the samples was less than 1 mm.

Besides fibers length, a very important property is their thermal stability. It was examined by thermogravimetric analysis (TG) (Fig. 3). Before the experiment, fibers were dried at 60 °C for 24 h. Despite drying, about 5 wt % of water confined in flax fibers was evaporated during heating to 100 °C. It was also found that fibers were thermally stable to about 200 °C and for that reason the sample processing temperature was set below this value. Using natural fibers as reinforcement in thermoplastics one has to keep in mind that temperature during extrusion and injection molding can be a crucial factor affecting mechanical properties of the composites as previously discussed [13].

A very important factor affecting mechanical properties of polymer blends is their structural morphology. As examined previously [5], the morphology of PLA/PCL blend depends mainly on the mass ratio of these polymers. Based

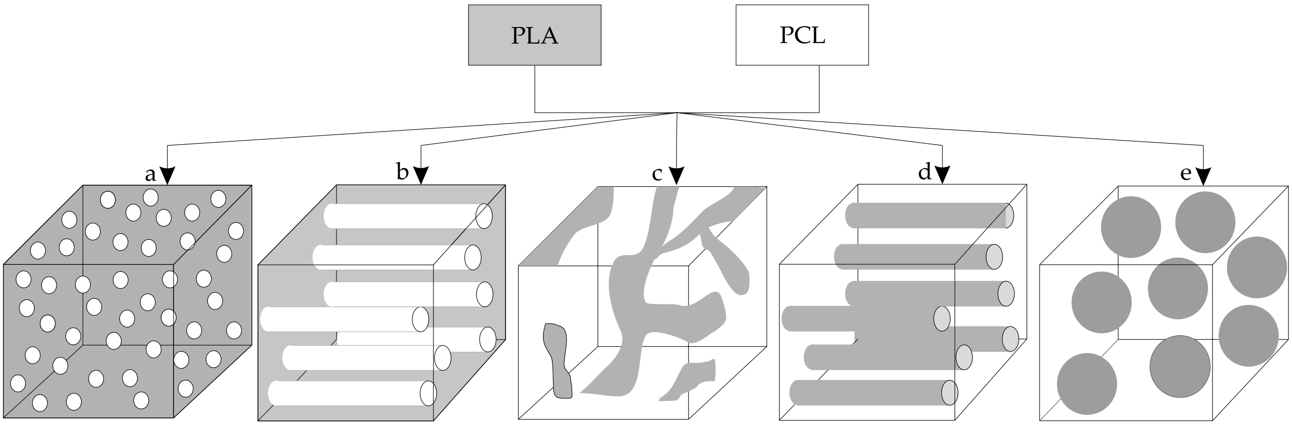

Fig. 4. Graphical representation of morphological evolution dependent on the ratio of PLA and PCL (explanation in text)

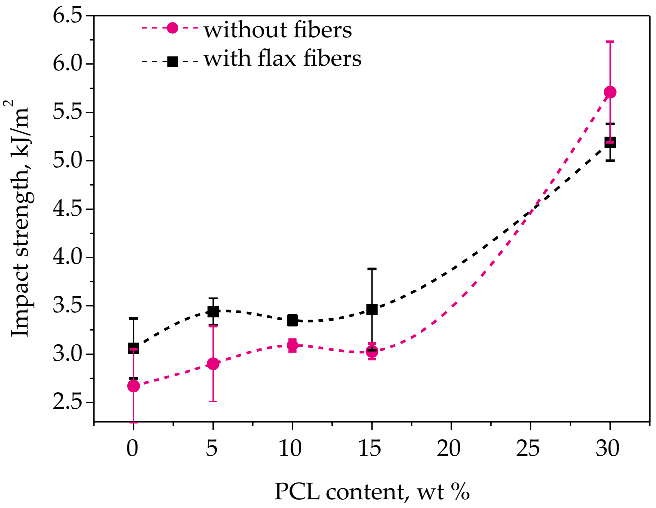

Fig. 5. Impact strength *versus* PCL content for the samples with or without flax fibers

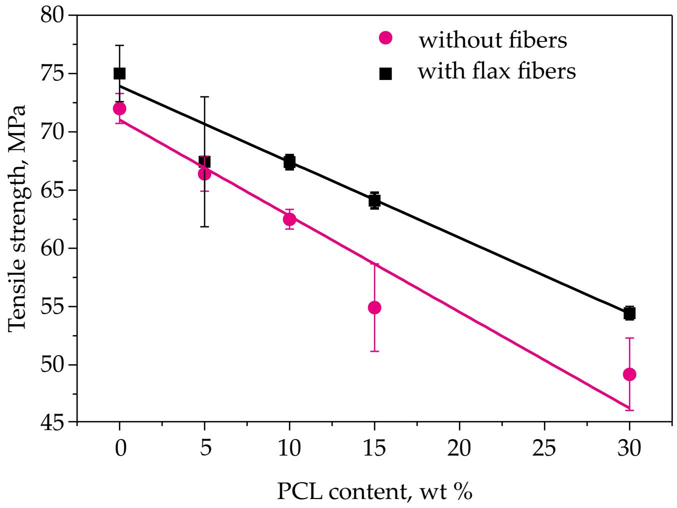

Fig. 6. Tensile strength *versus* PCL content for the samples with or without flax fibers

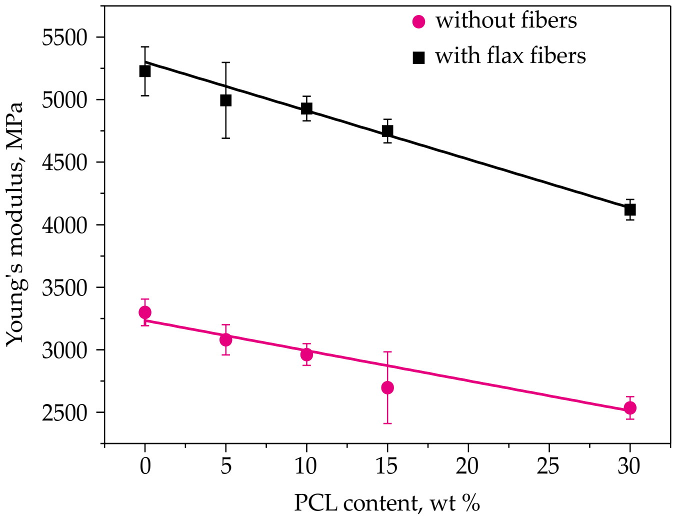

Fig. 7. Young's modulus *versus* PCL content for the samples with or without flax fibers

on this study, graphical representation of morphological evolution due to the ratio of PLA and PCL is schematically presented in Fig. 4. Depending on the PLA to PCL ratio, three morphology systems can be distinguished: spherical dispersion (Figs. 4a, 4e), lamellar dispersion (Figs. 4b, 4d) and co-continuous blend (Fig. 4c). As presented in Fig. 5, flax fibers increased the impact strength of PLA/PCL blends. A significant change in impact strength was observed for the samples containing 30 wt % PCL. These results suggest that between 15 and 30 wt % PCL, the morphology of PLA/PCL blend was significantly transformed, which is consistent with previous study [5].

Samples with flax fibers had higher tensile strength as compared to those without fibers (Fig. 6). However, tensile strength was decreasing with increasing content of PCL for the samples containing or not flax fibers. This resulted mainly from the lower tensile strength of PCL as compared to PLA. Due to the immiscibility of PLA and PCL interphase adhesion could additionally contribute to this decrease.

Flax fibers significantly increased Young's modulus, however, increasing content of PCL resulted in a decrease of this value (Fig. 7). Alike for tensile strength, this decrease was characteristic for the samples whether or not containing the fibers. Despite the decrease in Young's modulus for the sample containing flax fibers and 30 wt % PCL, its final reduced value (4100 MPa) was still higher than that of neat PLA without fibers (3300 MPa).

As presented in Figs. 6 and 7, linear regression was fitted fairly well within the standard deviation interval for tensile strength and Young's modulus. Comparing these data with nonlinear trend observed for impact strength (Fig. 5), one has to keep in mind that phase transformation often will not be reflected at relatively low strain, where cohesive and interfacial adhesion forces are counteracting the forces of deformation. On the other hand, high rate impact strength can reveal formation of co-continuous phase structure of impact resistant PCL blended with brittle PLA.

Crystallization and melting enthalpies were determined by differential scanning calorimetry for cooling and second heating cycles. The DSC curves for PLA and PLA with 20 wt % flax fibers are presented in Fig. 8. It follows from Fig. 8 that fibers acted as nucleant for cold crystallization of PLA. This effect was also reported elsewhere [22, 23]. In this study, it was found that PCL had great impact on crystallization of PLA with no flax fibers whereas for the samples containing flax fibers it was not reflected (Fig. 9). Crystallization and melting enthalpies (H) were calculated separately for each PLA or PCL fraction of the composites, due to the formula:

$$H = \frac{H_{\text{sample}}}{\alpha} \tag{2}$$

where: H_{sample} – enthalpy for the composite sample, and α – mass fraction of PLA or PCL in the composite sample.

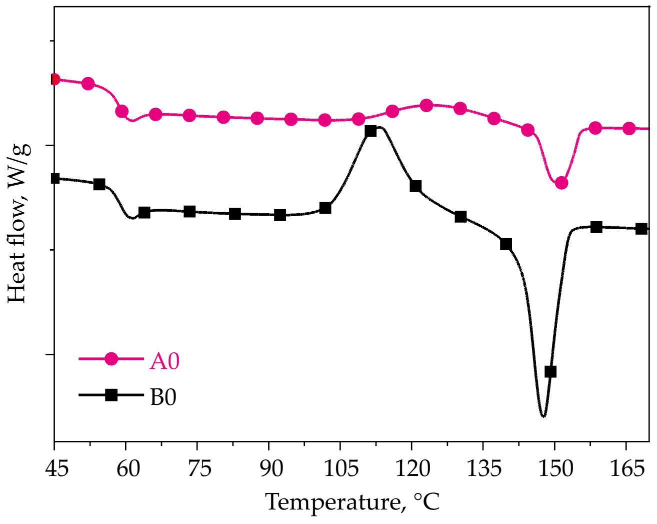

Fig. 8. DSC curves for samples A0 and B0 (second heating cycle)

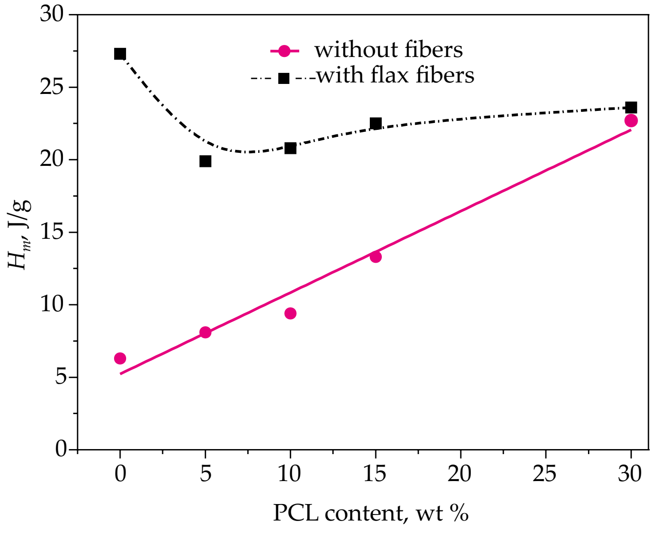

Fig. 9. Melting enthalpy (H_m) for PLA as dependent on PCL content for the samples with and without (reference samples) flax fibers

Table 2. Results of differential scanning calorimetry of studied samples

Sample	PLA				PCL	
	H_{cc}, J/g	T_{cc}, °C	H_m, J/g	T_m, °C	H_c, J/g	T_c, °C
A0	6.6	125.2	6.3	150.9	–	–
A1	8.01	124.7	8.1	150.4	15.2	33.1
A2	9.8	124.6	9.4	149.9	29.7	24.9
A3	13.7	122.6	13.3	149.3	27.2	35.8
A4	22.4	119.0	22.7	148.4	25.4	36.1
B0	27.2	113.4	27.3	147.7	–	–
B1	19.9	121.8	19.9	149.6	19.0	22.4
B2	20.8	121.7	20.8	149.6	16.2	35.0
B3	22.4	117.3	22.5	148.1	47.6	34.5
B4	23.4	118.8	23.6	148.3	33.6	34.4

H_c – enthalpy of crystallization, H_{cc} – enthalpy of cold crystallization, H_m – enthalpy of melting, T_c – point of crystallization, T_{cc} – point of cold crystallization, T_m – point of melting.

With increasing PCL content H_m value for PLA significantly increased from 6.3 to 22.7 J/g (Table 2). These results are consistent with other studies, proving that PCL promotes the crystallization process of PLA [9]. After addition of flax fibers H_m value for PLA also increased to 27.3 but 5 wt % PCL reduced it to about 20 J/g and further increase in PCL content slightly increased H_m value to 23.6 J/g. Generally, it is considered that the plant fibers act as nucleating agent for PLA, which is in line with the presented results. On the other hand, PCL was not able to promote further PLA crystallization as in the case of samples without fibers, probably because the saturation of this process resulted from the presence of fibers. PCL even slightly decreased crystallinity of PLA, potentially because of some alteration of phase morphology.

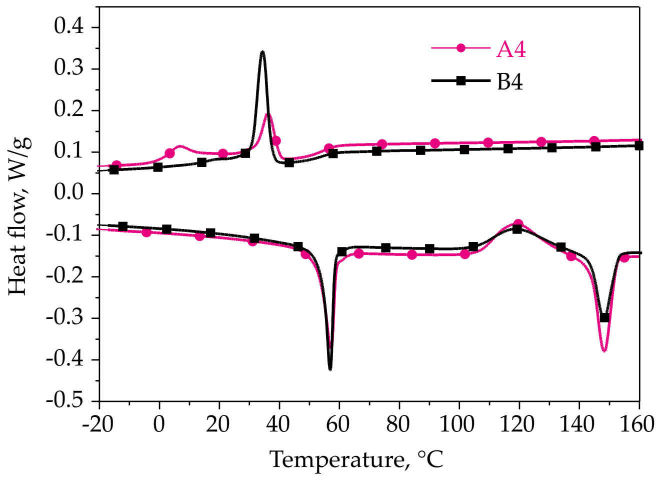

Fig. 10. DSC curves for samples A4 and B4 (cooling and second heating cycles)

Because melting enthalpy of PCL is overlapped with PLA glass transition (Fig. 10), it could not be the subject of quantitative analysis. However, crystallization of PCL was well separated from PLA glass transition in a cooling cycle. It was concluded that crystallization of PCL was more intensive at higher PCL content and also when flax fibers were added, however, this trend had some irregularities (Table 2). In previous publications a nucleating effect of PLA on crystallization of PCL was also noticed [24].

DMA results were consistent with the findings from DSC analysis (Figs. 11 and 12). The effect of fibers on cold crystallization of PLA is well reflected by the increase in storage modulus at the temperature range of cold crystal-

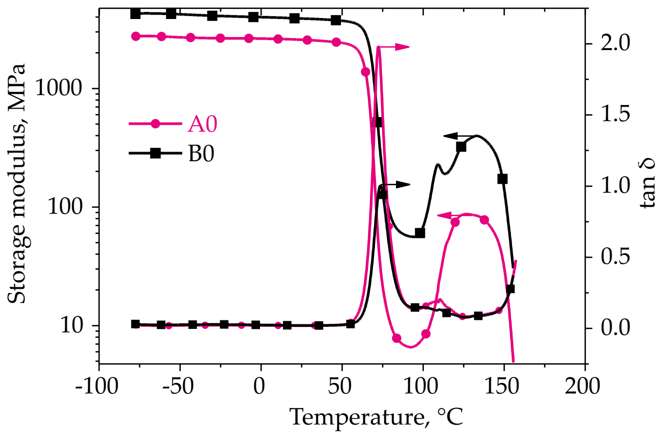

Fig. 11. Storage modulus and tan δ for samples A0 and B0

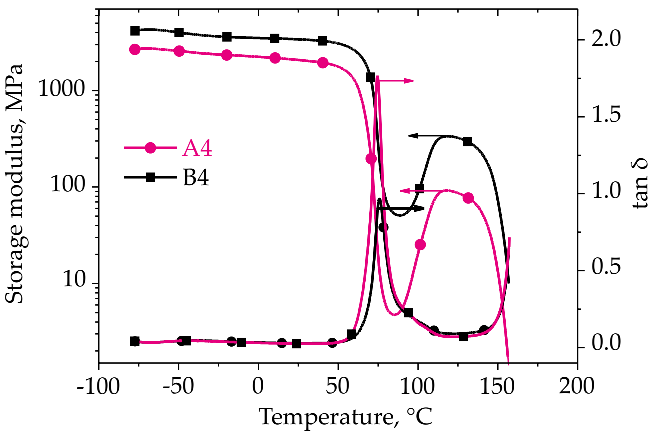

Fig. 12. Storage modulus and tan δ for samples A4 and B4

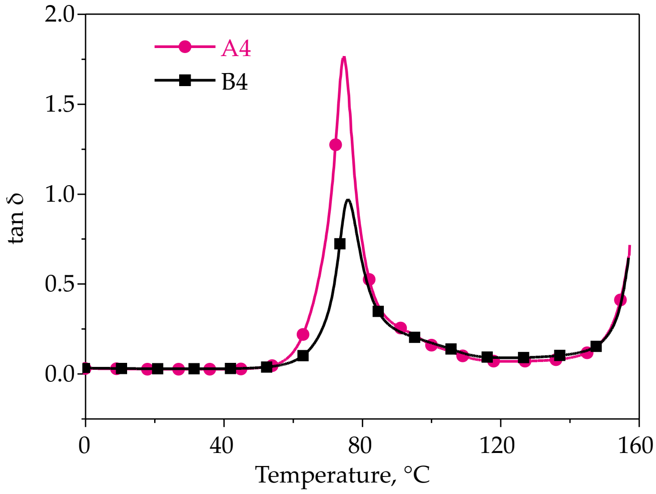

Fig. 13. Tan δ of PLA for samples A4 and B4

lization (from about 100 to 130 °C). This increase is due to the formation of PLA crystallites which led to the stiffening of the material structure. Another very important area of DMA study was glass transition of amorphous polymer phase. Glass transition of PLA occurred from 55 to 90 °C with its maximum at 75 °C, whereas for PCL from -67 to 0 °C with maximum at about -43 °C, as determined based on the changes of damping coefficient (tan δ) (Figs. 13 and 14). A slight increase in this temperature can be noticed for samples containing fibers.

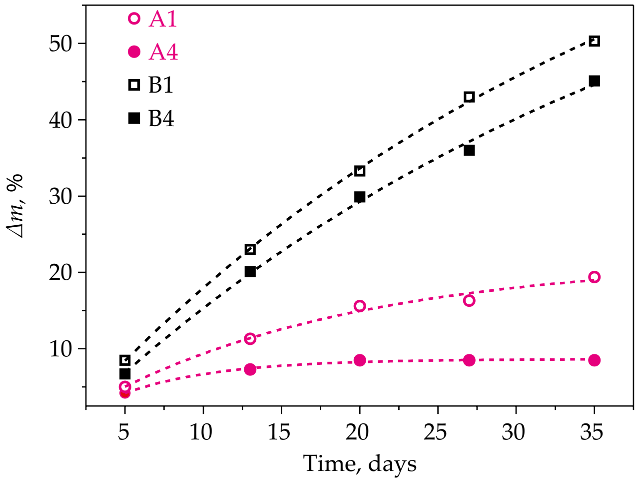

Fig. 15. Mass loss for selected samples (A1, A4, B1, B4) subjected to enzymatic degradation

Table 3. Mass loss of studied samples for specified days of treatment in proteinase K

Sample	Δm (%) after days of treatment				
	5	13	20	27	35
A0	1.5	11.6	15.7	17.3	18.4
A1	5.0	11.3	15.6	16.3	19.4
A2	1.2	4.9	6.1	9.2	9.2
A3	3.7	4.9	8.6	8.6	6.7
A4	4.2	7.3	8.5	8.5	7.9
B0	12.1	34.5	45.6	48.9	49.6
B1	8.5	23.0	33.3	43.0	50.3
B2	7.8	15.7	27.5	35.9	43.1
B3	5.3	14.0	24.7	31.3	37.3
B4	6.7	20.1	29.9	36.0	45.1

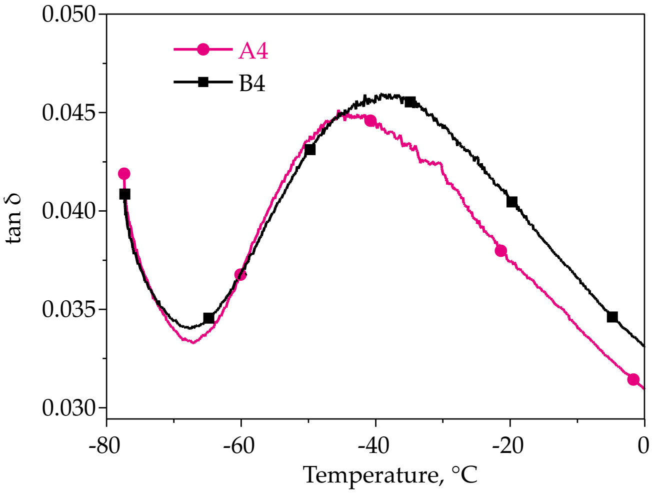

Fig. 14. Tan δ of PCL for samples A4 and B4

Addition of PCL and flax fibers affected biodegradation rate of the studied samples. It was found that polycaprolactone content decreased whereas flax fibers significantly increased enzymatic degradation rate of the examined samples (Table 3 and Fig. 15 only for selected samples). The mass loss of sample A4 after 35 days of treatment was less than 10 % whereas for sample B4 (with flax fibers) it was about 50 %. High impregnability of natural fibers and voids formed between them and polymer provided an opportunity for greater penetration of water and enzymes.

CONCLUSIONS

It was found, that during extrusion and injection molding, flax fibers were shortened from 5 to less than 1 mm as a result of processing conditions. Although this effect can be detrimental to some mechanical properties, it facilitates the use of this filler in injection molding of high quality biocomposite products. Flax fibers were thermally stable up to 200 °C. The extrusion temperature of PLA and thus thermal degradation of natural fibers can be reduced when co-compounded with PCL of low melting temperature (below 60 °C). It was found that 30 wt % PCL significantly increased the impact strength of fiber-reinforced PLA. Flax fibers also increased elastic modulus, biodegradation rate and affected crystallization of PLA and PCL. It was found that PCL had great impact on the crystallization of PLA with no flax fibers (reference samples) but this trend was not observed for the samples containing flax fibers. PLA also affected crystallization of PCL.

PLA with 20 wt % flax fibers and 30 wt % PCL has 25 % higher Young's modulus, 94 % higher impact strength, 145 % higher biodegradation after 35 days of enzymatic treatment and only tensile strength was 24 % lower as compared to the neat PLA. For that reason, PLA modified by melt-compounding with short flax fibers and PCL can be effective material for injection molding of high quality biodegradable products.

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