

DEVELOPMENT OF POLY(D,L-LACTIC ACID) WITH POLYBENZOXAZINE VIA SOLUTION BLENDING

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ABSTRACT: Polybenzoxazine was synthesized by using bisphenol A, formaldehyde and diamine as precursor via condensation reaction. Triethylenetetramine was used as diamine precursor. Polybenzoxazine was characterized by FTIR technique in order to confirm the obtained polybenzoxazine. The ratio of poly(D,L-lactic acid)/polybenzoxazine ($M_w = 10,000$ and $20,000$ g/mol) was 0:100, 1:99, 3:97 and 5:95, respectively. The poly(D,L-lactic acid)/polybenzoxazine films were characterized by using Scanning Electron Microscope (SEM). The results showed homogenous and smooth films. Thermal stability of poly(D,L-lactic acid)/polybenzoxazine films was better than pure polybenzoxazine film. Moreover, 3:97 ratio of polybenzoxazine mixed with poly(D,L-lactic acid) ($M_w = 20,000$ g/mol) film showed good tensile strength, because the stress at break was 24.06 ± 7.99 when determined by Universal Tinting Machine. It was concluded that poly(D,L-lactic acid) improved the property of the polybenzoxazine film.

Keywords: Biodegradable polymers, polybenzoxazine, poly(D,L-lactic acid)

1. INTRODUCTION

The research of biodegradable polymers has gained considerable momentum in latest years with the growing public attention to environment problems. Poly(lactic acid), a biodegradable polymer which can also be produced from annually renewable resources, has extended recently an increasing attention [1].

Lactic acid (2-hydroxy propanoic acid) is a hydroxyl acid containing an asymmetric carbon atom. The lactic acid exists in two optically active configurations: D- and L-lactic acids. These lactic acids are produced by fermentation using bacterial systems. However, the chemical process was used to produce a racemic or D,L-lactic acid. The poly(L-lactic acid) and poly(D-lactic acid) are semi-crystalline, while the poly(D,L-lactic acid) is amorphous. The mechanical and thermal properties of poly(D,L-lactic acid) are usually lower than poly(lactic acid) [2]. Moreover below T_g in the range of $50 - 60$ °C, amorphous poly(D,L-lactic acid) is rigid and brittle having the elastic modulus about 3-3.5 GPa and low ability to plastic deformation. The transition from brittle to ductile behavior in the plasticized polylactide occurs when T_g is shifted to 35°C.

Polybenzoxazine is a new class of phenolic resins which is very accepted and useful in polymer research. There are three common types of chemical needed to synthesize polybenzoxazine, including various aromatic/aliphatic amines, mono/diphenols, and formaldehyde. Accordingly, phenol and amine could be varied and this is one of the most advantages of polybenzoxazine in excellent

molecular design flexibility. The preparation of polybenzoxazine is also easy and low cost. Moreover, polybenzoxazine has good properties in high glass-transition temperature (T_g), high thermal stability, good mechanical properties, and low shrinkage upon polymerization thermal stability [3].

Polybenzoxazine precursors have been synthesized from various aromatic/aliphatic amines, mono/diphenols, and formaldehyde [3,4]. One approach was to synthesize polybenzoxazine from a low molecular weight monomer, using monofunctional amine, phenol, and formaldehyde as reactants [4]. However, polybenzoxazines obtained via this approach usually suffered from brittleness. Another method was the preparation of polybenzoxazine from high molecular weight oligomers from diamine, bisphenol-A, and formaldehyde [5]. The properties of the polybenzoxazines derived from these high molecular weight oligomers, especially brittleness, have been greatly improved when compared with cured films from the typical low molecular weight precursors. This enables polybenzoxazine to be an excellent candidate for flexible film applications. Therefore, a combination of polybenzoxazine with poly(D,L-lactic acid) could improve the film properties when compared to the pure polymer.

2. MATERIALS AND METHOD

2.1 Materials

Analytical grade 1,4-dioxane (99%) was purchased from Sigma-ALDRICH. Bisphenol-A (BPA, 97 % purity) and Triethylenetetramine

(TETA, 60% w/w) were obtained from Aldrich, Germany. Formaldehyde was gained from Ajax Finechem. D,L-lactic acid was purchased from Acros Organics. All chemicals were used as received.

2.2 Synthesis of Poly(D,L-lactic acid)

In a typical synthesis experiment in this work, approximately 200 g of D,L-lactic acid were added into a 500 mL round-bottomed flask which contained about 2 g of p-toluene sulfonic acid (PTSA) as catalyst (1% by weight). The flask was then heated at 170 °C in a conventional short-path distillation apparatus for 4 hours. The pressure of the system was reduced (ca. -25 inch Hg) for 2 hours to facilitate further removal of water and to increase the polymer yield. The molecular weight of products was consisting of 10,000 and 20,000 g/mol.

2.3 Synthesis of Polybenzoxazine

The polybenzoxazine precursors were prepared by mixing bisphenol-A, TETA, and formaldehyde at a mole ratio of 1:1:4, respectively [6,7]. Firstly, bisphenol-A (6.84 g, 30 mmol) was dissolved in 1,4-dioxane (15 mL) in a 50 mL glass bottle and was stirred until a clear solution was obtained. A formaldehyde solution (9.73 g, 324 mmol) was then added to the bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath. TETA was then added dropwise to the mixture while continuously stirring for approximately 1 hour until a transparent yellow viscous liquid was obtained [8]. The process of chemical precursor was shown in Fig.1

2.4 Preparation of Poly(D,L-lactic acid)/Polybenzoxazine films

The benzoxazine precursors were mixed with poly(D,L-lactic acid) ($M_w=10,000$ and $20,000$ g/mol) with 100:0, 99:1, 97:3, 95:5 and 0:100 ratio cast on glass plates at room temperature. The membranes were dried at room temperature in air for one day, followed by drying at 80 °C in an air-circulating oven for 24 hours to remove excess solvent.

2.5 Characterization of Poly(D,L-lactic acid)/Polybenzoxazine

FTIR results were obtained by using Thermo Nicolet Nexus 670 (Vacuelli55) used to determine the chemical structure. The sample was mixed with KBr powder then it was compressed in sample preparation equipment to obtain the thin plate. The measurement wavelength was $500-4000\text{ cm}^{-1}$.

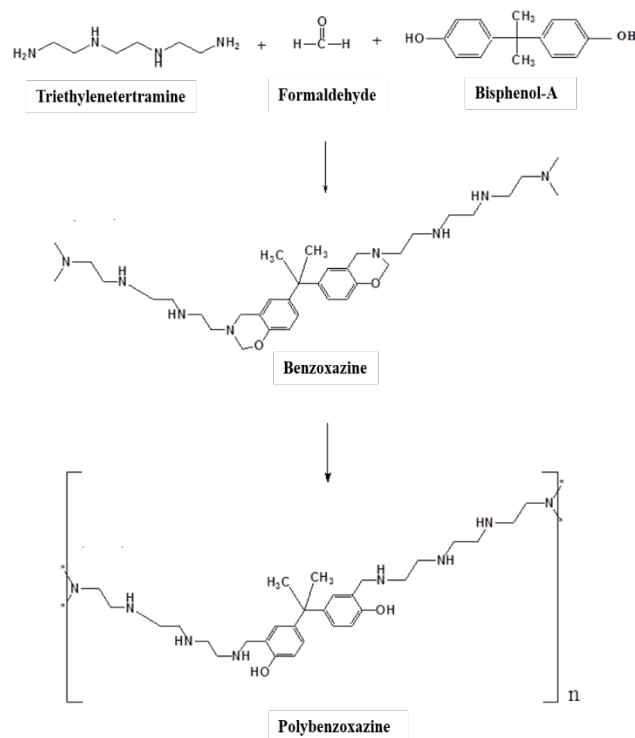


Fig.1 Synthesis of polybenzoxazine

Morphological observations of poly(D,L-lactic acid)/polybenzoxazine films were performed using a JEOL JSM-6460LV scanning electron microscopy. The samples were sputter-coated with gold to produce a conductive coating and to prevent charging.

The thermal transition properties of the poly(D,L-lactic acid), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine films were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples of 5 – 10 mg in weight were heated at 10 °C/min over a temperature range of 0 to 250 °C to observe their melting temperature (T_m) and glass transition temperature (T_g). Thermogravimetric analyses (TGA) were done on TA-Instrument (TG SDT Q600) instrument from 30 to 800 °C using nitrogen. The heating rate was 10 °C /min.

Mechanical properties including stress at break, percentage Strain at Break and initial Young's modulus, of the poly(D,L-lactic acid), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine films were determined at 25 °C and 65% relative humidity with a Lloyds LRX+ Universal Mechanical Testing Machine. The film samples (80 x 10 mm) were tested with a gauge length of 25 mm and a crosshead speed of 10 mm/min. The mechanical properties were determined from the average of three measurements for each sample.

3. RESULTS AND DISCUSSION

The photographs of poly(D,L-lactic acid) ($M_w=10,000$ and $20,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine films were shown in Fig.2-3.

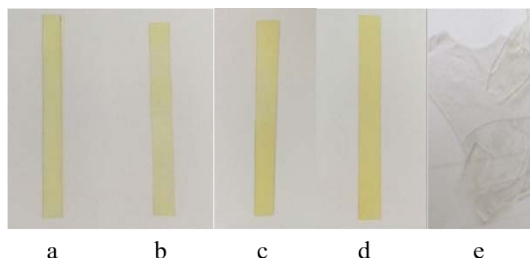


Fig. 2 The photographs of poly(D,L-lactic acid) ($M_w=10,000$ g/mol)/polybenzoxazine films a=0PDLLA/100PBZ, b=1PDLLA/99PBZ, c=3PDLLA/97PBZ, d=5PDLLA/95PBZ and e =100PDLLA/0PBZ

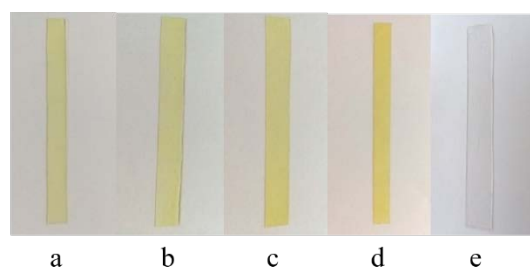


Fig. 3 The photographs of poly(D,L-lactic acid) ($M_w=20,000$ g/mol)/polybenzoxazine films a=0PDLLA/100PBZ, b=1PDLLA/99PBZ, c=3PDLLA/97PBZ, d=5PDLLA/95PBZ and e=100PDLLA/0PBZ

The chemical structure of the prepared poly(D,L-lactic acid), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine films were also confirmed using FTIR technique. The band of N-H stretching of the TETA was observed at around 3400 cm^{-1} . The band at 1502 cm^{-1} represents the stretching of the tri-substituted benzene ring. The out-of-plane bending vibration of C-H was observed at 932 cm^{-1} . In addition, bands assigned to the asymmetric stretching of C-O-C and C-N-C were found at 1233 and 1128 cm^{-1} , respectively. Furthermore, the CH_2 wagging of the oxazine ring was also observed at 1378 cm^{-1} . These FTIR results are in agreement with the study of Ning and Ishida [3], who also observed the asymmetric stretching of C-O-C (1234 cm^{-1}), the asymmetric stretching of C-N-C (1180 to 1187 cm^{-1}), the CH_2 wagging of oxazine (1325 to 1328 cm^{-1}), the tri-substituted benzene ring (1502 to 1511 cm^{-1}), and the out-of-plane bending vibrations of C-H (1502 to 1511 cm^{-1} and 937 to 943 cm^{-1}). The band of O-H and C=O

of poly(D,L-lactic acid) was observed at around 3500 cm^{-1} and 1725 cm^{-1} , respectively as shown in Fig 5.

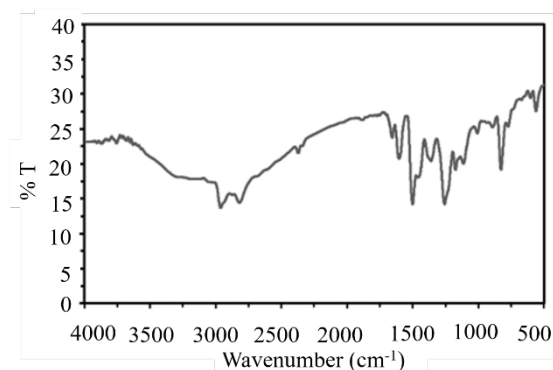


Fig. 4 The FTIR spectrum of polybenzoxazine

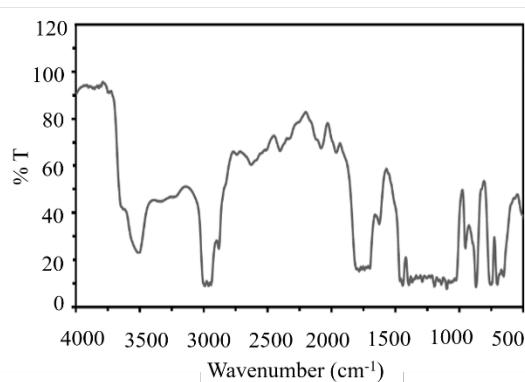


Fig. 5 The FTIR spectrum of poly(D,L-lactic acid)

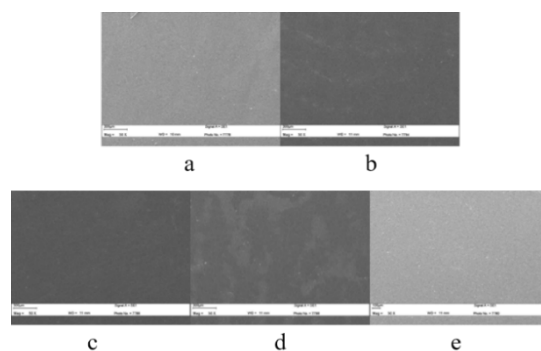


Fig. 6 The SEM results of polybenzoxazine (a), poly(D,L-lactic acid)($M_w=10,000$ g/mol)/polybenzoxazine 99:1 (b), 97:3 (c), 95:5 (d) and poly(D,L-lactic acid) (e)

3.1 Morphology

Morphology of the blend films was studied from SEM images. Figure 6 and 7 show SEM images of poly(D,L-lactic acid)/polybenzoxazine films with ($M_w=10,000$ g/mol) and ($M_w=20,000$ g/mol), respectively. The blend films show smooth surface.

The increasing ratio of poly(D,L-lactic acid) shows the higher rough surface.

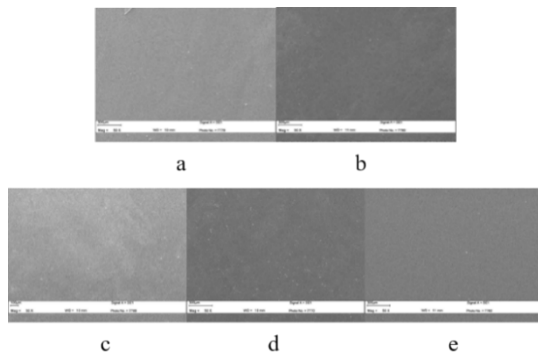


Fig. 7 The SEM results of polybenzoxazine (a), poly(D,L-lactic acid)($M_w=20,000$ g/mol) /polybenzoxazine 99:1 (b), 97:3 (c), 95:5 (d) and poly(D,L-lactic acid) (e)

3.2 Thermal Transition Properties

The thermal transition properties of the blend films were obtained from DSC thermograms to obtain melting temperature (T_m) glass transition temperature (T_g) as shown in Fig. 8-9. The T_g of the blend films were around 30-29 °C. The raising T_g was gained with high molecular weight because the polymer chain was more disorder. Addition of poly(D,L-lactic acid) also increased T_g . The formation of polymer chain affected by the thermal transition properties. The blend films with 3PDLLA/97PBZ and 5PDLLA/95PBZ show the T_m at around 117-143 °C according to some part of polymer chain was order formation to get crystallinity. The thermal stability of the poly(D,L-lactic acid), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine was investigated using TGA as shown in Fig. 10-11. The blend films show 3 steps of degradation, 150-200 °C, 250-400 °C and 400-450 °C

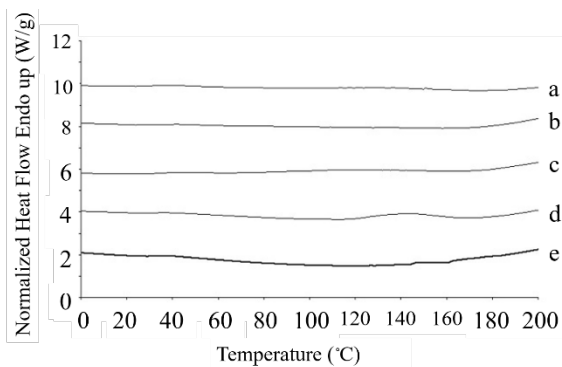


Fig. 8 The DSC results of polybenzoxazine (a), poly(D,L-lactic acid)($M_w=10,000$ g/mol) /polybenzoxazine 99:1 (b), 97:3 (c), 95:5 (d) and poly(D,L-lactic acid) (e)

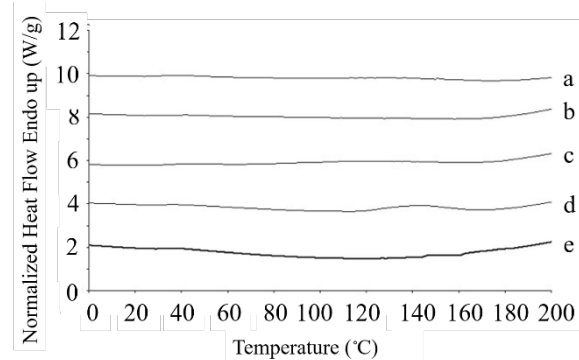


Fig. 9 The DSC results of polybenzoxazine (a), poly(D,L-lactic acid)($M_w=20,000$ g/mol) /polybenzoxazine 99:1 (b), 97:3 (c), 95:5 (d) and poly(D,L-lactic acid) (e)

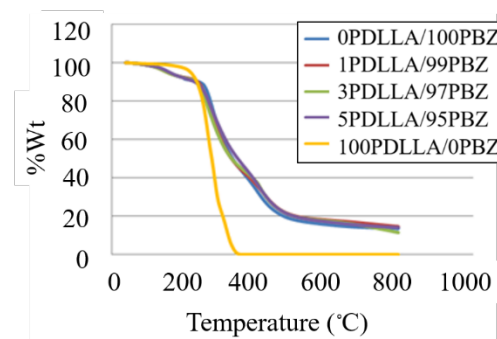


Fig. 10 The TGA results of poly(D,L-lactic acid)($M_w=10,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine.

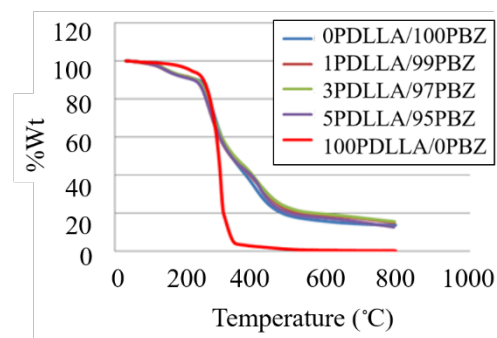


Fig. 11 The TGA results of poly(D,L-lactic acid)($M_w=20,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine.

3.3 Mechanical Properties

The mechanical properties, stress at break, percentage strain at break and Young's modulus, of poly(D,L-lactic acid), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine were determined from tensile testing. The results of mechanical properties of the blend films were compared in Table 1-2 for stress at break,

percentage strain at break and Young's Modulus, respectively. It can be seen that Young's modulus of blend films significantly increased as the poly(D,L-lactic acid) ratio increased. Especially 3PDLLA:97PBZ ratio showed high stress at break and good flexibility. This due to the poly(D,L-lactic acid) can increase free volume of polybenzoxazine molecules. The tensile results suggested that poly(D,L-lactic acid) showed good potential to mix with polybenzoxazine.

Table 1 Tensile properties of poly(D,L-lactic acid)($M_w=10,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine.

Sample PDLLA: PBZ	Stress at Break (MPa)	Percentage Strain at Break	Young's Modulus (MPa)
0:100	12.69 ± 3.97	77.82 ± 25.83	374.53 ± 95.61
1:99	10.52 ± 5.83	45.90 ± 84.58	352.49 ± 114.93
3:97	9.05 ± 6.96	2.59 ± 1.55	581.90 ± 128.10
5:95	19.18 ± 6.25	27.15 ± 37.06	588.80 ± 153.21
100:0	nd	nd	nd

nd = not detected

Table 2 Tensile properties of poly(D,L-lactic acid)($M_w=20,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine.

Sample PDLLA: PBZ	Stress at Break (MPa)	Percentage Strain at Break	Young's Modulus (MPa)
0:100	12.69 ± 3.97	77.82 ± 25.83	374.53 ± 95.61
1:99	12.37 ± 6.44	2.83 ± 1.36	668.92 ± 106.60
3:97	24.06 ± 7.99	6.04 ± 3.72	657.23 ± 137.45
5:95	15.29 ± 2.79	34.16 ± 17.49	466.33 ± 67.39
100:0	15.56 ± 4.89	7.03 ± 2.98	491.29 ± 81.41

4. CONCLUSIONS

In conclusions, it was successfully synthesized of poly(D,L-lactic acid) ($M_w=10,000$ and $20,000$ g/mol), polybenzoxazine and poly(D,L-lactic acid)/polybenzoxazine with 0PDLLA/100PBZ, 1PDLLA/99PBZ, 3PDLLA/97PBZ, 5PDLLA/95PBZ and 100PDLLA/0PBZ. It was found that the blend films showed better thermal properties than the pure polymer due to the good formation of the polymer blend. The SEM images were confirmed well-blending poly(D,L-lactic

acid)/polybenzoxazine. Increasing the amount of poly(D,L-lactic acid) gave the film a more smooth and homogeneous. It was also approved by mechanical properties using tensile testing. The 5PDLLA/95PBZ ratio with poly(D,L-lactic acid) $M_w = 10,000$ g/mol and 3PDLLA/97PBZ ratio with poly(D,L-lactic acid) $M_w = 20,000$ g/mol show the best flexibility compare with other ratio. It was concluded that a mixture of poly(D,L-lactic acid) with polybenzoxazine improved the performance of the blend film.

5. ACKNOWLEDGEMENTS

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