

EFFECT OF POLY(D-LACTIC ACID) ON PHYSICAL PROPERTIES OF POLY(LACTIC ACID)/NATURAL RUBBER BLENDS

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Abstract

In this study, poly(lactic acid) (PLA) was melt blended with a natural rubber (NR) at the ratios of 95/5, 90/10, 85/15, and 80/20 by weight. It was found that the impact strength and elongation at break of PLA/NR blends increased with increasing NR content up to 5 wt%. While tensile strength and Young's modulus decreased. The most significant improvement in Izod impact strength and elongation at break was found for the blend containing 15 wt% NR. Therefore, PLA/NR at a ratio of 85/15 wt% was chosen to study the effect of poly (D-lactic acid) (PDLA) on mechanical properties and heat distortion temperatures (HDT) of PLA/NR blend. The amount of PDLA applied was 1, 3, and 5 percent by weight based on PLA content in the blend. The results showed that impact strength and elongation at break of PLA/NR blend decreased with increasing amount of PDLA. However, the values were still higher than those of pure PLA. HDT of the blend with 1 wt% PDLA based on PLA content was improved in comparison to that of PLA/NR blend and pure PLA.

Keywords: Poly(lactic acid), Poly(D-lactic acid), natural rubber, HDT

Introduction

Poly(lactic acid) (PLA) is a biodegradable polymer derived from renewable resources. PLA provides good strength and easy processability with perfect degradable in most products. However, PLA suffers from low heat

distortion temperature (HDT), because its T_g is only 54-60°C and low toughness. Hence, PLA is not suitable for some applications, for example, microwavable trays and hot-fill applications. To achieve high toughness PLA,

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natural rubber (NR) has been one of desirable impact modifiers for PLA (Bitinis *et al.*, 2011; Bitinis *et al.*, 2012; Juntuek *et al.*, 2011; Pongtanayut *et al.*, 2013). The rubber particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately result in a material with improved toughness (Pongtanayut *et al.*, 2013). NR exhibits a unique combination of toughness, flexibility and biodegradability that together with its low cost makes it an ideal candidate to improve the brittleness of PLA. HDT of a polymeric material is an index of its heat resistance towards applied load. There are several ways to improve HDT of PLA such as blending with a high thermal stability polymer, addition of high thermal stability filler. Moreover, the easy way to increase the HDT value of polymer is to increase the crystallinity of PLA. Interestingly, in the 1980s, it was found that an equivalent mixture of poly (L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) formed a stereocomplex. The stereocomplex has a melting temperature, T_m , of 230°C that was approximately 50°C higher than the T_m of either PLLA or PDLA (Ikada *et al.*, 1987). This significant increase in melting temperature was due to the strong van der Waals interactions in the stereocomplex crystalline structure (Brizzolara *et al.*, 1996). Tsuji *et al.* investigated the isothermal and non-isothermal crystallization behavior of PLLA blend with a small amount of PDLA (0.1–10 wt%). The higher PDLA content was in PLLA matrix, the faster crystallization rate was gained, which revealed that PDLA was an effective nucleating agent for PLLA. The stereocomplex crystallites were consistent

with the increased content of the PDLA (Tsuji *et al.*, 2006). Therefore, in the present work, PLA was blended with NR first in order to obtain high toughness PLA. High toughness and high HDT blend was expected to achieve after the addition of PDLA.

Materials and Methods

Materials

Poly(lactic acid) (PLA, 4043D) was supplied from Nature works LLC. Poly (D-lactic acid) (PDLA) was provided by Department of Chemistry, Chiang Mai University. Natural rubber (STR 5L) was purchased from Thai Hua Rubber Co., Ltd.

Preparation of Blends

PLA blends were prepared using an internal mixer (Hakke Rheomix) at the temperature of 170°C with a rotor speed of 60 rpm for 10 min. Before mixing, PLA and PDLA were dried in an oven at 70°C for 4 h. The compositions in percentage by weight (wt%) of all blends are shown in Table 1. After mixing in an internal mixer, the blend specimens were prepared by compression molding machine (LabTech, LP20-B) at melting temperature of 170°C.

Mechanical and HDT Analysis

The unnotched and notched Izod impact test were performed according to ASTM D256 using an impact testing machine (Instron). Tensile properties were obtained according to ASTM D638 using an Instron universal testing machine with a load cell of 5 kN and a crosshead speed of 10 mm/min.

Table 1. Blend compositions

Code	PLA (wt%)	NR (wt%)	PDLA (wt%)
PLA	100	-	-
PLA/NR (95/5)	95	5	-
PLA/NR (90/10)	90	10	-
PLA/NR (85/15)	85	15	-
PLA/NR (80/20)	80	20	-
PLA/NR/PDLA (1)	84.15	15	0.85 (1) ^a
PLA/NR/PDLA (3)	82.45	15	2.55 (3) ^a
PLA/NR/PDLA (5)	80.75	15	4.25 (5) ^a

^a wt% of PDLA based on the amount of PLA in the blends.

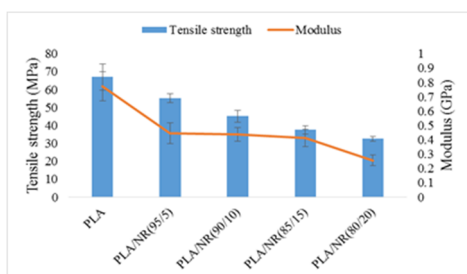


Figure 1. Tensile strength and Young's modulus of PLA, PLA/NR blends at various NR contents

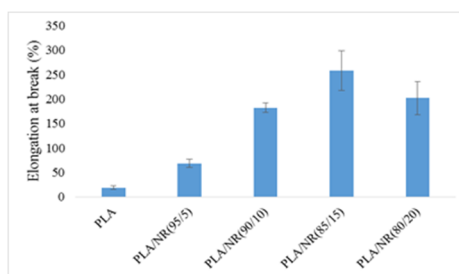


Figure 2. Elongation at break of PLA, PLA/NR blends at various NR contents

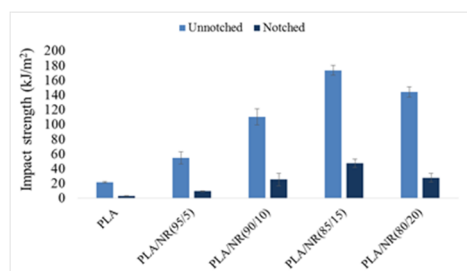


Figure 3. Izod impact strength of PLA, PLA/NR blends at various NR contents

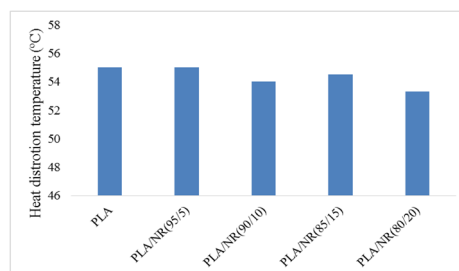


Figure 4. Heat distortion temperatures of PLA, PLA/NR blends at various NR contents

The heat distortion temperature of PLA, and PLA/NR, PLA/NR/PDLA blends was measured using a HDT/VICAT manual heat deflection tester (model HDV1). The dimension of the test bars was 127 mm × 13 mm × 3 mm and the test procedure was conformed to the ASTM D648 standard. The loading pressure was 0.455 MPa (66 psi) and samples were heated at a rate of 2°C/min from room temperature.

Results and Discussion

Effect of NR Content on Mechanical Properties and HDT of PLA

Figure 1 shows the tensile strength and Young's modulus of PLA, PLA/NR blends at various NR contents. Modulus and tensile strength of PLA/NR decreased with increasing NR content. The reduction in these mechanical properties was due to the result of the rubbery nature of NR. Also, the reduced PLA phase in

the blend and the poor interfacial adhesion between PLA and NR may be the reasons for a decrease in tensile strength and Young's modulus (Xu *et al.*, 2014). Elongation at break of PLA and PLA/NR blends is shown in Figure 2. Elongation at break was increased from 18.54% for neat PLA to 257.85% for PLA/NR (85/15).

Figure 3 shows the unnotched and notched Izod impact strength of PLA, PLA/NR blends at various NR contents. Notched condition was designed to reduce the toughness of materials. In the other words, the notched condition gives much lower absorbed energy to the samples (Tjong *et al.*, 1996). Hence, Notch specimen is better measure the resistance of the polymer to crack propagation and we can determine how resistant the specimen absorbs energy when given some defects on it. The unnotched and notched Izod impact strength of neat PLA were 20.70 and 2.91 kJ/m², respectively. Impact strength of PLA/NR blends increased with increasing NR content up to 15 wt%. When

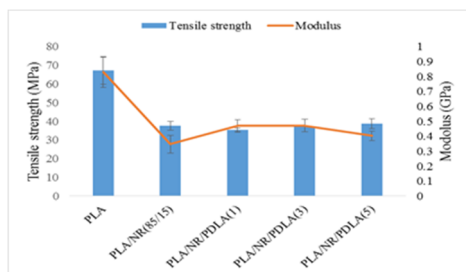


Figure 5. Tensile strength and Young's modulus of PLA, PLA/NR(85/15) and PLA/NR/PDLA blends

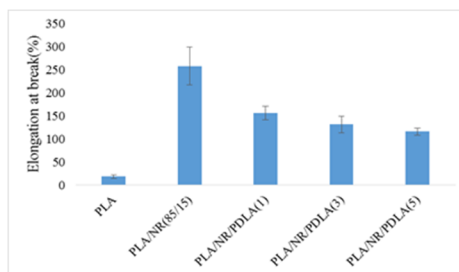


Figure 6. Elongation at break of PLA, PLA/NR (85/15) and PLA/NR/PDLA blends

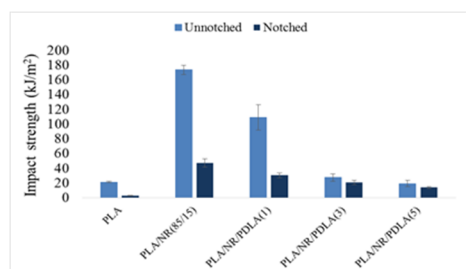


Figure 7. Izod impact strength of PLA, PLA/NR(85/15) and PLA/NR/PDLA blends

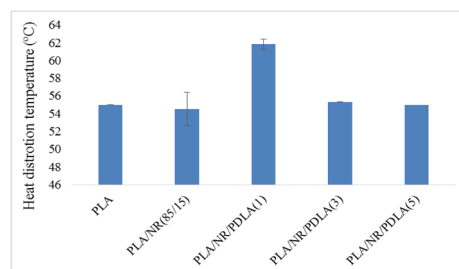


Figure 8. HDT of PLA, PLA/NR (85/15) and PLA/NR/PDLA blends

NR content was 15 wt%, unnotched and notched izod impact strength of the PLA/NR blend were 167.22 and 54.31 kJ/m², respectively. When NR content was increased to 20 wt%, unnotched and notched Izod impact strength of PLA/NR blend were decreased to 139.09 and 28.05 kJ/m², respectively. However, this value was still higher than that of neat PLA. The high flexibility of NR resulted in more energy absorption.

Figure 4 shows the values of heat distortion temperatures for the PLA and PLA/NR blends. Generally, the heat distortion temperature decreased as NR content increased. The decrease of HDT of PLA/NR blend could be resulted from soft NR phase. Furthermore, the incorporation of NR into the PLA decreased stiffness of specimens.

Effect of PDLA Content on Mechanical Properties and HDT of PLA/NR Blend

To study the effect of PDLA content on

mechanical properties of PLA/NR blends, NR content was fixed at 15 wt% according to the highest impact strength of PLA/NR (85/15) blend. The total amount of PLA and PDLA in the blend was kept constant at 85 wt% and the PDLA content in the blends was designed to be 1, 3, and 5 wt% based on the amount of PLA. Therefore, the ratios of PLA to PDLA were 84.15/0.85, 82.45/2.55, and 80.75/4.25 wt% as shown in Table 1.

Figure 5 shows the tensile strength and Young's modulus of PLA, PLA/NR and PLA/NR/PDLA blends at various PDLA contents. Modulus and tensile strength of PLA/NR/PDLA increased with increasing PDLA content. This indicated that PDLA could enhance stiffness of PLA/NR blends (Tsuiji and Ikada, 1999; Sarasua *et al.*, 2005).

Elongation at break of PLA, PLA/NR and PLA/NR/PDLA blends is shown in Figure 6. Elongation at break was decreased with an increase in PDLA content. The lowest

Table 2. Tensile strength, modulus, and elongation at break of PLA, PLA/NR and PLA/NR/PDLA blends

Sample	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
PLA	67.11 ± 7.23	0.83 ± 0.10	18.54 ± 3.66
PLA/NR(95/5)	55.15 ± 2.42	0.52 ± 0.07	68.54 ± 8.64
PLA/NR(90/10)	45.15 ± 3.43	0.44 ± 0.04	182.35 ± 9.67
PLA/NR(85/15)	37.63 ± 2.30	0.35 ± 0.06	257.85 ± 40.83
PLA/NR(80/20)	32.65 ± 1.29	0.31 ± 0.04	201.99 ± 33.66
PLA/NR/PDLA(1)	35.30 ± 2.30	0.47 ± 0.03	156.14 ± 14.83
PLA/NR/PDLA(3)	37.44 ± 0.21	0.47 ± 0.04	131.43 ± 17.79
PLA/NR/PDLA(5)	38.87 ± 2.66	0.40 ± 0.03	115.81 ± 8.18

Table 3. Izod impact strength and HDT of PLA, PLA/NR and PLA/NR/PDLA blends

Sample	Izod impact strength (J/m ²)		HDT (°C)
	Unnotched	Notched	
PLA	21.16 ± 0.94	2.85 ± 0.15	55.0
PLA/NR(95/5)	56.19 ± 13.98	9.12 ± 0.83	55.0
PLA/NR(90/10)	110.16 ± 11.15	25.22 ± 8.65	54.0
PLA/NR(85/15)	173.34 ± 6.49	46.95 ± 5.65	54.5
PLA/NR(80/20)	143.94 ± 6.87	27.44 ± 5.99	53.3
PLA/NR/PDLA(1)	108.68 ± 17.22	30.20 ± 3.59	61.8
PLA/NR/PDLA(2)	27.38 ± 5.07	20.71 ± 2.18	55.3
PLA/NR/PDLA(3)	19.18 ± 4.21	13.71 ± 1.38	55.0

elongation at break of 115.81 ± 8.18 % was found for PLA/NR/PDLA(5). However, it was significantly higher than that of pure PLA.

Figure 7 shows the unnotched and notched Izod impact strength of the PLA, PLA/NR and PLA/NR/PDLA blends. The unnotched and notched Izod impact strength were 20.70 and 2.91 kJ/m² for neat PLA and 173.34 and 46.95 kJ/m² for PLA/NR (85/15), respectively. When PDLA was added into PLA/NR blend, unnotched and notched Izod impact strength of PLA/NR/PDLA were decreased. The reduction of impact strength and elongation at break indicated that PLA/NR/PDLA blend was more rigid but less toughness than PLA/NR (85/15).

HDTs for the PLA, PLA/NR and PLA/NR/PDLA blends are shown in Figure 8. The HDT of PLA/NR blend containing 1 wt% PDLA based on the amount of PLA was higher than that of neat PLA. It might be because of high crystallinity and small spherulite size of PLA/NR/PDLA(1) (Tang *et al.*, 2012).

The summaries of tensile strength, modulus, and elongation at break of PLA and

all blends are shown in Table 2. Table 3 shows Izod impact strength and HDT of PLA and all blends.

Conclusions

Impact strength of PLA was found to be dramatically improved with the addition of 15 wt% NR. At this content, unnotched and notched Izod impact strength were higher than those of pure PLA about 7 and 10 times, respectively. However, tensile strength and Young's modulus of the blends decreased with increasing NR content. When 1 wt% PDLA based on PLA content was incorporated into PLA/NR blend, HDT of PLA/NR blend was significantly improved. On the other hand, the impact strength and elongation at break of PLA/NR blend decreased with an increase of PDLA content. Nevertheless, with an exception of unnotched Izod impact strength, the values were still higher than those of neat PLA. Hence, the addition of PDLA at 1 wt% based

on PLA content into PLA/NR blend led to the blend with higher impact strength and HDT compared to neat PLA.

Acknowledgements

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