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Impact strength enhanced bioplastic polylactic acid by interfacial bonding with hydroxylated natural rubber

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Abstract. The effect of functionality of HNR and weight composition of PLA:HNR on the mechanical properties, impact strength, water vapour and oxygen gas transmission rates was studied. From morphology result, co-continuous phases in PLA:HNR050 and PLA:HNR035 were more obvious than PLA:HNR025. The observed co-continuous phases might be caused by the interfacial bonding between PLA phase and HNR phase. Better compatibility between HNR035 and PLA was believed to result in the considerably improvement of impact strength and slight reduction of mechanical properties of PLA. It is interesting that water vapour and oxygen gas transmission rates of PLA significantly increased with HNR035 loading. As a result, the appropriate weight composition of HNR035 blended with PLA was clarified to be 70:30 that was about tippie higher than the composition of NR as reported in the previous studies.

1. Introduction

Toughness properties of PLA could be developed by blending with epoxidized natural rubber (ENR) compared to NR[1]. The rubber phase of NR was clarified to disperse in the continuous PLA matrix with small droplet. Increasing of NR content, the large droplet size of rubber and the partially compatible between PLA and ENR were observed. The amount of NR at 10 %w was claimed to give optimum property. Wahit M U et al [2] prepared PLA/ENR-50 blends by melt extrusion followed by injection molding to fabricate the test samples. The toughness of the blend was improved with ENR-50 loading up to 20 %w but flexural and tensile strength decreased. SEM showed good distribution and increased ENR particle size as ENR content increased from 10 to 30 %w. Water absorption was observed to increase with ENR loadings. Recently, the synthesized NR-graft-PLA (NR-PLA) via esterification of maleated NR (NR-MAH) with PLA was used as a compatibilizer in the PLA/NR blends[3]. The addition of 5 %w NR-PLA [36.6 %w grafted PLA content] into PLA/NR blend [80/20 (w/w)] was found to increase Izod impact strength of PLA from 28.9 J/m to 62.7 J/m due to partial miscibility of blends.

This research aims to investigate the effect of the functionality of hydroxylated natural rubber (HNR) and the blend ratio on the compatibility and mechanical properties including impact strength of PLA. The water vapor and oxygen transmission rates of the PLA:HNR blends were also investigated.



2. Experimental

2.1. Materials

Polylactic acid (Grade 4043D, NatureWorks®). Natural rubber (low ammonia (LA) 60% DRC purchased from Num Rubber & Latex Co., Ltd., Thailand). Hydrogen peroxide (Analytical Grade 35% purchased from T.S.Interlab, Thailand). Formic acid (Analytical Grade 85% from Fisher Chemical, UK). Triton-x 100 (Fisher Chemical, UK). Liquid nitrogen purchased from Linde Co., Ltd., Thailand.

2.2. Preparation hydroxylated natural rubber

NR latex 500 g was added with titron-x100 50 mL followed by addition of the mixture of hydrogen peroxide (H₂O₂) and 85% w/w formic acid (CH₂O₂) using the mole ratio of rubber : hydrogen peroxide : formic acid = 1 : 0.25 : 0.25 for HNR025, 1 : 0.35 : 0.35 for HNR035 and 1 : 0.50 : 0.50 for HNR050. The reaction was carried out for 2 hours at 70°C, subsequently, the obtained HNRs were washed with distilled water until the pH of washed water became 7 and then dried at the temperature of 50-55°C.

2.3. Mixing PLA with HNR

Various compositions of PLA:HNR blends from 90:10, 80:20 to 70:30 were prepared by melt blending using the internal mixer at 190°C with a rotor speed of 40 rpm for 10 minutes. Subsequently, they were compression molded into sheets for further property testing under the condition with temperature 200°C, pressure 150 kg/cm² for 10 minutes.

2.4. Morphology study

Morphology of the blends was investigated using Scanning Electron Microscope (SEM) (JEOL, JSM-6610LV). Fresh surfaces were created by immersing the samples in liquid nitrogen and then the fractured samples obtained were coated with gold by sputter coater (Cressington, 108 Auto).

2.5 Mechanical property testing

The impact strength of PLA and their blends were tested by notched Izod impact tester according to ASTM D256. The tensile strength, elongation at break and modulus of them were also tested by universal testing machine (model LR 50K, LLOYD International) with a load cell of 50 kN and crosshead speed of 5 mm/minute according to ASTM D638.

2.6 Glass transition temperature determination

Glass transition temperatures were determined using Mettler-Toledo Differential Scanning Calorimeter (DSC) (Perkin Elmer Pyris-7). Heating was run from -100 °C to 300 °C with the rate of 10°C/minute.

3. Results and Discussion

The FTIR spectra clarified the presence of the -OH in the range of 3388-3409 cm⁻¹ and the C=O of the ester groups in the range of 1732-1735 cm⁻¹ for HNR whereas these peaks were not found to present on the NR molecules[4]. The functionality of HNR were confirmed by the glass transition temperatures as summarized in table 1 that increased with the number of the functional groups.

Table 1. Glass transition temperatures of HNR and NR.

Rubber type	T _g (°C)
HNR050	-46.22
HNR035	-57.98
HNR025	-59.24
NR	-63.94

Figure 1 shows clear droplets of HNR025 phase that distributed in the PLA matrix (c) whereas co-continuous phases in the molded PLA:HNR050 (a) and PLA:HNR035 (b) were obvious. However, the increasing HNR035 composition ratio was found not to change the morphology of the PLA:HNR035 blends as shown in figure 2. The co-continuous phases observed might be resulted from the interfacial bonding between PLA phase and HNR phase.

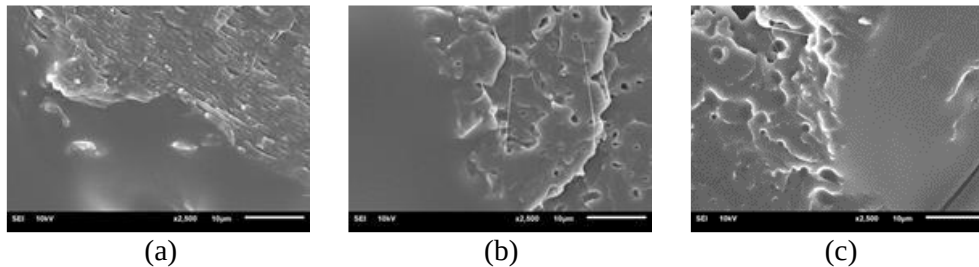


Figure 1. SEM images of PLA:HNR050 (a), PLA:HNR035(b) and PLA:HNR025(c) with the composition ratio of 90:10

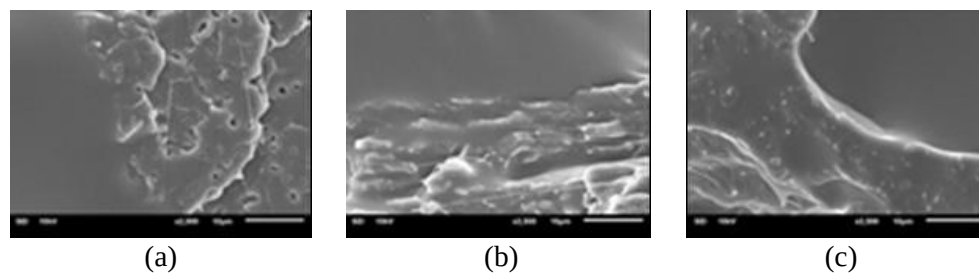


Figure 2. SEM images of PLA:HNR035 = 90:10 (a), 80:20 (b) and 70:30 (c)

The mechanical and impact strength properties of PLA/HNR compared to PLA were studied. Figure 3 shows that PLA:HNR035 gave the highest tensile strength (34.26 MPa), elongation at break (11.56%) and modulus (313.63 MPa) compared to those of PLA:HNR050 and PLA:HNR025. The appropriate ratio of PLA:HNR035 was found being 70:30 w/w that gave the highest tensile strength of 36.18 MPa, and the elongation at break of 23.47% as shown in the figure 4. On the other hand, it was significant that the impact strength of PLA was drastically improved by HNR035 loading as shown in figure 5. However, the impact strength of PLA:HNR035 was found to slightly decrease with HNR035 loading but still remain higher than that of PLA as shown in figure 6.

Water vapor and oxygen transmission rates of PLA:HNR035 and neat PLA films as summarized in table 2 were measured using the Modulated Infrared Sensor at the condition regarding to ASTM F1249-06 and ASTM D 3985-05, respectively. It was remarkable that water vapor and oxygen gas transmission rates of both PLA:HNR035= 70:30 and PLA:HNR035= 60:40 significantly higher than those of neat PLA. As a result, HNR035 considerably enhanced the gas barrier property of PLA due to well incorporation of HNR in the PLA matrix.

Table 2. Water vapor and oxygen gas transmission rates

Samples	Water vapor transmission rate* (g/m ² /day)	Oxygen gas transmission rate** (cm ³ /m ² /day)
PLA:HNR035 60:40	13	130
PLA:HNR035 70:30	11	22
Neat PLA[5]	116	511

*38°C, relative moisture 90% **23°C, relative moisture 0%

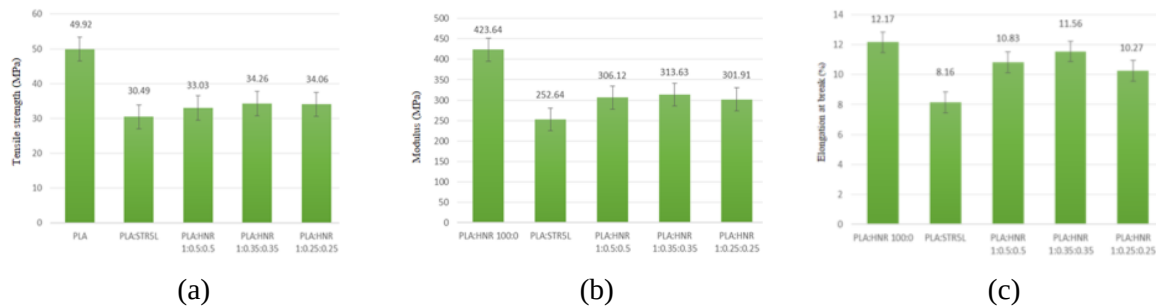


Figure 3. Mechanical properties of neat PLA and its blends with various types of HNR in the same composition of PLA:HNR=90:10.

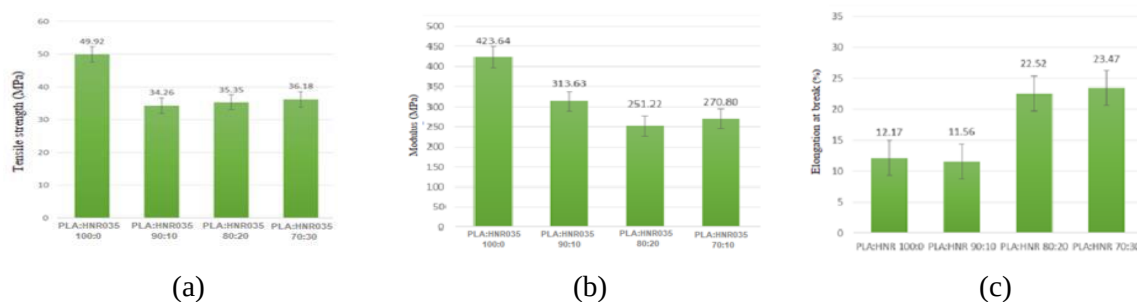


Figure 4. Mechanical properties of neat PLA and its blends with HNR035 at different compositions.

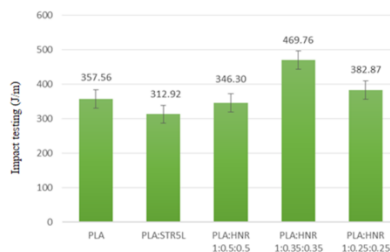


Figure 5. Impact strength of the PLA and its blends with various types of HNR.

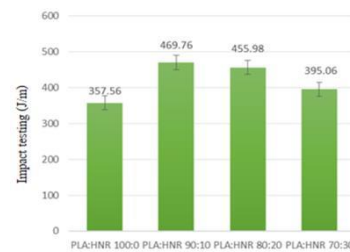


Figure 6. Impact strength of PLA and its blends with HNR035 at different compositions.

4. Conclusion

The observed co-continuous phases and the compatibility between PLA phase and HNR phase might be caused by the interfacial bonding. The remarkable improvement of impact strength and slight reduction of mechanical properties of PLA were obvious. HNR035 enhanced the highest impact strength of PLA with the appropriate blend ratio of PLA:HNR035 =70:30. Furthermore, HNR035 was also found to significantly improve the gas barrier property of PLA.

5. References

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