

Preparation of Polylactic Acid Graft Polyvinyl Acetate Compatibilizers for 50/50 Starch/PLLA Blending

S. Buchatip, A. Petchsuk

Abstract—Polylactic acid-g-polyvinyl acetate (PLLA-g-PVAc) was used as a compatibilizer for 50/50 starch/PLLA blend. PLLA-g-PVAc with different mol% of PVAc contents were prepared by grafting PVAc onto PLLA backbone via free radical polymerization in solution process. Various conditions such as type and the amount of initiator, monomer concentration, polymerization time and temperature were studied. Results showed that the highest mol% of PVAc grafting (16 mol%) was achieved by conducting graft copolymerization in toluene at 110°C for 10 h using DCP as an initiator. Chemical structure of the PVAc grafted PLLA was confirmed by ¹H NMR. Blending of modified starch and PLLA in the presence compatibilizer with different amounts and mol% PVAc was acquired using internal mixer at 160°C for 15 min. Effects of PVAc content and the amount of compatibilizer on mechanical properties of polymer blend were studied. Results revealed that tensile strength and tensile modulus of polymer blend with higher PVAc grafting content compatibilizer showed better properties than that of lower PVAc grafting content compatibilizer. The amount of compatibilizer was found optimized in the range of 0.5-1.0 Wt% depending on the mol% PVAc.

Keywords—starch, PLLA, compatibilizer, free radical polymerization, blending

I. INTRODUCTION

POLYESTER are being investigated as an alternative to conventional non-degradable or slowly degrading synthetic polymers in order to reduce their impact on the environments. Poly (lactic acid) (PLA) is a compostable polymer derived from renewable sources (mainly starch and sugar). With good biodegradability, high mechanical strength, and excellent shaping and molding properties, PLA was regarded as one of the most promising biodegradable polymers and was expected to substitute some of the non-biodegradable plastics[1-2]. However, PLA is an expensive material which limits its uses for disposable items. A possible problem-solving strategy is by blending PLA with inexpensive, readily available and biodegradable materials. Starch is a good candidate for blending with PLA due to an inexpensive renewable natural biopolymer.

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However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible, leading to poor adhesion between the two components and irreproducible performance. Such an operation therefore requires a compatibilizer to enhance the compatibility between the two immiscible phases and to improve the mechanical properties of the composite[3-4]. Due to the absence of suitable functionality for covalently coupling with biomolecular of PLA, we want to introduce more reactive groups by graft copolymerization onto the PLA side chain.

In this work, polylactic acid-g-polyvinyl acetate (PLLA-g-PVAc) was synthesized and used as a compatibilizer for 50/50 starch/PLLA blend. PLLA-g-PVAc was prepared by grafting PVAc onto PLLA backbone via free radical polymerization of vinyl acetate (VAc) in solution process. Various conditions such as type and the amount of initiator, monomer concentration, polymerization time and temperature were studied. In addition, effects of PVAc content and the amount of compatibilizer on properties of polymer blend were also investigated.

II. EXPERIMENTAL

A. Materials

Lactide monomer was obtained from PURAC (Netherlands). Poly(lactic acid)(PLLA) and modified starch were prepared in our laboratory. Vinyl acetate monomer, benzoyl peroxide (BPO) and dicumyl peroxide (DCP) were purchased from Sigma-Aldrich (Singapore). All solvents such as chloroform, methanol, tetrahydrofuran, toluene and acetone were obtained from RCI Lab Scan (Thailand) and were used as received.

B. Preparation of polylactic acid-g-polyvinyl acetate (PLLA-g-PVAc)

Polylactic acid-g-polyvinyl acetate was prepared by graft polymerization of vinyl acetate onto PLLA polymer chain using peroxide as an initiator in solution process as illustrated in Fig 1. Polymerization conditions such as type and the amount of initiator, polymerization time and temperature as well as monomer concentration were varied to obtain different mol% PVAc contents. The final product was precipitating in an excess ethanol before vacuum dried at 45°C for overnight.

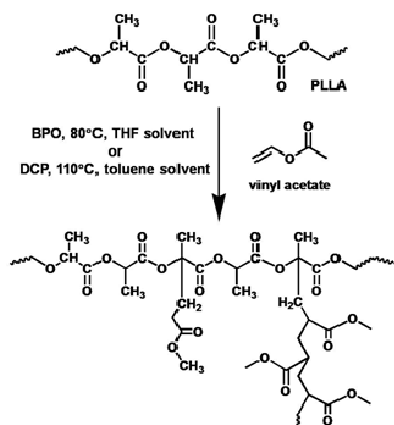


Fig. 1 Synthesis route to polylactic acid-g-polyvinyl acetate

C. Preparation of starch/polylactic acid blending

The blending of 50/50 modified starch and commercial PLLA in the presence of compatibilizer was acquired in ternary system. Effects of the amount of the compatibilizer and mol% PVAc grafting on properties of polymer blend were studied. The polymer blend was prepared using internal mixer at 160°C for 15 min. The speed of the rotation was set at 40 rpm. The specimen for mechanical testing was prepared by hot pressing the pulverized polymer blend at 160°C and was cut into rectangular shape.

D. Characterizations

The structural information of graft copolymer was measured using AVANCE 300 MHz Digital Nuclear Magnetic Resonance spectrometer (Bruker Biospin; DPX-300) (NMR). All samples were characterized at room temperature (20±1°C). ¹H NMR spectra were recorded at a frequency of 300 MHz. The spectral parameter used were as follows: 64 numbers of scan (NS), relaxation delay of 2 s., spin rate of 25 Hz and spectral size 16 K with 32 K time domain size. Tensile testing was carried out on an Instron tensile testing machine with a crosshead speed of 50 mm/min, using rectangular specimens with 50 mm gauge length and 15 mm width, according to ASTM D882.

III. RESULTS AND DISCUSSION

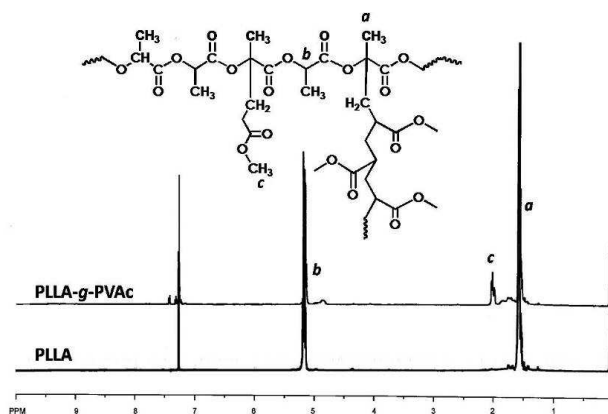
Chemical structure of the resulting PLLA-g-PVAc was confirmed by ¹H NMR. Figure 2 showed NMR spectra of PLLA-g-PVAc compared to that of PLLA. The characteristic chemical shifts at 1.5-1.7 (a) and 5.1-5.2 (b) ppm were related to methyl protons and methine proton of LA repeat unit, respectively. The observed new peak at 2.1 ppm (c) in PLLA-g-PVAc spectra was assigned to methyl protons connected to the oxygen atom and carbonyl group of PVAc unit insisting the graft copolymerization of VAc. The mol% grafting of PVAc was calculated from the integration ratio of peak at chemical shift 2.1 ppm to that of 5.1-5.2 ppm and was summarized in Table 1 where Graft copolymerization of PLLA-g-PVAc was taken place at various polymerization conditions. By varying the polymerization conditions, mol% grafting of PVAc can be varied.

The highest mol% PVAc grafting was achieved by conducting graft copolymerization in toluene at 110°C for 10

h using DCP as an initiator where 16 mol% PVAc grafting was obtained.

TABLE I
SUMMARY OF GRAFT COPOLYMERIZATION CONDITIONS AND THE RESULTING MOL% GRAFTING OF PLLA-G-PVAc

VAc feeding	conditions (initiator/solvent/temp./time)	% PVAc grafting (¹ H NMR)
50% wt PLA	BPO/THF/80°C/4 h.	5.8
50% wt PLA	BPO/THF/80°C/10 h.	4.3
50% wt PLA	DCP/toluene/110°C/10 h.	7.0
1:1 mol PLA	DCP/toluene/110°C/4 h.	13.2
1:1 mol PLA	DCP/toluene/110°C/10 h.	16.0

Fig. 2 ¹H NMR spectra of PLLA-g-PVAc compared to that of PLLA

The preparation of modified starch and commercial PLLA blend was acquired using internal mixer at 160°C for 15 min. Blending of 50:50 starch/PLLA was conducted in ternary system where 6 and 16 mol% PVAc grafting compatibilizer were added in different amount (0.5 and 1.0 wt %).

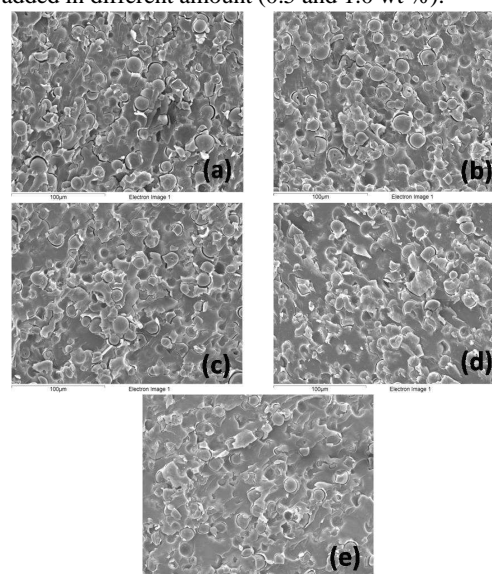


Fig. 3 SEM micrographs of starch / PLLA blend with and without PLLA-g-PVAc compatibilizers (a) without compatibilizer, (b) 0.5 Wt % of compatibilizer with 6 mol% PVAc, (c) 1.0 Wt % of compatibilizer with 6 mol% PVAc, (d) 0.5 Wt % of compatibilizer with 16 mol% PVAc and (e) 1.0 Wt % of compatibilizer with 16 mol% PVAc

Micrographs of all the modified starch blended with compatibilizer were hardly differentiated from polymer blend without compatibilizer. Therefore, mechanical properties of all polymer blends were then investigated. Mechanical properties of all polymer blends with and without compatibilizer were summarized in Table 2 and tensile strength, tensile modulus and elongation at break were shown in Fig 4.

Comparing same wt% of compatibilizer, as the mol% PVAc of compatibilizer increased from 6 to 16 mol%, tensile strength and tensile modulus of the polymer blend increased whereas the elongation at break decreased. This probably because the interfacial interaction between starch and PLLA increased as mol% PVAc increased, resulting in enhancing of mechanical properties.

TABLE II
MECHANICAL PROPERTIES OF STARCH /PLLA BLEND WITH AND WITHOUT
PLLA-G-PVAc COMPATIBILIZERS

Compatibilizers		Tensile strength	Modulus	Elongation
mol% PVAc	wt%	(MPa)	(MPa)	(%)
-	-	160.3 + 21.6	8912.1 + 1607.5	4.0 + 0.6
6	0.5	127.3 + 16.8	11121.5 + 1129.6	2.1 + 0.3
6	1	133.2 + 26.2	15130.3 + 2719.5	1.5 + 0.1
16	0.5	189.7 + 47.1	18190.2 + 3590.6	1.8 + 0.3
16	1	154.6 + 32.4	17470.4 + 2729.0	1.5 + 0.1

However for 16 mol% PVAc compatibilizer, only 0.5 wt% compatibilizer was enough to improve mechanical properties of polymer blend. An excess amount of the compatibilizer resulted in the decrease of tensile strength and modulus. This can be deduced that properties of polymer blend were strongly depended on the amount of functionalities (mol% PVAc) rather than the amount of the compatibilizer. The decrease of the elongation at break of the polymer blend was probably due to the interaction between acetate groups of compatibilizer and hydroxyl groups of starch resulting in the hardening of the polymer blend. To improve this hardness, plasticizer may be used.

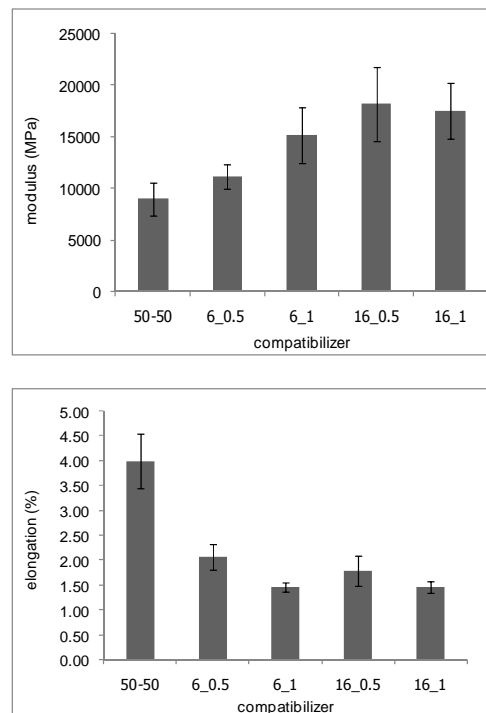
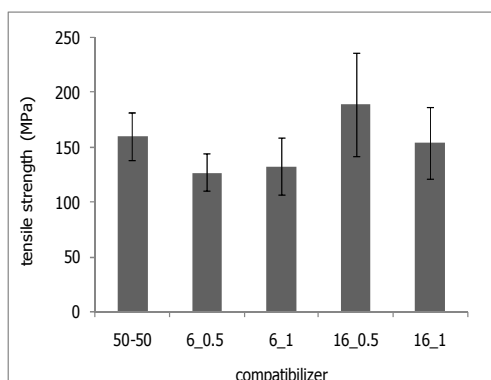


Fig. 4 Mechanical properties of starch / PLLA blend with and without PLLA-g-PVAc compatibilizer

IV. CONCLUSION

PLLA-g-PVAc can be prepared by graft polymerization of VAc onto PLLA backbone using free radical initiator in solution process. By varying the polymerization conditions, mol% PVAc can be varied from 4.3-16 mol%. Tensile strength and tensile modulus of polymer blend can be improved by adding small amount of high mol% PVAc grafting compatibilizer.

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