FABRICATION AND CHARACTERISATION OF POLYLACTIC ACID AND NATURAL RUBBER BLEND BIOPLASTICS FOR ORGANIC FERTILISER PACKAGING

Devaki Kariyappa Gounder, Nadzirah Mohd Mokhtar

Abstract

The global fertiliser market is huge, and their packaging is typically made from synthetic polymers that are not sustainable and environmentally friendly. In view of this, the goal of this study is to produce biodegradable plastic made of polylactic acid (PLA) and natural rubber (NR) for fertiliser packaging. The bioplastic was prepared by blending PLA and NR via solvent-casting technique. The bioplastics were then characterised based on morphological, mechanical, thermal resistance, water absorption and degradation properties. Based on the morphological analysis, a larger NR agglomeration was detected as the concentration of NR increased from 0.5 to 1.5 wt% in the PLA/NR mixtures. This could be the reason for the bioplastic to break easily, due to the weak spot on the agglomeration area. Nevertheless, the addition of NR enhances the melting point, water absorption and biodegradability of the PLA/NR bioplastics, which are important features for sustainable packaging.

Keywords Bioplastic, Natural Rubber, Polylactic Acid, Biodegradable Plastic, Fertiliser.

Introduction

To date, the development of biopolymer-based packaging films has received much attention in wide applications because of their

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environment-friendly nature (Pellis et al., 2021). The need arises when synthetic polymers produced from petrochemical products are not easily degraded in the environment (Chamas et al., 2020). New research on biopolymer-based packaging films supports the use of biodegradable polymers such as poly (lactic acid) (PLA), poly(glycolic acid) (PGA), poly(e-caprolactone) (PCL) and poly (3- hydroxybutyrate) (PHB). Among these, PLA has received the greatest attention owing to its advantages of being eco-friendly, biocompatible, high strength and high modulus.

In general, PLA is a semi-crystalline substance with relatively slow levels of nucleation and crystallisation, and is used as the primary component of bioplastics. This type of polymer is obtained from ring opening polymerisation of lactide, a dimer of lactic acid through the fermentation process of corn starch (Haniff et al., 2018). PLA was proved to be superior to petroleum-based plastics in terms of energy consumption and carbon dioxide emissions in the life-cycle assessment. Unfortunately, the inherent brittleness of PLA is a major drawback that restricts its applications. To address this issue, blending PLA with other polymers is the most practical and economical way to harden PLA. Elastomers are generally considered an effective hardener in plastics. Elastomeric particles act as stress concentrators that improve the fracture energy absorption of fragile polymers and eventually result in a hardened material. Numerous elastomers have been blended with PLA, such as polycarbonate (PC), acrylonitrile butadiene styrene (ABS), polypropylene (PP) and polyethylene terephthalate (PET) (Bijarimi et al., 2021). While these elastomers have in fact cured PLA, most of them are synthetic rubbers based on petroleum.

Recently, attractive elastomers from renewable resources like natural rubber (NR) have drawn attention. NR is a major product of the rubber processing industries and is normally used for a variety of downstream rubber products such as automobile, healthcare and other related industries. It is derived from rubber latex that possesses characteristics such as toughness, biocompatibility and biodegradability which make it an ideal candidate for modifying the brittleness of PLA (Huang et al., 2020; Wang et al., 2020; Chen et al., 2018; Buys et al., 2018). Apart from NR latex production, studies have been conducted to use NR waste from natural rubber processing plants to produce organic fertilisers. In view of this, this study intends to make greater use of NR for the production of biofilm as a packaging material for NR waste organic fertiliser. The PLA/NR biofilm will be characterised based on its morphological, mechanical strength, thermal resistance, and water absorption and degradation properties. It is hoped that this study can be the initiative to support the United Nations Sustainable Development Goals (SDGs) program by reducing dependence on non-biodegradable plastic bags.

Methodology

Materials

The commercial PLA $(C_3H_4O_2)_n$ (pellets diameter, 3-4 mm; average molecular weight, 150 kDa; density, 1.24 g/cm^3; melting temperature, 145-160 °C) was purchased from Sigma-Aldrich. Chloroform was also acquired by Sigma-Aldrich and used as a solvent for PLA and NR. Meanwhile, Standard Malaysian Rubber (SMR10) was used as the NR material in this research, which was obtained from Lee Rubber Co. (Pte) Ltd. Kuala Kangsar, Perak. The plasticity retention index (PRI) of the SMR10 is 50. Organic fertiliser was collected from a vermicomposting process of NR waste.

Preparation of PLA/NR Bioplastic

Prior to use, PLA and NR were dried in a drying oven at 80°C for 1 hour to remove moisture. The blend solution was first prepared by dissolving NR in 35 mL of chloroform while stirred at 60˚C for 30 minutes. PLA was then added to the mixing solution until the final solution was homogenised. The composition of NR varied between 0.5% and 1.5% by weight per total weight of PLA, as presented in Table 1. The final solution was then poured onto a glass plate in order to produce a flat sheet film. In this project, PLA/NR blend films were prepared using the solvent-casting technique. The film was immersed in water for the phase inversion process, where the film will be naturally peeled off from the glass plate. The peeled films were placed in the oven at 60°C for 3 hours to leave it dried. The films were then cut into 10 × 12 cm sizes. The pouches were made by using a heat sealer with one side of the film was kept open for packing the organic fertiliser. Once the vermicompost organic fertiliser is inserted into the pouch, the other side will be sealed to prevent it from leaving the plastic. The final product is shown in Figure 1.

Table 1: Ratio of PLA and NR blends.

Sample	NR (g)	PLA (g)
PLA	0	5
PLA/NR*0.5	0.025	5
PLA/NR*1.0	0.050	5
PLA/NR*1.5	0.075	5

Figure 1: PLA/NR bioplastic packaging with the organic fertiliser.

Characterization of PLA/NR Blend Bioplastic

Scanning Electron Microscopy Analysis

The surface morphological structure of the PLA/NR bioplastics was investigated by using Scanning Electron Microscope (SEM) (TM-3030 Plus, Hitachi). Samples were mounted with carbon tape on aluminium stubs and then sputter-coated with platinum to make them conductive prior to SEM observation. This analysis was carried out to observe the physical compatibilities between the PLA and NR in the polymer blends.

Tensile Strength Analysis

The tensile test was conducted in accordance with ASTM 638 standard using an Instron 5967 universal test machine. The samples were cut into a rectangular shape based on the 5 cm × 1 cm size. The sample was clamped at both ends and pulled in tension at a constant elongation rate of 3 mm/min with an initial gauge length of 75 mm.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was used to determine the melting temperature (T_m) of the PLA/NR bioplastics. DSC analysis was carried out in a TA/Q1000 under nitrogen atmosphere, using 5-7 mg sample sealed into aluminium pans. In order to avoid any effect of moisture, all test specimens were pre-dried at 90°C prior to measurements. The samples were initially heated from 30-200°C with a heating rate of 10°C min^{-1}, and then cooled down to 30 °C with a cooling rate of 5°C min^{-1}.

Water Absorbent Test

All samples of 5.0 x 1.0 cm PLA/NR bioplastics were dried in an oven at 80°C for 24 hours to remove moisture. The samples were then immersed in water at room temperature. During the periods of 30, 60, 120, 180 and 240 minutes, the samples were taken out from the water. Excess surface water was removed using tissue and the weight of the bioplastics was immediately measured over time. Three replicates were measured on each sample and averaged. The percentage of water absorption (% WA) was calculated using Equation (1) (Hemsri et al., 2015).

$$\%\ WA = [(W_s - W_0)/W_0] \times 100 \qquad (1)$$

where W_s and W_0 are the weight of the bioplastic after and before submersion, respectively.

Hydrolytic Degradation Test

Alkaline hydrolytic degradation tests were conducted to determine the degradation behaviour of the PLA/NR bioplastics. The samples were cut into 10 mm x 10 mm x 1 mm and immersed in 25 ml of NaOH aqueous solution for 24 hours at room temperature. The pH of the alkaline solution was set to 13. After hydrolysis, the samples were cleaned with distilled water and dried at room temperature for one hour. The samples were then dried in the oven at 80°C for 4 hours to remove the remaining moisture, and the final weight of the samples was recorded. Similar procedures were carried out by Buys et al. (2018).

Results and Discussion

Morphology Analysis

Figure 2 presents the morphological surface images of the PLA/NR bioplastics with the magnification of 2,500 times. Detection of NR particles was observed to be larger while increasing the weight percentage of NR in the PLA/NR mixtures. The compatibility factor between PLA and NR makes it possible to infer this occurrence. The higher the NR particles, the harder it becomes to be mixed well. Given that NR is non-polar, the mixture of polar PLA and non-polar NR resulted in an incompatible mixture due to the large polarity difference of these polymers. From the SEM images, poor adhesion between the NR particles and the PLA matrix can be seen where the NR particles have been agglomerated (see PLA/NR*1.0 and PLA/NR*1.5 images). As two distinct phases are observed, this figure also emphasises the inference that PLA/NR is immiscible during the mixing process. This may be attributed to poor blending during the solution preparation. The findings are supported by the rough surface of the bioplastics when used.

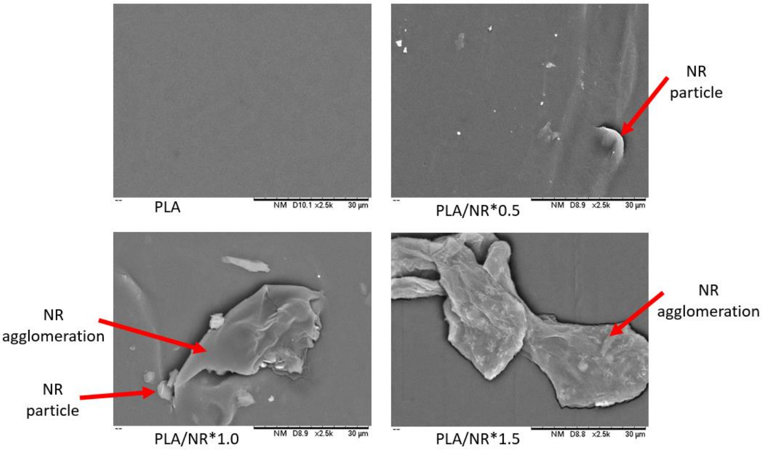

Figure 2: SEM analysis of PLA/NR bioplastics.

Mechanical Strength Analysis

Figure 3 shows the Force-Displacement diagram of the PLA/NR bioplastics obtained during the tensile tests. Because the thickness of the sample was only 0.0220 m, bioplastics tend to rupture very quickly. It can be observed that as the NR content increased in the mixture, the more rapidly the sample broke with a displacement of just 2 mm. These trends are understandable, given that the PLA/NR mixtures are immiscible, and the interface between PLA and NR has not been fully optimised. As can be seen in the SEM images (see Figure 2), the NR agglomeration was clearly observed in the PLA/NR*1.5 sample. The agglomeration area is the easy breakpoint of bioplastics. This is the reason why the bioplastic cannot withstand high pressure. However, compared to pure PLA, PLA/NR*0.5 and PLA/NR*1.0 performed better on a displacement basis. The results confirm that NR has the potential to enhance the strength of the PLA polymer. For organic fertiliser packaging purposes, the bioplastic must be able to maintain its mechanical properties to store the fertiliser and prevent leakage. At this rate, further studies are needed to improve the mechanical resistance of the PLA/NR bioplastics.

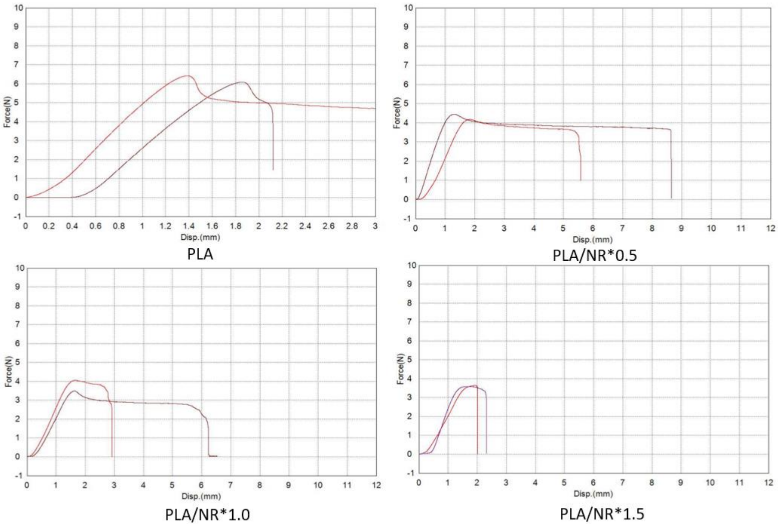

Figure 3: Force-Displacement analysis of PLA/NR bioplastics.

Thermogravimetric Analysis

DSC analysis of the PLA/NR bioplastics is illustrated in Figure 4. The melting point, T_m of PLA from this analysis is 167.1°C, whereas T_m for PLA/NR*0.5 and PLA/NR*1.0 was recorded at 168°C. A marginal increase of T_m was achieved for the PLA/NR*1.5 bioplastics, which is 168.5°C. The addition of NR did not significantly change the thermal behaviour of PLA, since the quantity of NR is very low compared to the primary polymer. The shift of T_m to a higher degree can be attributed to the decrease in chain mobility. It could be explained that crystallisation was involved in the re-arrangement of polymer chains, while the rubber network limited the mobility of PLA chains (Huang et al., 2020).

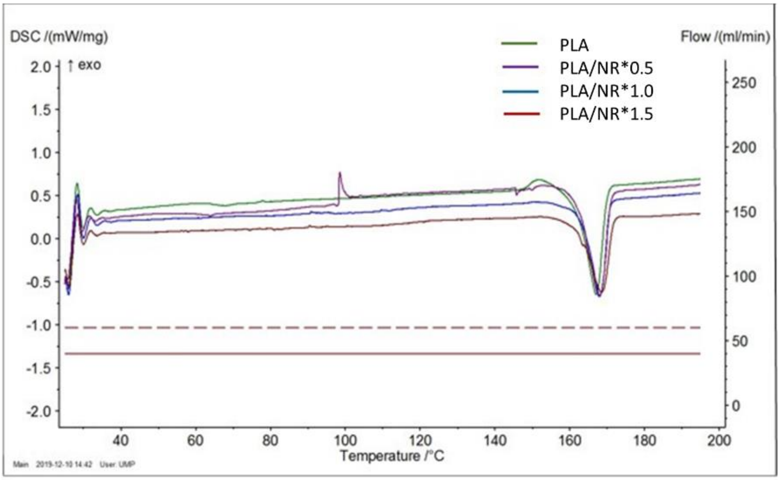

Figure 4: DSC analysis of PLA/NR bioplastics.

Water Absorption Analysis

Water absorption from polymer mixtures is an important analysis to assess their stability on the water. The percent water uptake (%WA) achieved by the samples determines their long-term feasibility. For organic fertiliser packaging, the diffusion of water into bioplastics could affect the quality of organic fertiliser within the packaging. Therefore, a smaller percentage of water absorption is desired for the packing material. The water absorption results for the PLA and PLA/NR bioplastics are shown in Figure 5. It is clear that the PLA bioplastics generally absorb more water than the PLA/NR bioplastics. During 4 hours of the test period, the PLA sample absorbed 3.41% of its original weight in water, indicating a very poor water resistance. On the other hand, a declining trend in water absorption was observed for the PLA/NR bioplastics and the best water-resistant bioplastic is PLA/NR*1.5. Thus, the incorporation of NR into PLA significantly improved the water resistance of PLA/NR blends over pure PLA. This is because NR is hydrophobic, while PLA is hydrophilic due to the polar amino acids within the PLA structure. The water likes and dislikes behaviour affects the degree of water absorption. The water resistance of the PLA/NR mixtures increased as the rubber content increased, due to the presence of non-polar rubber in the mixtures, thereby reducing water diffusion in the bioplastics. However, the performance of the bioplastic PLA/NR*1.5 decreases after 180 minutes, which can be explained by the poor adhesion between the NR particles and the PLA matrix. The bioplastics were unable to withstand high water resistance for a prolonged period of time and began to absorb water after 180 minutes. A similar pattern was observed with PLA/NR*1.0 bioplastics at 120 minutes.

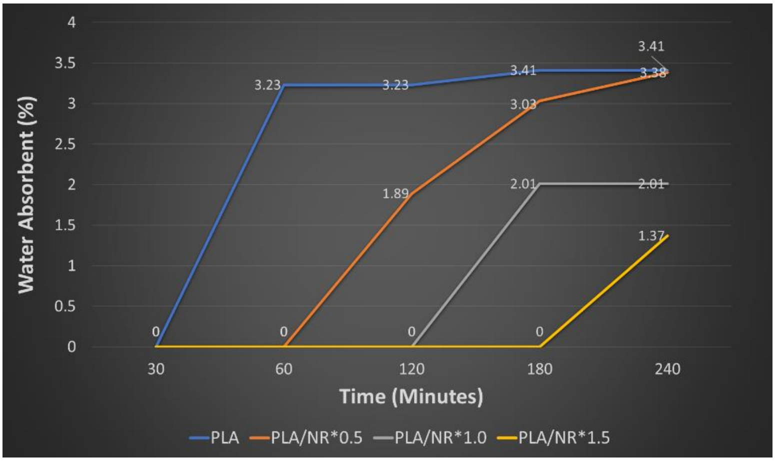

Figure 5: Water absorbent analysis of PLA/NR blend.

Hydrolytic Degradation Test

Weight loss of samples within 24 hours for the bioplastics to degrade was tested with a hydrolytic degradation test. In this study, it was observed that the rate of degradation of the PLA/NR bioplastics was very slow (0% weight loss), compared to pure PLA that lost 2.35% weight in 24 hours. As the amount of NR in the composition increased, the rate of degradation decelerated. Prior to the packaging of organic fertilisers, the bioplastic must maintain its mechanical, chemical and physical properties until it is placed in the soil. A slower degradation rate for PLA bioplastic is important when filled with fertiliser and takes time to be used. Therefore, mixing NR with PLA reduces the rate of hydrolytic degradation that is appropriate for the packaging of organic fertilisers.

Conclusion

This project involves the production of bioplastics from the mixtures of PLA and NR using a solvent-casting method. The effects of PLA/NR on morphology, mechanical strength, thermal stability, water absorption and hydrolytic degradation properties were investigated. With regard to mechanical strength, sample displacement decreased with the addition of NR in PLA/NR mixtures. This demonstrated that PLA and NR do not mix well during the solution preparation. The immiscibility of PLA and NR mixtures has also been proven by SEM analysis, which showed visible NR particles in the fabricated PLA/NR bioplastics. Apart from this, thermal analysis by DSC showed that the melting point of PLA/NR mixtures increased due to the presence of NR. Water absorption of the PLA/NR mixtures decreases with the increasing NR composition, and plastic degradation is slower with high NR composition. These low water absorption and slow degradation properties allow the use of the PLA/NR bioplastics without being easily degraded by exposure to water or alkaline solution. Certainly, an optimisation of the PLA/NR blending ratio will be required to improve the quality of the PLA/NR bioplastics for ready exploitation in the materials industry.

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