Comparative study of physical and chemical properties of PLA-based films obtained by solution casting and flat-slot die melt extrusion

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Abstract. In this study the effect of processing methods on physical and chemical properties of polylactide (PLA) (Mn 130 kDa, L-93/ D-7) was investigated. PLA-films were obtained by solution casting and melt extrusion using Bestfiilament extruder equipped with flat-slot die. SEM, AFM, FTIR-spectroscopy and DSC were used for characterization of the films. The films obtained by flat-slot die melt extrusion had a relief surface with prominent strands and inclusions, while the cast films had a smooth surface with pores or gaps ranging in size from 20 to 60 μm. The average roughness (Ra) and root-mean-square roughness (Rq) of the surface of cast films were at the level of 45-48 and 37-39 nm, respectively. Meanwhile, for the melt films these values increased and corresponded to 122 and 65 nm, respectively. According to FTIR, both types of films were characterized by an increase in the absorption peaks at 1800-1700, 1450-1470 and 1350-1320 cm-1, which correspond to stretch vibrations of ester bond and bending vibrations of the C-H bond, respectively. DSC data showed decrease in crystallinity of PLA and change in its internal structure from amorphous-crystalline to amorphous after the processing.

1 Introduction

Polylactide (PLA) is a polymer of lactic acid and its cyclic esters (L,L-lactide, D,L-lactide, D,D-lactide, meso-lactide) and is one of the widely used biodegradable polymers in the world [1]. PLA has drawn interest due to its availability and degradability affected by environmental factors [2]. At present, PLA is mainly applied in biomedicine [3], packaging industry [4] and agriculture [5]. It is known that the ester bonds of PLA tend to break down under the influence of temperature, resulting in a change in the crystallinity of the polymer [6]. Therefore, the mechanical and thermal properties of PLA products as well as their biodegradation rate depend on their production conditions [2].

Factors determining the heat resistance of PLA are its phase state, stereochemical structure and molecular weight. The presence of crystallites promotes the amorphous phase of the poly-L-lactide (PLLA) to be highly elastic below the melting point. The amorphous poly-D,L-lactide (PDLA) compared to the amorphous-crystalline PLLA changes from highly

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elastic to a plastic state at much lower temperatures [7]. Depending on applied processing methods of PLA products, its crystals may grow in three structural positions called α-, β- and γ-forms. They are characterized by different helix conformation and cell symmetry [8]. The α-form develops during melt or cold crystallization, and the β-form develops during mechanical stretching of the more stable α- and γ-forms [9].

Crystallinity increase of PLA contributes to its processing options and increases physical and mechanical characteristics of the resulting products. However, it should be taken into account that PLA processing methods (e.g., injection molding, melt extrusion, solution casting) lead to a significant change in the original properties. In the study by Krul et al. (2011) PLLA films obtained by solution casting demonstrated a high degree of crystallinity up to 39 % [10]. Meanwhile, when using injection molding phase structure of the cast products goes to the amorphous phase since crystallization processes do not have time to develop due to rapid cooling of PLLA melt.

It should be noted that PLA crystallization rate is significantly lower than that of other thermoplastics, which limits its high-scale production. The main method of PLA processing is melt extrusion which involves a mechanical forcing of the molten polymer through a gauge die with a diameter corresponding to the resulted product. During the extrusion of biodegradable polymers, premature degradation may occur. In the case of PLA, different types of degradation can occur simultaneously.

At high temperatures (above 180 °C) the increase in melt flowability of PLA leads to a decrease in its viscosity and the start of mechanical degradation. This is due to the vibrational energy of polymer bonds, which increases with temperature, making the bonds more prone to cleavage. In addition, an increase in temperature of the extrusion leads to oxygen molecules becoming more mobile, thus promoting oxidative degradation [11].

In contrast to conventional strand die extrusion, flat-slot die extrusion involves distributing the melt over the width of the die, exiting it as a strip and winding it on a cooling drum, which prevents the growth of large spherulites and promotes rapid crystallization.

In the present study, PLA film obtained by flat-slot die extrusion was cooled at room temperature, so that the natural crystallization processes could be clarified, and compared with PLA film obtained by solution casting. Thus, the aim of this study was to investigate the crystallinity and thermal characteristics of PLA films obtained by solution casting and flat-slot die melt extrusion.

2 Materials and methods

2.1 Materials

In this study, polylactide (PLA) (“NatureWorks”, USA) with M_w = 115 kDa, C_x = 62%, T_m = 170º C was used. The ratio of L- to D- isomers was determined by the modified method described in [16] after derivatization with α-menthol. Chloroform (“Ekos-1”, Russia) was used as a solvent. It was determined that the used PLA had a 7 % content of D-isomer. Thus, it was characterized as being in an amorphous-crystalline state, and its thermal behavior can be altered during processing.

2.2 Obtaining of the PLA products

PLA cast films were obtained by solution casting. First, PLA was dissolved in chloroform (3% solution). The resulting solution was then poured into Petri dish and placed in a fume hood at room temperature for 48 h for complete evaporation of the solvent. PLA melt films were obtained using a single screw extruder (“Bestfilament”, Russia) at a melting

temperature of 170º C, with a screw rotation speed of 12 rpm. A steel flat-slot die designed in RCCU "SAS" of Reshetnev Siberian state university (Krasnoyarsk, Russia) was used for the forming of the film.

2.3 Scanning electron microscopy (SEM), contact angle measurements and atomic force microscopy (AFM)

Microstructure of the obtained films was studied by scanning electron microscopy (SEM) (TM-4500, equipment of Krasnoyarsk Regional Center of Research Equipment of Federal Research Center "Krasnoyarsk Science Center SB RAS"). Previously, the samples were coated with platinum (at 10 mA, for 45 s) with Emitech K575X sputter coater.

The surface properties of the obtained polymer films were studied using an OCA 25 measuring device for contact angle measurements and the drop shape analysis. The subsequent data processing was performed using SCA 20 software.

The surface roughness of the films was studied by atomic force microscopy (AFM) using atomic-force microscope "INTEGRA-AURA" (NT-MDT, Russia) in the semi-contact mode with calculation of the average (Ra) and root-mean-square roughness (Rq).

2.4 Fourier-transform infrared spectroscopy

Chemical structure of the samples was studied by infrared spectroscopy with Fourier transform using the Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA) and the ITX Smart prefix (Thermo Scientific, USA) with a diamond crystal by disturbed total internal reflection method (DTIR). The analyses were carried out with a spectral resolution of 4 cm–1, averaged over 32 scans, in the range of 4000 - 400 cm–1. The obtained IR-Fourier spectra were processed in the OMNIC software applying advanced correction of disturbed total internal reflection.

2.5 Differential scanning microscopy

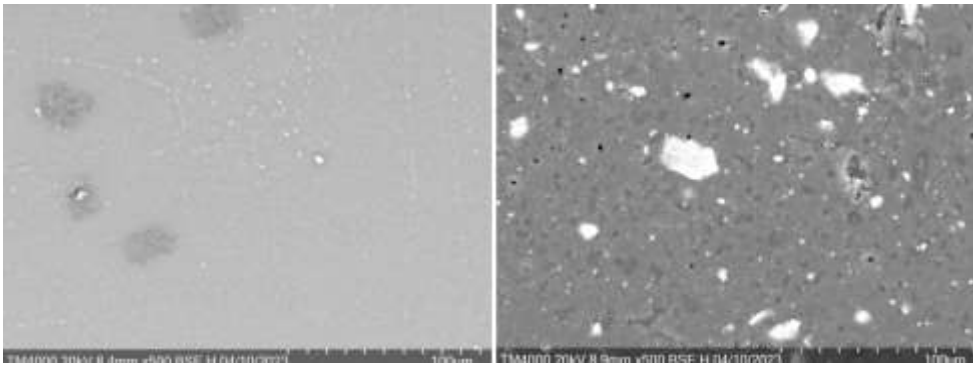
Temperature modulated differential scanning calorimetry of the samples was performed using DSC25 differential scanning calorimeter (TA Instruments, USA) in standard aluminum crucibles, in an atmosphere of pure N_2 , at a flow rate of 70 ml/min. The samples were heated in the temperature range from -10 to 150 °C at a rate of 10 °C/min. The first heating to 150 °C was performed at a rate of 20 °C/min. The sinusoidal heat flow was modulated with a period of 60 s and an amplitude of ±1 °C. Glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting point (T_m) peaks were identified on the obtained DSC curves. ΔH_m was calculated from the area of the melting peak using TRIOS software.

3 Results

3.1 Microstructure and surface properties of the obtained PLA films

The films with a thickness up to 150 μm and up to 190 μm were obtained by solution casting and flat-slot die melt extrusion, respectively. The films obtained by flat-slot die melt extrusion had some visual differences and a relief surface with prominent strands and inclusions, which is also notable on electron microphotographs (Figure 1). In contrast, the cast films had a smooth surface with pores or gaps ranging in size from 20 to 60 μm. The

inclusions on the surface of melt films are most likely due to uneven melting of the polymer and the exit of the PLA through the flat-slot die.



a) b)

Fig. 1. Surface microphotographs of PLA films obtained by solution casting (a) and flat-slot die extrusion (b). Magnification x500.

To determine the surface properties of the studied films, sessile drop technique was used which implies measuring of the contact angle made by the intersection of the liquid/solid interface and the liquid/air interface (Table 1). High hydrophobicity and hydrophilicity can have different effects on wettability and degradation of the sample surface.

Table 1. Contact angles and components the solid's surface energy of water droplets on PLA product samples.

PLA product sample	Contact angle, °	Dispersive component, mN/m	Polar component, mN/m
cast PLA film	86,1 ± 7,7	42,2	5,1
melt PLA film	96,1 ± 5,7	41,9	5,7

The application of the solution casting method with subsequent evaporation of the solvent leads to the formation of a hydrophobic surface of the PLA film with a contact angle 86.1 ± 7.7 °. For the film, obtained by flat-slot die extrusion, the corresponding value was slightly higher and amounted to 96.1 ± 5.7 °. Dispersive and polar component values for both films were at the level of 42 mN/m and 5,7 mN/m respectively, corresponding to the values characteristic for hydrophobic films [12].

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AFM study of the surface of PLA films obtained by solution casting and flat-slot die extrusion (Figure 2) showed that the method of processing affects the indicators of surface roughness.

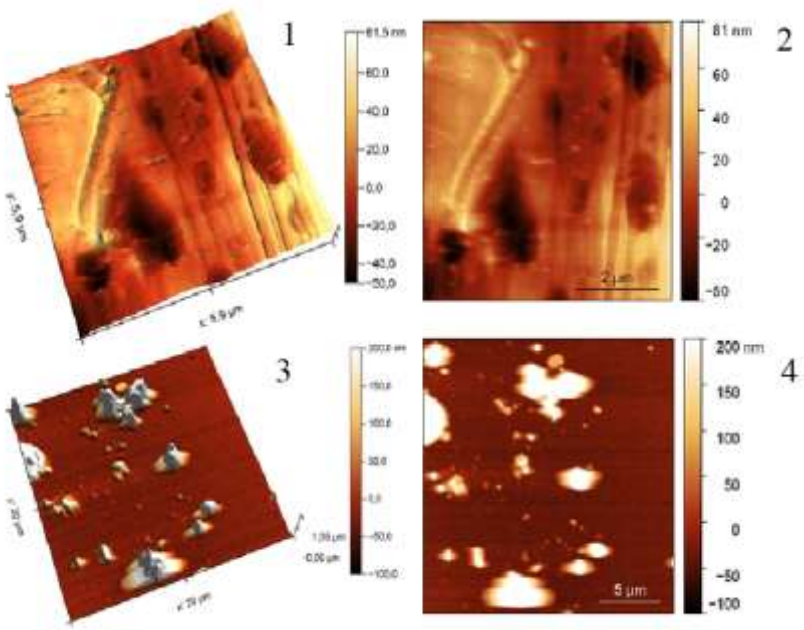

Fig. 2. AFM images of PLA films: 1,3 – AMF topography images of PLA films obtained by solution casting and flat-slot die extrusion, respectively; 2,4 – AMF phase images of PLA films obtained by solution casting and flat-slot die extrusion, respectively.

Thus, despite the hydrolysis susceptability of PLA, the surface of the resulted products is quite hydrophobic. However, the method of processing should be taken into account since it affects the structure and relief of the products surface.

3.2 FTIR spectroscopy

Using FTIR spectroscopy, IR spectra of neat PLA and resulted cast film and melt film were obtained. Figure 3 shows IR spectra of PLA films with characteristic bands. Stretch vibrations of -CH in the CH_3 group, which correspond to bands at 2940-2996 cm^{-1} (symmetrical vibrations) were visible. Stretch vibrations of the carbonyl group C=O (band 1747 cm^{-1}) and stretch vibrations of oxygen (in the C-O-C group) corresponding to a range of bands from 1081 cm^{-1} to 1229 cm^{-1} were also noted along with symmetrical and asymmetrical stretch vibrations of C-O-C in the range 860-956 cm^{-1} and bending vibrations of CH_2 at 703 cm^{-1}.

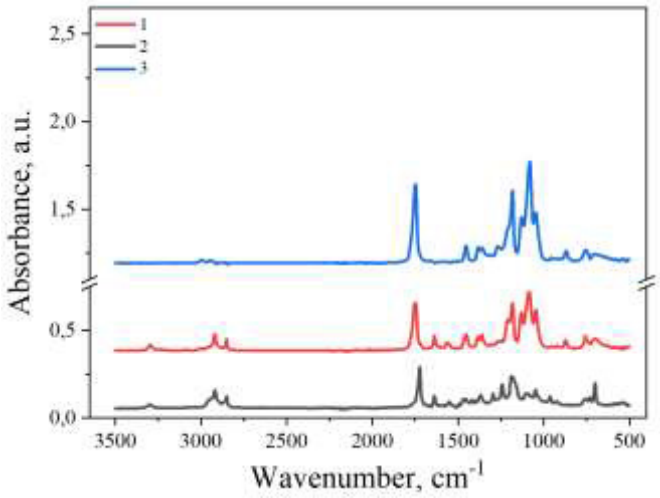

Fig. 3. IR spectra of neat PLA (1) and PLA films obtained by solution casting (2) and flat-slot die extrusion (3).

The differences in IR spectra of the obtained samples and the neat PLA were also found. Specifically, the absence of pronounced bands in the range of 2800-1900 cm-1 was noted for the obtained samples, whereas for the neat PLA a peak in the region of 2849.50 cm-1, characteristic for stretch vibrations of CH3, was observed. In 3400-2700 cm-1 region FTIR spectra of the neat polymer also had a pronounced peak at 3350-3250 cm-1, which corresponds to the vibrations of alkyl bonds ≡C-H. In 1900-900 cm-1 region increased vibrations of the bonds were observed for both types of PLA films compared to the neat PLA. In particular, the films were characterized by an increase in the absorption peaks at 1800-1700, 1450-1470 and 1350-1320 cm-1, which correspond to stretch vibrations of ester bond and bending vibrations of the C-H bond, respectively.

3.3 DSC

To understand the thermal processes occurring during PLA processing differential scanning calorimetry (DSC) was performed. According to differential scanning calorimetry (DSC) curves, during primary and secondary heating of neat PLA two peaks can be observed: a slight glass transition peak and a melting peak. First heating Tg was 59.1ºC, but it decreased down to 56.3º C according to second heating, while Tm decreased from 152, 3 ºC to 147 ºC. This effect could be due to water evaporation during first heating, small amounts of which could be absorbed during PLA synthesis. It was found earlier that the used PLA represents a blend of L-and D-isomers (93/7 %) and has an amorphous structure at room temperature [7], which was confirmed by the absence of the cold crystallization peak according to DSC data. A tenfold decrease in enthalpy indicates negligible heat loss during second heating. Crystallinity values of neat PLA and resulted films were preliminary calculated according to the following formula [13]:

$$\chi = \Delta H_{exp}/\Delta H_{stand} \quad (1)$$

where χ – the degree of crystallinity, ΔH_{exp} – melting enthalpy of the sample measured at the melting point, ΔH_{stand} – melting enthalpy of 100% crystalline PLA (~ 93.7 J/g) measured at the equilibrium melting point.

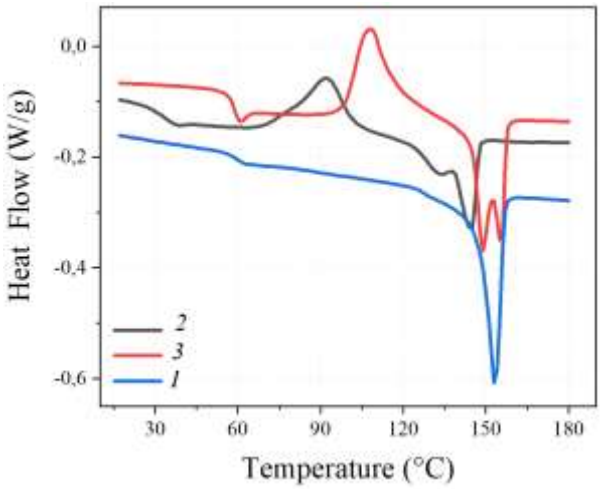

Fig. 4. DSC curves of neat PLA (1) and PLA films obtained by solution casting (2) and flat-slot die extrusion (3).

According to the calculated theoretical data, first heating crystallinity of the neat PLA was at the level 34.2%. However, second heating crystallinity significantly drops down to 3%, which means that after first heating a tenfold drop in crystallinity occurred probably due to changes in the structure of PLA. In general, these results support the assumption of the polymer having an amorphous state. Melting enthalpy is the heat energy required to break the intermolecular bonds in the polymer crystal lattice. Melting enthalpy of the neat PLA probably decreased due to the destruction of the crystal structure.

On the DSC curve of PLA film obtained by solution casting the peaks referring to glass transition temperature (~32.8°C), melting point (~144.6°C) and cold crystallization temperature (~92.7°C) shift to high temperatures after first heating (Table 4). At the same time, the enthalpy of melting increases insignificantly to 21 J/g. These processes can be explained by the slow crystallization of the film due to solvent evaporation. According to the calculated data, the crystallinity of the film was 21.3 %.

Table 2. Thermal characteristics of neat PLA and PLA-based products obtained using different processing methods

Sample	Heating	T_g , ºC	T_{cc} , ºC	T_m , ºC	Δ H_m, J/g
neat PLA	1st	59,1	-	153,2	32
	2nd	56,3		147,2	3
cast PLA film	1st	28,3	83,5	144,0	19
	2nd	32,8	92,7	144,6	21
melt PLA film	1st	57,7	106,9	148,9/155,4	24,6
	2nd	58,3	108,3	149,1/155,3	24,9

The DSC curve of PLA film obtained by flat-slot die extrusion demonstrated the presence of all four peaks that shift to higher temperatures during second heating: The respective Tg, Tcc and double Tm were 58.3, 108.3°C and 141.1/155.3°C. The occuring of double melting point was noted only for melt films, indicating the formation of two types of crystals of different sizes.

Thus, the change of PLA properties after processing is also confirmed by DSC data, indicating the neat PLA undergoing significant changes when exposed to heat. The applied

processing methods led to changes in crystallinity, decrease in glass transition temperature and melting point of the PLA products compared to the neat polymer. This effect is most prominent when comparing the neat PLA and the film obtained by solution casting. Tg and Tm of the cast film decreased by 1.7 and 3 °C respectively compared to the neat polymer.

4 Conclusion

Two processing methods (solution casting and flat-slot die extrusion) were used to obtain PLA films. The films obtained by flat-slot die melt extrusion had some visual differences and a relief surface with prominent strands and inclusions, which is also notable on electron microphotographs. In contrast, the cast films had a smooth surface with pores or gaps ranging in size from 20 to 60 μm.

Dispersive and polar component values for both films were at the level of 42 mN/m and 5,7 mN/m respectively, corresponding to the values characteristic for hydrophobic films.

The application of the solution casting method with subsequent evaporation of the solvent leads to the formation of a hydrophobic surface of the PLA film with a contact angle 86.1 ± 7.7 °. For the film, obtained by flat-slot die extrusion, the corresponding value was slightly higher and amounted to 96.1 ± 5.7 °. Dispersive and polar component values for both films were at the level of 42 mN/m and 5,7 mN/m respectively, corresponding to the values characteristic for hydrophobic films.

AFM study of the surface of PLA films obtained by solution casting and flat-slot die extrusion showed that the method of processing affects the indicators of surface roughness.

In general, the change of PLA properties after processing was confirmed by DSC data, indicating the neat PLA undergoing significant changes when exposed to heat. The applied processing methods led to changes in crystallinity, decrease in glass transition temperature and melting point of the PLA products compared to the neat polymer. This effect is most prominent when comparing the neat PLA and the film obtained by solution casting. Tg and Tm of the cast film decreased by 1.7 and 3°C respectively compared to the neat polymer.

The obtained results can be practically used in manufacturing to predict the properties of polymer products after applying specific processing methods.

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