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RESEARCH ARTICLE

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ABSTRACT

Introducing plasticizer poly(ethylene glycol) (PEG400) was applied into poly(lactic acid) (PLA) to produce film matrix packaging by direct casting. Non mechanical properties were carried out plasticized PLA including morphology, crystallinity structure and degree, thermal properties and oxygen barrier properties. Plasticized PLA revealed improving surface structure of PLA film matrix form fractures and homogenous film were achieved at 5% PEG 400. Chromatogram PLA and plasticized PLA were categorized crystal structure an α-form crystal. Intercalated and exfoliated structure did not occur significantly due to dispersion PEG 400 in the matrix but indicated dispersion structure. Thermal properties did not improve plasticized PLA significantly for both glass temperature and melting temperature. PEG 400 accelerated crystal formation that increased the crystallinity degree from 17.71% to 34.64%. Plasticized PLA enhanced permeability value about 20% while largest fraction PEG400 reduced ability to prevent from oxygen through pass the film. The oxygen barrier properties was significantly affected degree of crystalline in the film with a correlation number 0.85.

KEY WORDS

crystallinity, morphological, oxygen, PEG, PLA

1.0 INTRODUCTION

Poly(lactic acid) or PLA is a biobased thermoplastic produced from renewable agricultural sources by fermentative respiration, which produces lactic acid. PLA has a mechanical properties similar to polystyrene such as high strength and modulus. As a biopolymers, PLA also offers excellent biocompatibility [1]. However, brittleness and stiffness limit PLA's applications [2]. Blending PLA with other polymers offers opportunities to mitigate PLA's material property issues. Attempts to modify properties of PLA have been done using plasticizers [3-5] and reinforcing fillers such as fibers, layered silicates and nanoparticles [6-10].

Recently, work on plasticized PLA have been reported. It has been shown to be possible to copolymerize plasticized PLA with other monomers to enhance flexibility. On the other hand, simply blending PLA with suitable plasticizers offers a cost effective alternative to copolymerization. As a plasticizer, polyethylene glycol (PEG) has been shown to be one suitable copolymerization agent via interaction hydrophilic group from PEG with hydrophobic group from PLA [11].

PEG offers good miscibility with PLA and does not show a separation phase at lower molecular weights and plasticizer loading [12]. On the other hand, solubility and miscibility of PEG decreases with increasing molecular weight [13] or concentrations exceeding 10% PEG1000 into PLA [14]. Addition of low molecular PEG is most suitable to improve miscibility [15] and formation of homogenous PLA + plasticizer blends [11,16]. PEG is rich in hydroxyl groups, which are believed to develop hydrogen bonds with the lactide polymer. By interfering with lactide-lactide interactions, a plasticizing effect is realized. Optical properties of blended PLA+PEG400 are not significantly changed. However, spectra patterns from FTIR and Raman spectroscopy have shown slight decreased carbonyl groups, which is expected due to PLA+PEG hydrogen bonding [17].

Thermal properties PLA represented as glass transition temperature (Tg) and melting temperature (Tm) have Tg range 43.9-70^{o}C and Tm 150-170^{o}C [2,11,12,16,18,19]. Copolymerization of PLA with PEG reduces both T_g and T_m. Blending PLA+PEG has been reported lower glass transition temperature (T_g) and melting temperature (T_m) [4,13]. As pure polymer, PEG has T_g, T_m and ΔH_m at -29^{o}C, 62.25^{o}C and 72.64 J/g, respectively. Decreasing effect of T_g and T_m on plasticized PLA is due to free movement of PLA chains [12]. Corresponding to intrinsic properties, PLA can be found in crystalline and amorphous phase. Degree of crystallinity of pure PLA is typically 3-23% [2, 11,12,18,19]. As a crystallizable polymer, PEG enhances degree crystallization PLA [14]. WAXD analysis of PLA+PEG showed sharper peak, which implies increasing degree of crystallinity [19]. Crystalline structures present in PLA hinder amorphous chain mobility.

PLA+PEG400 blends should be in the right composition to improve certain properties. Introduction of right amount of PEG may not just effectively enhance hydrophilicity, flexural and toughness of PLA, but may also improve crystallization kinetics of PLA [14]. Crystalline regions enhance gas barrier properties since gas diffusion occurs through amorphous regions of the polymer [20]. PLA enantiomers influence some properties such as melting temperature, degree of crystallinity and barrier properties. High L-lactide content results in higher barrier properties of the polymer. Oxygen permeability of pure has been measured as PLA 4.9 x 10^{-14} kg m/ (m^2 s Pa) at 30^{o}C [21]; 2.45 x 10^{-13} kg m/ (m^2 s Pa) at 25^{o}C [11]. Adding plasticizer has a potential decrease barrier properties of PLA [4]. However, a PEG content 16.6% can provide a favorable compromise between PLA barrier and mechanical properties [22].

In previous research, the researcher worked with oxygen barrier properties at various temperature measurement of plasticized PLA. However, no attempt was made to correlate barrier effects

crystallization [23]. So, this research is aimed to investigate morphological, structural, and thermal properties as well as degree of crystallinity for improving the oxygen barrier property in plasticized PLA at different PEG400 concentration.

2.0 EXPERIMENTAL

2.1 Material

Poly(lactic acid) (PLA) A-101 (m.w. 80,000 g/mole, density 1.24 g/cm^3) was purchased from Shenzen Esun (China). Chlorofom C606-4 HPLC grade, was purchased from Fisher Scientific, USA. Polyethylene Glycol-400 was purchased from from Fisher Scientific, USA with average molecular weight 380-420, density 1.13 g/mol.

2.2 Preparation Matrix Film PLA/PEG400 Blend

Before processing, PLA was oven dried for 6 hours at 45^{o}C. PLA+PEG matrix films were cast in glass petri dishes by mixing method. PLA was diluted into chlorofom at 5% weight (w/v). In detail, 20 gram PLA were dissolved in 400 ml chlorofom and stirred vigorously for 60 minutes at 55^{o}C. Then, PEG was added, stirring was continued for 15 minutes. PEG was added into PLA solution at concentrations of 0, 1, 5 and 10% (w/w), respectively. Solutions ere poured onto glass petri dishes. Then, solutions were dried into films at 35^{o}C for 15 hours. Resultant PLA films were peeled from petri dishes and thicknesses were measured in 10 locations using a micrometer. Then, an oxygen transmission rate (OTR) was measured for each film at 30^{o}C.

2.3 Scanning Electron Microscope

Morphological measurement using scanning electron microscopy measurement, the sample were cutted at 1 x 1 cm. Then, samples were mounted on bevel samples holder and laminated with aurum in a vacuum. SEM pictures were taken by Zeiss scanning electron microscopy (1-5 kV, 10-17 mm width, 500x magnification).

2.4 Wide Angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) analysis was carried out by XRD-7000, M/s Shimadzu, Japan using a monochromatic and a Cu radiation source (wave length 1.54 A at 40 kV and 30 mA). A $d_{spacing}$ was calculated using Bragg's law equation [18].

$$2\ d \sin\theta = n\lambda$$

where θ is the Bragg's angle, n (=1,2,3..) is the order of diffraction and λ is wavelength.

2.5 Differential Scanning Calorimetry (DSC)

Glass transition (T_g), crystalllization (T_c) and melting temperature (T_m) of neat PLA, PLA+PEG blend samples have been studied using Perkin-Elmer Diamond DSC. Samples of 3.5 mg were heated from 30 to 400^{o}C at a rate 20^{o}C/min under a constant flow rate of 20 ml/min nitrogen gas purging through the calorimeter. Degree of crystallinity can be calculated by using following equation:

$$X_c\% = (100\ \Delta H_m)/(\Delta H_f\ W_{PLA})$$

Where ΔH_m is the heat of fusion of sample, ΔH_m corresponds to the heat of fusion for 100% crystalline PLA. Crystallinity of plasticized PLA and pure PLA was calculated, where heat of fusion of crystalline PLA was 93.6 J/g.

2.6 Oxygen Transmission Rate

Oxygen permeability of neat PLA and PLA+PEG 400 blended films was measured using Dynamic Accumulation (ASTM F3136-15). Samples were mounted in gas permation chambers (Oxysense, Inc., Dallas, TX) and measurements

were performed at 23°C. PLA+PEG 400 blended film samples consisted of four thicknesses and were measured in triplicate. The permeation accumulation chamber had a sample area 16.62 cm^2 and volume 8.3 cm^3. Initially, the cell was purged with more than 10 volumes of industrial grade compressed nitrogen. Purge completeness was followed by monitoring oxygen concentration decrease to a constant zero level using the Oxysense Model 310 device (Oxysense, Inc., Dallas, TX). Next, commercial-grade oxygen (100%) was used to purge the test-gas chamber. Oxygen concentration in the DA chamber was measured and recorded periodically using commecially available oxygen fluorescence sensor (Model 310; Oxysense, Inc, Dallas, TX). Oxygen transmission rate (OTR) was subsequently calculated as previously described [24].

3.0 RESULTS AND DISCUSSION

3.1 Morphological Properties

Scanning electron microscopy was used to observe the surface appearance of film samples. SEM permits observation of phase morphology in composite material and enhance interfacial adhesion information [25]. Fig 1. shows surface morphology of neat PLA film and plasticized PLA films.

Based on the SEM investigation, the pure PLA surface film appeared smooth and dark. Interestingly, crack patterns were found in neat PLA film. This may be explained by the fact of pure PLA polymer is naturally brittle so the fractures formed after the film dried. Surprisingly, the plasticized PLA film results showed a significantly different appearance on the film surface. The SEM showed that PEG 400 covered the PLA with a bright and cloudy appearance. SEM suggests that beyond 5% PEG 400, PLA was saturated, which led to PEG blooming on the surface. In contrast, loadings lower that 5% PEG 400 loadings did not become saturated, but also did not reach uniform distribution throughout the samples. Additionally, loadings greater than 10% resulted in phase separation. Several reports have shown that lower molecular weight plasticizer incorporated in the PLA matrix resulted a uniform film morphology, which prevented phase separation [3,14].

3.2 PLA+PEG 400 Film Structure

The structure of PLA+PEG400 blend is represented WAXD analysis at low angle ($2\theta < 20^o$) due to the distance between PLA+PEG400 peak can be estimated in WAXD results. WAXD patterns of neat PLA and PLA+PEG400 are shown in Fig 2. Diffractograms of neat PLA exhibit two peak reflections at $2\theta = 16.9$ as strongest peak and $2\theta = 19.3$ as medium peak. Two peaks of pure PLA have been reported at $2\theta = 16.6$ and 19.1^o [18]. Sharpen peak at $2\theta = 16.9$ showed the neat PLA structure was semi-crystalline [18,26]. Furthermore, neat PLA offered details at 15.04^o; 16.94^o; 19.25^o and 22.60^o, respectively, which correspond to crystalline structures in α form [18,27].$d_{spacing}$ was calculated from the peak position using Bragg's law. Interlayer distance between PLA polymer was 2.64 nm at $2\theta = 16.95^o$. After adding PEG400 to PLA, the strongest peak of PLA+PEG400 blends remained stable at around $2\theta = 16.90\text{-}16.95^o$ for all PEG400 concentrations. Diffractograms of neat PLA and PLA+PEG400 films pattern did not significantly change, except introducing PEG400 5%. WAXD diffraction intensity of α-form crystalline regions became stronger and peaks were sharper than neat PLA. Sharper peaks from PLA+PEG400 blends indicate higher crystallinity, suggesting PEG400 promotes crystal formation of PLA [14], while the plasticizer improves chain mobility [12]. The crystal size was measured using Debye Scherrer equation revealed decreasing when PEG400 was introduced into PLA. Neat PLA have an average crystallinity degree 21.55 nm whereas plasticized PLA was 18.99 nm.

Adding PEG 400 to PLA showed similar

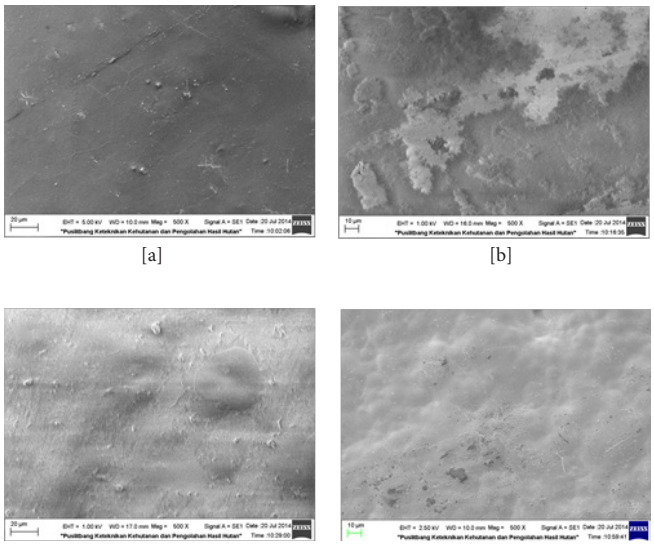

Figure 1. Scanning electron micrographs of the surface section of: (a) neat PLA; (b) PLA+PEG 400 1%; (c) PLA+PEG 400 5%; (b) PLA+PEG 400 10%.

diffractogram patterns although a slight difference appeared at certain diffraction angle. Contrary to expectations, this result did not find a significant difference between neat PLA with plasticized PLA. One interesting finding from the diffractogram is the PEG400 dispersed thoroughly in the PLA matrix during film production. This result did not detect any significantly exfoliated and intercalated film structure. Although, presenting PEG400 5% showed small peak angle shift into 16.9° indicated a slight intercalated structure.

3.3 Thermal Properties

Thermal properties of neat PLA were measured including Glass transition temperature (T_g), melting temperature (T_m), enthalphy fusion (ΔH_m) and crystallinity degree (X). Thermograms of pure PLA exhibited T_g, T_m, ΔH_m and X at 55.8°C, 167.72°C, 16.579 J/g, 17.71%, respectively. These thermal properties were within ranges provided by other authors [11,12,19]. Thermal properties of pure PLA and plasticized PLA are summarized in Table 1.

PEG thermal properties are generally lower than those of PLA. As expected, introducing PEG400 in PLA during blending reduced glass transition temperature. This finding is similar with other research the glass transition temperature of PLA+PEG200 decreased with increasing PEG200 concentration into PLA [1]. Other research investigated that introducing PEG1000 into PLA at amount 10% resulted decreasing T_g plasticized film PLA+PEG1000 from 63°C into 39°C. A possibility is to introduce a plasticizer affect reducing intermolecular force between polymer chains that change in free volume [14].

Then, melting temperature did not significantly improve with PEG400 concentration into PLA (between 166.31°C and 167.66°C). Table 1 shows that degree of crystallinity of PLA increases with increasing PEG concentration. However, introduction of PEG400 at 10% reduced degree of crystallinity. Results suggest phase separation occurred at higher PEG400 loadings. In general, increasing molecular weight may increase the entanglements between PLA and PEG400 chains. Crystallization

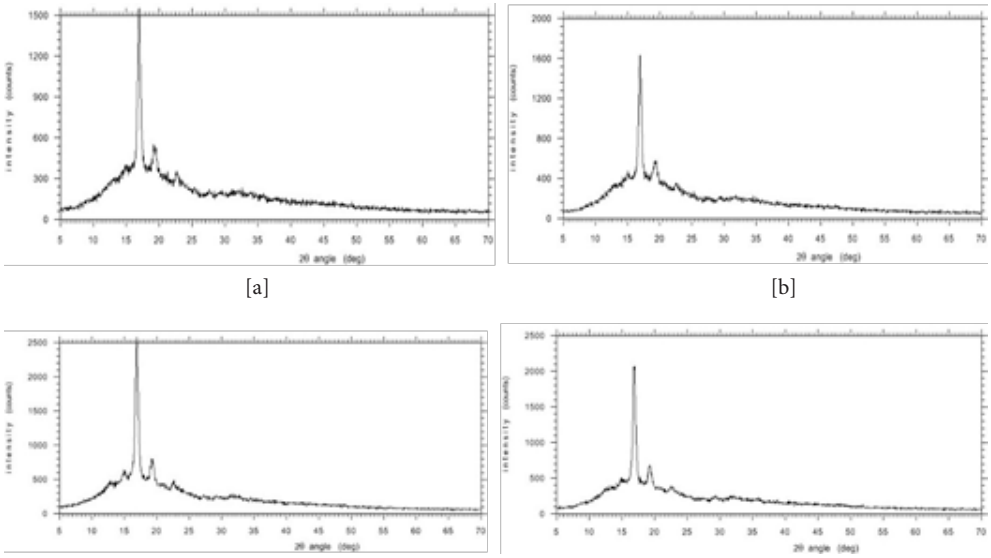

Fig 2. Diffractograms of: (a) neat PLA; (b) PLA+PEG 400 1%; (c) PLA+PEG 400 5%; (b) PLA+PEG 400 10%.

Table 1. DSC data of neat PLA and plasticized PLA with PEG400.

Film	T_g(°C)	T_m(°C)	ΔH_m(J/g)	X(%)
PLA	55.8	167.72	16.58	17.71
PLA+PEG 1%	54.2	167.26	21.31	22.76
PLA+PEG 5%	53.2	167.26	32.43	34.64
PLA+PEG 10%	51.6	166.31	22.83	24.39

PLA+PEG400 has a similar with other researcher result that degree of crystallinity decreased is extended due to phase separation [19].

3.4 Oxygen Transmission Rate (OTR)

Oxygen permeability tended to decrease with increasing PEG 400. Oxygen barrier improved with increasing PEG400. Data suggest that 5% PEG400 plasticized PLA offered greatest increase to barrier of about 20%. Results are shown in Table 2.

Surprisingly, degree of crystallinity had a significant effect toward oxygen barrier properties. Increasing crystallinity degree PLA plasticized films were followed reducing oxygen permeability number. It can be say that the crystallinity region has a role to prevent the oxygen diffusion through pass the PLA film. Presenting PEG400 may configure relatively small crystalline regions being formed in significant number. WAXS analysis resulted in α-form crystal, which created a stable polymorph because improve interchain interaction [28-30] and resulted better barrier properties [31]. As semicrystalline polymers, shape and size of a crystallites, crystal structures and degree of crystallinity have an important influence on the permeability process [32]. WAXS analysis PLA/cellulose showed increasing crystallinity that offered a positive influence on oxygen barrier [10]; oxygen permeability was reduced with increasing degree of crystallinity [33]; solubility and diffusion decreased with increasing crystallinity [34].

Table 2. Degree of crystallinity and oxygen permeability correlation

Film	Crystallinity (%)	Oxygen permeability ($x10^{-18}$ kg m/m^2 s Pa)
PLA	17.71	7.02
PLA /PEG400 1%	22.76	5.98
PLA/PEG400 5%	34.64	5.61
PLA/PEG400 10%	24.39	5.99

CONCLUSIONS

Characterization of plasticized PLA with PEG400 for film packaging were carried out. Morphological film showed good miscibility during formulation of PLA with 5% PEG 400. WAXD analysis showed good miscibility of PEG400 into PLA as represented with a similar diffractograms. As a plastizable polymer, introduction PEG400 into PLA enhanced crystallization formation in all concentrations studied. Therefore, crystal structure of PLA/PEG400 blend resulted in α-form. Degree of Crystallinity increased to 34.64% at PEG400 5% addition and followed with decreasing glass transition temperature and melting temperature. Degree of crystallinity improved oxygen barrier properties as showed. Therefore, PEG400 has been shown to be an effective plasticizer for PLA, which also improves. However, care must be taken to not overload PLA with PEG400.

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