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RESEARCH ARTICLE

Mechanical, thermal, and morphological properties of poly(lactic acid) (PLA)/ recycled tyre rubber waste compatibilised with chain extender

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ABSTRACT - The accumulation of waste tires in our society is a pressing issue due to their short lifespan and increasing demand. This research delves into effective methods for recycling waste tires, with a particular focus on utilising biopolymers. Polylactic acid (PLA), a completely biodegradable polymer, has gained popularity for its biocompatibility, biodegradability, mechanical strength, and ease of processing. To overcome its toughness and thermal stability limitations, PLA has been blended with commercial polymers, such as rubber. Furthermore, the addition of 10% recycled tyre waste to 90% PLA has been shown to increase its durability and strength. Joncryl® ADR is used as a chain extender and reactive compatibiliser to enhance the chemical interactions in the binary blend. The samples were prepared using a twin-screw extruder with the temperature between 150 and 190 ºC and 60 rpm of screw speed. These blends are then analyzed using a range of characterization techniques, including Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), tensile testing, and notched Izod impact testing. The blends were then characterized by chemical changes, thermal transitions, and thermal degradation. It was found that the 90/10/0.6 (PLA/RW/ADR) nanocomposite exhibited maximum thermal degradation.

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1.0 INTRODUCTION

In recent years, recycled product manufacturing has gained popularity. One of the benefits associated with this practice is the enhancement of economic and environmental appeal of the technology through material recycling(Ayrilmis et al., 2009). The escalating demand for tyres in conjunction with their limited lifespan has resulted in a significant rise in the accumulation of waste tyres, making them a prominent issue within the realm of advancing civilization's waste materials. Consequently, it becomes imperative to explore and establish techniques for the effective recycling of waste tyres.Several strategies have been suggested to utilize the substantial quantity of waste rubber, with one such technique being the implementation of biopolymers. Biopolymers are organic compounds made up of repeating monomers that are linked together by covalent bonds to form a polymer chain. These polymers can be obtained from various natural sources such as plants, animals, microorganisms, and agricultural wastes. However, they are known to be expensive and have inherent limitations in terms of their properties or processing capabilities (Martin & Avérous, 2001). The bio resins with the highest durability now accessible in commercial markets are predominantly derived from polylactic acid (PLA).

PLA stands out as a fully biodegradable polymer, earning recognition as a highly promising bio-based material due to its excellent biocompatibility, capacity for biodegradation, impressive mechanical strength, lack of toxicity, non-irritating nature, and ease of processing(Piah et al., 2023). Synthesizing PLA using energy-efficient methods is a promising solution that can help us reduce our dependence on petroleum resources(Wu et al., 2023). PLA could replace petroleum-based polymers due to its comparable mechanical properties, thermal flexibility, biocompatibility, and low toxicity. Its unique features, like high crystallinity and mechanical strength, make it ideal for packaging, textiles, and medical devices(Lee et al., 2021; Li et al., 2021).

In an attempt to address the primary drawbacks of polylactic acid (PLA), including its limited toughness and low thermal stability, researchers have sought to incorporate PLA into blends with commercial polymers. An instance of blending rubber with PLA (Bijarimi et al., 2013; Fekete et al., 2021; Iordanskii, 2021; Rosli et al., 2016; Xu et al., 2014), Polypropylene (PP), Polyamide 6 (PA6), Linear low-density polyethylene (LLDPE), polyoxymethylene (POM)(Bijarimi et al., 2019; Haniff et al., 2018; Hoseini & Haghtalab, 2017; Rudzaimi et al., 2021). Previously, PLA was primarily utilized in medical fields for things like implant devices, tissue scaffolds, and internal sutures. However, PLA is now being utilized in new composite material technology due to its biodegradability, which lessens the amount of non-

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degradable plastic products that landfills have to handle. Studies conducted in the past have shown that incorporating recycled tire waste into PLA can significantly improve its durability and strength(Bijarimi et al., 2013, 2014, 2023; Fekete et al., 2021; Iordanskii, 2021; Rosli et al., 2016; Zhang et al., 2022). In this study, we use Joncryl® ADR as a chain extender and reactive compatibilizer that can substantially enhance the processability and final characteristics of specific polymers and immiscible polymer blends.

2.0 EXPERIMENTAL

2.1 Materials and blend preparation

The PLA Biopolymer 2002D resin was provided by Unic Technology Ltd., China. It has a melting temperature between 160 and 170 °C. The density is 1.24 g/cm^3, and the melt flow index is 4–8 g/min. Recycled tire waste (RW) was obtained from the Rubber Product Recycle Industry, Kuantan, Malaysia. The PLA and RW resin compositions were fixed at 90/10 (PLA/RW) for binary blends. The ADR was added to the binary blend (PLA 90/ RW10/ADR0.6). The temperature profile of the extruder barrel was set between 150 and 250 °C.

2.2 Mechanical properties (Stress-strain analysis)

The mechanical properties of different blend compositions were tested and compared. To conduct the tensile test, the ASTM D638 standards were followed using a Testometric M350-10CT tensile machine (made by Testometric Company, Ltd., UK). The test was carried out under ambient conditions with crosshead speeds of 50 mm/min. The values of stress-strain properties were taken from an average of five specimens.

2.3 Characterization

Changes in chemical composition during blending were studied using Fourier transform infrared (FTIR) spectroscopy. The infrared (IR) spectra were captured using a Spectra 400 FT-IR spectrometer, which had a resolution of 4 cm^{-1} for a total of 33 scans within the 4000–500 cm^{-1} range of the IR spectrum. Differential scanning calorimetric (DSC) was performed under a nitrogen atmosphere on samples of 1–2 mg using a DSC (TA instruments apparatus). DSC used to investigate the thermal properties of the nanocomposites. All samples will be placed in standard aluminium pans with pierced lids and heated from 25 °C to 300 °C at a scan rate of 10 °C / min. The glass transition (T_g), crystallization temperature (T_c), and melting temperatures (T_m) will be evaluated. Polymer crystallinity is determined with DSC using the heat associated with the melting (fusion) of the polymer. The degree of crystallinity (X_c) was calculated using Eq.

$$X_c = \frac{\Delta H_m}{\Phi_{PLA}\,(\Delta H_m^o)} \times 100\%$$

where ΔH_m is the measured enthalpy of melting, and ΔH_m^o is the melting enthalpy assuming 100% crystalline PLA at 93.0 J/g. The ϕ_PLA is the weight fraction of PLA in the blend (Bijarimi et al., 2017).

2.4 Morphological analysis

Morphological analysis was performed to evaluate the structural detail of the composites using the Scanning Electron Microscopy (SEM) technique. Small pieces of the fractured specimens were observed using a JEOL/JSM-IT200 Scanning Electron Microscope (JSM-IT200 Ltd., Japan) after the tensile test. The fractured surfaces were coated with a thin layer of gold before microscopic observation. This technique also provides insights into the distribution of components in binary blends.

2.5 Impact properties

The material's impact resistance was tested using the notched Izod method, following ASTM 256 standards. The Ray-Ran Universal Impact tester, manufactured by Ray-Ran Test Equipment Ltd. in the UK, was used for the examination. Compression moulding was used to prepare the rectangular specimen, resulting in a thickness of 3 mm, a width of 12.7 mm, and a length of 64 mm. Before testing, the samples were notched at a 60-degree angle with a depth of 2.54 mm using a motorized Ray-Ran cutter. The impact tests were conducted at room temperature, and the results were reported in kilojoules per square meter. The values were calculated based on an average of five specimens.

3.0 RESULTS AND DISCUSSION

3.1 Mechanical properties

Based on the sample, it appears that neat PLA has a brittle structure. However, the addition of RW improves its plastic deformation, resulting in a decrease in stress yield and an increase in elongation at the break of PLA. Figure 1 demonstrates the impact of adding 10% wt RW to PLA on its tensile strengths. It displays a significant increase in strain and a slight decrease in stress compared to neat PLA. Additionally, adding 0.6 % wt ADR to PLA90/RW 10 results in a slight increase in strain but a decrease in stress compared to PLA/RW.

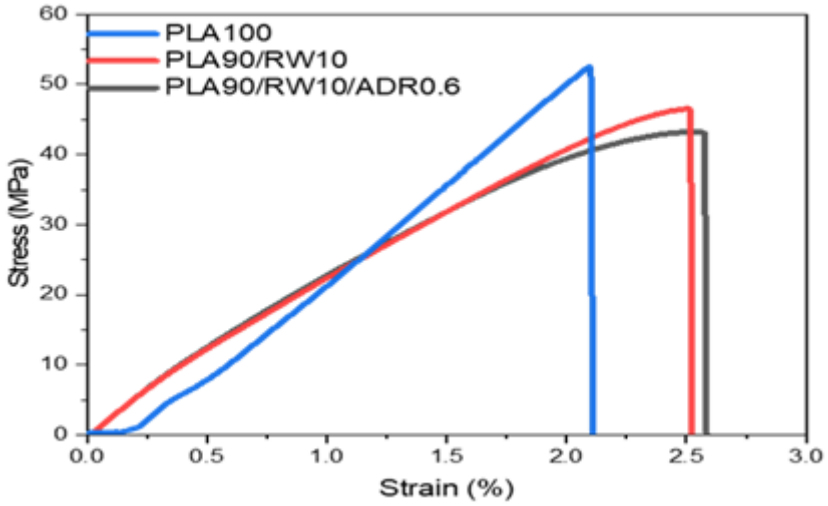

Figure 1. Stress-strain curves for pure PLA, PLA/RW and PLA/RW/ADR.

3.2 Fourier transform infrared analysis

Figure 2 illustrates the FT-IR spectra of PLA100, PLA90/RW10, and PLA90/RW10/ADR0.6 respectively. The pure PLA and PLA/RW spectrum reflects four major regions, which are –CH stretching at 2933-3017 cm^{-1}, C–H bending at 1316-1476 cm^{-1}, –C=O stretching at 1700-1804 cm^{-1}, and –C–O stretching at 1000-1236 cm^{-1}. The FT-IR spectra analysis indicates that there is no chemical interaction between PLA and RW in the binary complex, evidenced by shifts in characteristic peaks.

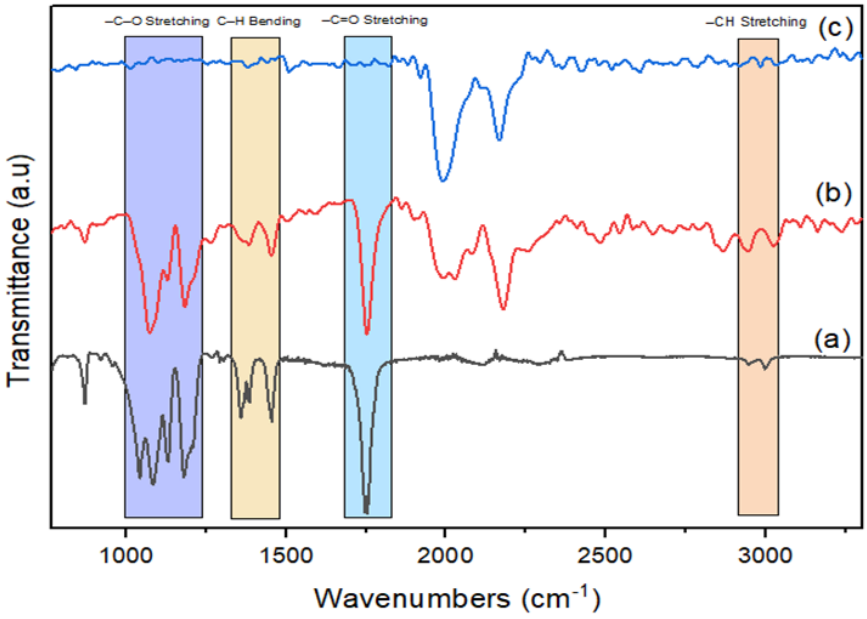

Figure 2. FTIR curve for (a) PLA, (b) PLA90/RW10 and (c) PLA90/RW10/ADR0.6.

3.3 Differential scanning calorimetry (DSC)

Figure 3 illustrates the DSC analysis that revealed distinct thermal behavior among the studied materials. Pure PLA displayed a sharp endothermic peak corresponding to its melting temperature. This T_m value indicates the temperature at which the crystalline regions of PLA transition from a solid to a molten state. The observed T_m for pure PLA is 168°C. Another significant feature in the DSC curve was the glass transition temperature T_g at which PLA transitions from a glassy, rigid state to a rubbery, amorphous state. For pure PLA, the T_g was found to be 58°C. In the blend, the T_m value might show some changes compared to pure PLA. This can be attributed to the interaction between PLA and the recycled tire materials, potentially leading to variations in the crystallinity and melting behavior. Similar to T_m, the T_g of the blend could be influenced by the presence of RW. It may shift due to the introduction of amorphous components from the tires.

The presence of Joncryl® ADR may influence the T_m of the blend further. Depending on its compatibility with PLA and RW, it could lead to changes in crystallinity and melting behaviour. Joncryl® ADR might also affect the Tg of the

blend. It can act as a compatibiliser or modifier, impacting the amorphous regions of the material. This may result in alterations in T_g compared to the PLA/RW blend without Joncryl® ADR.

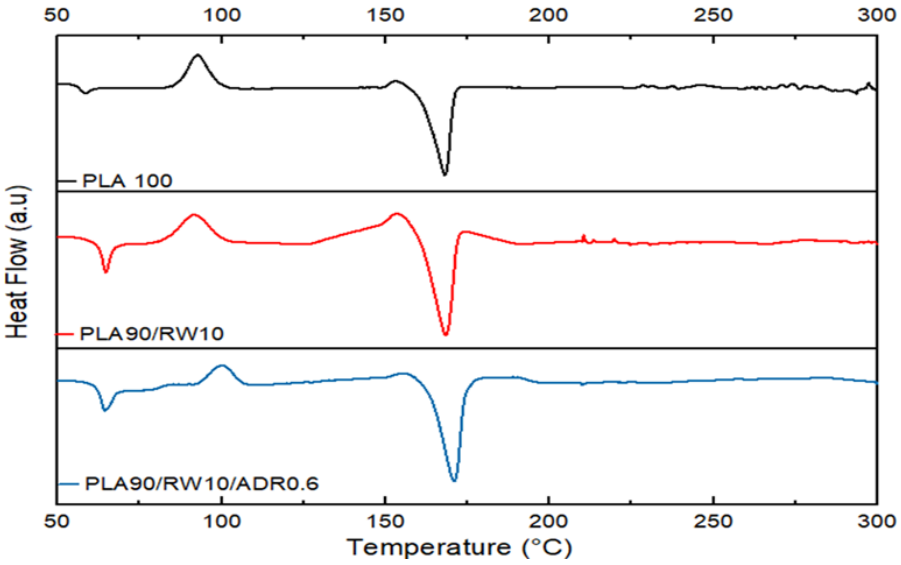

Figure 3. curve for DSC of PLA90/RW10, and PLA90/RW10/ADR0.6.

Table 1. DSC results for PLA, PLA/RW, and PLA/RW/ADR.

Sample	Glass transition temperature T_g °C	Crystallization temperature T_c °C	Melting temperature T_m °C	Degree of crystallinity X_c %
PLA100	58	92.8	168	14.6
PLA90/RW10	64.8	91.7	168	14.9
PLA90/RW10/ADR0.6	64.5	99.6	171	19.3

3.4 Scanning Electron Microscopy (SEM)

Figure 4 shows the SEM analysis of the PLA pure sample that revealed a distinct microstructure characterized by a smooth surface with ductility. Moreover, it was detected that the PLA90/RW10 blend behaved according to a highly immiscible polymer blend, with distinct particle interfaces and large dispersed phase particles with smoothness, showing poor interfacial adhesion. The fracture surface represents RW particles and disperses in the PLA matrix. This corresponds to the significant increase in elongation at break.

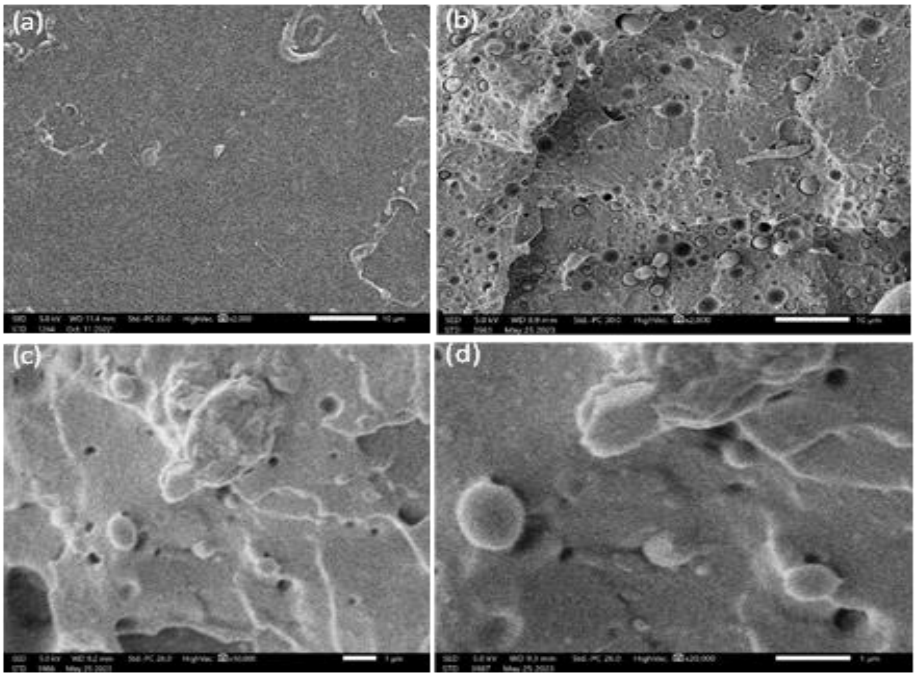

Figure 4. SEM images for a) PLA 2K, b) PLA90/RW10 2K, c) PLA90/RW10 10K, d) PLA90/RW10 20K magnifications.

Figure 5 shows the SEM analysis of the PLA/RW/ ADR blend, further changes in microstructure were evident compared to the PLA/RW blend, improved particle dispersion, and changes in phase boundaries. The addition of Joncryl® ADR appears to have a notable influence on the blend's microstructure. The SEM images suggest that Joncryl® ADR may contribute to enhanced compatibility between PLA and RW components, potentially leading to improved mechanical properties and material performance.

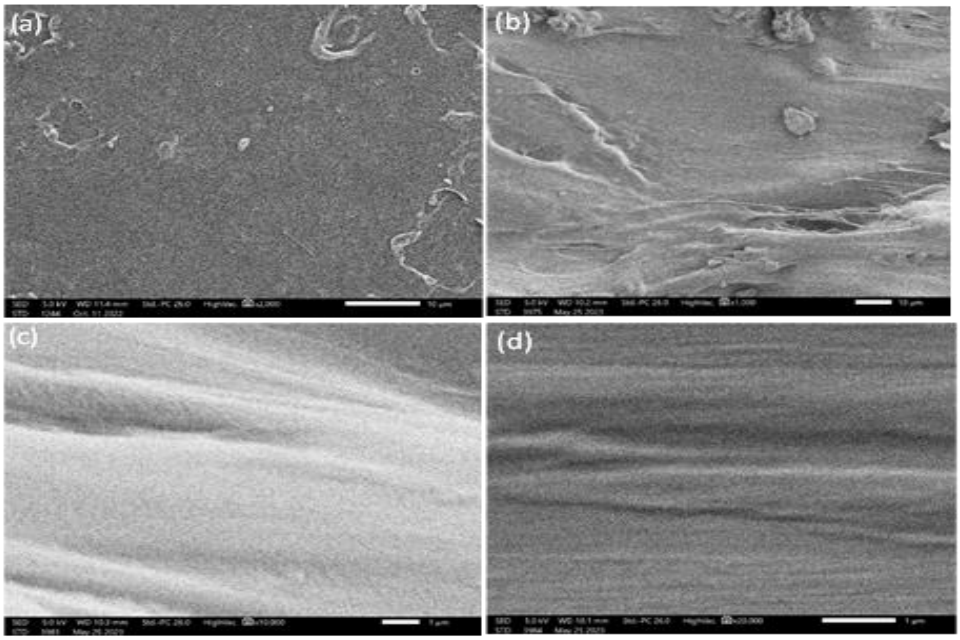

Figure 5. SEM images for a) PLA 2K, b) PLA90/RW10/0.6 ADR 2K, c) PLA90/RW10/0.6 ADR 10K, d) PLA90/RW10/0.6 ADR 20K magnifications.

3.5 Impact test

Figure 6 shows the impact strength increasing sharply from PLA100 (2.0950kJ/m^2) to PLA90/RW10/ADR 0.6 (4.940 kJ/m^2) when 0.6 % of ADR was added as a toughening agent for PLA/RW blend. This represents a significant improvement in the material's ability to withstand sudden forces without breaking. It is important to recognize that multiple factors contribute to the improvement of this process, including the distinct properties of the ADR employed and its interaction with the PLA and RW. By preventing the propagation of cracks within the material, the ADR can effectively enhance its durability.

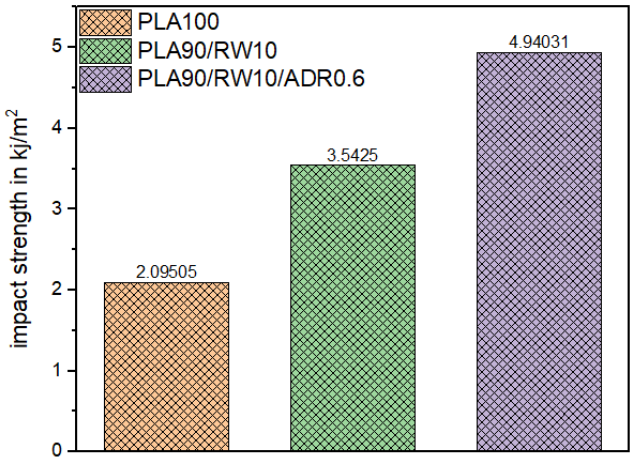

Figure 6. Impact strengths of PLA/RW and PLA/RW/ADR.

5.0 CONCLUSION

In this study, the PLA, RW, and ADR blends were successfully prepared and characterized for chemical interactions, thermal transitions, and thermal degradability. The addition of Joncryl® ADR as a chain extender and reactive compatibilizer played a pivotal role in enhancing the chemical interactions within the binary blend. When 0.6% of ADR was added to the PLA90/RW10 blend, it led to an improvement in impact strength by 57% and elongation at break by

18% during the tensile test as compared to pure PLA. Furthermore, when 0.6% wt ADR was added to the PLA90/RW10 blend, the T_c, T_m, and X_c increased by 6.8 °C, 3.0 °C, and 4.6%, respectively, in comparison to pure PLA. This result signifies the successful development of a more robust and thermally stable biocomposite material that can serve as a promising alternative to conventional plastics in various applications.

6.0 CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7.0 AUTHORS CONTRIBUTION

Mohd Bijarimi (Conceptualisation; Resources)

Ramzi Qasem (Methodology; Data curation; Writing - original draft; Writing - review & editing; Resources; Investigation)

Waleed Alhadadi (Supervision; Visualisation)

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9.0 REFERENCES

[1] Ayrilmis, N., Buyuksari, U., & Avci, E. (2009). Utilization of waste tire rubber in the manufacturing of particleboard. *Materials and Manufacturing Processes*, *24*(6), 688–692.

[2] Bijarimi, M., Abdulsalam, Y., Norazmi, M., Normaya, E., Alhadadi, W., & Desa, M. S. Z. (2023). Preparation and characterization of poly(lactic acid)/linear low density polyethylene/recycled tire waste/graphene nanocomposites. *Materials Today: Proceedings*, *xxxx*, 6–9. https://doi.org/10.1016/j.matpr.2023.03.568

[3] Bijarimi, M., Ahmad, S., & Alam, A. K. M. M. (2017). Toughening effect of liquid natural rubber on the morphology and thermo-mechanical properties of the poly(lactic acid) ternary blend. *Polymer Bulletin*, *74*(8), 3301–3317. https://doi.org/10.1007/s00289-016-1889-7

[4] Bijarimi, M., Ahmad, S., & Rasid, R. (2013). Melt Blends of Poly(lactic acid)/Natural Rubber and Liquid Epoxidised Natural Rubber. *Journal of Rubber Research*, *17*, 57–68.

[5] Bijarimi, M., Ahmad, S., & Rasid, R. (2014). Mechanical, thermal and morphological properties of poly(lactic acid)/epoxidized natural rubber blends. *Journal of Elastomers and Plastics*, *46*(4), 338–354. https://doi.org/10.1177/0095244312468442

[6] Bijarimi, M., Amirul, M., Norazmi, M., Ramli, A., Desa, M. S. Z., & Desa, A. (2019). *Preparation and characterization of poly (lactic acid) (PLA)/ polyamide 6 (PA6)/ graphene nanoplatelet (GNP) blends bio-based nanocomposites Preparation and characterization of poly (lactic acid) (PLA)/ polyamide 6 (PA6)/ graphene nanoplatel*. *6*.

[7] Fekete, I., Ronkay, F., & Lendvai, L. (2021). Highly toughened blends of poly(lactic acid) (PLA) and natural rubber (NR) for FDM-based 3D printing applications: The effect of composition and infill pattern. *Polymer Testing*, *99*, 107205. https://doi.org/https://doi.org/10.1016/j.polymertesting.2021.107205

[8] Haniff, M., Bijarimi, M., Zaidi, M. S., & Sahrim, A. (2018). Preparation and characterization of poly(Lactic acid) (PLA)/ polyoxymethylene (POM) blends. *Materials Science Forum*, *917 MSF*(July), 3–6. https://doi.org/10.4028/www.scientific.net/MSF.917.3

[9] Hoseini, M., & Haghtalab, A. (2017). *Rheology and morphology study of immiscible linear low-density polyethylene / poly (lactic acid) blends filled with nanosilica particles*. *45526*, 1–12. https://doi.org/10.1002/app.45526

[10] Iordanskii, A. (2021). *Structural Features and Properties ' Characterization of Polylactic Acid / Natural Rubber Blends with Epoxidized Soybean Oil*.

[11] Lee, J.-S., Hwang, G.-H., Kwon, Y. S., & Jeong, Y. G. (2021). Highly Tough and Thermally Stable Polylactide Blends Compatibilized with Glycidyl Methacrylate-Grafted Polypropylene. *Macromolecular Materials and Engineering*, *306*(8), 2100122. https://doi.org/https://doi.org/10.1002/mame.202100122

[12] Li, N., Qiao, D., Zhao, S., Lin, Q., Zhang, B., & Xie, F. (2021). 3D printing to innovate biopolymer materials for demanding applications: A review. *Materials Today Chemistry*, *20*, 100459. https://doi.org/https://doi.org/10.1016/j.mtchem.2021.100459

[13] Martin, O., & Avérous, L. (2001). Poly (lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer*, *42*(14), 6209–6219.

[14] Piah, M. B. M., Ahmad, M. N., Abdullah, E. N., & Muzakkar, M. Z. (2023). Modifications of Poly(lactic Acid) with Blends and Plasticization for Tenacity and Toughness Improvement. *Indonesian Journal of Chemistry*, *23*(4), 1161–1180. https://doi.org/10.22146/ijc.80830

[15] Rosli, N. A., Ahmad, I., Anuar, F. H., & Abdullah, I. (2016). Mechanical and thermal properties of natural rubber-modified poly(lactic acid) compatibilized with telechelic liquid natural rubber. *Polymer Testing*, *54*, 196–202. https://doi.org/https://doi.org/10.1016/j.polymertesting.2016.07.021

[16] Rudzaimi, M., Bijarimi, M., Hafidzah, F., Alhadadi, W., Desa, M. S. Z., & Ahmad, M. N. (2021). Biodegradable binary blend of poly(lactic acid) / polypropylene via twin-screw extruder: Preparation and characterization. *AIP Conference Proceedings*, *2409*(December). https://doi.org/10.1063/5.0067619

[17] Wu, Y., Gao, X., Wu, J., Zhou, T., Nguyen, T. T., & Wang, Y. (2023). Biodegradable Polylactic Acid and Its Composites: Characteristics, Processing, and Sustainable Applications in Sports. *Polymers*, *15*(14). https://doi.org/10.3390/polym15143096

[18] Xu, C., Yuan, D., Fu, L., & Chen, Y. (2014). Physical blend of PLA/NR with co-continuous phase structure: Preparation, rheology property, mechanical properties and morphology. *Polymer Testing*, *37*, 94–101. https://doi.org/https://doi.org/10.1016/j.polymertesting.2014.05.005

[19] Zhang, H., Yuan, W.-Q., Weng, Y., Zeng, J.-B., & Li, Y.-D. (2022). Morphological control and interfacial compatibilization of fully biobased PLA/ENR blends via partial crosslinking ENR with sebacic acid. *Industrial Crops and Products*, *180*, 114707. https://doi.org/https://doi.org/10.1016/j.indcrop.2022.114707