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Properties of poly(lactic acid)/Ecoflex rigid foil sheets applied in thermoforming process

RAPID COMMUNICATION

Summary — Selected properties of rigid foil sheets made of poly(lactic acid) (PLA) and their blends with Ecoflex modifier for thermoforming have been presented in this paper. The products have been subjected to strength, gas permeability, gel permeation chromatography (GPC), light transmission and haze as well as surface wettability investigation. The advantageous influence of Ecoflex on processing parameters and sheet quality have been stated. However, this modifier slightly lowered strength parameters and sheet transparency as well.
Key words: biodegradable polymers, poly(lactic acid), rigid foil sheets, biodegradable packagings.

WŁAŚCIWOŚCI SZTYWNYCH FOLII POLI(KWAS MLEKOWY)/ECOFLEX PRZEZNACZONYCH DO TERMOFORMOWANIA
Streszczenie — W artykule przedstawiono wybrane właściwości sztywnych folii wytworzonych z poli(kwasu mlekowego) (PLA) oraz jego mieszanin z modyfikatorem Ecoflex przeznaczonych do termoformowania. Metodą chromatografii żelowej (GPC) wyznaczono ciężary cząsteczkowe otrzymanych polimerów. Wyroby poddano badaniom wytrzymałościowym, przenikalności gazów, transmitancji światła, zamglenia oraz zwilżalności (tabele 1—4). Stwierdzono, że dodatek Ecoflex ma korzystny wpływ na parametry przetwórcze i jakość folii, natomiast nieznacznie pogarsza właściwości wytrzymałościowe i transparentność produktów.
Słowa kluczowe: polimery biodegradowalne, poli(kwas mlekowy), folie sztywne, opakowania biodegradowalne.

The biodegradable materials are a new group of products, whose world consumption increased 15 times in last ten years [1]. The dynamic production growth of those materials results, first of all, from care about natural environment, economy, exploitation of coming to an end deposits of energetic raw materials and last but not least, legislature. Biodegradable materials are used in specialist industry (tissue engineering), in mass production (packaging) and also have been applied as modifiers accelerating decomposition of synthetic polymers in natural environment [2, 3].

The biggest producer of biodegradable materials is American Company LLC Nature Works producing various types of poly(lactic acid) (PLA). Nowadays, this polymer is the most popular in the world and may be processed using standard machines, equipment and technologies for classic polymers [4—11]. PLA in spite of many favorable advantages such as ease of processing, biodegradation and wide possibilities of application, has defects, of which the most important are rigidity, brittleness, water sorption and the possibility of degradation during processing. One way to eliminate or reduce those disadvantageous properties is development of new polymer blends with other biodegradable polymers with suitable properties that can not be used alone. One of such polymers is poly(butylene adipate-*co*-terephthalate) (PBAT) [12—15].

The objective of this study was to examine the influence of commercial PBAT (Ecoflex) on processing and physicochemical properties of PLA sheets.

EXPERIMENTAL

Materials

Poly(lactic acid) (PLA) type 2002D Ingeo (Nature Works LLC, USA) was used for thermoforming of sheets. PLA is characterized by: melting point temperature T_m = 210 °C, glass temperature T_g = 55—58 °C, density 1240 kg/m^3, and melt flow rate of 5—7 g/10 min (210 °C/2.16 kg).

Poly(butylene adipate-*co*-terephthalate) (PBAT) with trade name Ecoflex type C17893 (BASF, Germany),

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applied to improve properties of sheets, was characterized by: T_m = 120 °C and density 1250 kg/m^3.

As an antiblocking agent PLA dc S511 (SUKANO, Switzerland) with T_m about 65 °C and density 1230 kg/m^3 were used.

Preparation of sheets

Three types of sheets were prepared:

— sheet 1: PLA/antiblocking agent of composition specified by mass ratio of 98/2,

— sheet 2: PLA/Ecoflex/antiblocking agent of composition 96/2/2,

— sheet 3: PLA/Ecoflex/antiblocking agent of composition 96/2/2 (extruded at higher temperatures).

All biodegradable materials in pelletized form were prepared by co-rotating twin-screw extrusion provided with gravimetric dosing unit. Polymers as granulates were subjected to sheets extrusion using industrial DIAMAT equipment. The technological line is provided with a single-screw extruder (screw diameter 100 mm) and sheet extrusion die-head of width 1120 mm. For the tests a new plasticizing system, especially screw for PLA has been designed and used. The single screw, of length L/D = 28 with barrier winding and variable groove depth was used for better homogenizing action of the extruded polymer.

Before extrusion all granulates were dried for 4 h at 75 °C in the drier over molecular sieves. The temperatures of the plasticizing system along the cylinder for sheet 1 and sheet 2 ranged between 210 and 240 °C. The temperatures of the extrusion die-head ranged between 230 and 235 °C. Sheet 3 was extruded at temperatures along the cylinder ranging from 230 to 245 °C to check the influence of increased temperatures on sheets properties of PLA/Ecoflex blend. The output capacity of the PLA extrusion attained approx. 140 kg/h. The speed of the screw was 30 min^{-1}.

Methods of testing

Barrier abilities of thermoformed sheets were determined using water vapor permeation and gas permeation devices Lyssy L80-500 and Lyssy 100-500, respectively, according to requirements of standards PN-EN ISO 15106-1 and PN-EN ISO 2556. The analyses were carried out for water vapor, oxygen and carbon dioxide.

Tensile strength has been determined using TIRAtest27025 according to PN-EN ISO 527-1 standard.

Light transmission and haze were determined using Spherical Hazemeter BS 2782 according to PN-EN ISO 13468-1 and PN-84/C-89100 standards.

Surface wettability of sheets was determined by testers (IMPIB Institute) according to ISO 8296 standard.

Molecular weights were determined by size exclusion chromatography (SEC). Chromatographic system was composed of a 1100 Agilent isocratic pump, degasser, autosampler, photometer MALLS DAWN EOS (Wyatt Technology Corporation, Santa Barbara, CA), and differential refractometer Optilab-REX. ASTRA 4.90.07 software (Wyatt Technology Corporation) was used for data collecting and processing. Two PL Gel columns 5 microns MIXED-C were used for separation. Samples were injected as a solution in methylene chloride.

The industrial research of printing sheets was carried on using flexographic printer of speed 7 m/min. The ink from Huber Italia Spa was used for this purpose.

RESULTS AND DISCUSSION

The extrusion of sheet 1 (PLA without Ecoflex) was connected with high energy consumption. After trimming this sheet had feather edges. The sheet sides were uneven, jerked and torn. Sheet 2 (modified with Ecoflex) showed better quality (the sheet after trimming was even without feather edges) and energy consumption during extrusion was lower by about 30 % in comparison to sheet 1. The best quality and processing parameters showed sheet 3 (modified with Ecoflex and extruded at higher temperature).

T a b l e 1. Light transmission coefficient and haze of investigated sheets

Sample	Light transmission coefficient, %	Haze, %
Sheet 1	91.5 ± 0.1	3.8 ± 0.0
Sheet 2	79.1 ± 0.2	71.9 ± 0.2
Sheet 3	83.9 ± 0.1	25.5 ± 0.1

T a b l e 2. Strength properties of investigated sheets when stretching; MD — machine (extrusion) direction, TD — transversal direction

Parameter	Sheet 1		Sheet 2		Sheet 3	
	MD	TD	MD	TD	MD	TD
Tensile strength, MPa	63	62	60	59	64	60
Elongation at break, %	3	3	3	3	3	3
Elasticity modulus, MPa	2535	2167	2689	2417	2844	2815

In industrial tests of sheet extrusion a sheet of thickness 0.45 mm and width 450 mm was obtained. Light transmission coefficients and haze values for prepared sheets are listed in Table 1. Sheet 1 containing only an antiblocking agent showed high transparency of 91.5 %. Addition of modifier (sheet 2) caused substantial decrease of light transparency. The sheet was opaque. However, higher processing temperatures improved transparency by 6 % and lowered its haze 3 times. The changes in light transparency and haze result from changes in crystalline structure of the extruded sheet at higher temperature.

Based on mechanical results, presented in Table 2, it has been stated that the tensile strength at break of PLA samples slightly diminished after adding modifier and the elongation at break remained unaffected. The changes lie within the range of measuring error. The value of elasticity modulus however grew up for modified sheets and was the highest for sheet 3. The reason of those changes may be crosslinking process between PLA chains which is initiated by high temperature.

The results of determination of number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) are presented in Table 3. Chromatographic analysis of PLA substrate and investigated sheets show that the degradation processes occur in the polymer when extruding. The average molecular weights $\overline{M}_n$ and $\overline{M}_w$ for the prepared sheets (1—3) are lower then for neat PLA.

T a b l e 3. Results of average molecular weights and polydispersion degrees

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Pure PLA	89 340	120 900	1.35
Sheet 1	77 590	117 800	1.52
Sheet 2	77 950	110 000	1.41
Sheet 3	83 160	116 200	1.40

$\overline{M}_n$ for sheets 1 and 2 (received in the same temperature) in comparison to pure PLA diminished by about 13 %. For samples extruded at higher temperature profile (sheet 3) one may notice lower diminishing of $\overline{M}_n$ compared to sheets 1 and 2 (fall by 7 %). It may be caused by crosslinking reactions of degraded polymer chains at elevated temperatures. Those processes also cause the growth of elasticity modulus of sheet 3. Decrease of $\overline{M}_w$ as a results of extrusion was smaller than for $\overline{M}_n$. Higher temperatures of processing cause increase of $\overline{M}_w$.

T a b l e 4. Results of barrier abilities of investigated sheets concerning selected media

Sample	Water vapor permeation (38 °C, 90 % Δ*RH*) g/m²/24 h	Oxygen permeation (23 °C, 0.1 MPa) cm³/m²/24 h	Carbon dioxide permeation (23 °C, 0.1 MPa) cm³/m²/24 h
Sheet 1	14.68	70.79	56.49
Sheet 2	15.68	67.14	60.36
Sheet 3	13.16	60.05	58.85

The sheet 1 showed lowered values of wettability than Ecoflex containing sheets (2 and 3). It may confirm the positive influence of this agent on surface wettability of sheet which is extremely important in further processes of sheet processing like printing, coating, gluing. Wettability value for sheets 2 and 3 were 40 mJ/m^2, and for sheet 1 was 38 mJ/m^2. The temperature of processing did not affect the wettability of sheets with Ecoflex. In industrial printing tests it has been stated that in the first case sheet surface did not need any further treatment; in the second one however (sheet 1), the print was not stable and underwent blurring.

The barrier properties were listed in Table 4. Ecoflex has positive influence on oxygen permeation values, the permeation for CO_2 and water vapor however is much higher. Elevated processing temperatures have positive influence on permeation values of all investigated sheets.

CONCLUSIONS

Based on obtained results one can state that Ecoflex as additive for PLA sheets causes their haze and lower transparency. Higher temperature of sheets processing improve their transparency. It considerably improves their processing properties but negatively influences the strength properties. However, the fall of those values was negligible. Ecoflex also improves the barrier properties of the sheet against water vapor (only when higher processing temperature was used) and oxygen but worsens them against carbon dioxide CO_2. During extrusion the polymer undergoes slight thermal and mechanical degradation.

The packagings obtained in the processes mentioned above show good physicochemical and utility properties and may be applied for packaging of food. The products worked out in the Institute IMPIB in Toruń are first products of this type in Poland on industrial scale.

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