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Biodegradable polymer packaging materials based on polycaprolactone, starch and polyhydroxybutyrate

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Abstract

In this work, novel multicomponent blends were prepared. These blends were based on three main components: polycaprolactone, native corn starch and polyhydroxybutyrate. All mixtures were prepared using twin screw extruder by two different techniques. The mechanical properties of these materials were evaluated for comparison of influence of different preparation processes on blend's properties. The description of morphology of blends was based on SEM micrographs. The developed three-component materials (polycaprolactone/corn starch/polyhydroxybutyrate) composed mostly of materials from renewable resources were designed, prepared and tested as well.

Keywords: biodegradable polymer materials, corn starch, packaging materials, polycaprolactone, polyhydroxybutyrate

Introduction

Traditional plastic materials exhibit very long time of environmental decomposition, which represents a serious problem with long life of plastic waste. Relatively large part of such waste originates from packaging materials. One possibility of solution of this problem is development of packages from biodegradable polymer materials. On the other hand, these materials usually have problematic processing characteristics as well as lower mechanical properties. These problems can be reduced by blending of two or more polymers in the final blend, where the benefits of individual components can be combined. For example polycaprolactone (PCL) exhibits very good processing stability, but its problem is a high price and low melting point. Corn starch (M100) is a cheap biopolymer, but it is very brittle.

Polyhydroxybutyrate (PHB) has good values of tensile strength, but its main drawbacks are poor processability and high brittleness, which can be eliminated by addition of suitable plasticizer. PHB belongs to a group of biopolymers produced from renewable resources by biotechnology synthesis. In our previous works several two–component blends based on polycaprolactone and various types of starch were prepared (Bugaj 2007; Krošlák 2007). These blends were processed using film blown technology problematically. In our present work, polycaprolactone, corn starch and polyhydroxybutyrate were blended together for preparation of fully biodegradable blends, suitable for environmental friendly packaging materials.

Materials and Methods

The following chemicals were used: Poly(ε-caprolactone) - (PCL) - CAPA 6800 was made by Solvay Caprolactones, UK - is an aliphatic polyester; Native corn starch Meritena 100 – (M100) – was supplied by Amylum Slovakia, Slovakia – containing 27,3% amylose; Polyhydroxybutyrate – (PHB) – was supplied by Biomer, Germany; Glycerol, H_2O – the plasticizers for starch; Triacetine – the plasticizer for PHB; Stearin III – mixture of stearic and palmitic acid was used as processing aid.

Preparation of materials

The two-component blends composed of polycaprolactone (PCL) and native corn starch were modified by addition of polyhydroxybutyrate (PHB). In screening experiments, we investigated the influence of addition of the PHB on the properties of PCL/thermoplastic starch blends. Influence of technology of blend preparation on blend properties was investigated as well. Blends were prepared by one step as well as two steps method.

All the blends were prepared using twin screw extruder with screw diameter 16 mm, L/D = 40 with three kneading zones and with one venting zone situated at 38 D for removing of water from the mixture before extruder head. Screws speed was 300 rpm and temperature profile was as follows (from head to feeder –Table 1):

Table 1: Used temperature profile of heated zones of the twin screw extruder

Heating zone	die	9	8	7	6	5	4	3	2	1
Temperature [°C]	110	120	140	140	140	140	140	130	120	100

Extruder was equipped by one-hole die. Extruded strand was cooled down by air and cut into pellets. In one step process all components were mechanically blended at laboratory temperature and such mechanical mixture was dosed into twin screw extruder. In two step process, at first the blends of PCL, corn starch and plasticizers were extruded using twin screw extruder. In the second step, prepared pellets of PCL/corn starch mixture were blended with PHB using twin screw extruder again. In the first step, glycerol and water were used as plasticizers for starch. In second step, triacetine was used as plasticizer for PHB. Prepared pellets were processed using single screw extruder with screw diameter 19 mm and L/D = 25. Compression ratio was 1:2. Extruder was equipped with rectangular die for production of tapes with dimensions approx. 1 mm thickness and 19 mm width. Test pieces for tensile test were cut from prepared tapes and measured according to ISO 527 standard.

Mechanical properties measurement

For tensile test the Metrotest 5kN machine was used at cross-head speed 1 mm/min in the deformation range of 0 - 3% and after this value of elongation the speed increased up to 50 mm/min. The tensile strength (σb) and the elongation at break (εb) were determined based on recorded tensile curve. The energy necessary to break of the sample was represented by the area under the tensile curve, calculated by integration of tensile curve.

Preparation of the samples for the SEM

Fracture surfaces of the samples were made by breaking of extruded tapes in liquid nitrogen. The fragments with fracture surfaces were glued on metal holder and covered by gold layer in argon atmosphere.

SEM

Scanning electron microscope Tesla BS300 was used for SEM measurements at voltage 20kV. The microscope was equipped with electronic control unit TESCAN, with connection on PC. The picture was scanned electronically in the form of BMP files directly on HDD of controlling computer. Consequently, the picture was processed by software WinTip 3.1.

Results and Discussion

The two-component blends composed of polycaprolactone and native corn starch were prepared as master blend which was in the next experiments modified (composition of the blend is shown in table 2 under no.1). PHB was added to this blend in increasing concentration. In this first series of experiments we investigated the influence of addition of the PHB on the properties of PCL/thermoplastic starch blends as well as influence of technological process at preparation of such blends on final properties. Two technological processes (one step and two step method according to experimental part) were applied for blend preparation. The composition of all prepared blends is listed in Table 2, 3 and 4.

Table 2: The composition of blends prepared using one step technology

Designation of the blend	M 100 [g]	Glycerol [g]	PCL [g]	H_2O [g]	Stearin III [g]	PHB [g]	Weight % of PHB on blend no.1	Triacetine [g]
1	177.6	95.6	225	9.6	1.8	0	0	0
2	177.6	95.6	225	9.6	1.8	50	10	12.5
3	177.6	95.6	225	9.6	1.8	100	20	25
4	177.6	95.6	225	9.6	1.8	150	30	37.5

Table 3: The composition of first mixing step of the blends prepared using two step technology

1. mixing step					
Designation of the blend	M 100 [g]	Glycerol [g]	PCL [g]	H_2O [g]	Stearin III [g]
5	177.6	95.6	225	9.6	1.8
6	177.6	95.6	225	9.6	1.8
7	177.6	95.6	225	9.6	1.8

Table 4: The composition of second mixing step of the blends prepared using two step technology

2.mixing step			
Designation of the blend	Granulate from 1.step [g]	PHB [g]	Triacetin [g]
5	500	50	12.5
6	500	100	25
7	500	150	37.5

The mechanical properties were evaluated to determine the influence of technology on properties of blends with the same composition. Dependencies of mechanical properties on PHB content in the blends are shown in Fig. 1 – 3. The SEM micrographs of fracture surfaces of prepared blends are shown in Fig. 4.

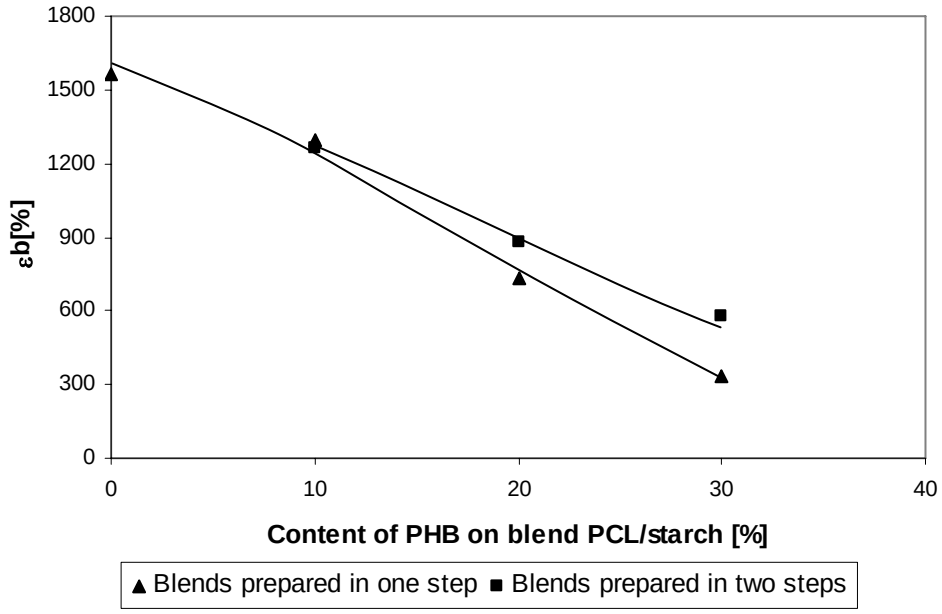

Fig.1: The dependence of elongation at break on the content of PHB in polymer mixture.

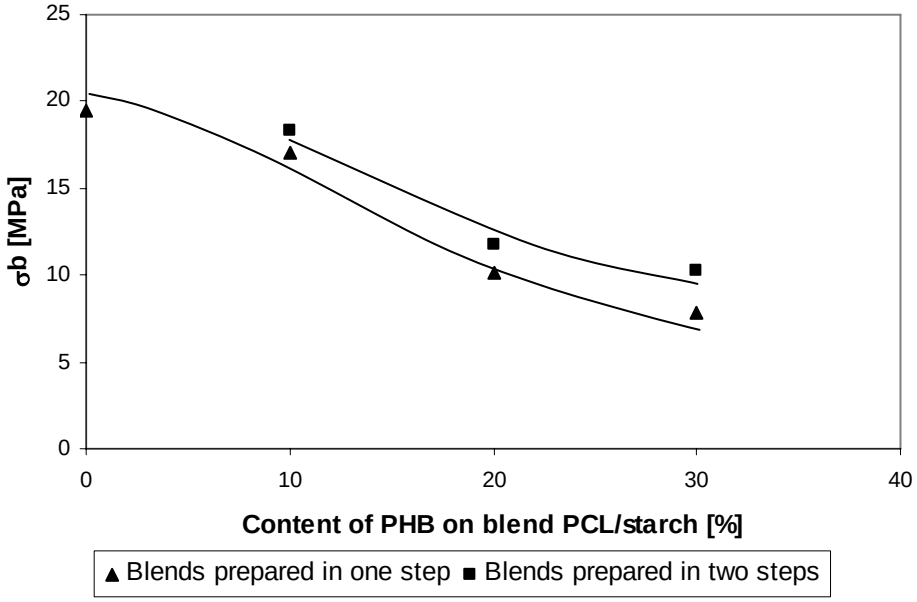

Fig.2: The dependence of tensile strength on the content of PHB in polymer mixture.

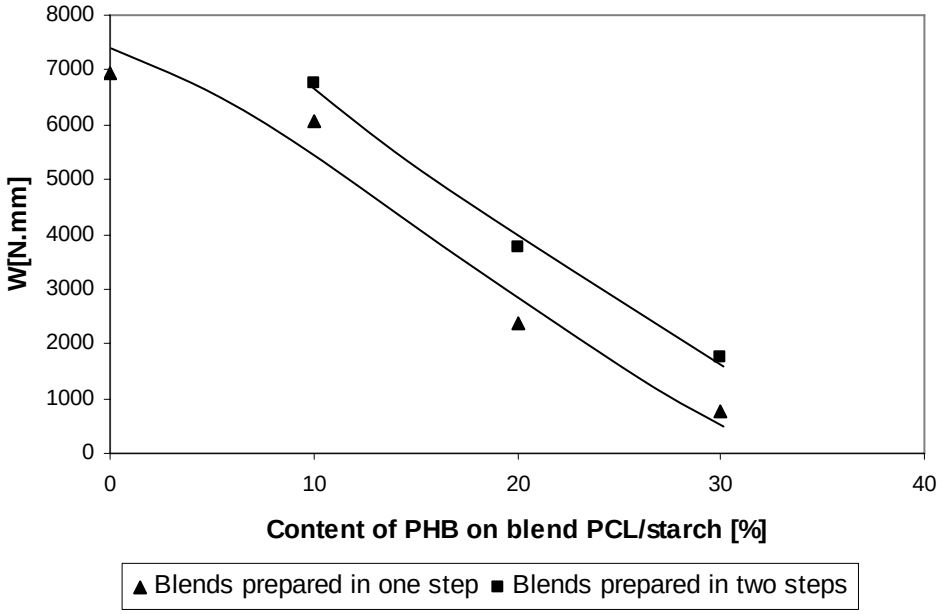

Fig.3: The dependence of the energy necessary to break the sample on the content of PHB in polymer mixture.

From the dependences on Fig.1, 2, and 3, it is obvious that the tensile strength, elongation at break and energy necessary to break the sample decrease with increasing content of polyhydroxybutyrate in the blends. It could be also observed that blends mixed in two steps exhibit slightly better mechanical properties in comparison to blends prepared in only one

step. This difference is more significant at higher content of PHB. This effect can be caused by more effective distribution of corresponding plasticizer into starch and PHB.

On the SEM pictures (Fig. 4), difference in structure of blends prepared in one step and in two steps is evident. All fracture surfaces of samples prepared in two steps show more homogeneous structures than the same blends prepared in one-step mixing technology. This effect might be demonstrated for example at sample no. 4, containing 30 weight % of PHB on the basic PCL/starch blend. There are clearly visible large domains of dispersed component in the matrix, if one step technology was applied. On the other hand, blend with the same composition but prepared using two step technology gives more compact structure without visible larger domains. The more uniform and finer structure results in higher values of mechanical properties.

Based on obtained results, it was shown that both composition and technology of preparation can significantly influence the final morphology of the structure as well as the final properties of prepared materials. Two-step process provides better incorporation of individual plasticizers into reasonable part of polymer blends. Moreover, a better dispergation can be also achieved in comparison with one step process. The obtained results give a good chance for development of real three–component biodegradable blends with increased content of polymers from renewable resources. In the next work optimization of composition will be necessary with respect to concentration of plasticizers for both starch and PHB components as well as the ratios between individual polymers.

Abbreviations and symbols:
εb- Elongation at break
GL – Glycerol
M 100 – Native corn starch Meritena 100
PCL – Polycaprolactone
PHB – Polyhydroxybutyrate
S III – Stearin – mixture of stearic and palmitic acid
σb – Tensile strength
SEM – Scanning electron microscopy
W - Energy necessary to break the sample

Acknowledgement

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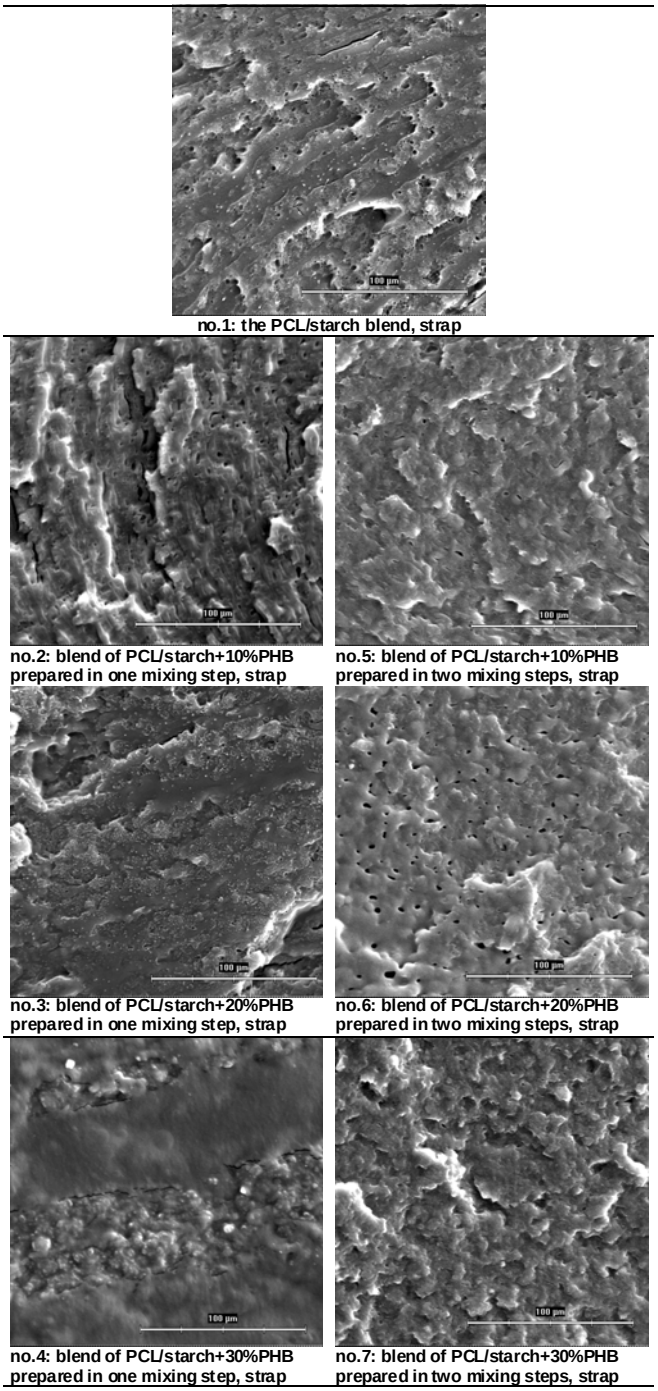

Fig.4: The SEM - micrographs of all prepared samples.

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