



Characterization of polylactide/poly(ethylene glycol) blends via direct pyrolysis mass spectrometry



Esra Ozdemir^a, Teoman Tinçer^{a,b}, Jale Hacaloglu^{a,b,*}

^a Middle East Technical University, Department of Polymer Science and Technology, TR-06800 Ankara, Turkey

^b Middle East Technical University, Department of Chemistry, TR-06800 Ankara, Turkey

ARTICLE INFO

Article history:

Received 15 June 2016

Received in revised form 12 August 2016

Accepted 20 September 2016

Available online 21 September 2016

Keywords:

Poly(lactide)

Poly(lactide)/poly(ethylene glycol) blends

Thermal degradation

Pyrolysis mass spectrometry

ABSTRACT

In this study, melt blended poly(lactic acid) and poly(ethylene glycol), (PLA)/PEG samples involving 10, 15 and 20 wt% PEG were prepared and characterized by direct pyrolysis mass spectrometry technique in addition to classical techniques such differential scanning calorimetry, thermogravimetric analyses and mechanical tests. The incorporation of PEG resulted in consistent and significant decrease in the tensile strength and modulus, and reduction in endothermic melting peak of PLA due to the plasticizing effect of PEG with the virgin PLA matrix. Both TGA and DP-MS analyses pointed out that the thermal decomposition of the blend occurred mainly in two steps. In addition, the pyrolysis mass spectrometry analyses indicated presence of chains generated by the interactions of ether linkages of PEG and COOH groups of PLA, present either as end groups or due to reactions with water, during the blending and/or pyrolysis process. As a consequence, decrease in the thermal stability of PEG chains was detected. Analyses of the blends prepared by solution mixing for variable periods confirmed that these interactions took place mainly during the blending process. In addition, increase in the thermal stabilities of both components for the blends prepared by stirring for prolonged times was detected and associated with generation of a crosslinked structure.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Among all bio-based biodegradable polymers, poly(lactic acid) (PLA), a promising polyester, has drawn significant attention not only due to its comparable properties with conventional polymers but also relatively better properties than other biodegradable polymers [1–7]. Even though PLA presents environmentally friendly properties like biocompatibility, it still shows limited thermal, mechanical and barrier properties for many applications [6,8–12]. Mechanical and thermal properties of PLA can be improved by copolymerization, blending with other polymers, plasticization using biocompatible plasticizer and incorporation of filler materials. Among these, being a simple and more economic way, blending of PLA with various polymers has been investigated by many authors [13–15]. Poly(ethylene glycol), (PEG), due to its miscibility, biodegradability, and food contactable application, is almost the most suitable material which has been used as an impact modifier for PLA [16–20].

It has been determined that both the molecular weight and the amount of PEG has significant effects on the properties of PLA/PEG blends [17,21–25]. A limit of miscibility and brittleness characteristics depending upon the plasticizer content and the molecular weight were detected [17,21]. The plasticizing efficiency was increased with decreasing molecular weight of PEG [23,24]. Sheth et al. found that PLA/PEG blends varied from completely miscible to partially miscible, depending upon the PEG concentration [22]. Kim and coworkers showed that in the presence of 40% high molecular weight PEG percentage of elongation at break is improved significantly [23].

PEG, being a plasticizer, shows plasticization effect, gives rise to increase in PLA chain mobility, allows the rearrangement of the chains. PEG by disturbing the intermolecular forces, decreases the glass transition temperature, T_g of PLA [21–26]. Increasing the amount of PEG leads to decrease in T_g and improvement in crystallization [21]. Ahmed and coworkers determined that the incorporation of PEG as a plasticizer reduces T_g and melting point, T_m of neat PLA significantly, as expected [25]. In a recent research, Stoehr and coworkers examined the effect of PEG amount and recorded that PEG content affects T_g and cold crystallization temperature, T_{cc} [26].

* Corresponding author at: Middle East Technical University, Department of Polymer Science and Technology, TR-06800 Ankara, Turkey.
E-mail address: jale@metu.edu.tr (J. Hacaloglu).

Several studies on thermal degradation characteristics of PLA and PEG were also appeared in the literature [27–34]. However, there is insufficient information about thermal degradation behaviors of PLA/PEG blends. Therefore, the main objective of this research was to focus on both thermal properties and degradation mechanisms of plasticized PLA. For this purpose we also applied direct pyrolysis mass spectrometry, DP-MS that has been shown as a valuable tool for analyses of polymers [35–39]. The applications of DP-MS for thermal characterization involve investigation of thermal stability, degradation products and decomposition mechanism of homopolymers, copolymers, polymer blends and composites. The technique has great potential for identification of additives and structure in complex polymer matrices without time consuming extractions or derivatizations, as components are separated as a function of their volatilities and/or thermal stabilities [35].

2. Experimental

2.1. Materials

Poly lactide, PLA, (number average molecular weight, $M_n \sim 190000$), and poly (ethylene glycol) ($M_n \sim 8000$), were purchased from Cargill Dow. PLA and PEG were dried at 60 °C overnight under reduced pressure prior to the mixing processes. The mixtures of PLA/PEG with appropriate blend ratios, (90/10, 85/15 and 80/20 wt/wt) were melt-compounded using a DSM Xplore twin screw micro compounder at 190 °C, with a screw speed 100 rpm for 8 min. PLA/PEG 80/20 wt/wt blends were also prepared by solution mixing by magnetic (1000 rph) stirring for 1, 12 and 24 h in chloroform and dried at 60 °C overnight under reduced pressure.

Samples of PLA and PLA/PEG blends were dried in vacuum at 60 °C before mechanical testing. The dog-bone shaped specimens of PLA and its blends (dimension 50.0, 7.6, 2.0 mm length, width and thickness respectively) were obtained by Dac injection molding instrument at a barrel temperature of 190–195 °C and mold temperature of 40 °C. The extruded samples were forced to mold cavities at 8 bar pressure. The dog bone shaped specimens obtained after injection molding, were dried again at 65 °C overnight under vacuum before tensile testing.

2.2. Characterization

The universal testing machine (Lloyd LR30K) as per ASTM D638, at crosshead speed of 50 mm/min and cell load of 5 kn was used for tensile tests.

Differential Calorimetry, (DSC) and Thermogravimetry Analyses (TGA) were performed on a Perkin Elmer Instrument STA6000 under nitrogen atmosphere at a flow rate of 20 mL/min and a heating rate of 10 °C/min. Direct pyrolysis mass spectrometry (DP-MS) analyses were performed using 5973 HP quadruple mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. 70 eV EI mass spectra, at a rate of 2 scan/s, were recorded. Samples (0.10 mg) in the flared glass sample vials were heated to 450 °C at a rate of 10 °C/min. Experiments were repeated at least twice to ensure reproducibility.

3. Results and discussions

3.1. Mechanical properties

The variation of mechanical properties of PLA and PLA/PEG blends as a function of PEG loading are collected in Table 1. The neat PLA is typically brittle and rigid. Thus, it has high tensile strength and elastic modulus (Young's modulus) but very low% elongation at

Table 1
Mechanical properties of PLA and PLA/PEG blends prepared by melt blending.

	Tensile Strength (MPa)	% Elongation at Break	Young's Modulus (MPa)
PLA	64.5 ± 1.3	11.0 ± 0.5	1180 ± 30
PLA/PEG 90/10	48.9 ± 0.7	12.1 ± 2.1	950 ± 30
PLA/PEG 85/15	31.5 ± 2.6	8.1 ± 0.8	650 ± 40
PLA/PEG 80/20	16.1 ± 1.6	43.1 ± 10.4	330 ± 30

break, as brittleness is inversely proportional to elongation at break. The incorporation of PEG resulted in consistent and significant decrease in the tensile strength and modulus, due to the plasticizing effect of PEG with the virgin PLA matrix. The blend prepared at PLA/PEG ratio of 80/20, exhibited a decrease in tensile strength to the tune of 75.0% and tensile modulus to 72.0% respectively, as compared with the pristine PLA matrix. The variation in elongation at break for the blends involving 10 and 15 wt% PEG, showed no constituency with addition of PEG, however, it seems that there existed almost no significant change in elongation within the experimental errors. Finally, the elongation at break was increased noticeably only for the blend containing 20 wt% PEG, indicating significant decrease in brittleness of PLA. The blends with high elongation at break were characterized by relatively weak impact values.

3.2. Differential scanning calorimetry and thermogravimetry analyses

DSC images of the melt blended PLA/PEG samples involving 10, 15 and 20 wt% PEG prepared by melt blending, are shown in Fig. 1. The endothermic melting peak of PLA at around 172.3 °C was shifted to 165.7, 166.7 and 165.9 °C with the addition of 10, 15 and 20% PEG blends respectively, mainly due to the plasticizing effect of PEG and indicated generation of a compatible system [12]. The cold crystallization temperature (T_c) of PLA appeared at 86.2, 77.3 and 88.4 °C with addition of 10, 15 and 20 wt% PEG respectively.

The TGA curves of PLA, PEG and the melt blended PLA/PEG samples are shown in Fig. 2 and the relevant data are listed in Table 2. Thermal stability of PEG was noticeably higher than that of PLA. Thermal degradation of PLA/PEG blends occurred in two steps. The thermal decomposition of PLA was shifted to lower temperatures in the presence of PEG. The second step of decomposition associ-

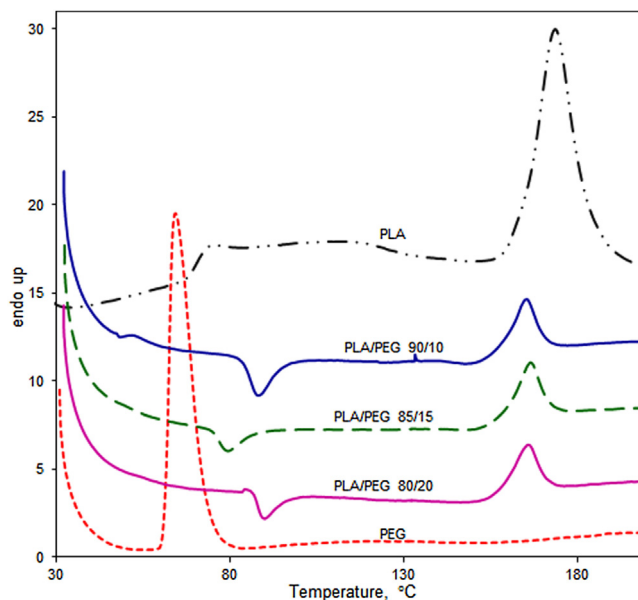


Fig. 1. DSC curves of PLA, PEG and PLA/PEG blends.

Download English Version:

<https://daneshyari.com/en/article/5134783>

Download Persian Version:

<https://daneshyari.com/article/5134783>

[Daneshyari.com](https://daneshyari.com)