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Synthesis of Some Novel Blends of Polylactide with Polylactide-b-Poly (ethylene glycol) Block Copolymers

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The synthesis of polylactide (PLA)-b-polyethylene glycol (PEG) linear block copolymers and their use in blends with pure-PLA is described. PLA-b-PEG linear block copolymers were obtained by the reaction between poly(ethylene glycol) bis (2-aminopropyl ether) (molecular weight 2000 Dalton) with PLA in the presence of stannous octoate via trans esterification. Molecular weight measurements of the block copolymers indicated that AB and ABA type block copolymers were obtained by controlling the feed ratio in the trans esterification reactions. The copolymers obtained were purified by the fractional precipitation and then characterized by ¹H-NMR, FTIR, GPC and DSC techniques. Blends of pure PLA with PLA-b-PEG displayed improved mechanical properties compared to pure PLA. Thermal, mechanical and morphological characterization of the blends were also conducted.

Keywords: Polylactide, block copolymers, poly(ethylene glycol)

1 Introduction

Aliphatic polyesters have been extensively investigated for several decades because of their biocompatibility and biodegradability. They offer an attractive platform for biomedical, drug delivery, and tissue engineering applications. This is due to the ability to synthesize well-defined oligomers and polymers and oligomers over a range of chain architectures that produce benign degradation products (1–17). Significant attention has recently been paid to the technical properties and commercialization of poly(lactide) (PLA) due to its biodegradability and biocompatibility as well as the fact that it can be derived from several renewable resources, including corn. PLA has found a wide range of applications from biomedical sutures (18) to biodegradable packaging for food (19). It possesses good barrier properties and excellent transparency. In addition, PLA is hydrophobic and biodegradable, it adapts well to a biological environment, and it does not have adverse effects on tissues. However, there is still a great need to improve other properties, such as thermal and mechanical proper-

ties to increasing the scope of applications in biomedical or environmental plastic fields. One of the most effective methods for enhancing the thermal and mechanical properties of PLA is its copolymerization with other monomers or polymers (20–32). Many of these polymers are also widely used in everyday life as packaging films or fibers for functional clothes. But the main focus of the current research in biocompatible polyesters is oriented towards materials for biomedical applications, such as drug delivery systems, surgical sutures, resorbable plating and the use of renewable resources for the production of food packaging. Poly(ethylene glycol) PEG is one candidate polymer for combining with PLA as it is hydrophilic and biocompatible. Block copolymers composed of PLA and PEG units with an AB or ABA architecture have received broad interest over the last decades for applications in the fields of pharmaceuticals and biomedicine (33–37). In fact, these materials can be used either as drug carriers in the form of nanoparticles, solution dispersed micelles, or hydrogels, or as scaffolds for tissue engineering in the hydrogel form.(38–40).

Our studies have been focused on the modification reactions of biodegradable polyesters in order to improve their mechanical, thermal and/or hydrophilic properties (41–46). Continuing the research to improve the properties of PLA, we describe the synthesis of PLA-b-PEG and PLA-b-PEG-b-PLA block copolymers via transesterification reactions. The mechanical properties of the blends of PLA with these copolymers have also been evaluated.

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2 Experimental

2.1 Materials

PLA (PLLA) was a gift from RESINEX-BMY Plastik Kimya Sanayi Ve Ticaret A.Ş. Bursa Turkey. Poly (ethylene glycol) bis (2-aminopropyl ether) with MW 2000 g/mol (PEGNH₂) was a gift from Huntsman Corp. (Switzerland). Stannous octoate (SnOct₂), isophorone diisocyanate (IPDI) and the other chemicals used were purchased from Aldrich.

2.2 Synthesis of PLA-b-PEG Block Copolymers

PLA was transesterified with PEGNH₂ under reflux condition in chloroform. As an example for the transesterification reaction, 3 g of PLA, 3 g of PEG and 0.02 g Sn(oct)₂ were dissolved in 50 ml of chloroform, and the solution was refluxed for 3. The solvent was evaporated by using a rotary evaporator. The resulting PLA-b-PEG copolymer was redissolved in 10 mL of chloroform and precipitated in 100 mL of methanol and dried under vacuum overnight at 40°C.

2.3 Fractional Precipitations of the PLAs

Copolymers obtained were further purified by the fractional precipitation method described previously (43). Briefly, a vacuum-dried copolymer sample was dissolved in 30 ml (V₁) of chloroform. MeOH was added dropwise until completion of the first precipitation and noted as V₂. The γ -value was calculated as the ratio of the volume of MeOH (V₂) used to the volume of CHCl₃ (V₁). The γ -values for the related homopolymers were also determined in order to compare with those of the copolymers. Methanol was added under continuous stirring until precipitation of the polymer was complete. The precipitated polymer was removed and this method was repeated until the precipitation of the polymer was complete and gamma-values of each fraction were calculated. Each polymer fraction was dried under vacuum and weighed.

2.4 Preparation of the Blends of PLA with PLA-b-PEG Block Copolymers

A mixture of PLA and PLA-b-PEG block copolymer were dissolved in 10 mL of chloroform. The solution was filtered and poured in a Petri dish ($\Phi = 7.5$ cm). Petri dish was covered with a piece of paper so that the solvent evaporated slowly. A transparent, smooth polymer film was obtained in one day after the solvent evaporated. The film was subsequently dried under vacuum for one day at room temperature.

2.5 Polymer Characterization

FTIR-ATR (Attenuated Total Reflectance Spectroscopy) spectra were recorded using a Nicolet 520 model FT-IR Fourier Transform Infrared Spectrometer and Perkin-

Elmer FT-IR. ¹H-NMR spectra were recorded in CDCl₃ with a tetramethylsilane internal standard using a 400 MHz NMR Varian XL 200. SEC measurements of the polymer samples in tetrahydrofuran (THF) solutions were carried out by using a Polymer Laboratories Gel Permeation Chromatography (GPC) Setup as an integrated instrument with a UV (254 nm), RI detector and a HPLC pump. Calibration was carried out using poly (styrene) standards provided by Polymer Laboratories. M. W. of seven standards are 1260 (PDI: 1.06), 4920 (PDI: 1.03), 9920 (PDI: 1.02), 30300 (PDI: 1.02), 60450 (PDI: 1.02), 170800 (PDI: 1.02), 299400 (PDI: 1.02) g/mol. The eluent (THF) was used at 40°C and at a flow rate of 1 mL/min.

Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Diamond to determine the glass transition temperatures (T_g), the melting temperatures (T_m), and decomposition temperatures (T_d). Samples were heated from -65 to 180°C (for T_g and T_m) and 20 to 600°C (for T_d) in a nitrogen atmosphere at a rate of 10°C/min.

2.6 Stress–Strain Measurements

Stress–strain measurements of the film samples were performed on a SDL Testometric model Universal Tensile Testing Machine using a 50 kg load cell with a stretch speed 100 mm/min. The solvent cast film samples from CHCl₃ were cut to a rectangular shape with size (0.1–0.3) × 10 × 50 mm. At least three samples from each blend composition were measured.

2.7 Scanning Electron Microscopy (SEM)

The morphology of the fractured surfaces was elucidated by SEM to investigate the microstructure of the polymer blends. Scanning electron micrographs were taken on a JEOL JXA-6335 FS scanning electron microscope (SEM). The specimens were frozen under liquid nitrogen then fractured, mounted, and coated with palladium, gold, and carbon. The SEM was operated at 15 kV, and the electron images were recorded directly from the cathode ray tube on a Polaroid film.

3 Results and Discussion

3.1 Transesterification Reactions

PLA-b-PEG diblock and PLA-b-PEG-b-PLA triblock copolymers were obtained by transesterification. Because aliphatic polyesters are very sensitive to hydrolysis and transesterification between alcohol groups and ester groups at high temperature (47), PEG with amine end groups were used. Transesterification reactions of PLA with PEG containing amine end-groups were performed in chloroform solution under mild reflux conditions (at 65–70°C for 3 h).

Table 1. Synthesis of PLA block copolymers via transesterification reactions in chloroform under reflux conditions for 3 h

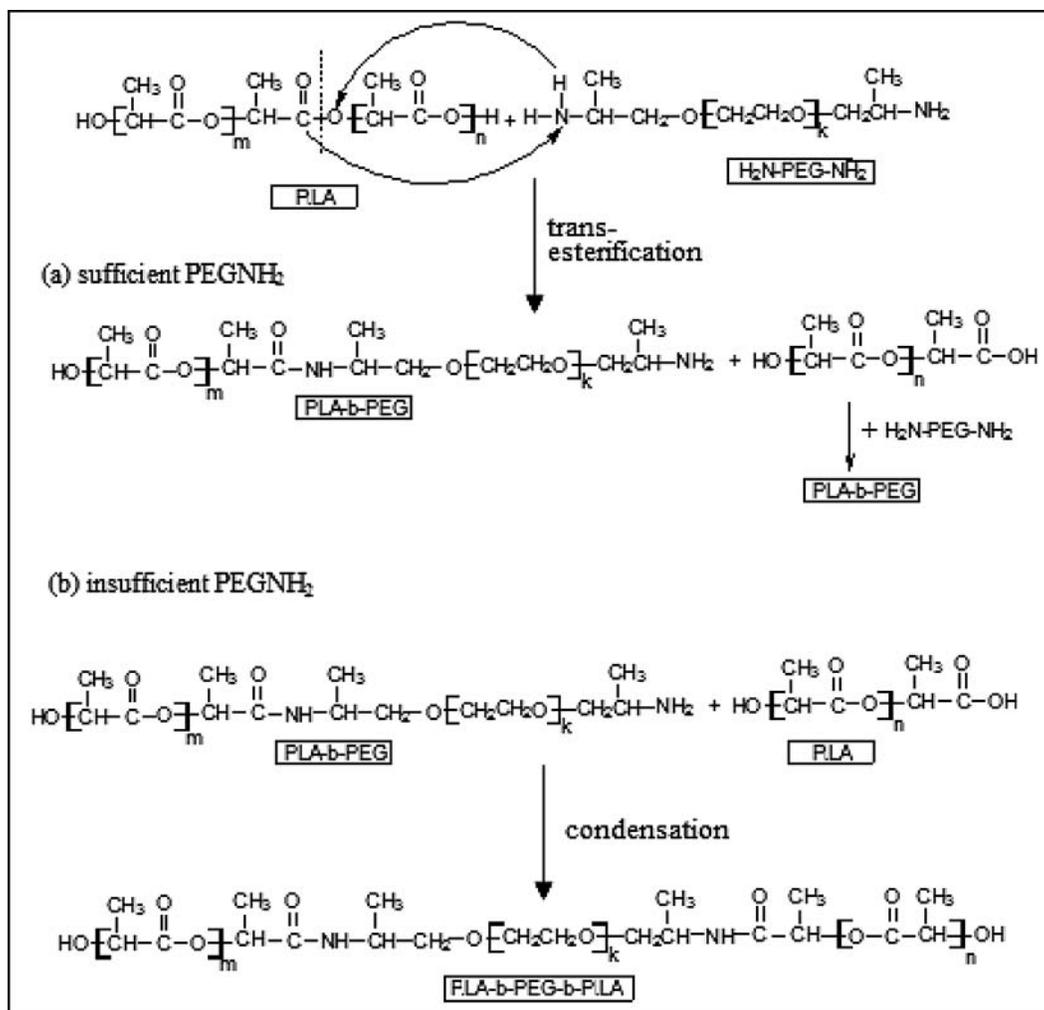
| Run No | PLLA (g) | PEGNH ₂ 2000 (g) | Yield (g) | Copolymer Analysis | | | | |
|--------|-------------|--------------------------------|--------------|-------------------------------------|----------|---------------------------|---------------------------|------|
| | | | | PEG ^a (mol% in copol. | γ | M _n (g/mol) | M _w (g/mol) | MWD |
| 304 | 3 | 3 | 4.35 | 28 | 1.6–1.8 | 4659 | 11539 | 2.48 |
| 305 | 3 | 1.5 | 3.11 | 20 | 1.5–1.7 | 12932 | 21323 | 1.65 |
| 306 | 3 | 0.6 | 2.81 | 9 | 1.4–1.6 | 27961 | 41965 | 1.50 |
| PLA | - | - | - | - | 1.2–1.4 | 10475 | 26571 | 2.54 |

^acalculated from ¹H-NMR spectrum.

Control of the M. W. of the copolymers obtained was successfully established by using different feeding ratios of the PEG with amine endgroups use of excess PEG resulted in diblock copolymer formation, while the use of low amounts of PEG resulted in triblock copolymer formation. Table 1 lists the results and conditions of the transesterification reactions in order to obtain PLA-b-PEG and PLA-b-PEG-b-PLA.

3.2 Fractional Precipitation

After block copolymer synthesis, precipitation of the copolymer into methanol removes the unreacted PEG. Fractional precipitation was applied to the block copolymers obtained for further purification. γ -Values, the ratio of the precipitant volume (methanol) to solvent volume (CHCl₃) were also determined during precipitation.



Sch. 1. Transesterification reactions of PLA with (a) excess (sufficient) PEGNH₂ and (b) limited (insufficient) PEGNH₂.

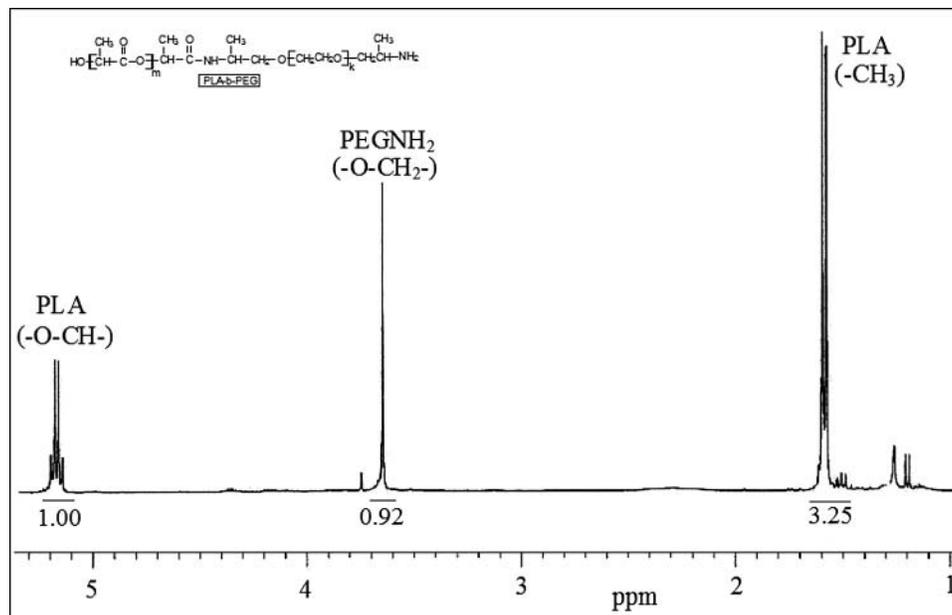


Fig. 1. NMR spectrum of PLA-b-PEG (sample #305 in Table 1).

When compared to pure-PLA the γ -values of the PLA-PEG block copolymers were shifted to the higher values because of the hydrophilic PEG units. γ -values of the block copolymers listed in Table 1 were found between 1.4 to 1.8 for PLA-b-PEG while for PLA the γ -values were between 1.2–1.4.

When we analyze M. W. of the copolymers, it is observed that the higher ratio of PEGNH₂ in the beginning causes

the degradation of the polyester during transesterification and forms the AB type of copolymer with lower M. W.; in turn, the use of lower PEGNH₂ in feeding causes higher M. W. of the ABA type of block copolymer. The envisaged reactions were given in Scheme 1.

In the case of the use of higher PEGNH₂ in the beginning of the transesterification reaction, carboxyl end groups of all PLA fragments have been capped by amine

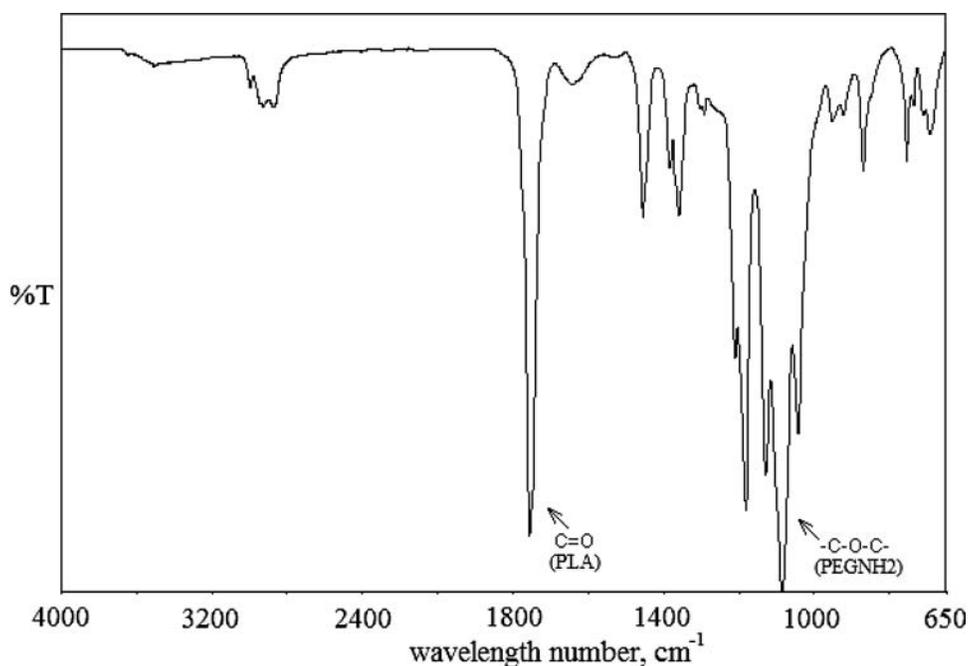


Fig. 2. IR spectrum of PLA-b-PEG (sample #305 in Table 1).

Table 2. Thermal properties of PLA graft copolymers

| Run No | T_{m1} | T_{m2} | T_{m3} | T_{d1} | weight loss (%) | T_{d2} | weight loss (%) |
|--------|----------|----------|----------|----------|-----------------|----------|-----------------|
| 304 | 27 | 142 | 151 | 252 | 50 | 400 | 50 |
| 305 | nd | 144 | 155 | 275 | 80 | 390 | 10 |
| 306 | 55 | 160 | 168 | 305 | 95 | - | - |

nd: not determined.

end groups of PEG. Then, AB type of PLA-b-PEG type of block copolymers occur (Run nos. 304 and 305 in Table 1). In the case of the use of limited PEGNH₂ in the beginning, amine end group of the PLA-b-PEG block copolymer has been capped by carboxyl end of free PLA fragments leading to the ABA type, PLA-b-PEG-b-PLA triblock copolymers. The sample run #306 has the nearly two times higher molecular weight (M_n 27,961 g/mol) than that of pure PLA (M_n 10,475 g/mol), which confirms that the PLA (10,475)-b-PEG (2000)-b-PLA (10,475) triblock structure. Characterization of the block copolymers obtained was performed by the ¹H-NMR and FTIR spectroscopy techniques. ¹H-NMR spectra of the PLA-b-PEG, PLA-b-PEG-b-PLA, PLA-b-PEG-b-PHO block copolymers all had the characteristic signals of the related polymer blocks: (δ , ppm): 1.6 ppm (-CH₃ of PLA), 3.6 ppm (-O-CH₂ of PEG), and 5.2 ppm (-O-CH- of PLA). The PEG content (mol%) in the graft copolymer samples was calculated from the integral ratio of the PEG signal at 3.6 ppm to total integral value in the ¹H-NMR spectra. Figure 1 shows a typical ¹H-NMR spectrum of a diblock copolymer sample (sample #305). The PEG content of the PLA-b-PEG-b-PLA triblock copolymer (sample #306 in Table 1) was two times greater than that of PLA-b-PEG diblock copolymer (sample #305 in Table 1), as expected. FTIR spectra of the copolymer samples obtained were also had the characteristic signals of ether bands of PEG at 1086 cm⁻¹ and ester carbonyl of PLA at 1755 cm⁻¹ (Fig. 2).

3.3 Thermal Analysis

Glass transition (T_g), melting transition (T_m) and decomposition temperatures (T_d) of the block copolymers were

Table 3. Mechanical properties of the polymer blends

| Sample Code | The ratio of the PLA/ PLA-b-PEG | Tensile strength (MPa) | Strain in (%) |
|-------------|---------------------------------|------------------------|---------------|
| PLA | | 23.5 ± 5.1 | 2 ± 0.9 |
| BL-5 | 1 : 0.1 | 16 ± 3.3 | 60 ± 3.3 |
| BL-6 | 1 : 0.3 | 12 ± 3.1 | 80 ± 12 |

measured by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The block copolymers obtained had two to three T_m 's related to the block copolymer segments. Pure PLA has T_g 61°C, T_m 170°C and T_d 309°C (48, 49). Pure PEG2000 has T_m 60°C. Because of the plasticization effect of the PEG inclusion, block copolymers indicated the lower glass transition and melting transitions than that of the pure PLA. Results of the thermal analysis of the graft copolymers were listed in Table 2. PLA segments decompose at around 250–300°C. Because of the strong hydrogen bonds of amide groups in the copolymer (Sch. 1) higher decomposition at 390–400°C were observed. Melting transition of the triblock copolymer (sample #306 in Table 1) was found to be higher than that of the diblock copolymers, as expected.

3.4 Morphology of the Block Copolymers

The morphology of the fractured surfaces was elucidated by SEM to investigate the microstructure of modified materials. The SEM in Figure 3a-b compares the fractured surface of PLA-b-PEG block copolymer films to the pure PLA. In Figure 3a, pure PLA showed a smooth and dense morphology as observed previously. Minor cracks were observed, as a result of cutting the brittle PLA. The diblock copolymer sample #305 showed a distribution of small pieces fused together on the surface (Fig. 3b). The microstructure of the triblock copolymer sample #306 indicated an interesting morphology like a rose blossom. This multi-layer structure was also observed as an onionlike structure of poly(ethylene-co-1-butene)-b-poly(D-lactide) (50).

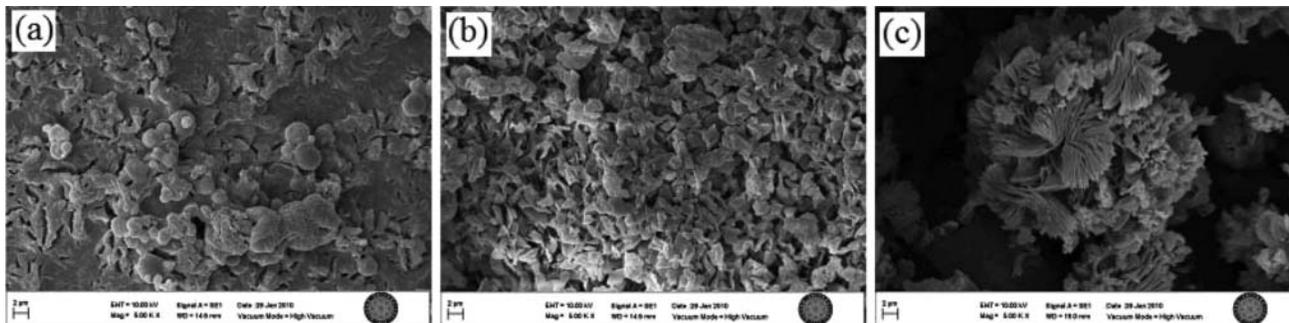


Fig. 3. SEM micrograph of a) PLA, b) PLPEGN2105 (305), c) PLPEGN2102 (306) (bar shows 2 μ m).

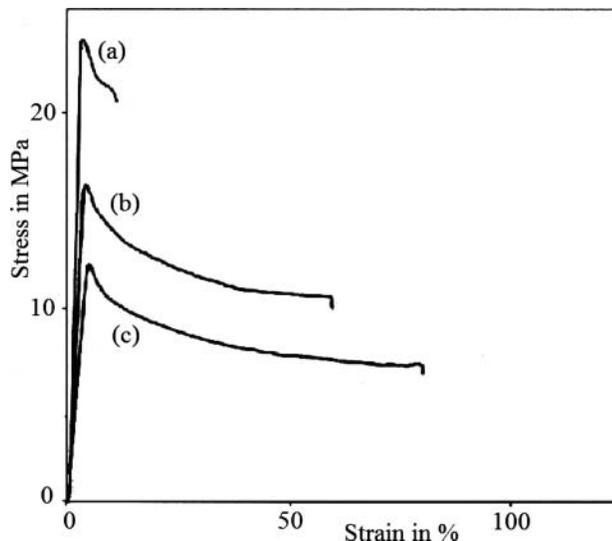


Fig. 4. Stres-strain curves of the polymer blends: (a) pure PLA, (b) PLA/PLA-b-PEG (1:0.1), (c) PLA/PLA-b-PEG (1:0.3).

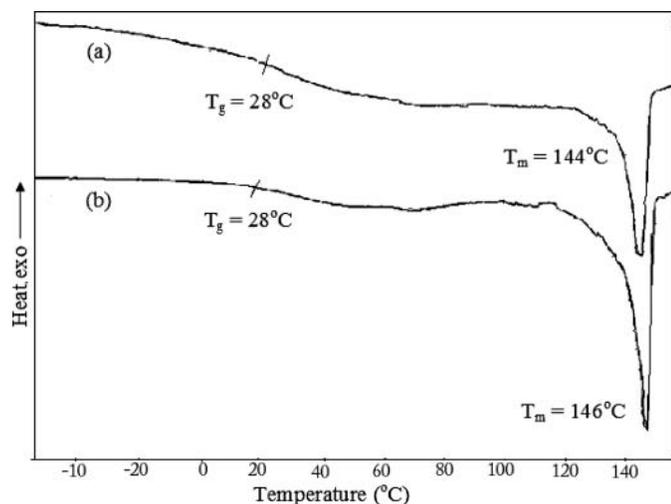


Fig. 5. DSC curves of blends of PLA/PLA-b-PEG with the ratio (1/0.1) (BL-5) (a) and 1/0.3 (BL-6) (b).

3.5 Blends of PLA with Diblock Copolymer

Pure PLA was blended with PLA-b-PEG diblock copolymer (sample #305) in two different ratio of PLA/PLA-b-PEG: 1/0.1 which was coded as BL-5, and 1/0.3 which was coded as BL-6. The mechanical properties and the morphology of the polymer blend films obtained by solvent casting were evaluated by means of stres-strain measurement and SEM technique. Figure 4 indicates the stres-strain curves of the polymer blends with pure PLA. PLA materials are stiff, brittle and exhibit limited extendibility. The blends of PLA substantially improved the mechanical properties. Various mechanical properties of the prepared polymer blends are summarized in Table 3. The prepared new materials have a very high elongation at break, but with lower tensile strength. The ultimate strain in the polymer blends increased with the addition of diblock copolymer while mechanical strength decreased with the addition of diblock copolymer. For the polymer blends, elongation at break increased from 2% to 80%, tensile strength was decreased from 23.5 MPa to 12 MPa.

3.6 Thermal Analysis of the Polymer Blends

Thermal analysis of the polymer blends was also performed by using DSC. T_g and T_m of the polymer blends were determined to be lower than that of the pure PLA. Figure 5 shows the DSC curves of the polymer blends. Plasticizer effect of the PLA-b-PEG diblock copolymers caused the T_g and T_m come down from 170 and 61°C to 144 and 28°C, respectively.

3.7 Morphology of the Polymer Blends

Fracture surface of the polymer blend films was analyzed by using SEM technique. Figure 6 shows the morphology of the fractural surface of the blends. While minor cracks were observed in pristine PLA (Fig. 6a), the morphology of the fractured surfaces of polymer blends changed substantially. The cut surface of the polymer blends showed no cracks and

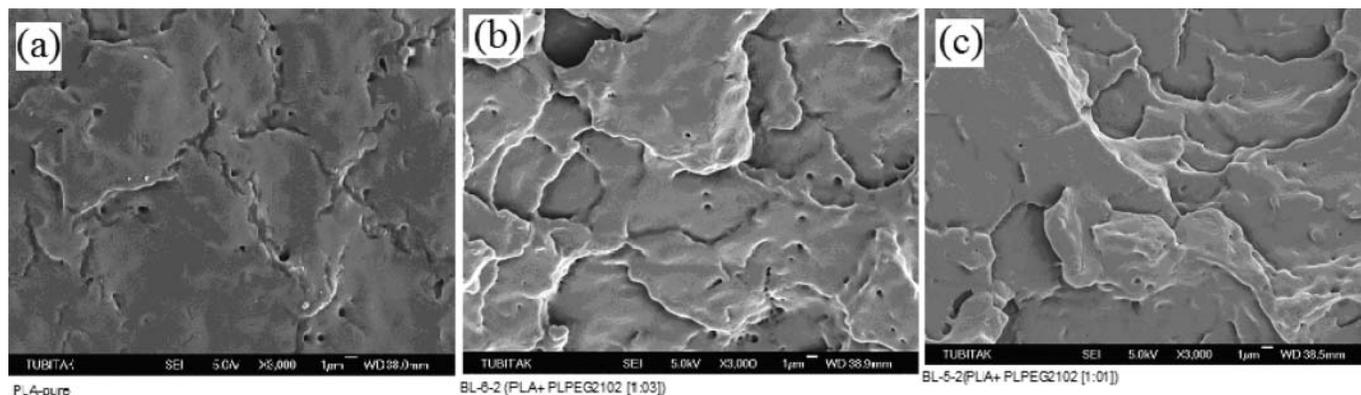


Fig. 6. SEM pictures of (a) the pristine PLA, blends of PLA/PLA-b-PEG with the ratio (1/0.1) (BL-5) (b) and 1/0.3 (BL-6) (c).

exhibited a finely interconnected multilayer structure (Figs. 6 (b and c)).

4 Conclusions

Block copolymers of PLA and PEO can be obtained by transesterification reactions with PEG containing amine ends at moderate temperatures for short reaction times. Di- or triblock copolymers can also be produced by changing feed ratio. Blends of PLA with these block copolymers have good film properties improving the poor mechanical property of PLA. The PLA-b-PEG block copolymers and their blends with of PLA can be promising material for biomedical applications and environmentally friendly packing.

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