APPENDIX

PUBLICATIONS

List of Publications

Rong-or, C., Pongputthipat, W., Ruksakulpiwat, Y., Chumsamrong, P. (2023). Poly(Lactic acid)/ Natural Rubber/ Rice straw Bio-composite films for Agricultural application. Proceedings of the International Polymer Conference of Thailand (PCT 13 Conference), Bangkok, Thailand, June 8–9

Rong-or, C., Pongputthipat, W., Ruksakulpiwat, Y., Chumsamrong, P. (2024). Soil burial degradation of bio-composite films from poly(lactic acid), natural rubber, and rice straw. Polymer Bulletin, 1-18. https://doi.org/10.1007/s00289-024-05229-6

PBCG-P1

Sustainable Biocomposite Films from Poly(Lactic acid)/Natural Rubber/Rice straw

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Abstract

The aim of this research is to develop sustainable and biodegradable biocomposite films for agricultural applications using components derived from renewable resources, including poly(lactic acid) (PLA), natural rubber (NR), and rice straw (RS). The PLA/NR blend, at a fixed ratio of 60/40 wt.%, was filled with 3%, 5%, and 10 wt.% RS powder, respectively. All the films were successfully produced with the cast film extrusion process. However, at 10 wt.% RS, many large holes were presented on the obtained film, which disallowed further testing. The brittleness of neat PLA changed into a ductile fracture when NR was added. The tensile strength and modulus of the biocomposite films decreased with increasing RS contents. Nevertheless, their elongation at break was still significantly higher than that of neat PLA. The MFI of the composites increased as the fiber content increased. FE-SEM micrographs of tensile fracture surfaces of PLA/NR blend, and PLA/NR/RS films showed smooth surfaces with phase-separated morphology. After 90 days of soil burial, the biocomposite with 5 wt.% RS showed the greatest weight loss of 15%. The information above demonstrates that PLA/NR/RS biocomposite materials have the potential to be used as biodegradable and low-cost agricultural films.

Keywords: Biocomposite, Biodegradable film, Poly(lactic acid), Natural rubber, Rice straw

1. Introduction

Thailand, an agricultural country, has high agricultural output. Consequently, amount of plastic waste from agricultural sector has been increased. One of them is plastic films such as seedling bags and mulch film. Films for agricultural applications, generally made from polyethylene plastic, are used worldwide because they are inexpensive and lightweight[1]. As polyethylene is not biodegradable and becomes microplastics in the environment, it could have significant deleterious consequences for the health of organisms, also across the food chain[2]. Hence, replacing traditional polymers with biodegradable and compostable ones is essential.

Among biodegradable polymers, poly (lactic acid) (PLA), a biodegradable polyester derived from renewable resources, is of interest. Though PLA is strong, it is also very brittle. PLA has frequently been blended with flexible materials to solve these issues. Blending PLA with biodegradable and renewable NR without various modifications is a good choice to improve toughness and elongation at break and enhance the degradation rate of PLA, which is an ideal candidate to improve the brittleness of PLA[3]. The addition of NR increased the amorphous region in the matrix, thus increasing the percentage of water absorption. This occurs because the amorphous region is flexible and can facilitate the diffusion of water [4-6]. One of basic parameters control the hydrolytic degradation of a PLA is quantity of absorbed water[7]. Additionally, since NR is less expensive than PLA, blending the two materials reduces the cost.

Rice straw is an organic waste that is the large quantities as a by-product of rice cultivation. The most popular way to dispose of rice straw is to burn it. In various areas of Thailand, most farmers rely on the natural burning of straw, which is leading to numerous ecological, environmental, health, and economic problems[8-9]. Because of this, rice straw fibers were studied from many research for use in the production of reinforcing agents for polymer composites and improve the biodegradability of PLA[10,11]. Rice straw is a valuable waste product that provides several substantial advantages, including ease of accessibility, low cost, biodegradability, little risk to health, and environmental friendliness. This will all lead to the production of sustainable PLA/NR/Rice straw biocomposite films that are low cost, biodegradable, flexible, and strong films.

2. Experimental methods

2.1 Materials

Poly(lactic acid) (PLA, 4043D) was purchased from Nature Works LLC. Natural rubber (NR, STR 5L) was purchased from Natural Art and Technology Co., LTD. Rice straw (RS) was collected from a rice processing factory in Nakhon Ratchasima Province, Thailand.

2.2 Preparation of PLA/NR/RS biocomposites

PLA was dried in an oven at 80 °C for 10 hours before mixing with 10-minute masticated NR. Biocomposites produced from PLA, NR, and RS powder (53 microns long) were made with different compositions, as shown in Table 1. The amount of rice straw in the polymer composite varied in the range of 3, 5, and 10 wt.% based on the total weight of the PLA/NR blend. The ratio of PLA to NR was fixed at 60/40 wt. %. All polymer composite compositions were mixed in an internal mixer (Haake Rheomix, 3000P) for 10 minutes at 170 °C with a rotor speed of 60 rpm. After that, the polymer composite was crushed into smaller pieces in a plastic recycling machine (Tranekaer, DK-5953).

Table 1. Formulations of PLA/NR/Rice straw composites.

Sample code	PLA (%wt.)	NR (%wt.)	RS (%wt.)
Neat PLA	100	-	-
PLA/NR	60	40	-
PLA/NR/3%RS	58.2	38.8	3
PLA/NR/5%RS	57	38	5
PLA/NR/10%RS	54	36	10

2.3 Biocomposite films preparation

PLA/NR/RS biocomposites films were produced using cast film extrusion (Betol, BC 32). The temperature of the barrel (zones 1, 2, 3, and 4) was 45, 165, 180, and 190 °C, and the slit die zone was 190 °C. The screw speed was 50 rpm. The chill roll speed and temperature were 6 rpm and 60 °C, respectively.

2.4 Characterization of PLA, PLA/NR, and PLA/NR/RS biocomposite films

According to the ASTM D1238 standard, the melt flow index (MFI) measurements of PLA, PLA/NR, and PLA/NR/RS composites were done using a melt indexer (Kayeness, D40004HV) by applying a weight of 2.16 kg at a melt temperature of 190 °C. At least 6 extrudates from each formulation were cut and weighed at regular intervals before the average was calculated. The melt flow index is obtained using the following equation (1).

$$\text{MFI (g/10 min)} = \frac{600 \times W}{t} \quad (1)$$

where MFI is the melt flow index (g/10 min), W is weight of material extruded (g), and t is cutting time (s).

The universal testing machine (Instron, 5565) is used to measure the tensile properties of PLA, PLA/NR, and PLA/NR/RS biocomposite films according to the tensile test standard ASTM D882 (thickness less than 1.0 mm (0.04 in.)) with a load cell of 5 kN, a crosshead speed of 12.5 mm/min, and a gauge length of 50 mm.

Morphological properties of PLA/ NR/ RS biocomposite films were investigated using a field emission scanning electron microscope (FE-SEM; ZEISS, AURIGA). Osmium tetroxide was used to stain the

rubber phase for 24 hours to distinguish the various phases. Before FE-SEM analysis, the surfaces of the samples was coated with carbon. FE-SEM images of the samples were collected using a 3 kV acceleration voltage.

The 3x3 cm samples of films were buried in a box of soil that was kept at a 30% moisture by weight condition. The samples were buried between 12-15 centimeters deep. Each sample was retrieved from the soil after being buried for 15, 30, and 60 days. The obtained samples were cleaned in distilled water and dried to a constant weight in a vacuum oven at 40 °C. The percentage weight loss of the film samples was calculated by following equation (2).

$$\text{Weight loss (\%)} = \left(\frac{W_i - W_t}{W_i}\right) \times 100 \qquad (2)$$

where W_i is the initial dry weight of the samples and W_t is the dry weight of the sample retrieved from soil burial.

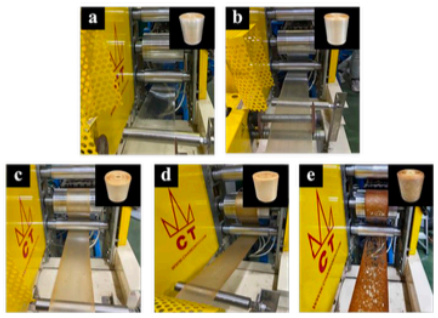

Figure 1. Physical characteristics of (a) neat PLA, (b) PLA/NR, and PLA/NR/RS biocomposite films; (c) 3%, (d) 5%, and (e) 10%.

3. Results and Discussion

Figure 1 (a-e) shows the physical characteristics of neat PLA, PLA/NR blends, and PLA/NR/RS biocomposite films. All biocomposite films exhibited an opaque light brown tint, while neat PLA film was slightly yellow and clear, and PLA/NR blends film was semi-opaque. The surface appearance of the neat PLA, PLA/NR blend, PLA/NR/3%RS, and PLA/NR/5%RS films was smooth. The surface of the PLA/NR/10 % RS film, on the other hand, contained numerous huge holes; hence, this film had not been subjected to further characterization. The PLA films were 0.20±0.01 mm thick. The thickness of the films decreased to 0.054±0.01 mm with the addition of NR. This might be because NR improved the melt strength of PLA/NR film, thus facilitating stretchability. The thickness of the biocomposite films was 0.14±0.01, 0.16±0.01, and 0.24±0.01 mm for the films at 3, 5, and 10 %wt. RS, respectively. The thickness of the biocomposite films tended to increase with an increase in RS content, which was consistent with the increase in melt flow rate.

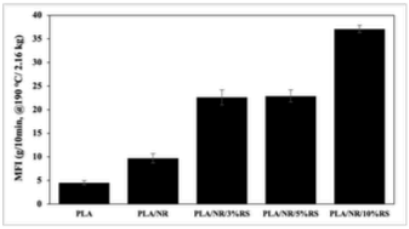

Figure 2. Melt flow index (MFI) of neat PLA, PLA/NR, and PLA/NR/RS biocomposites.

One of the most important measurements for polymer processing is the melt flow index (MFI). MFI is indicative of the molten polymer's processing abilities and flow characteristics, enabling a basic evaluation of the processing characteristics of thermoplastic polymers. Figure 2 shows the MFI values of neat PLA, PLA/NR blend, and all PLA/NR/RS biocomposites. The MFI of the PLA/NR blend was higher than that of neat PLA. The addition of 40 %wt. NR might improve the melt flow properties of neat PLA. The MFI values of the composites containing 3 and 5 %wt. RS were similar and approximately twice that of PLA/NR. The higher the amount of fiber added during composite manufacturing causes an increase in shear[12]. When RS content was increased to 10 %wt., the MFI increased to around 37±0.79 g/10 min, which could not be used to produce a smooth

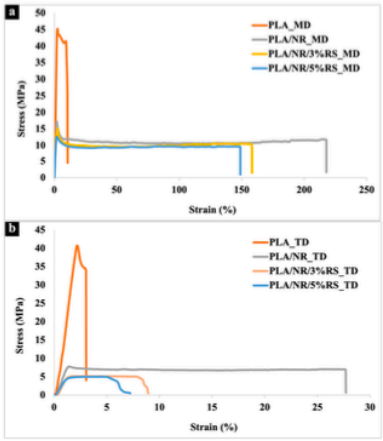

Figure 3. Stress-strain curve of neat PLA, PLA/NR, and PLA/NR/RS biocomposite films; (a) machine direction (MD) and (b) transverse direction (TD).

film. In general, the range of MFI that is suitable for cast film is around 9-15 g/10 min, which makes the cast film extrusion process smoother[13]. The large and numerous holes were then occurred in the films at 10 %wt. RS.

Tensile test results of neat PLA, PLA/NR, and PLA/NR/RS biocomposites are shown in Figure 3 (a-b), where the tensile stress-strain curves can be seen. The neat PLA showed brittle fractures. The brittleness of neat PLA changed into a ductile fracture when NR was added. At the RS contents of 3–5 %wt., the fracture behavior of the films was still ductile.

The tensile properties of neat PLA, PLA/NR, and PLA/NR/ RS biocomposite films in machine (MD) and transverse direction (TD) are compared in Figure 4 (a-c).

In MD, PLA/NR blend and PLA/NR/RS biocomposites films showed lower tensile strength and modulus values (Figure 4 (a-b)) than neat PLA. The rubbery nature of NR leads to a decrease in tensile strength and modulus. Also, the tensile strength and modulus of PLA/NR/RS biocomposites films were lower compared to neat PLA and PLA/NR blends, and they decreased with increasing RS contents. This is common in natural fiber composites. The PLA are hydrophobic, but the most natural fibers are hydrophilic, which prevents them from forming good interfacial adhesion[14]. The tensile strength and modulus of the films are lower in the transverse direction (TD) than they are in the machine direction, but both directions exhibit the same trend.

Elongation at break of neat PLA, PLA/NR, and PLA/NR/RS biocomposite films is shown in figure 4 (c). When RS is added, the elongation at break of PLA/NR/RS biocomposite films is decreased. As a result of poor interfacial adhesion. Moreover, the presence of RS fiber limits the mobility of PLA and NR polymeric chains, which hinders the chains ability to elongate. As a result, elongation at break decreases. However, all biocomposite films still showed a significantly higher elongation at break than that neat PLA. The films' elongation at break is much lower in the transverse direction than it is in the machine direction.

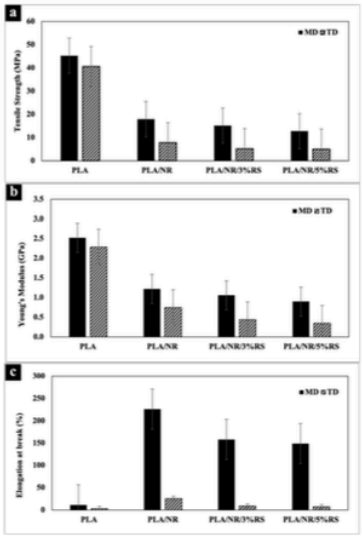

Figure 4. Average tensile properties of neat PLA, PLA/NR, and PLA/NR/RS biocomposite film; (a) Tensile strength, (b) Young's Modulus, and (c) Elongation at break.

Figure 5 (a–d) shows the FE-SEM micrographs of the tensile fracture surfaces of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films. Figure 5 (a) shows that the surface of the neat PLA film was smooth, which is typical for brittle polymers. Phase separated morphology could be seen in the PLA/NR blends (figure 5(b)), many NR droplets were found in the PLA matrix. This indicated that blends of PLA and NR were immiscible.

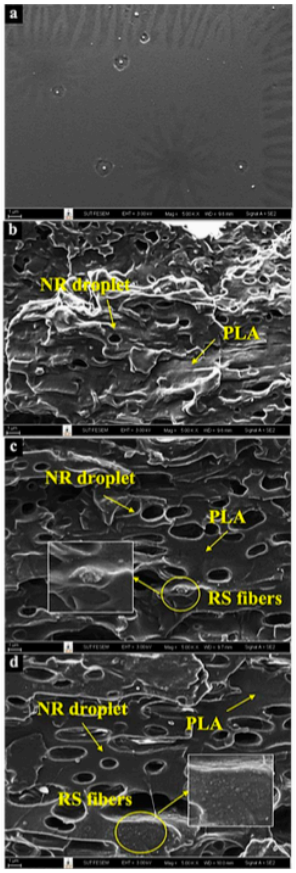

Figure 5. FE-SEM micrographs at 5000×magnification of tensile fracture surface of (a) neat PLA, (b) PLA/ NR, and PLA/NR/RS biocomposite films at RS contents of; (c) 3%, and (d) 5%.

When RS fibers were added to PLA/NR, it was discovered that the lager extent of phase separation. (Figure 5 (c-d)). This occurs from the difference in polarity of the composite system. Only a little amount of the RS fiber could be observed on the fracture surface of PLA/NR/RS biocomposite films. It shows that the RS fiber was well embedded in the polymer matrix.

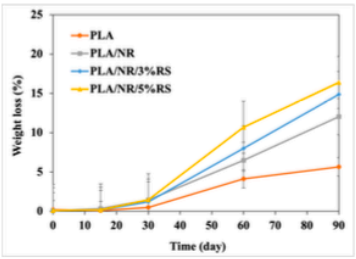

Figure 6. Weight loss percentage of PLA, PLA/NR, and PLA/NR/RS biocomposite films.

The biodegradability of the film samples was followed by measuring the percent weight loss of samples after 15, 30, 60, and 90 days of soil burial, as shown in Figure 6. PLA was discovered to have the lowest weight loss percentage, which refers to the slowest degradation, when compared to the PLA/NR blend and the PLA/NR/RS biocomposites. By adding NR to PLA, the percentage of weight loss increased. This is due to the incompatibility of PLA and NR. Heterogeneous structures are usually destroyed faster than homogeneous ones [5]. It was observed that NR influences the hydrolysis, which is the initial stage of the PLA degradation process [15]. Moreover, other factors such as temperature, moisture, water absorption, bacteria, and mold in the soil influence its reactivity and accessibility. The percentage of water absorption increased when NR was present because it made the matrix's amorphous region larger [6]. This could be the explanation why PLA/NR observed greater weight loss than PLA. With an increase in RS content, the weight loss percentage increased. The natural fibers' hydrophilic properties led to a higher degradation rate [14]. The

degradation rate of all polymers was found to be slow in the initial degradation rate, with the onset of more decomposition occurring after several months.

4. Conclusions

In this study, biocomposite films were made using PLA/NR/RS composites, which were developed by adding RS powder to the PLA/NR blend at concentrations of 3, 5, and 10% by weight, to investigate the production and properties of biocomposite films that could be used in agriculture. From the test results, it was found that the MFI values of the PLA/NR blend and the composites were higher than PLA. Except for the biocomposite films containing 10 %wt. RS, all the films showed a smooth surface and could be subjected to mechanical and biodegradable tests. The brittleness of neat PLA changed into a ductile fracture when NR was added. The tensile strength and modulus of PLA/NR/RS biocomposites films were lower compared to neat PLA and PLA/NR blends, and they decreased with increasing RS contents. However, the biocomposite films still showed a significantly higher elongation at break than neat PLA. FE-SEM analysis revealed phase separated morphology in PLA/NR blends and PLA/NR/RS biocomposites films. When the biodegradability of the film samples was evaluated after 15, 30, 60, and 90 days of soil burial, PLA was found to have the lowest weight loss percentage. The percentage of weight loss increased when the NR and RS were added. The biocomposite with 5 wt.% RS showed the greatest weight loss. From the above results, low-cost and biodegradable agricultural films are possibly produced from PLA/NR/RS biocomposite.

Acknowledgements

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5. References

1 Haase, D. L.; Bouzza, K.; Emerton, L.; Friday, J.B.; Lieberg, B.; Aldrete, A.; Davis, A.S. *Land*. 2021, 10(8), 826.

2 Da Costa, J.P.; Nunes, A.R.; Santos, P.S.M.; Girão, A.V.; Duarte, A.C.; Rocha-Santos, T. *J. Environ. Health,* 2018, 53(9); pp 866-875.

3 Buys, Y.F.; Aznan, A.N.A.; Anuar, H. *Mater. Sci. Eng.,* 2017, 290(1); pp 1-8.

4 Huang, Y.; Zhang, C.; Pan, Y.; Zhou, Y.; Jiang, L.; Dan, Y. *Polym. Degrad. Stab.,* 2013, 98(5); pp 943-950.

5 Tertyshnaya, Y. V.; Karpova, S.G.; Podzorova, M.V.; Khvatov, A.V.; Moskovskiy, M.N. *Polym,* 2022, 14(5); pp 1-16.

6 Rosli, N.A.; Ahmad, I.; Anuar, F.H.; Abdullah, I. *J. Clean. Prod.,* 2018, 198; pp 987-995.

7 Zaaba, N.F.; Jaafar, M. *Polym Eng Sci,* 2020, 60(9); pp 2061-2075.

8 Kophimaia, Y.; Cheenacharoenb, S.; Simisterc, R.; Gomezc, L.D.; McQueen-Masonc, S.J.; Vuttipongchaikij., S. *J Agric Nat Resour,* 2020, 54; pp 617-622.

9 Singh, G.; Arya, S. K. *J. Clean. Prod.,* 2021, 291(125278); pp 1-64.

10 Beniwal, P.; Toor, A.P. *Ind Crops Prod.,* 2023, 192(116098); pp 1-9.

11 Pongputthipat, W.; Ruksakulpiwat, Y.; Chumsamrong, P. *Polym. Bull.*, 2022; 1-19.

12 Eselini, N.; Tirkes, S.; Akar, A.O.; Tayfun, U. *J. Elastomers Plast*., 2019; 1-16.

13 Van Krevelen, D. W.; Te Nijenhuis, K. *Properties of Polymers*, 2009.

14 Alias, N. F.; Ismail, H.; Ishak, K.M.K. *Iran. Polym. J,* 2021, 30(7); pp 737-749.

15 Rahmani, M.; Khani, M.M.; Rabbani, S.; Mashaghi, A.; Noorizadeh, F.; Faridi-Majidi, R.; Ghanbari, H. *Mater. Sci. Eng. C.*, 2020, 110626; pp 1-15.

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ORIGINAL PAPER

Soil burial degradation of bio-composite films from poly(lactic acid), natural rubber, and rice straw

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Abstract

Agricultural activities contribute to numerous waste problems and have emerged as a significant environmental concern. Nondegradable plastic residues decompose, releasing microplastics and affecting ecosystems and the environment. Consequently, biodegradable bio-composite films consisting of polylactic acid (PLA), natural rubber (NR), and rice straw (RS) have been developed with the aim of using them in agricultural applications. In this study, the PLA/NR blend, at a fixed ratio of 60/40 wt%, was filled with 3 and 5 wt% RS powder and extruded through a slit die into films. The biodegradability of all films was examined after being buried for 90 days in soil with a moisture content of 30% by weight. The neat PLA film showed the lowest weight loss percentage, 3.33%, suggesting a comparatively slower degradation rate in comparison to the PLA/NR(60:40) blend and all bio-composite films. The presence of 40 wt% NR in the film helped accelerate the biodegradation process during soil burial. The film produced from PLA/NR 60:40 wt% matrix filled with RS at 5 wt% led to rapid degradation, leading to a weight loss of 8.30%. From SEM micrographs, the morphology of all polymers after burial in soil showed fractures, the formation of pores, and obvious surface indications of fungi growing. The content of carbon decreased after soil burial, while oxygen content increased, and nitrogen was detected. The XRD analysis revealed low crystallinity in the neat PLA, consistent with the DSC analysis. The addition of NR and RS to the composites led to an increase in the crystallinity of PLA phase. All investigated materials exhibited an increase in crystallinity after being buried in soil. This research demonstrates that bio-composite films manufactured from the PLA/NR(60:40) blend filled with RS degrade more easily than unmodified PLA film.

Keywords Biocomposite · Biodegradability · Poly(lactic acid) · Natural rubber · Rice straw

Extended author information available on the last page of the article

Introduction

Across the globe, the agricultural sector is regarded as being essential to the economy and society. But on the other hand, there is also a lot of waste generated from agricultural activities. Plastic films, like mulch film and seedling bags, are one of them. The remaining plastic is hard-to-remove waste and can cause many environmental problems if disposed of improperly. Proper disposal requires time and space, and different categories of garbage require specific procedures and approaches. This disparity in disposal practices can lead to complications in managing plastic waste effectively. The presence of these nondegradable plastic residues in the environment will begin to degrade because of the effects of the environment around them, releasing microplastics ranging from 1 μm to 5 mm in size [1]. Microplastics have significant negative effects on the health of organisms as well as across the food chain [2]. One possible approach to solving the problem of plastic waste involves the use of biodegradable plastic. The utilization of biodegradable plastic offers eco-friendly alternatives to synthetic plastic, but poor mechanical and barrier properties necessitate the development of fillers and composites [3].

This study focuses on poly (lactic acid) (PLA), a type of biodegradable plastic. PLA is a semi-crystalline thermoplastic polyester synthesized from the ring-opening polymerization of lactides derived from the bacterial fermentation of food residues and natural polysaccharides such as corn starch, sugar beet, and wheat [4, 5]. PLA can be naturally degraded through ester bond hydrolysis under specific conditions. This process, involving moisture, oxygen, and microorganisms, results in chemical reactions like photoionization and chain scission. Exposure to moisture causes ester groups to cleave, reducing PLA's molecular weight and enhancing its crystallinity. Microbial and enzyme processes are crucial in the degradation process. Microbial degradation converts organic compounds to less toxic or useful forms, while enzymes like lipase, esterase, and alcalase play a crucial role in breaking down PLA. The increased nitrogen content accelerates PLA degradation, with bacteria colonizing PLA surfaces and releasing enzymes that hydrolyze its polymeric structure. These enzymes are consumed by bacterial cells as a nutrient substrate, facilitating total degradation on both the surface and inside the material [6]. In addition, fungi are attention in biodegradation research due to their ability to colonize extreme environments, produce enzymes for chemical compound degradation, and their hydrophobin proteins, which enable them to adhere to surfaces like plastics [7]. Nevertheless, polylactic acid (PLA) is still expensive and exhibits a higher degree of resistance to degradation compared to other types of biodegradable plastics [8]. Despite its compatibility with various processing techniques, its high glass transition temperature causes brittleness in final products [9, 10]. Consequently, PLA is frequently blended with other biopolymers to enhance its original characteristics. Blending with natural rubber (NR) is a common method for reducing PLA brittleness due to its excellent elasticity, ductility, and low cost [11–13], and natural rubber can also reduce PLA degradation time and improve decomposition [14–16]. However, it was reported that the degradation behavior of PLA/NR blends is affected by composition of the blends [14, 17].

Furthermore, PLA, a hydrophobic polymer, exhibits a long process of biodegradation in landfill environments. To attain biodegradability, hydrophilic fillers such as starch or cellulose are preferred due to their ability to produce lactic acid. Due to this, the process of landfill biodegradation involves hydrolysis and hydrolytic degradation, where the absorption of water plays a critical role. The addition of hydrophilic fillers has the potential to improve the degradation of PLA in landfills by enhancing its ability for water absorption. The enzymatic hydrolysis of cellulose results in the formation of lactic and silicic acids. These acids act as catalysts in the hydrolytic degradation process, leading to the generation of carboxylic acid end groups. These end groups increase the rate of deterioration, as observed in the study on the degradation of PLA reinforced with high-lignin-containing microfibrillated cellulose [17–20]. It was discovered that the biocomposites did not have any antibacterial properties. This was attributed to the bacterial degradability of the lignocellulosic components, which led to the degradation of the composites. Rice straw (RS) is an agricultural waste consisting of 12% lignin, 38% cellulose, and 25% hemicellulose [21]. The surface of rice straw contains polar groups like hydroxyl, which renders it polar [22, 23]. Therefore, using rice straws assists in PLA degradation [24].

Biodegradability of biodegradable and bio-composite materials for agricultural films has been widely assessed by soil burial test, which determine material weight loss with time [25–29]. Soil components like fungi, bacteria, earthworms, and insects can break down plastic films by bio-fragmentation, which is crucial for enhancing the film's surface area accessible to microorganisms [30]. Soil burial test also allows for detailed examination of the sample's transformations during testing, such as changes in chemical composition (using energy dispersive X-ray analysis (EDX)), biological erosion of the film surface (via electron microscopy), or alterations in physical properties associated with degradation. Additionally, agricultural films are prone to being ploughed into the soil and buried in the ground at the end of a growing season. If the biodegradability of the films in soil is known, it can ensure the successive biodegradation process, which consequently gives rise to compost, which is a fertilizer for the ground.

As mentioned earlier, PLA is a biobased and biodegradable polymer that has low toughness, a slow biodegradation rate, and remains expensive. The biodegradable, elastic, and cost-effective natural rubber (NR) was blended with polylactic acid (PLA) to create flexible agricultural films. Consequently, the blend was filled with rice straw (RS), which is an agricultural waste, to enhance its biodegradability. A prior study [31] successfully produced a bio-composite film made of a PLA/NR blend ratio of 70:30 wt% filled with RS powder. Their mechanical and morphological characteristics, as well as their weight loss after being buried in soil for 90 days, have been proposed. To further study the blending of a higher amount of NR with PLA to obtain lower-cost films, the amount of NR was increased to 40 wt%. In addition, the thinner film was designed in the current work, so the screw speed of the single screw extruder during casting films was 40 rpm, whereas 50 rpm was used in the previous study. The increased amount of NR and reduced screw speed led to a decrease in film thickness. The maximum amount of RS that could be filled in the PLA/NR(60:40) blend and cast into film was 5 wt%. The tensile test findings indicated that the incorporation of NR changed the brittleness of neat PLA into a ductile fracture. With an increase in

RS concentration, the tensile strength and modulus of bio-composite films dropped. Despite this, the elongation at break remained notably higher than that of neat PLA, and all bio-composite films have the potential to be formed into eco-friendly planting bags [32]. The interesting point of the current work is to know the biodegradation behavior in soil of bio-composite films prepared using a high amount of NR and the lower film thickness. This study investigated the biodegradation of PLA/NR/RS film with a fixed ratio of PLA/NR of 60:40 wt% through soil burial. The study observed weight loss percentage and changes in crystallinity, chemical composition, and thermal properties to assess biodegradability for potential applications in designing or utilizing biodegradable films in the future.

Methodology

Materials

Poly(lactic acid) (PLA, Ingeo 4043D) was purchased from NatureWorks. Natural rubber (NR, STR 5 L) was purchased from Natural Art and Technology Co., Ltd. Rice straw (RS) was collected from a rice processing factory in Nakhon Ratchasima Province, Thailand.

Preparation of PLA/NR/RS masterbatch

Poly(lactic acid) (PLA) and rice straw (RS) powder (~53 μm long) were dried overnight in an oven at 80 °C to eliminate moisture. The mastication process was employed for mixing the natural rubber (NR) and RS powder using a two-roll mill (Yong Fong Machinery, YFY-R-6). This process was carried out over a period of 10 min, using a roller speed of 10 rpm. The RS content varied within the range of 3 and 5 wt% based on the overall weight of the PLA/NR blend. The ratio between PLA and NR was maintained at a constant value of 60/40 wt%. Then, PLA was mixed with the NR/RS for 10 min at a temperature of 170 °C with a rotor speed of 60 rpm using an internal mixer (Haake Rheomix, 3000P). The masterbatch obtained is subsequently processed into sheets using a two-roll mill at a roller speed of 10 rpm. The sheets were sliced into long strips in preparation for the PLA/NR/RS masterbatch (MB).

Preparation of PLA/NR/RS bio-composites

The PLA/NR/RS masterbatch was mixed with PLA in a 50/50 ratio of MB/PLA using a twin-screw extruder (Brabender, PL2100). The temperatures of the barrel in zones 1, 2, 3, 4, and 5 were 150, 165, 175, 180, and 170 °C, respectively. The screw speed was 40 rpm. Subsequently, the PLA/NR/RS bio-composites were crushed into smaller pieces in a plastic recycling machine (Tranekaer, DK-5953). The composition of the PLA/NR(60:40) blend and the composites is shown in Table 1.

Table 1 Formulations of PLA/NR(60:40) blend and PLA/NR/RS bio-composites

Sample code	PLA (wt%)	NR (wt%)	RS (wt%)
Neat PLA	100.0	-	-
PLA/NR (60:40)	60.0	40.0	-
PLA/NR/3%RS	58.2	38.8	3.0
PLA/NR/5%RS	57.0	38.0	5.0

Composite films preparation

The neat PLA, the PLA/NR(60:40) blend, and the PLA/NR/RS bio-composites were packed and melted in the extruder. The temperature in the barrel (zones 1, 2, 3, and 4) was set at 45, 165, 180, and 190 °C, and the slit die zone was 190 °C. The screw speed, chill roll speed, and temperature of the chill roll were 40 rpm, 6 rpm, and 60 °C, respectively.

Soil burial biodegradation

The film samples, dimensions 3×3 cm, were buried in soil with a moisture content of 30% by weight and at a depth of 15 cm. The samples were retrieved after being buried for periods of 15, 30, 60, and 90 days. The retrieved samples went through a cleaning process using distilled water and were subsequently dried in a vacuum oven at a temperature of 40 °C until a constant weight was achieved. The calculation of the weight loss percentage for the film samples was done using Eq. (1).

$$\text{Weight loss}\,(\%) = \left(\frac{W_i - W_t}{W_i}\right) \times 100 \tag{1}$$

Where w_i represents the initial dry weight of the samples, while w_t represents the dry weight of the sample retrieved after being buried in soil for a determined time [33].

Morphological characterization

The morphological characteristics of all films (0.3×0.3 cm) were examined using a field emission scanning electron microscope (FE-SEM) (Zeiss AURIGA FE-SEM). To be able to separate the different phases, the rubber phase was stained with osmium tetroxide for 24 h. Before performing FE-SEM analysis, a carbon coating on the surfaces of the samples was applied. The samples were imaged using a FE-SEM with a 3 kV acceleration voltage.

Chemical components characterization

The chemical components of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite film samples were obtained using JEOL JSM-7800 field emission scanning electron microscopy (FESEM) with energy dispersive X-ray analysis (EDX) at 3 kV. The sample was prepared using a methodology like that employed for FE-SEM analysis, with the difference that a gold coating was applied to the surfaces of the samples.

Thermal characterization

The thermal characteristics of all films were determined using a differential scanning calorimeter (METTLER TOLEDO, DSC 3+). For the measurements, 5–10 mg of samples was sealed in an aluminum pan. The sample was heated from 25 to 200 °C at a rate of 5 °C/min (the first heating) and held for 2 min under a nitrogen atmosphere, then cooled to 25 °C at a rate of 5 °C/min (cooling) before being heated to 200 °C at a rate of 5 °C/min (the second heating). The degree of crystallinity (Xc) of the PLA phase in polymer composites was calculated based on the enthalpy value of a 100% crystalline PLA using the following Eq. (2).

$$X_c\,(\%\text{crystallinity}) = \left(\frac{\Delta H_m - \Delta H_c}{w \times \Delta H_m^0}\right) \times 100 \tag{2}$$

Where ΔH_m is the measured endothermic enthalpy of melting and ΔH_c is the cold crystallization exothermic enthalpy during the heating scans. $\Delta H_m^0 = 93.7$ J/g, and w is the weight fraction of PLA in the sample [34].

Crystalline structure characterization

X-ray diffraction (XRD) investigations were conducted on the neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite film samples (3×3 cm) using an X-ray diffractometer (Bruker, D2 PHASER) equipped with a CuKα (λ=1.54 Å) to identify the crystalline phases present in the materials. The samples were scanned in the range of 5 degrees to 50 degrees.

Results and discussion

Physical characteristics of the neat PLA, PLA/NR(60:40) blend, and Bio-composite films

Figure 1 (a–d) shows the physical characteristics of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films. The PLA film was yellow and translucent, the PLA/NR(60:40) blend film was semi-opaque, and the bio-composite films were opaque light brown.

Table 2 illustrates the thickness of all films produced in the current work. The film thickness is notably thinner compared to the films produced in the prior study [31]. Adding 40 weight% of natural rubber (NR) to polylactic acid (PLA) as a matrix for bio-composite production and using a screw speed of 40 rpm during film casting resulted in significantly thinner films.

Biodegradability

The degradation of neat PLA, PLA/NR(60:40) blend, and bio-composites was confirmed by visually observing the physical appearance of the samples and measuring

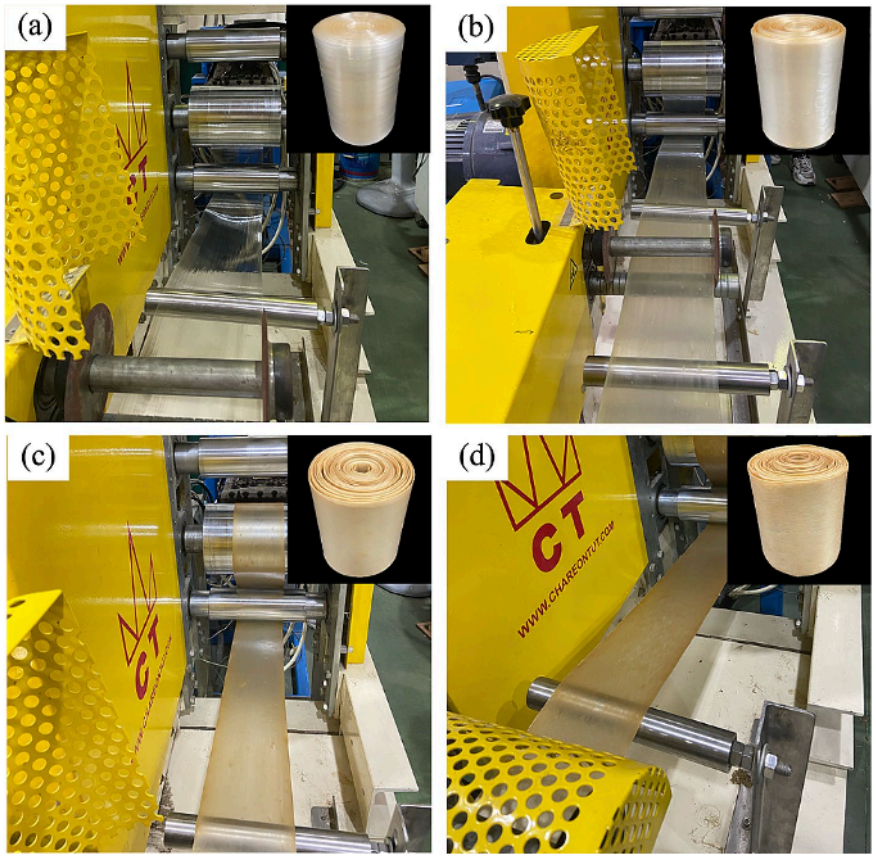

Fig. 1 Photographs of the cast films: neat PLA (**a**), PLA/NR(60:40) blend (**b**), and PLA/NR/RS bio-composite at RS contents of 3 wt% (**c**) and 5 wt% (**d**)

Table 2 The thickness of the films prepared in the present study and in the previous study

Cast film	Thickness (mm)	Source
Neat PLA	0.336±0.010	Previous study [31]
PLA/NR(70:30)	0.251±0.043	
PLA/NR/RS(3%)	0.296±0.029	
PLA/NR/RS(5%)	0.298±0.031	
Neat PLA	0.202±0.011	Present study
PLA/NR(60:40)	0.054±0.010	
PLA/NR/3%RS	0.140±0.011	
PLA/NR/5%RS	0.160±0.013	

the percentage of weight loss. Figure 2 displays the photographs of film samples that were taken both before and after the burial test. After 90 days of burial in soil, the transparency of the neat PLA was replaced by an opaque white. The PLA/NR(60:40) blend and PLA/NR/RS bio-composite showed a slight color change, and the trace of fungi was obviously detected on the surface.

The weight loss percentages of the film samples after being buried in soil for different durations (15, 30, 60, and 90 days) are plotted in Fig. 3. The study results show that neat PLA exhibits the lowest weight loss percentage, indicating a slower degradation rate in comparison to both the PLA/NR(60:40) blend and the PLA/NR/RS bio-composite. Generally, PLA degradation occurs through hydrolytic and microorganism processes, with high temperatures, humidity, and water absorption enhancing this process [34, 35]. In this study, soil temperature and moisture may not be high enough to enhance the degradation of PLA. According to other reports, if the temperature remains below the Tg value, the degradation of the PLA is limited to its surface [36, 37].

The addition of the NR led to an increase in the percentage of weight loss. This results from the incompatibility of PLA and NR. In general, heterogeneous structures disintegrate more rapidly than homogeneous ones [16]. The heterogeneous structure of the PLA/NR blend causes an increased percentage of water absorption [38, 39]. The presence of NR enhances the process of water absorption, which is the primary PLA degradation mechanism and involves hydrolysis. This phenomenon results in an increase in the crystallinity section, which remains even after biodegradation [40, 41].

Higher weight loss percentages are associated with increased fiber content in composite materials. The hydrophilic properties of natural fibers, including cellulose and hemicellulose, indicate higher degradation rates and water absorption in composite

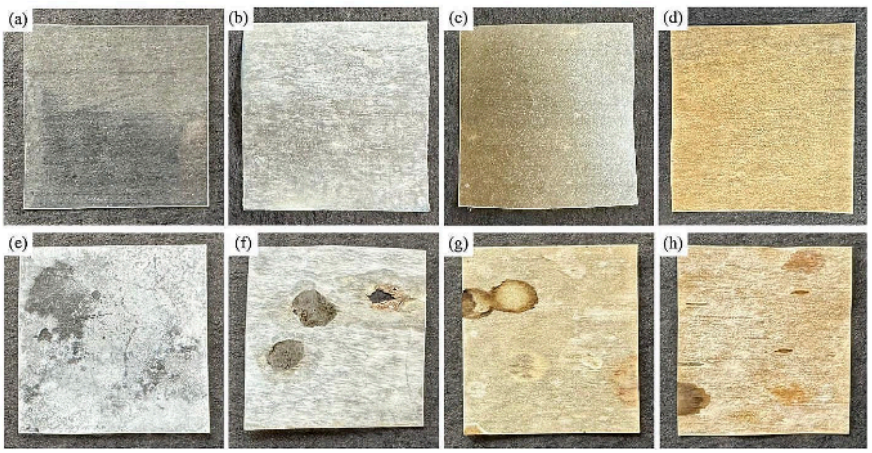

Fig. 2 Physical appearance of neat PLA (**a**), PLA/NR(60:40) blend (**b**), PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**) before soil burial test and neat PLA (**e**), PLA/NR(60:40) blend (**f**), and PLA/NR/RS bio-composite films at RS contents of 3 wt% (**g**) and 5 wt% (**h**) after soil burial test for 90 days

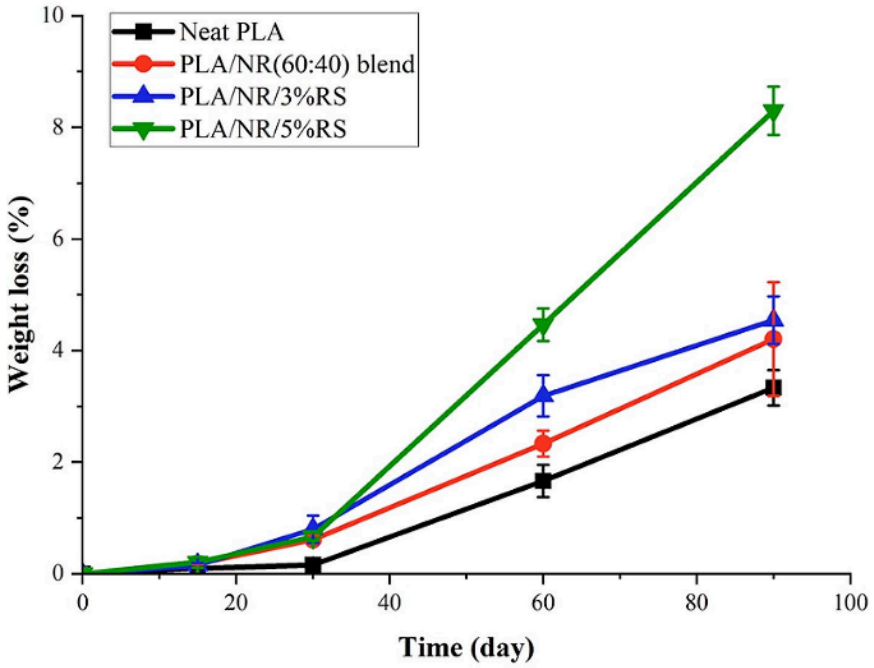

Fig. 3 Weight loss percentage of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films

materials [42–44]. As a result of higher water absorption, the molecular chain of PLA in the composites underwent hydrolytic degradation and was shortened. The small molecules can be assimilated by microorganisms during the degradation process. Consequently, the PLA/NR/RS bio-composite films showed a higher degradation rate. The initial degradation rate of all films appears to be slightly slow, with the onset of more decomposition occurring a few months later.

Prior research included developing bio-composite films using a PLA/NR ratio of 70:30 wt% [31]. The film sample's weight loss was observed to rise when NR and RS were present. A bio-composite matrix was created in this study by combining PLA and NR in a 60:40 weight ratio and employing a reduced screw speed to produce thinner films. The films deteriorated faster when buried in soil, as demonstrated in Table 3. There are reports in research that the thinner bioplastic sample tends to show higher water absorption [45] or a higher percentage weight loss [46]. NR facilitates water penetration into the test samples, accelerating the degradation of PLA. Increased NR content leads to higher water absorption [38].

Morphological properties

Figure 4 displays the FE-SEM micrographs depicting the surface characteristics of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films prior to their exposure to soil burial. The neat PLA film exhibited a smooth surface, in contrast

Table 3 Comparing the weight loss percentage of the neat PLA, PLA/NR blend, and PLA/NR/RS bio-composite films after being buried in soil for 90 days

Cast film	PLA (wt%)	NR (wt%)	RS (wt%)	Weight loss (%)	Source
Neat PLA	100	-	-	1.7351±0.6257	Previous study [31]
PLA/NR(70:30)	70.0	30.0	-	1.7811±0.5817	
PLA/NR/RS(3%)	67.9	29.1	3.0	2.1230±0.2910	
PLA/NR/RS(5%)	66.5	28.5	5.0	2.7230±0.3417	
Neat PLA	100	-	-	3.3324±0.3167	Present study
PLA/NR(60:40)	60.0	40.0	-	4.2029±1.0196	
PLA/NR/3%RS	58.2	38.8	3.0	4.5424±0.4242	
PLA/NR/5%RS	57.0	38.0	5.0	8.2979±0.4307	

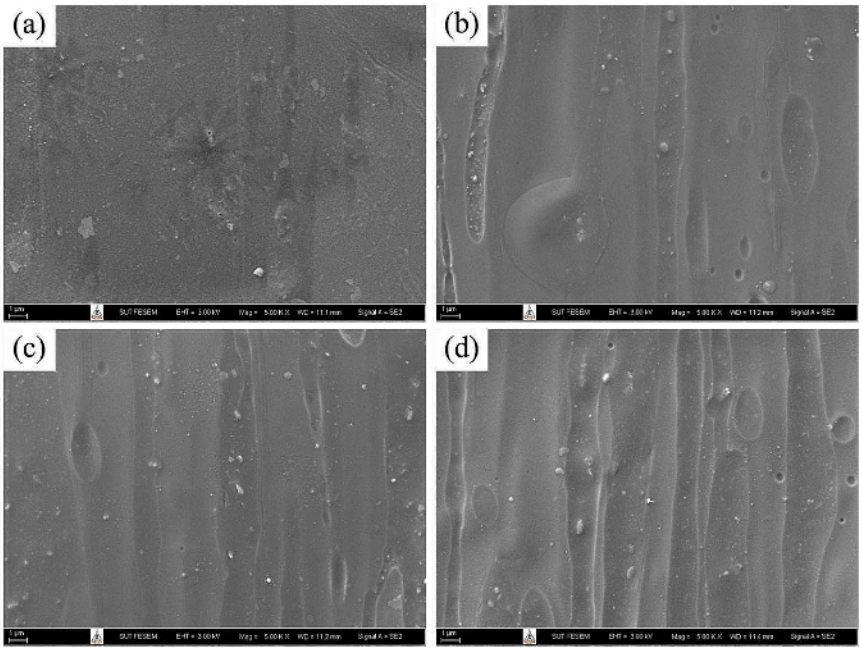

Fig. 4 FE-SEM micrographs at 5000x magnification of film surface of neat PLA (**a**) PLA/NR(60:40) blend (**b**), and PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**)

to the PLA/NR(60:40) blends and PLA/NR/RS bio-composite, which exhibited surface roughness and a heterogeneous phase surface. This occurrence arises due to the immiscibility of all polymers.

After a 90-day soil burial, the morphology of all films changed, as seen in Fig. 5. The surfaces of the neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films displayed numerous fractures and pores, as well as obvious indications of fungus growth on the blend and composite film surfaces. These results are similar to those from earlier studies that found bacterial and fungal propagules, such as repro-

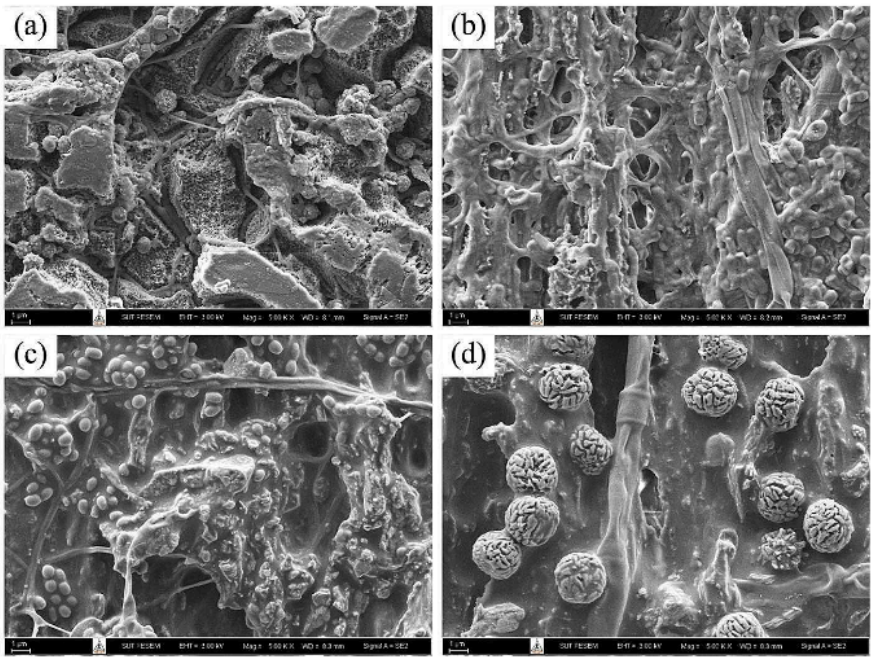

Fig. 5 FE-SEM micrographs at 5000x magnification of film surface after soil burial for 90 days of neat PLA (**a**) PLA/NR(60:40) blend (**b**), and PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**)

ductive hyphae and spores, on plastic surfaces that were breaking down [47, 48]. Moreover, the addition of RS to PLA has been seen to result in an increase in fungal populations as well as a growth in their size. The water absorption ability of RS [49] leads to polymer swelling, which in effect enhances microbial attack and increases microbial activity. This rise in microbial activity is dependent on the presence of water and oxygen [50].

EDX analysis

The chemical composition of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films was analyzed using SEM-EDX both before and following a 90-day period of soil burial. The data in Table 4 shows that the main elements found in the neat PLA, the PLA/NR(60:40) blend, and the PLA/NR/RS bio-composite samples before being buried in soil were carbon (C) and oxygen (O). After soil burial for a period of 90 days, nitrogen (N) was detected. The presence of nitrogen can be explained by the release of biological compounds from fungal spores, specifically proteins [51]. Nitrogen is a vital element of plant nucleic acids, enzymes, and proteins, playing a crucial role in facilitating a wide range of metabolic reactions after decomposition [21]. Furthermore, it was observed that the element C content decreased after the burial of all polymer films in soil, whereas the element O content

Table 4 EDX analysis of element contents of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio- composite film before and after burial in soil for 90 days

Sample code	Before burial in soil		After burial in soil		
	C/wt%	O/wt%	C/wt%	O/wt%	N/wt%
Neat PLA	84.97	15.03	61.65	24.63	13.72
PLA/ NR(60:40)	75.33	24.67	55.27	31.35	13.38
PLA/NR/3%RS	73.93	26.08	53.14	33.21	13.65
PLA/NR/5%RS	74.12	25.89	51.36	32.89	15.75

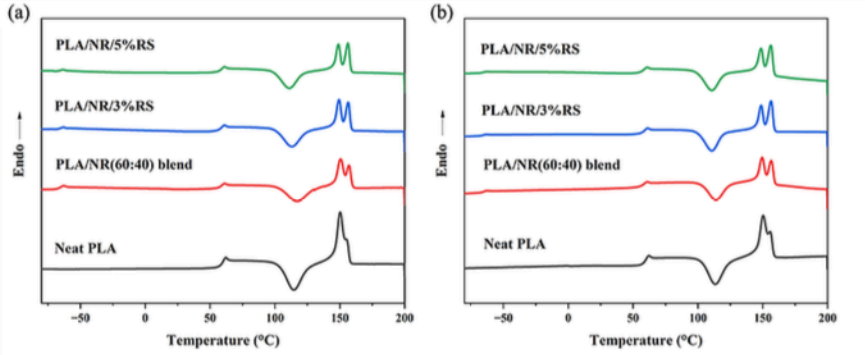

Fig. 6 DSC thermograms of neat PLA, PLA/NR(60:40) blend, PLA/NR/3%RS, and PLA/NR/5%RS bio-composite films before (**a**) and after (**b**) burial in soil for 90 days

increased. The confirmation of biodegradation is supported by the observed decrease in carbon content, while the increase in oxygen percentage serves as an offset to the decrease in carbon atomic percentage. This indicates that oxidation reactions occur on all polymers during the process of biodegradation [52].

DSC analysis

Differential scanning calorimetry (DSC) is used for evaluating the thermal characteristics of polymers. Phase transitions, crystallization behaviors, and thermal heat capacity are a few of these features. When analyzing changes in thermal characteristics during polymer processing, DSC makes it simpler to find and examine the degradation that is produced [53]. For the purpose of understanding the structural changes of materials, this study only presented data from the first heating scan (Fig. 6), which reveals the PLA in its crystalline form in the molded samples [54]. To study the change of thermal behavior from degradation, the glass transition temperature (Tg), melting temperature (Tm), cold crystallization temperature (Tcc), and degree of crystallization (Xc) of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite film samples were measured before and after they were buried in soil, as shown in Table 5.

The neat PLA exhibited a glass transition temperature (Tg) of 62.67°C. When natural rubber (NR) was added to PLA, two distinct Tg values were observed at -67.68°C and 63.83°C, which corresponded to the NR and PLA phases, respectively.

Table 5 DSC Results of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films before and after burial in soil for 90 days

Sample code	$Tg_{(NR)}$ (°C)	$Tg_{(PLA)}$ (°C)	Tcc (°C)	Tm_1 (°C)	Tm_2 (°C)	Xc (%)
Neat PLA	-	62.67	100.65	148.41	153.58	3.97
Neat PLA After	-	63.47	100.68	150.83	156.17	4.31
PLA/NR(60:40) Before	-67.68	63.83	89.54	147.25	154.75	7.92
PLA/NR(60:40) After	-67.78	63.16	91.18	147.42	155.25	9.62
PLA/NR/3%RS Before	-68.80	63.20	92.95	139.90	155.33	9.54
PLA/NR/3%RS After	-67.51	63.62	93.68	144.20	155.92	10.78
PLA/NR/5%RS Before	-68.24	62.53	91.60	145.01	155.08	11.63
PLA/NR/5%RS After	-67.69	63.37	93.63	147.67	158.92	13.03

The incompatibility of PLA and NR blends is responsible for the presence of two glass transition temperatures (Tg) [12]. Two distinct melting peaks in a polymer indicate the presence of two different crystalline forms. The higher temperature at which the melting peak was established indicates a more well-formed crystalline structure. The occurrence of two distinct melting peaks in the PLA phase is attributed to the transformation of α' crystals into α crystals [55]. The addition of NR and RS to the PLA did not result in any significant change in the Tg and Tm values. Incorporating NR leads to a decrease in Tcc, leading to a shift to lower temperatures. Previous studies have demonstrated that elastomers enhance the mobility of polymer chains and expedite the process of crystallization in PLA [56, 57]. A slight increase in Tcc was seen after the addition of RS to the PLA/NR(60:40) blend, while it decreased in comparison to the neat PLA. RS exhibited potential as a nucleating agent, hence enhancing the crystallization process [58, 59]. In addition, the addition of NR to PLA results in an obvious increase in crystallinity (Xc), and it increases significantly more when RS is added. This information is related to NR and RS, which may operate as nucleating agents to increase the crystallization process of PLA [60, 61].

After a 90-day period of soil burial, the Tg of all polymers was similar, suggesting that the soil burial had no effect on the Tg of all polymers. Tcc and Tm rose by 1–3 °C after the degradation process. The crystallinity (Xc) of all polymers got higher, with a somewhat higher level observed in the blend and composites. NR and RS could facilitate the degradation process by enhancing water penetration into the amorphous phase, which is usually less resistant to microbial activity and hydrolysis than the crystalline phases. This process broke molecular chains in the disordered regions, facilitating the movement and reorganization of the remaining molecular chains into a crystalline structure [50, 62, 63].

XRD analysis

XRD analysis was used to monitor changes in the crystalline structure of the polymers resulting from degradation. Figure 7 shows the X-ray diffraction (XRD) patterns of the samples both before and after being buried in soil for 90 days. The XRD patterns of PLA exhibited a broad peak at approximately $2\theta = 16°$, showing the absence of distinct diffraction peaks and thus demonstrating its mainly amorphous structure [64]. The obtained results are in accordance with the DSC analysis, which indicated

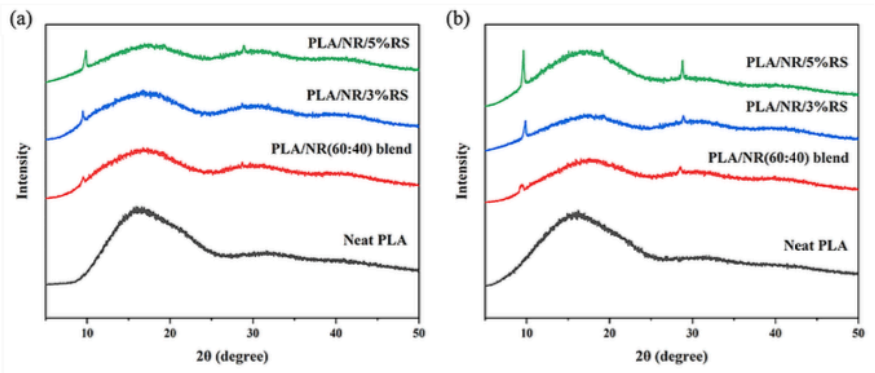

Fig. 7 XRD patterns of neat PLA, PLA/NR(60:40) blend, PLA/NR/3%RS, and PLA/NR/5%RS bio-composite films before (**a**) and after (**b**) burial in soil for 90 days

a significantly low degree of crystallinity. The degree of crystallinity was so low that it could not be detected using XRD analysis. The observed XRD pattern of PLA/NR(60:40) blend and PLA/NR/RS bio-composite revealed the appearance of diffraction peaks at $2\theta = 10°$ and $2\theta = 28°$. This indicates that the presence of NR and RS produced an effect on the crystalline structure of PLA. Following soil burial, it was noted that the intensity of all diffraction peaks increased, with a corresponding increase as the RS concentration increased. With the increase in RS content, the composites were degraded more effectively, leading to the generation of more low-molecular-weight chains. This resulted in enhanced molecular mobility and higher intensity in the diffraction peaks. This occurrence has also been observed in PLA/starch composites [65]. The finding corresponds with the earlier indicated % weight reduction.

Conclusions

This study aims to assess the biodegradation behavior of PLA/NR/rice straw bio-composite films manufactured using a PLA/NR blend ratio of 60:40 wt% filled with 3–5 wt% rice straw powder when buried in soil for 90 days. The bio-composite films in the present study showed a higher weight loss compared to the films made from a PLA/NR blend with a ratio of 70:30 wt% filled with the same amount of rice straw powder in the previous study [31]. The neat PLA film showed the lowest weight loss percentage, 3.33%, suggesting a comparatively slower degradation rate in comparison to the PLA/NR blend and all bio-composite films. The film produced from PLA/NR 60:40 wt% matrix filled with RS at 5 wt% led to rapid degradation, leading to a weight loss of 8.30%. FE-SEM micrographs revealed the occurrence of fractures, the formation of pores, and the visible signs of fungi on the film after being buried in soil. The EDX analysis showed the presence of nitrogen element and the content of carbon decreased after soil burial, while the oxygen content increased, indicating oxidation reactions during biodegradation. The XRD analysis revealed low crystallinity in the PLA, consistent with the DSC analysis. The addition of NR and RS to the composites led to an increase in the crystallinity of PLA. All investigated materials exhibited an increase in crystallinity after being buried in soil with lowest increase found for

neat PLA. This study shows that bio-composite films manufactured from the PLA/NR(60:40) blend filled with RS deteriorate more easily than unmodified PLA film.

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Author contributions C.R. wrote the main manuscript.W.P. and C.R. prepared all the figures and tables.P.C. and Y.R. proved the manuscript.All authors reviewed the manuscript.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

References

1. Malafeev KV, Apicella A, Incarnato L, Scarfato P (2023) Understanding the impact of biodegradable microplastics on living organisms entering the Food Chain: a review. Polymers 15:1–26. https://doi.org/10.3390/polym15183680
2. Da Costa JP, Nunes AR, Santos PSM, Girão AV, Duarte AC, Rocha-Santos T (2018) Degradation of polyethylene microplastics in seawater: insights into the environmental degradation of polymers. J Environ Sci Health Part A 53:866–875. https://doi.org/10.1080/10934529.2018.1455381
3. Raj VA, Sankar K, Narayanasamy P, Moorthy IG, Sivakumar N, Rajaram SK, Karuppiah P, Shaik MR, Alwarthan A, Oh TH, Shaik B (2023) Development and characterization of Bio-based Composite films for Food Packing Applications using boiled Rice Water and Pistacia vera Shells. Polymers 15:1–18. https://doi.org/10.3390/polym15163456
4. Rebelo RC, Goncalves LPC, Fonseca AC, Fonseca J, Rola M, Coelho JFJ, Rola F, Serra AC (2022) Increased degradation of PLA/PBAT blends with organic acids and derivatives in outdoor weathering and marine environment. Polymer 256:125223. https://doi.org/10.1016/j.polymer.2022.125223
5. Taib NAAB, Rahman MR, Huda D, Kuok KK, Hamdan S, Bakri MKB, Julaihi MRMB, Khan A (2023) A review on poly lactic acid (PLA) as a biodegradable polymer. Polym Bull 80:1179–1213. https://doi.org/10.1007/s00289-022-04160-y
6. Zaaba NF, Jaafar M (2020) A review on degradation mechanisms of polylactic acid: Hydrolytic, photodegradative, microbial, and enzymatic degradation. Polym Eng Sci 60:2061–2075. https://doi.org/10.1002/pen.25511
7. Janczak K, Dabrowska GB, Raszkowska-Kaczor A, Kaczor D, Hrynkiewicz K, Richert A (2020) Biodegradation of the plastics PLA and PET in cultivated soil with the participation of microorganisms and plants. Int Biodeterior Biodegrad 155:1–10. https://doi.org/10.1016/j.ibiod.2020.105087
8. Bubpachat T, Sombatsompop N, Prapagdee B (2023) Isolation and role of polylactic acid-degrading bacteria on degrading enzymes productions and PLA biodegradability at mesophilic conditions. Polym Degrad Stab 152:75–85. https://doi.org/10.1016/j.polymdegradstab.2018.03.023
9. Rakmae S, Lorprayoon C, Ekgasit S, Suppakarn N (2013) Influence of heat-treated bovine bone-derived Hydroxyapatite on Physical properties and in vitro degradation behavior of poly (lactic acid) composites. Polym Plast Technol Eng 52:1043–1053. https://doi.org/10.1080/03602559.2013.769580
10. Iglesias-Montes ML, D'Amico DA, Malbos LB, Seoane IT, Cyras VP, Manfredi LB (2023) Thermal degradation kinetics of completely biodegradable and Biobased PLA/PHB blends. Thermochim Acta 725:179530. https://doi.org/10.1016/j.tca.2023.179530
11. Chen Y, Yuan D, Xu C (2014) Dynamically vulcanized biobased polylactide/natural rubber blend material with continuous cross-linked rubber phase. ACS Appl Mater Interfaces 6:3811–3816. https://doi.org/10.1021/am5004766

12. 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. Polym Test 37:94–101. https://doi.org/10.1016/j.polymertesting.2014.05.005
13. Mohammad NNB, Arsad A, Rahmat AR, Abdullah Sani NS, Ali Mohsin ME (2016) Influence of compatibilizer on the structure properties of polylactic acid/natural rubber blends. Polym Sci Ser A 58:177–185. https://doi.org/10.1134/S0965545X16020164
14. Buys YF, Aznan ANA, Anuar (2017) Mechanical properties, morphology, and hydrolytic degradatio, behavior of polylactic acid / natural rubber blends. Mater Sci Eng 290:1–8. https://doi.org/10.1088/1757-899X/290/1/012077
15. Sookprasert P, Hinchiranan N (2017) Morphology, mechanical and thermal properties of poly(lactic acid) (PLA)/natural rubber (NR) blends compatibilized by NR-graft-PLA. J Mater Res 32:788–800. https://doi.org/10.1557/jmr.2017.9
16. Tertyshnaya YV, Karpova SG, Podzorov MV, Khvatov AV, Moskovskiy MN (2022) Thermal properties and dynamic characteristics of Electrospun Polylactide/Natural Rubber fibers during disintegration in Soil. Polymers 14:1–16. https://doi.org/10.3390/polym14051058
17. Lertphirun K, Srikulkit K (2019) Properties of Poly(Lactic Acid) filled with hydrophobic Cellulose/SiO2 composites. Int J Polym Sci 2019:1–8. https://doi.org/10.1155/2019/7835172
18. Yetis F, Liu X, Sampson WW, Gong RH (2023) Biodegradation of composites of Polylactic Acid and Microfibrillated Lignocellulose. J Polym Environ 31:698–708. https://doi.org/10.1007/s10924-022-02583-2
19. Budin S, Jaafar M (2022) Comparative study on mechanical properties of virgin and recycled polylactic acid aging in natural weathering and seawater environment. Polym Bull 79:4841–4858. https://doi.org/10.1007/s00289-021-03756-0
20. Gois GS, Santos ASF, Hernandez EP, Medeiros ES, Almeida YMB (2023) Biodegrada-tion of PLA/CNC composite modified with non-ionic surfactants. Polym Bull 80:11363–11377. https://doi.org/10.1007/s00289-022-04618-z
21. Yadav S, Kumar P (2023) Effect of neem leaves and stock density of earthworm (Eisenia fetida) on quality of rice straw vermicompost. Adv Environ Res 12:51–64. https://doi.org/10.12989/aer.2023.12.1.051
22. Yang Q, Ruan F, Wu H, Kan C, Wang G, Wang Z, Wang H, Xu Z, Wang H (2023) Effect of Chemical Treatment on Rice Straw Fiber Surface and properties of Straw/Polylactic Acid composites. J Nat Fibers 20:1–14. https://doi.org/10.1080/15440478.2023.2228486
23. Beniwal P, Toor AP (2023) Advancement in tensile properties of polylactic acid composites reinforced with rice straw fibers. Ind Crops Prod 192:1–9. https://doi.org/10.1016/j.indcrop.2022.116098
24. Sakai E, Qiu JH, Murata T, Kazushi I, Kobayashi J, Takahashi T (2011) Degradation characteristics of Rice Straw/Poly(Lactic Acid) composites. Adv Mat Res 391–392:1268–1272. https://doi.org/10.4028/www.scientific.net/amr.391-392.1268
25. Barragán H, Pelacho A, Martín-Closas L (2016) Degradation of agricultural biodegradable plastics in the soil under laboratory conditions. Soil Res 54:216–224. https://doi.org/10.1071/SR15034
26. Han Y et al (2020) Effects of Tensile stress and soil burial on mechanical and chemical degradation potential of Agricultural Plastic films. Sustainability 12:7985. https://doi.org/10.3390/su12197985
27. La Mantia FP, Ascione L, Mistretta MC, Rapisarda M, Rizzarelli P (2020) Comparative investigation on the Soil Burial degradation Behaviour of Polymer films for Agriculture before and after photo-oxidation. Polymers 12:753. https://doi.org/10.3390/polym12040753
28. Hongsriphan N, Pinpueng A (2019) Properties of Agricultural films prepared from biodegradable poly(Butylene Succinate) adding natural sorbent and fertilizer. J Polym Environ 27:434–443. https://doi.org/10.1007/s10924-018-1358-5
29. Chen Y et al (2024) Biodegradable cellulose-base aerogel films with high solar emissivity for agricultural thermal management. https://doi.org/10.1007/s10570-024-05751-w. Cellulose
30. Kyrikou I, Briassoulis D (2007) Biodegradation of Agricultural Plastic films: a critical review. J Polym Environ 15:125–150. https://doi.org/10.1007/s10924-007-0053-8
31. Pongputthipat W, Ruksakulpiwat Y, Chumsamrong P (2022) Development of biodegradable biocomposite films from poly(lactic acid), natural rubber and rice straw. Polym Bull 80:10289–10307. https://doi.org/10.1007/s00289-022-04560-0
32. Rong-or C, Pongputthipat W, Ruksakulpiwat Y, Chumsamrong P (2023) Poly(Lactic acid)/ Natural Rubber/ Rice straw Bio-composite films for Agricultural application. Proceedings of the International Polymer Conference of Thailand (PCT 13 Conference), Bangkok, Thailand, June 8–9

33. Boonmee C, Kositanont C, Leejarkpai T (2016) Degradation of poly (lactic acid) under simulated landfill conditions. Environ Nat Resour 14:1–9. https://doi.org/10.14456/ennrj.2016.8
34. Matta AK, Rao RU, Suman KNS, Rambabu V (2014) Preparation and characterization of biodegradable PLA/PCL Polymeric blends. Procedia Mater Sci 6:1266–1270. https://doi.org/10.1016/j.mspro.2014.07.201
35. Fabian DRC, Durpekova S, Dusankova M, Cisar J, Drohsler P, Elich O, Borkova M, Cechmankova J, Sedlarik V (2023) Renewable poly(lactic acid)lignocellulose biocomposites for the enhancement of the Water Retention Capacity of the Soil. Polymers 15:1–18. https://doi.org/10.3390/polym15102243
36. Elsawy MA, Kim KH, Park JW, Deep A (2017) Hydrolytic degradation of polylactic acid (PLA) and its composites. Renew Sust Energ Rev 79:1346–1352. https://doi.org/10.1016/j.rser.2017.05.143
37. Karamanlioglu M, Alkan U (2019) Influence of time and room temperature on mechanical and thermal degradation of poly(lactic) acid. Therm Sci 23:383–390. https://doi.org/10.2298/TSCI181111051K
38. Rosli NA, Ahmad I, Anuar FH, Abdullah I (2018) The contribution of eco-friendly bio-based blends on enhancing the thermal stability and biodegradability of poly(lactic acid). J Clean Prod 198:987–995. https://doi.org/10.1016/j.jclepro.2018.07.119
39. Huang Y, Zhang C, Pan Y, Zhou Y, Jiang L, Dan Y (2013) Effect of NR on the hydrolytic degradation of PLA. Polym Degrad Stab 98:943–950. https://doi.org/10.1016/j.polymdegradstab.2013.02.018
40. Rosli NA, Karamanlioglu M, Kargarzadeh H, Ahmad I (2021) Comprehensive explora-tion of natural degradation of poly(lactic acid) blends in various degradation media: a review. Int J Biol Macromol 187:732–741. https://doi.org/10.1016/j.ijbiomac.2021.07.196
41. Kalita NK, Damare NA, Hazarika D, Bhagabati P, Kalamdhad A, Katiyar V (2021) Biodegradation and characterization study of compostable PLA bioplastic containing algae biomass as potential degradation accelerator. Environ Chall 3:1–10. https://doi.org/10.1016/j.envc.2021.100067
42. Zandi A, Zanganeh A, Hemmati F, Mohammadi-Roshandeh J (2019) Thermal and biodegradation properties of poly(lactic acid)/rice straw composites: efects of modifed pulping products. Iran Polym J 28:1–13. https://doi.org/10.1007/s13726-019-00709-3
43. Alias NF, Ismail H, Ishak KMK (2021) Poly(lactic acid)/natural rubber/kenaf biocomposites production using poly(methyl methacrylate) and epoxidized natural rubber as co–compatibilizers. Iran Polym J 30:737–749. https://doi.org/10.1007/s13726-021-00927-8
44. Rosdi FNM, Salim N, Roslan R, Bakar NHA, Sarmin SNS (2023) Potential Red Algae Fibre Waste as a raw material for Biocomposite. J Adv Res Appl Sci Eng Technol 30:303–310. https://doi.org/10.37934/araset.30.1.303310
45. Shirazi RN, Aldabbagh F, Ronan W, Erxleben A, Rochev Y, McHugh P (2016) Effects of material thickness and processing method on poly(lactic-co-glycolic acid) degradation and mechanical performance. J Mater Sci: Mater 27:154. https://doi.org/10.1007/s10856-016-5760-z
46. Tserki V, Matzinos P, Panayiotou C (2003) Effect of compatibilization on the performance of biodegradable composites using cotton fiber waste as filler. J Appl Polym Sci 88:1825–1835. https://doi.org/10.1002/app.11812
47. Sriyapai P, Chansiri K, Sriyapai T (2018) Isolation and characterization of polyester-based plastics-degrading Bacteria from Compost soils. Microbiology 87:290–300. https://doi.org/10.1134/S0026261718020157
48. Gkoutselis G, Rohrbach S, Harjes J, Obst M, Brachmann A, Horn MA, Rambold G (2021) Microplastics accumulate fungal pathogens in terrestrial ecosystems. Sci Rep 11:1–14. https://doi.org/10.1038/s41598-021-92405-7
49. Banthao C, Kumpolsan P, Baimark Y, Wongkasemjit S, Pakkethati K (2020) Improvement the properties of poly(l-lactide) films with cellulose fiber from rice straw waste in agricultural products. Int J GEOMATE 18:43–48. https://doi.org/10.21660/2020.70.5716
50. Yaacob ND, Ismail H, Ting SS (2016) Soil Burial of Polylactic Acid/Paddy Straw Powder Biocomposite. Bioresour 11:1255–1269. https://doi.org/10.15376/biores.11.1.1255-1269
51. Diaz-Hernandez JL, Sanchez-Soto PJ, Serrano-Delgado A (2012) Biological nanostructures associated to iberulites: a SEM study. Curr Microscopy Contrib Adv Sci Technol 1:154–161
52. Wufuer R, Li W, Wang S, Duo J (2022) Isolation and degradation characteristics of PBAT Film degrading Bacteria. Int J Environ Res Public Health 19:1–12. https://doi.org/10.3390/ijerph192417087
53. Velghe I, Buffel B, Vandeginste V, Thielemans W, Desplentere F (2023) Review on the degradation of poly(lactic acid) during Melt Processing. Polymers 15:1–33. https://doi.org/10.3390/polym15092047
54. Feng Y, Hu Y, Yin J, Zhao G, Jiang W (2013) High impact poly(lactic acid)/Poly(ethylene octene) blends prepared by reactive blending. Polym Eng Sci 53:389–396. https://doi.org/10.1002/pen.23265

55. Lorenzoa MLD, Androsch R (2016) Melting of α'- and α-Crystals of Poly(lactic acid). Proceedings of Paper presented at the AIP Conference (VIII International Conference on Times of Polymers and Composites), Naples, Italy, June
56. Thongpin C, Klatsuwan S, Borkchaiyapoom P, Thongkamwong S (2013) Crystallization behavior of PLA in PLA/NR compared with dynamic Vulcanized PLA/NR. J Met Mater Min 23:53–59
57. Burkov A, Kraev A, Grishin M, Vesnin R, Fomin S, Iordanskii A (2021) Structural features and properties' characterization of Polylactic Acid/Natural Rubber blends with Epoxidized Soybean Oil. Polymers 13:1–12. https://doi.org/10.3390/polym13071101
58. Tisserat B, Joshee N, Mahapatra AK, Selling GW, Finkenstadt VL (2013) Physical and mechanical properties of extruded poly(lactic acid)-based Paulownia elongata biocomposites. Ind Crops Prod 44:88–96. https://doi.org/10.1016/j.indcrop.2012.10.030
59. Bomfim ASC, Oliveira DM, Benini KCC, Cioffi MOH, Voorwald HJC, Rodrigue D (2023) Effect of spent Coffee grounds on the crystallinity and viscoelastic behavior of Polylactic Acid composites. Polymers 15:1–16. https://doi.org/10.3390/polym15122719
60. Suksut B, Deeprasertkul C (2011) Effect of Nucleating agents on Physical properties of Poly(lactic acid) and its blend with Natural Rubber. J Polym Environ 19:288–296. https://doi.org/10.1007/s10924-010-0278-9
61. Ming R, Yang G, Li Y, Wang R, Zhang H, Shao H (2015) Flax Fiber-Reinforced Polylactide Stereocomplex composites with enhanced Heat Resistance and Mechanical properties. Polym Compos 38:472–478. https://doi.org/10.1002/pc.23605
62. Lv S, Zhang Y, Gu J, Tan H (2018) Soil burial-induced chemical and thermal changes in starch/poly (lactic acid) composites. Int J Biol Macromol 113:338–344. https://doi.org/10.1016/j.ijbiomac.2018.02.139
63. Silva APD, Pereira MDP, Passador FR, Montagna LS (2020) PLA/Coffee grounds composites: a study of Photodegradation and Biodegradation in Soil. Macromol Symp 394:1–9. https://doi.org/10.1002/masy.202000091
64. Palsikowski PA, Kuchnier CN, Pinheiro IF, Morales AR (2017) Biodegradation in Soil of PLA/PBAT blends compatibilized with Chain Extender. J Polym Environ 26:330–341. https://doi.org/10.1007/s10924-017-0951-3
65. Lv S, Liu X, Gu J, Jiang Y, Tan H, Zhang Y (2017) Microstructure analysis of polylactic acid-based composites during degradation in soil. Int Biodeterior Biodegrad 122:53–60. https://doi.org/10.1016/j.ibiod.2017.04.017

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