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Research Note

Compatibility Study of Pectin and Polylactic Acid (PLA) Blends Using Molecular Dynamics and Characterization of Thermally Pressed Blend Film

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Pectin was used to modify poly (lactic acid) (PLA) to develop an amphiphilic packaging material. Molecular dynamics was employed to assess the compatibility of pectin and PLA. The structure and the hydrophilicity of the pectin–PLA blend films, prepared using graded hot-pressing, were characterized. The results showed that pectin and PLA were not compatible in molecular dynamic simulation, and the thermodynamic test of pectin–PLA blend films also indicated the incompatibility which showed two glass transition temperatures (62.2 °C and 157.3 °C, respectively). Moreover, the thermal stability of the blend films increased with increasing pectin content in the films, and the films maintained good hydrophilic property with the contact angle less than 90°. This study could inspire further macroscopic and microscopic evaluation of blend films.

Key Words: amphiphilic, FTIR, polymer compatible, simulation and modelling, thermal analysis

Abbreviations: PLA – poly (lactic acid), MD – molecular dynamic simulation, DSC – differential scanning calorimeter, TGA – thermo gravimetric analysis, FTIR – fourier transform infrared, Ebb – energy distributions of base and base molecule, Ebs – energy distributions of base and screen molecule, Ess – energy distributions of screen and screen molecule, T_g – glass transition temperature

INTRODUCTION

Poly (lactic acid) (PLA) has special properties, such as high rigidity, biodegradability and biocompatibility (Armentano et al. 2013), and can be modified by preparing PLA copolymers and composites for wide ranging applications (Nampoothiri et al. 2010). However, the drawbacks of PLA, particularly its hydrophobicity, limit its application as a carrier (Oksman et al. 2003). To overcome these deficiencies, much research has focused on the modification of PLA using blending, grafting, and copolymerization techniques (Oksman et al. 2003). Nevertheless, little has been reported regarding the development of PLA-based amphiphilic materials for use in active food packaging.

Pectins are a group of anionic hydrophilic polysaccharides isolated from plant cells (Zhang et al. 2013). As a polymer modifier, pectin can change the hydrophilicity of a polymer matrix through blending (Zhou et al. 2013). In binary blending systems, modifiers should be miscible with matrixes, making it necessary to assess the compatibility of the two polymers (Yang et al. 2013).

In binary blending system, modifiers should be miscible with matrix, so it becomes necessary to assess the compatibility of two polymers (Yu et al. 2006). Molecular dynamic simulation (MD) is an efficient way to estimate the miscibility behavior of binary mixtures, and can

predict the thermodynamics of mixing directly from the chemical structures of the two components (Fu et al. 2013).

This study aimed to assess the compatibility of pectin and PLA, before being mechanically blended and hot-pressed into a novel amphiphilic film, to evaluate the dynamic intermolecular interactions between pectin and PLA using MD software. The morphology and water resistance performance of the blended films with varying pectin concentrations were also determined.

MATERIALS AND METHODS

Materials

PLA pellets (REVODE 190) with a density of 1.25 ± 0.05 $g.cm^{-3}$ were provided by Zhejiang Hisun Biomaterials Co., Ltd. (China). Pectin (P9135), purchased from Sigma-Aldrich (USA), was composed of 74% galacturonic acid on a dry weight basis.

Compatibility Assessment of Pectin and PLA

Software designed for materials science, Materials Studios, was used to perform molecular dynamics simulations. The force field was COMPASS and the summation methods were atom-based for electrostatics. Van der Waals interactions were no truncation cut off limits (Oksman et al. 2003). The compatibility of pectin and PLA was then screened in the Blends module using the tutorials.

Preparation of Thermally Pressed Pectin-PLA Films

Pectin and PLA were dried in a hot-air oven at 105 °C for 24 h. Blends with different pectin contents were prepared using a Haake rheometer (HAAKE, Poly Lab OS, Germany) at 60 rpm and 180 °C for 15 min, and ground into small pieces with a herb grinder. For each sample, PLA-based composite (3.5 g) was melted at 180 °C for 10 min on the heated plates and then compressed into a film using a hot press (Carver Inc., Wabash, Indiana, USA). A three-stage heating method was used to prepare films of the same thickness (Kaya et al. 2014).

Thermal Property Analysis and Structural Characterization

Thermal property of the film was tested using the method of Zhang et al. (2013) with some modifications. Briefly, for differential scanning calorimetry (DSC) analysis, samples were heated at a rate of 20 °C/min under nitrogen and the calorimeter (DSC 204 F1, Netzsch) was calibrated with indium before each run. For thermo gravimetric analysis (TGA, Perkin Elmer STA 6000), samples were heated at a rate of 20 °C/min^{-1}, under less than 40% nitrogen, from 30 to 600 °C, to observe weight changes. The chemical compositions of samples were evaluated using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) spectrometer in total reflection mode. Spectra were obtained at a resolution of 4 cm^{-1}, averaging over 64 scans in the range of 4000–600 cm^{-1}.

Moisture Content, Water Solubility and Contact Angle of Films

Moisture content, water solubility (Zhong and Li 2011) and contact angle (Zhang et al. 2003) were measured using methods based on previous studies.

RESULTS AND DISCUSSION

The pectin–PLA blends exhibited very different Ebb, Ebs and Ess energy distributions (-10, -3, and 28 $kcal.mol^{-1}$, respectively) (Fig. 1A), which showed that PLA was not miscible with pectin. Both the mixing energy (E_{mix}) and χ increased with increasing temperature, but were still below 0 (Fig. 1B, 1C). The blends model was unable to create a phase diagram for mixing, because no critical point was found between 1 and 10,000 K. In the test, if there was no critical point, the molecules might be completely miscible and, therefore, no phase diagram could be plotted, which further indicated the incompatibility of the composites. In conclusion, pectin and PLA were not compatible within a workable temperature range. Based on these results, mechanical blending with thermal pressing was a suitable procedure for preparing blended films of pectin and PLA.

DSC analysis indicated that there were two glass transition temperatures (T_g) in the blend films, which showed that pectin and PLA were immiscible (Fig. 2A). These observations agreed with the results of molecular simulation calculations. TGA showed that there was a three-step weight loss within the temperature ranges 35–95 °C, 200–290 °C, and 230–370 °C, which were attributed to free water evaporation, bound water and glycerol evaporation, and PLA decomposition, respectively. Meanwhile, there was two-step weight loss below 500 °C with 35% residue (Fig. 2B). These results showed that the blend films became more hygroscopic and thermally stable when pectin was incorporated. This phenomenon was due to PLA being strongly hydrophobic and pectin being hydrophilic. Characteristic bands were found at 3410 cm^{-1} (O–H stretching), 2943 cm^{-1} (C–H stretching), 1750 cm^{-1} (C=O stretching), and 1638 cm^{-1} (δ(O–H) in water) in the pectin powder FTIR spectrum (Fig. 2C), and at 1746 cm^{-1} (C=O stretching) and 1077 cm^{-1} (C–O–C

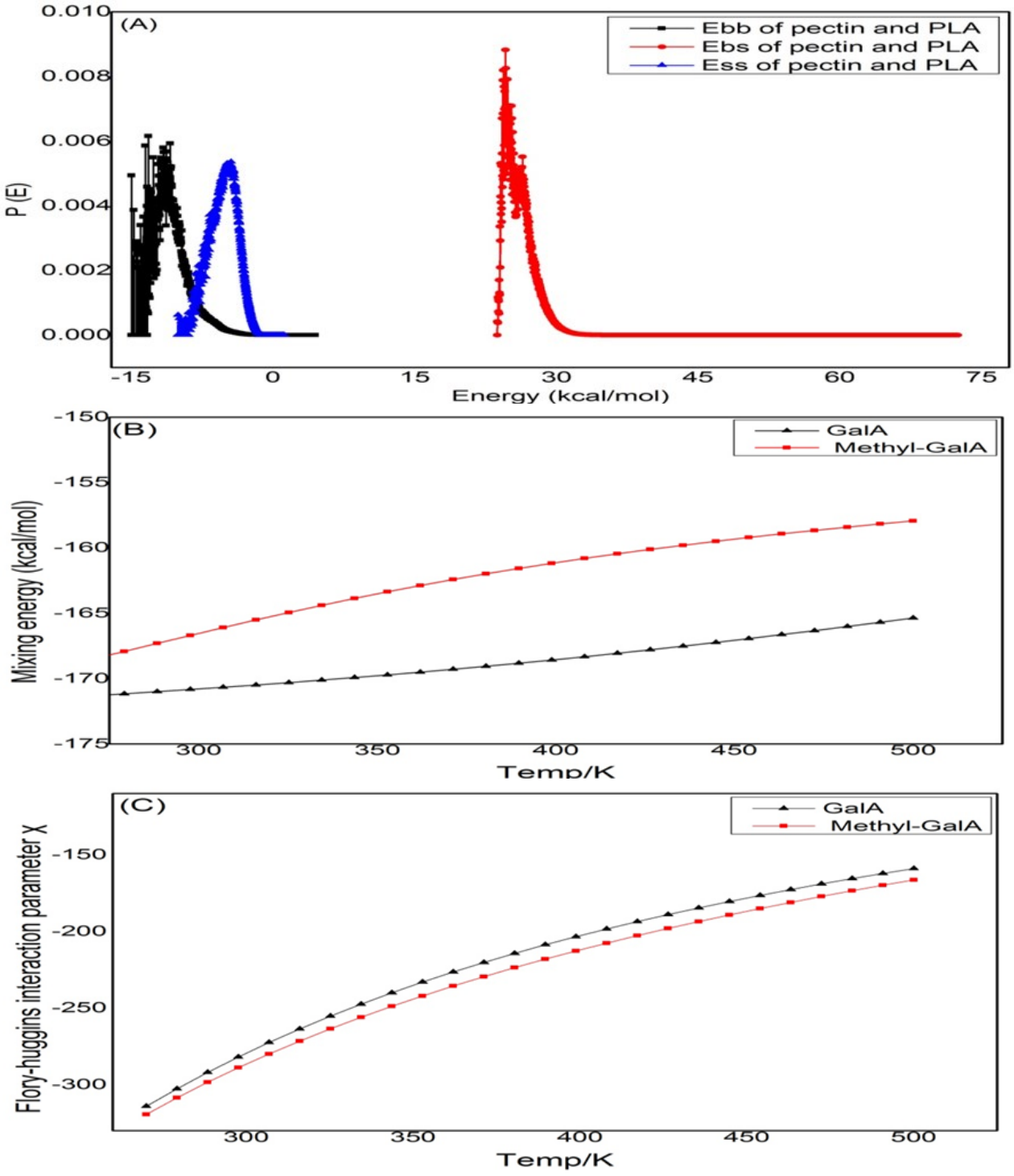

Fig. 1. Compatibility assessment of pectin and polylactic acid (PLA) through molecular dynamics simulations: (A) Binding energy distributions of pectin and PLA, (B) Mixing energy of pectin and PLA and (C) Flory-Huggins interaction parameter χ of PLA and pectin. GalA and Methyl–GalA are the main basic structural units of pectin.

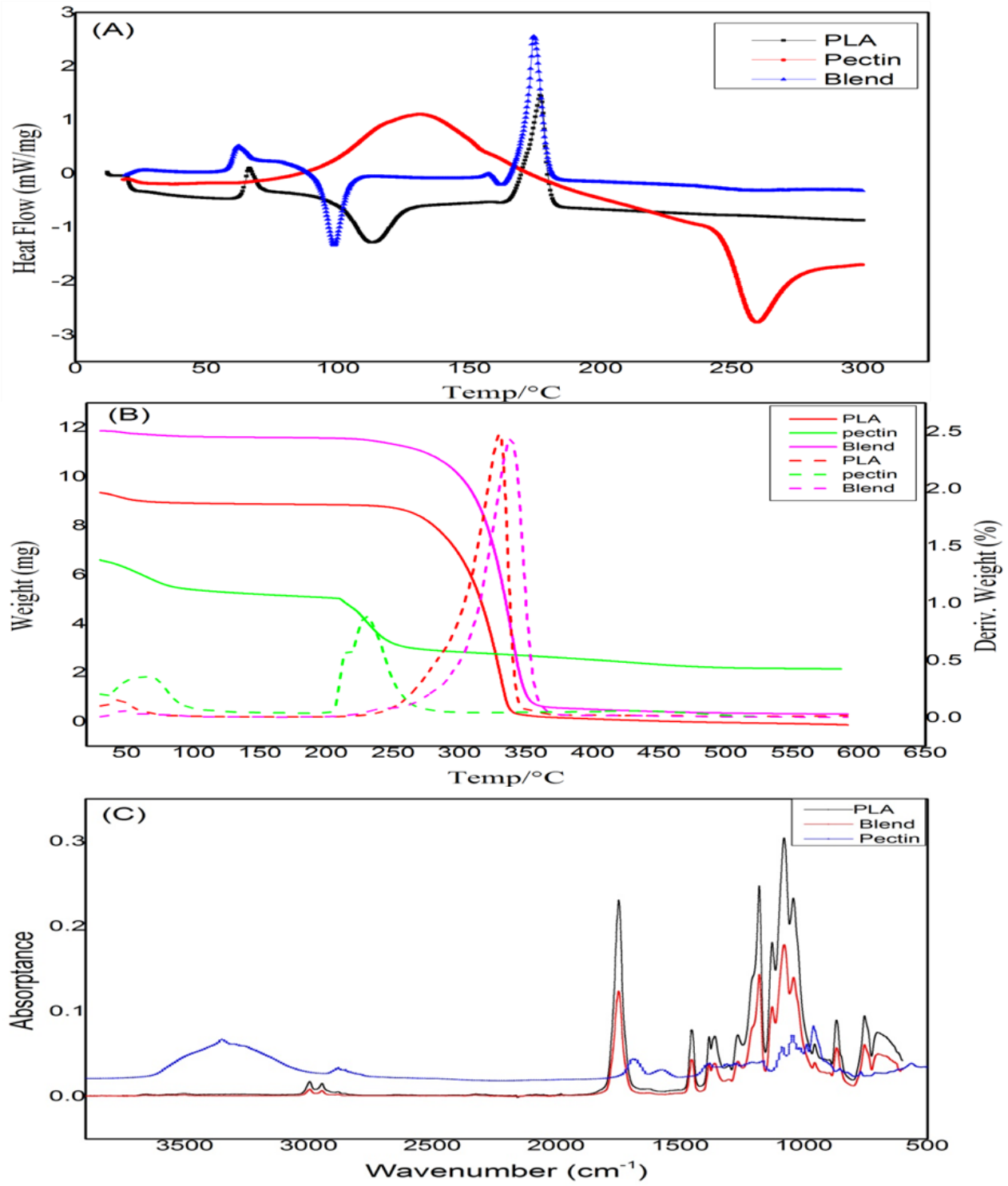

Fig. 2. (A) DSC, (B) TGA and (C) FTIR spectra of PLA, pectin and pectin–PLA blend film.

Table 1. The water content, water solubility and contact angle of blend films.

Pectin Content (%)	Water Content (%)	Water Solubility (%)	Contact Angle (°)
0	0.57 ± 0.08[a]	0.29 ± 0.11[a]	80.50 ± 0.20[d]
2	0.90 ± 0.02[b]	0.97 ± 0.13a[b]	78.00 ± 1.25[c]
4	1.12 ± 0.06[c]	2.23 ± 0.92b[c]	77.07 ± 0.40b[c]
6	1.42 ± 0.06[d]	2.89 ± 0.12[c]	75.93 ± 0.71[b]
10	1.74 ± 0.04[e]	5.00 ± 0.11[d]	70.80 ± 0.61[a]

Each value is expressed as an average ± standard deviation (n = 3). Means in the same column with the same lowercase letters are not significantly different (P < 0.05).

stretching) in the PLA FTIR spectrum, which were similar to those previously reported (Zhou et al. 2013). In contrast, C–H and C=O stretching signals were more obvious in the composites, while no water bonding and O–H stretching were present in the hot-press-treated blend films (Oksman et al. 2003). The pectin and PLA blend clearly showed that no new chemical bonds were formed in the mechanical blending mix. These results were consistent with molecular simulation calculations.

The absorption of the blend films was demonstrated by changes in water contents (Table 1). At lower pectin contents, the water content increased linearly with pectin content, from 0.5% to 2.0% active water. As increasing pectin contents led to an increasing moisture content, the water content in the film was highly dependent on the pectin content. The water content results showed that PLA film without pectin contained only a little water, which was attributed to its slight hygroscopicity. Water solubility, a measure of the water resistance of the film, was evaluated from the percentage of soluble matter in the initial dry matter of the sample. The water solubilities of blend films with varying pectin contents were 0.29 ± 0.11%, 0.97 ± 0.13%, 2.23 ± 0.92%, 2.89 ± 0.12% and 5.00 ± 0.12%, respectively (Table 1). The solubility of the film was mainly attributed to the water solubility of pectin. However, about 40–50% pectin was still protected by the PLA matrix. Therefore, the water resistance properties of the blend films were maintained by the presence of PLA, a highly hydrophobic macromolecule. The contact angles decreased from 80 to 70° as pectin content was increased from 0 to 10% (Table 1). Pectin altered the wettability of PLA, giving the blend film hydrophilic character.

CONCLUSION

The thermodynamic compatibility, structure, and water resistance performance of a pectin and PLA mixture were investigated using both computer simulations and laboratory tests. The results of MD, DSC, TGA, and FTIR showed that pectin and PLA were incompatible due to complex interactions between the molecules. The hygroscopic and thermal stability of PLA were modified significantly by blending with different ratios of pectin. This study provides valuable information for the application of PLA in food packaging and biomedical devices.

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