
อิทธิพลของมาเลอิกแอนไฮไดรด์และโปแตสเซียมเปอร์ซัลเฟตต่อสมบัติเชิงกลของพอลิแลคติกแอซิดคอมปาวด์

Effect of Maleic Anhydride and Potassium Persulfate on Mechanical Properties of Poly(Lactic acid) Compound

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บทคัดย่อ

พอลิแลคติกแอซิดเป็นพอลิเมอร์ย่อยสลายได้ทางชีวภาพที่รู้จักกันดี การผสมพอลิแลคติกแอซิดกับพอลิเมอร์ชนิดอื่นๆ ที่ได้มาจากแหล่งปลูกทดแทนได้กำลังเป็นวิธีการนิยมสำหรับการลดต้นทุนการผลิตและการปรับปรุงสมบัติของพอลิแลคติกแอซิดโดยที่ยังคงรักษาคุณลักษณะความเป็นพอลิเมอร์ชีวภาพได้ แป้งมันสำปะหลังเป็นพอลิเมอร์ชีวภาพที่นำมาผสมกับพอลิแลคติกแอซิด เร็วๆ นี้ ได้มีการนำยางธรรมชาติเป็นสารเพิ่มความเหนียวของพอลิเมอร์ผสมระหว่างพอลิแลคติกแอซิดและแป้งมันสำปะหลัง วัตถุประสงค์ของการศึกษานี้คือการตรวจสอบอิทธิพลของมาเลอิกแอนไฮไดรด์และโปแตสเซียมเปอร์ซัลเฟตต่อความเหนียวทนแรงของพอลิแลคติกแอซิดคอมปาวด์ที่มีส่วนผสมของพอลิแลคติกแอซิด 80% แป้งมันสำปะหลัง 20% และยางธรรมชาติ 10 ส่วนต่อร้อยละของน้ำหนักพอลิแลคติกแอซิดและแป้งมันสำปะหลัง พอลิแลคติกแอซิดคอมปาวด์นี้เตรียมด้วยเครื่องอัดรีดแบบสกรูคู่ที่ 150°C และขึ้นรูปด้วยเครื่องอัด ทำการตรวจสอบสมบัติความทนต่อแรงดึงและความต้านทานต่อแรงกระแทก เติมนสารริเริ่มชนิด Luperox®L101 ในปริมาณ 10% และ 25% โดยน้ำหนักของมาเลอิกแอนไฮไดรด์ พบว่าที่ปริมาณ 25% ช่วยปรับปรุงสมบัติเชิงกล อิทธิพลของปริมาณโปแตสเซียมเปอร์ซัลเฟตที่ศึกษาอยู่ในช่วง 0.25-1.00% พบว่าโปแตสเซียมเปอร์ซัลเฟตเพิ่มความต้านทานต่อแรงกระแทก ทำการศึกษาคุณลักษณะเฉพาะของพอลิแลคติกแอซิดคอมปาวด์ด้วยเทคนิคการวิเคราะห์เชิงกลอุณหพลศาสตร์ เทคนิคสแกนนิ่งแคลอริเมตตรี เทคนิคเทอร์โมกราวิเมตตรี และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด

คำสำคัญ : พอลิเมอร์ย่อยสลายทางชีวภาพ แป้งมันสำปะหลัง ยางธรรมชาติ พอลิแลคติกแอซิด แหล่งทดแทนได้

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Abstract

Poly(lactic acid) (PLA) is a well-known biodegradable polymer. The blending of PLA with other polymers derived from renewable resources is now becoming a common method for reducing production costs and for producing improvements to the PLA properties while still remaining its bio-based characteristics. Cassava starch is a common biopolymer that has been incorporated into PLA. Recently, natural rubber (NR) was also employed to enhance the toughness of PLA/cassava starch blend. The objective of this study was to examine the effects of maleic anhydride (MA) and potassium persulfate (PPS) on the toughness of a PLA compound that contained 80 wt% of PLA, 20 wt% of cassava starch and 10 pph of NR. This PLA compound was prepared by using a twin screw extruder at 150°C and fabricated by means of a compression molding technique. Its tensile properties and impact strength were investigated. An initiator, Luperox®L101, was added at 10 and 25 wt% based on its MA content. The latter content improved the mechanical properties of PLA compound. The effect of the MA content, at 0.25, 0.5 and 1 wt%, was evaluated. The optimum content of MA was 0.5%. The effect of PPS was determined in the range of 0.25-1.00%. PPS produced higher impact strength than MA. Characterization of the blends was made by using dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

Keywords : Biodegradable polymers; Cassava starch; Natural rubber; Poly(lactic acid); Renewable resources

Introduction

Poly(lactic acid) (PLA) is a well-known biodegradable polyester and it has already been commercialized. PLA is also referred to as a bio-based polymer because the starting material, lactic acid, can arise from a renewable resource such as cassava starch or corn starch. The manufacturing cost of PLA is relatively high compared to more conventional polymers such as polyethylene, polypropylene and poly(ester terephthalate). Therefore, a biodegradable polymer such as starch was blended with PLA in order to reduce the costs of production. There have been many published reports on PLA/starch blends (Park *et al.*, 1999; Ke & Sun, 2003a; Ke *et al.*, 2003; Mihai *et al.*, 2007; Lu *et al.*, 2009; Yokesahachart *et al.*, 2011; Cai *et al.*, 2011; Zhang & Sun, 2004a). Starch has been used as a native starch or a thermoplastic starch. It was found that the PLA/starch blend is a brittle material and its mechanical properties are decreased when compared to virgin PLA. There are many methods to increase the mechanical properties of the PLA/starch blend such as an addition of a reactive additive or a compatibilizer, such as maleic anhydride (Zhang & Sun, 2004a; Zhang & Sun, 2004b; Huneault & Li, 2006; Orozco *et al.*, 2009; Leadprathom *et al.*, 2010; Muenprasat *et al.*, 2010), methylene diisocyanate (Wang *et al.*, 2002; Wang *et al.*, 2003), dioctyl maleate (Zhang & Sun, 2004c), fomamide (Wang *et al.*, 2007) and glycidyl methacrylate (Shi *et al.*, 2011), or the addition of a third polymer, i.e., poly (ϵ -caprolactone) (Sasazin *et al.*, 2008; Liao & Wu, 2009), poly (vinyl alcohol) (Ke & Sun, 2003b), PLA-g-starch copolymer (Wootthikanokkhan *et al.*, 2012; Chen *et al.*, 2006) and poly (hydroxylester-ether) (Shogren *et al.*, 2003). To the best of our knowledge, there has been no previous report on the properties of PLA/starch/natural rubber blends. It was expected that natural rubber (NR) would enhance the toughness of the PLA/starch blend. NR is used as a toughening agent for PLA (Jaratrotkamjorn *et al.*, 2012), and a thermoplastic elastomer prepared from a PLA/NR blend has been established (Tanrattanakul *et al.*, 2012). Thus, the

properties of this PLA/starch/NR blend have been studied in the present work. There were some differences between the present study and the previous study (Jaratrotkamjorn *et al.*, 2012). The present blend was a ternary blend of a PLA/starch/NR blend that used natural rubber latex and had a lower content than the binary PLA/NR blend. However, it was not the objective of this work to compare the present blend with that of the binary blend. The ternary blend may contain stress concentrators more than the binary blend. Consequently, a compatibilizer was required for the PLA/starch/NR blend. Maleic anhydride (MA) acted as the compatibilizer in the PLA-based blend with and without an initiator such as benzoyl peroxide and Luperox®101. Potassium persulfate (PPS) is a well-known initiator used for graft copolymerization in starch-based systems such as those where cassava starch was grafted with polystyrene (Kaewtatip & Tanrattanakul, 2008), cassava starch grafted with polyethylene (Tanrattanakul & Panwiriyarat, 2009), cassava starch grafted with natural rubber (Tanrattanakul & Chumeka, 2010) and sago starch grafted with poly (methyl methacrylate) (Qudsieh *et al.*, 2004). There have been no publications on the use of PPS in PLA/starch blends.

The objectives of the present study were to investigate the mechanical properties of the PLA/cassava starch/NR latex blend and to determine the effect of MA and PPS on the mechanical properties of this ternary blend. The effect of MA and PPS on the miscibility of the blend was investigated in terms of a shift in the glass transition temperature and the interfacial adhesion between the dispersed phase and the matrix was determined from the blends morphologies.

Experimental

Materials

All polymers used are commercial grade. Ingeo®3051D was produced by Natureworks LLC. A high ammonium concentrated latex was employed and produced by Jana Concentrated Latex Co., Songkla,

Thailand. A non-ionic surfactant (Trinton®X-100PRS) was used for the dispersion of latex and supplied by Dow Chemical Co. Ltd. (Thailand). Cassava starch was kindly supplied by the General Starch Co. Ltd. (Thailand). Maleic anhydride (MA), benzoyl peroxide (BPO) and 2,5-bis (ter-butylperoxy), 2,5-dimethylhexane (Luperox®101) were produced by Sigma-Aldrich Co. and potassium persulfate (PPS) was supplied by Ajax Finechem Co..

Polymer blend preparation

Poly (lactic acid) (PLA) and cassava starch were dried before use. Starch and natural rubber latex were mixed together prior to adding the non-ionic surfactant and water, and this mixture was called as a starch compound. The starch compound was dried before blending with PLA and reactive additives (MA, PPS and BPO). Melt blending was carried out in a twin screw extruder (PRISM®16TC) at 160°C. Owing to short screws, extrusion was performed twice. The screw speed of the first and the second extrusion was 150 and 190 rpm, respectively. The extrudates were air cooled and successively pelletized by using a pelletizer. The resulting blends were dried and kept in a desiccator prior to use. A list of the blend formulations is provided (Table 1). Compression molding was carried out at 160°C for 13 min to obtain a 2 mm-thick sheet. The blends were kept in a desiccator before testing.

Testing of mechanical properties

The tensile properties and Charpy impact resistance were carried out at room temperature (25-27°C) according to ASTM D412 and ASTM D256, respectively. At least five specimens were used for every sample. The tension speed was 5 mm/min. The impact strength was investigated by using v-notched and un-notched specimens.

Polymer blend characterization

Dynamic mechanical thermal analysis (DMTA) was performed by using Rheometric Scientific® DMTA V under the following condition: frequency 1 Hz, heating rate 3°C/min, strain control 0.01% and a dual cantilever mode. Perkin Elmer® DSC7 was used for measurement of the thermal properties at a heating scan of 10°C/min from 20°C to 200°C. The DSC thermograms were recorded from the first heating scan. The heat of fusion of pure crystalline PLLA (ΔH_c) was 93 J/g (Jaratrotkamjorn *et al.*, 2012). Scanning electron micrographs were produced using JEOL®5800LV and Quanta®400 FEI. All specimens were immersed in liquid nitrogen for 4 h and immediately fractured prior to coating with gold. NR particles were removed by etching with petroleum ether for 24 h and then dried at 50°C for 24 h before coating with gold.

Table 1 Blend formulation in weight unit

Sample	PLA	Starch	NR ^a	L101 ^b	MA	PPS
0NR	80	20	-	-	-	-
Control	80	20	10	-	-	-
0.25MA	80	20	10	25%	0.25	-
0.5MA	80	20	10	25%	0.5	-
1.0MA	80	20	10	25%	1.0	-
0.25PPS	80	20	10	-	-	0.25
0.5PPS	80	20	10	-	-	0.5
1.0PPS	80	20	10	-	-	1.0

^adry rubber content, based on MA content

Results and discussion

Mechanical Properties and Morphology of Blends without MA and PPS

The aim of the present study was to improve the toughness of the PLA/starch blend. The addition of cassava starch in PLA reduces costs but increases the brittleness due to the unplasticized starch as was the case in the present study. As a result, NR was added into the PLA/starch blend to enhance the toughness of the blend. The PLA/starch/NR blend was referred to as the “control” sample; the PLA/starch blend was referred to as the “ONR” sample. Generally, impact testing measures the toughness of materials. The impact strength and the mechanical properties of the ONR sample and the control sample are shown in Table 2. The addition of NR increased the impact strength of the PLA/starch blend and did not affect the strain at break (ϵ_b). NR decreased the Young’s modulus (E) and the stress at break (σ_b). Typically, the tensile toughness obtained from an area under a stress-strain curve also is an indicator of the toughness of the materials. It showed that NR decreased the tensile toughness of the blend. This may be due to the lower tensile strength of the control sample that was attributed to the smaller area under the stress-strain curve.

It has been reported that although NR is a toughening agent that can significantly increase the impact strength of PLA, but it shows little affect on the strain at break of PLA (Jaratrokamjorn *et al.*, 2012). The polymer blend in the present study was a ternary blend (PLA/starch/NR), and the NR content was less than that of the starch content. Therefore, the contribution of the NR in

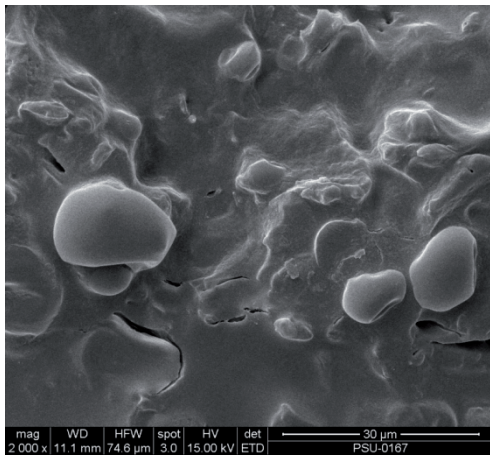
the present blend was a lower efficiency than that in the PLA/NR blend used in earlier work. Normally the rubber toughened polymer has a lower modulus and tensile strength than the virgin polymer because rubber is weaker than the polymeric matrix. Based on the rule of mixture, the properties of polymer blends also depend on the intrinsic properties of each polymer. Typical properties of NR are a low modulus, low tensile strength, high strain at break and high impact resistance. Consequently, the control sample did show lower tensile properties and a higher impact strength than the ONR sample. The strain at break of polymer blends is also controlled by the particle size of the rubber. It has been published that the molecular weight of NR is related to the NR particle size that has a strong influence on the strain at break of PLA (Jaratrokamjorn *et al.*, 2012). For example, the PLA/NR blend containing high molecular weight NR ($M_n = 1,485,000 \pm 32,000$ g/mol) showed the average diameter of NR particle at 2.50 ± 1.16 μm and the strain at break of the blend was $6 \pm 2\%$. The lower molecular weight NR ($M_n = 202,000 \pm 5,000$ g/mol) provided the rubber particle diameter at 0.95 ± 0.44 μm and the strain at break of the blend was $21 \pm 1\%$. The lower molecular weight provides smaller rubber particles that led to the higher strain at break, and there is an optimal size of the rubber particles for the highest strain at break.

The NR latex that was used in the present study produced a good mixing between the latex and the cassava starch. Thus, the molecular weight of the NR was high, and in particular was higher than in the rubber block such as STR5L. NR particles were observed by using SEM.

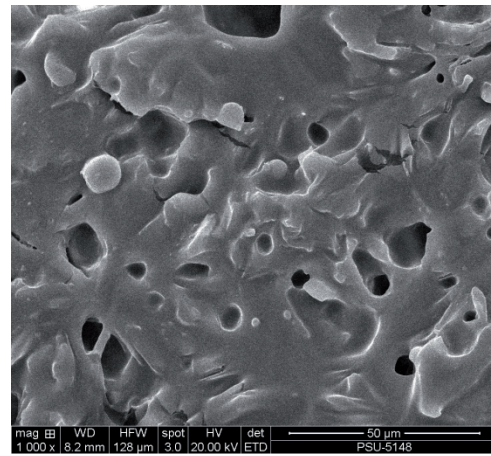
Table 2 Effect of NR on the mechanical properties of the PLA/starch blend

Sample	Impact strength (kJ/m^2)		Tensile properties			
	Notched	Unnotched	E (MPa)	σ_b (MPa)	ϵ_b (%)	A^a
ONR	1.78 ± 0.25	6.28 ± 0.95	1734 ± 24	43.9 ± 2.5	3.8 ± 0.2	60.2
control	1.98 ± 0.23	6.77 ± 1.10	1177 ± 18	27.4 ± 0.7	3.8 ± 0.2	41.5

^aan area under the stress-strain curve



(a)

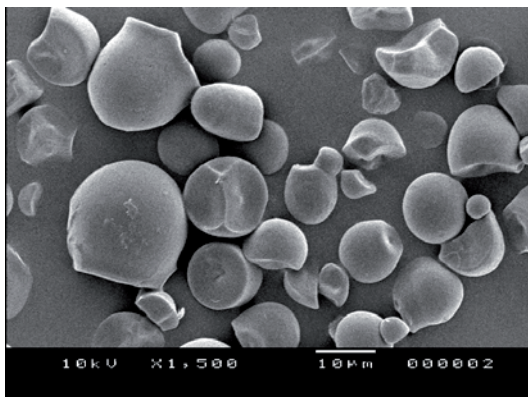


(b)

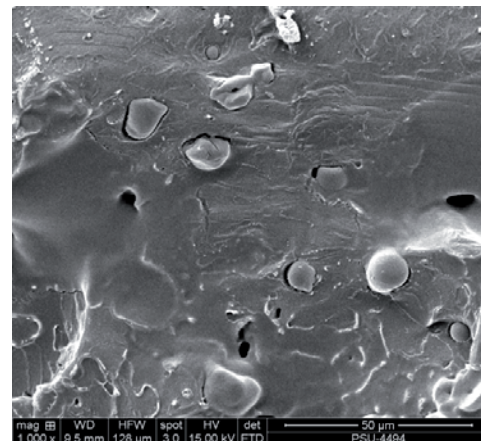
Figure 1 SEM micrographs of the “control” sample: (a) regular surface and (b) surface etched with petroleum ether to remove NR particles.

Figure 1 is SEM micrographs of the control sample. The sample was freeze fractured. One piece was a regular sample, an un-etched specimen (Figure 1a). The presence of NR particles was unclear in the un-etched specimen. Another piece of the fractured surface was etched with petroleum ether in order to remove the NR particles from the fractured surface (Figure 1b). The NR particles in the present blend were very large ($5.13 \pm 2.45 \mu\text{m}$) as shown by the big holes in Figure 1b, whereas the submicron particles obtained in the PLA/NR blend provided the higher strain at break (Jaratrotkamjorn *et al.*, 2012).

The starch granules of the blends observed in Figure 1 were verified by the morphology of the virgin starch in Figure 2a which showed relatively spherical shape. Without plasticization, the starch granules remained in the PLA matrix and some were distorted as seen in Figure 1. Figure 2b is a SEM micrograph of the PLA/starch blend, the 0NR sample. It looked similarly to the control sample, except the interfacial adhesion between PLA matrix and starch granules in the control sample (the blend with NR) was better than that in the 0NR sample.



(a)



(b)

Figure 2 SEM micrographs of (a) the native cassava starch and (b) the PLA/starch blend (0NR sample).

Table 3 Effect of L101 content on the mechanical properties of the PLA/starch/NR blend containing 0.5 pph of maleic anhydride

L101 (%) ^a	Impact strength (kJ/m ²)		Tensile properties			
	Notched	Unnotched	E (MPa)	σ_b (MPa)	ϵ_b (%)	A ^b
0	1.62 ± 0.14	6.26 ± 0.51	1184 ± 35	24.2 ± 1.2	3.5 ± 0.3	35.1
10	1.86 ± 0.31	6.90 ± 0.66	1206 ± 15	27.0 ± 1.0	3.7 ± 0.1	40.9
25	2.07 ± 0.06	7.10 ± 0.70	1171 ± 20	29.6 ± 0.6	4.5 ± 0.3	61.3

^a based on maleic anhydride content; ^b an area under the stress-strain curve

Effect of MA and PPS on Mechanical Properties

Based on the mechanical properties of the control sample, an enhancement of the impact resistance of the PLA/starch/NR blend was required. It has been claimed that maleic anhydride (MA) reacts as a compatibilizer in the PLA/starch blend and L101 is used as an initiator (Zhang & Sun, 2004a; Zhang & Sun, 2004b; Huneault & Li, 2006). Hence, MA was introduced into the control sample and the optimum content of L101 was determined. In this experiment the MA content was 0.5 parts per hundred of the PLA/starch blend and referred to as 0.5 pph. The L101 content was based on the MA content. The effect of the L101 content on the impact strength and the tensile properties of the control sample are displayed in Table 3. The impact strength increased with an increasing amount of L101, and 25% L101 showed the highest impact resistance that was higher than the control sample, the blend without MA. The Young's moduli were in the same range while for tensile strength, the strain at break and

the tensile toughness of the blends increased as the L101 content increased. The sample containing 25% L101 showed a higher impact resistance, tensile strength and strain at break than the control sample. These results indicated that MA with the initiator was required to increase the mechanical properties of the PLA/starch/NR blend.

It was necessary to verify the optimal content of MA. The MA content was selected in the range of 0.25-1 pph. Due to the previous results it was required to add MA with 25% L101. It seemed that the addition of MA provided a higher toughness than the control sample (Table 4); however, the MA content should be ≤ 0.5 pph because the impact strength, the strain at break and the tensile toughness were lowest at 1.0 pph of MA.

Potassium persulfate (PPS) is a well-known redox initiator. It is soluble in water and used in graft copolymerization as described earlier. The present study employed PPS at a range of 0.2-1.0 parts per hundred of PLA and

Table 4 Effect of maleic anhydride content on the mechanical properties of the PLA/starch/NR blend containing 25% L101

MA (pph)	Impact strength (kJ/m ²)		Tensile properties			
	Notched	Unnotched	E (MPa)	σ_b (MPa)	ϵ_b (%)	A ^a
0.25	2.14 ± 0.11	6.92 ± 0.27	1146 ± 13	26.6 ± 0.3	4.7 ± 0.2	65.7
0.5	2.07 ± 0.06	7.10 ± 0.70	1171 ± 20	29.6 ± 0.6	4.5 ± 0.3	61.3
1.0	2.01 ± 0.31	6.43 ± 0.41	1161 ± 17	28.0 ± 0.4	4.0 ± 0.1	49.2

^a an area under the stress-strain curve

Table 5 Effect of potassium persulfate content on the mechanical properties of the PLA/starch/NR blend

PPS (pph)	Impact strength (kJ/m ²)		Tensile properties			
	Notched	Unnotched	E (MPa)	σ_b (MPa)	ϵ_b (%)	A ^a
0.2	2.13 ± 0.12	7.22 ± 0.44	1209 ± 29	26.8 ± 1.7	4.1 ± 0.4	60.0
0.5	2.47 ± 0.40	7.56 ± 1.30	1201 ± 45	27.0 ± 0.8	4.6 ± 0.2	77.6
1.0	2.14 ± 0.15	6.60 ± 0.37	1200 ± 33	24.0 ± 1.1	4.1 ± 0.4	51.9
0.5PPS +0.5BPO	1.90 ± 0.34	4.55 ± 0.78	1039 ± 41	22.0 ± 1.3	3.4 ± 0.2	31.7

^a an area under the stress-strain curve

starch, that was similar to the MA content. The effect of the PPS on the impact strength and the tensile properties are shown in Table 5.

The amount of 0.5 pph of PPS without benzoyl peroxide (BPO) generated the highest impact strength and tensile properties; any further increase of the PPS content reduced these mechanical properties. The previous studies (Tanrattanakul V. & Panwiryarat W. (2009) and Tanrattanakul V. & Chumekae, W. (2010)) showed the synergistic behavior when a combination of BPO and PPS was used in the LDPE/starch blend and NR/starch blend. In contrast, the addition of BPO in the present study caused a reduction in the tensile properties. This may be due to the high amount of BPO that induced chain scission

as indicated by the yellow color of the extrudate. The sample containing 0.5 pph of PPS without BPO showed the highest mechanical properties among all the blends; therefore, it proved to be the best formula for enhancing the toughness of the PLA/starch/NR blend.

Blend characterization

Characterization of the ternary blend is more complicated than the binary blend. It is difficult to identify the interaction of each polymeric pair when the compatibilizer can react among the three polymers. MA and PPS could provide an interaction in the PLA/starch, PLA/NR and starch/NR pair. Moreover, it was not possible to compare the reactivity of the MA and PPS among those binary blends. Due to the low NR content (< 10%), a

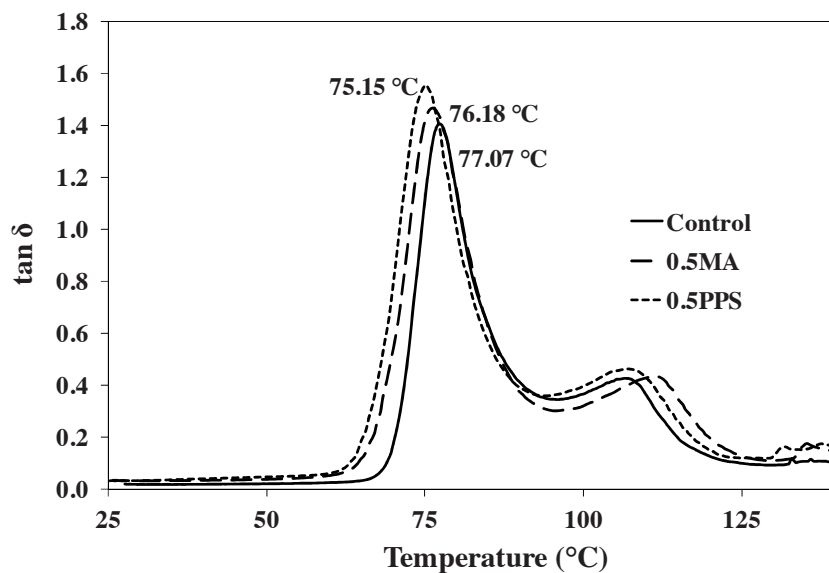


Figure 3 SEM micrographs of (a) the native cassava starch and (b) the PLA/starch blend (0NR sample).

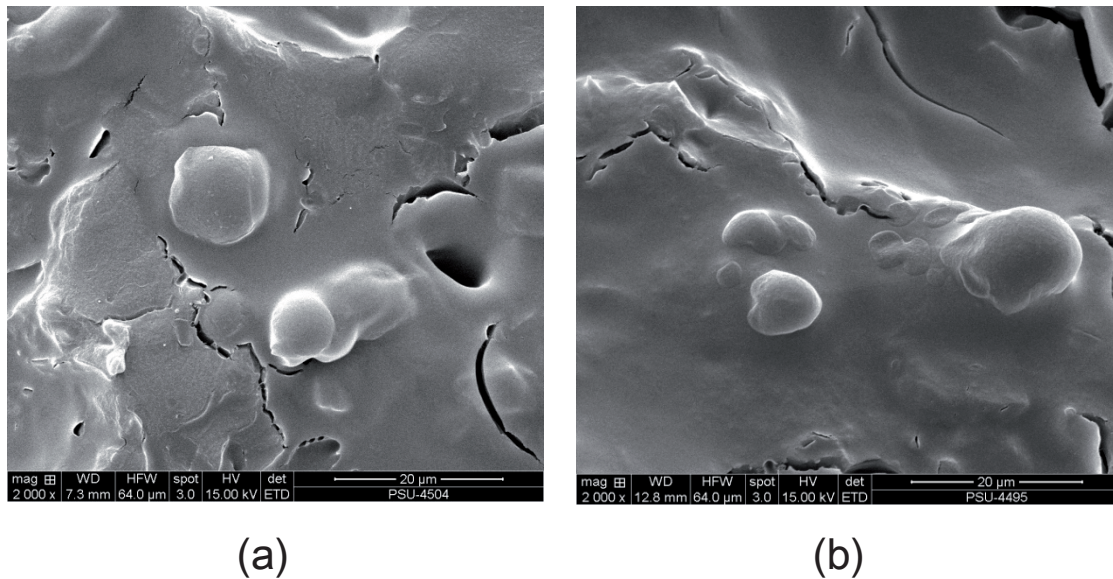


Figure 4 SEM micrographs of the PLA/starch/NR blends : (a) containing 0.5 pph of MA and (b) containing 0.5 pph of PPS

compatibilization effect may occur in the PLA/starch pair more than in the other pairs.

The dynamic mechanical thermal analysis (DMTA) was employed to determine the α -relaxation temperature or the glass transition temperature (T_g) of the blends. The control sample had a maximum $\tan \delta$ at 77.07°C (Figure 3). The addition of 0.5 pph of MA and 0.5 pph of PPS decreased this relaxation temperature, i.e., to 76.18°C

and 75.15°C, respectively. It is known that MA and PPS have been used to prepare the reactive blends and graft copolymers. For this reason, it was expected that MA and PPS increased the interfacial adhesion between the PLA and the dispersed phases and this was confirmed by the DMTA result and the SEM micrographs. A shift to a lower temperature of T_g reflected the good adhesion between the PLA and the NR.

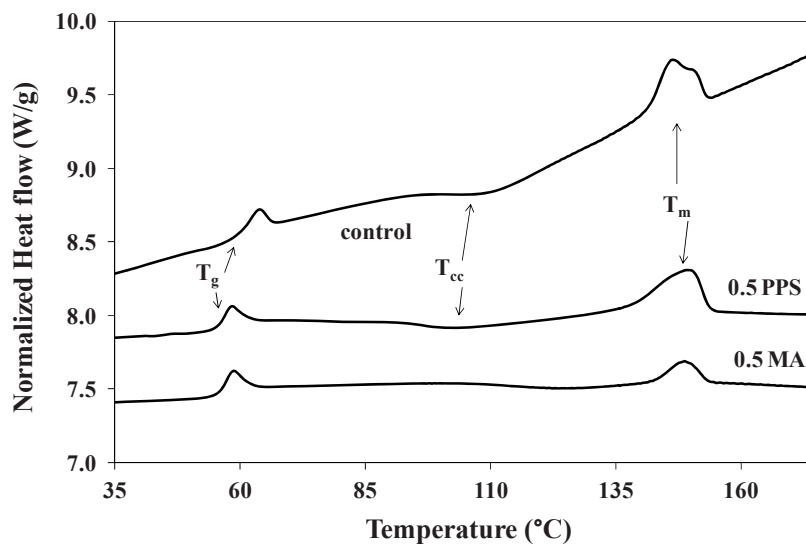


Figure 5 DSC thermograms of the PLA/starch/NR blends with and without reactive additive.

Table 6 Thermal properties of PLA in the PLA/starch/NR blends obtained from DSC

Sample	T _g (°C)	T _{cc} (°C)	T _m (°C)	X _c (%)
Control	59.9	111.2	146.2	2.01
0.5MA	56.0	123.7	148.8	2.40
0.5PPS	55.8	102.7	149.1	13.2

The SEM micrographs of the blend containing MA and PPS are provided in Figure 4a and 4b, respectively. The starch granules in Figure 4a and 4b showed a stronger adhesion with the PLA matrix than those appeared in Figure 1 because a sharper boundary was observed between the starch granules and the PLA matrix in

Figure 1. Unfortunately, it was difficult to observe the NR particles without etching. The evidence of an interfacial adhesion between the PLA and NR may have been destroyed by the etching-solvent. Thus, it was not possible to identify the improvement of the interfacial adhesion of PLA/NR from the SEM micrographs.

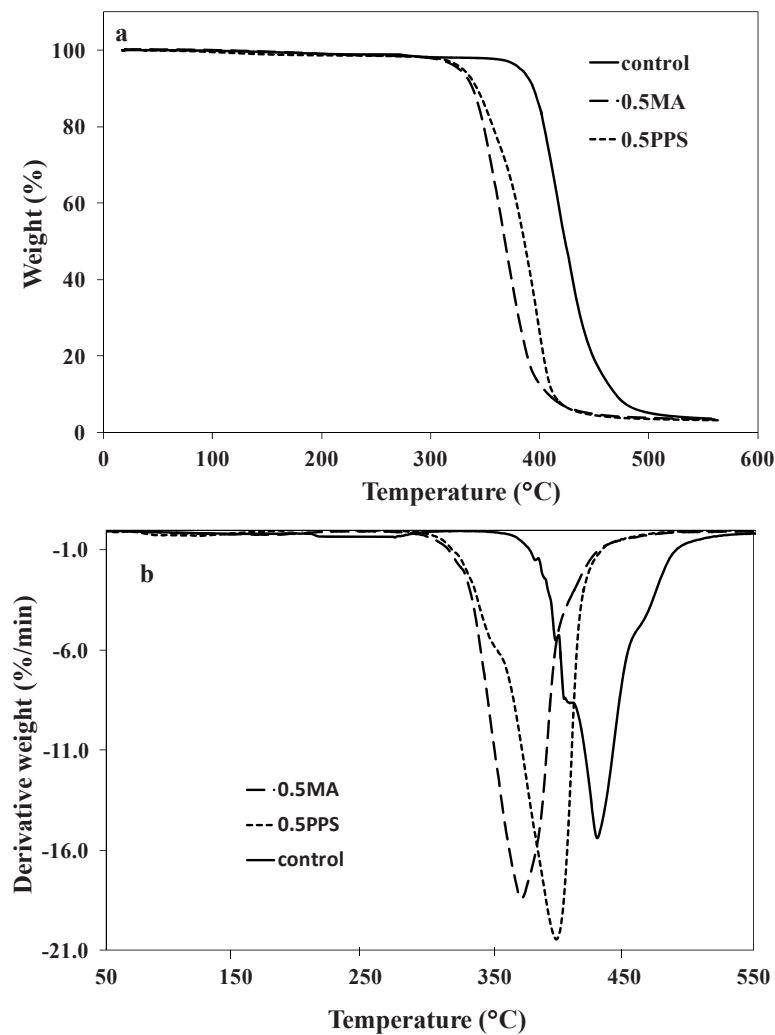


Figure 6 TGA thermograms (a) and DTG thermograms (b) of the PLA/starch/NR blends with and without reactive additive.

Table 7 Thermal degradation temperature and weight loss of the PLA/starch/NR blends obtained from TGA

Sample	Stage 1		Stage 2		Stage 3	
	Onset T (°C)	Lost Weight (%)	Onset T (°C)	Lost Weight (%)	Onset T (°C)	Lost Weight (%)
Control	101	1.1	391	80.3	453	14.2
0.5MA	139	1.5	337	95.1	-	-
0.5PPS	113	1.5	360	95.3	-	-

The effect of MA and PPS on the thermal properties of the blend is exhibited in Figure 5 and their transition temperatures are listed in Table 6. A melting peak was observed in all blends. In theory, the data obtained from the first heating scan depends on the thermal history of each sample and is related to the physical and mechanical properties of the sample. A second heating scan is required when the same thermal history is needed. In the present study, only the first heating scan was used. The T_g of the blend decreased when either MA or PPS was added. In a similar way to the results of the DMTA, this may indicate a higher compatibility between the PLA and the NR in the 0.5MA and the 0.5PPS samples. All samples had a cold crystallization temperature (T_{cc}). MA increased the T_{cc} of PLA while PPS decreased this transition. The rigid structure of MA may obstruct the cold crystallization of the PLA chains and produced a higher T_{cc} . The melting temperature was higher in the blends containing MA or PPS. PPS played a role in the crystallization of PLA while MA did not have any observed effect on this property. The higher degree of crystallinity in the blend containing 0.5 pph of PPS may be involved with ease of the cold crystallization that provided more crystallinity during the heating scan.

The thermal stability of the blends was evaluated from the TGA and DTG curves (Figure 6). Typically, a derivative curve in Figure 6b is derived from the TGA curve. It represents the rate of change in weight loss in terms of %/min. The thermal degradation temperatures of the blends are tabulated in Table 7. The control sample showed 3 stages of thermal degradation but the 0.5MA

blend and the 0.5PPS blend exhibited 2 stages. The first degradation stage of all blends was above 100°C when a small weight loss occurred, e.g., 1-2%. The second and the third stages of thermal degradation in the control sample began at 391°C and 453°C, respectively, whereas the maximum degradation rate appeared at 430°C. Although the 0.5MA blend and the 0.5PPS blend showed a higher thermal stability than the control sample in the first stage, their thermal stability in the second stage was lower. The main thermal degradation occurred in the second stage because the maximum weight loss appeared during this stage. The maximum rate of loss of the 0.5MA blend and the 0.5PPS blend was at 368°C and 400°C, respectively, and both were lower than the control sample. The reduction of thermal stability due to MA or PPS may result from the chain scission of PLA.

Conclusions

A poly(lactic acid) – polymer blend was formed by blending poly (lactic acid) with cassava starch and natural rubber latex. Two reactive additives: maleic anhydride and potassium persulfate were used as compatibilizers in order to increase the toughness of the poly (lactic acid) compound, poly(lactic acid)/starch/natural rubber blend. The toughness of the blends was evaluated in terms of their impact strength and tensile toughness (an area under a stress-strain curve). The blend of 0.5 pph of maleic anhydride was found to be the most appropriate for increasing the toughness, and the addition of 25% of Luperox[®] 101 in the maleic anhydride further enhanced the toughness of the blend. Potassium persulfate produced

a higher toughness and tensile properties than maleic anhydride. The optimal formula was 0.5 pph of potassium persulfate without benzoyl peroxide. The increase in the interfacial adhesion between the dispersed phases and the poly (lactic acid) matrix due to the maleic anhydride and potassium persulfate was evident by a reduction in the glass transition temperature of PLA determined from the dynamic mechanical thermal analysis and the differential scanning calorimetry and by the morphology observed from scanning electron micrographs. The drawback of the maleic anhydride and potassium persulfate was that they both decreased the thermal stability of the blends.

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References

- Cai, J., Liu, M. & Wang, L. (2011). Isothermal crystallization kinetics of thermoplastic starch/poly(lactic-acid) composites. *Carbohydrate Polymers*, *86*, 941-947.
- Chen, L., Qiu, K., Xie, Z., Hong, Z., Sun, J., Chen, X. & Jing, X. (2006). Poly(l-lactide)/starch blends compatibilized with poly(l-lactide)-g-starch copolymer. *Carbohydrate Polymers*, *65*, 75-80.
- Huneault, M.A. & Li, H. (2007). Morphology and properties of compatibilized polylactide/thermoplastic starch blend. *Polymer*, *48*, 270-280.
- Jaratrotkamjorn, R., Khaokong, C. & Tanrattanakul, V. (2012). Toughness enhancement of poly(lactic acid) by melt blending with natural rubber. *Journal of Applied Polymer Science*, *124*, 5027-5036.
- Kaewtatip, K. & Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers*, *73*, 647-655.
- Ke, T. & Sun, X. (2003a). Melting behavior and crystallization kinetics of starch and poly(lactic acid) composites. *Journal of Applied Polymer Science*, *89*, 1203-1210.
- Ke, T. & Sun, S.X. (2003b). Starch, poly(lactic acid), and poly(vinyl alcohol) blends. *Journal of Polymers and the Environment*, *11*, 7-14.
- Ke, T., Sun, S.X. & Seib, P. (2003). Blending of poly (lactic acid) and starches containing varying amylose content. *Journal of Applied Polymer Science*, *89*, 3639-3646.
- Leadprathom, J. & Suttiruengwong, S. (2010). Compatibilized polylactide/thermoplastic starch by reactive blend. *Journal of Metals Materials and Minerals*, *20*, 87-90.
- Liao, H.T. & Wu, C.S. (2009). Preparation and characterization of ternary blends composed of polylactide, poly(caprolactone) and starch. *Materials Science and Engineering*, *515*, 207-214.
- Lu, D.R., Xiao, C.M. & Xu, S.J. (2009). Starch-based completely biodegradable polymer materials. *Express Polymer Letters*, *3*, 366-375.
- Mihai, M., Huneault, M.A., Favis, B.D. & Li, H. (2007). Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends. *Macromolecular Bioscience*, *7*, 907-920.
- Orozco, V.H., Brostow, W., Chonkaek, W. & Lopez, B.L. (2009). Preparation and characterization of poly (lactic acid)-g-maleic anhydride and starch blends. *Macromolecular Symposia*, *277*, 69-80.
- Park, J.W., Lee, D.J., Yoo, E.S. & Im, S.S. (1999). Biodegradable polymer blends of poly (lactic acid) and starch. *Journal of Korea Polymer*, *7*, 93-101.
- Qudsieh, I.Y.M., Fakhru'l-Razi, A., Muyibi, S.A., Ahmad, M.B., Rahman, M.Z.Ab. & Yunus, W.M.Z. (2004). Preparation and characterization of poly(methyl methacrylate) grafted sago starch using potassium persulfate as redox initiator. *Journal of Applied Polymer Science*, *94*, 1891-1897.

- Sarazin, P., Li, G., Orts, W.J. & Favis, B.D. (2008). Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer*, *49*, 599-609.
- Shi, Q., Chen, C., Gao, L., Jiao, L., Xu, H. & Guo, W. (2011). Physical and degradation properties of binary or ternary blend composed of poly(lactic acid), thermoplastic starch and GMA grafted POE. *Polymer Degradation and Stability*, *96*, 175-182.
- Shogrena, R.L., Doane, W.M., Garlotta, D., Lawton, J.W. & Willetta, J.L. (2003). Biodegradation of starch/poly(lactic acid)/poly(hydroxyester-ether) composite bars in soil. *Polymer Degradation and Stability*, *79*, 405-411.
- Suttirungwong, S. & Tongpin, C. (2010). Functionalization of poly(lactic acid) with maleic anhydride for biomedical application. *Journal of Metals Materials and Minerals*, *20*, 189-192.
- Tanrattanakul, V. & Panwiriyarat, W. (2009). Compatibilization of low-density polyethylene/ cassava starch blends by potassium persulfate and benzoyl peroxide. *Journal of Applied Polymer Science*, *114*, 742-753.
- Tanrattanakul, V. & Chumeka, W. (2010). Effect of potassium persulfate on graft copolymerization and mechanical properties of cassava starch/natural rubber foams. *Journal of Applied Polymer Science*, *116*, 93-105.
- Tanrattanakul, V., Bunkaew, P. & Boonlong, N. (2012). Influence of rubber mastication on mechanical properties of poly(lactic acid)-based thermoplastic natural rubber. *Journal of Biobased Materials and Bioenergy*, *6*, 1-7.
- Wang, H., Sun, X. & Seib, P. (2002). Effects of starch moisture on properties of wheat starch/poly(lactic acid) blend containing methylenediphenyl diisocyanate. *Journal of Polymers and the Environment*, *10*, 133-138.
- Wang, H., Sun, X. & Seib, P. (2003). Properties of poly(lactic acid) blends with various starches as affected by physical aging. *Journal of Applied Polymer Science*, *90*, 3683-3689.
- Wang, N., Yu, J., Chang, P.R. & Ma, X. (2008). Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers*, *71*, 109-118.
- Wootthikanokkhan, J., Kasemwananimit, P., Sombatsompop, N., Kositchaiyong, A., Isarankurana Ayutthaya, S. & Kaabuuathong, N. (2012). Preparation of modified starch-grafted poly(lactic acid) and a study on compatibilizing efficacy of the copolymers in Poly(lactic acid)/ thermoplastic starch blends. *Journal of Applied Polymer Science*, *126*, 388-395.
- Yokesahachart, C. & Yoksan, R. (2011). Effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with poly(lactic acid). *Carbohydrate Polymers*, *83*, 22-31.
- Zhang, J.F. & Sun, X. (2004a). Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. *Biomacromolecules*, *5*, 1446-1451.
- Zhang, J.F. & Sun, X. (2004b). Physical characterization of coupled poly(lactic acid)/starch/maleic anhydride blends plasticized by acetyl triethyl citrate. *Biomacromolecules*, *4*, 1053-1060.
- Zhang, J.F. & Sun, X. (2004c). Mechanical and thermal properties of poly(lactic acid)/starch blends with dioctyl maleate. *Journal of Applied Polymer Science*, *94*, 1697-1704.