JOURNAL OF RADIATION RESEARCH AND APPLIED SCIENCES 6 (2013) 11–20

Available online at www.sciencedirect.com

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journal homepage: http://www.elsevier.com/locate/jrras

Effects of gamma irradiation on the crystallization, thermal and mechanical properties of poly(L-lactic acid)/ethylene-co-vinyl acetate blends

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ARTICLE INFO

Article history:
Received 25 June 2013
Accepted 6 August 2013

Keywords:
Poly(L-lactic acid) blends
Microstructure
Rheological
Crystallization
Mechanical properties
Gamma irradiation

ABSTRACT

Poly(L-lactic acid)/ethylene vinyl acetate polymer blends (PLLA/EVA) with various blend ratios were prepared through melt blending process. The structural-property behavior of the polymer blends before and after they had been exposed to gamma irradiation was investigated. The hydrolytic degradation was investigated. The interfacial interaction between PLLA and EVA was visualized by Mechanical testing and FTIR. The crystallization behaviors of the blends were investigated by Differential scanning calorimetry (DSC), and the thermal stability was studied by thermogravimetric analysis (TGA). The results show that the hydrolytic degradation rate of PLLA/EVA blend can be widely controlled by exposing the PLLA/EVA to gamma-irradiation and also by EVA content. In alkaline solution, the hydrolytic degradation rate of the blends exposed 100 kGy and whose EVA content is higher than 50 wt% was decelerated while the rate of the unirradiated blends whose EVA content is lower than 20 wt% was accelerated. The tensile strength and modulus of the PLLA–EVA blend were increased by increasing PLLA content in the polymer blends and irradiation dose. FTIR spectra showed that some modifications occurred, after they had been exposed to gamma irradiation. The crystallization behavior was studied with differential scanning calorimetry and the composition-dependent changed of degree of crystallinity (X_c) of the PLLA phase indicated that PLLA and EVA were immiscible over the composition range investigated. However, there is a sharp decrease in the crystallinity with increasing EVA and irradiation dose. The TGA thermograms showed that the irradiated blends were less thermally stable than the unirradiated blends, at higher temperatures, the opposite situation was seen.

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Peer review under responsibility of The Egyptian Society of Radiation Sciences and Applications

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jrras.2013.10.001

1. Introduction

Recently, much attention has been paid to poly(L-lactide) (PLLA) and its copolymers not only because they are biodegradable but also they can be made from renewable natural resources such as corn starch. Therefore, utilization of PLLA will be one of the methods to reduce consumption in fossil fuels. PLLA has various advantages such as high mechanical property and transparency, somehow its brittleness and low heat resistance are shortages of PLLA in the case of being used as commodity materials. Polymer blend has been widely utilized for the control of biodegradation as well as the improvement for the mechanical properties and the heat resistance (Ma et al., 2012). The blends of PLLA with biodegradable polymers such as poly(D-lactide) (PDLA) (Mauduit, Perouse, & Vert, 1996; Tsuji, 2003). poly(3-caprolactone) (PCL) (Tsuji & Ikada, 1998; Tsuji & Ishizaka, 2001), poly(3-hydroxybutyric acid) (PHB) (Blumm & Owen, 1995; Yoon et al., 2000), poly(ethylene oxide) (PEO) (Nijenhuis, Colstee, Grijpma, & Pennings, 1996), and poly(vinyl alcohol) (PVA) (Tsuji & Muramatsu, 2001) were studied because the biodegradability and the biocompatibility were required for some applications such as medical materials. But in some cases and in other applications such as some part of car and electronic products, non-biodegradability is required. Poly(L-lactide) (PLLA) is one of the biodegradable and biocompatible polymers and has received increased attention in the decades due to its comprehensive mechanical properties. Similar to other semicrystalline polymers, the properties of PLLA, including the mechanical behavior, thermal properties, and degradation profile, are strongly dependent on the degree of crystallinity [X_c (%)] and crystalline morphology (Kulinski & Piorkowska, 2005; Pluta, 2004; Tsuji & Ikada, 1995). However, the crystallization of PLLA is very slow to develop significant crystallinity, especially, during the normal processing involved the non-isothermal conditions, such as extrusion and injection molding, it is hard to achieve high X_c (%) in PLLA. In this case, the amorphous content of PLLA plays a very important role on the final properties of the particles. Consequently, the fracture toughness is very poor, and the particles are brittle and very sensitive to the environment stress and other impact load. On the other hand, the processability of PLLA is inferior to that of the polyolefin. Thus, the wide application of PLLA in packaging, which needs a certain degree of ductility, is greatly limited. Blending with plasticizer is now widely adopted in modification of PLLA materials due to the dual effects of plasticizer in PLLA. Plasticizer can greatly improve the mobility of PLLA chain segments, and consequently, the glass transition temperature (T_g) of PLLA is decreased, and the crystallization is improved greatly on the one hand (Martin & Averous, 2001; Xiao, Lu, & Yeh, 2009; Yu et al., 2008) On the other hand, the presence of plasticizer improves the processability and ductility of PLLA greatly (Li & Shimizu, 2009). However, large reduced tensile strength and Young's modulus have been reported simultaneously due to the decrease of the macromolecular chain cohesion density (Anderson, Schreck, & Hillmyer, 2008; Lemmouchi et al., 2009).

Recently, blending PLLA with other polymers has been the main subject of many researches. Most research is mainly focused on PLLA blends miscibility (Li & Woo, 2008; Sakai, Nishikawa, Inoue, & Yazawa, 2009; Zhang, Goh, & Lee, 1998) and rheological properties (Gu, Zhang, Ren, & Zhan, 2008; Ko et al., 2009; Wu, Zhang, Zhang, & Zhou, 2008; Zhang, Wu, Zhang, Zhou, & Xu, 2009). However, few works has been done to investigate the toughening of PLLA by elastomers. In this regard, four different elastomers into PLLA and it was found that the smaller the dispersed particles are, the better the impact strength is (Ishida, Nagasaki, Chino, Dong, & Inoue, 2009). They also suggested that elastomers with a high polarity are more suitable for toughening PLLA. The toughening effect of acrylonitrile–butadiene–styrene copolymer on PLLA was studied and it was found that the blends exhibit poor mechanical properties with low elongation at break and decreased impact strength due to the poor miscibility (Li & Woo, 2008; Tsuji & Ikada, 1995). Other work has proved that linear low-density polyethylene exhibits toughening effect for PLLA to a certain extent (Anderson & Hillmyer, 2004; Anderson, Lim, & Hillmyer, 2003). It is well known that the biodegradability of PLLA is strongly related to its crystallinity, higher-order structure and morphology. It is also known that the crystallinity and structure of polymer blend are largely influenced by its blend ratio. That is biodegradability of PLLA/EVA blend is varied depending on these two factors, i.e. crystalline structure and blend ratio. Because the two factors are not independent, the biodegradability of crystallized PLLA/EVA blends is difficult to discuss.

Irradiation can, and is well known to, induce crosslinking to polymers. It is a very powerful technique that has been widely used in both product manufactures and research laboratory (Gehring, 2000; Oshima, Ikeda, Seguchi, & Tabata, 1997). Our recent work on the effects of gamma irradiation on the PLLA/EVA blends has extended the understanding of irradiation-induced crosslinking and enhanced compatibility at the inter-phase boundaries of the two phases in the blends.

2. Experimental

2.1. Materials

Poly(L-lactic acid) was used as biodegradable polyester, with M.wt = 3.2×10^5 was supplied by Aldrich. The melt index of the PLLA is 0.63 g/10 min and the optical purity is 98.3%. EVA with 18 wt% VA contents was purchased from DuPont Industrial Polymers, Wilmington, USA.

2.2. Preparation of PLLA/EVA blends

The pellets of both polymers were dried in a vacuum oven at 60 °C for 24 h before use. Blends of EVA and PLLA were prepared (containing different ratios of the two individual polymers (20/80), (50/50) and (80/20) wt%) by melt mixing in a laboratory mixer (Brabender Plasticorder PL2100), equipped with two rotors running in a counter-rotating way. The rotor speed was 60 rpm and the set temperature was 160 °C. The blends were prepared using the following sequence: first EVA pellets were introduced into the hot mixer, after melting, PLLA was added. The polymer mixture was immediately transferred from the mixer to an open roll-mill to make into a sheet.