Mechanical properties, morphology, and hydrolytic degradation behavior of polylactic acid / natural rubber blends

Y F Buys¹, A N A Aznan¹, H Anuar¹
¹Department of Manufacturing and Materials Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia

Email: yose@iium.edu.my

Abstract. Due to its biodegradability and renewability, polylactic acid (PLA) has been receiving enormous attention as a potential candidate to replace petroleum based polymers. However, PLA has limitation due to its inherent brittleness. In order to overcome this limitation, blending PLA with elastomeric materials such as natural rubber (NR) are commonly reported. In previous, several researches on PLA/NR blend had been reported, with most of them evaluated the mechanical properties. On the other hand, study of degradation behavior is significance of importance, as controlling materials degradation is required in some applications. This research studied the effect of blend composition on mechanical properties, morphology development, and hydrolytic degradation behavior of PLA/NR blends. Various compositions of PLA/NR blends were prepared by melt blending technique. Tensile test and impact test of the blends were performed to evaluate the mechanical properties. Addition of NR improved the elongation at break and impact strength of the blends, but reduced the tensile strength and stiffness of the specimens. Dynamic Mechanical Analysis (DMA) measurements of the blends displayed two peaks at temperature -70°C which corresponded to $T_g$ of NR and 65°C which corresponded to $T_g$ of PLA. Field Emission Scanning Electron Microscopy (FE-SEM) micrograph of 70/30 PLA/NR specimen also showed two distinct phases, which lead to indication that PLA/NR blends are immiscible. Hydrolytic degradation behavior was evaluated by measuring the remaining weight of the samples immersed in sodium hydroxide solution for a predetermined times. It was shown that the degradation behavior of PLA/NR blends is affected by composition of the blends, with 100 PLA and 70/30 PLA/NR blend showed the fastest degradation rate and 100 NR displayed the slowest one.

1. Introduction
Nowadays, most of common type of plastic shopping bag uses polyethylene. It is made from petroleum-derived polymer and technically non-biodegradable products. Non-biodegradable materials do not break down easily. It took more than hundreds year to degrade and certain materials might not be destroyed over time. The harm caused by products that non-biodegradable will continue to pile up over time, demanding more and more land devoted to holding waste with increasing of demand on plastics production. Besides, it brings harmful effect toward the environment such as global warming and pollution. Therefore, it is very important to have a biodegradable plastic to replace the petroleum based plastics which caused the environmental issues.
Among the many types of disposable plastic packaging, Polylactic Acid (PLA) has been intensively attracting attention as it is one of the biodegradable thermoplastic polyester. It can be used to reduce the environmental impact on plastic production and waste since it is biodegradable. PLA is an ideal material for the food packaging and for other consumer products since it is biodegradable thermoplastic polyester which gives excellent physical and mechanical properties [1]. PLA is strong but it is very brittle [2]. In order to overcome these problems, blending PLA with flexible materials has been widely used.

Natural rubber (NR) is an elastic material and it has been considered as a good candidate to the blended with PLA to improve the brittleness of PLA. The addition of 10% of NR into PLA improves the ductility and its crystallization [3]. Several studies had been reported on PLA/NR blend specifically on physical and mechanical properties [3]. However, there are no studies that related to degradation behavior of PLA/NR blend.

It is very significance to aware with rate of degradation since difference application required dissimilarity rate of degradation. Degradation behavior of polymer blend is affected by composition miscibility and morphology of the blends. Therefore, this research attempts to address this issue.

2. Experimental procedures

2.1 Materials

In this experiment, PLA 3051 D from NatureWorks LLC was used. The density of the PLA is 1.24 g/cm$^3$ and its melt flow index is 10-25 g/10 min. Meanwhile the NR used was the Standard Malaysian Rubber (SMR-L) supplied by Rubber Research Institute of Malaysia (RRIM), with 0.93 g/cm$^3$ density.

2.2 Sample Preparation

Prior of being used, PLA was dried in an oven at 80°C for one hour to remove the moisture. Received NR was extruded through a two-roll mill (Kodaira) at room temperature for three min to obtain the standard thickness for mixing procedure. PLA was melt blended with NR in various blend composition (vol %) by using internal mixer (Brabender Plastograph) with 50 rpm rotating speed at temperature 190°C for 10 min. The mixtures were then crushed by a crusher machine before compression moulded by using XH-406B Tablet Press at temperature 190°C under 15 MPa for 5 min.

2.3 Tensile Test

In order to determine the tensile strength, Young’s modulus and elongation at break of the samples, tensile tests were conducted under ASTM D638 standard. The tests were performed by a Universal Tensile Machine LR 10K (Lloyd) with a 5 mm/min strain rate at room temperature. The values of tensile strength, Young’s modulus, and elongation at break were obtained by Nexxygen software support.

2.4 Impact Test

Impact tests were performed to determine the amount of energy absorbed by the material during fracture. The tests were carried out according to ASTM D256 standard by using Advance Pendulum Impact (Dynisco Polymer), with 7.5 J hammer. Samples dimension was 60 mm x 13 mm x 3 mm. Prior to the tests, a V-notch was used to notch the rectangular specimens.

2.5 Dynamic Mechanical Analysis (DMA) Measurement

DMA measurements were performed to study viscoelastic properties as well as determine the miscibility of PLA/NR blends. The measurements were carried out by a Pyris Diamond DMA (Perkin Elmer Instruments) with single cantilever using 3 point bending mode at 1 Hz frequency. The dimension of the samples were 40 mm x 13 mm x 3 mm. Liquid nitrogen were used to cool the samples and nitrogen gas were purged during the measurement to avoid oxidation. The DMA tests were performed from -100°C to 100°C, with 5°C/min heating rate.
2.6 Scanning Electron Microscopy (SEM) Observation

In order to study the morphology of PLA/NR blends, SEM observations were performed by using a Field Emission SEM (FE-SEM) Jeol JSM-670 at room temperature. Observations were conducted on liquid nitrogen fractured surface of the specimens. Before inserted to the observation chamber, the samples were coated with Au in order to impart conductivity.

2.7 Hydrolytic Degradation Test

Alkaline hydrolytic degradation tests were performed in order to determine the degradation behavior of PLA/NR blends. Specimens sized 10 mm x 10 mm x 1 mm were placed in 25 ml of NaOH aqueous solution with pH 13 for a predetermined time at room temperature. After hydrolysis, the samples were washed in distilled water and dried in open air at room temperature for a few hours. Subsequently, the samples were dried in oven with temperature 80˚C for 24 hours to remove remaining moisture and then the remaining weight of the samples were recorded.

3. Results and Discussion

3.1 Mechanical Properties

Figure 1 shows the Young’s modulus, tensile strength, as well as elongation at break of PLA/NR blends obtained from tensile tests. The error bars represent the standard deviation. From figure 1 (a) and (b), it can be observed that as NR content increased, the Young’s modulus and tensile strength of the blends decreased. Meanwhile, figure 1 (c) indicates that the elongation at break of the blends experienced slight increase when the NR content increase. These trends are understandable as the elastic and flexible nature of the NR reduce the stiffness of PLA. Similar trends had been also reported elsewhere [3-7]. However, only slight increase in the elongation at break also indicates that in current system, the interface between PLA and NR has not fully optimized. It is believed that existence of suitable compatibilizer may optimize the increase in elongation at break [7-9].

![Figure 1](image-url)

**Figure 1.** (a) Young’s modulus, (b) tensile strength, and (c) elongation at break of PLA/NR blends.
The impact strength data of PLA/NR blends is shown in Figure 2. The error bars represent the standard deviation. As NR content in the blends increased, increment trend in the impact strength was observed. The value of impact strength had dramatically increased from 4.14 kJ/m² of the neat PLA to 17.97 kJ/m² of 50/50 PLA/NR. From this figure, it is clear that the low toughness of PLA had been improved by NR blending. It is also interesting to note that 10% addition of NR showed higher value compared to 95/5 or 85/15 blends, which had also been highlighted by other research in previous [9]. Nevertheless, in general, it can be deduced that addition of NR into PLA results in increase in the impact strength, as also reported elsewhere [10].

![Figure 2. Impact strength of PLA/NR blends.](image)

### 3.2 Miscibility and Morphology

Figure 3 illustrates the tangent delta versus temperature of PLA, NR and PLA/NR blends obtained from DMA measurement. The peak represented glass transition temperature ($T_g$). From figure 3, it is observed that pure PLA has a $T_g$ around 65°C, and pure NR shows its $T_g$ around -70°C. Meanwhile for composition of 65/45 PLA/NR, 60/40 PLA/NR and 55/45 PLA/NR, two tangent delta peaks were observed at every curve, i.e. at temperature of -70°C and 65°C. Therefore, it can be concluded that PLA/NR blends are immiscible in conjunction with the presence of two peaks.

![Figure 3. Tangent delta of PLA, NR and PLA/NR blends](image)

Field Emission Scanning Electron Microscope (FE-SEM) was used to examine the fracture surface morphology between PLA/NR blends. Figure 4 represents the composition of 70/30 PLA/NR blends
with magnification of 2000 times. It was observed that the fracture surface of the blends shows the sea-island structure in composition of 70/30 PLA/NR. Since the composition of NR is 30%, it is considered that NR is the minority phase (island phase) meanwhile PLA is majority (sea phase) as its composition is 70%. Since two distinct phases are observed, this figure also re-emphasize the deduction that PLA/NR is immiscible.

![SEM image of 70/30 PLA/NR blend](image)

**Figure 4.** SEM images of 70/30 PLA/NR blend

3.3 *Degradation Behavior*

Figure 5 indicated the weight loss of the samples with the time consuming (days) for the samples to degrade. It took 35 days for PLA to completely degrade. Composition of 70/30 PLA/NR blends similar degradation behavior with that pure PLA. However, figure 5 of pure NR displayed that there was slight changed in the result. It showed that the rate of degradation at NR was very slow compared to the pure PLA and PLA/NR blends. The detail of physical change of PLA, NR and PLA/NR blends can be seen in figure 6.

![Degradation graph](image)

**Figure 5.** Weight loss of different samples over time.
Figure 5. Weight loss of PLA, NR and PLA/NR blends

Figure 6. Physical change of PLA, NR and PLA/NR blends

The rate of degradation was increased when the amount of PLA increased in the compositions. When the amount of NR increased in the composition, the rate of degradation became slower.

4. Conclusion
Polylactic Acid (PLA) is a biodegradable matrix which is blend with the Natural Rubber (NR) in order to overcome the brittleness of the PLA. Through the tensile test, it proved that PLA is brittle. By addition of NR in PLA, it can reduce the brittleness of PLA. The result clearly can be seen in elongation of break in tensile test and impact test as it increased along the addition of NR. Meanwhile for DMA, there were two peaks visible in the tangent delta graph which represented the PLA and NR in the blend. From the storage modulus graph in DMA also provided information of Tg which constituent revealing the immiscibility of blends. The immiscibility of the blends also can be proved through the FE-SEM morphology. The imaged of blends produced the sea island structure at composition 70/30 PLA/NR blends and co-continuous structure at 50/50 PLA/NR. Degradation test result showed that PLA faster in degradation rate compared to NR. The addition of NR caused degradation rate decreased. Pure PLA and 70/30 PLA/NR were completely degraded after 35 days. Therefore, it can be concluded that the miscibility and morphology of blends strongly affected the degradation rate.
Acknowledgement
This work was supported by Research Initiative Grant Scheme RIGS16-085-0249, International Islamic University Malaysia

References
[1] Conn R, Kolstad J, Borzelleca Dixler J F, File R Jr, La Du J R and Pariza M W, 1995. Safety assessment of polylactide (PLA) for use as a food-contact polymer. Food and Chemical Toxicology, 33, 273-283.
[2] Gupta B, Revagade N, Hilbornb J, 2007. Poly(lactic acid) fiber: an overview. Progress in Polymer Science, 32, 455-482.
[3] Bitinis N, Verdejo R, Cassagnau P and Lopez-Manchado M A, 2011. Structure and properties of polylactide/natural rubber blends. Materials Chemistry and Physics, 129 (3), 823-83.
[4] Jaratrotkamjorn R., Khaokong C and Tanrattanakul V, 2012. Toughness enhancement of poly(lactic acid) by melt blending with natural rubber. Journal of Applied Polymer Science, 124 (6), 5027-5036.
[5] Pongtanayuta K, Thongpina C, and Santawitee O, 2013. The effect of rubber on morphology, thermal properties and mechanical properties of PLA/NR and PLA/ENR blends. Energy Procedia, 34, 888 – 897.
[6] Mohammad N N B, Arshad A, Rahmat A R and Abdullah Sani N S, 2015. Effects of maleated natural rubber on mechanical properties of polylactic acid/natural rubber blends. Material Science Forum, 819, 284-289.
[7] Mohammad N N B, Arshad A, Rahmat A R, Abdullah Sani N S and Ali Mohsin M E, 2016. Influence of compatibilizer on the structure properties of polylactic acid/natural rubber blends. Polymer Science, Series A, 58 (2), 177–185.
[8] Chumeka W, Tanrattanakul V, Pilard J F, and Pasetto P, 2013. Effect of poly(vinyl acetate) on mechanical properties and characteristics of poly(lactic acid)/natural rubber blends. Journal of Polymers and the Environment, 21, 450-460.
[9] Juntuek P, Ruksakulpiwat C, Chumsamrong P and Ruksakulpiwat Y, 2012. Effect of glycidyl methacrylate - grafted natural rubber on physical properties of polylactic acid and natural rubber blends. Journal of Applied Polymer Science, 125 (1), 745-754.
[10] Zhang C, Man C, Pan Y, Wang W, Jiang L, and Dan Y, 2011. Toughening of polylactide with natural rubber grafted with poly(butyl acrylate). Polymer International, 60, 1548–1555.