

18 RUŽIČKINI DANI

DANAS ZNANOST – SUTRA INDUSTRIJA

16. – 18. rujna 2020. |



ZBORNIK RADOVA

Preparation and characterization of biodegradable poly(lactid acid) and poly(ethylene oxide) blends

Miće Jakić*, Sanja Perinović Jozić, Tina Slatina, Mihaela Storić

*Faculty of Chemistry and Technology, University of Split,
Ruđera Boškovića 35, 21 000 Split, Croatia
Corresponding author: mjakic@ktf-split.hr

Summary

The aim of this work was to prepare blends of biodegradable polylactid acid (PLA) with poly(ethylene oxide) (PEO) and to investigate possible interactions within prepared polymer blends. Investigated blends were prepared by hot melt extrusion (HME) process in a laboratory extruder. The thermal characteristics of neat polymers and their blends were investigated by differential scanning calorimetry (DSC) in a nitrogen atmosphere. The glass transition temperature of PLA in the PLA/PEO blends could not be determined because it was overlapped with an endothermic peak of PEO melting. The change of melting temperatures at higher PLA or PEO content indicated that PLA and PEO are only partially miscible in the melt. Fourier transform infrared spectroscopy (FT-IR) was used to investigate possible interactions between polymers. The observed shifting of peak maxima in FT-IR spectra of blends with higher PLA or PEO content are significant enough to confirm the interactions between the investigated polymers in blends, as well as the results of DSC analysis. Thermal stability of PLA/PEO blends has been investigated by thermogravimetric analysis (TG) in non-isothermal heating regime in a nitrogen atmosphere. Neat polymers exhibit single stage degradation, while a two-stage degradation pattern is seen in the case of all PLA/PEO blends. From characteristic of TG curves, it could be concluded that the degradation of PLA/PEO blends starts at lower temperatures and occurs more slowly by addition of PEO.

Keywords: polylactid acid, poly(ethylene oxide), differential scanning calorimetry, Fourier transform infrared spectroscopy, thermogravimetric analysis

Introduction

Poly(lactic acid) (PLA) as an environmentally friendly biodegradable polymer, derived from renewable agricultural resources such as corn and sugar cane, is a promising alternative to petroleum-based polymers because of its renewability, biodegradability, compostability and non-toxicity. PLA is one of the most frequently used biodegradable polymers, especially in packaging and medical applications due to its high strength, high modulus, good transparency, processability and biocompatibility. However, PLA also has the drawbacks of inherent brittleness and poor toughness, which limit its large-scale commercial applications. In order to compete with the low-cost commodity polymers, many strategies such as blending PLA with other polymers, modifying PLA with plasticizers, blending with inorganic nano-fillers or copolymerization have been devised. The blending of PLA with other biocompatible polymers, i.e. poly(ethylene oxide), is considered as a practical and economical approach (Yang et al 2001; Chieng et al. 2014; Saha et al. 2018).

Poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) are the most commercially important polyethers. PEG refers to an oligomer (molecular weight below 20,000) and PEO is polymer of ethylene oxide commercially available in the wide range of molecular weights (20,000–8,000,000). Besides the differences in molecular weight they have different end groups (PEG: –OH and PEO :–CH₃) and different physical properties. However, due to chain length effects, their chemical properties are nearly identical (Vrandečić et al. 2010). As a biodegradable plasticizer, low-molecular weight PEG, due to its miscibility, biodegradability and food contactable application, has proved to be the most suitable as an impact modifier for PLA (Mohapatra et al. 2014). Sheth et al. (1997) have investigated PLA/PEG blends and concluded that depending upon the PEG concentration miscibility varied from completely miscible to partially miscible. Recent studies on PLA plasticized with PEG in various contents have shown a limit of miscibility of polymer blends. The plasticizing efficiency increased with decreasing molecular weight of PEG. However, the same showed brittle nature at higher content because of a lack of adhesion between the separate phases. The addition of PEG also reduced the glass transition temperature and the melting temperature of the virgin polymer (Mohapatra et al. 2014). Chieng et al. (2013) employed PEG to improve the ductility of PLA. PEG acted as plasticizer and reduced glass transition temperature of PLA. Likewise, PLA/PEG blend was not stable due to phase separation at ambient temperatures leading to the formation of PLA-rich and PEG-rich phases (Hu et al. 2003b). However, papers dealing with high molecular PEO in the blend with PLA are only few (Nijenhuis et al. 1996, Oliveira et al. 2013, Saha et al. 2018). Nijenhuis et al. (1996), by using differential scanning calorimetry, concluded that blends containing up to 50 weight % PEO showed single glass transition temperatures. Likewise, the PLA and PEO melting temperatures were found to decrease on blending. Finally, later authors concluded that the PLA and PEO are miscible in the amorphous phase. On the other hand, Oliveira et al. (2013) investigated the properties of mixtures of PLA and PEO in polymer solutions (chloroform) by dilute solution viscometry and infrared spectroscopy. Their results revealed interactions, which authors attributed to dipole–dipole interactions between the ester groups of PLA and the ether groups of PEO.

In this work, an attempt was made to prepare blends of biodegradable PLA with high molecular PEO by hot-melt extrusion, technique commonly used in plastic industry. Likewise, in order to elucidate possible interaction of PLA and PEO in the melt, infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis were utilized.

Materials and Methods

PEO, supplied by Sigma-Aldrich (100 000 g/mol), and PLA, supplied by NatureWorks (72 000 g/mol), were utilized. The PLA/PEO blends of different mass fraction of polymers (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) were prepared by extrusion in a laboratory extruder (Dynisco, Qualitest North America) at 170 °C and screw speed 120 rpm. Fig. 1 represent the extruded samples used for further characterization. It is evident (colour) that neat polymers and their blends didn't undergo thermal degradation during preparation process.

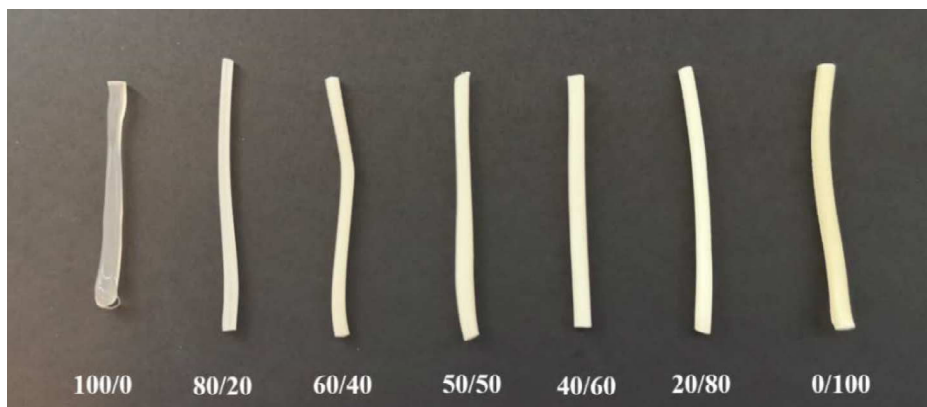


Figure 1. The extruded samples of PLA/PEO blends

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer by the Horizontal Attenuated Total Reflectance (HATR) technique. The internal reflection crystal, made of zinc selenide (ZnSe), had a 45° angle of incidence to the IR beam. Spectra were acquired in the measurement range 4000-650 1/cm at the room temperature. Signals were collected in 10 scans at a resolution of 4 1/cm and were ratiomed against a background spectrum recorded from the empty ZnSe crystal at the room temperature.

Differential scanning calorimetry (DSC)

The thermal characteristics of PLA/PEO blends were investigated by the differential scanning calorimetry (Mettler Toledo DSC 823^o) in the nitrogen atmosphere (30 mL/min). The calibration was performed with indium and the samples were pressed in aluminium pans. The samples of approximately 15 mg were heated at a rate of 20 °C/min from (-90) to 210 °C, cooled at the same rate to (-90) °C and reheated to 210 °C. All thermal transition parameters of the PLA/PEO blends (glass transition, melting and crystallization) were determined according to international standards ISO 11357-2 and ISO 11357-326. More information can be found in the work of Jakić et al. (2016) and Perinović Jozić S. et al (2020).

Thermogravimetric analysis (TG)

Thermogravimetric measurements of the PLA/PEO blends were conducted by using PerkinElmer Pyris 1 TGA thermobalance at the heating rate of 10 °C/min in a temperature range 50-550 °C under a steady flow of nitrogen (20 mL/min). Samples weighing approximately 10 mg for the analysis were used. To evaluate the thermal stability of the investigated polymers different criteria were used (Jakić et al., 2013).

Results and Discussion

Fourier transform infrared spectroscopy

The FT-IR spectra of neat polymers and PLA/PEO blends are presented in Figs. 2 and 3. The spectra of neat polymers contain absorption bands that are characteristic only for PLA or PEO, respectively, and these peaks can be used as an indication of the specific interactions between polymers in the blend. Selected polymers spectrum characteristic peaks and corresponding assignments of interest are summarized in Table 1.

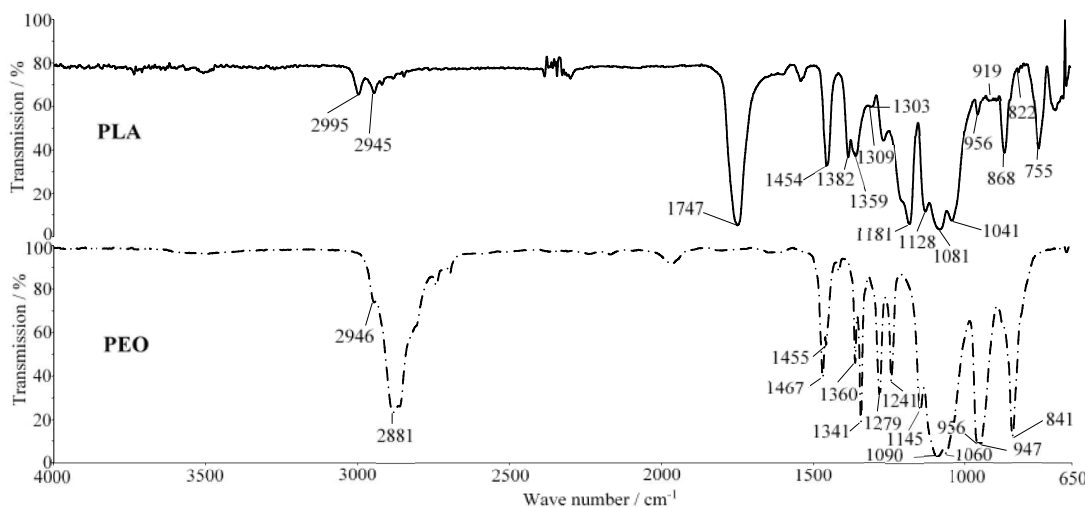


Figure 2. Comparison of the FT-IR spectra of neat PLA and neat PEO

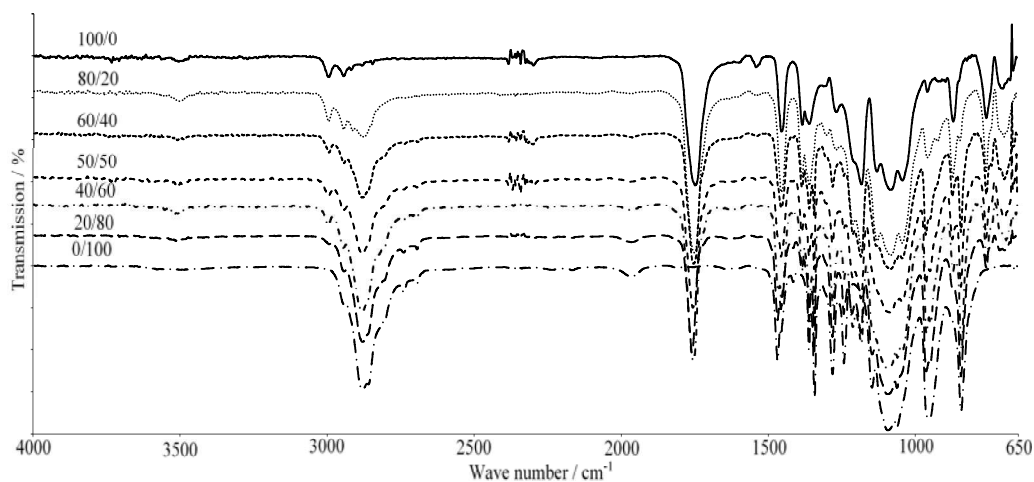


Figure 3. FT-IR spectra of PLA/PEO blends

Table 1. Selected wave numbers (cm^{-1}) and assignments of IR bands of interest, exhibited by neat polymers (Auras et al., 2010, Sim et al., 2010) in the PLA/PEO blends

PLA/PEO	100/0	80/20	60/40	50/50	40/60	20/80	0/100
C=O							
<i>asym. stretching</i>	1747	1750	1753	1756	1756	1759	-
C-O-C							
<i>stretching asym./sym.</i>	1181/ 1081	1181/ 1082	1182/ 1082	1182/ 1084	1183/ -	1183/ -	
C-O-C sym. stretching (triplet)	-/-/-	-/ -	-/ 1060	-/ 1060	-/ 1060	1144/ 1092/ 1060	1145/ 1090/ 1060
CH₂ rocking; C-O-C scissor/ deformation	-	845	842	842	842	841	841

The C=O stretching region that appeared in FT-IR spectra at 1747 cm^{-1} as a broad asymmetric band is characteristic of the ester (PLA). Upon PEO addition, the C=O band is shifted by 12 cm^{-1} (blend 20/80) to higher wave number. In the spectral range of $1000\text{-}1300 \text{ cm}^{-1}$, the crystalline phase of PEO is featured by the characteristic *triplet* with the sharp central peak of strong intensity (Sim et al., 2010). Changes in the intensity, shape, and position of the characteristic triplet can be associated with the interaction between PEO and PLA. The triplet maintains its shape while at the initial addition of PLA (20 %) the position of the maximum peak is shifted from 1090 cm^{-1} to 1092 and 1096 cm^{-1} , respectively. Likewise, in the same spectral range, the bands at 1181 and 1081 cm^{-1} are related to the asymmetric and symmetric C-O-C stretching of the crystalline phase of PLA (Auras et al., 2010), respectively. From Fig. 3 and Table 1 it is evident that in afore mentioned spectral range characteristic *triplet* of PEO is overlapped with C-O-C stretching of PLA or *vice versa*. On the contrary, all other characteristic peaks in the spectrum of investigated polymer blends are practically identical to neat ones which could be strong evidence of the non-existence of any interactions within the blends (Chieng et al. 2013, Saha et al. 2019). However, in our opinion the observed shifting of the broad asymmetric band (C=O) is the result of the weak interaction between the two polymers in solid state. These conclusions are partially in agreement with the work of Oliveira et al. (2013) which concluded that the nature of the interaction was most likely a result of dipole–dipole interactions between the ester groups of PLA and the ether groups of the PEO.

Differential scanning calorimetry

The results of the DSC measurements are shown as normalized DSC curves of neat polymers (Figs. 4 and 5) and PLA/PEO blends (Figs. 6 and 7). Thermal transition parameters of all investigated samples are listed in Table 2.

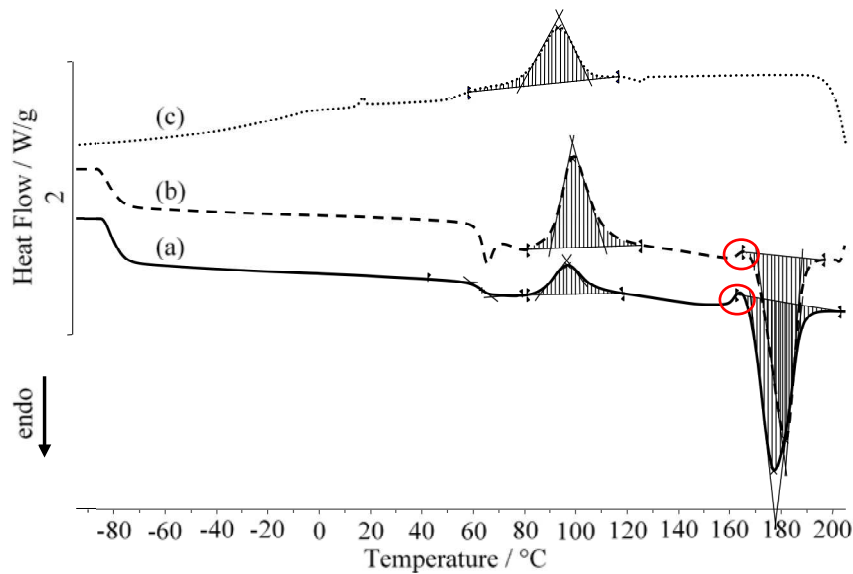


Figure 4. Normalized DSC curves of neat PLA: (a) second heating, (b) first heating and (c) cooling

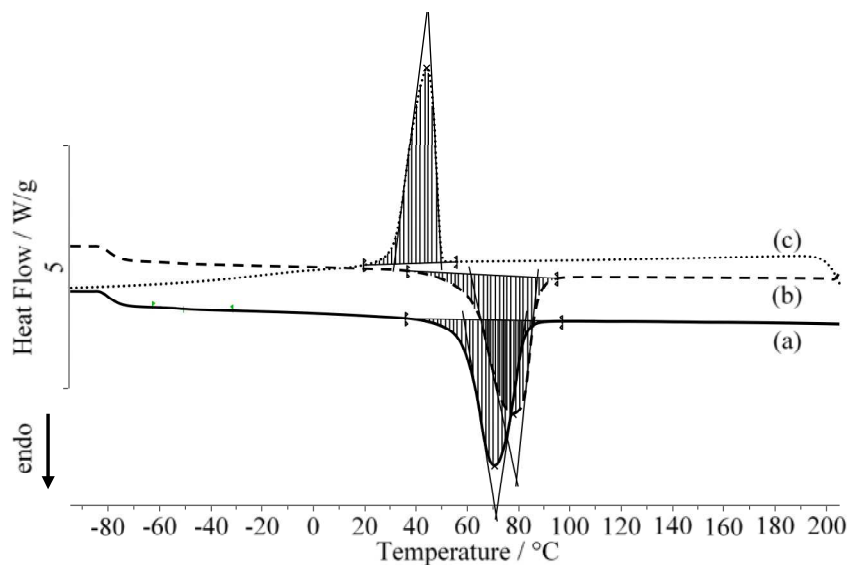


Figure 5. Normalized DSC curves of neat PEO: (a) second heating, (b) first heating and (c) cooling

The DSC heating curves of PLA/PEO blends (Fig. 6) show one glass transition temperature, which corresponds to the PEO, two endothermic peaks, which correspond to the melting of the PLA and PEO crystal phase, respectively, and one exothermic peak which corresponds to the premelting crystallization of the PLA. Likewise, the DSC cooling curves of all investigated blends (Fig. 7) show also two exothermic peaks which represents the melt crystallization of PLA and PEO, respectively.

It must be emphasized that only neat PLA has the exothermic peak of cold crystallization (Fig. 4) at temperature 86 °C (T_{eicc}), 97 °C (T_{pcc}) and 109 °C (T_{efcc}) with corresponding enthalpy of cold crystallization (ΔH_{cc}) -10.3 J/g. The cold crystallization is not visible in the other samples because PEO prevents PLA to crystallize during heating at even smallest addition of PEO (Fig.6).

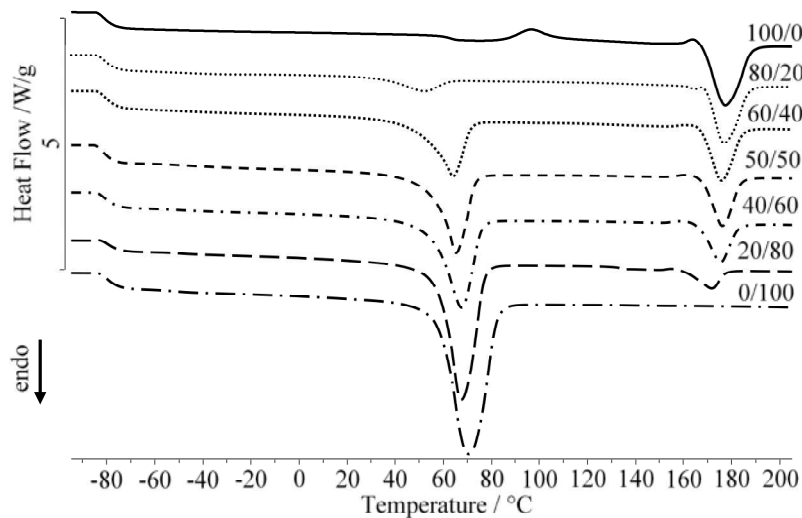


Figure 6. Normalized DSC curves of PLA/PEO blends, glass transition and melting (second heating)

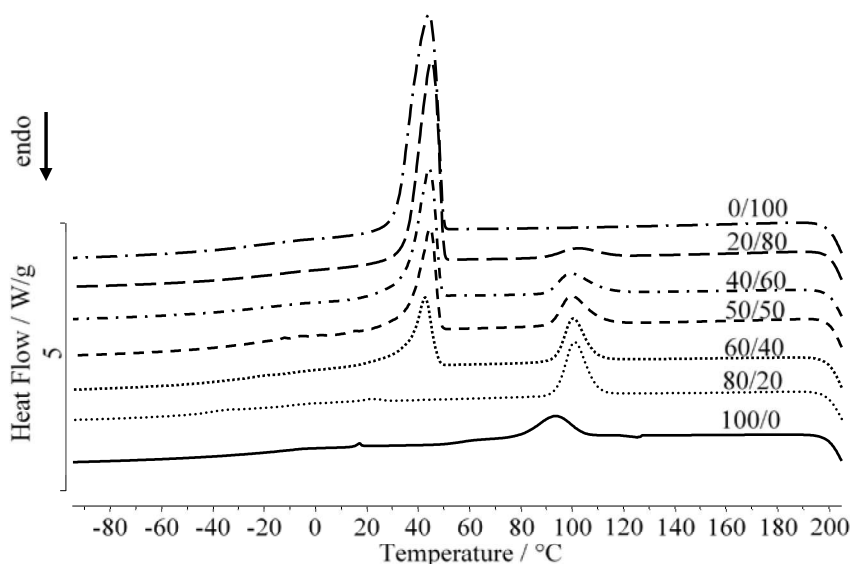


Figure 7. Normalized DSC curves of PLA/PEO blends, crystallization

The melting characteristics of the PEO in the blend 80/20 are determined but they are under the huge effect of glass transition from PLA that occurs in the same temperature region, so this melting appears at lower temperatures than melting of the PEO in other samples, while the glass transition of PLA is not visible. Because of this overlapping the melting of PEO cannot be taken as the indicator of miscibility between these two polymers. The glass transition of PLA is not visible, but it does not mean that it does not exist, so the visible glass transition of PEO cannot be considered for the miscibility too. Hence, the melting of PLA was used as the only miscibility criterion. As the PLA content increased in the investigated blends upon 50 %, the T_{mg} of PEO remains almost unchanged, while for samples with 60 % and 80 % of PLA content corresponding temperatures are increased toward T_g of PLA by 20–24 °C, as shown in Table 2. Likewise, in the case of melting temperature of the PEO, values of T_{eim} decreased from 58 °C for neat PEO to 35 °C for blend 80/20. Contrary, the melt crystallization temperatures of PEO depicted as T_{eimc} remained almost unchanged in all investigated blends. The T_{eipmc} of PLA decreases with the increase of PEO content in the blends, from 159 to 151 °C, with the exception at 80/20 blend (Table 2). On the other hand, the T_{eim} of PLA decreased upon higher PEO addition (>60 %); from 168 °C for neat PLA to 160 °C for blend 20/80. Corresponding melt crystallization temperatures (T_{eimc}) of PLA immediately increased by addition of minimum quantity of PEO from 106 °C for neat PLA to 110 °C for blend 80/20. Upon further addition of PEO, the change of values of T_{eimc} of PLA are more pronounced (117 °C for blend 20/80). This result also confirms the influence of PEO on the crystallization process of PLA that was noticed with the cold crystallization, but here it results with the earlier crystallization compared to the neat PLA. Upon PLA (PEO) addition values of corresponding enthalpies of melting (ΔH_m) and melt crystallization (ΔH_{mc}) of the PEO (PLA) in the blends are decreased (Table 2), as can be seen from the area of endothermic and exothermic peak, respectively (Figs. 6 and 7). The values of the corresponding enthalpy of premelting crystallization (ΔH_{pmc}) changes irregularly upon PEO addition, but they are all smaller in the blends than in the neat PLA (Table 2) pointing on the same conclusion according to PLA crystallization in the presence of PEO. The values of specific heat capacity (Δc_p) of the PEO are not affected by PLA addition. These results agree with FT-IR results and confirm the existence of possible interaction within PLA/PEO system. Finally, it can be concluded that the PLA and PEO are partially miscible at higher PLA or PEO content (80 %) in the melt. This is in accordance with the work of Seth et al. (1997), Zoppi et al. (2001) and Hu et al. (2003a,b).

Table 2. Thermal transition parameters of the PLA/PEO blends for DSC measurements

Parameter	PLA/PEO							
	100/0	80/20	60/40	50/50	40/60	20/80	0/100	
T_g (°C)	T_{eig}	58	-/-52	-/-55	-/-54	-/-56	-/-55	-56
	T_{mg}	63	-/-30	-/-26	-/-46	-/-50	-/-49	-50
	T_{efg}	67	-/-37	-/-35	-/-37	-/-46	-/-44	-47
Δc_p (J/g °C)	0.35	-/0.10	-/0.14	-/0.15	-/0.12	-/0.01	0.12	
T_{eipmc}	159	164/-	155/-	154/-	152/-	151/-	-	
T_{pmc} (°C)	T_{ppmc}	163	167/-	160/-	160/-	158/-	154/-	-
	T_{efpmc}	166	168/-	165/-	165/-	163/-	157/-	-
ΔH_{pmc} (J/g)	1.2	0.2/-	0.6/-	0.8/-	0.7/-	0.2/-	-	
T_m (°C)	T_{eim}	168	169/35	167/52	167/56	166/55	160/58	58
	T_{pm}	176	176/51	174/63	175/65	174/66	171/66	69
	T_{efm}	188	186/62	184/71	184/73	182/75	177/77	82
ΔH_m (J/g)	44.6	34.3/13.0	32.4/47.0	28.1/61.8	22.4/73.9	10.7/109.2	147.1	
T_{mc} (°C)	T_{eimc}	106	110/-	110/48	112/49	114/49	117/50	50
	T_{pmc}	94	102/-	101/43	100/45	100/45	103/47	46
	T_{efmc}	79	94/-	94/34	92/36	91/35	90/36	31
ΔH_{mc} (J/g)	21.7	29.8/-	23.3/39.4	20.5/52.0	16.3/69.2	7.8/103.6	143.2	

Thermogravimetric analysis

The dynamic thermogravimetric curves (mass versus degradation temperature), and corresponding derivative thermogravimetric (DTG) curves (mass loss rate versus temperature) of neat PLA and PEO are presented in Fig. 8. A one-stage degradation pattern is seen in the case of PLA. Thermal degradation of PLA begins at 335 °C (T_{onset}) with a peak temperature at 365 °C (T_{max}) and proceeds almost totally without residue which is supported by the fact that total weight loss through single degradation stage is 99.1 %.

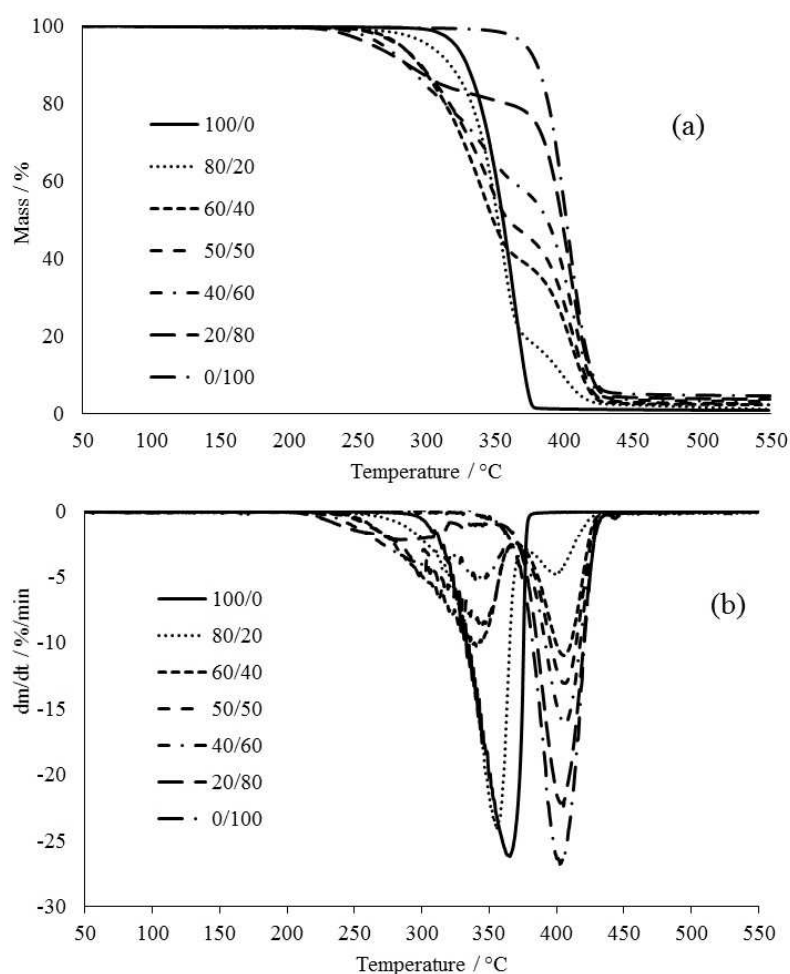


Figure 8. TG (a) and DTG (b) curves of the thermal degradation of the PLA/PEO blends

Likewise, thermal degradation of the neat PEO is also characterized by only a single degradation stage that begins at 382 °C (T_{onset}) with a peak temperature at 403 °C (T_{max}) confirming its superior thermal stability to PLA. The total weight loss is found to be 95.3 %. *Vice versa*, a two-stage degradation pattern is seen in the case of the PLA/PEO blends. Evidently, the first degradation stage corresponds to thermal degradation of PLA, while the second one corresponds to thermal degradation of PEO (Fig. 8). The dependence of the characteristics of TG and DTG curves on the blend composition is presented in Table 3. From these data it could be concluded that the degradation of PLA/PEO blends starts at even lower temperatures than neat PLA and occurs more slowly by addition of PEO (PLA). In the first degradation stage, a total increase of T_{onset} by 95 °C is observed as the PEO content is increased. Similarly, the temperature at 5 % mass loss and peak temperature also show the same change pattern. The sample with 80 % of PEO content showed the lowest values of all investigated blends, indicating its apparent destabilizing effect on PLA. Similar conclusions were reached by Chieng et al. (2013) and Bijarimi et al. (2016). Chieng et al. (2013) explained the decrease of the PLA thermal stability by the presence of PEG (PEO) as plasticizer.

PEG promotes a decrease in thermal stability by its action to intersperse itself around polymers and by breaking polymer-polymer interactions, which are predicted in the lubricity theory and gel theory of plasticization. Additionally, Hassouna et al. (2011) investigated new approach on the development of plasticized PLA with PEG via reactive extrusion. Latter authors pointed out that the products of PEG degradation (generated above 280 °C) could promote PLA degradation. The reaction between hydroxyl terminated groups of PEG and PLA ester functions, acidity, catalysts or some impurities could be the sources of such degradation. Finally, authors concluded that the addition of PEG makes certainly PLA more sensitive to thermal stability at higher temperatures (> 300 °C). However, in the second degradation stage, changes of T_{onset} and T_{max} value are minor and practically negligible. The mass loss in the first degradation stage decreased linearly as the PEO content increased in the blend, while mass loss in the second degradation stage increased. The final mass losses in the first and second stage increased linearly as the PEO content increased, that could be an additional indicator of PEO destabilising effect on PLA.

Table 3. The characteristics of thermal degradation curves of the PLA/PEO blends

PLA/PEO	$T_{5\%}$ (°C)	T_{onset} (°C)	T_{max} (°C)	R_{max} (% 1/min)	m_f (%)	Δm (%)
<i>First degradation stage</i>						
100/0	321	335	365	26.3	0,9	99,1
80/20	301	329	355	24.1	18.4	81.6
60/40	281	296	341	10.2	39.3	60.7
50/50	279	293	344	8.6	47.0	53.0
40/60	268	275	340	5.3	58.7	41.3
20/80	261	240	284	2.2	80.7	19.3
0/100	371	382	403	26.8	4.7	95.3
<i>Second degradation stage</i>						
100/0	-	-	-	-	-	-
80/20	-	389	400	4.8	1.1	17.2
60/40	-	390	405	11.0	2.4	37.0
50/50	-	389	406	13.1	2.6	44.4
40/60	-	389	407	16.2	3.1	55.5
20/80	-	385	403	22.2	3.9	76.9
0/100	-	-	-	-	-	-

Conclusions

In this work, blends of biodegradable PLA with high molecular PEO were prepared by hot-melt extrusion, technique commonly used in plastic industry. The extruded samples, used for further characterization, didn't undergo thermal degradation during preparation process. The observed shifting of the broad asymmetric band (C=O) is the result of the weak interaction between the two polymers in solid state, which can be attributed to the dipole–dipole interactions between the ester groups of PLA and the ether groups of the PEO.

As the PLA content increased in the investigated blends upon 60 % and 80 %, the T_{mg} of PEO are increased toward T_{mg} of PLA by 20-24 °C. Likewise, the similar pattern could be seen in the case of melting temperature of PLA and PEO in the blends. DSC results are in agreement with FT-IR results and confirm that the PLA and PEO are partially miscible at higher PLA or PEO content (80 %) in the melt. Thermal degradation of neat PLA and neat PEO proceeds almost totally without residue by only a single degradation stage confirming PEO's superior thermal stability to PLA. A two-stage degradation pattern is seen in the case of the PLA/PEO blends where the first degradation stage corresponds to thermal degradation of PLA and the second one to thermal degradation of PEO. From TG data it could be concluded that the degradation of PLA/PEO blends starts at even lower temperatures than neat PLA and occurs more slowly by addition of PEO (PLA). Moreover, the sample with 80 % of PEO content showed the lowest values of all investigated blends, indicating its apparent destabilizing effect on PLA.

References

- Auras, R., Lim, L., Selke, S., Tsuji, H. (2010): Poly(lactic acid): Synthesis, Structures, Properties, Processing and Applications, John Wiley & Sons Inc., New Jersey.
- Bijarimi, M., Ahmad, S., Rasid, R., Khushairi, M. A., Zakir, M. (2016): Poly(lactic acid)/Poly(ethylene glycol) blends: Mechanical, thermal and morphological Properties, AIP Conference Proceedings 1727, 020002 (2016); doi: 10.1063/1.4945957.
- Chiang, B. W., Ibrahim, N. A., Yunus, W. M. Z. W., Hussein, M. Z. (2013): Plasticized Poly(lactic acid) with Low Molecular Weight Poly(ethylene glycol): Mechanical, Thermal, and Morphology Properties, *J. Appl. Polym. Sci.* 130, 4576-4580.
- Chiang, B. W., Ibrahim, N. A., Yunus, W. M. Z. W., Hussein, M. Z. (2014): Poly(lactic acid)/Poly(ethylene glycol) Polymer Nanocomposites: Effects of Graphene Nanoplatelets, *Polymers* 6, 93-104.
- Hassouna, F., Raquez, J-M., Addiego, F., Dubois, P., Toniazzo, V., Ruch, D. (2011): New approach on the development of plasticized polylactide (PLA): Grafting of poly(ethylene glycol) (PEG) via reactive extrusion, *Eur. Polym. J.* 47, 2134–2144.
- Hu, Y., Topolkaev, V., Hiltner, A., Baer, E. (2003a): Crystallization and phase separation in blends of high stereoregular poly(lactide) with poly(ethylene glycol), *Polym.* 44, 5681–5689.
- Hu, Y., Topolkaev, V., Hiltner, A., Baer, E. (2003b): Aging of poly(lactide)/poly(ethylene glycol) blends. Part 2. Poly(lactide) with high stereoregularity, *Polymer.* 44, 5711–5720.
- ISO 11357-2: 2009 Plastics-Differential scanning calorimetry (DSC)-Part 2: Determination of glass transition temperature.
- ISO 11357-3: 2009 Plastics - Differential scanning calorimetry (DSC) - Part 3: Determination of temperature and enthalpy of melting and crystallization.
- Jakić, M., Stipanelov Vrandečić, N., Klarić, I. (2013): Thermal degradation of poly(vinyl chloride)/poly(ethylene oxide) blends: Thermogravimetric analysis, *Polym. Degrad. Stab.* 98, 1738-1743.
- Jakić, M., Stipanelov Vrandečić, N., Ocelić Bulatović, V., Govorčin Bajsić, E. (2016): Miscibility of Poly(Vinyl Chloride) with Poly(Ethylene Oxide) of Different Molecular Weights, *Chem. Biochem. Eng. Q.* 30 (1) 61–71.
- Mohapatra, A. K., Mohanty, S., Nayak, S. K. (2014): Effect of PEG on PLA/PEG Blend and Its Nanocomposites: A Study of Thermo-Mechanical and Morphological Characterization, *Polym. Compos.* 35, 283-293.

- Nijenhuis, A. J., Colstee, E., Grijpma, D. W., Pennings, A. J. (1996): High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: thermal characterization and physical properties, *Polymer*. 37, 5849-5857.
- Oliveira, J. E., Moraes, E. A., Marconcini, J. M., Mattoso, L. H. C., Glenn, G. M., Medeiros, E. S. (2013): Properties of Poly(lactic acid) and Poly(ethylene oxide) Solvent Polymer Mixtures and Nanofibers Made by Solution Blow Spinning, *J. Appl. Polym. Sci.* 129, 3672-3681.
- Perinović Jozić, S., Jozić, D., Jakić, J., Andričić, B. (2020): Preparation and characterization of PLA composites with modified magnesium hydroxide obtained from seawater, *J. Therm. Anal. Calorim.* 142, 1877-1889.
- Saha, D., Samal, S., Biswal, M., Mohanty, S., Nayak, S. (2018): Preparation and characterization of poly(lactic acid)/poly(ethylene oxide) blend film: effects of poly(ethylene oxide) and poly(ethylene glycol) on the properties, *Polym. Int.* 68, 164-172.
- Sheth, M., Kumar, R., Dave, V., Gross, R., Mccarthy, S. (1997): Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol), *J. Appl. Polym. Sci.* 66, 1495-1505.
- Nijenhuis, A., Colstee, E., Grijpma, D., Pennings, A. (1996): High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: thermal characterization and physical properties, *Polym.* 37, 5849-5857.
- Sim, L., Gan, S. N., Chan, C. H., Yahya, R. (2010): ATR-FTIR studies on ion interaction of lithium perchlorate in polyacrylate/poly(ethylene oxide) blends. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 76, 287-292.
- Zoppi, R., Duek, E. A., Coraça, D., Barros, P. (2001): Preparation and Characterization of Poly (L-Lactic Acid) and Poly (Ethylene Oxide) Blends, *Materials Resh.* 4, 117-125.
- Yang, X., Kang, S., Shaw Ling Hsu, S. L., Stidham, H. D., Smith, P. B., Leugers, A. (2001): A Spectroscopic Analysis of Chain Flexibility of Poly(lactic acid). *Macromolecules.* 34, 5037-5041.