POLY(LACTIC ACID)/ NATURAL RUBBER/ RICE STRAW BIOCOMPOSITE FILMS FOR AGRICULTURAL APPLICATION

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ฟิล์มคอมโพสิตชีวภาพจากพอลิแลกติกแอซิด ยางธรรมชาติ และฟางข้าว เพื่อใช้ในงานด้านการเกษตร

นางสาวชนาธินาถ ร่องอ้อ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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คำสำคัญ: พอลิแลกติกแอซิด/ยางธรรมชาติ/ฟางข้าว/คอมโพสิตชีวภาพ/การย่อยสลายทางชีวภาพ

งานวิจัยนี้มุ่งเน้นการพัฒนาฟิล์มคอมโพสิตชีวภาพที่ยั่งยืนและย่อยสลายได้ทางชีวภาพสำหรับการใช้งานทางการเกษตรจากวัสดุที่ย่อยสลายได้ทางชีวภาพและทดแทนได้ในระยะเวลาสั้น ได้แก่ พอลิแลกติกแอซิด, ยางธรรมชาติ, และฟางข้าว อย่างไรก็ตามพอลิแลกติกแอซิด และยางธรรมชาติ มีความไม่เข้ากัน นำไปสู่การแยกเฟสและคุณสมบัติเชิงกลต่ำ ดังนั้นในงานวิจัยนี้จึงได้ทำการปรับปรุงความเข้ากันได้ผ่านการบด (mastication) ยางธรรมชาติด้วยเครื่องบดผสมสองลูกกลิ้ง (two-roll mill) ระยะเวลาในการบดคือ 10, 20, และ 30 นาที ยางธรรมชาติถูกนำไปผสมเข้ากับพอลิแลกติกแอซิดด้วยเครื่องบดผสมภายใน (internal mixer) อัตราส่วนระหว่างพอลิแลกติกแอซิดและยางธรรมชาติเท่ากับ 60/40 เปอร์เซ็นต์โดยน้ำหนัก (wt.%) จากการตรวจสอบผลของดัชนีการไหล พบว่า เมื่อเวลาที่ใช้ในการบดยางธรรมชาตินานขึ้นจะส่งผลให้ดัชนีการไหลของพอลิเมอร์ผสมเพิ่มสูงขึ้น โดยเวลาในการบดยาง 10 นาที ดัชนีการไหลมีค่า 9.69 ± 1.01 กรัม/10นาที และที่เวลาในการบดยางเท่ากับ 30 นาที ค่าดัชนีการไหลเพิ่มเป็น 60.27± 0.31 กรัม/10นาที จากการตรวจสอบสมบัติการดึงของชิ้นทดสอบพอลิเมอร์ผสมซึ่งขึ้นรูปด้วยกระบวนการกดอัด (compression molding) พบว่า ค่าความยืดสูงสุด ณ จุดขาด ของพอลิเมอร์ผสมระหว่างพอลิแลกติกแอซิดกับยางธรรมชาติที่ผ่านการบดเป็นเวลา 10 นาที มีค่าสูงสุดเท่ากับ 231.33 ± 34.43 เปอร์เซ็นต์ (%) ดังนั้นระยะเวลาในการบดยาง 10 นาทีจึงถูกนำไปใช้ศึกษาต่อในการผลิตฟิล์มคอมโพสิตชีวภาพ

ในการศึกษาถัดมาเป็นการศึกษาผลของปริมาณฟางข้าวที่มีต่อดัชนีการไหล สมบัติการดึงและสัณฐานวิทยาของฟิล์มคอมโพสิตชีวภาพระหว่างพอลิแลกติกแอซิด ยางธรรมชาติและฟางข้าว ฟางข้าวถูกเติมที่อัตราส่วน 3, 5, และ 10 wt.% ของพอลิเมอร์ผสมระหว่างพอลิแลกติกแอซิดและยางธรรมชาติที่อัตราส่วนคงที่เท่ากับ 60/40 wt.% ชิ้นงานทดสอบถูกขึ้นรูปด้วยกระบวนการหลอมอัดรีดขึ้นรูปเป็นฟิล์ม (cast films extrusion) จากการขึ้นรูปเป็นฟิล์ม พบว่า ฟิล์มคอมโพสิตชีวภาพที่มีการเติมฟางข้าว 10 wt.% มีรูขนาดใหญ่จำนวนมากปรากฏบนพื้นผิว ซึ่งทำให้ไม่สามารถทำการทดสอบเพิ่มเติมได้ ความไม่ต่อเนื่องของเนื้อฟิล์มสอดคล้องกับค่าดัชนีการไหลที่สูงของคอมโพสิตที่มีปริมาณฟางข้าว 10 wt.% (37 ± 0.79 กรัม/10 นาที) ซึ่งสูงกว่าช่วงดัชนีการไหลที่เหมาะสม (ประมาณ 9-15 กรัม/10 นาที) สำหรับการผลิตฟิล์มผ่านกระบวนการอัดรีดขึ้นรูปอย่างมีนัยสำคัญ การศึกษาสมบัติการดึงของฟิล์มคอมโพสิตที่เติมฟางข้าวอัตราส่วน 3 และ 5 wt.% พบว่า พฤติกรรม

การแตกหักของพอลิแลกติกแอซิดยังคงเป็นแบบเหนียว แม้ว่าความต้านทานแรงดึงและมอดุลัสของฟิล์มคอมโพสิตชีวภาพจะลดลงเมื่อมีปริมาณฟางเพิ่มขึ้น แต่ค่าความยืดสูงสุด ณ จุดขาด ยังคงสูงกว่าพอลิแลกติกแอซิด สัณฐานวิทยาของพื้นที่ผิวแตกหักจากการดึงของฟิล์มคอมโพสิตชีวภาพแสดงให้เห็นถึงความไม่เข้ากัน

ผลการตรวจสอบพฤติกรรมการย่อยสลายของฟิล์มคอมโพสิตชีวภาพโดยการฝังดินที่มีความชื้นเท่ากับ 30% โดยน้ำหนัก เป็นระยะเวลา 3 เดือน แสดงให้เห็นว่า ฟิล์มพอลิแลกติกแอซิดมีเปอร์เซ็นต์การสูญเสียน้ำหนักต่ำสุดที่ 3.33% ในขณะที่ฟิล์มที่เติมฟางข้าว 5 wt.% มีอัตราการสูญเสียน้ำหนักมากที่สุดคือ 8.30% สอดคล้องกับผลของน้ำหนักโมเลกุลที่ลดลง สัณฐานวิทยาแสดงให้เห็นถึงการเกิดรอยแตกและการมีอยู่ของเชื้อราบนพื้นผิวฟิล์มหลังจากถูกฝังลงในดิน การวิเคราะห์องค์ประกอบทางเคมีด้วยเทคนิครังสีเอกซ์แบบกระจายพลังงาน (energy dispersive X-ray, EDX) แสดงให้เห็นว่ามีองค์ประกอบไนโตรเจนและปริมาณคาร์บอนลดลงหลังจากการฝังดิน ในขณะที่ปริมาณออกซิเจนเพิ่มขึ้น เทคนิควิเคราะห์การเลี้ยวเบนของรังสีเอ็กซ์ (X-ray diffraction, XRD) เผยให้เห็นความเป็นผลึกต่ำในพอลิแลกติกแอซิด สอดคล้องกับการวิเคราะห์ทางความร้อนด้วยเทคนิคดิฟเฟอเรนเชียลสแกนนิ่งแคลอรีมิเตอร์ (differential scanning calorimeter, DSC) การเติมยางธรรมชาติและฟางข้าวลงในคอมโพสิตชีวภาพทำให้ค่าความเป็นผลึกของพอลิแลกติกแอซิดเพิ่มขึ้น นอกจากนั้น ยังพบว่า ความเป็นผลึกของฟิล์มทุกชนิดมีค่าเพิ่มขึ้นหลังจากฝังดินเป็นเวลา 3 เดือน สอดคล้องกับค่ามอดุลัสที่มีแนวโน้มเพิ่มขึ้น ในทางตรงกันข้ามพบว่าค่าความต้านทานแรงดึงและค่าความยืดสูงสุด ณ จุดขาดลดลง การศึกษานี้แสดงให้เห็นว่าฟิล์มคอมโพสิตชีวภาพที่เติมฟางข้าวเสื่อมสภาพได้ง่ายกว่าฟิล์มพอลิแลกติกแอซิด เพื่อประเมินประสิทธิภาพของฟิล์มคอมโพสิตชีวภาพในการใช้งานทางการเกษตร ฟิล์มทุกชนิดได้แก่ พอลิแลกติกแอซิด พอลิเมอร์ผสมระหว่างพอลิแลกติกแอซิดและยางธรรมชาติ และฟิล์มคอมโพสิตชีวภาพถูกนำมาใช้ในการผลิตถุงเพาะชำและฟิล์มคลุมดินสำหรับการปลูกต้นพริกเป็นเวลา 3 เดือน เมื่อครบกำหนดการปลูก 3 เดือน พบว่า รากของพริกสามารถแทงทะลุออกมาจากถุงเพาะชำ โดยเฉพาะถุงที่ทำจากฟิล์มคอมโพสิตชีวภาพ บ่งชี้ว่าถุงเพาะชำไม่ได้ขัดขวางการเจริญเติบโตของต้นพริก นอกจากนี้ ยังพบว่า ต้นพริกมีแนวโน้มการเจริญเติบโตได้ดีที่สุดในถุงเพาะชำจากฟิล์มคอมโพสิตชีวภาพที่เติมฟางข้าว 3 wt.% โดยมีค่าน้ำหนักแห้งเท่ากับ 33.33 ± 4.16 กรัม ฟิล์มคอมโพสิตชีวภาพย่อยสลายเร็วเมื่อใช้เป็นฟิล์มคลุมดินสำหรับปลูกพริก โดยฟิล์มเริ่มมีการขาดออกจากกันตั้งแต่เดือนแรก และในเดือนที่สองพบว่าฟิล์มมีการแตกกระจายออกจนไม่สามารถคลุมดินได้ ทำให้หญ้าและวัชพืชเกิดขึ้นตามบริเวณรอยแตกนั้น แสดงให้เห็นว่า การใช้ฟิล์มคอมโพสิตชีวภาพเป็นฟิล์มคลุมดินสำหรับการปลูกพริกนั้นอาจไม่เหมาะสม

สาขาวิชา วิศวกรรมวัสดุ
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ลายมือชื่อนักศึกษา..............................
ลายมือชื่ออาจารย์ที่ปรึกษา..............................

CHANATINAT RONOG-OR: POLY(LACTIC ACID)/ NATURAL RUBBER/ RICE STRAW BIOCOMPOSITE FILMS FOR AGRICULTURAL APPLICATION.
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The aim of this study is to develop sustainable and biodegradable biocomposite films for agricultural applications using biodegradable and renewable resources including poly(lactic acid) (PLA), natural rubber (NR), and rice straw (RS). However, the incompatibility between PLA and NR results in phase separation and poor mechanical properties. To enhance compatibility, NR mastication was conducted by a two-roll mill, with mastication durations of 10, 20, and 30 minutes. Masticated NR was then blended with PLA using an internal mixer. The weight ratio of PLA and NR was fixed at 60/40 wt.%. The melt flow index (MFI) of the polymer blend increased with the duration of NR mastication, from 9.69 ± 1.01 g/10 min at 10 minutes to 60.27 ± 0.31 g/10 min at 30 minutes. The tensile test of the compression-molded polymer blend specimens revealed that the NR mastication time at 10 minutes showed the highest percentage elongation at break, which was 231.33 ± 34.43 %. Therefore, a mastication time of 10 minutes was selected to further investigate the production of biocomposite films.

The subsequent study aimed to investigate the effect of rice straw (RS) content on the MFI, tensile, and morphological characteristics of the bicomposite films. RS was added to a PLA/NR blend at weight ratios of 3, 5%, and 10%, with a PLA and NR weight ratio fixed at 60/40 wt.%. Test specimens were produced using cast film extrusion procedure. Examination revealed numerous large holes on the surface of the biocomposite film containing 10 wt.% RS, which limited further testing. The film's discontinuity is attributed to the elevated melt flow index value of the composite containing 10 wt% rice straw content (37 ± 0.79 g/10 min), which is significantly above the recommended melt flow index range (about 9–15 g/10 min) to produce films using a cast film extrusion process. The tensile tests of biocomposite films containing 3 and 5 wt.% RS still show ductile fracture behavior. Even though the tensile strength and modulus decrease as the RS content increases, the elongation at break remains higher than PLA. The morphology of the fracture surface area exhibits incompatibility.

The results of examining the degradation behavior of biocomposite films by burying them in soil with a moisture content of 30% by weight for a period of 3 months showed that the polylactic acid film had the lowest percentage weight loss at 3.33%, while the film with 5 wt.% RS had the highest weight loss rate at 8.30%. This is consistent with the decrease in the molecular weight of the PLA phase in biocomposite films. The morphological analysis reveals numerous pores and fungus growth on the film surface after soil burial. Energy dispersive X-ray (EDX) analysis indicated a reduction in carbon contents while the oxygen and nitrogen content increased during the burial process. The X-ray diffraction (XRD) study indicated a low degree of crystallinity in the PLA, which is in accordance with the results obtained from the differential scanning calorimeter (DSC). Following the addition of NR and RS to the biocomposites, the crystallinity of the PLA trended to increase. Additionally, after 3 months of soil burial, each type of film showed increased crystallinity and modulus, while tensile strength and elongation at break decreased. This indicates that biocomposite films filled with RS exhibit a higher susceptibility to degradation compared to PLA films.

To evaluate the efficacy of biocomposite films in agricultural applications, all types of films, including PLA, PLA/NR blend, and biocomposite films, were used to fabricate seedling bags and mulch films for the cultivation of chili plants over a three-month period. After a period of three months, the chili roots effectively penetrated the seedling bags. Specifically, bags made from biocomposite materials. These findings indicate that the utilization of seedling bags did not hinder the growth of the chili plants. In addition, the growth of chili plants in the bags made from biocomposite film containing 3 wt.% RS appeared to be better and resulted in a maximum dry weight of 33.33 ± 4.16 grams. Biocomposite film decomposes quickly when used as a mulch for growing chili plants. The film began to fall apart after the first month. In the second month, the film had expanded to such an extent that it could no longer adequately cover the soil. This causes grass and weeds to grow in the cracked area. This suggests that using biocomposite films as mulch films for chilli cultivation may not be appropriate.

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CHAPTER I

INTRODUCTION

1.1 General Background

With the world's population increasing and various activities that human being must rely on natural resources more than in the past, natural resources are decrease rapidly. Therefore, humans have invented and developed thing that will replace natural resources, which is "plastic", durable materials lasted for hundreds of years. However, the overutilization of plastic gives rise to a multitude of issues. A portion of plastic rapidly becomes waste. Conventional plastic, which is non-biodegradable, can contaminate our environment for many decades if not disposed of correctly. Currently, enormous amounts of plastic are accumulating in landfills and in the environment. With rising consumption, there is a pressing need for innovation and comprehensive solutions to address this issue. Plastic which are biodegradable or made from renewable resources including poly(lactic acid) (PLA), polybutylene adipate terephthalate (PBAT) and polybutylene succinate (PBS) represent an alternative potential in the improvement of materials for utilization in environmental preservation. The discovery of biodegradable plastics has made it possible for humans to find a substitute for traditional petrochemical plastics because there are features in use that are comparable.

Thailand, a country mostly reliant on agriculture, exhibits a significant amount of agricultural production. The abundance of soils and favorable terrain, along with sufficient water resources and a tropical climate, enable multiple crop cycles per year. Consequently, amount of plastic waste from agricultural sector has been increased. One of them is plastic films such as seedling bags and mulch films. When seedlings are planted, plastic films cannot be quickly decomposed in the soil. The seedlings may not grow as well as they should. Waste plastic from films is also a problem for the environment. The residual plastic is a stubborn waste with the potential to contaminate the atmosphere when burned. Therefore, focusing on the ecosystem by using biodegradable films is a proactive strategy for reducing plastic waste, decrease waste disposal costs, and avoid diverse environmental issues. It can also biodegrade naturally within a reasonable period of environmental conditions.

Films for agricultural applications generally made from polyethylene plastic, are used worldwide because they are inexpensive and lightweight (Haase et al., 2021). Such films often have a short service life, resulting in massive amounts of plastic waste. Therefore, it has presented numerous problems. Despite its non-biodegradable nature, polyethylene can transform into microplastics in the environment. This can have substantial adverse effects on the health of organisms, as well as on the entire food chain (Da Costa et al., 2018). Therefore, it is crucial to substitute conventional polymers with biodegradable and compostable alternatives to decrease the quantity of post-consumer plastics that are hard and costly to recycle and pose risks to the environment.

Poly(lactic acid) (PLA) is a biodegradable polymer that is especially suitable for use in agricultural film. Renewable sources such as corn, wheat, potato starch, or sugarcane produce this biodegradable polyester. This thermoplastic biopolymer is highly promising due to its biocompatibility and excellent mechanical characteristics (Zhou and Butchosa, 2016). Nevertheless, PLA has certain disadvantages, such as low toughness, slower decomposition rate, hydrophobic nature, and absence of reactivity side-chain groups. In addition to having mechanical properties that are either superior to or equivalent to those of conventional plastics, PLA must also have undergone bulk modification, primarily to increase its toughness and degradation rate, for it to be successfully used in consumer commercial applications (Ren, 2011). For example, Garcia-Garcia et al. (2020) applied epoxidized karanja oil (EKO) to PLA to increase its flexibility. They discovered that the compositions, including EKO, produced an increase in elongation at break and, as the EKO content increased, reduced the glass transition temperature. The PLA composition, including 5 wt.% EKO, demonstrated the best possible balance between increasing the material's strength and increasing its elongation at break to 77%. Furthermore, under composting conditions, all of it decomposed. In addition, Arrieta et al. (2020) discovered that oligomeric lactic acid (OLA) enhanced the rate of crystallisation in PLA. The PLA composite containing 15 wt.% of OLA exhibited superior structural and mechanical capabilities, along with suitable degradation in compost. These findings suggest that this composite could be used as an agricultural mulch film.

This research specifically emphasizes developing sustainable and biodegradable agricultural films to solve the above-mentioned problems. PLA was the polymer base chosen for this purpose, with natural rubber and rice straw as additional components.

Blending PLA with NR without various modification is a good choice to improve toughness and elongation at break and enhance degradation rate of PLA (Buys, Aznan and Anuar, 2017). Natural rubber, derived from the latex found in the sap of certain plants, is a renewable resource that can effectively enhance the flexibility of PLA, as well as its low cost (Bitinis, Verdejoa, Cassagnau, and Lopez-Manchadoa, 2011). However, the different polarity and molecular weights of PLA and NR cause the blends to be immiscible, leading to phase separation and poor mechanical properties. A study conducted by Jaratrotkamjorn, Khaokong, and Tanrattanakul (2012) discovered that the polarity, viscosity, and molecular weight of NR can be improved through NR mastication using a two-roll mill. This results in improved compatibility as well as an increase in impact strength and elongation at break in the PLA/NR blend. Furthermore, NR has been observed to disrupt the crystalline structure of PLA (Huang et al., 2013). It will have a positive effect on the degradability of PLA. The hydrolysis of PLA is partially regulated by the water diffusion rate in the amorphous areas of the polymer. The diffusion of water through crystalline areas is limited (Kale et al., 2007). Incorporating NR resulted in an augmentation of the amorphous region within the matrix, thereby resulting in an elevation in the rate of water absorption. This phenomenon arises because of the amorphous area's inherent flexibility, which allows for rapid water diffusion (Rosli, Ahmad, Anuar, and Abdullah, 2018). One of basic parameters controlling control the hydrolytic degradation of a PLA is quantity of absorbed water (Zaaba and Jaafar, 2020).

In Thailand, rice serves as both the predominant staple crop and the key agricultural export of the country (Suebpongsang, Ekasingh and Cramb, 2020). To serve the growing demands, rice is grown yearly; as a result, the product of rice increased by around 30% in 2022 compared to 2021 (Thai Rice Exporters Association, 2022). Rice harvesting leaves behind a waste called rice straw. Rice straw is either stacked or spread over the field, depending on the harvesting methods employed. Removing the remaining rice straw from the field is a difficult task. Burning is the simple method. Remaining rice straw burning influences greenhouse gas emissions and a direct effect on the environment, ultimately leading to climate change (Singh et al, 2021). And with these problems that have spread throughout several global regions. There are many researchers who understand its importance. To encourage the sustainable disposal of this agricultural waste and increase the value of rice straw for farmers, rice straw has been studied for a variety of purposes, including its possible use as a reinforcing ingredient in polymer composites. The research conducted by Xu et al. (2022) provides a practical approach to optimize the utilization of rice straw waste. Green wall insulation based on PLA offer the benefits of environmental preservation and renewability. However, their limited usage is attributed to their poor efficiency. To solve this issue, the researchers employed the azodicarbonamide (AC) as the foaming agent and utilized the molded foaming method to manufacture PLA/rice straw (RS) biocomposite foams. To enhance the performance of foams, degradable polycaprolactone (PCL) was added. This study found that foams exhibited enhanced impact strength, compression strength, and water resistance following the addition of 40 wt.% PCL. Therefore, all the foams demonstrated exceptional insulating capabilities. Xie et al. (2022) proposes strong proof in support of the development and production of green composites reinforced with rice straw. The researchers found that the stalk consists of a central core and an outer sheath. The epidermal tissue within the outer layer of the core is thicker compared to that of the sheath, and its thickness plays a significant role in determining composite mechanical characteristics.

The information above suggests that PLA, NR, and RS biocomposite could potentially produce low-cost, biodegradable, flexible, and strong agricultural films.

1.2 Research objectives

(i) To study the effect of mastication time of natural rubber on the melt flow index and tensile properties of PLA/NR blends.

(ii) To study the preparation method of biocomposite films from PLA/NR/RS.

(iii) To study the effect of an amount of rice straw on tensile, thermal, morphological, and biodegradable properties of PLA/NR/RS biocomposites films.

(iv) To study the agricultural application of PLA/NR/RS biocomposites films.

1.3 Scope and limitation of the study

This study initially investigated the influence of different mastication times (10, 20, and 30 minutes) in a two-roll mill on the tensile characteristics of a blend of PLA and NR, with a blend ratio of 60/40 wt.%. The blend that shows optimum tensile properties was chosen and used as a matrix for PLA/NR/Rice straw biocomposites. A ground RS with a diameter of about 53 μm was applied. An internal mixer was used to prepare the biocomposites with 3, 5, and 10% RS based on the amount of PLA/NR blend matrix. Biocomposite films were produced by cast film extrusion. Mechanical, thermal, morphological, and biodegradable properties of biocomposite films were characterized. In addition, the potential applications of PLA, NR, and RS biocomposite films as agricultural films, including seedling bags and mulch films, were investigated. The plant's growth efficiency and degradation during the planting period were examined.

CHAPTER II

LITERATURE REVIEW

2.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is a renewable resource-based biodegradable polymer. It is a thermoplastic aliphatic polyester that is biocompatible, biodegradable, and mechanically strong. It is similar to polystyrene (PS) or poly(ethylene terephthalate) (PET) in rigidity and clarity (Vasile et al., 2019). PLA has come to prominence as a leading environmentally friendly bioplastic derived from renewable resources with large-scale commercial applications. Rigid packaging, flexible film packaging, clothing, fiber, injection molded items, extrusion, and other applications are produced using PLA.

2.1.1 Synthesis of poly (lactic acid)

PLA is synthesized through two main processes: direct polycondensation (DP) of lactic acid (LA) and ring-opening polymerization (ROP) of lactide. These processes are illustrated in Figure 2.1. Although DP is a less complex method compared to ROP for producing PLA, ROP is the predominant approach for producing high molecular weight PLA.

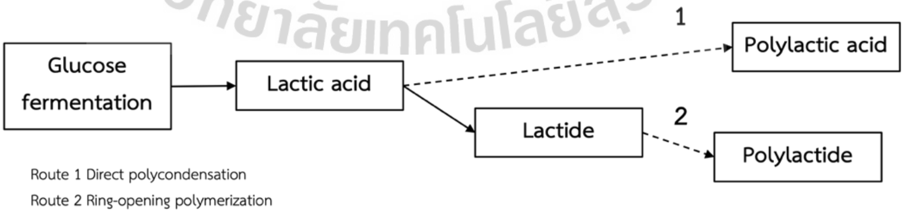

Figure 2.1 General routes of poly(lactic acid) production (Sin and Bee, 2019).

The LA for the procedure is derived through the process of fermenting sugar. LA is transformed into lactide and subsequently turned into PLA. It is important to mention that there are two distinct words, "poly(lactic acid)" and "polylactide," used to refer to the polymer of LA. Both names, polylactide and PLA, are sometimes used interchangeably. However, from a scientific perspective, there is a distinction between them. Polylactide is formed by the ROP process, whereas PLA is generated utilizing the DP process. Typically, the phrase "poly(lactic acid)" is commonly used to refer to the polymer that is derived from LA (Sin and Bee, 2019).

Lactic acid, also known as 2-hydroxypropanoic acid, is a kind of hydroxy acid that has two different optically active forms. Bacteria ferment carbohydrates derived from renewable sources, such as starch, potato and corn, producing L-lactic and D-lactic acid. Figure 2.2 illustrates the two isomers of lactic acid, specifically L-lactic acid and D-lactic acid. The synthesis of PLA requires either neat L-lactic acid, neat D-lactic acid, or a combination of both (Xiao, Wang, Yang, and Gauthier, 2012).

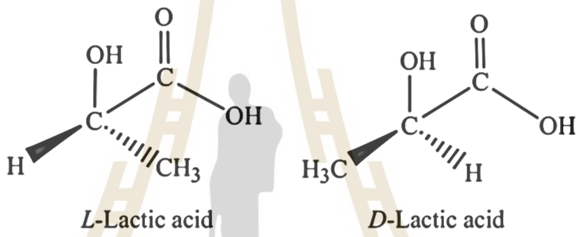

Figure 2.2 The stereoisomers of L-lactic acid and D-lactic acid (Xiao, Wang, Yang, and Gauthier, 2012).

2.1.2 Physical and chemical properties of PLA

The overall characteristics of the polymer were identified by the stereochemical the structure of the lactide monomers (Drumright, Gruber and Henton, 2000). Table 2.1 demonstrates the influence of stereochemistry and crystallinity on the mechanical characteristics of PLA.

Table 2.1 The influence of stereochemistry and crystallinity on the mechanical properties (Garlotta, 2001).

Mechanical Properties	Amorphous L-PLA	Annealed L-PLA	Amorphous D,L-PLA
Tensile strength (MPa)	59.0	66.0	44.0
Yield strength (MPa)	70.0	70.0	53.0
Elongation at break (%)	7.0	4.0	5.4
Modulus of elasticity (MPa)	3750.0	4150.0	3900.0

The homopolymer of PLA has a glass transition temperature of approximately 55°C and a melt temperature of around 175°C. High molecular weight polylactic acid (PLA) is a thermoplastic polymer that is colorless, shiny, and hard. The two isomers of LA can generate four different materials. Poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) have a regular chain structure and are semi-crystalline. Poly(D,L-lactic acid) (PDLLA) is amorphous, while meso-PLA is generated through the polymerization of meso-lactide. Generally, polylactic acids (PLA) can dissolve in typical solvents such as benzene, chloroform, and dioxane. The solubility of these substances, on the other hand, is increased in these solvents when they are heated to their boiling points. In addition, PLA's crystalline is undissolved in acetone, ethyl acetate, and tetrahydrofuran (Garlotta, 2001).

2.1.3 The advantages and limitations of PLA

2.1.3.1 The advantages of PLA

2.1.3.1.1 Biocompatibility

In contemporary biomedical applications, PLA is the predominant biodegradable polymer. The primary appeal of PLA, particularly in relation to biomedical applications, lies in its exceptional biocompatibility. A biocompatible material must not induce harmful or carcinogenic effects in nearby tissues. Furthermore, it is critical that degradation byproducts do not impede tissue regeneration. When transplanted into live organisms, PLA undergoes hydrolysis and breaks down into its constituent hydroxy acid (Rasal, Janorkar, and Hirt, 2010). Instances encompass medication delivery, tissue engineering, and both temporary and long-term embedded devices, with continuous expansion into novel domains (Da Silva et al., 2018).

2.1.3.1.2 Eco-friendly polymer

PLA is derived from renewable resources, such as cassava, corn starch, and sugarcanes. PLA polymers are classified as both biodegradable and compostable (McKeen, 2017). In addition, the production of PLA also necessitates energy consumption, however the amount of energy required, and the resulting carbon dioxide (CO_2) emission are less than 50% when compared to traditional polymer production. (Gironi and Piemonte, 2011). The sustainability and eco-friendly features of PLA enhance its appeal as a biopolymer.

2.1.3.1.3 Processibility

PLA has better thermal processibility compared to other biopolymers such as poly(hydroxy alkanoates) (PHAs), poly(ethylene glycol) (PEG), poly(ε-caprolactone) (PCL), etc. It can be processed by injection molding, extrusion molding, blow molding, thermoforming, and fiber spinning (Karkri, 2017).

2.1.3.1.4 Energy savings

PLA exhibits a reduction in energy consumption of 25–55% compared to polymers derived from petroleum. It is expected that this percentage could potentially decrease to less than 10% in the future. PLA production must be cost-effective because it uses less energy than other manufacturing processes (Vink, Rabago, Glassner and Gruber, 2003).

2.1.3.2 The limitations of PLA

2.1.3.2.1 Slow degradation rate

PLA breaks down when the ester groups in its backbone undergo hydrolysis. Several variables may affect the rate of degradation. Important factors to examine include the chemical structure of the polymer, its crystallinity, molecular weight, morphology, water diffusion rate into the polymer, and water concentration in the polymer (Janorkar, Metters and Hirt, 2004).

2.1.3.2.2 Hydrophobicity

PLA is characterized by a surface that is very hydrophobic and has a static water contact angle of around 80 degrees (Tham, Abdul Hamid, Ahmad, and Ismail, 2014). As a result, there is less interaction between materials. However, to enhance its biocompatibility, researchers have demonstrated that making changes to both the surface and interior of the material can increase its affinity for water. The surface adjustments have been carried out through the application of grafting, treatments, and coatings. On the other hand, bulk modifications have involved the copolymerization or blending of PLA with polymers that are more hydrophilic (Hendrick and Frey, 2014).

2.1.3.2.3 Lack of reactive side-chain groups

PLA is characterized by its chemical inertness, as it lacks any reactive side-chain groups. This poses a significant challenge when attempting to modify its surface or bulk properties (Farah, Anderson, and Langer, 2016).

2.1.3.2.4 Poor toughness

PLA is intrinsically brittle, exhibiting less than 10% elongation at break of fracture (Zhao et al., 2020). Although it possesses comparable tensile strength and elastic modulus to PET and PS, the limited toughness of PLA restricts its usage in various industrial and medical applications that involve high stress levels and require plastic deformation (Hamad, Kaseem, Yang, Deri, and Ko, 2015).

2.1.4 Crystallization of PLA

PLA can have an amorphous or semi-crystalline polymer structure, depending on its thermal history and chemical composition. The crystal shape and structure of PLA have a significant influence on its mechanical characteristics and biodegradability. PLA typically crystallizes slowly, resulting in a low degree of crystallinity. However, applications that require strong mechanical characteristics and excellent heat resistance often value a high degree of crystallinity. Therefore, modifications to the formulation and/or processing are required. Three methods were typically used to accelerate the crystallization of PLA: (i) adding nucleating agents to reduce the surface free energy barrier towards nucleation, thereby causing crystallization at higher temperatures upon cooling; (ii) using plasticizers to decrease the chain folding energy, thereby increasing the chain/segment mobility and the rate of crystallization; and (iii) forming stereo complex (SC) crystallites between enantiomeric poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) (Jiang et al., 2015).

2.1.5 Degradation of PLA

The degradation of a polymer can result in alterations to its mechanical, thermal, and optical properties, which can appear as crazing, cracking, erosion, discoloration, or phase separation. PLA demonstrates an incredibly slow breakdown rate. Temperature and humidity both influence the rate of PLA degradation. Elevated temperatures and increased humidity accelerate the breakdown rate of PLA. (Sookprasert and Hinchiranan, 2014).

PLA can be broken down into several different types of degradation methods, including hydrolytic or enzymatic degradation, end-chain scission and random-chain scission, and surface or bulk degradation. The characteristics of PLA, such as its crystallinity and molecular weight, as well as the environment in which hydrolysis takes place, are the main factors that exhibit an influence on the degradation process (Feng et al., 2021). The prevalent mechanism for the biodegradation of PLA involves a two-step degradation process. In the beginning, the moisture and heat in the organic matter break down the PLA chains, resulting in the generation of low-molecular-weight polymers and, subsequently, lactic acid. Subsequently, the microorganisms present in the compost and soil break down the oligomer fragments and lactic acid into methane and carbon dioxide (CO2) through anaerobic and aerobic processes, respectively (Luo, Lin and Guo, 2019).

Typically, the rate at which PLA breaks down is mostly influenced by the polymer's ability to react with water and any catalysts that may be present. Temperature is an essential factor that influences PLA decomposition. Usually, as the temperature increases, both the rate at which hydrolysis occurs and the level of microbial activity increase consistently. Nevertheless, when exposed to very high temperatures, the activity of bacteria may decrease significantly or cease entirely. UV light is a significant additional environmental factor that affects PLA deterioration. Research has revealed that exposure to UV radiation causes a reduction in PLA's structural strength, leading to an increase in its weakness, stress at fracture break, and average molecular weight (Teixeira, Eblagon, Miranda, Pereira and Figueiredo, 2021).

2.1.5.1 Processes and factors controlling the hydrolytic degradation of PLA

Semicrystalline polyesters degrade in aqueous environments via a two-stage process. The initial stage begins with water diffusion into the disorganized amorphous regions, which facilitates its penetration. The next stage commences once all the amorphous regions have degraded. The hydrolytic action progresses from the outer edges towards the core of the crystalline domains. The amorphous PDLLA has a significantly higher hydrolysis rate compared to the semicrystalline PLLA (Hakkarainen, 2002).

After chain scission occurs, the carboxylic end groups have a catalytic function in the hydrolytic breakdown of PLA through a self-catalyzed and self-sustaining process. The hydrolytic degradation occurs in a heterogeneous manner, with higher rates observed within the molecular structure compared to the surface. The mechanism depicted in Figure 2.3 was attributed to the internal autocatalytic impact of the carboxyl end groups (Elsawy, Kim, Park and Deep, 2017).

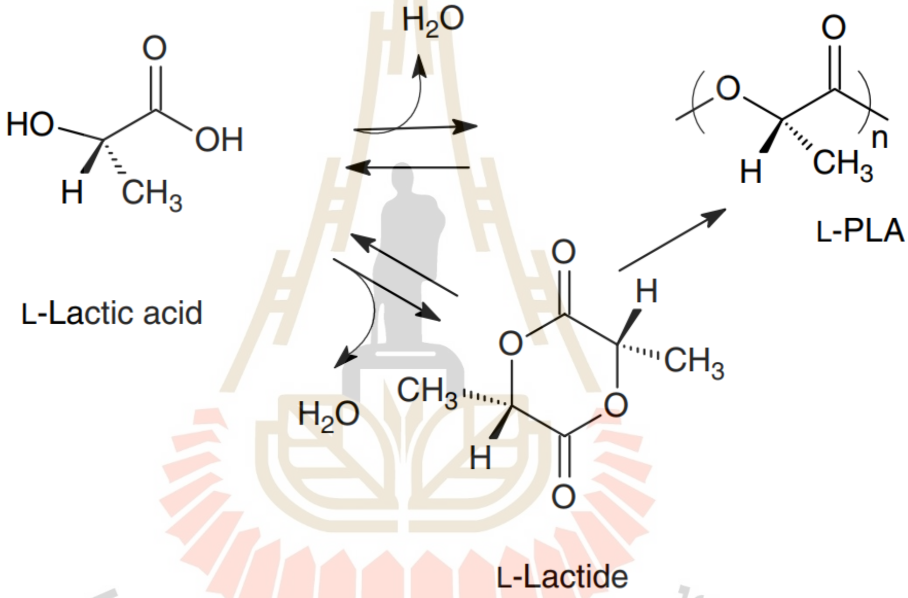

Figure 2.3 Polymerization degradation routes for polylactic acid (Elsawy, Kim, Park and Deep, 2017).

The hydrolytic degradation of PLA in water occurs through the random separation of the ester bond. Four key factors influence this process: the rate constant, the amount of water absorbed, the diffusion coefficient of chain fragments within the polymer, and the solubility of degradation products (Schliecker, Schmidt, Fuchs and Kissel, 2003).

According to those investigations' findings, PLA crystallinity tends to rise as it degrades. Hydrolytic chain cleavage occurs frequently in the amorphous areas of the polymer, leading to a rise in crystallinity. As a result, determining a sample's crystallinity before and after degradation can be used as a supplement to measure degradation progress (Elsawy, Kim, Park and Deep, 2017).

2.1.5.2 Improving PLA degradation

PLA is a biodegradable material that takes a long time to degrade. There has been a lot of research on how to reduce the above-mentioned disadvantages:

Van Cong et al. (2012) investigated the combination of polylactic acid (PLA) with ethylene-vinyl acetate (EVA) in their research. It was discovered that increasing the EVA concentration of the blends (40 wt.%) resulted in an increase in PLA degradation, as indicated by the weight loss results seen after 15 months. The presence of crystalline structures and phase separation between PLA and EVA contributes to the observed rise in weight loss of the PLA/EVA blend. In addition, Singla et al. (2017) discovered that adding EVA to PLA decreases its crystallinity and decreases its Tg. During the amorphous phase, the decreased crystallinity leads to improved water absorption and increases microbe attack. Furthermore, during the continuous PLA phase, the addition of more EVA content resulted in an increased dispersion of EVA droplets. The presence of EVA droplets, which are isolated from the PLA phase, enhances the diffusion of water, and increases microbiological activity.

Taiatele et al. (2019) examined the breakdown of films produced from a combination of thermoplastic starch (TPS) and poly(lactic acid) (PLA), as well as the process of composting these films. When composted, PLA blends with TPS, which breaks down after 21 days and undergoes a more severe and faster breakdown during composting. The addition of starch to PLA blends resulted in increased water absorption, suggesting an improvement in the blends' hydrophilic properties. This improvement in water absorption leads to swelling of the polymer and an accelerated rate of biodegradation. Akrami et al. (2016) found that adding starch into PLA not only enhances its hydrophilic properties, but also destroys its crystalline structure, leading to an accelerated breakdown rate of PLA blends. The hydrolysis reaction rate is considerably lower in the crystalline region compared to the amorphous region, which has less organization. The amorphous region is more susceptible to hydrolysis due to the higher permeability of water compared to the crystalline zone. Consequently, the process of blending can modify the crystalline structure of PLA, resulting in samples that degrade at different rates.

Rahmani et al. (2020) examined the decomposition of poly(mannitol sebacate) (PMS)/PLA blends in a controlled environment using a phosphate-buffered saline solution with a pH of 7.4 and sodium azide at a temperature of 37 °C. Due to the significant mass loss, PMS improves PLA's biodegradability. Compared to PLA, PMS is a biodegradable polyester that degrades rapidly. PMS, which incorporates hydroxyl groups from mannitol moieties into its polymer chain, enhances the hydrophilicity of PLA blends. Water contact angle analysis evidenced the enhanced hydrophilicity of PLA blends, showing a decrease in the angle as the amount of PMS in the blend increased. The increased hydrophilicity significantly improved water permeability, resulting in an accelerated rate of PLA biodegradation.

Furthermore, alternative methods exist to enhance the PLA degradation rate. These entail the use of natural rubber and hydrophilic natural fibers, such as rice straw. The next topic will address this issue.

2.2 Natural Rubber (NR)

The chemical structure of NR is cis-1,4-polyisoprene, which is the product of its biosynthesis. NR is a biopolymer and is widely used in everyday life. It possesses a distinctiveness that sets it apart from other rubber types. NR, being an agricultural commodity, is considered renewable. Carbon dioxide is used as the starting ingredient in the biosynthesis of natural rubber, resulting in a carbon-neutral process. Consequently, it does not have any impact on the phenomenon of global warming. Upon reaching the end of its lifespan, it undergoes decomposition, resulting in the production of carbon dioxide. As a result, there is no rise in the quantity of this gas (Kohjiya and Ikeda, 2014).

2.2.1 Properties of NR

The several beneficial characteristics of natural rubber (NR), including its high tensile strength, flexibility, resistance to crack formation, and less heat build-up, have drawn attention (Akhtar, Bhowmick, and De, 1986).

From a chemical perspective, natural rubber is primarily composed neat poly-cis-1.4 isoprene, with particles ranging in size from 0.15 to 3 μm and a molecular structure of C5H8 (Figure 2.4). Non-isoprene structural units may also be bonded at the ends of its macromolecules. The qualities of natural rubber are also significantly impacted by the presence of non-rubber component, which varies between 5 and 10%. The recurrent isoprene units possess a double bond that facilitates crosslinking or vulcanization, allowing the rubber's three-dimensional structure to exhibit its elastic capabilities. Vulcanization is the procedure of introducing vulcanization agents, such as sulfur, peroxide, resins, and metal oxides, into latex to improve the characteristics of rubber. This transformation involves the formation of a network of interconnected molecules, converting the rubber from a plastic-sensitive substance to a technologically valuable material. In other words, it changes the rubber from a thermoplastic to a thermoset (Ansari, Jakarni, Muniandy, and Hassim, (2021).

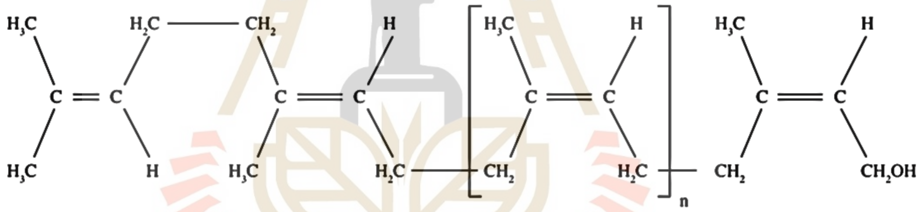

Figure 2.4 The chemical structure of natural rubber's cis-1,4-polyisoprene (Herculano et al., 2011).

2.2.2 Toughness improvement for PLA by blending with NR

Toughness is the ability of a substance to absorb energy and undergo plastic deformation without breaking. According to Chen, Zhang, Jin, and Park (2018), the stiffness of PLA's backbone chain results in low toughness, which restricts its application in various industries. As a result, the toughness of PLA has been enhanced using several methods, including plasticization, melt blending with various tough polymers or rubbers, thermoplastic elastomers, and copolymerization (Nagarajan, Mohanty and Misra, 2016). However, blending with natural rubber is one of the most common approaches since it is a bio-based material with excellent elasticity, ductility, and low cost, making it a good choice for toughening PLA, as has been widely reported.

Bitinis Verdejo, Cassagnau, and Lopez-Manchado (2011) improved the high brittleness and poor crystallization characteristics of PLA through blending it with NR at different ratios. A blend of PLA and NR was produced utilizing an internal mixer. The researchers discovered that the ductility of PLA was greatly enhanced with the incorporation of NR. The addition of 10 wt.% NR significantly enhanced the elongation at break of neat PLA, increasing it from 5% to 200%. Furthermore, the use of NR not only accelerated the process of crystallization but also improved the capacity of PLA to crystallize.

Pongtanayut, Thongpin, and Santawitee (2013) conducted a study to improve PLA's toughness characteristics by combining it with NR at weight ratios ranging from 0% to 30%. The researchers found that the continuous PLA matrix evenly distributed the NR phase as small droplets. The presence of excessive NR concentrations will lead to the formation of larger rubber droplets. Adding NR would improve PLA's ability to crystallize, but it would also reduce its thermal stability. Blending PLA with NR has greatly enhanced its ductility. The concentration of NR at 10% weight appears to have the most favorable characteristics. When the NR content is high, its tensile properties appear to decrease.

Thongpin, Klatsuwan, Borkchaiyapoom, and Thongkamwong (2013) conducted a study to investigate the crystallization behavior and thermal stability of PLA when various ratios of NR were added. They discovered that rubber particles formed a spherical dispersed phase in PLA for initial systems with a low NR of 10-30 wt.%. However, with higher NR content of 40-50 wt.%, the rubber particles were observed to form a co-continuous phase. The inclusion of NR in PLA did not impact the plastic's glass transition temperature (Tg), but it did have the potential to initiate cold crystallization (Tc) and subsequently increase the plastic's crystallinity. This resulted in a modification in the melting temperatures (Tm) of PLA. Remarkably, the heating process at temperatures higher than the Tm of PLA revealed exothermic behavior, specifically when the NR concentration ranged from 10-30 wt.%. The cross polymerization between NR and PLA molecules results in an increased fast the decomposition temperature of the polymer blend. When NR vulcanized was added to PLA, it was observed that NR particles dispersed in the continuous phase of PLA.

Nevertheless, when the NR contents increased, the particles exhibited a larger size. The impact of NR particles on the crystallization of PLA was seen to be like the previous instance. However, the process of combining two polymers through cross polymerization was not detected in the DSC thermograms. Therefore, the blends exhibited two separate stages of degradation and PLA showed lower stability during TGA compared to the previous system.

Chen, Yuan, and Xu (2014) developed a highly durable PLA/NR blend material using a dynamic vulcanizing process. It was found that the cross-linked NR phase exhibited a continuous dispersion resembling a network structure. The interfacial compatibility is enhanced when PLA is grafted onto NR using melt-blending. The mixture containing 35 wt.% of NR exhibited a distinct shift from being brittle to becoming ductile, with an impact strength of 58.3 kJ/m^2, approximately 21 times higher than that of the neat PLA. This network exhibited strong adhesion at the interfaces, resulting in enhanced impact resistance and elongation at the point of failure of the blend. In addition, the FTIR analysis indicated that the PLA-NR grafts were created by introducing peroxide and increasing the NR content. This demonstrates that the interfaces between PLA and NR are chemically compatible. According to their suggestion, when the blend of dynamically vulcanized materials is loaded, the PLA phase effectively transfers fracture energy to the deformed continuous NR phase across the strong interface. This leads to a significant improvement in toughness and elongation.

Xu, Yuan, Fu, and Chen (2014) examined the brittle-ductile transition of PLA in the addition of NR at varying concentrations ranging from 10 to 40 wt.%; there was no modification to the interface. According to the researchers, the PLA/NR blend is incompatible and forms a two-phase structure. NR exhibits a slightly greater viscosity and storage modulus compared to PLA when in its molten state. The dispersed NR droplets, which have a relatively high modulus, function as "hard particles" that increase the viscosity of the PLA melt at low NR concentrations. At high concentrations of NR, the droplets combine to form co-continuous phases. In this situation, the NR phase preserves zonal dispersion, while the PLA continuous phase, with its significantly lower viscosity, acts as a lubricant, allowing the rotor to move smoothly between the

NR zonal phases. This results in blends with low viscosity. The 35 wt.% NR phase exhibited a continuous structure resembling a network, resulting in an improved impact strength of around 500 J/m. This value is roughly 7 times higher than that of neat PLA. Enhancements in the mechanical characteristics of PLA/NR blends are anticipated through the resolution of interfacial interaction between the two materials.

Mohammad, Arsad, Rahmat, Abdullah Sani, and Ali Mohsin (2016) examined the effect of the compatibilizer on the structure and characteristics of PLA/NR blends. The addition of 5–20 wt.% of NR decreased the brittleness of PLA. Two distinct compatibilizers, PLA-g-MA and NR-g-MA, were employed as coupling agents. A notable improvement in mechanical properties, specifically in elongation at break, was observed when 10 wt.% of NR was added. Furthermore, with the addition of 15 wt.% of NR content, the impact strength increased. This improvement was obtained by including NR-g-MA in the polymer blend. The addition of compatilizers dramatically reduced the Tg to a level like that of neat PLA. This improvement in compatibility between PLA and NR polymer blends was attributed to the presence of compatilizers. In addition, the thermal stability of the compatible blends is increased by approximately 5–10% compared to neat PLA due to the interaction and dispersion of the components. The SEM observation revealed a small enhancement in interfacial adhesion with no void formation, as well as a significant reduction in the presence of spherical NR particles in the polymer blend.

2.2.3 Effect of NR on degradation of PLA

PLA is a biodegradable polymer with a long degradation time. There has been a lot of research into how to reduce the time it takes for PLA to degrade, and adding natural rubber is the best option due to its low cost and assistance in improving PLA decomposition. Several research studies have reported the impact of NR on the degradation of PLA;

Huang et al. (2013) investigated the effect of NR on the hydrolytic breakdown process of PLA. The researchers discovered that NR could increase the hydrophobicity of the PLA surface, but it does not lead to a reduction in water absorption within the bulk of PLA. In contrast, as the NR content increases, water absorption rises. The hydrolysis takes place throughout the whole volume of the specimens rather than being limited to the surface, demonstrating a type of degradation known as bulk erosion. NR does not appear to influence PLA's hydrolysis process, thereby promoting PLA biodegradation when blended with NR. Furthermore, the thermal properties examination revealed that NR has a negative impact on PLA crystallization. These findings will be advantageous for maintaining the biodegradability of PLA when blended with NR.

The study conducted by Sookprasert and Hinchiranan (2017) investigated the hydrolytic degradation of PLA, PLA/NR, and PLA/NR/NR-graft-PLA blends, both with and without the incorporation of NR-graft-PLA (with a grafted PLA content of 36.7 wt.%). The results show that adding NR slowed down the hydrolytic breakdown of the blend because NR is hydrophobic. Adding NR-graft-PLA makes the PLA and NR phases more compatible, which makes it easy for water to diffuse into the amorphous PLA matrix in the blends. Consequently, the enhanced compatibility of PLA/NR/NR-graft-PLA blends allows for the preservation of the hydrolytic degradation rate, which is like that of neat PLA.

Rosli, Ahmad, Anuar, and Abdullah (2018) conducted a study to examine the thermal stability and biodegradability characteristics of poly(lactic acid)-natural rubber (PLA-NR) with and without liquid natural rubber (LNR) as a compatibilizer. It was discovered that the addition of NR improved the ability of PLA to withstand high temperatures by behaving as a thermal stabilizer. However, the inclusion of LNR did not have a substantial impact on the thermal stability of the PLA-NR blend. The biodegradability of PLA in soil was significantly improved by adding NR up to 300%, with water absorption identified as a key factor influencing the degradation process. In addition, the biodegradability was seen to enhance with the inclusion of 8 weight percent of LNR due to its significant water absorption capacity. Nevertheless, the biodegradability experiences a minor decline when incorporating low LNR concentration, because of chemical bonding and enhanced adhesion between PLA and LNR. The incorporation of LNR resulted in a significant improvement in water contact angle analysis. The water contact angle of PLA decreased from 54° to 39° upon the addition of NR. However, the addition of LNR significantly raised the water contact angle to 73°.

Buys, Aznan, and Anuar (2017) investigated the impact of blend content on the mechanical characteristics, morphological development, and hydrolytic degradation behavior of PLA/NR blends. According to their report, the addition of NR improved the blends' elongation at break and impact strength but decreased the samples' tensile strength and stiffness. The blends exhibited two peaks in the Dynamic Mechanical Analysis (DMA) measurements at a temperature of -70°C. These peaks corresponded to the Tg of NR and at 65°C, which is the Tg of PLA. The FE-SEM micrograph of the 70PLA/30NR specimen revealed the presence of two clearly distinguishable phases, suggesting that the PLA/NR blends are immiscible. The hydrolytic degradation behavior was assessed by quantifying the residual weight of the samples after they were submerged in a sodium hydroxide solution for a specific duration. The deterioration behaviour of PLA/NR blends is influenced by the composition of the blends. The neat PLA and 70PLA/30NR blend exhibited the highest degradation rate, with complete degradation occurring after 35 days. In contrast, the 50PLA/50NR, 30PLA/70NR blend, and neat NR had the slowest degradation rates, respectively. Thus, they deduced that the ability of blends to be combined and their structure significantly influenced the rate at which they degraded.

Tertyshnaya et al. (2022) studied the thermal and dynamic characteristics of PLA/NR blend substrates both before and after degradation in soil over a period of 60 and 220 days. The researchers discovered that the soil had a significant impact on the physical structure of the PLA/NR blend, resulting in the development of fractures and a rough surface. After 220 days of being exposed to soil, the level of crystallinity in neat PLA increases, whereas in the PLA/NR blend it slightly declines. The breakdown of PLA/NR blends by living organisms is obviously affected by the proportion of components and the structural characteristics of the resulting composites. The PLA/NR blend's incompatibility is beneficial for the degradation process. Homogeneous structures tend to be stronger than heterogeneous ones. The influence of NR on the degradation of PLA is evident. The values of Tm and Tg in samples of PLA/NR blends of all compositions exhibit a tendency to decrease, whereas in neat PLA, they show an increase. Typically, the Tg value drops when the polymer disintegrates. Moisture that is absorbed during weathering causes the polymer to become more flexible, which in turn enhances the movement of the polymer chains and leads to lower Tg. This study found that the breakdown of PLA was not extensive enough. Instead, the crystallizing polymers underwent a process akin to polymer annealing, resulting in an increase in both the degree of crystallinity and the Tg. Furthermore, the crystalline grains exhibit a high level of compaction of macromolecules and possess resistance against harsh environmental conditions. Their degradation is linked to reduced permeability for all categories of low-molecular-weight liquids and gases.

2.2.4 Improving the compatibility between PLA and NR

The properties of NR are excellent toughness, flexibility, and low cost. Additionally, NR is a sustainable and decomposable substance. Several studies have demonstrated that the direct blending of PLA with NR can enhance PLA's toughness. However, the concern lies in the poor interfacial adhesion force between the PLA and NR phases due to their differing polarities and NR's high molecular weight. This results in a low level of compatibility between the two polymers. This results in a lack of effective improvements in PLA's mechanical properties. Therefore, researchers conducted numerous studies to enhance the compatibility between PLA and NR. This study focused only on investigating the improvement of mechanical compatibility. The reason for choosing that method is its environmental safety and cost-effectiveness.

The research conducted by Jaratrotkamjorn, Khaokong, and Tanrattanakul (2012) improved the mechanical properties of PLA/NR blend by modifying the polarity, molecular weight, and viscosity. This study utilized rubber mastication in a two-roll mill, with a varying number of mastication passes from 20 to 240. It was discovered that the molecular weight and viscosity of NR reduced when the number of mastication increased. NR mastication improved the impact strength of PLA/NR blends. The optimum number of mastications was found to be between 80 and 180, resulting in the achievement of an optimal particle size. In addition, the number of mastications at 100 times improved the elongation at break of PLA/NR blends.

Zhang et al. (2013) conducted investigations to enhance the compatibility of PLA/NR blend with pre-hot shearing. The NR sample was put through shearing for 5 minutes and 10 minutes using an internal mixer, to compare it with the non-sheared sample. It was found that its mechanical properties improved after shearing for 10 minutes. Furthermore, rheological investigations have also demonstrated an enhanced compatibility of the PLA/NR blend when subjected to long pre-hot shearing.

Pattamaprom et al. (2016) investigated the influence of increasing mastication speed on the viscosity reduction of NR and its effect on the properties of impact strength. The optimal rotational speed for mastication was determined to be 40 rpm for a duration of 15 minutes. This speed was shown to result in a smaller size of the NR phase and increased compatibility of the PLA/NR blend. The study revealed that the impact strength of the blends could be enhanced by using masticated NR.

The study conducted by Phattarateera and Pattamaprom (2019) investigates the various impacts of viscosity on natural rubber (NR), because viscosity influences the compatibility of the PLA/NR blend. The NR was masticated using an internal mixer for various times, ranging from 0 to 24 minutes. It was discovered that an overly extended masticating time (24 minutes) resulted in a substantial decrease in viscosity and an abrupt decrease in mechanical properties. This occurs because of the rapid aggregation of NR particles.

2.3 Rice Straw (RS)

Rice has played a significant role in Thailand's culture, economy, and politics for more than 2,000 years. In addition to being the principal crop used as a staple in the nation, rice is also its largest agricultural export (Suebpongsang, Ekasingh and Cramb, 2020). The stalks and leaves of rice plants that are still present after the grains have been harvested are referred to as "rice straw." It is a byproduct of rice farming and is widely distributed in rice-growing regions. The characteristic color of rice straw is tan or golden, and it has a hollow, cylindrical shape. Rice straw, a significant agricultural biomass waste produced in South-east Asia and Thailand, is frequently incinerated in the field, resulting in enormous environmental issues. Thailand reportedly produces over 20 million metric tons of rice straw each year, and during the busiest rice harvesting periods, 90% of rice paddies burn the straw to dispose of it

(Kophimaia et al., 2020). Burning straw increases atmospheric pollutants such sulfur oxides, CO_2, CO, and hydrocarbons, which are harmful to the climate and crop yields. Rice straw burning releases particulate matters (PM), namely PM 2.5 (particles with a size of 2.5 m) and PM 10 (particles with a size of 10 m), which remain suspended in the air for an extended period. A significant number of individuals suffer from asphyxiation and respiratory distress because of particulate matter (PM) (Singh and Arya, 2021). Rice straw, despite being a significant waste, poses significant hazards when burned. However, by transforming rice straw into reinforcing agents for polymer composites, we may both benefit humanity and increase the value of the rice straw.

2.3.1 General Properties

Rice straw is the remaining byproduct from the process of harvesting rice. It is either stacked or distributed around the field, depending on the methods used for harvesting. The total amount of rice straw removed from the field is contingent upon the height at which it is cut. The straw-to-paddy ratio can range from 1.0 to 4.3 and from 0.74 to 0.79. Rice straw is a type of plant material that is made up of 38% cellulose, 25% hemicellulose, and 12% lignin. It is classified as a lignocellulosic biomass. Rice straw has a lower cellulose and lignin content compared to other plants, such as softwood, but it has a higher hemicellulose degree. The moisture level of rice straw is a crucial factor in identifying the appropriate processing methods and potential applications since it directly impacts both the heating value and volume reduction. Furthermore, a low bulk density leads to poor blending and an uneven distribution of temperature (Hung et al, 2020).

2.3.2 Rice straw composites with PLA

Over the past ten years, natural fiber/filler reinforced composites have gained a lot of attention due to their excellent mechanical properties, substantial processing advantages, chemical resistance, low density ratio, and cheap cost. The resulting composite is eco-friendly and sustainable due to its incorporation of biodegradable thermoplastic polymers and renewable agricultural ingredients like rice straw. There have been numerous published research studies on rice straw composites made of PLA.

In their study, Zhu, Qiu, Liu, and Sakai (2019) utilised an eco-friendly physical technique to enhance the compatibility of rice straw (RS) with a PLA matrix. They achieved this by attaching attapulgite (ATP) nanorods onto the surface of the RS, resulting in a modified rice straw (MRS). The MRS/PLA composites exhibited enhanced tensile strength and modulus compared to the RS/PLA composites, owing to better interfacial adhesion between the RS and PLA matrix. The newly formed PLA-ATP interlayer resulted in improved interfacial adhesion. ATP's heat barrier effect resulted in greater thermal stability for MRS/PLA composites compared to RS/PLA composites. The findings revealed that the interlayer of attapulgite on the surface of rice straw enhanced the properties of MRS/PLA composites, resulting in greater compatibility between the two materials.

Nizamuddin et al. (2021) presented a new idea of incorporating rice straw hydrochar (HC) into PLA at various loadings. Rice straw undergoes hydrothermal carbonization (HTC) when exposed to microwaves, resulting in the production of hydrochar. The research showed that the storage modulus of PLA/HC composites was higher than that of neat PLA. This suggests that PLA and hydrochar have formed a network structure. SEM images reveal that neat PLA has a soft and smooth surface, while PLA/HC blends display irregular holes and fissures due to the porous characteristics of hydrochar. The addition of hydrochar to PLA/HC composites at loadings of 5%, 10%, 15%, and 20% resulted in a rise in the tensile modulus of neat PLA from 2.627 GPa to 4.376 GPa, 4.895 GPa, 5.217 GPa, and 6.182 GPa, respectively. Despite being slightly less stable than neat PLA, it remains stable across the entire range of PLA procedures and applications (30–240 °C).

Beniwal and Toor (2023) utilised rice straw (RS) for producing eco-friendly composites. The modified fibers were incorporated with PLA to produce composite films. These films exhibited enhanced thermal stability and crystallinity. The results of the mechanical tests revealed a significant 94.9% improve in the tensile strength of the film, as well as a substantial approximately 605% increase in its toughness. Compared to PLA films, the modified films exhibited reduced water permeability and increased hydrophobicity, indicating successful incorporation of fillers into the matrix. The synthesised films exhibited enhanced physiochemical and physical properties, suggesting their potential suitability for packaging purposes.

Freitas, Gonzalez-Martinez, and Chiralt (2023) conducted study on PLA-TPS bilayer films composed of thermoplastic corn starch (TPS) and PLA, with or without the inclusion of rice straw (RS). Their findings revealed that these films had improved functional properties for food preservation. PLA offered a wet food contact alternative with the ability to prevent water vapor from passing through, while TPS provided the laminates with the ability to prevent oxygen from passing through. Incorporating cellulose fiber (CF) into TPS enhanced the barrier properties and reinforced the structural integrity of the films. The PLA's elongation at break had a slight decrease due to the RS extract, however, its oxygen barrier capacity was enhanced. The tensile and barrier characteristics of bilayer films were modified due to the migration of low molecular weight compounds from each monolayer to the other, resulting in changes in the functionality of each layer. Although the addition of RS extract in the PLA sheet had a minimal impact on the water vapor permeability (WVP) and caused a decrease in the resistance and elongation at break of the bilayers, the bilayers that included CF in the TPS sheet exhibited the lowest levels of oxygen permeability. The bilayers with CF have reduced oxygen permeability.

2.3.3 Effect of Rice straw on degradation of PLA

Several studies demonstrate that PLA can undergo degradation in the environment, resulting in the release of carbon dioxide, water, and methane. The rate of degradation ranges from several months to 2 years, depending on the specific environmental conditions. Typically, the decomposition of PLA in the soil is gradual and requires a significant amount of time. Adding hydrophilic fillers to the PLA matrix is expected to improve the degradation of PLA. The study investigated the biodegradability of PLA/RS composites by combining rice straw (RS), an agriculturally derived waste material with inherent hydrophilic properties, with PLA. The addition of rice straw improves PLA decomposition. Researchers have reported numerous studies on the impact of rice straw on PLA degradation.

Sakai et al. (2011) conducted a study to examine the water absorption and degrading abilities of rice straw/PLA composites. The study focused on utilising agricultural wastes effectively. The researchers found that the addition of a greater amount of hydrophilic rice straw substantially raised the optimal water content of PLA composites. After subjecting the PLA composites to natural weathering for a duration of 6 months, the materials exhibited the development of supplementary microcracks on their surface. Furthermore, during the periods of testing with the highest amount of precipitation, there was a notable decrease in both the tensile strength and fracture strain. The results may be attributed to the water absorption facilitated by hydrophilic rice straw. Upon burial in soil, a greater amount of microcrack development was detected on the PLA composites compared to the neat PLA. Furthermore, due to the prolonged testing time, there was a notable reduction in the tensile strength and fracture strain of the PLA composites containing 30 wt.% rice straw. The findings indicated that certain bacteria were carried through water absorption, hence accelerating the process of biodegradation.

Zandi, Zanganeh, Hemmati, and Mohammadi-Roshandeh (2019) developed PLA/rice straw biocomposites with a higher rate of biodegradation at a lower cost by chemically modifying rice straw (RS). The results indicated that the addition of RS led to a reduction in the Tg and Tm thermal transitions of PLA, while simultaneously increasing its degree of crystallinity. This can be attributed to the presence of heterogeneous nucleation sites and an accelerated growth stage. A soil burial experiment conducted indoors for a duration of 128 days demonstrated that polymer composite samples underwent rapid degradation, particularly when subjected to higher loadings of RS fillers.

Pongputthipat, Ruksakulpiwat, and Chumsamrong (2022) developed sustainable and biodegradable biocomposite films by utilising renewable materials including poly(lactic acid) (PLA), natural rubber (NR), and rice straw (RS). The PLA/NR blend with an NR content of 30 wt.% was decided on for mixing with RS powder due to its better elongation at break, measuring 372.10%. RS was incorporated into the PLA/NR/RS biocomposite at several concentrations ranging from 3, 5, and 10 wt.% of the blend. The inclusion of RS fiber resulted in a reduction in the tensile characteristics of the film. The biocomposite films, which had 3 and 5 wt.% of RS, exhibited a ductile fracture behaviour. The tensile strength and elongation at break of the PLA/NR/RS biocomposite films exhibited a reduction with an increase in the RS component. The biodegradability of the neat PLA, PLA/NR blend, and all biocomposite films was evaluated by determining the percentage of weight loss in the film samples after being buried in soil for 90 days. The weight loss of the composite film increased as the amount of RS increased after 90 days of soil burial. The biocomposite at 10 wt.% of RS exhibited the greatest decrease in weight. Following burial in soil, the molecular weights of the PLA phase in all the films reduced as determined by GPC analysis.

2.4 Seedling bags and mulch films

2.4.1 Seedling bags

Plants can be cultivated in various methods. Although direct seed sowing into seedbeds is easy, it can be successful in some situations, and it also depends on having strong seeds and suitable environmental circumstances. Therefore, raising seedlings in seedling bags is a viable alternative and crucial for safeguarding against pest predation. Furthermore, it can help increase seedling survival rates and reduce cultivation loss. When transplanting seedlings into the soil, it is essential to tear and get rid of the plastic seedling bags, as the bags are non-biodegradable in the soil. This action causes the seedlings' roots to tear off. Seedlings may exhibit inefficient growth. In addition, the waste from plastic seedling bags has been an important environmental issue in recent years. The remaining plastic becomes waste that is difficult to dispose of and has the potential to cause air pollution when burned. These methods are used because of the expensive operation required for the efficient removal of these films after they are applied, as well as the lack of a cost-effective disposal solution. Another issue arises from the films' challenging recyclability, mostly due to the substantial presence of organic objects that cling to the material. Although the nursery bag may have the ability to break down naturally, it is crucial that it does not undergo decomposition at an excessively fast rate. An important property of a seedling bag is its resistance to both adverse weather conditions and pest infestations. It is possible to keep the seedlings in the seedling bag until they have grown strong and are ready for planting. When considering the replacement of traditional film for nursery bags, it is important to consider the new film's mechanical properties and bag-molding abilities. For the above reasons, many researchers have studied and developed numerous biodegradable nursery bags.

The study by Amir-Hashim, Roslim, and Rosni (2012) investigated the properties of seedling bags produced using a composite of natural rubber latex (NR). It was discovered that the tensile strength was sufficient for holding the anticipated amount of soil for the bag's size without any fractures. Despite having discovered that the lowest measured tensile strength was 12.6 MPa, it was still sufficient for holding the amount of the soil contained in the bag. The study discovered that NR latex films used for seedling bags exhibit excellent tensile strength, however stiffness drops as the amount of non-rubber components used in filling increases. The film with 30% corn starch had the highest modulus value was 1.87 MPa, but the unfilled film demonstrated the highest elongation at break. Subsequently, the combination of calcium carbonate and fertilizer resulted in an enhancement of stiffness and a reduction in the degree of elongation at the point of fracture of the film. This suggests that the physical form of the filler substance and its interaction in the rubber matrix have an impact on its properties.

Suaduang et al. (2019) did a study on the use of films for packaging purposes, such as nursery bags and greenhouse bags. These films were produced using a combination of polylactic acid (PLA) and spent coffee grounds (SCG). The researchers discovered that as the amount of SCG increased, the tensile properties exhibited more elongation at break. Simultaneously, the hardness, brittleness, and modulus at break decreased. The tensile strength drops as the content of SCG increases, due to the dispersion of SCG within the PLA matrix. When the concentration of SCG rises to 10 wt.%, the modulus at break of neat PLA lowers to 22.13% and 19.11%, respectively. This decrease indicates a reduction in brittleness compared to neat PLA. This study demonstrates the feasibility of improving the brittle PLA for film applications due to its favourable mechanical properties and ability to biodegrade in natural surroundings.

Bilck, Olivato, Yamashita, and Pinto de Souza (2014) developed biodegradable bags using a combination of thermoplastic starch and PBAT. They planted the seeds without removing them from the bag. Following 240 days of transplanting into planters, the seedling bags underwent complete biodegradation. The dry mass of these plants showed no discernible difference from those transplanted without the seedling bags. They can produce biodegradable seedling bags that can be instantly transplanted into the soil without the need to remove the bag, thereby preventing root damage. This is an alternative replacement for non-biodegradable plastic.

2.4.2 Mulch films

For decades, people have applied mulch films directly to the soil's surface for a variety of purposes, such as providing protection of seedlings and young shoots, preserving soil moisture, inhibiting weed growth, and preventing soil erosion. Due to its excellent mechanical properties, low cost, and ability to operate as a barrier for sunlight and water, in general, polyethylene (PE) plastic has been the most effective material for mulch films. However, because of the potential for plastic pollution and health dangers connected with its usage, it is also costly and time-consuming to dispose of these plastic leftovers from the field either before or after harvest. So, a good option for mulch material is biodegradable polymers made from fossil fuels, microbes, animals, and plants (Mansoor et al., 2022).

2.4.2.1 Properties of mulch films

The integrity of mulch films is crucial, and it must be resistant to weather conditions such as wind, rain, light, oxygen, heat, humidity, and microorganisms. As they are being used, biodegradable polyester mulch films are vulnerable to the elements. To modify the polymers used in the production of mulch film, it is necessary to study important characteristics of mulch films, such as their mechanical, thermal, and spectral properties. These are important decisions to consider (Adhikari et al., 2016).

2.4.2.1.1 Mechanical properties

Mulch films must have mechanical properties to retain their integrity and resist damage from environmental factors. The films' mechanical properties, including tensile strength, elongation at break, and modulus, are directly influenced by their natural weathering. PE plastic is commonly used to produce mulch film, as previously mentioned. However, if alternative materials are to be used, it is important that they exhibit corresponding mechanical properties with PE.

These properties include a tensile strength at yield of about 6.8 MPa, a Young's modulus of around 0.1 GPa, and an elongation at break of about 410% (ExxonMobil, 2021). The produced films on MD and TD have varied mechanical properties depending on the orientation of the film process; as a result, each one needs to be studied separately. It was discovered that mulch can be made from biodegradable materials (Stachowiak, Postawa, Malinska, Drózdz, and Pudełko, 2022). A lot of research has been done on the mechanical characteristics of mulch films produced from biodegradable materials to be utilized as a replacement to conventional plastics. Nuinu, Samosorn, Srilatong, Tongbut, and Saengsuwan (2013) studies mulch film from the PLA/ENR blends filled with rutile TiO_2 as fillers. They discovered that adding ENR content can improve the elongation at breaks in PLA films. Tan et al. (2016) conducted studies on the physical properties of mulch films produced from biodegradable polymers and natural fibers. The fiber consisted of waste fibers from ramie and cotton, which were combined with poly(vinyl alcohol), polyacrylate, and starch. According to the results of the experiments, it was determined that these fiber/polymer films have desirable physical properties that were suitable for usage in mulch film applications.

2.4.2.1.2 Thermal properties

The thermal characteristics of the materials are critical for applications, especially when they must perform under temperature-relevant conditions. Thermal degradation breaks the molecular bonds of polymers, thereby influencing the material's properties. Thermal decomposition, thermo-oxidative degradation, and thermo-mechanical degradation are the three mechanisms that can occur when heat occurs. Variables such as temperature and molecular weight influence the thermal degradation kinetics (Li, Qiang, Chena, and Ren, 2019). Mulch film is often used outdoors, exposing it to sunlight, heat, and changing weather for a long period of time. Therefore, thermal, and light factors directly impact the mulch film. According to Fa, Wang, Ge, and Chao (2020), the PE composite film breaks down first through photo- or thermo-oxidative processes and then completely by microorganisms in the natural environment. The composite film can undergo both procedures simultaneously. The first abiotic oxidation is essential for subsequent biodegradation by microorganisms. The abiotic degradation process occurs through free radical processes, which are produced on the polymer chain because of thermal or light. Also, crop growth is affected by weather, especially the temperature of the soil. It was reported that, when transparent film mulch raised the soil temperature, the growth season was reduced and crop yields and quality decreased (Ning, Liang, Sun, Liu, and Sun, 2020).

2.4.2.1.3 Light transmission

Mulch films are often used in the wide outdoors. This means it was exposed to sunlight for a considerable amount of time. For this reason, polyester film may be exposed to the sun's light. Weathering of polyester mulch films occurs naturally in the presence of sunlight, leading to the breakdown of bonds of ester and the resulting photooxidation (Zhang et al., 2023). In addition, light is a crucial factor to weed growth (Wang et al., 2022). For this reason, the standard mulch film seems to be black. Since plants, including weeds, rely on photosynthesis for their survival, black films reduce their access to the vital photochemically active radiation (PAR) range of 400 to 700 nm. (Carruthers, Longstaff, Dennison, Abal, and Aioi, 2001). Because of its significance, the study of light transmission has attracted a great deal of attention.

Merino, Zych, and Athanassiou (2022) found that the interaction between light and mulches has a substantial effect on their functionality. Mulches that are opaque to the photosynthetically active radiation (PAR) range inhibit the growth of weeds and increase the temperature of the soil. Black mulches increase soil temperature, but white and silver mulches deflect light and are used to reduce soil temperature in situations where elevated temperatures can be detrimental to plants and reduce crop yields. Ning, Liang, Sun, Liu, and Sun (2020) found that a relative light transmission value below 3% was discovered to be necessary for black or opaque mulch films; therefore, their measured coefficients should meet this criterion. Because solar radiation is strongest at 500 nm wavelength, the transmittance of this wavelength was measured to be 1.68%. This percentage is below the specified requirement of 3%. Zhang et al. (2023) studied the natural weathering behavior of films in high-temperature dry and high-temperature humid. They found that natural weathering reduces the film's light transmittance. Surface undulation and haze increased when higher natural weathering broke molecular chains, which are the source of haze in films.

2.4.2.2 Biodegradable mulch films

Mulch films, commonly made of PE, can enhance the cultivation of crops by conserving water and moisture, preventing weed spread, and more. However, after the harvest is over, the crops must be harvested and appropriately disposed of, which is a difficult and costly undertaking for farmers. Finally, this results in the implementation of unfavorable removal methods such as the utilization of burning for mulch films in outdoor environments or their disposal in local landfills. These polymers undergo a process of degradation, transforming into microplastics that possess toxicity towards both living organisms and the environment. Consequently, extensive research has been conducted to develop mulch films that are capable of decomposing naturally. Furthermore, it is possible to incorporate this substance into the soil through harvesting without causing any harmful effects on the environment.

The study by Merino et al. (2022) investigates the application of mulch films made from PLA and plasticized PLA (PPLA) in combination with various industrial vegetable wastes. The researchers discovered that the inclusion of 20% spinach stems in PPLA had an important effect on its biodegradability, resulting in about 40 wt.% biodegradation after 6 months. The GPC results indicated a slight decrease in molecular weight in a period of 6 months, confirming a process of biodegradation. The addition of plasticizer or filler had a slight effect on the biodegradability of PLA. The produced films exhibited a diverse range of nutrients, which are advantageous for the growth and development of plants. Tan et al. (2016) conducted a study on mulch films made from natural fibers and biodegradable polymers. The films were composed of fiber/polyacrylate (VA), fiber/poly(vinyl alcohol) (PVA), and fiber/starch (ST) and were originally white in color. The experimental findings demonstrated that these fiber/polymer films showed acceptable physical characteristics that were suitable for use in mulch films. The fiber/starch and fiber/PVA films were produced using entirely biodegradable materials and exhibited the capacity to replace non-biodegradable films. Nevertheless, the fiber/starch film shows possibilities as a mulch film for crops with short growth cycles, as its rapid soil breakdown (1-2 months) renders it unsuitable for long-term usage. The fiber/PVA and fiber/PA films undergo total degradation after a period of 2-3 months and 3-4 months, respectively.

2.5 Cast Film Extrusion

Plastic films are thin, continuous materials that are usually less than 200 μm (0.008 in.) in thickness. Plastic films are manufactured using several resins, each with distinct physical properties that are ideally suited for specific applications. Film extrusion, cast film extrusion, blown film extrusion, and film casting are all methods used to manufacture plastic films. The research focused on the cast film extrusion process.

Cast film is manufactured by extruding the molten material through a narrow opening called a slit die (as shown in Figure 2.5) and then rapidly cooling it either by encountering a chilly roll or by rapidly cooling it in a water bath. Both techniques exhibit elevated melt temperatures as well as rapid film cooling rates. Consequently, the production of films that exhibit little haze, great clarity, and a high level of gloss is achieved. The melt flow indexes for cast film grades are typically between 5.0 and 12.0 g/10 minutes.

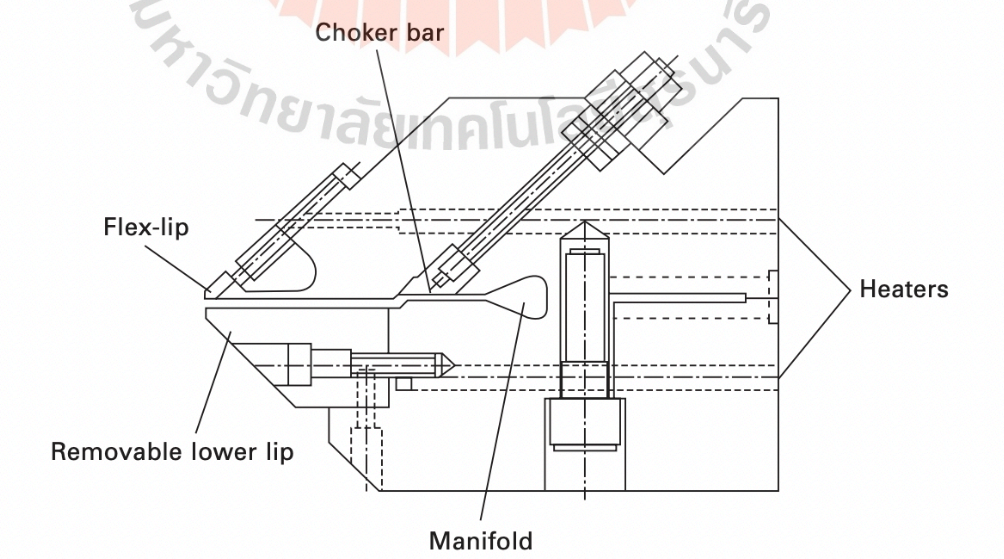

Figure 2.5 Slit die for cast film (Casalini and Perale, 2016).

In the chill-roll cast film process, a plastic film is formed by extruding it through a narrow opening onto the surface of a chill roll. The die is configured to extrude the film material in a vertical or oblique downward direction, causing it to be transferred to the roll surface in a tangential manner. The die functions similarly to a sheet die, typically without a restrictor bar. Both the die lips' gap and the rotational speed of the chill roll are utilized to regulate the thickness of the film by drawing down and thinning the melt web. Consequently, the die gap has been configured to exceed the intended film thickness.

The recommended die gap values for most thermoplastics are 0.4 mm for films up to 0.25 mm (0.01 in.) thick, and 0.75 mm (0.03 in.) for film gauges ranging from 0.25-0.6 mm (0.01-0.024 in.). To modify the thickness of the film in the transverse direction, the die lip adjusters should enable the die gap to be changed at each adjustment point across the width of the die. If the deviation in transverse thickness exceeds ± 5% of the desired thickness, the quality of the film reel will be affected. To ensure consistency in film drawdown rates and physical qualities, it is important to maintain a constant temperature across the die, which will in turn be reflected in the film web. Modifying the temperature profile across the die to change the film thickness will disturb these parameters, leading to subpar film quality. When the process is properly controlled, the consistency of the thickness in chill-roll cast film is far better than in blown film (Drobny, 2020).

Slit die extrusion has been used in film preparation in a variety of studies:

Xie et al. (2014) examined the use of flexible biopolymers like PBS to improve the toughness of PLA. However, the process faced challenges such as reduced strength and stiffness due to unexpected phase arrangement and inadequate interfacial contacts. The study used a single-screw extruder with a slit die and hot stretching to create fibrils for the PBS phase. The extrudate was then cooled in a cold-water bath to solidify the fibrils, resulting in ribbons of in situ fibrillar composites with a thickness of 0.3 mm. The study highlighted the need to generate nanosized PBS droplets during extrusion compounding for nanofibrillar PBS creation. The mean diameter of PBS nanofibrils increased with the PBS content, creating a hybrid structure called a shish-kebab superstructure. Composites containing 40wt.% PBS nanofibrils showed superior properties in terms of strength, modulus, and ductility compared to neat PLA. These composites showed a 31% increase in strength, a 51% increase in modulus, and a 72% increase in elongation at break. PLA exhibits unprecedented levels of strength, modulus, and ductility, making it highly promising for various packaging applications. For the conditions of this study, the temperature profiles were sequentially set at 130, 170, 170, 170, and 165 °C from the hopper to the nozzle. The slit-die's dimensions were 20 mm in width and 2 mm in height. The rolling speed was constant at 50 rpm, and the stretch ratio was estimated to be around 6.7. The flow of cooling water maintained the roll temperature at 30 °C. After stretching, we promptly cooled the extrudate in a cold-water bath at 20 °C to solidify the fibrils in the composites.

Murphy et al. (2017) studied the enhancement of the Young's modulus, yield stress, and elongation to break of PLA through the addition of poly(e-caprolactone) (PCL), indicating a potential alternative, despite the inherent immiscibility of many polymers with PLA. This work utilised high-pressure carbon dioxide (CO_2) to improve the miscibility of two polymers that are typically immiscible when blended. The process of melt blending, utilising carbon dioxide (CO2), was employed to create blends. These blends were then compared to blends produced through solvent casting and melt blending using a single-screw extruder. The pellet condition, including the mixes, barrel temperature, and die temperature, was changed to 160 °C and 170 °C, respectively. The samples were forced through a narrow opening of 1 mm using a slit-die and then transferred onto a moving belt with the help of cooled rollers. Speeds of 20 and 30 revolutions per minute (rpm) were used. The researchers discovered that the use of CO_2-assisted blends led to a notable decrease in the size and quantity of PCL domains inside a PLA matrix. This, in turn, enhanced the adhesion between phases at the microscale. The optimal composition for Young's modulus, yield stress, and elongation to break was determined to be a melt blend consisting of 75% PLA and 25% PCL. The mechanical characteristics of PLA were enhanced through the utilization of CO_2 aided melt blending.

Voznyak, Morawiec, and Galeski (2016) studied the use of slit die extrusion to improve the properties of polylactide (PLA) and poly(1,4-butylene succinate) (PBS) nanocomposites. The researchers used a single-screw extruder with a 12 mm wide, 0.8

mm thick, and 100 mm long slit die, with temperatures ranging from 170°C to 135°C. The slit die was set at 130°C and pressure of 65.0 MPa. The extrudates were then deposited onto a conveyor belt at 25°C, resulting in a film with dimensions of 0.75 mm thickness and 10 mm width. The researchers found that the extrusion process of PLA and the combination of PLA with 3 wt.% PBS resulted in numerous inactive shear bands within the extruded material. The primary deformation process was crazing, with the thickness of PLA/PBS extrudate crazes increasing as strain increased. The surfaces of the craze were coated with PBS nanofibers, which were oriented perpendicular to the craze planes. When the strength of PLA nanofibrils stretched across a craze became too strong, PBS nanofibrils replaced them, preventing breakage. The presence of pre-existing shear bands and nanosized PBS fibers in the PLA/PBS composite enhanced ductility while maintaining high strength and stiffness. The study concluded that the slit die extrusion process at low temperature in a single screw extruder is an efficient technique for manufacturing environmentally friendly nanocomposites.

Voznyak, Morawiec, and Galeski (2018) conducted research on the production of environmentally friendly nanocomposites. They achieved this by melting two polymers and forming nanofibers of one polymer within the other polymer. Shear-induced crystallization stabilized these nanofibers. They created a PLA-PHA nanocomposite using a slit die extrusion process in a single screw extruder, using the same conditions as their studies in 2016. The results indicated improved ductility, stiffness, and strength at low temperatures. The study compared the mechanical properties of neat PLA and PLA/PHA composites under identical conditions. Extrusion processing enhances the strain at break by 17.2% for neat PLA and 18.1% for PLA/PHA composites, while Young's modulus increases to 2.35 GPa.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Poly(lactic acid) (PLA) (Ingeo 4043D) was bought from NatureWorks. Natural rubber (NR, STR 5L) was purchased from Natural Art and Technology Co., Ltd. The rice straw (RS) was obtained from a rice processing facility located in Nakhon Ratchasima Province, Thailand. Dimethylsulphoxide (DMSO) (AR grade), hexane (AR grade), methyl alcohol (AR grade), and chloroform (HPLC grade) were supplied by RCI Labscan Limited.

3.2 Preparation and characterization of PLA blended with masticated NR at different mastication times

3.2.1 Preparation of PLA/NR blends

PLA was dried in an oven at 80 °C overnight to eliminate moisture. Before blending with PLA, NR was masticated at various times (10, 20, and 30 min) with a roll speed of 10 rpm in two roll mill (Yong Fong Machinery, YFY-R-6). PLA/NR blends were mixed in an internal mixer (Haake Rheomix, 3000P) at a temperature of 170 °C with a rotor speed of 60 rpm for 10 min. The ratio of PLA to NR was fixed at 60/40 wt.%. The polymer blends were cut down into smaller pieces using a plastic recycling machine (Tranekaer, DK-5953), and after that, blend films were produced using compression molding (Labtech, LP20-B). The thickness of the film was 0.5 mm.

3.2.2 Melt flow index

In accordance with the ASTM D1238 standard, a melt flow indexer (Kayeness, D40004HV) was used to measure the melt flow index (MFI) of neat PLA and PLA/NR blend. A weight of 2.16 kg was applied at a melt temperature of 190 °C. The average MFI value was determined after cutting and weighing at least 6 extrudates from each formulation at regular intervals. Equation (3.1) is used to determine the melt flow index.

$$\mathrm{MFI} = \frac{600 \times m}{t} \tag{3.1}$$

where MFI is the melt flow index (g/10 min), m is mass (g), and t is cut time (s) (Djellali, Sadoun, Haddaoui, and Bergeret, 2015).

3.2.3 Tensile properties

Tensile properties of all PLA/NR blend films were evaluated following ASTM D882 (thickness less than 1.0 mm (0.04 in.)) using a universal testing machine (Instron, 5565) with a load cell of 5 kN, a crosshead speed of 12.5 mm/min, and a gauge length of 50 mm. The specimen dimension was 15 mm width and 120 mm length. The average data for at least 10 specimens was reported.

3.3 Preparation and characterization of PLA/NR/RS biocomposite films

3.3.1 Rice straw fiber preparation

Rice straw was dried in an oven at 60 °C overnight and ground using a mechanical crusher (Hight speed multi-function mill) at a rotor speed of 1,500 rpm to obtain 44-250 µm particles. After that, ground rice straw was sieved to get <53 µm particles.

3.3.2 Preparation of PLA/NR/RS biocomposites

PLA/NR/RS biocomposites were prepared in various compositions, as shown in Table 3.1. The PLA/NR/NR blend that showed the best properties was used as a composite matrix. The amount of rice straw in the polymer composite was varied in the range of 3, 5, and 10 wt.% based on the total weight of the PLA/NR blend. All compositions of polymer composites were mixed using an internal mixer (Haake Rheomix, 3000P) at a temperature of 170 °C with a rotor speed of 60 rpm for 10 min. The polymer composite was subsequently crushed into small pieces in a plastic recycling machine (Tranekaer, DK-5953).

Table 3.1 Formulations of PLA/NR/RS biocomposites.

Sample code	PLA (%wt.)	NR (%wt.)	Rice straw (%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
PLA/NR/10%RS	54.0	36.0	10.0

3.3.3 Biocomposite films preparation

Cast film extrusion (Betol, BC 32) was used to produce neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films. The barrel (zones 1, 2, 3, 4) temperature was 45, 165, 180, 190 °C, respectively, and the slit die zone was 190 °C. The screw speed and chill roll speed were 40 and 6 rpm, respectively.

3.3.4 Characterization of PLA/NR/RS biocomposite films

In this study, the melt flow index (MFI), tensile properties, thermal properties, and morphological properties of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were observed. The MFI was determined using the same testing method as described in Section 3.2.2. The tensile properties were evaluated using the same testing method as described in Section 3.2.3. The thermal properties were assessed using a differential scanning calorimeter (DSC), while the morphological properties were examined using a field emission scanning electron microscope (FE-SEM).

3.3.4.1 Thermal properties

A differential scanning calorimeter (METTLER TOLEDO, DSC 3+) was used to determine the thermal characteristics of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films. An aluminum pan was used to hold the sample, which weighed between 5 and 10 mg and was sealed with an aluminum cover. To remove the prior thermal history, during the first heating process, the sample increased in temperature from -100 °C to 200 °C at a rate of 5 °C/min. Subsequently, it was maintained at a temperature of 200 °C for a duration of 2 minutes in a nitrogen atmosphere. The sample was subsequently cooled to a temperature of -100 °C at a rate of 5 °C/min (cooling) and then heated to a temperature of 200 °C at a rate of 5 °C/min for the second heating process. The crystallinity degree (Xc) of the PLA phase in polymer composites was determined by utilizing the enthalpy value of a crystalline PLA, as defined by equation (3.2).

$$X_c(\%) = \frac{(\Delta H_m - \Delta H_c)}{\Delta H_m^{\infty}} \, x \, 100 \tag{3.2}$$

where ΔH_m is a measured endothermic enthalpy of melting and ΔH_c is the cold crystallization exothermic enthalpy during the heating scans. The theoretical melting enthalpy of 100% crystalline PLA (93.7 J/g) will be taken to be ΔH_m^{∞} (Tang, Zhang, Liu, and Zhu, 2012).

3.3.4.2 Morphological properties

The morphological properties of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were investigated using a field emission scanning electron microscope (FE-SEM) (Zeiss AURIGA FE-SEM). To identify different phases, the rubber phase of the tensile fractured surfaces was stained with osmium tetroxide for 24 hours and coated with gold. FE-SEM images of the samples were collected using a 3 keV acceleration voltage.

3.4 Biodegradability of neat PLA, PLA/NR blend and the PLA/NR/RS biocomposite films

3.4.1 Soil burial biodegradability

At least 5 samples of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films (30x30 mm) were buried in a box containing soil having a pH of 7 and maintained at 30% moisture by weight. The samples were buried at a depth of 120-150 mm. After being buried for 30, 60, and 90 days, each sample was retrieved from the soil. The obtained specimens were washed with DI water and dried in a vacuum oven at 40 °C to a constant weight. The degradation of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films in soil was assessed using various methods. These included measuring the weight loss percentage, analyzing the chemical components using X-ray analysis and EDX, determining the molecular weight using gel permeation chromatography (GPC), examining the crystalline structure using wide-angle X-ray scattering (XRD), evaluating the tensile properties, analyzing the thermal properties using differential scanning calorimetry (DSC), and studying the morphology using field-emission scanning electron microscopy (FE-SEM). The testing techniques for the tensile, thermal, and morphological properties were conducted according to the methods specified in Sections 3.2.3, 3.4.4.1, and 3.4.4.2, respectively.

3.4.1.1 Weight loss percentage

The weight loss percentage for the specimen test was determined using equation (3.3).

$$\text{Weight loss (\%)} = \left(\frac{w_i - w_t}{w_i}\right) \times 100 \qquad (3.3)$$

where w_i is the samples' initial dry weight and w_t is the dry weight of the samples after being buried in soil for a certain period (Boonmee, Kositanont, and Leejarkpai, 2016).

3.4.1.2 Molecular weight characterization

To extract the PLA phase from the PLA/NR blend and PLA/NR/RS biocomposite films, which were collected both before and after the soil burial test, the film samples were dissolved in dimethyl sulfoxide (DMSO). The solution was transferred into the separatory funnel, and hexene was added. The mixture was shaken to facilitate the separation of the components into two different layers. The DMSO layer was drained out and subsequently precipitated using methanol. After the extracted PLA was obtained, it was dried in a hot air oven at a temperature of 40 °C for a duration of 24 hours. Gel permeation chromatography (GPC, Waters Alliance e2695) was employed to examine the molecular weight and polydispersity index (PDI) of both neat PLA and the PLA extracted from each composite film. Chloroform was used as a solvent and a flow rate of 0.5 ml/min. The volume that was injected was 40 µl, and the concentration of the sample was 0.7% w/v. A calibration curve was generated using polystyrene standards from Waters Corporation, USA.

3.4.1.3 Morphological properties

Morphological properties of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were investigated using a FE-SEM (Zeiss AURIGA FE-SEM). To identify different phases, the rubber phase was stained with osmium tetroxide for a duration of 24 hours. Before performing FE-SEM analysis, a carbon coating on the surfaces of the samples was applied. FE-SEM images of the samples were collected using a 3 keV acceleration voltage.

3.4.1.4 Chemical component characterization

The chemical composition of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite film samples was analyzed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7800) with energy dispersive X-ray analysis (EDX) at an acceleration voltage of 3 kV. The analysis was conducted both before and after the samples were buried in soil. The samples were prepared using a similar technique to that utilized for FE-SEM analysis, with the only distinction being the use of a gold coating on the sample surfaces.

3.4.1.5 X-ray diffraction analysis

Neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite film samples were exposed to X-ray diffraction (XRD) investigations. The analyses were conducted using a Bruker D2 PHASER X-ray diffractometer equipped with a CuKα (λ = 1.54 Å) source. The objective was to identify the crystalline phases present in the materials. The samples were scanned in the angular intervals ranging from 5 - 50 degrees.

3.5 An application of biocomposite films as Seedling bags

The neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite film were cut, and two pieces were connected by heat sealing to produce seedling bags sized 10x15 cm. Each seedling bag was punctured to create 12 holes, each about 0.5 cm in diameter, as shown in Figure 3.1. Subsequently, the chili seedlings were transferred into bags filled with soil and placed in a plant pot filled with soil. Watering is carried out every day, while fertilizer takes place once a month. To evaluate the efficacy of plant development in biocomposite bags, various parameters, including the plant's dry weight, stem diameter, height, and total weight of chili fruits per plant, were assessed after a three-month period. The measurements were taken from three chili plants, and the results were averaged. For dry weight evaluation, the plants were washed with deionized water and then dried in a vacuum oven at 100 °C until a constant weight was achieved. Subsequently, the dry plants were weighed.

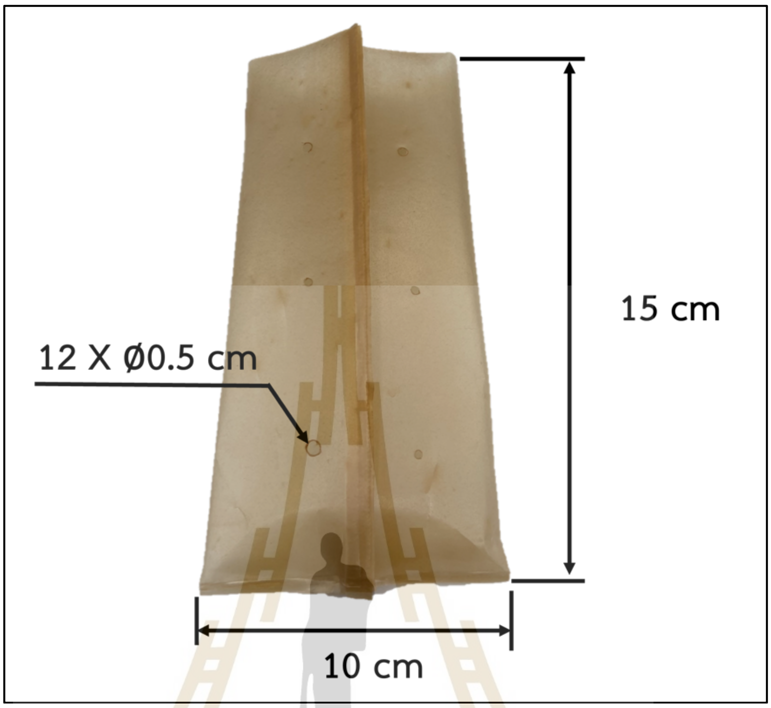

Figure 3.1 Dimensions of seedling bags.

The biodegradability of the seedling bags was assessed after a three-month period of growing chili plants. The evaluation was conducted using various methods, including measuring the percentage of weight loss, characterizing the molecular weight using GPC, analyzing the tensile properties, conducting wide-angle x-ray scattering (XRD), examining the thermal properties using DSC, and assessing the morphological properties using FE-SEM. The testing was performed using the procedures stated above.

3.6 An application of biocomposite films as mulch film

To produce a mulch film, two 4 strips of cast film measuring around 10 cm in width and 100 cm in length were combined using chloroform, resulting in a single film measuring 40x100 cm. Subsequently, the films were punctured to form a pair of holes at midpoints sized 5 cm, 50 cm apart (see Figure 3.2). After that, the film was used as mulch for chili plants. Five replications were conducted for neat PLA, PLA/NR blend, and PLA/NR biocomposite films. To examine the effectiveness of different types of films used for mulch in plant development, several parameters were measured after a three-month period. This data included the plant's dry weight, stem diameter, height, and total weight of chili fruits per plant. Measurements were obtained from three chili plants and were averaged. The biodegradability of the mulch films was assessed using techniques that include molecular weight characterization (GPC), wide-angle x-ray scattering (XRD), thermal analysis (DSC), and examination of morphological features (FE-SEM). The testing was carried out employing the methods stated above.

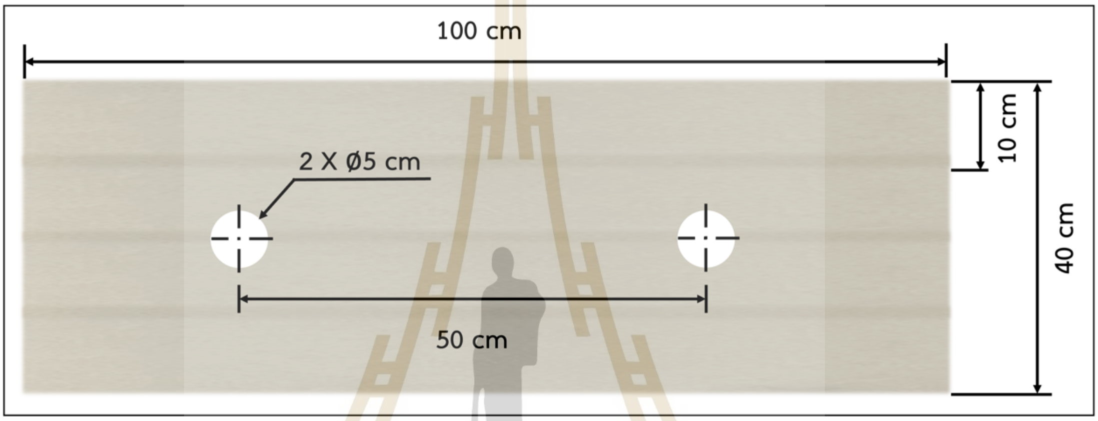

Figure 3.2 Dimensions of mulch films.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of natural rubber's mastication time on the melt flow index and tensile properties of PLA/NR blends

4.1.1 Melt flow index (MFI)

The melt flow index (MFI) is an essential indicator in polymer processing that assesses the flow properties of thermoplastic polymers. It indirectly indicates the molecular weight and viscosity of the melt, providing important information about the processing abilities of these materials. As the MFI increases, the viscosity and molecular weight decrease. (Chaiwutthinan, Chuayjuljit, Srasomsub, and Boonmahitthisud, 2019). Figure 4.1 shows the MFI values of the neat PLA and PLA/NR blends at various mastication times of NR, including 10, 20, and 30 min. The melt flow index (MFI) of the PLA/NR blends was higher than that of neat PLA and showed an increase with the NR's mastication time.

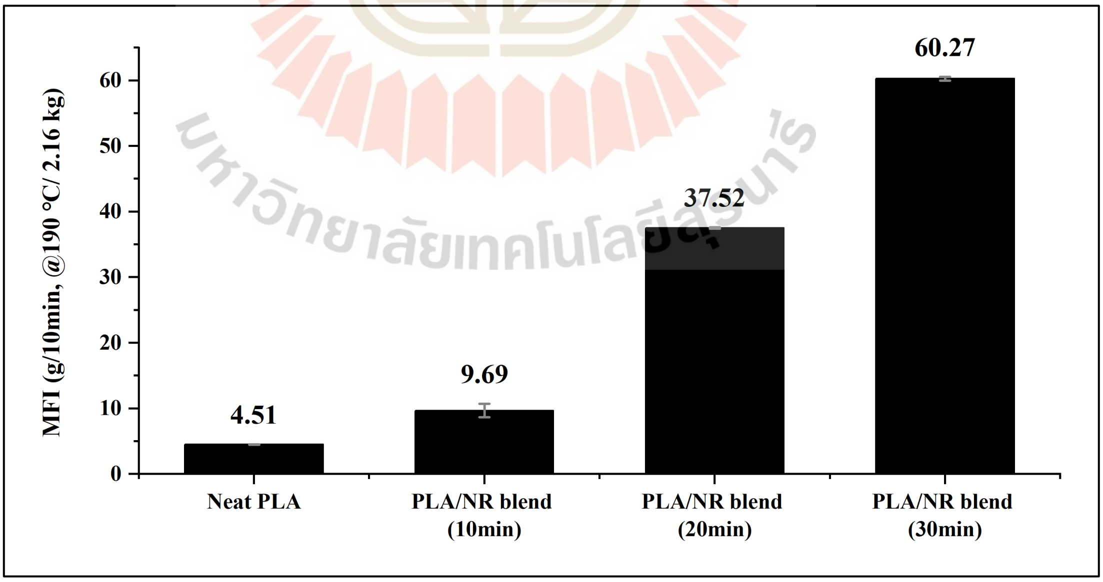

Figure 4.1 Melt flow index (MFI) of neat PLA and its blends with masticated NR at different mastication times.

The results that were observed correspond to the presence of NR, which acts as an attribute of a plasticizer and enhances the chain mobility of PLA (Tessanan, Chanthateyanonth, Yamaguchi, and Phinyocheep, 2020). Additionally, a decrease in viscosity occurred because of long mastication time (Phattarateera and Pattamaprom, 2019).

4.1.2 Tensile properties

Tensile stress-strain curves for neat PLA and PLA/NR blends at various mastication times of NR are shown in Figure 4.2. The addition of NR to the PLA matrix transformed the PLA's brittle fracture characteristics into ductile fracture behavior. Table 4.1 shows the summary of the tensile strength, Young's modulus, and elongation at break of the neat PLA and PLA/NR blends.

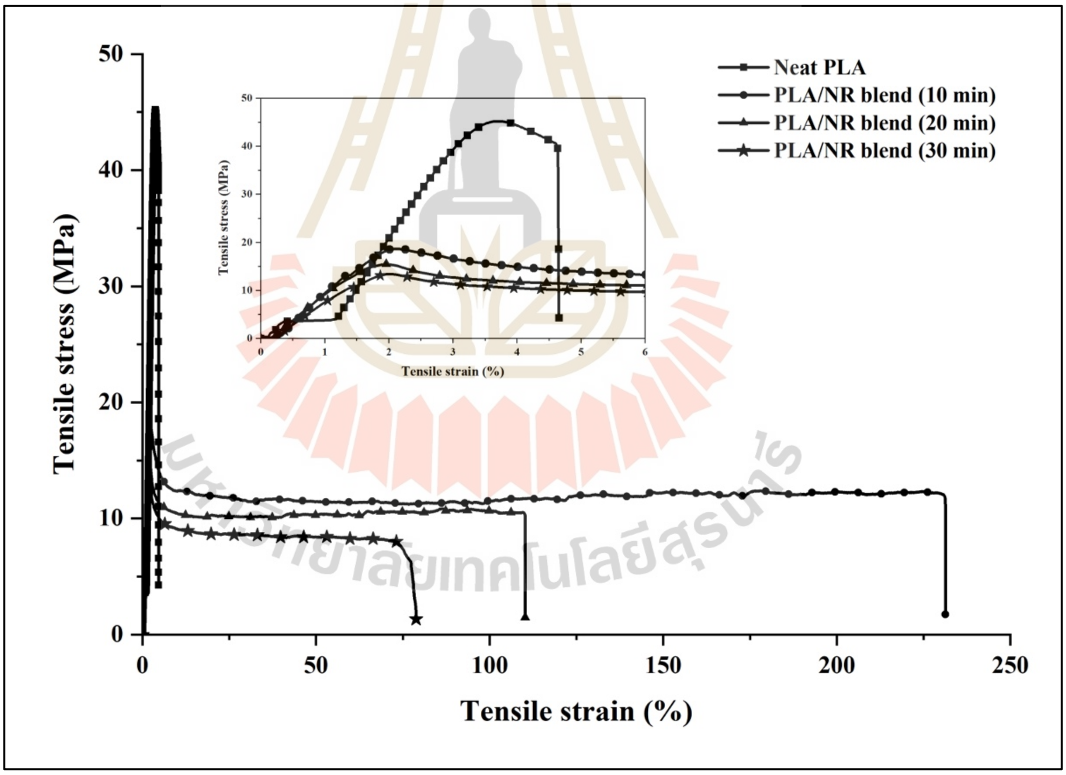

Figure 4.2 Stress-strain curves of neat PLA and its blends with masticated NR at different mastication times.

The tensile properties of neat PLA and the blends of PLA and masticated NR at various mastication times are compared in Figure 4.3 (a-c). The addition of NR into the PLA matrix resulted in a decrease in both tensile strength and modulus. The decrease in both properties was more significant with an increase in the mastication time of NR. Due to its elastic properties that help lessen PLA's brittleness, NR's rubbery nature causes a decrease in the blends' tensile strength and modulus (Buys et al., 2017). Bitinis et al. (2011), Pongtanayut et al. (2013), and Xu et al. (2014) have all discovered similar tendencies.

The addition of NR enhanced the elongation at break of PLA. The flexibility and softness of natural rubber (NR) would enhance the elongation of the blend. The mastication of NR could decrease its molecular weight, improving the interfacial adhesion between PLA and NR, which leads to improved compatibility with PLA. However, throughout the process of mastication, when the time was extended to 20 and 30 minutes, it was seen that there was a significant decrease in the elongation at break. At overly long masticating time resulted in a reduction in viscosity. The decreased viscosity of the rubber led to the formation of a combined rubber particle, which is a low-entanglement network that caused a decrease in elongation at break, but it remained greater than that of PLA (Jaratrotkamjorn et al., 2012; Phattarateera and Pattamaprom, 2019). Therefore, if the objective is to enhance the toughness of PLA, a 10-minute mastication time for NR seems to be the most appropriate choice for continued study.

Table 4.1 Summary of tensile properties of neat PLA and its blends with masticated NR at different mastication times.

Sample	**Tensile strength (MPa)**	**Young's Modulus (GPa)**	**Elongation at break (%)**
Neat PLA	45.21 ± 1.03	2.11 ± 0.63	4.66 ± 1.15
PLA/NR blend (10min)	18.66 ± 0.36	1.27 ± 0.28	231.33 ± 34.43
PLA/NR blend (20min)	15.46 ± 0.17	1.02 ± 0.12	110.26 ±14.23
PLA/NR blend (30min)	13.40 ± 0.19	0.85 ± 0.03	78.84 ± 5.41

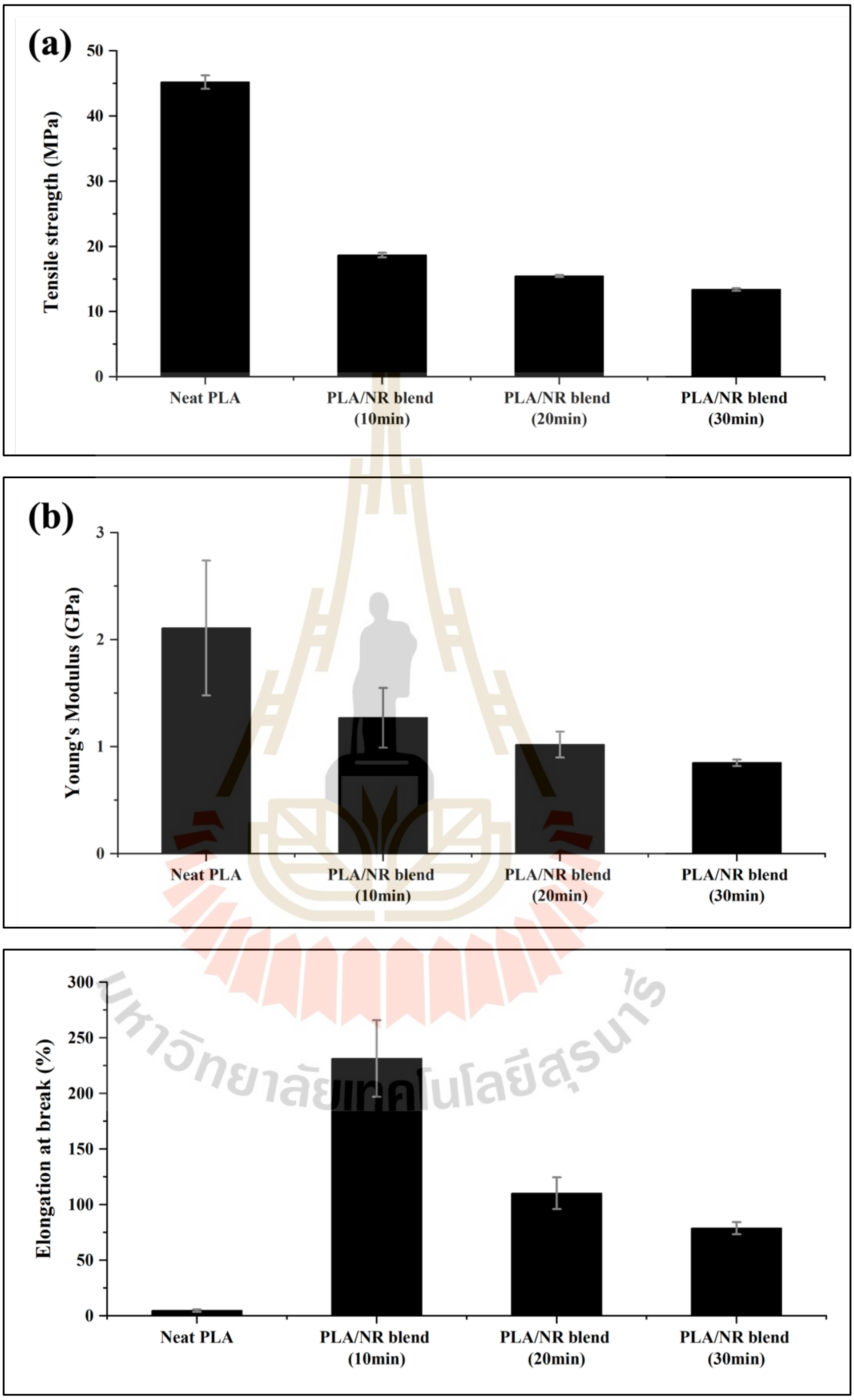

Figure 4.3 Tensile properties of neat PLA and its blends with masticated NR at different mastication times: Tensile strength (a), Young’s Modulus (b), and Elongation at break (c).

4.2 Effect of an amount of rice straw on melt flow index, tensile properties, and morphological characteristics of PLA/NR/RS biocomposite films

This study intends to create environmentally friendly and biodegradable biocomposites using renewable and biodegradable materials, which include PLA, NR, and rice straw (RS). After determining the most effective mastication time for NR to be mixed with PLA, the 10-minute masticated NR was chosen to be blended with PLA at a constant ratio of 60% PLA and 40% NR by weight. The PLA/NR blend matrix was then filled with RS at weight percentages of 3%, 5%, and 10%. The RS fiber was expected to decrease the cost of biocomposites without compromising their mechanical properties while simultaneously enhancing their biodegradability. Subsequently, the effect of RS content on the melt flow index (MFI), tensile properties, and morphological properties of the bicomposite films were investigated.

4.2.1 Physical characteristics

Figure 4.4 (a-e) shows the physical characteristics of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films. All biocomposite films exhibited an opaque light brown tint, while neat PLA film was slightly yellow and transparent, and PLA/NR blend 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 0.05 ± 0.01 mm with the addition of NR.

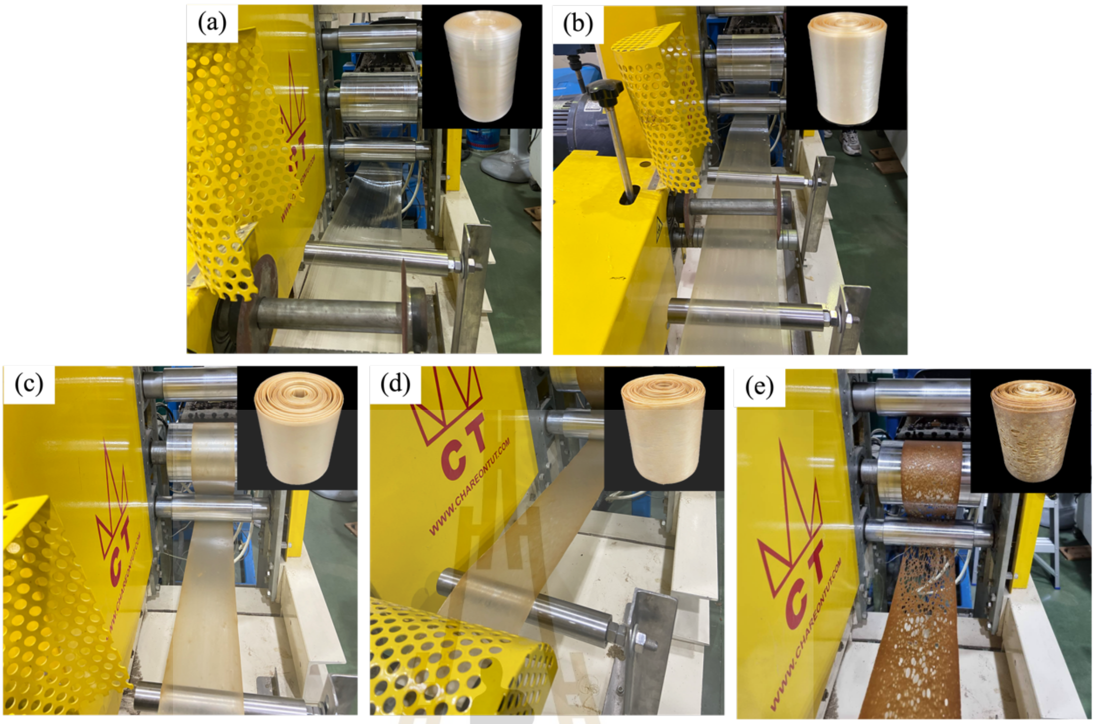

Figure 4.4 Physical characteristics of neat PLA (a), PLA/NR blend (b), and PLA/NR/RS biocomposite films; 3 wt.% (c), 5 wt.% (d), and 10 wt.% RS (e).

This might be because NR improved the melt strength of PLA/NR film, thus facilitating stretchability (Zhao et al., 2023). 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. Table 4.2 shows the thickness and width from extrusion process of the neat PLA and PLA/NR blend and PLA/NR/RS biocomposite films at 3, 5, and 10 wt.% RS. 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.

Table 4.2 The thickness and width of the neat PLA and PLA/NR blend and PLA/NR/RS biocomposite films.

Sample	Thickness (mm)	Width (mm)
Neat PLA	0.20 ± 0.01	123.98 ± 0.02
PLA/NR blend	0.05 ± 0.01	109.02 ± 0.01
PLA/NR/3%RS	0.14 ± 0.01	103.23 ± 0.02
PLA/NR/5%RS	0.16 ± 0.01	104.14 ± 0.02
PLA/NR/10%RS	0.24 ± 0.01	116.27 ± 0.07

4.2.2 Melt flow index (MFI)

Figure 4.5 shows the MFI values of neat PLA, PLA/NR blend, and all PLA/NR/RS biocomposites. The PLA/NR blend had a higher MFI than neat PLA. The addition of 40 %wt. NR improves the melt flow properties of neat PLA because it acts as an attribute of a plasticizer and enhances the chain mobility of PLA, as mentioned above in Topic 4.1.1. 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 (Eselini, Tirkes, Akar, and Tayfun, 2019). 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 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 (Van Krevelen and Te Nijenhuis, 2009). The large and numerous holes were then occurred in the films at 10 %wt. RS.

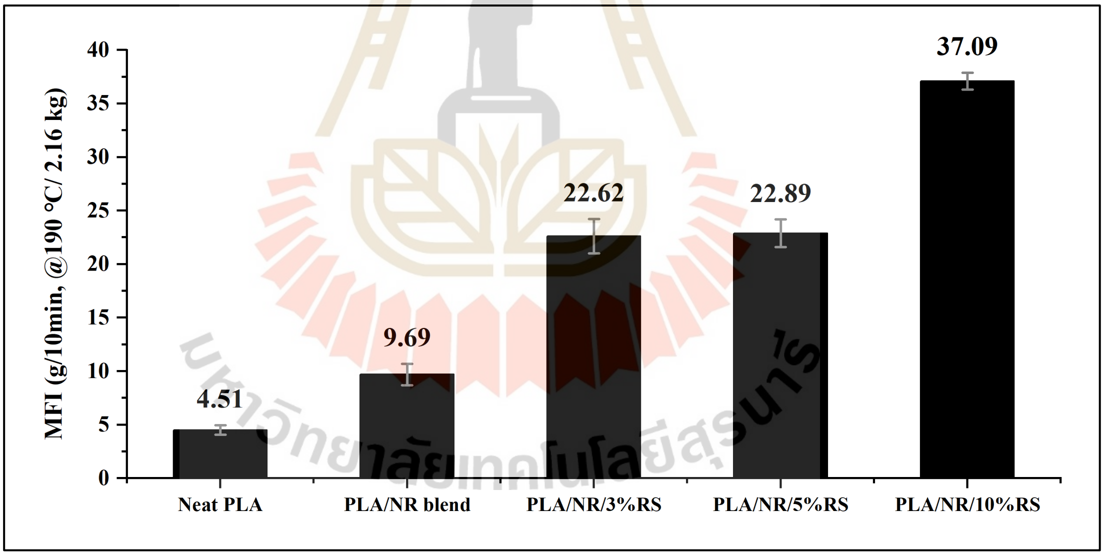

Figure 4.5 Melt flow index (MFI) of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites.

4.2.3 Tensile properties

Tensile stress-strain curves of neat PLA, PLA/NR, and PLA/NR/RS biocomposites are shown in Figure 4.6 (a-b). The neat PLA showed brittle fractures. The natural brittleness of neat PLA transformed into a more 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 4.7 (a-c). In addition, a comparison is performed with the characteristics of HDPE to evaluate its features for use as an agricultural film.

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 (Alias, Ismail, and Ishak, 2021). 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 rearrangement (Yaisun and Trongsatitkul, 2023). 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.

The neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films exhibit better tensile strength and modulus characteristics compared to HDPE. While the elongation at break of all films was less than HDPE, indicating their lower elasticity, both the PLA/NR blend and PLA/NR/RS biocomposite films were able to produce film. Table 4.3 shows the summary of the tensile strength, Young's modulus, and elongation at break of the HDPE, neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films.

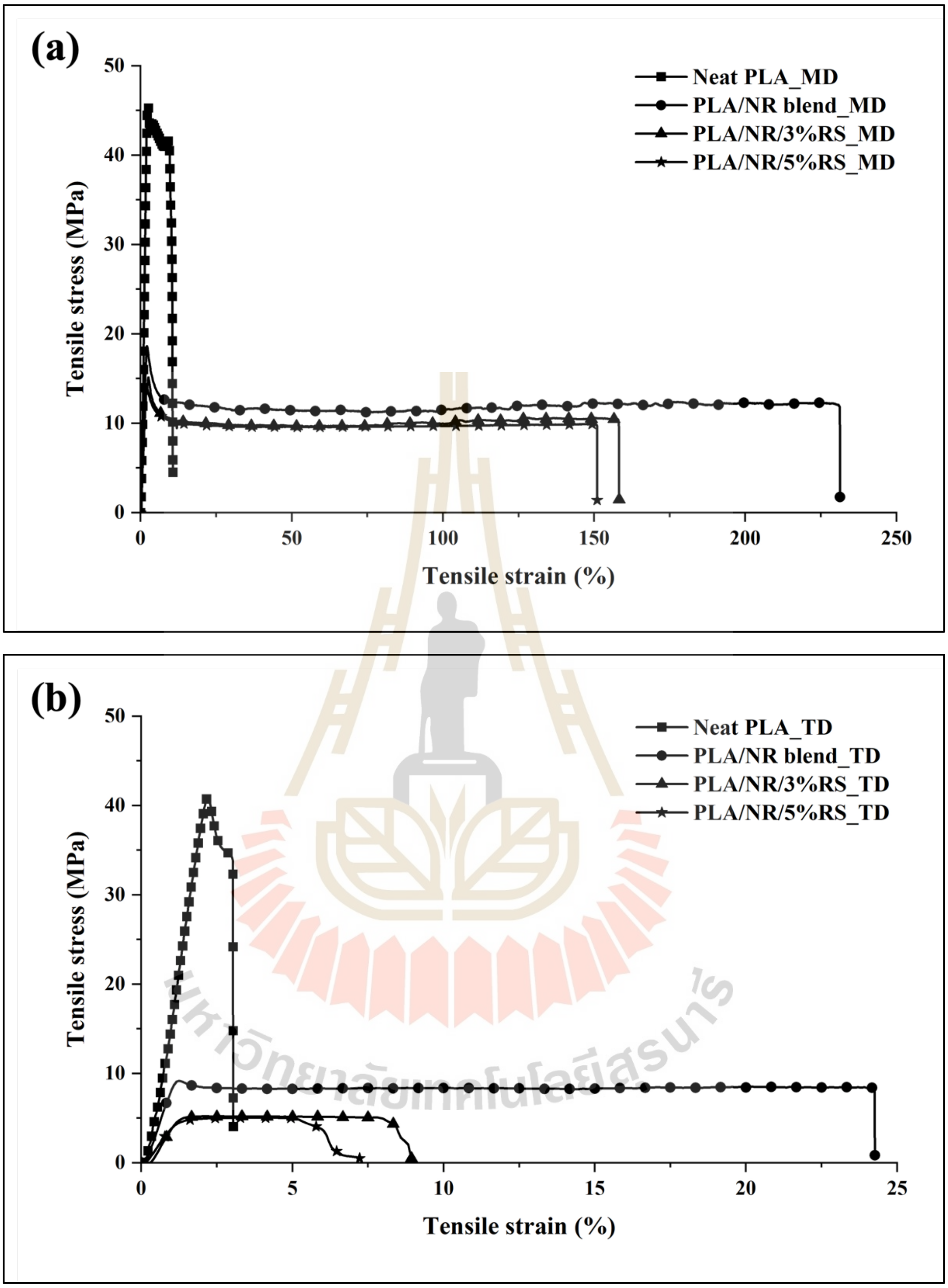

Figure 4.6 Stress-strain curve of neat PLA, PLA/NR, and PLA/NR/RS biocomposite films; machine direction (MD) (a) and transverse direction (TD) (b).

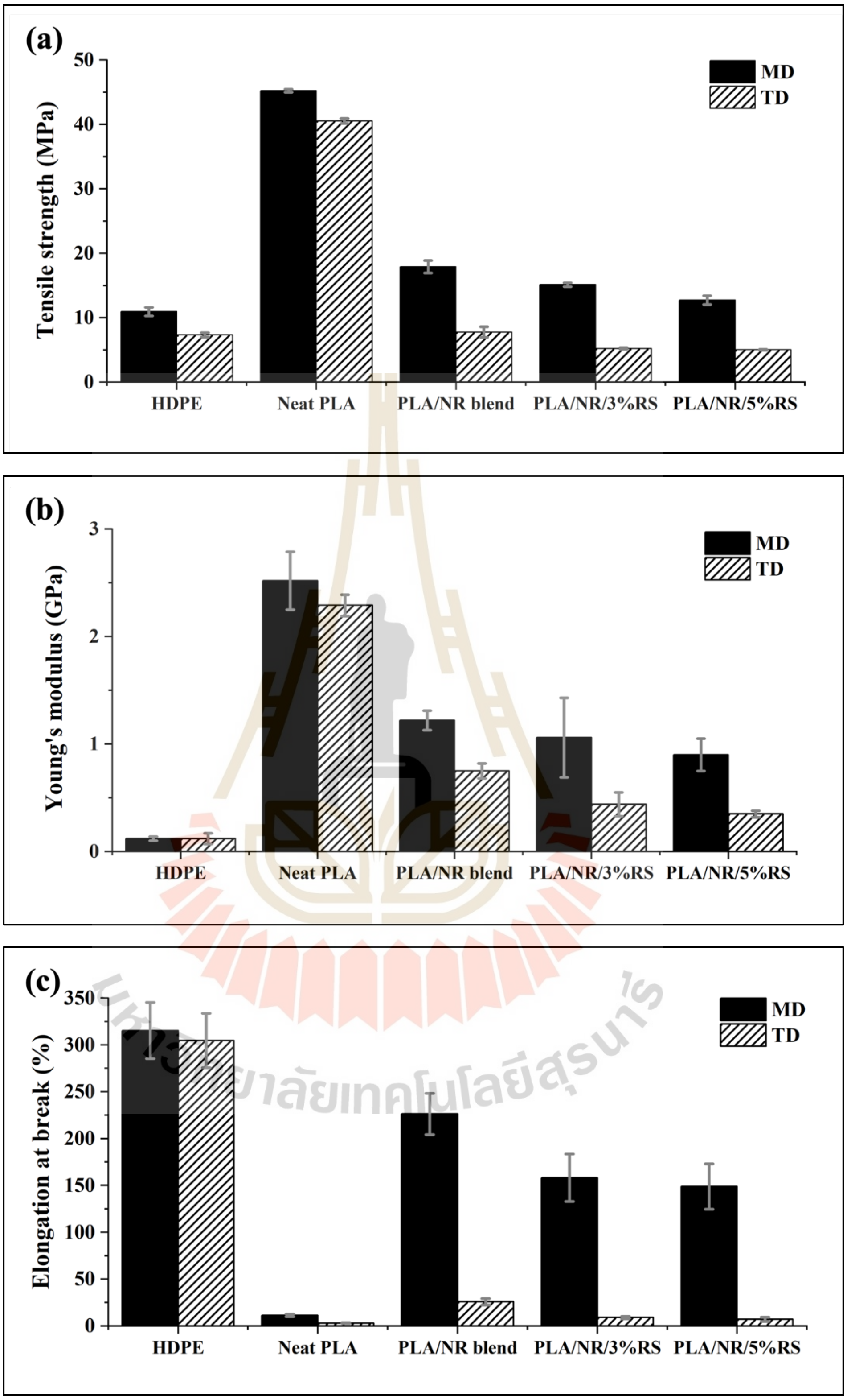

Figure 4.7 Tensile properties of HDPE, neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films; Tensile strength (a), Young’s Modulus (b), and Elongation at break (c)

Table 4.3 Summary of tensile properties of HDPE, neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films.

Sample		Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
HDPE	MD	11.86 ± 0.66	0.12 ± 0.02	314.93 ± 35.49
	TD	11.29 ± 0.36	0.12 ± 0.05	307.43 ± 35.15
Neat PLA	MD	45.22 ± 0.25	2.52 ± 0.27	11.26 ± 1.38
	TD	40.55 ± 0.38	2.29 ± 0.10	3.10 ± 0.34
PLA/NR blend	MD	19.11 ± 0.98	1.22 ± 0.09	226.31 ± 28.43
	TD	10.58 ± 0.85	0.75 ± 0.07	25.86 ± 3.46
PLA/NR/3%RS	MD	15.14 ± 0.30	1.06 ± 0.37	158.24 ± 25.30
	TD	5.22 ± 0.12	0.44 ± 0.11	8.94 ± 1.36
PLA/NR/5%RS	MD	14.38 ± 0.62	0.90 ± 0.15	148.90 ± 24.12
	TD	5.04 ± 0.06	0.35 ± 0.03	7.21 ± 2.22

4.2.4 Morphological properties

Figure 4.8 (a–d) shows the FE-SEM micrographs of the tensile fractured surfaces of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films. 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, many NR droplets were found in the PLA matrix. This indicated that blends of PLA and NR were immiscible. When RS fibers were added to PLA/NR, it was discovered that the lager extent of phase separation. 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.

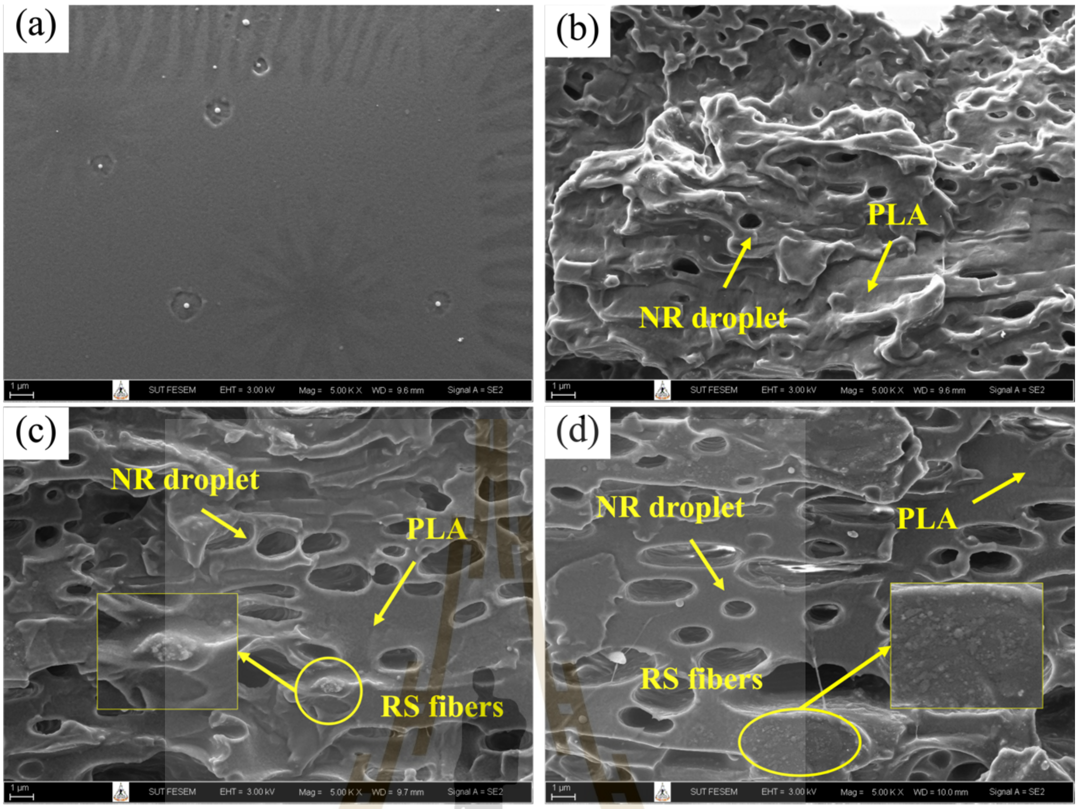

Figure 4.8 FE-SEM micrographs at 5000x magnification of tensile fracture surface of neat PLA (a) PLA/NR blend (b), and PLA/NR/RS biocomposite films with RS concentrations of 3 wt.% (c) and 5 wt.% (d).

4.3 Soil burial degradation of PLA/NR/RS biocomposite films

4.3.1 Physical appearance

The degradation of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites was confirmed by visually observing the physical appearance of the samples. Figure 4.9 shows the appearance of film samples before and after the burial test. After being buried in soil for a period of 90 days, the previously clear, neat PLA became opaque and turned white. The PLA/NR blend and PLA/NR/RS biocomposite exhibited a little alteration in colour, and the presence of fungi was noticeably observed on the surface.

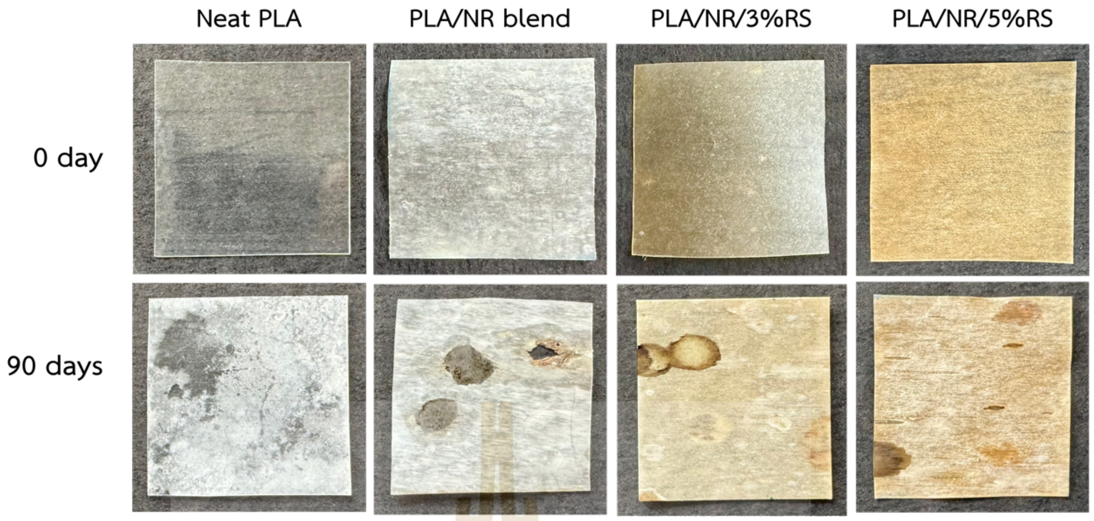

Figure 4.9 Physical appearance of the films before and after soil burial test for 90 days.

4.3.2 Biodegradability

4.3.2.1 Weight loss percentage

The film samples' weight loss percentages, following burial in soil for various durations (15, 30, 60, and 90 days), are graphically represented in Figure 4.10. The study findings indicate that neat PLA demonstrates the lowest percentage of weight loss. This suggests a comparatively slower degradation rate when compared to both the PLA/NR blend and the PLA/NR/RS biocomposite. PLA breakdown occurs primarily through hydrolytic and microbial processes, which are accelerated by high temperatures, humidity, and water absorption (Matta, Rao, Suman, and Rambabu, 2014; Fabian et al., 2023). The study suggests that the soil temperature and moisture conditions may not reach the optimal conditions required to facilitate the decomposition of PLA. According to additional reports, if the temperature remains below the Tg, the deterioration of the PLA is confined to its surface (Elsawy et al., 2017; Karamanlioglu and Alkan, 2019).

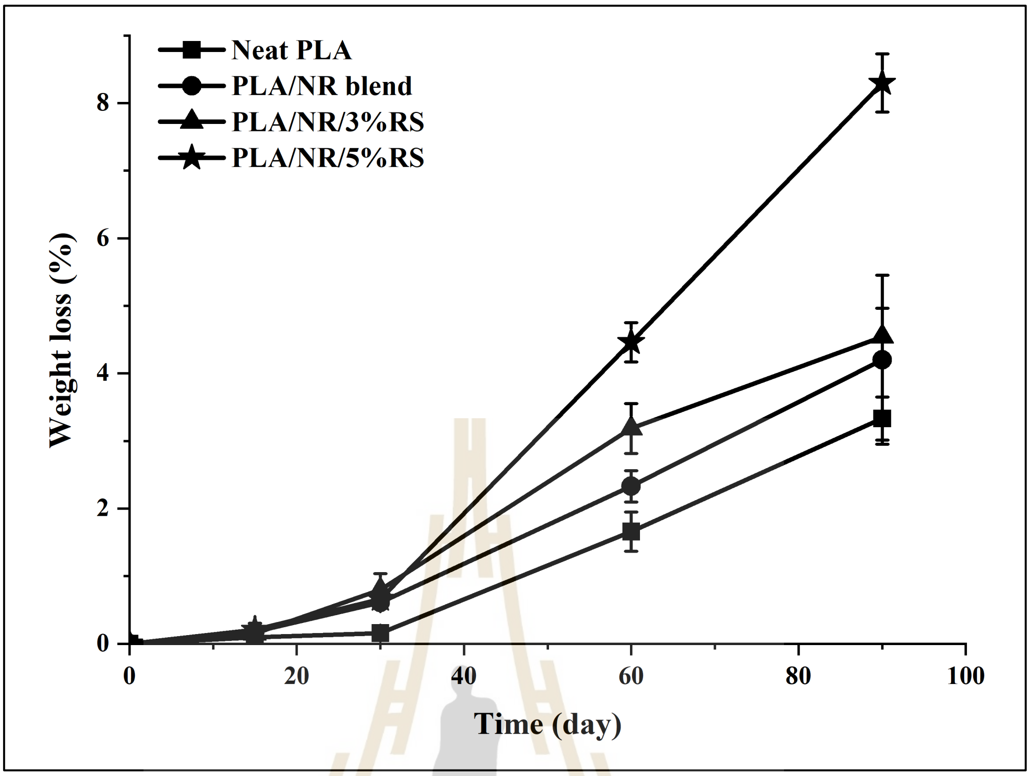

Figure 4.10 Weight loss percentage of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after being buried in soil for 90 days.

The incorporation of the NR and PLA resulted in an increase in the weight loss percentage. This is the result of the incompatibility between PLA and NR. Structures composed of heterogeneous materials typically undergo faster destruction than those composed of homogeneous ones (Tertyshnaya et al., 2022). The heterogeneous structure of the PLA/NR blend causes an increased percentage of water absorption (Huang et al., 2013; Rosli et al., 2018). NR increases the efficiency of water absorption, which is the primary mechanism for PLA degradation and involves hydrolysis. This phenomenon leads to an augmentation in the crystallinity section, which remains even through the biodegradation process (Rosli et al., 2021; Kalita et al., 2021). In composite materials, increased weight loss percentages correspond to increased fiber content. Natural fibers such as cellulose and hemicellulose have hydrophilic qualities, which means they have the potential to absorb water and degrade at a faster pace when used in composite materials (Zandi et al., 2019; Alias et al., 2021; Rosdi, Salim, Roslan, Bakar, and Sarmin, 2023). Because of increased water absorption, the molecular chain of PLA in the composites experienced hydrolytic degradation and became shorter. Microorganisms can assimilate small molecules during the degradation process. As a result, the PLA/NR/RS biocomposite films exhibited higher rates of deterioration. The initial stage of degradation for all films seems to be rather slow, with a more significant decomposition starting in the next few months. The PLA/NR/RS bio-composite films still exhibited a greater rate of degradation. Therefore, using films, particularly PLA/NR/RS biocomposites at 5 wt.%, presents an interesting option for future use. Table 4.4 provides a summary of the weight loss percentage in neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films following a 90-day soil burial period.

Table 4.4 Summary of weight loss percentage of the neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after being buried in soil for 90 days.

Sample	Weight loss (%)
Neat PLA	3.33 ± 0.32
PLA/NR blend	4.20 ± 1.02
PLA/NR/3%RS	4.54 ± 0.42
PLA/NR/5%RS	8.29 ± 0.43

4.3.2.2 Molecular weight determination using GPC technique

The neat PLA and the PLA phase in PLA/NR blend, and PLA/NR/RS biocomposite film samples were analyzed using GPC both before and after degradation investigations. The results obtained from the analysis are shown in Table 4.5. An observed reduction in the molecular weight of the PLA phase occurred after 90 days of soil burial biodegradation. This observation is consistent with earlier investigations (Juntuek, Chumsamrong, Ruksakulpiwat, and Ruksakulpiwat, 2015; Vasile et al., 2018). Moreover, the addition of NR and RS to the PLA matrix has led to a further decrease in the average molecular weight. This result corresponds to the results obtained from the analysis of weight loss percentages in PLA/NR blend and PLA/NR/RS bio-composite films. Similar results were obtained by Pongputthipat et al. (2023), who reported a decrease in the molecular weight of PLA when rice straw was added to the

PLA/NR blend. This addition of rice straw was found to increase PLA hydrolysis (Sakai et al., 2011).

Table 4.5 The number-average molecular weights (Mn), weight-average molecular weights (Mw), and polydispersity index (PDI) of neat PLA, PLA extracted from each film were determined before and after being buried in soil for 90 days.

Sample	Before burial in soil			After burial in soil		
	Mn (g/mol)	Mw (g/mol)	PDI	Mn (g/mol)	Mw (g/mol)	PDI
Neat PLA	38,487	160,328	4.17	35,983	153,098	4.25
PLA/NR	33,510	84,639	2.52	31,800	84,183	2.65
PLA/NR/3%RS	32,132	80,510	2.50	29,332	73,050	2.49
PLA/NR/5%RS	30,039	70,716	2.35	28,211	72,781	2.58

4.3.2.3 Tensile properties

Figure 4.11 (a-b) shows the tensile stress-strain curves of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites after being buried in soil for 90 days. The fracture behavior of both the neat PLA and PLA/NR blend in machine direction (MD) was like that before burial, with neat PLA displaying a brittle fracture and PLA/NR blend displaying a ductile fracture. PLA/NR/RS biocomposite exhibits a transition from ductile to brittle fractures. The transverse direction (TD) of both neat PLA and PLA/NR/RS biocomposite exhibit lower stress-strain curve compared to the machine direction (MD). However, both directions show a similar pattern. It is worth noting that the PLA/NR blend tends to be more brittle. The tensile strength of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films before and after the soil burial test for 90 days are compared in Figure 4.12 (a-b). After being buried in the soil for a period of 90 days, it was seen that the tensile strength of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films decreased. The observed outcome is a consequence of the deterioration of the films that takes place throughout the process of soil burial. During the process of decomposition in a landfill, the chain structure of films may undergo a breakdown and the formation of pores on the surface. This leads to concentrated stress around these pores, which reduces their ability to support loads and finally results in a decrease in tensile strength (Chuayjuljit, Wongwaiwattanakul, Chaiwutthinan, and Prasassarakich, 2016; Zhang, Cao, and Jiang, 2023). The presence of NR and RS fiber will enhance the breakdown process. It is evident that the addition of NR and fibers resulted in more of a decrease in tensile strength compared to the case without them. However, a pattern that is similar can be seen in both MD and TD directions.

Figure 4.13 (a-b) shows the elongation at break of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites before and after soil burial testing. The elongation at break exhibited the same trend as the trend observed in tensile strength. It was observed that the elongation at break has exhibited significant changes in PLA/NR blend, and PLA/NR/RS biocomposite.

Young's moludus of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films before and after soil burial testing are shown in Figure 4.14 (a-b). Which found that modulus of all films is increased especially PLA/NR/RS biocomposite films. It is seen that the modulus of all films has increased, especially in the case of PLA/NR/RS biocomposite films. The presence of RS fiber results in rapid deterioration due to the high probability of natural fibers being subjected to hydrolytic degradation by soil microbes such as fungus and bacteria (Brunsek, Kopitar, Schwarz, and Marasovic, 2023). The initial step of PLA degradation is well recognized to involve crystallization within its structure. Usually, natural fibers act as natural nucleating agents (Lubos, Martin, and Jozef, 2014), leading to enhanced crystallinity and a more compacted arrangement of polymer chains. Consequently, this results in an increase in modulus. Similar patterns have been observed in both the MD and TD directions.

Following 90 days of soil burial, the tensile strength, Young's modulus, and elongation at break of the neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films are summarized in Table 4.6.

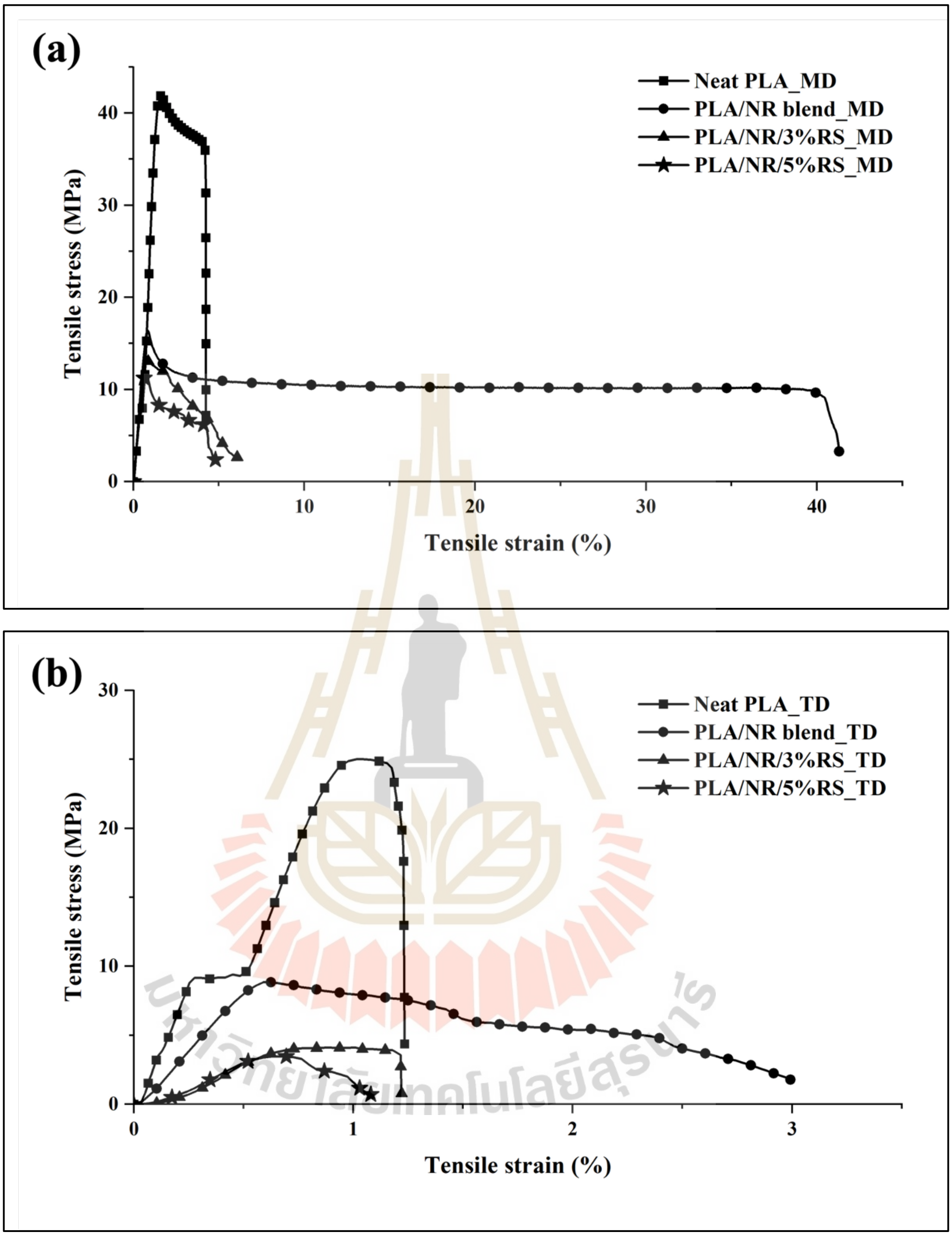

Figure 4.11 Stress-strain curve of neat PLA, PLA/NR, and PLA/NR/RS biocomposite films; machine direction (MD) (a) and transverse direction (TD) (b) after being buried in soil for 90 days.

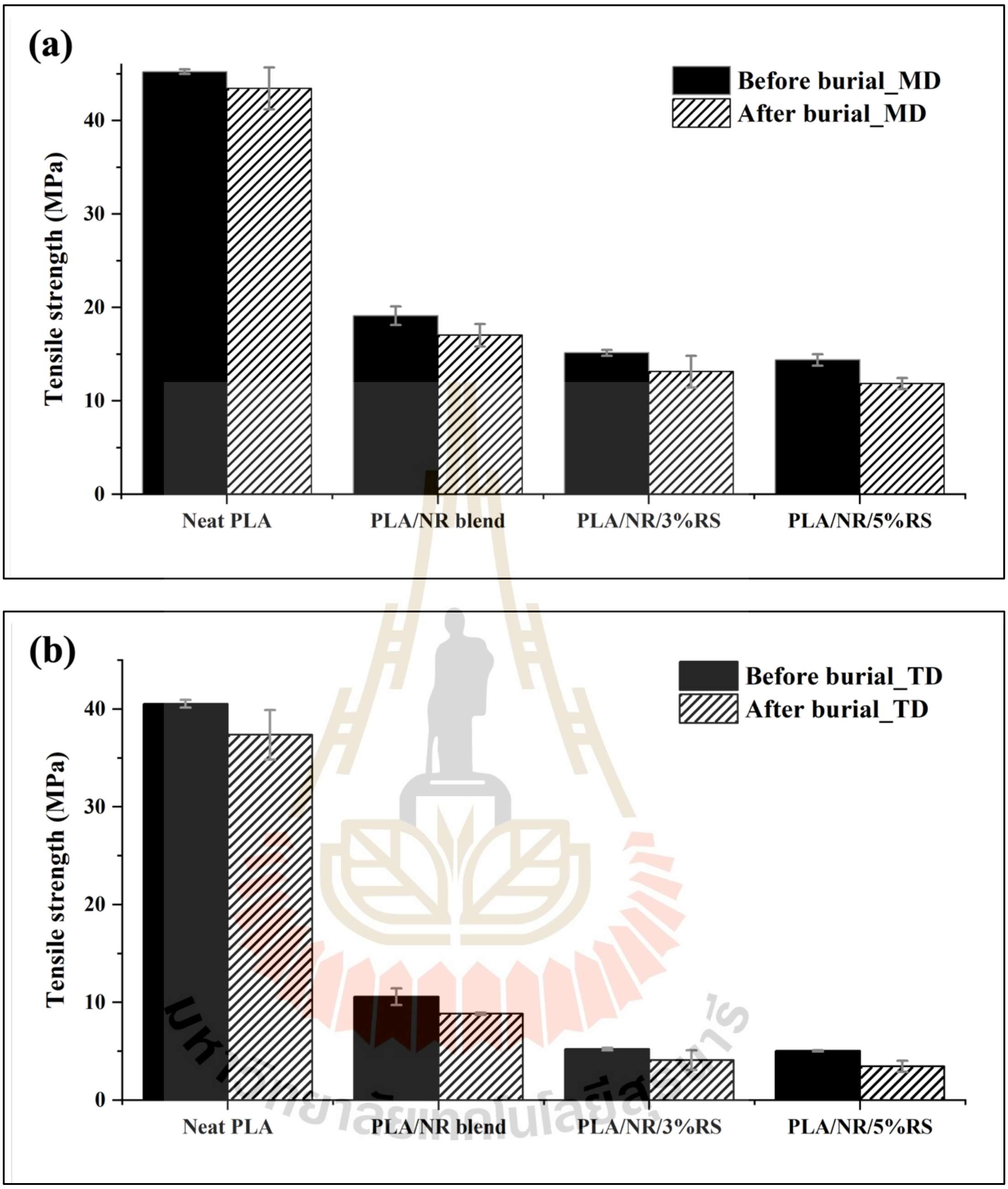

Figure 4.12 Tensile strength of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films; MD (a), TD (b) before and after soil burial test for 90 days.

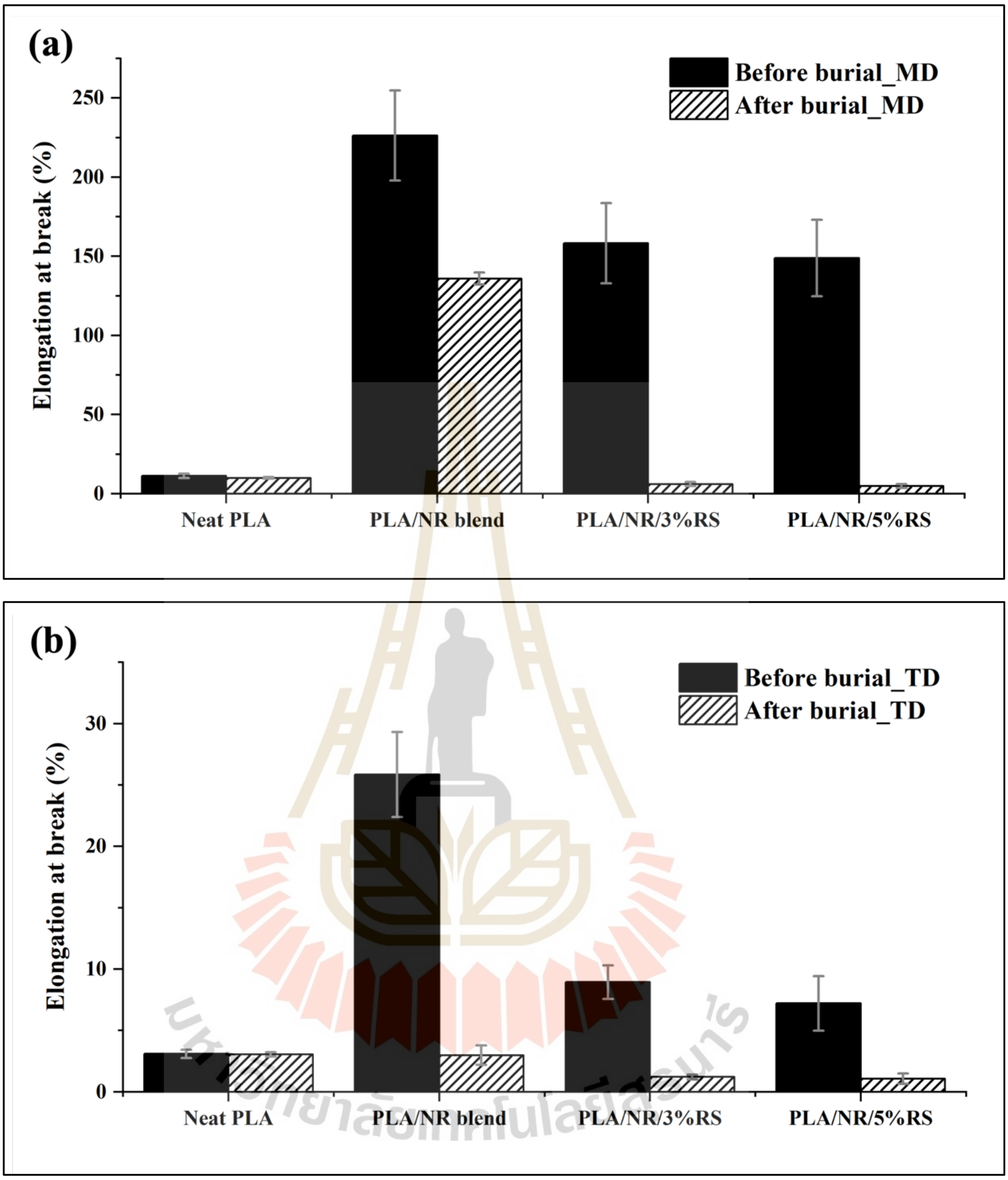

Figure 4.13 Elongation at break of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films; MD (a), TD (b) before and after soil burial test for 90 days.

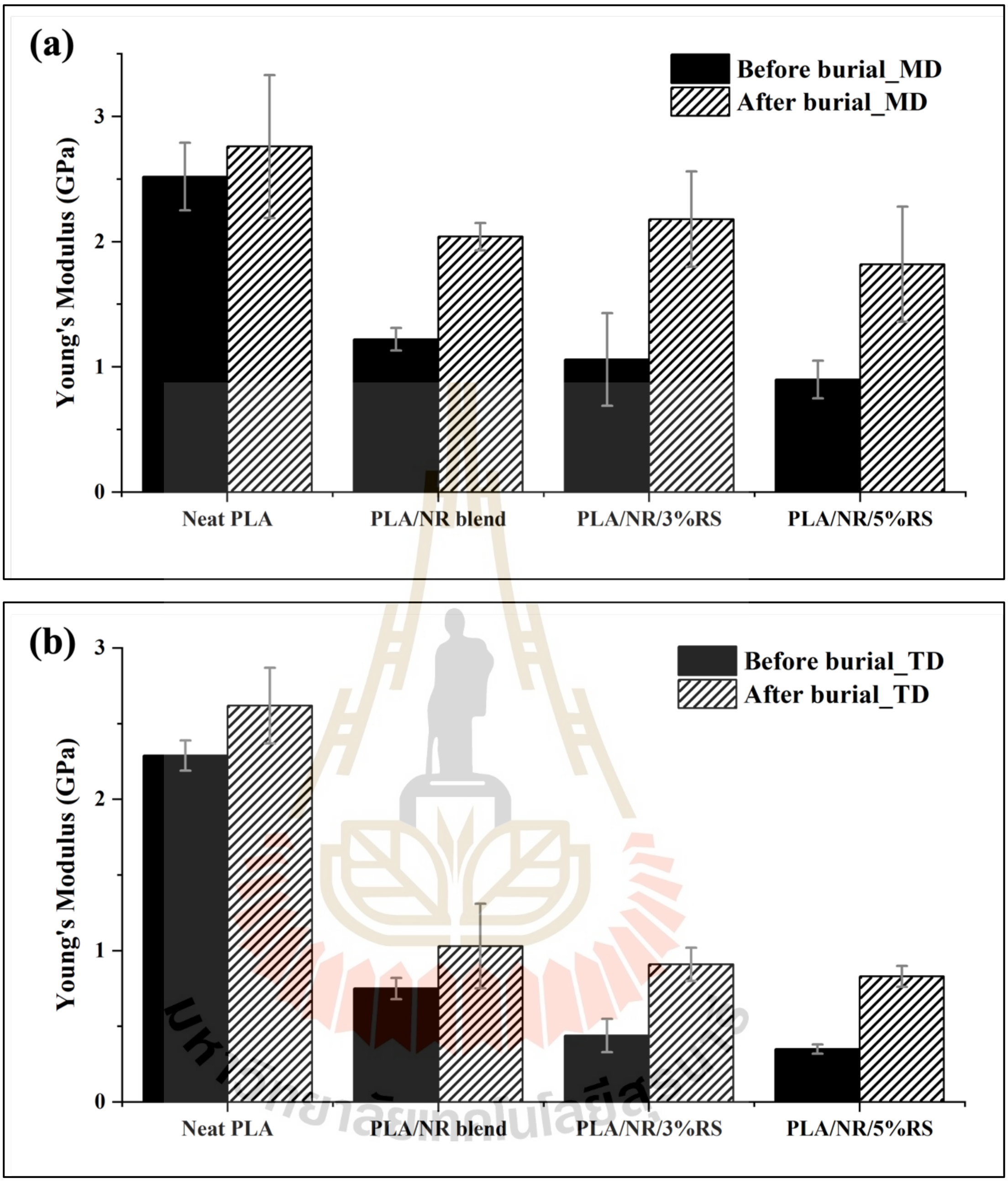

Figure 4.14 Young’s Modulus of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films; MD (a), TD (b) before and after soil burial test for 90 days.

Table 4.6 Summary of tensile properties of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after being buried in soil for 90 days.

Sample		Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
Neat PLA	MD	41.87 ± 2.25	4.74 ± 0.57	4.25 ± 0.42
	TD	32.4 ± 2.54	3.61 ± 0.25	1.23 ± 0.17
PLA/NR blend	MD	16.42 ± 1.21	2.44 ± 0.11	41.30 ± 3.80
	TD	8.85 ± 0.11	1.62 ± 0.28	2.99 ± 0.79
PLA/NR/3%RS	MD	13.13 ± 1.70	2.18 ± 0.38	6.08 ± 1.30
	TD	4.09 ± 1.02	0.91 ± 0.11	1.22 ± 0.19
PLA/NR/5%RS	MD	11.85 ± 0.60	1.82 ± 0.46	4.80 ± 1.21
	TD	3.46 ± 0.58	0.83 ± 0.07	1.08 ± 0.43

4.3.2.4 Morphological properties

Figure 4.15 exhibits the FE-SEM micrographs of the surface characteristics of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films before they were exposed to soil burial. The PLA film had a smooth surface, whereas the PLA/NR blend and PLA/NR/RS biocomposite had a rough surface and a heterogeneous phase surface. This phenomenon occurs because of PLA and NR polymers' immiscibility.

After a 90-day period of soil burial, the morphology of all films underwent alterations, as depicted in Figure 4.16. The surfaces of the neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films exhibited numerous fractures and pores, along with evident indications of fungal growth on the blend and composite film surfaces. The findings are consistent with previous research that observed the presence of bacterial and fungal propagules, including reproductive hyphae and spores, on deteriorating plastic surfaces (Sriyapai, Chansiri, and Sriyapai, 2018; Gkoutselis et al., 2021).

Furthermore, the incorporation of RS into PLA has been seen to lead to an augmentation in fungal populations, accompanied by an expansion in their size (Banthao, Kumpolsan, Baimark, Wongkasemjit, and Pakkethati, 2020). The water absorption property of RS results in the swelling of the polymer, hence increasing microbial attack and intensifying microbial activity. The increase in microbial activity is dependent upon the existence of both water and oxygen (Yaacob, Ismail, and Ting, 2016).

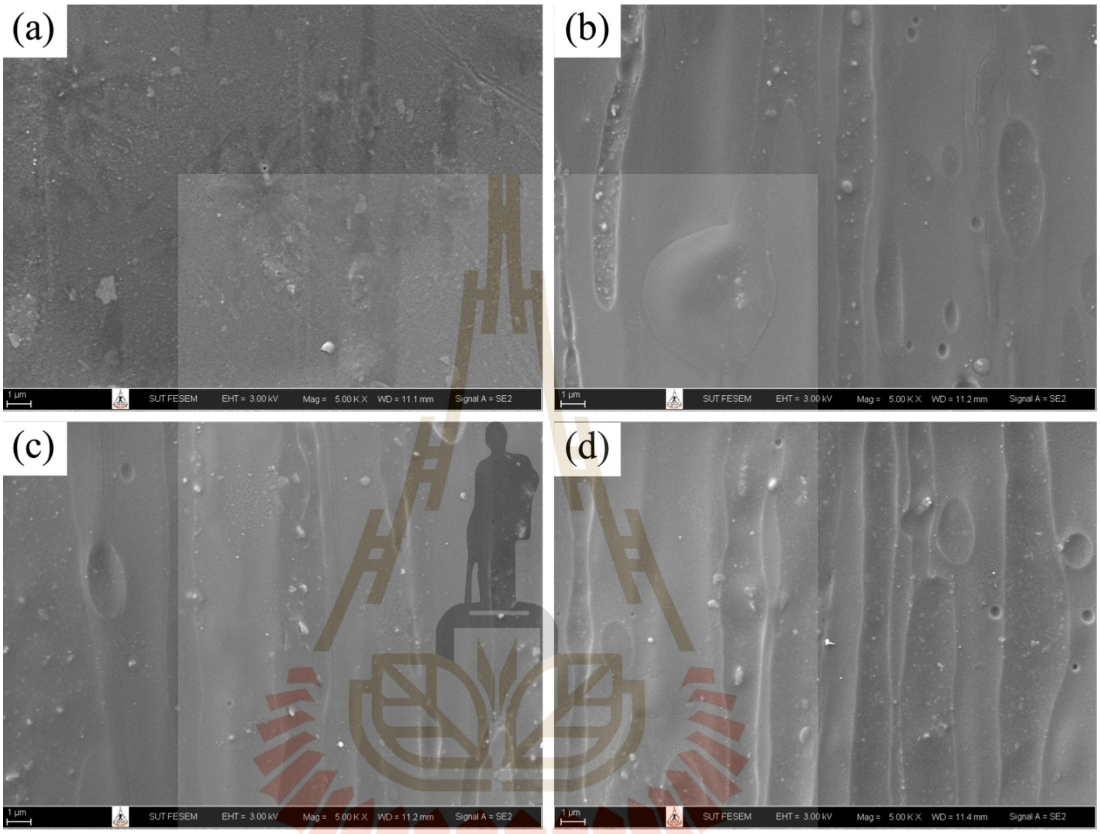

Figure 4.15 FE-SEM micrographs at 5000x magnification of film surface of neat PLA (a) PLA/NR blend (b), and PLA/NR/RS biocomposite films at RS contents of; 3 wt.% (c), and 5 wt.% (d).

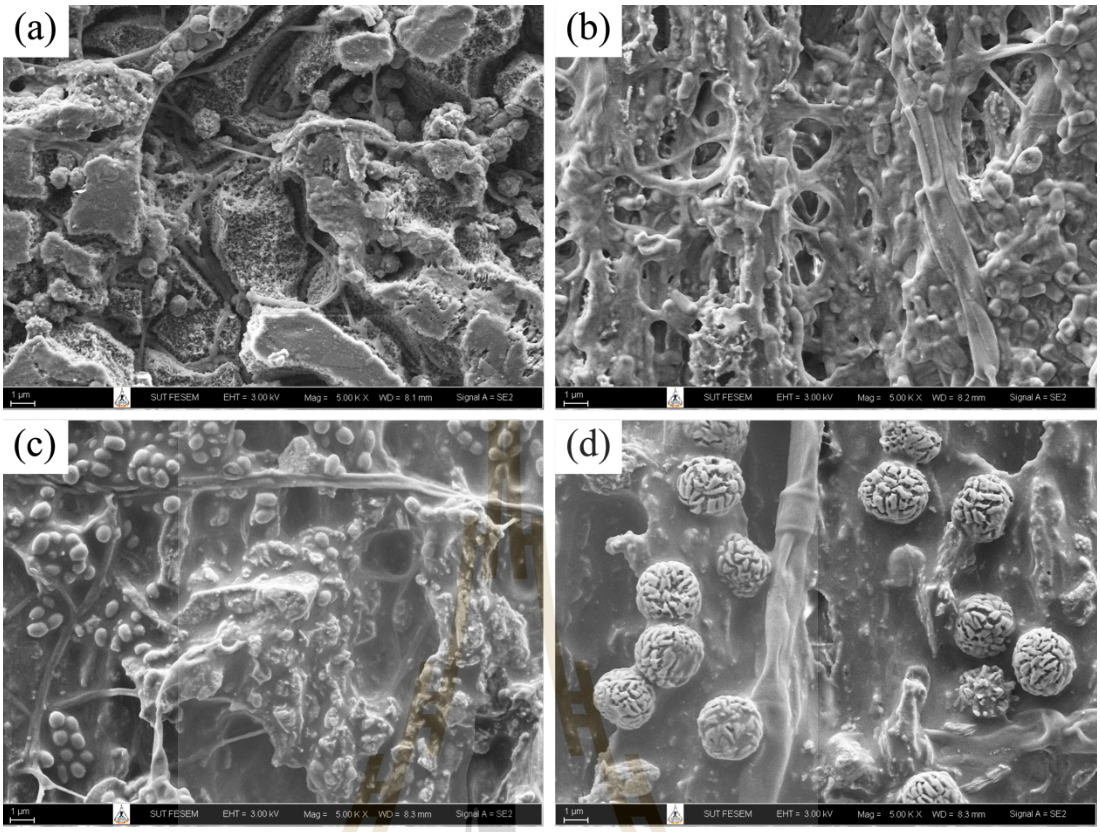

Figure 4.16 FE-SEM micrographs at 5000x magnification of film surface after soil burial for 90 days of neat PLA (a) PLA/NR blend (b), and PLA/NR/RS biocomposite films at RS contents of; 3 wt.% (c), and 5 wt.% (d).

4.3.2.5 EDX analysis

Table 4 displays the data revealing that the primary elements present in the neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite samples, prior to being buried in soil, were carbon (C) and oxygen (O). Nitrogen (N) was detected after a 90-day interval of soil burial. The presence of nitrogen can be attributed to the emission of biological substances from fungal spores, particularly proteins (Diaz-Hernandez, Sanchez-Soto, and Serrano-Delgado, 2012). Nitrogen is an essential component of plant nucleic acids, enzymes, and proteins, and it provides an important role in assisting several metabolic pathways following degradation (Yadav and Kumar, 2023). Moreover, it was discovered that the C content dropped after the burial of all polymer films in soil; in contrast, the O content increased. The observed reduction in carbon content confirms biodegradation, while the rise in oxygen percentage counteracts the decrease in carbon atomic percentage. This is evident that oxidation processes are occurring on all polymers during the biodegradation process. (Wufuer, Li, Wang, and Duo, 2022).

Table 4.7 EDX analysis of element contents of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films before and after in soil for 90 days.

Sample	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	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

4.3.2.6 DSC analysis

Differential scanning calorimetry (DSC) has been used to assess the thermal properties of polymers. Some of these characteristics include phase transitions, crystallisation behaviours, and thermal heat capacity. DSC simplifies the identification and analysis of degradation that occurs during polymer processing by facilitating the examination of changes in thermal properties (Velghe, Buffel, Vandeginste, Thielemans, and Desplentere, 2023). This study just analysed data from the first heating scan (Figure 4.17) to examine the structural changes of materials during using. The results showed the PLA in its crystalline form in the molded samples (Feng, Hu, Yin, Zhao, and Jiang, 2013). To investigate the thermal changes resulting from degradation, the glass transition temperature (Tg), melting temperature (Tm), cold crystallisation temperature (Tcc), and degree of crystallisation (Xc) of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite film samples were measured both before and after being buried in soil. The measured values are presented in Table 4.8.

The neat PLA demonstrated a Tg of 62.67°C. Upon the addition of NR to PLA, two different Tg values were identified at -67.68°C and 63.83°C. These values related to the NR and PLA phases, respectively. The presence of two glass transition temperatures can be attributed to the incompatibility of PLA and NR blends (Xu et al., 2014). The presence of two different crystalline forms in a polymer is indicated by the occurrence of two distinct melting points. The elevated temperature at which the melting point was seen indicates a more well-defined crystalline structure. The presence of two distinct melting peaks in the PLA phase can be attributed to the transformation of alpha’-form crystals into alpha-form crystals (Taib et al., 2023). The incorporation of NR and RS into the PLA did not lead to any substantial change in the Tg and Tm values. Adding NR results in a reduction in Tcc, causing a transition towards lower temperatures. Prior research has shown that elastomers improve the mobility of polymer chains and accelerate the crystallization process in PLA (Thongpin et al., 2013; Burkov et al., 2021). After the addition of RS to the PLA/NR blend, there was a slight increase in Tcc, although it remained lower than that of the neat PLA. RS demonstrated potential as a nucleating agent, hence improving the crystallization process (Tisserat, Joshee, Mahapatra, Selling, and Finkenstadt, 2013; Bomfim et al, 2023). Furthermore, the addition of NR to PLA leads to a significant enhancement in crystallinity (Xc), and this increase is even more pronounced when RS is added. This is related to NR and RS, which can function as nucleating agents to enhance the crystallization process of PLA (Suksut and Deeprasertkul, 2011; Ming et al., 2015).

Table 4.8 DSC Results of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite 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 Before	-	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 blend Before	-67.68	63.83	89.54	147.25	154.75	7.92
PLA/NR blend 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

After a 90-day duration of soil burial, the Tg of all polymers remained unchanged, indicating that the soil burial had no effect on the Tg of the polymers. The degradation process resulted in an increase of 1-3 °C in both Tcc and Tm. All polymers showed an increase in crystallinity (Xc), with blends and composites exhibiting a somewhat higher level. NR and RS can enhance the degradation process by increasing the absorption of water into the less resistant amorphous phase, which is often more susceptible to microbial activity and hydrolysis compared to the crystalline phases. This action disrupted molecule bonds in the amorphous regions, enabling the motion and rearrangement of the remaining molecular bonds into a crystalline structure (Yaacob et al., 2016; Lv, Zhang, Gu, and Tan, 2018; Silva, Pereira, Passador, and Montagna, 2020).

4.3.2.7 XRD analysis

X-ray diffraction (XRD) analysis was employed to monitor transformations in the crystalline structure of the polymers attributed to degradation. Figure 4.18 displays the XRD patterns of the samples before and after a 90-day burial in soil. The XRD patterns of PLA showed a broad peak at about 2θ = 16°, indicating there were no clear diffraction peaks and confirming that its structure was mostly amorphous (Palsikowski, Kuchnier, Pinheiro, and Morales, 2017). The results obtained correspond to the DSC analysis's findings, which revealed a significantly low degree of crystallinity. The XRD examination identified the low degree of crystallinity. The PLA/NR blend and the PLA/NR/RS biocomposite both had clear diffraction peaks at 2θ = 10° and 2θ = 28° on the XRD pattern. These findings suggest that the presence of NR and RS influences the crystalline structure of PLA. The intensity of all diffraction peaks increased after being buried in the soil, as did the increase in RS content. As the RS content increased, the composites exhibited more degradation, resulting in the generation of more low-molecular-weight chains. As a result, molecular mobility increased, and diffraction peaks became more intense. This phenomenon has also been reported in PLA/starch composites (Lv et al., 2017). The finding accords with the previously indicated decrease in weight loss percentage and molecular weight.

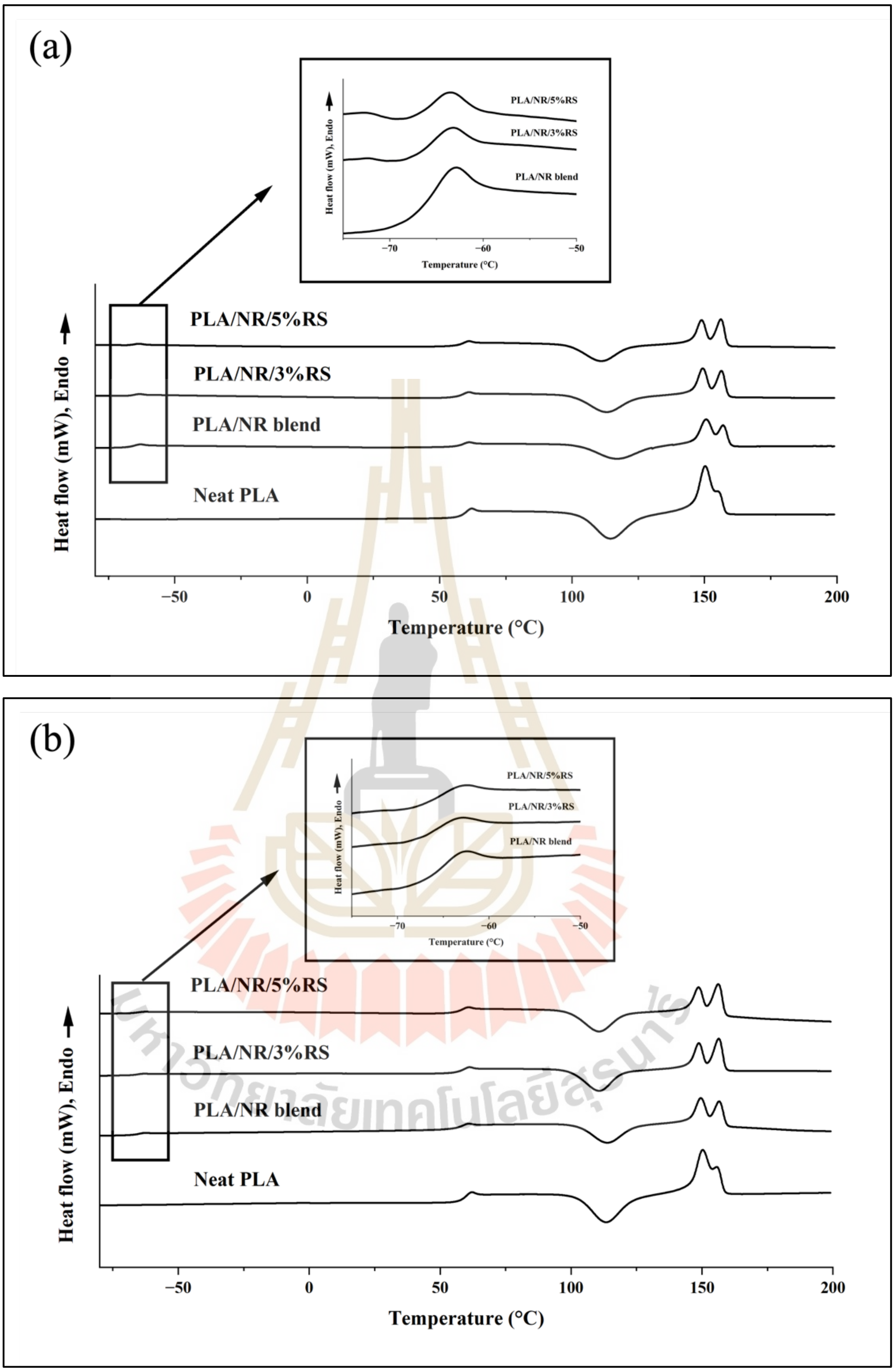

Figure 4.17 DSC thermograms of neat PLA, PLA/NR blend, PLA/NR/3%RS, and PLA/NR/5%RS biocomposite films before (a) and after (b) burial in soil for 90 days.

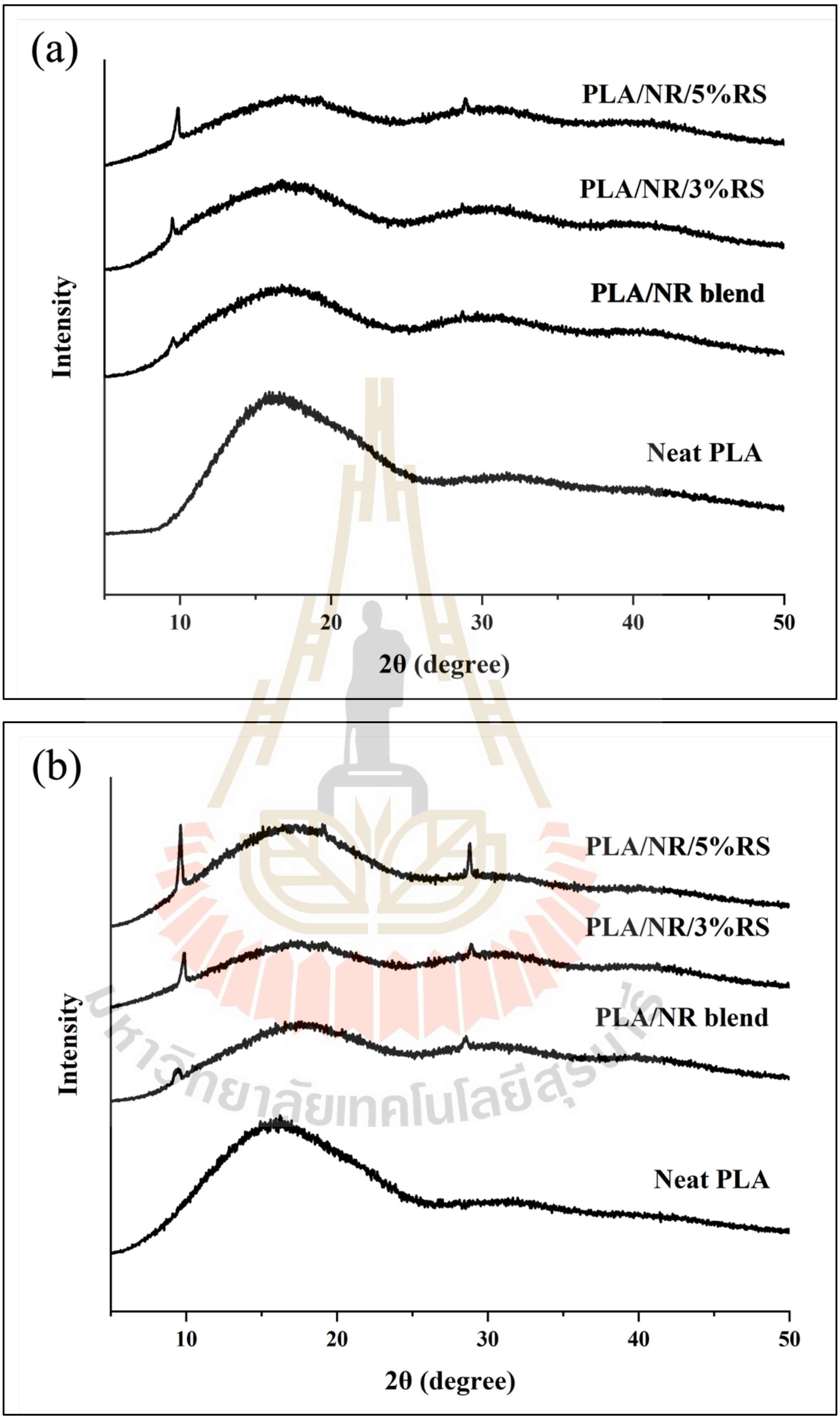

Figure 4.18 XRD patterns of neat PLA, PLA/NR blend, PLA/NR/3%RS, and PLA/NR/5%RS biocomposite films before (a) and after (b) burial in soil for 90 days.

4.4 Examples of Agricultural Applications of the biocomposite films

4.4.1 Seedling bags

The neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were utilized to produce a seedling bag measuring 10x15 cm, with holes of approximately 0.5 cm in diameter, as shown in Figure 4.19. Chili plants were cultivated in seedling bags, which were then placed in a plant pot filled with soil for a period of 3 months, starting on August 7th, and finishing on November 7th, 2023. Figure 4.20 shows the first day of the chili planting. The progress of the chili's growth can be visually seen in Figures 4.21, 4.22, and 4.23, which correspond to time periods of 1, 2, and 3 months, respectively. The results from observing the growth of the chili plant's root in seedling bags after 90 days of planting are depicted in Figure 4.24.

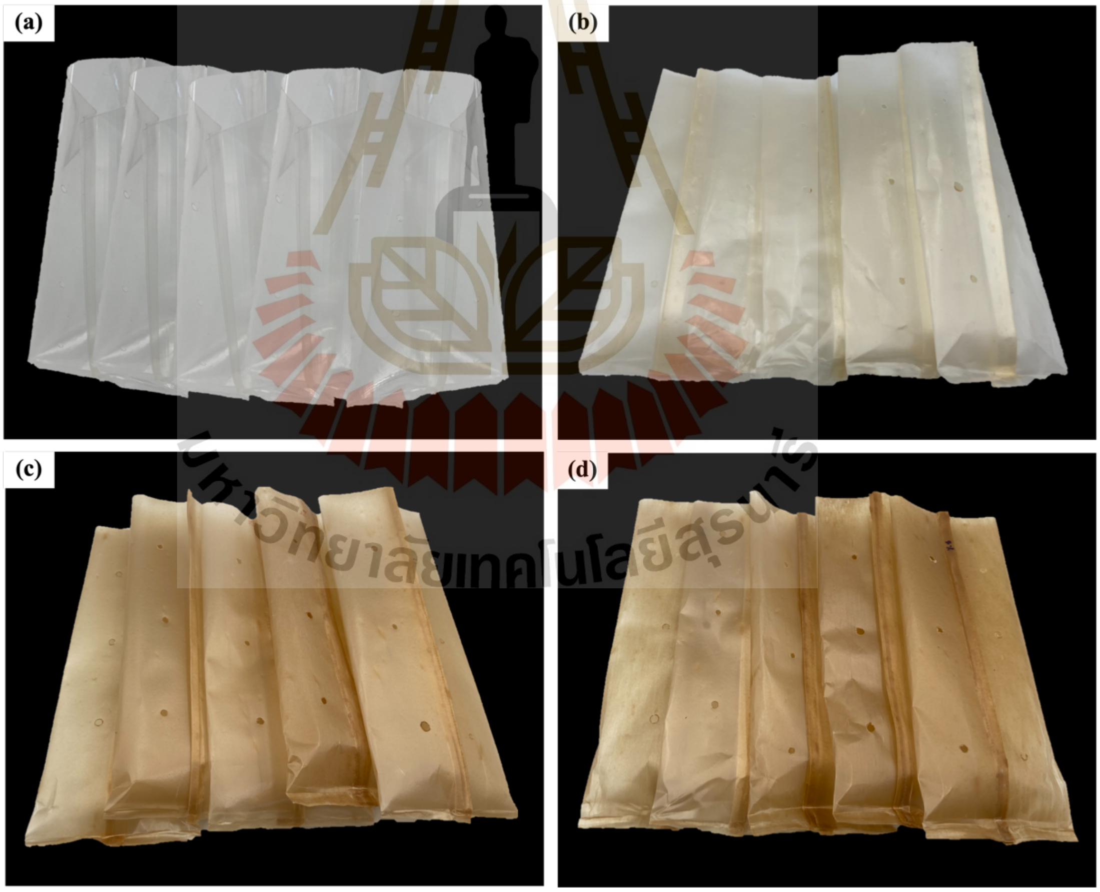

Figure 4.19 Seedling bags produced from neat PLA (a), PLA/NR blend (b), PLA/NR/3%RS (d), and PLA/NR/5%RS (e) biocomposite films.

Figure 4.20 Chilli plants in seedling bags made from different types of film: (a) HDPE, (b) neat PLA, (c) PLA/NR blend, (d) PLA/NR/3%RS, and (e) PLA/NR/5%RS at 0 month. (All bags were placed in a plant pot filled with soil.)

Figure 4.21 Chilli plants in seedling bag made from HDPE (a), neat PLA (b), PLA/NR blend (c), PLA/NR/3%RS (d), and PLA/NR/5%RS (e) biocomposite films at 1 month of cultivation.

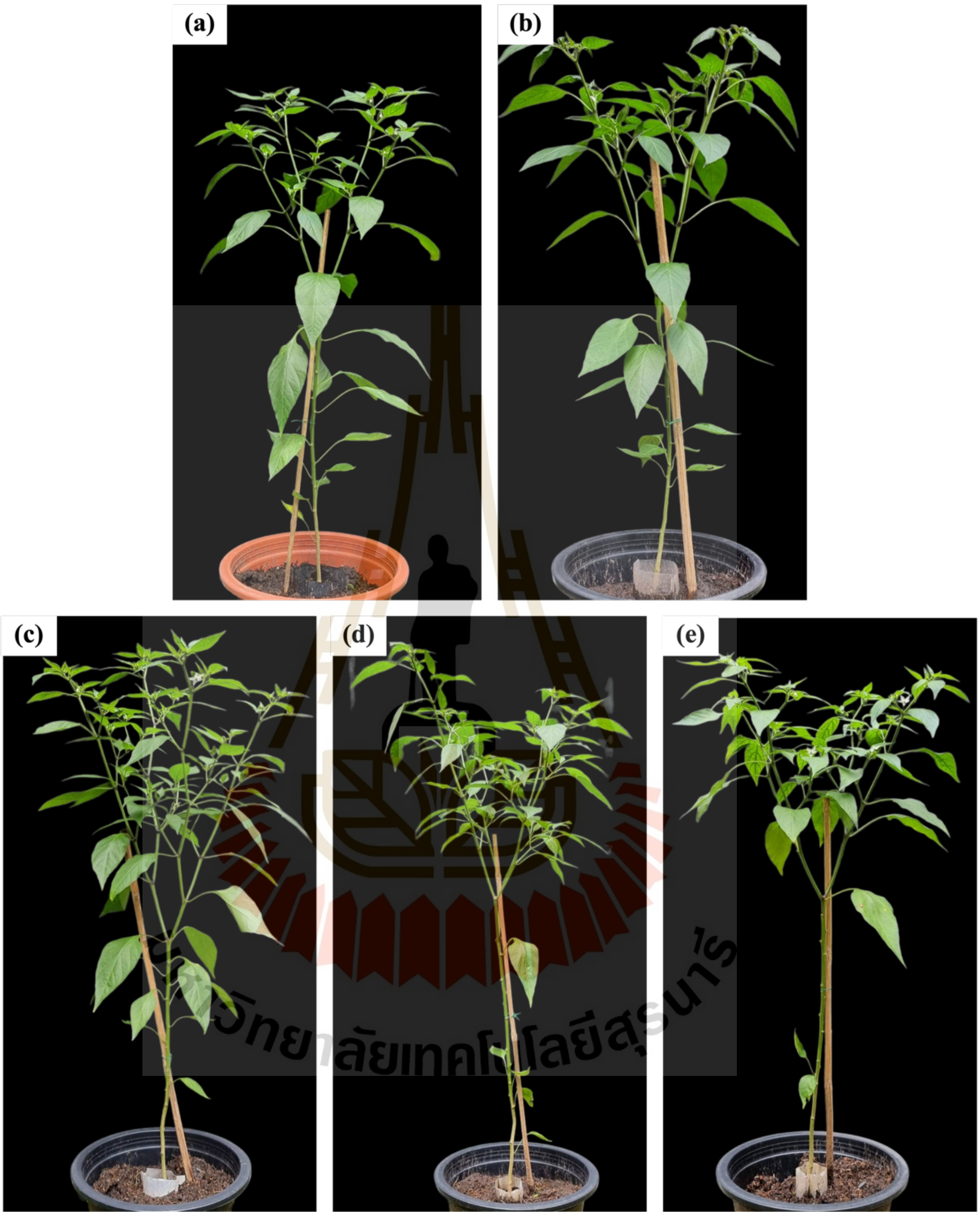

Figure 4.22 Chilli plants in seedling bag made from HDPE (a), neat PLA (b), PLA/NR blend (c), PLA/NR/3%RS (d), and PLA/NR/5%RS (e) biocomposite films at 2 months of cultivation.

Figure 4.23 Chilli plants in seedling bag made from HDPE (a), neat PLA (b), PLA/NR blend (c), PLA/NR/3%RS (d), and PLA/NR/5%RS (e) biocomposite films at 3 months of cultivation.

After a period of 3 months, it was discovered that the roots had grown out (as shown in Figure 4.24) and caused significant damage to the seedling bags, especially those made of PLA/NR blend and PLA/NR/RS biocomposite films. These bags exhibited significant tearing in comparison with the bags made of HDPE and neat PLA. The root penetration provides an indicator of the efficacy of the seedling bags, which can facilitate plant growth. During the planting process, the seedling bags can be put directly into the ground without being required to pull it off. This will have no impact on the plant's root system. The bags can biodegrade organically, naturally breaking down within a suitable timeframe for each plant species.

To examine the influence of seedling bags on the growth of chili plants, multiple parameters, including dry weight, total weight of chili fruits, stem diameter, and height, were evaluated following a 3-month period of growth in the bags. Furthermore, the biodegradation of the seedling bags was investigated once the growth of the chili plant was completed.

Figure 4.24 The growth of chili plant's root from seedling bags made from HDPE (a), neat PLA (b), PLA/NR blend (c), PLA/NR/3%RS (d), and PLA/NR/5%RS (e) biocomposite films after planting for 3 months.

4.4.1.1 Dry weight, total weight of chili fruits per plant, stem diameter and height of chili plants

The use of seedling bags made from neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films in a 3-month chili planting experiment did not affect the growth of the plants, compared to traditional seedling bags made from HDPE. The chili plants grown in bags made from a blend of PLA/NR and biocomposite films of PLA/NR/RS had a higher dry weight, total weight of chili fruit per plant (Figure 4.25), stem size, and height (Figure 4.26) than plants grown in HDPE and neat PLA bags. As a result, the plants exhibited faster development. This could be due to the roots' ability to penetrate the bag and spread into the surrounding soil. Typically, when a plant's root system grows completely and becomes strong, it will lead to the development of a healthy stem and leaf system.

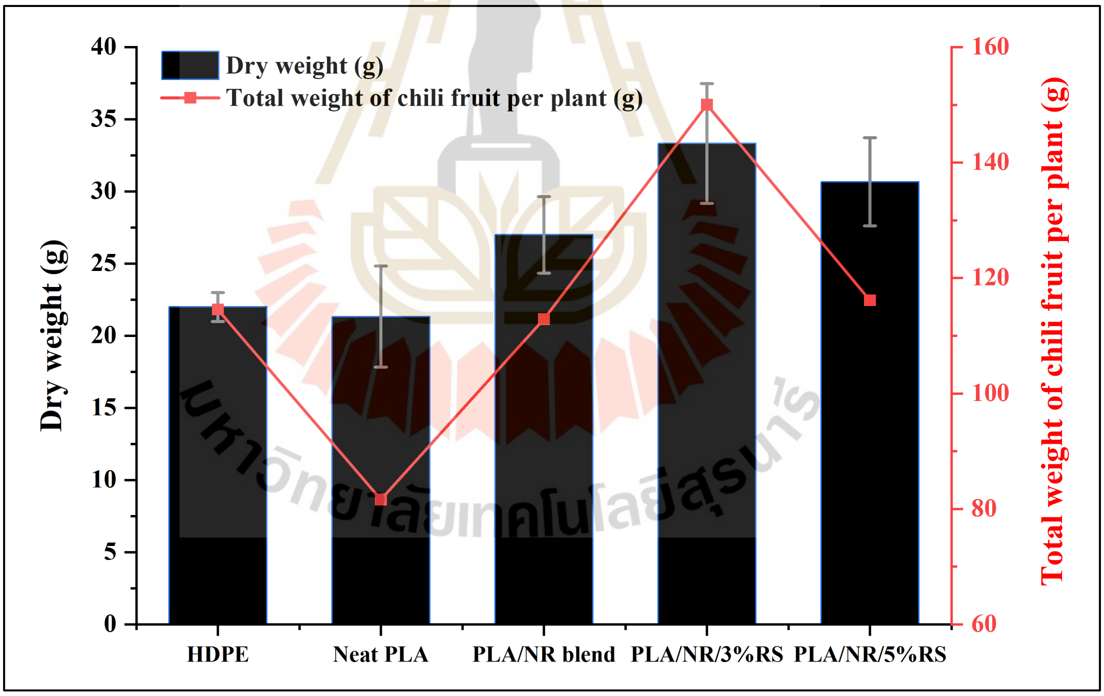

Figure 4.25 Comparison of the average dry weight and total weight of chili fruit per plant of the chili plant grown in different types of seedling bags for a period of 3 months.

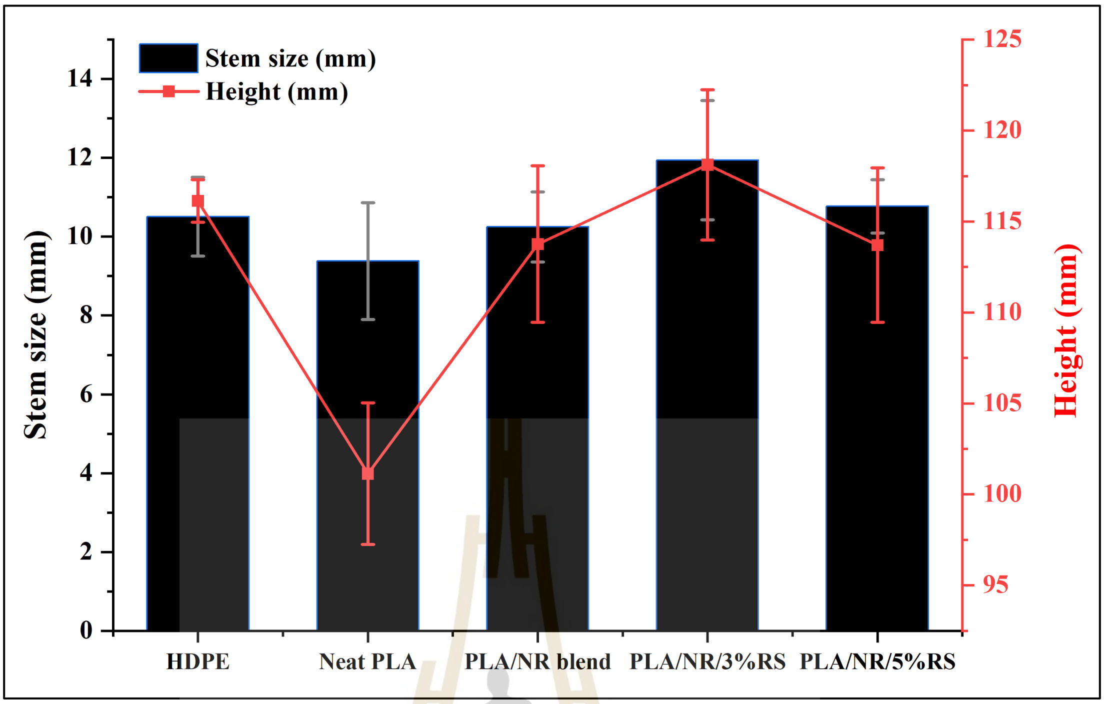

Figure 4.26 Comparison of the stem size and height of the chili plant grown in different types of seedling bags for a period of 3 months.

4.4.1.2 Biodegradation of seedling bags

4.4.1.2.1 Weight loss percentage

Figure 4.27 shows the percentage weight loss of the film samples after they had been shaped into seedling bags. The seedling bags made from PLA/NR/RS biocomposite film with 5% RS exhibited the highest percentage change in weight, determining 11.29 ± 0.37%. This was followed by PLA/NR/3%RS and PLA/NR blend, which showed weight losses of 8.48 ± 0.14% and 4.36 ± 0.24%, respectively. In contrast, neat PLA demonstrated low weight changes of 0.52 ± 0.08%. The weight loss percentage of seedling bags showed the same trend as the results of test films buried in the soil (Figure 4.10, page 58), with the seedling bag results being higher than the burial test.

PLA degradation primarily occurs through hydrolytic and microorganism activities, which are accelerated by humidity and water absorption. During the planting seed test using seedling bags, the film will be watered daily. Furthermore, the presence of NR and fibers improves the efficiency of the water absorption process. Because of increased water absorption, the PLA polymer chains in the composite break down into smaller molecules. Another thing is that the presence of microorganisms is influenced by humidity, and microbes can assimilate small molecules during the process of decomposition. As a result, it enhances the degradation of the seedling bags in comparison to films buried in the soil with only 30% moisture content. Moreover, the act of roots penetrating the seedling bags causes damage. As a result, deteriorating films may have a larger surface area available for water absorption.

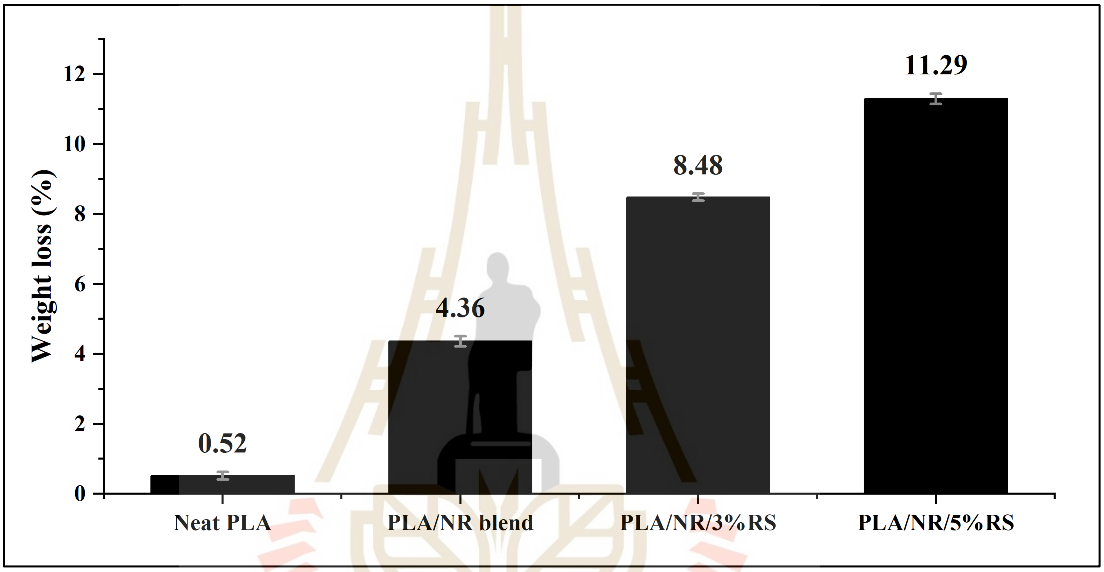

Figure 4.27 Weight loss percentage of seedling bags produced from neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after planting for 3 months.

4.4.1.2.2 Molecular weight determination using GPC technique

After cultivating chili plants for three months, the PLA phase was extracted from all bags and subjected to analysis using the GPC technique. This analysis aimed to evaluate the number-average molecular weights (Mn), weight-average molecular weights (Mw), and polydispersity index (PDI). The analysis results listed in Table 4.9 indicate a significant reduction in the molecular weight of all films due to degradation.

Table 4.9 The number-average molecular weights (Mn), the weight-average molecular weights (Mw), and the polydispersity index (PDI) of neat PLA and the PLA extracted from PLA/NR blend and PLA/NR/RS biocomposite film, as well as from the films cut from seedling bags and mulch films after 3 months of chili plant growth.

Sample	Film (As prepared)			Seedling bag (After growing chili plants)			Mulch film (After growing chili plants)		
	Mn (g/mol)	Mw (g/mol)	PDI	Mn (g/mol)	Mw (g/mol)	PDI	Mn (g/mol)	Mw (g/mol)	PDI
Neat PLA	38,487	160,328	4.17	35,693	153,924	4.31	35,092	129,125	3.68
PLA/NR blend	33,510	84,639	2.52	31,114	85,135	2.74	28,413	67,654	2.38
PLA/NR/3%RS	32,132	80,510	2.50	29,501	82,802	2.81	28,398	72,651	2.56
PLA/NR/5%RS	30,039	70,716	2.35	28,906	72,209	2.50	27,916	67,169	2.41

The decrease in molecular weight corresponded to the decrease in weight loss, with a more significant decrease observed when NR and RS were added. Furthermore, it aligns with the results obtained from the investigation of the soil burial film test.

4.4.1.2.3 Tensile testing

The tensile properties of the film specimens cut from seedling bags produced from neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were investigated before and after chili planting for 3 months to assess their degradability. The results are presented in Figure 4.28, and Table 4.10 shows the summary of the results. The tensile properties of any polymer undergo changes because of deterioration. The rate of degradation is influenced by various factors, including temperature, humidity, and the presence of microbes. The results showed that after using the film as a seedling bag for three months, both the tensile strength and the elongation at break decreased. This contrasts with the observed increase in Young's modulus. These results correspond to the results of the soil test for burial films, as shown in Table 4.6 (page 66). It can be observed that the test results acquired from seedling bags indicate that the film exhibits slightly more changes in mechanical properties compared to the film that was buried in the soil. These results are a direct consequence of the increased degradation caused by hydrolysis and microorganisms in the soil of the films. The film's surface deteriorates when the polymer structure chains are destroyed, leading to a loss in both tensile strength and elongation at break. An increase in Young's modulus is associated with an enhancement in the degree of crystallinity in the structure. The increase in crystallinity is a consequence of the degradation mechanism of PLA, so a rise in this property may suggest a higher rate of polymer degradation.

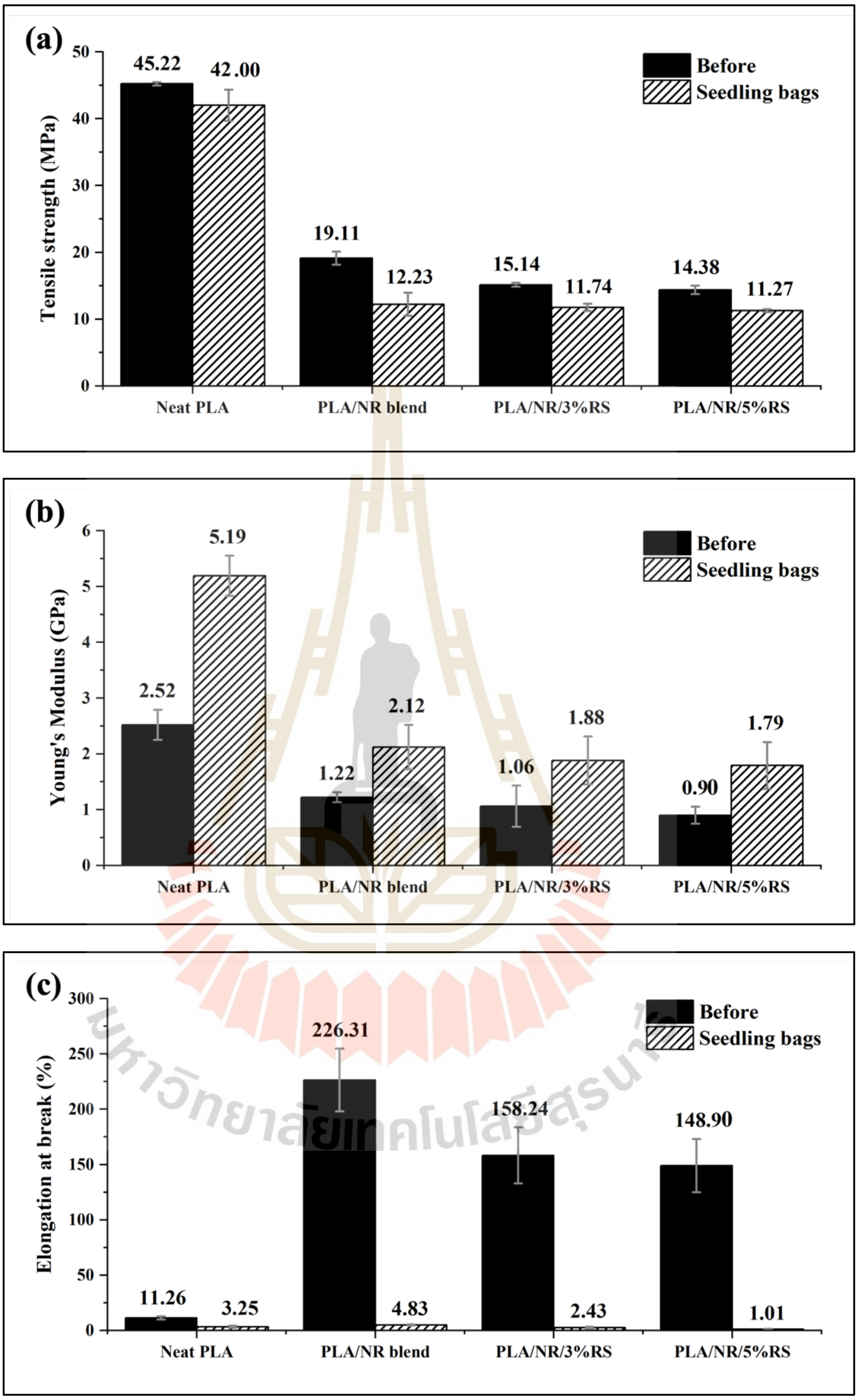

Figure 4.28 Tensile properties of the film specimens cut from seedling bags produced from HDPE, neat PLA, PLA/NR blend, and PLA/NR/RS biocomposites films; Tensile strength (a), Young's Modulus (b), and Elongation at break (c) before and after chili planting for 3 months.

Table 4.10 Summary of tensile properties of the film specimens cut from seedling bags produced from neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after planting for 3 months.

Sample	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
Neat PLA	42.01 ± 2.32	5.19 ± 0.36	3.25 ± 0.85
PLA/NR blend	12.23 ± 1.72	2.12 ± 0.40	4.84 ± 0.44
PLA/NR/3%RS	11.75 ± 0.54	1.88 ± 043	2.43 ± 0.73
PLA/NR/5%RS	11.27 ± 0.21	1.79 ± 0.42	1.01 ± 0.32

4.4.1.2.1 Morphological properties

The FE-SEM micrographs show the surface characteristics of neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after being used for seedling bags for a period of 3 months, as shown Figure 4.29. The figure shows that the surfaces of all films exhibit roughness and disorganized, indicating significant degradation of the surface. After the addition of NR and RS, it was discovered that the surface exhibited an increased presence of cracks and lacked smoothness. This confirms the increased degradation when NR and RS are added. The alteration in the surface characteristics of the film used for seedling bags was consistent with the film that had been buried in the soil for a duration of 3 months.

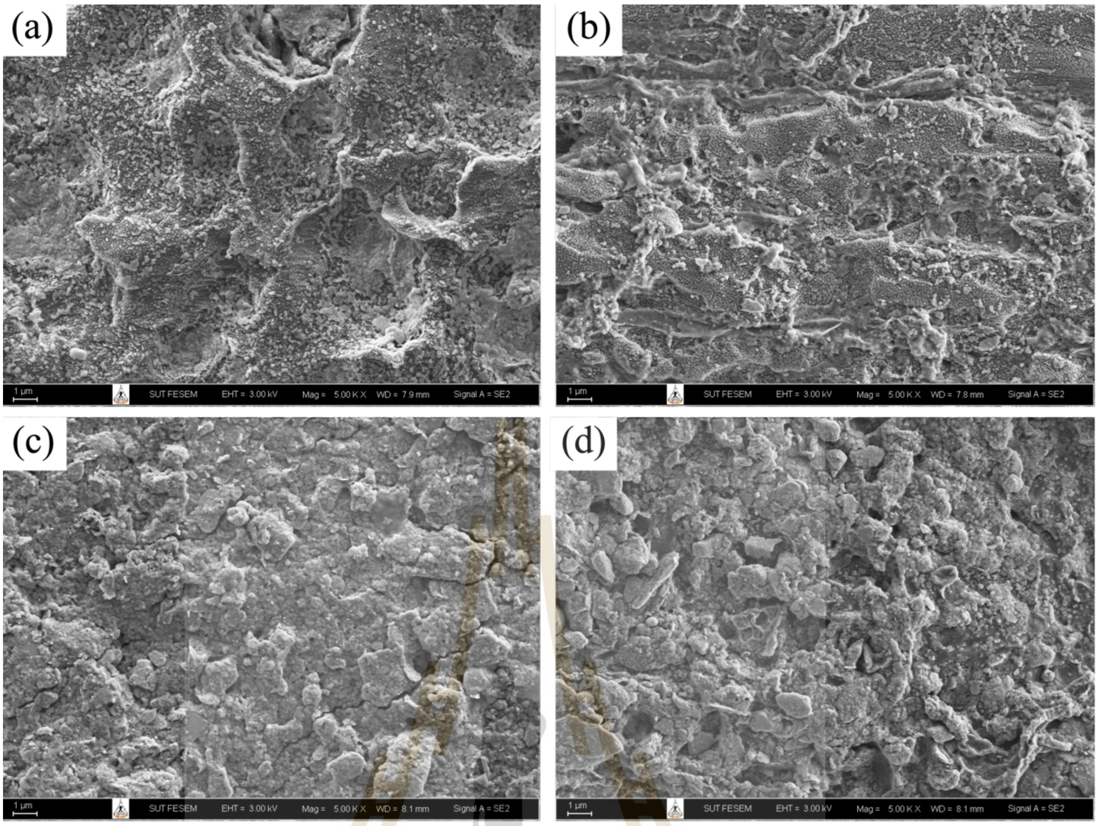

Figure 4.29 FE-SEM micrographs at 5000x magnification of the film specimens cut from seedling bags produced from neat PLA (a), PLA/NR blend (b), PLA/NR/3%RS (c) and PLA/NR/5%RS (d) biocomposite films after chili planting for 3 months.

4.4.1.2.2 DSC analysis

Figure 4.30 displays the DSC thermograms obtained during the first heating scan of the film samples taken from seedling bags, which were used for chili planting for a period of 3 months. This study investigated alterations in thermal characteristics during polymer degradation. An analysis revealed that the peak size of Tg increased in comparison to the DSC thermograms of the film sample before it was buried in soil for 3 months (Figure 4.17, page 72). This increase indicates the occurrence of a relaxation peak during the aging process, which arises when the sample is maintained at temperatures below its Tg for a long period of time (Parker, 2000). However, the transformation in Tg in almost all films did not demonstrate a significant shift when comparing films before and after their use as seeding bags for a period of 3 months, as shown in Table 4.11. Two distinct crystal forms were seen in the films that were used to produce the seedling bags, as indicated by the presence of two different Tm values. This crystal form represents a transformation in the crystal structure. From investigation, it was found that the alpha’- crystal form exhibited a reduced peak size, while the alpha- form crystals were larger in comparison to the before-buried film (Figure 4.17 (a), page 72). This result indicates a more organized and structured crystalline structure. Furthermore, the arrangement of the chain influences the decrease of the Tcc in all films. It was discovered that the value decreased in comparison to the value of the film that was not buried in the soil. The polymer's crystalline structure became more well-organized, resulting in a lower energy requirement for rearrangement. This leads to enhanced mobility of the polymer chains. Consequently, the polymer chains can be organized at lower temperatures (Maricilla and Beltran, 2017). Upon analyzing the crystallinity (Xc) of the PLA phase in the film samples taken from seedling bags used for growing chili plants for a duration of 3 months, it was observed that the Xc of the seedling bag films had increased. This finding aligns with the previously observed trend of increased Xc when the film is buried in soil.

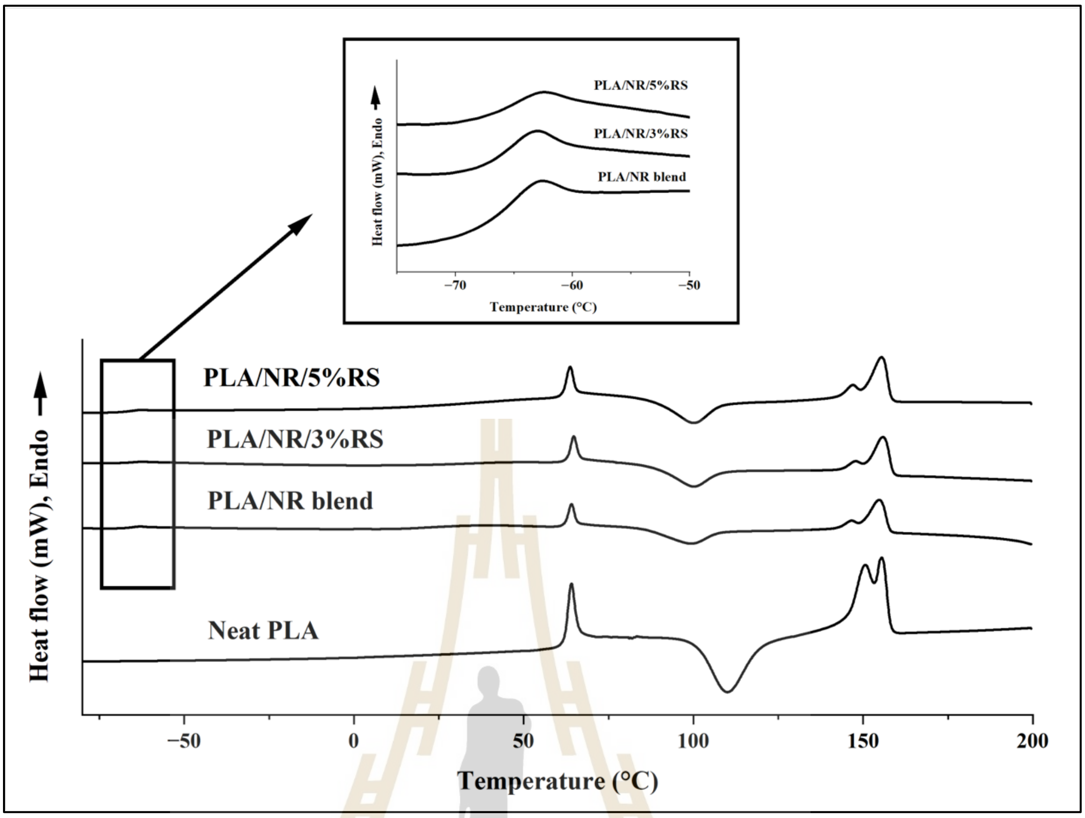

Figure 4.30 DSC thermograms of the samples taken from seedling bags after growing chili plants for a period of 3 months.

Table 4.11 The DSC results from the first heating scan of the cast film and the samples taken from seedling bags and mulch films after growing chili plants for 3 months.

Sample	Tg(NR) (°C)	Tg(PLA) (°C)	Tcc (°C)	Tm1 (°C)	Tm2 (°C)	Xc (%)
Neat PLA As prepared	-	62.67	100.65	148.41	153.58	3.97
Neat PLA Seedling bags	-	61.96	100.23	147.20	158.14	5.25
Neat PLA Mulch films	-	62.87	96.13	147.25	156.42	3.01
PLA/NR blend As prepared	-67.68	63.83	89.54	147.25	154.75	7.92
PLA/NR blend Seedling bags	-68.16	62.11	85.40	146.58	154.76	9.93
PLA/NR blend Mulch films	-66.27	60.10	86.27	-	154.75	7.68
PLA/NR/3%RS As prepared	-68.80	63.20	92.95	139.90	155.33	9.54
PLA/NR/3%RS Seedling bags	-67.96	62.78	88.71	144.94	155.83	10.49
PLA/NR/3%RS Mulch films	-	64.38	86.66	-	153.92	8.76
PLA/NR/5%RS As prepared	-68.24	62.53	91.60	145.01	155.08	11.63
PLA/NR/5%RS Seedling bags	-67.64	61.46	88.98	144.41	155.75	13.07
PLA/NR/5%RS Mulch films	-	63.70	83.64	-	152.92	10.02

4.4.1.2.3 XRD analysis

The XRD patterns, shown in Figure 4.31, indicated a change in the crystallinity of film samples taken from the seedling bags after a period of 3 months following chili planting. The neat PLA has a broad peak at 2θ degrees = 10°- 25°, which is attributed to the semicrystalline structure of PLA. The diffraction peaks of PLA/NR blend and PLA/NR/RS biocomposite films seen at 2θ degrees = 10° and 28°, corresponding with the test of film after being buried in soil (Figure 4.18 (b), page 73), indicate that PLA has undergone significant crystallization. It is possible that this is due to the presence of NR and RS, both nucleating agents that contribute to the degradation process.

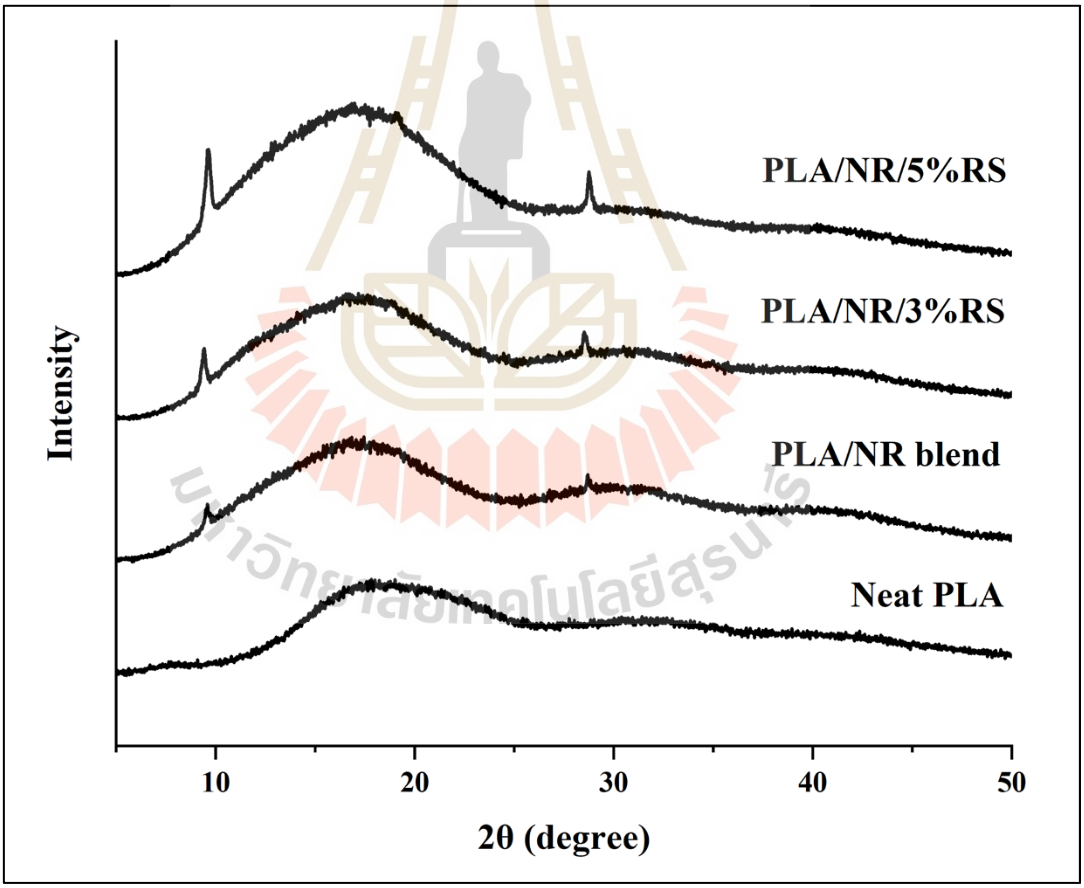

Figure 4.31 XRD patterns of film samples taken from seedling bags after growing chili plants for a period of 3 months.

4.4.2 Mulch films

In addition to their application in producing seedling bags, the neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films were employed to produce mulch films for cultivating chili plants in the field. The chili plants were cultivated for a period of 3 months, starting on April 3rd, and ending on July 3rd, 2023. Figure 4.32 presents the first day of growing chili plants, while Figures 4.33, 4.34, and 4.35 show the growth of chili plants and the physical changes that occur in the mulch films throughout periods of 1, 2, and 3 months, respectively.

Chili plants cultivated with mulch film exhibit a lower growth rate in comparison to those produced without mulch films, as seen in Figure 4.33. The use of neat PLA film as mulch resulted in the slowest growth of the chili plants. An examination of the mulch film's physical characteristics revealed that both the PLA/NR blend (d') and the PLA/NR/3%RS (e') biocomposite showed signs of cracking. Additionally, there is grass growing within the film.

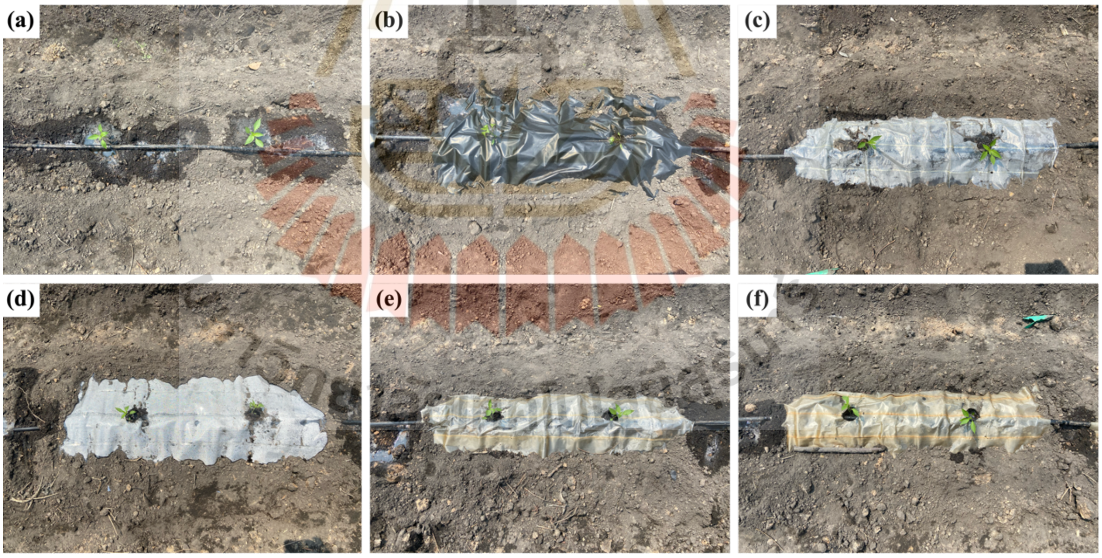

Figure 4.32 Chilli planting without mulch film (a) and with various types of mulch films: HDPE (b), neat PLA (c), PLA/NR blend (d), PLA/NR/3%RS (e), and PLA/NR/5%RS (f) biocomposite films on the first day of cultivation.

In the second month (Figure 4.34) of cultivating the chili plants, there was significant growth and production of several chili fruits. The plants cultivated with PLA mulch film grew inadequately and did not exhibit the expected growth. In addition, it was discovered that the mulch film made from PLA/NR blend and PLA/NR/RS biocomposite film had deteriorated to the extent that it could no longer hold its initial form. Consequently, a significant amount of grass began to sprout from the cracks. Decomposition may be the cause of the mulch film's degradation.

In the final month of the chili plants' cultivation (Figure 4.35), it was observed that they had thrived and produced a huge crop of chilies. On the contrary, the chili plants that were covered with neat PLA film showed limited growth. According to Ning et al.'s (2020) report, the use of transparent film mulch increased soil temperature, resulting in a decreased growth season and decreased crop yields and quality. Furthermore, it was observed that the mulch film made from a PLA/NR blend and a PLA/NR/RS biocomposite exhibited increased degradation, leading to a failure to maintain its film form. The deteriorated film breaks into tiny pieces and disperses across the ground. A lot of grass and weeds were discovered alongside the deteriorated film tracks.

To assess the impact of mulch films on the development of chili plants, various factors, such as dry weight, stem diameter, total weight of chili fruits per plant, and height, were measured after a 3-month growing period. Additionally, the process of biodegradation of mulch films was examined after the chili planting period had finished.

Figure 4.33 Chilli planting without mulch film (a, a’) and with various types of mulch films: HDPE (b, b’), neat PLA (c, c’), PLA/NR blend (d, d’), PLA/NR/3%RS (e, e’), and PLA/NR/5%RS (f, f’) biocomposite films at 1 month of cultivation.

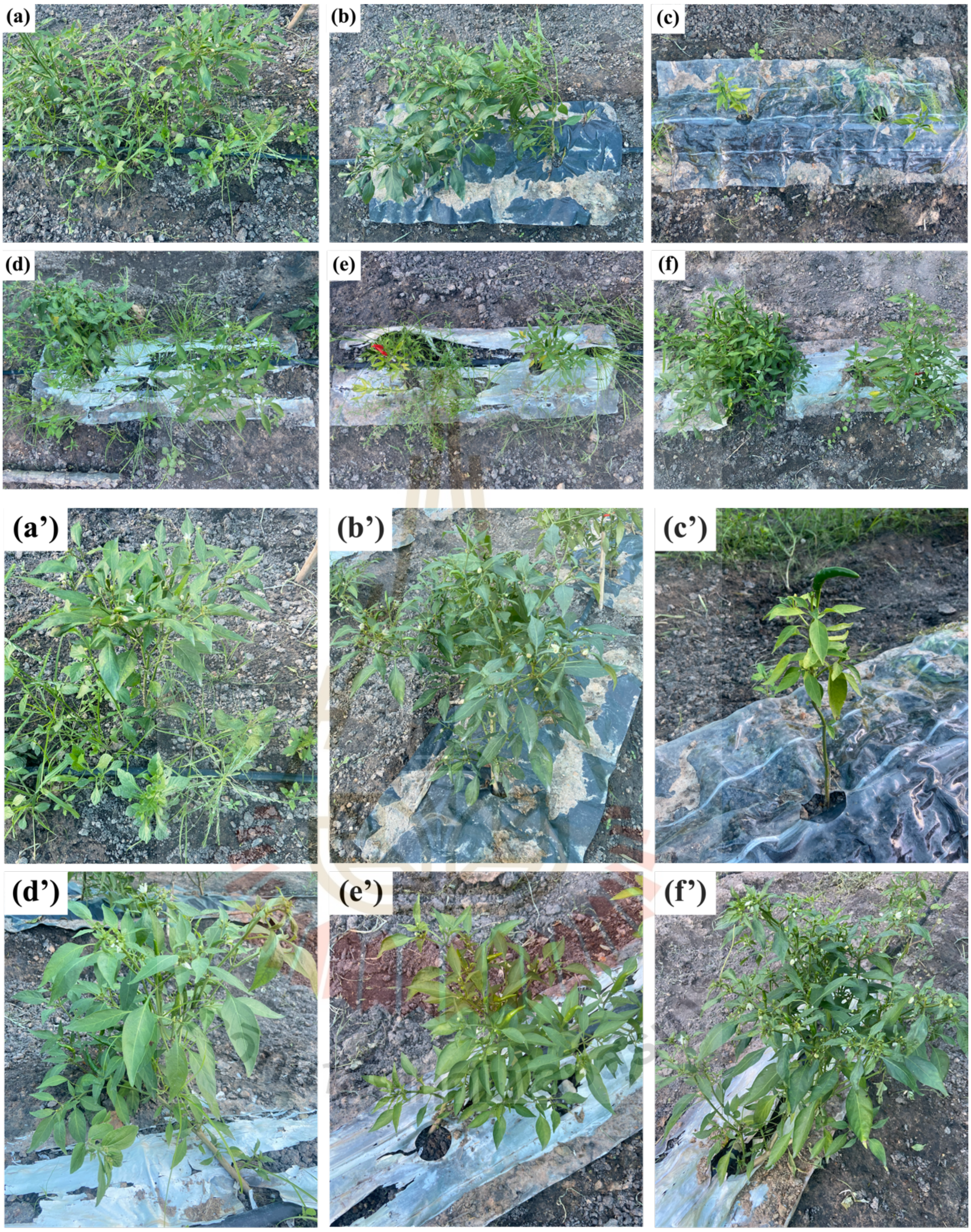

Figure 4.34 Chilli planting without mulch film (a, a') and with various types of mulch films: HDPE (b, b'), neat PLA (c, c'), PLA/NR blend (d, d'), PLA/NR/3%RS (e, e'), and PLA/NR/5%RS (f, f') biocomposite films at 2 months of cultivation.

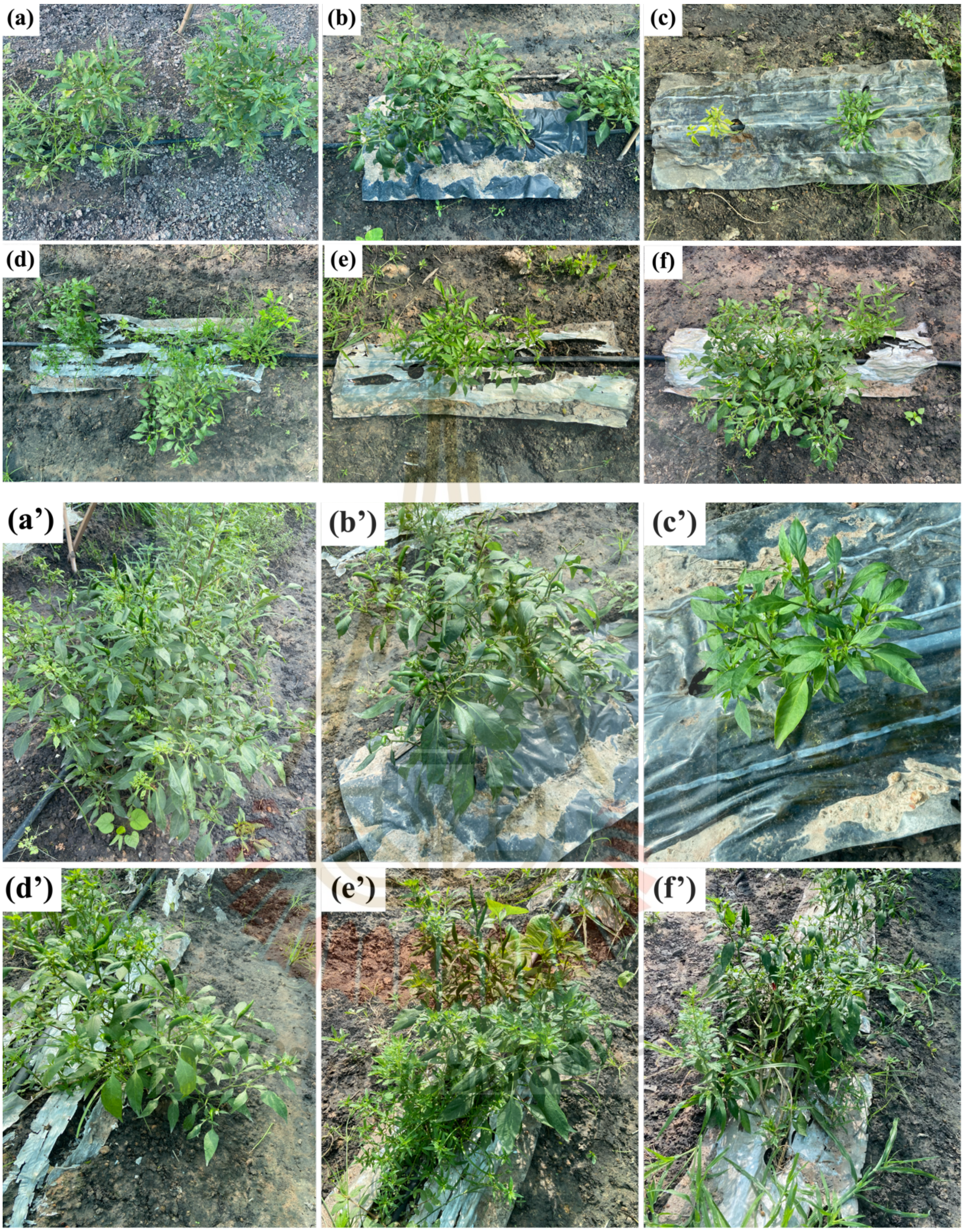

Figure 4.35 Chilli planting without mulch film (a, a’) and with various types of mulch films: HDPE (b, b’), neat PLA (c, c’), PLA/NR blend (d, d’), PLA/NR/3%RS (e, e’), and PLA/NR/5%RS (f, f’) biocomposite films at 3 months of cultivation.

4.4.2.1 Dry weight, total weight of chili fruits per plant, stem diameter and height of chili plants

Figures 4.36 and 4.37 present a comparison of the dry weight, total weight of chili fruit, height, and stem diameter of chili plants grown with and without mulch films. According to the results illustrated in those figures, the growth efficiency of chili plants with mulch films made from HDPE, PLA/NR blend, and biocomposite was not significantly different. Conversely, it was discovered that chili plants grown with neat PLA mulch film had a significantly lower growth rate. The soil's exposure to high temperatures may have directly caused this. This leads to an increase in soil temperature, which has an impact on the growth of chili plants. Furthermore, the deviation range indicated that the absence of mulch film can lead to inconsistent chili plant development.

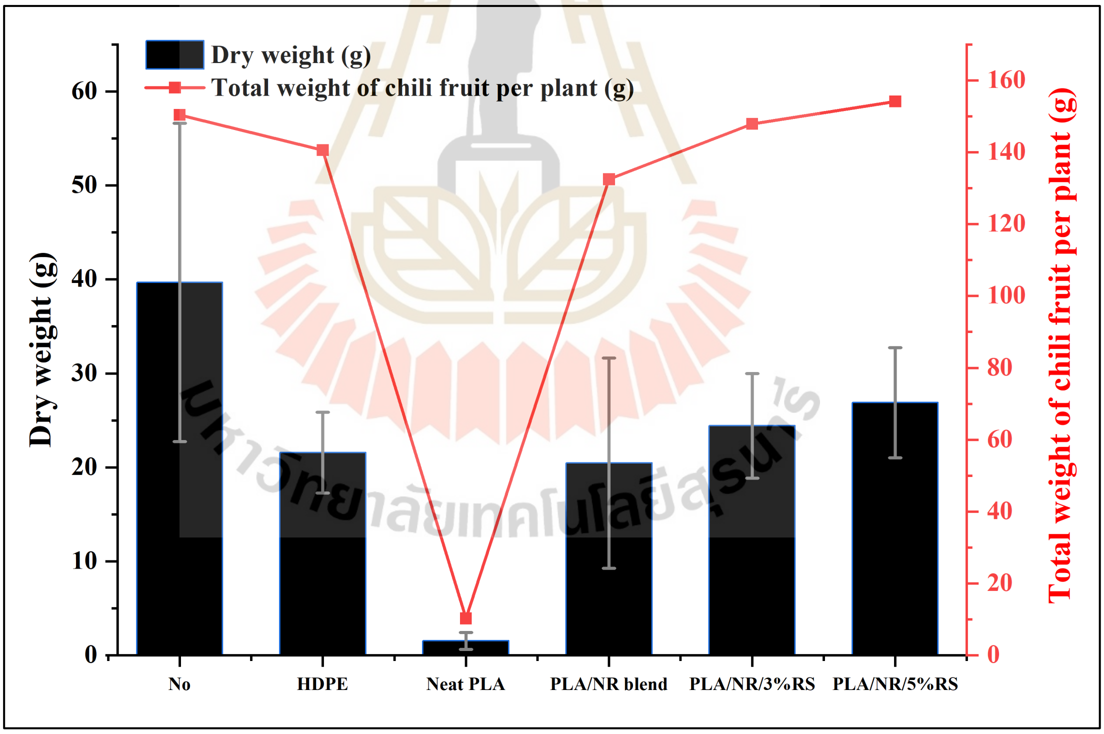

Figure 4.36 Comparison of the average dry weight and total weight of chili fruit of the chili plant grown in different types of mulch films for a period of 3 months.

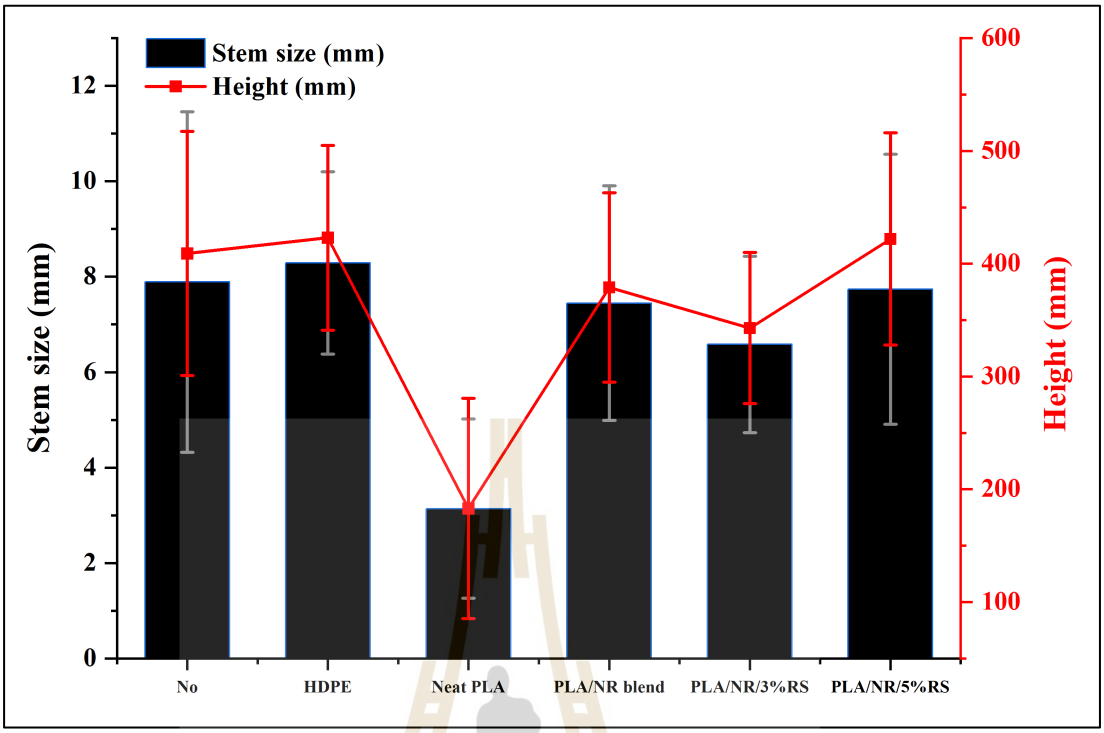

Figure 4.37 Comparison of the stem size and height of the chili plant grown in different types of mulch films for a period of 3 months.

4.4.2.2 Biodegradation of mulch films

The value for the mulch film's percentage weight loss was not available. Because of the mulch film's fragmentation and dispersion, total retrieval became impossible. This makes it impossible to obtain an accurate measurement of the percentage weight loss.

4.4.2.2.1 Molecular weight determination using GPC technique

The molecular weights of neat PLA and PLA that were extracted from PLA/NR blend and PLA/NR/ RS biocomposite film before and after being employed as seedling bags and mulch films for 90 days are shown in Table 4.9. The results from the 90-day study demonstrate a substantial decrease in the molecular weight of all films, especially those used as mulch films, due to degradation. Physical observation confirms that the mulch film breaks into tiny fragments, causing it to lose its shape, while the seedling bag remains intact. The testing of mulch films was conducted during the summer in Thailand, where the high temperatures were approximately 40 °C. Therefore, the mulch film will be exposed to direct sunlight and heat. While the seedling bags testing was performed during the rainy season in Thailand, the seedling bag was also buried within the pots. Hence, it can be concluded that the factors important for the rapid degradation of mulch film include light and heat, through photo- or thermo-oxidative processes (Ning et al., 2020), as well as microbial degradation in the surrounding environment. Correspondence with other research that has identified UV light exposure as a significant environmental factor that affects the degradation of PLA. The study conducted by Teixeira et al. (2021) revealed that exposure to UV light has detrimental effects on the physical properties of PLA, including decreased integrity, increased brittleness, stress at break, and reduced average molecular weight.

4.4.2.2.2 Morphological properties

As shown in Figure 4.38, the FE-SEM micrographs demonstrate the surface characteristics of mulch films made from neat PLA, PLA/NR blend, and PLA/NR/RS biocomposite films after a three-month usage period. The figure indicates that the surfaces of all films exhibit roughness and lack organization, resulting from significant degradation of the surface. Additionally, compared to the surface of the seedling bags (Figure 4.29, page 87), the mulch film's surface showed large pores and a distinct separation. This signifies a higher rate of degradation. Both the film used for producing seedling bags and the mulch film used in growing chili plants are watered daily. When water and moisture from both soil and weather permeate the films, they undergo hydrolysis, leading to their degradation. Furthermore, the process of decomposition takes place because of the activity of microorganisms present in the soil. However, because of the mulch film experiment, the film is exposed to sunlight, which generates more heat than burying it like a seedling bag would. Hence, heat and light have a significant impact on the accelerated degradation of the mulch film. The results of morphological investigations of films buried in soil and films used for seedling bags and mulch film indicate that the film surface with the addition of NR and RS exhibits higher deterioration compared to the film without the addition. Therefore, it was verified that both variables enhanced the water absorption rate of PLA, resulting in enhanced degradation.

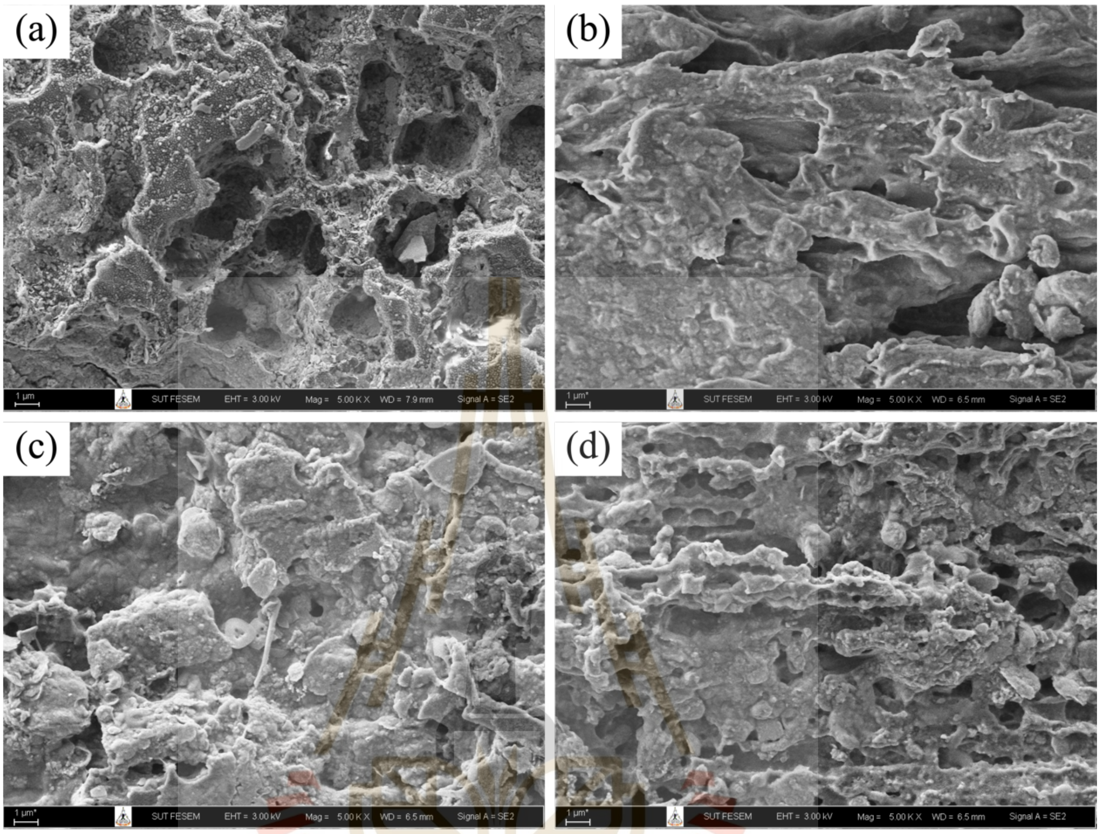

Figure 4.38 FE-SEM micrographs at 5000x magnification of mulch films produced from neat PLA (a), PLA/NR blend (b), PLA/NR/3%RS (c) and PLA/NR/5%RS (d) biocomposite films after chili planting for 3 months.

4.4.2.2.3 DSC analysis

Figure 4.39 shows the DSC thermograms obtained from film samples obtained from mulch films used for chili planting after a 3-month period. These thermograms were used for analysing changes in thermal characteristics during polymer degradation. The results of the DSC are summarized in Table 4.11. There was no significant shift in the glass transition temperature (Tg) of mulch films made from PLA/NR blend films. However, mulch films made from PLA/NR/RS biocomposite film showed a subtle change in Tg (NR) that was difficult to detect. The PLA films displayed two distinct crystal structures, as evidenced by two distinct Tm values. The analysis revealed that the alpha’-crystal form showed a decrease in peak size, while the alpha-form crystals were larger and more visibly apparent compared to the film used for seedling bags (Figure 4.30, page 88), including the film before and after being buried in soil (Figure 4.17, page 72). This crystal form indicates a transformation in the arrangement of the crystal structure towards a more organised crystalline structure. In other hand, it was observed that both the mulch films made from the PLA/NR blend and the PLA/NR/RS biocomposite films exhibited a single crystalline form. This could be attributed to the possible interference during the chain's move to rearrangement, resulting in PLA's crystallization behavior being reduced (Devin, Ahmadi, and Taromi, 2017; Akindoyo, Beg, Ghazali, and Heim, 2018).

The Tcc of all film samples was observed to decrease. This finding is consistent with the results obtained from films used in the production of seedling bags. After conducting an analysis of the crystallinity (Xc) of the PLA phase in film samples obtained from mulch films utilised to cultivate chilli plants over a period of 3 months, it was discovered that the Xc exhibited a reduced degree of crystallinity in comparison to the film before to being buried in the soil. This happens because it is under a lot of influence, which leads to a more rapid degradation process. This includes hydrolytic, photo-, and thermo-oxidative processes, as well as the actions of different microorganisms. These factors rapidly destroy molecular chains in amorphous regions, allowing them to further attack the crystalline regions. Therefore, it is possible that the number and size of crystals may decrease.

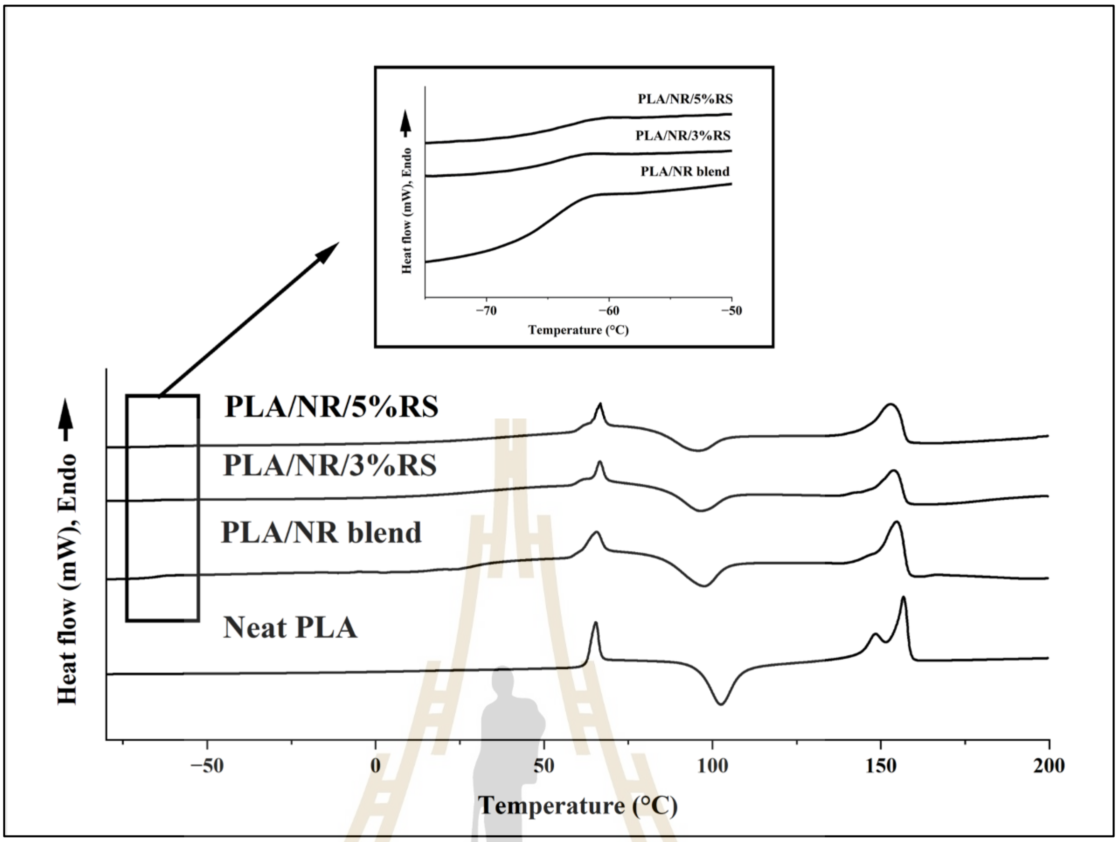

Figure 4.39 DSC thermograms of the samples taken from mulch films after growing chili plants for a period of 3 months.

4.4.2.2.1 XRD analysis

The XRD patterns displayed in Figure 4.40 demonstrate a change in the crystallinity of film samples obtained from the mulch films 3 months after planting chilli. The neat PLA exhibits a broad peak at 2θ degrees = 10° - 25°, attributed to its semicrystalline structure. The diffraction peaks of the PLA/NR blend and PLA/NR/RS biocomposite films are detected at a degree of 2θ = 10°. This investigation contrasts with the observations obtained from films that tested soil burial and used it to produce seedling bags, where diffraction peaks were discovered at 2θ degrees = 10° and 28°. In accordance with the result of a decrease in molecular weight and the results of physical observations. The mulch film had the highest rate of degradation. It is a well-known fact that PLA undergo degradation initially with its amorphous region. This results in the arrangement of the structure being more organized until the crystalline region increases. However, in this instance, there is a decrease in crystallinity when compared to other tests, and the peak that often occurs after X-ray diffraction, caused by the refraction of atoms in the crystal sample, is absent (Ali, 2023). The decomposition of mulch film is subject to many factors, therefore increasing the possibilities of its decomposition. This decomposition can lead to the reduction in size of the crystals, making them more susceptible to water, moisture, and microbe attacks. Finally, the amount of crystalline material was decreased to a degree where it could not be detected. There is a study by Phillips, Jolley, Zhou, and Smit (2021) indicating that temperature can influence the appearance of peaks in XRD patterns. Increased temperatures can induce atomic vibrations or displacements within a crystal, resulting in a shift or broadening of the diffraction peaks. This is consistent with the utilization of outdoor mulch film, which has a long exposure to high temperatures.

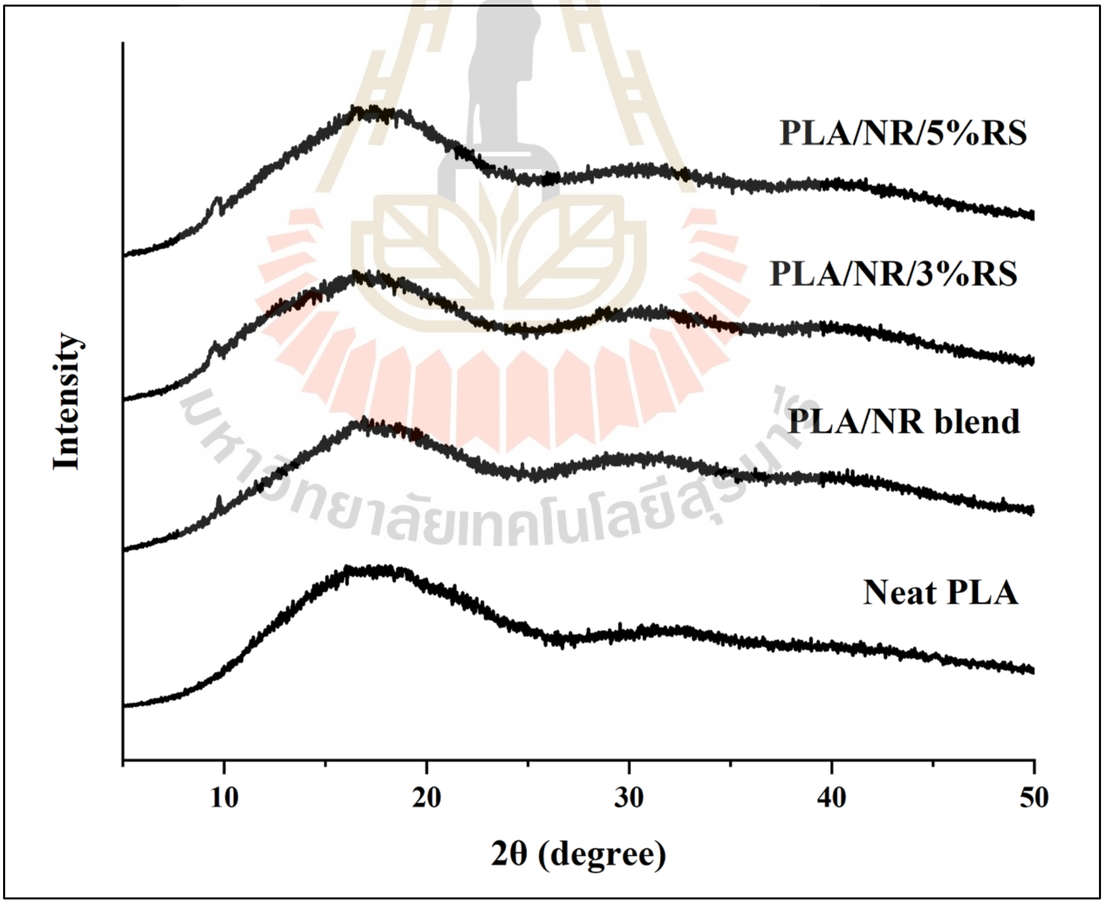

Figure 4.40 XRD patterns of film samples taken from mulch films after growing chili plants for a period of 3 months.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

To improve their compatibility, the study investigated the impact of NR's mastication period on the tensile properties and melt flow index (MFI) of the PLA/NR blend. The ratio of the PLA/NR blend was maintained at a constant weight percentage of 60/40 (wt.%). It was discovered that increasing the duration of NR masticating leads to a higher MFI of the polymer blend. The results of the tensile test showed that the NR mastication duration of 10 minutes had the maximum percentage of elongation at break, which was measured at 231.33 ± 34.43%. Thus, a mastication duration of 10 minutes was chosen for further investigation, as it was found to be the optimum period to significantly improve PLA's toughness properties.

After a suitable PLA/NR blend condition was achieved, the effects of rice straw (RS) content on the MFI, tensile properties, and morphology of biocomposite films were studied. The ratio of PLA and NR in the blend was kept constant at 60/40 wt.%. The blend was filled with RS fiberr at concentrations of 3, 5, and 10 wt.%, respectively. Observations revealed numerous holes in the biocomposite film, which contains 10 weight percent RS (PLA/NR/10%RS). According to the MFI results, increasing the RS content to 10%wt. resulted in an MFI of 37±0.79 g/10 min, which was unsuitable for producing a smooth film. Normally, the appropriate MFI range for cast film is approximately 9-15 g/10 min. Consequently, the biocomposite films comprising 3 and 5 weight percent were further examined. As the RS content increased, the biocomposite films' tensile strength and modulus decreased, but their elongation at break remained higher than PLA's. The morphology of the biocomposite film on the surface fracture under tension was shown to be incompatible.

The biodegrading behavior of the biocomposite films was assessed by burying them in soil for a duration of 3 months. The PLA film had the lowest percentage weight loss of 3.33%, indicating a relatively slow degradation rate in comparison to all the biocomposite films. The film containing 5 wt.% of RS exhibited the highest weight loss percentage of 8.30%, which is consistent with the result of decreased molecular weight. The morphological analysis reveals numerous pores and fungus growth on the film surface after burial in the soil. The chemical composition analysis using EDX revealed the presence of nitrogen and an increase in oxygen content, while the carbon contents decreased during the burial process. The DSC results and the XRD results both showed that PLA had a low level of crystallinity. The addition of NR and RS to the biocomposites resulted in an enhanced PLA crystallinity. All biocomposite films showed an increase in crystallinity after burial in the soil. Consistent with the results on mechanical properties, it was observed that the modulus value tended to increase. This study demonstrates that biocomposite films filled with RS exhibit a higher susceptibility to degradation compared to PLA films.

The biocomposite films were studied and evaluated for their potential agricultural applications including seedling bags and mulch films. Chili plants were cultivated for a period of 3 months. Chili plants grown in bags made from PLA/NR blend and PLA/NR/RS biocomposite films showed higher values of dry weight, stem diameter, total weight of chili fruits per plant, and height compared to plants grown with HDPE and neat PLA seedling bags. In addition, the roots of the chili plant had penetrated the pores in the seedling bags. Particularly, bags produced from biocomposite materials. The root penetration provides an indicator of the efficacy of the seedling bags, which can facilitate and unhindered plant growth. The investigation of the weight loss percentage of the seedling bags after a 3-month period revealed that the seedling bags made from PLA/NR/RS biocomposite film with 5% RS showed the highest percentage loss in weight, specifically 11.29 ± 0.37%. The increase in weight loss percentage after 3 months of chili planting is associated with the decrease in molecular weight. The results demonstrated the highest decrease in molecular weight in PLA/NR/RS biocomposite films with a 5% RS content. The morphological inspection of the film sample, which came from seedling bags used to grow chili plants for three months, shows that the surface of the biocomposites' film degrades more than that of neat PLA. Both the DSC and XRD data showed an increase in the seedling bag films' crystallinity. It is consistent with the observation that the Young's modulus of the film samples cut from the bags after three months of chili planting tends to increase.

The mulch films used for chili cultivation degraded rapidly, starting to degrade within the first month. Over the second month, the film fragmented into smaller pieces, spreading into the soil, and allowing grass and weeds to grow in the cracked areas. Chili plants grown for 3 months using mulch films made from PLA/NR blend and PLA/NR/RS biocomposite films had similar growth rates to those using HDPE films and without films. On the other hand, the study found that the growth rate of chili plants with neat PLA mulch films was significantly lower. The 90-day investigation shows a significant reduction in the molecular weight of PLA phase in all biocomposite films, with physical observations confirming the degradation. The mulch films' percentage weight loss was not available due to film degradation and fragmentation into small pieces that could not be completely recovered. The morphological characteristics of mulch films revealed rough and disorganized surfaces, indicating surface destruction. The DSC results revealed a decrease in crystallinity compared to the film prior to its burial in the soil. Finally, the crystallinity was decreased to a degree where it could not be detected by XRD inspection. As mentioned previously, it was found that biocomposite films were not suitable for mulch film application.

5.2 Recommendation

An investigation of the impact on the environment is essential, particularly the potential effects on soil when the film decomposes. Furthermore, there may be limitations on the future utilization of the film due to its degradation. Hence, it is imperative to select the appropriate film for use.

REFERENCES

Adhikari, R., Bristow, K.L., Casey, P.S., Freischmidt, G., Hornbuckle, J.W., and Adhikari, B. (2016). Preformed and sprayable polymeric mulch film to improve agricultural water use efficiency. *Agricultural Water Management, 169*, 1-13. https://doi.org/10.1016/j.agwat.2016.02.006

Akhtar, S., Bhowmick, A.K., De, P.P. and De, S.K. (1986). Tensile rupture of short fibre filled thermoplastic elastomer. *Journal of Materials Science, 21*(12), 4179-4184. https://doi.org/10.1007/BF01106527

Akindoyo, J. O., Beg, M.D.H., Ghazali, S., and Heim, H.P. (2018). Impact modified PLA-hydroxyapatite composites – Thermo-mechanical properties. *Composites Part A, 107*, 326-333. https://doi.org/10.1016/j.compositesa.2018.01.017

Akpan, E. I., Adeosun, S.O., Lawal, G.I., Balogun, S.A. and Chen, X.D. (2014). Structural Characteristics of Batch Processed Agro-Waste Fibres. *International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering, 8*(3), 223-230.

Akrami, M., Ghasemi, I., Azizi, H., Karrabi, M., and Seyedabadi, M. (2016). A new approach in compatibilization of the poly(lactic acid)/thermoplastic starch (PLA/TPS) blends. *Carbohydrate Polymers, 144*, 254-262. https://doi.org/10.1016/j.carbpol.2016.02.035

Ali, M. (2023). Qualitative Analyses of Thin Film-Based Materials Validating New Structures of Atoms. *Materials Today Communications, 36*(106552), 1-28. https://doi.org/10.1016/j.mtcomm.2023.106552

Alias, N. F., Ismail, H., and Ishak, K.M.K. (2021). Poly(lactic acid)/natural rubber/kenaf biocomposites production using poly(methyl methacrylate) and epoxidized natural rubber as co-compatibilizers. *Iranian Polymer Journal, 30*(7), 737-749. https://doi.org/10.1007/s13726-021-00927-8

Amir-Hashim, M. Y., Roslim, R. and Rosni, M.W. (2012). Physical Properties and Surface Morphology of Natural Rubber Latex Films Intended for Seedling Bag Application. *Journal of Rubber Research, 15*(4), 243-254.

Ansari, A.H., Jakarni, F.M., Muniandy, R. And Hassim, S. (2021). A review on the application of natural rubber as asphalt modifier. *Materials Science and Engineering, 1075*(1), 1-12. https://doi.org/10.1088/1757-899X/1075/1/012031

Arrieta, M. P., Perdiguero, M., Fiori, S., Kenny, J.M., and Peponi, L. (2020). Biodegradable electrospun PLA-PHB fibers plasticized with oligomeric lactic acid. *Polymer Degradation and Stability. 179*(109226), 1-7. https://doi.org/10.1016/j.polymdegradstab.2020.109226

Banthao, C., Kumpolsan, P., Baimark, Y., Wongkasemjit, S., and Pakkethati, K. (2020). Improvement the properties of poly(l-lactide) films with cellulose fiber from rice straw waste in agricultural products *International Journal of GEOMATE, 18*(70), 43-48. https://doi.org/10.21660/2020.70.5716

Beniwal, P., and Toor, A.P. (2023). Advancement in tensile properties of polylactic acid composites reinforced with rice straw fibers. *Industrial Crops & Prod, 192*(116098), 1-9. https://doi.org/10.1016/j.indcrop.2022.116098

Bilck, A. P., Olivato, J.B., Yamashita, F., and Pinto de Souza, J.R. (2014). Biodegradable bags for the production of plant seedlings. *Polímeros, 24*(5), 547-553. https://doi.org/10.1590/0104-1428.1589

Bitinis, N., Verdejoa, R., Cassagnau, P. And Lopez-Manchadoa, M.A. (2011). Structure and properties of polylactide/natural rubber blends. *Materials Chemistry and Physics, 129*, 823-831. https://doi.org/10.1016/j.matchemphys.2011.05.016

Bomfim, A. S. C., Oliveira, D.M., Benini, K.C.C., Cioffi, M.O.H., Voorwald, H.J.C., and Rodrigue, D. (2023). Effect of Spent Coffee Grounds on the Crystallinity and Viscoelastic Behavior of Polylactic Acid Composites. *Polymers, 15*(2719), 1-16. https://doi.org/10.3390/polym15122719

Boonmee, C., Kositanont, C., and Leejarkpai, T. (2016). Degradation of Poly (lactic acid) under Simulated Landfill Conditions. *Environment and Natural Resources, 14*(2), 1-9.

Brunsek, R., Kopitar, D., Schwarz, I., and Marasovic, P. (2023). Biodegradation Properties of Cellulose Fibers and PLA Biopolymer. *Polymers, 15*(3532), 1-20. https://doi.org/10.3390/polym15173532

Burkov, A., Kraev, A., Grishin, M., Vesnin, R., Fomin, S., and Iordanskii, A. (2021). Structural Features and Properties' Characterization of Polylactic Acid/Natural Rubber Blends with Epoxidized Soybean Oil. *Polymers, 13*(1101), 1-12. https://doi.org/10.3390/polym13071101

Buys, Y.F., Aznan, A.N.A. and Anuar, H. (2017). Mechanical properties, morphology, and hydrolytic degradation behavior of polylactic acid / natural rubber blends. *Materials Science and Engineering, 290*(1), 1-8. https://doi.org/10.1088/1757-899X/290/1/012077

Carruthers, T. J. B., Longstaff, B. J., Dennison, W. C., Abal, E. G., and Aioi, K. (2001). Measurement of light penetration in relation to seagrass *Global Seagrass Research Methods*, 369-292. https://doi.org/10.1016/B978-044450891-1/50020-7

Casalini, T., and Perale, G. (2016). Processing of bioresorbable and other polymers for medical applications. *Durability and reliability of medical polymers*, 49-76. https://doi.org/10.1533/9780857096517.1.49

Chaiwutthinan, P., Chuayjuljit, S., Srasomsub, S., and Boonmahitthisud, A. (2019). Composites of poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend with wood fiber and wollastonite: Physical properties, morphology, and biodegradability. Journal of Applied Polymer Science, 47543, 1-14. https://doi.org/10.1002/app.47543

Chen, J., Zhang, T.Y., Jin, F.L. and Park, S.J. (2018). Fracture Toughness Improvement of Poly(lactic acid) Reinforced with Poly(ε-caprolactone) and Surface-Modified Silicon Carbide. *Advances in Materials Science and Engineering, 2018*, 1-10. https://doi.org/10.1155/2018/6537621

Chen, Y., Yuan, D. And Xu, C. (2014). Dynamically vulcanized biobased polylactide/natural rubber blend material with continuous cross-linked rubber phase. *ACS Applied Materials & Interfaces, 6*(6), 3811-3816. https://doi.org/10.1021/am5004766

Chuayjuljit, S., Wongwaiwattanakul, C., Chaiwutthinan, P., and Prasassarakich, P. (2016). Biodegradable Poly(Lactic Acid)/Poly(Butylene Succinate)/Wood Flour Composites: Physical and Morphological Properties. *Polymer Composites, 38*(12), 1-11. https://doi.org/10.1002/pc.23886

Da Costa, J.P., Nunes, A.R., Santos, P.S.M., Girão, A.V., Duarte, A.C. and Rocha-Santos, T. (2018). Degradation of polyethylene microplastics in seawater: Insights into the environmental degradation of polymers. *Environmental Science and Health, Part A, 53*(9), 866-875. https://doi.org/10.1080/10934529.2018.1455381

Da Silva, D., Kaduri, M., Poley, M., Adir, O., Krinsky, N., Shainsky-Roitman, J. And Schroeder, A. (2018). Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems. *Chemical Engineering Journal, 340*, 9-14. https://doi.org/10.1016/j.cej.2018.01.010

Devin, T. P., Ahmadi, Z., and Taromi, F.A. (2017). Investigation on Crystallinity Behavior of the Polylactic Acid and Poly-3-hydroxybutyrate Bio-based Polymers in the Presence of the Pyromellitic Anhydride. *Journal of Applied Biotechnology Reports, 4*(3), 661-668.

Diaz-Hernandez, J. L., Sanchez-Soto, P.J., and Serrano-Delgado, A. (2012). Biological nanostructures associated to iberulites: a SEM study. *Current Microscopy Contributions to Advances in Science and Technology*(1), 154-161.

Ding, L., Zou, B., Shen, L., Zhao, C., Wang, Z., Guo, Y., Wang, X. And Liu, Y. (2014). A simple route for consecutive production of activated carbon and liquid compound fertilizer from rice husk. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 446*, 90-96. https://doi.org/10.1016/j.colsurfa.2014.01.055

Djellali, S., Sadoun, T., Haddaoui, N., and Bergeret, A. (2015). Viscosity and viscoelasticity measurements of low density polyethylene/poly(lactic acid) blends. *Polymer Bulletin 72,* 1177–1195. https://doi.org/10.1007/s00289-015-1331-6

Drobny, J. G. (2020). Introduction, *Applications of Fluoropolymer Films* (1st ed., pp. 3-38). Amsterdam: Elsevier Science. https://doi.org/10.1016/B978-0-12-816128-9.00001-5

Drumright, R.E., Gruber, P.R. and Henton, D.E. (2000). Polylactic Acid Technology. *Advanced Materials, 12*(23), 1841-1846. https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E

Elsawy, M.A., Kim, K.H., Park, J.W. And Deep, A. (2017). Hydrolytic degradation of polylactic acid (PLA) and its composites. *Renewable and Sustainable Energy Reviews, 79*, 1346-1352. https://doi.org/10.1016/j.rser.2017.05.143

Eselini, N., Tirkes, S., Akar, A.O., and Tayfun, U. (2019). Production and characterization of poly(lactic acid)-based biocomposites filled with basalt fiber and flax fiber hybrid. *Journal of Elastomers & Plastics*, 1-16. https://doi.org/10.1177/0095244319884716

ExxonMobil. (2021). Technical data sheets for Exceed XP. Retrieved from https://www.exxonmobilchemical.com/en/resources/product-data-sheets/polyethylene/exceed-xp-performance-pe-polymers.

Fa, W., Wang, J., Ge, S., and Chao, C. (2020). Performance of photo-degradation and thermo-degradation of polyethylene with photo-catalysts and thermo-oxidant additives. *Polymer Bulletin, 77*, 1417-1432. https://doi.org/10.1007/s00289-019-02813-z

Fabian, D. R. C., Durpekova, S., Dusankova, M., Cisar, J., Drohsler, P., Elich, O., Borkova, M., Cechmankova, J., and Sedlarik, V. (2023). Renewable Poly(Lactic Acid)Lignocellulose Biocomposites for the Enhancement of the Water Retention Capacity of the Soil. *Polymers, 15*(2243), 1-18. https://doi.org/10.3390/polym15102243

Farah, S., Anderson, D. G. And Langer, R. (2016). Physical and mechanical properties of PLA, and their functions in widespread applications – A comprehensive review. *Advanced Drug Delivery Reviews, 107*, 367-392. https://doi.org/10.1016/j.addr.2016.06.012

Feng, P., Jia, J., Liu, M., Peng, S., Zhao, Z. And Shuai, C. (2021). Degradation mechanisms and acceleration strategies of poly (lactic acid) scaffold for bone regeneration. *Materials & Design, 210*, 1-18. https://doi.org/10.1016/j.matdes.2021.110066

Feng, Y., Hu, Y., Yin, J., Zhao, G., and Jiang, W. (2013). High Impact Poly(lactic acid)/Poly(ethylene octene) Blends Prepared by Reactive Blending. *Polymer engineering and science 53*, 389-396. https://doi.org/10.1002/pen.23265

Freitas, P. A. V., Gonzalez-Martínez, C., and Chiralt, A. (2023). Using rice straw fractions to develop reinforced, active PLA-starch bilayers for meat preservation. *Food Chemistry, 405*(134990), 1-11. https://doi.org/10.1016/j.foodchem.2022.134990

Garcia-Garcia, D., Carbonell-Verdu, A., Arrieta, M.P., López-Martínez, J., and Samper M.D. (2020). Improvement of PLA film ductility by plasticization with epoxidized karanja oil. *Polymer Degradation and Stability, 179*(109259), 1-35. https://doi.org/10.1016/j.polymdegradstab.2020.109259

Garlotta, D. (2001). A Literature Review of Poly(Lactic Acid). *Journal of Polymers and the Environment, 9*(2), 63-84. https://doi.org/10.1023/A:1020200822435

Ghatge, S., Yang, Y., Ahn, J.H., and Hur, H.G. (2020). Biodegradation of polyethylene: a brief review. *Applied Biological Chemistry, 63*(27), 1-14. https://doi.org/10.1186/s13765-020-00511-3

Gironi, F. And Piemonte, V. (2011). Bioplastics and Petroleum-based Plastics: Strengths and Weaknesses. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 33*(21), 1949-1959. https://doi.org/10.1080/15567030903436830

Gkoutselis, G., Rohrbach, S., Harjes, J., Obst, M., Brachmann, A., Horn, M.A., and Rambold, G. (2021). Microplastics accumulate fungal pathogens in terrestrial ecosystems. *Scientifc Reports 11*(13214), 1-14. https://doi.org/10.1038/s41598-021-92405-7

Gorga, R.E.and Cohen, R.E. (2004). Toughness enhancements in poly(methyl methacrylate) by addition of oriented multiwall carbon nanotubes. *Journal of Polymer Science Part B: Polymer Physics, 42*(14), 2690-2702. https://doi.org/10.1002/polb.20126

Haase, D. L., Bouzza, K., Emerton, L., Friday, J.B., Lieberg, B., Aldrete, A. And Davis, A.S. (2021). The High Cost of the Low-Cost Polybag System: *A Review of Nursery Seedling Production Systems. Land, 10*(8), 826. https://doi.org/10.3390/land10080826

Hakkarainen, M. (2002). Aliphatic Polyesters: Abiotic and Biotic Degradation and Degradation Products. *Springer*, 113-138. https://doi.org/10.1007/3-540-45734-8_4

Hamad, K., Kaseem, M., Yang, H.W., Deri, F. And Ko, Y.G. (2015). Properties and medical applications of polylactic acid: A review. *Express Polymer Letters, 9*(5), 435-455. https://doi.org/10.3144/expresspolymlett.2015.42

Hendrick, E.and Frey, M. (2014). Increasing Surface Hydrophilicity in Poly(Lactic Acid) Electrospun Fibers by Addition of Pla-b-Peg Co-Polymers. *Journal of Engineered Fibers and Fabrics, 9*(2), 153-164. https://doi.org/10.1177/155892501400900219

Herculano, R.D., Tzu, L.C., Silva, C.P., Brunello, C.A., Queiroz, Á.A.A.d., Kinoshita, A. And Graeff, C.F.d.O. (2011). Nitric oxide release using natural rubber latex as matrix. *Materials Research, 14*(3), 355-359. https://doi.org/10.1590/S1516-14392011005000055

Huang, Y., Zhang, C., Pan, Y., Zhou, Y., Jiang, L., and Dan, Y. (2013). Effect of NR on the hydrolytic degradation of PLA. *Polymer Degradation and Stability, 98*(5), 943-950. https://doi.org/10.1016/j.polymdegradstab.2013.02.018

Hung, N. V., Maguyon-Detras, M.C., Migo, M.V., Quilloy, R., Balingbing, C., Chivenge, P., and Gummert, M. (2020). Chapter 1 Rice Straw Overview: Availability, Properties, and Management Practices. *Springer International Publishing*, 1-13. https://doi.org/10.1007/978-3-030-32373-8_1

Janorkar, A.V., Metters, A.T. and Hirt, D.E. (2004). Modification of Poly(lactic acid) Films: Enhanced Wettability from Surface-Confined Photografting and Increased Degradation Rate Due to an Artifact of the Photografting Process. *Macromolecules, 37*(24), 9151-9159. https://doi.org/10.1021/ma049056u

Jaratrotkamjorn, R., Khaokong, C., and Tanrattanakul, V. (2012). Toughness Enhancement of Poly(lactic acid) by Melt Blending with Natural Rubber. *Journal of Applied Polymer Science, 124*, 5027-5036. https://doi.org/10.1002/app.35617

Jiang, L., Shen, T., Xu, P., Zhao, X., Li, X., Dong, W., Ma, P. And Chen, M. (2015). Crystallization modification of poly(lactide) by using nucleating agents and stereocomplexation. *E-Polymers, 16*(1), 1-13. https://doi.org/10.1515/epoly-2015-0179

Juntuek, P., Chumsamrong, P., Ruksakulpiwat, Y., and Ruksakulpiwat, C. (2015). Effect of Vetiver Grass Fiber on Soil Burial Degradation of Natural Rubber and Polylactic Acid Composites. *International Polymer Processing, 29*(3), 379-388. https://doi.org/10.3139/217.2836

Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S. E., and Singh, S. P. (2007). Compostability of bioplastic packaging materials: an overview. *Macromol Biosci, 7*(3), 255-277. https://doi.org/10.1002/mabi.200600168

Kalita, N. K., Damare, N.A., Hazarika, D., Bhagabati, P., Kalamdhad, A., and Katiyar, V. (2021). Biodegradation and characterization study of compostable PLA bioplastic containing algae biomass as potential degradation accelerator. *Environmental Challenges, 3*(100067), 1-10. https://doi.org/10.1016/j.envc.2021.100067

Karamanlioglu, M., and Alkan, U. (2019). Influence of time and room temperature on mechanical and thermal degradation of poly(lactic) acid. *Thermal science, 23*(1), 383-390. https://doi.org/10.2298/TSCI181111051K

Karkri, M. (2017). Thermal Conductivity of Biocomposite Materials. In Sadasivuni, K.K., Cabibihan, J.J., Ponnamma, D., Al-Maadeed, M.A. and Kim, J (Ed.), *Biopolymer Composites in Electronics* (1 ed., pp. 129-153). Amsterdam: Elsevier. https://doi.org/10.1016/B978-0-12-809261-3.00004-8

Kohjiya, S. And Ikeda, Y. (2014). Introduction. In Kohjiya, S. And Ikeda, Y. (Ed.), *Chemistry, manufacture and applications of natural rubber* (pp. 18-27). Cambridge: Woodhead Publishing. https://doi.org/10.1016/B978-0-85709-683-8.50022-7

Kophimaia, Y., Cheenacharoenb, S., Simisterc, R., Gomezc, L.D., McQueen-Masonc, S.J., and Vuttipongchaikij., S. (2020). Straw digestibility of Thai rice accessions. *Agriculture and Natural Resources, 54*, 617-622.

Li, Y., Qiang, Z., Chena, X., and Ren, J. (2019). Understanding thermal decomposition kinetics of flame-retardant thermoset polylactic acid. *RSC Advances, 9*, 3128–3139. https://doi.org/10.1039/C8RA08770A

Lorenzoa, M. L. D., and Androsch, R. (2016). *Melting of **α**'- and **α**-Crystals of Poly(lactic acid).* Paper presented at the AIP Conference Proceeding, Naples, Italy. https://doi.org/10.1063/1.4949583

Lubos, B., Martin, S., and Jozef, D. (2014). Crystallization of Polylactic Acid Composites with Banana and Hemp Fibres by Means of DSC and XRD Methods. *Applied Mechanics and Materials, 616*, 325-332. https://doi.org/10.4028/www.scientific.net/AMM.616.325

Luo, Y., Lin, Z., & Guo, G. (2019). Biodegradation Assessment of Poly (Lactic Acid) Filled with Functionalized Titania Nanoparticles (PLA/TiO2) under Compost Conditions. *Nanoscale Research Letters, 14*(1), 1-10. https://doi.org/10.1186/s11671-019-2891-4

Lv, S., Liu, X., Gu, J., Jiang, Y., Tan, H., and Zhang, Y. (2017). Microstructure analysis of polylactic acid-based composites during degradation in soil. *International Biodeterioration & Biodegradation, 122*, 53-60. https://doi.org/10.1016/j.ibiod.2017.04.017

Lv, S., Zhang, Y., Gu, J., and Tan, H. (2018). Soil burial-induced chemical and thermal changes in starch/poly (lactic acid) composites. *International Journal of Biological Macromolecules, 113*, 338–344. https://doi.org/10.1016/j.ijbiomac.2018.02.139

Mansoor, Z., Tchuenbou-Magaia, F., Kowalczuk, M., Adamus, G., Manning, G., Parati, M., Radecka, I., and Khan, H. (2022). Polymers Use as Mulch Films in Agriculture-A Review of History, Problems and Current Trends. *Polymers, 14*(5062), 1-29. https://doi.org/10.3390/polym14235062

Mansor, M. K., Kamal, M.M., Dayang-Habibah, A.I.H., and Yusoff, M.F.H. (2015). Biodegradable Bags Properties Evaluation for Nursery Application. *Australian Journal of Basic and Applied Sciences, 9*(8), 126-131.

Maricilla, A. and Beltran, M. (2017). Mechanisms of Plasticizers Action. In *Handbook of Plasticizers* (3 ed., pp. 119-134): ChemTec Publishing.

Matta, A. K., Rao, R.U., Suman, K.N.S., and Rambabu, V. (2014). Preparation and Characterization of Biodegradable PLA/PCL Polymeric Blends. *Procedia Materials Science, 6*, 1266-1270. https://doi.org/10.1016/j.mspro.2014.07.201

McKeen, L. W. (2017). Environmentally Friendly Polymers. *In Permeability Properties of Plastics and Elastomers* (4 ed., pp. 305-323). Amsterdam: Elsevier Science. https://doi.org/10.1016/B978-0-323-50859-9.00013-0

Merino, D., Zych, A., and Athanassiou, A. (2022). Biodegradable and Biobased Mulch Films: Highly Stretchable PLA Composites with Different Industrial Vegetable Waste. *ACS Applied Materials & Interfaces, 14*, 46920–46931. https://doi.org/10.1021/acsami.2c10965

Ming, R., Yang, G., Li, Y., Wang, R., Zhang, H., and Shao, H. (2015). Flax Fiber-Reinforced Polylactide Stereocomplex Composites With Enhanced Heat Resistance and Mechanical Properties. *Polymer Composites, 38*(3), 472–478. https://doi.org/10.1002/pc.23605

Mohammad, N.N.B., Arsad, A., Rahmat, A.R., Abdullah Sani, N.S. and Ali Mohsin, M.E. (2016). Influence of compatibilizer on the structure properties of polylactic acid/natural rubber blends. *Polymer Science Series A, 58*(2), 177-185. https://doi.org/10.1134/S0965545X16020164

Murphy, S. H., Marsh, J.J., Kelly, C.A., Leeke, G.A., and Jenkins, M.J. (2017). Co2 Assisted blending of poly(lactic acid) and poly(ε-caprolactone). *European Polymer Journal, 88*, 34-43. https://doi.org/10.1016/j.eurpolymj.2016.12.013

Nagarajan, V., Mohanty, A.K. and Misra, M. (2016). Perspective on Polylactic Acid (PLA) based Sustainable Materials for Durable Applications: Focus on Toughness and Heat Resistance. *ACS Sustainable Chemistry & Engineering, 4*(6), 2899-2916. https://doi.org/10.1021/acssuschemeng.6b00321

Ndazi, B.S. and Karlsson, S. (2011). Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures. *Express Polymer Letters, 5*(2), 119-131. https://doi.org/10.3144/expresspolymlett.2011.13

Ning, R., Liang, J., Sun, Z., Liu, X., and Sun, W. (2020). Preparation and characterization of black biodegradable mulch films from multiple biomass materials. *Polymer Degradation and Stability, 183*(109411), 1-31. https://doi.org/10.1016/j.polymdegradstab.2020.109411

Nizamuddin, S., Hossain, N., Qureshi, S.S., Tanjung, F.A., Siddiqui, M.T.H., Baloch, H.A., Mubarak, N.M., Griffin, G, and Srinivasan, M. (2021). Experimental investigation of physicochemical, thermal, mechanical and rheological properties of polylactide/rice straw hydrochar composite. *Journal of Environmental Chemical Engineering*, 1-10. https://doi.org/10.1016/j.jece.2021.106011

Nuinu, P., Samosorn, K., Srilatong, K., Tongbut, S., and Saengsuwan, S. (2013). Thermal and Mechanical Properties of Mulch Film from Poly(Lactic Acid)/Expoxidized Natural Rubber Blends Filled with Rutile TiO2 as fillers *Advanced Materials Research, 844*, 65-68. https://doi.org/10.4028/www.scientific.net/AMR.844.65

Palsikowski, P. A., Kuchnier, C.N., Pinheiro, I.F., and Morales, A.R. (2017). Biodegradation in Soil of PLA/PBAT Blends Compatibilized with Chain Extender. *Journal of Polymers and the Environment, 26*, 330-341. https://doi.org/10.1007/s10924-017-0951-3

Parker, M. J. (2000). Test Methods for Physical Properties. *Comprehensive Composite Materials, 5*, 183–226. https://doi.org/10.1016/B0-08-042993-9/00074-7

Pattamaprom, C., Chareonsalung, W., Teerawattananon, C., Ausopron, S., Prachayawasin, P., and Puyvelde, P.V. (2016). Improvement in impact resistance of polylactic acid by masticated and compatibilized natural rubber. *Iranian Polymer Journal, 25*(2), 169-178. https://doi.org/10.1007/s13726-015-0411-7

Phattarateera, S., and Pattamaprom, C. (2019). The Viscosity Effect of Masticated Natural vs. Synthetic Isoprene Rubber on Toughening of Polylactic Acid. *International Journal of Polymer Science*, 1-9. https://doi.org/10.1155/2019/5679871

Phillips, R., Jolley, K., Zhou, Y., and Smith, R. (2021). Influence of temperature and point defects on the X-ray diffraction pattern of graphite. *Carbon Trends, 5*(100124), 1-12. https://doi.org/10.1016/j.cartre.2021.100124

Phonphuak, N. And Chindaprasirt, P. (2015). Types of waste, properties, and durability of pore-forming waste-based fired masonry bricks. *Eco-efficient Masonry Bricks and Blocks*, 103-127. https://doi.org/10.1016/B978-1-78242-305-8.00006-1

Pongputthipat, W., Ruksakulpiwat, Y., and Chumsamrong, P. (2022). Development of biodegradable biocomposite films from poly(lactic acid), natural rubber and rice straw. *Polymer Bulletin*, 1-19. https://doi.org/10.1007/s00289-022-04560-0

Pongtanayut, K., Thongpin, C.and Santawitee, O. (2013). The Effect of Rubber on Morphology, Thermal Properties and Mechanical Properties of PLA/NR and PLA/ENR Blends. *Energy Procedia, 34*, 888-897. https://doi.org/10.1016/j.egypro.2013.06.826

Rahmani, M., Khani, M.M., Rabbani, S., Mashaghi, A., Noorizadeh, F., Faridi-Majidi, R., and Ghanbari, H (2020). Development of poly (mannitol sebacate)/poly (lactic acid) nanofibrous scaffolds with potential applications in tissue engineering. *Materials Science & Engineering C, 110626,* 1-15. https://doi.org/10.1016/j.msec.2020.110626

Rasal, R.M., Janorkar, A.V. and Hirt, D.E. (2010). Poly(lactic acid) modifications. *Progress in Polymer Science, 35*, 338–356. https://doi.org/10.1016/j.progpolymsci.2009.12.003

Ren, J. (2011). *Biodegradable Poly(Lactic Acid): Synthesis, Modification, Processing and Applications* (1st ed.). Springer-Verlag, Berlin Heidelberg. https://doi.org/10.1007/978-3-642-17596-1_1

Rosdi, F. N. M., Salim, N., Roslan, R., Bakar, N.H.A., and Sarmin, S.N.S. (2023). Potential Red Algae Fibre Waste as a Raw Material for Biocomposite. *Journal of Advanced Research in Applied Sciences and Engineering Technology, 30*(1), 303-310. https://doi.org/10.37934/araset.30.1.303310

Rosli, N. A., Karamanlioglu, M., Kargarzadeh, H., and Ahmad, I. (2021). Comprehensive exploration of natural degradation of poly(lactic acid) blends in various degradation media: A review. *International Journal of Biological Macromolecules*, *187*, 732-741. https://doi.org/10.1016/j.ijbiomac.2021.07.196

Rosli, N.A., Ahmad, I., Anuar, F.H., and Abdullah, I. (2018). The contribution of eco-friendly bio-based blends on enhancing the thermal stability and biodegradability of Poly(lactic acid). *Journal of Cleaner Production, 198*, 987-995. https://doi.org/10.1016/j.jclepro.2018.07.119

Sakai, E., Qiu, J. H., Murata, T., Kazushi, I., Kobayashi, J., and Takahashi, T. (2011). Degradation Characteristics of Rice Straw/Poly (Lactic Acid) Composites. *Advanced Materials Research, 391-392*, 1268-1272. https://doi.org/10.4028/www.scientific.net/AMR.391-392.1268

Salmah, H., Marliza, M. And The, P.L. (2013). Treated Coconut Shell Reinforced Unsaturated Polyester. *International Journal of Engineering and Technology, 13*(2), 94-103.

Schliecker, G., Schmidt, C., Fuchs, S. And Kissel, T. (2003). Characterization of a homologous series of d, l -lactic acid oligomers; a mechanistic study on the degradation kinetics in vitro. *Biomaterials, 24*(21), 3835-3844. https://doi.org/10.1016/S0142-9612(03)00243-6

Silva, A. P. D., Pereira, M.D.P., Passador, F.R., and Montagna, LS. (2020). PLA/Coffee Grounds Composites: A Study of Photodegradation and Biodegradation in Soil. *Macromolecular Symposia, 394*(2000091), 1-9. https://doi.org/10.1002/masy.202000091

Sin, L. And Bee, S. (2019). *Polylactic Acid: A Practical Guide for the Processing, Manufacturing, and Applications of PLA* (2nd ed.). LLC Chadds Ford, PA, USA: Plastic Design Library (PDL).

Singh, G., and Arya, S. K. (2021). A review on management of rice straw by use of cleaner technologies: Abundant opportunities and expectations for Indian farming. *Journal of Cleaner Production, 291*(125278), 1-64. https://doi.org/10.1016/j.jclepro.2020.125278

Singh, G., Gupta, M.K., Chaurasiya, S., Sharma, V.S., and Pimenov, D.Y. (2021). Rice straw burning: a review on its global prevalence and the sustainable alternatives for its effective mitigation. *Environmental Science and Pollution Research,* 28(5), 32125-32155. https://doi.org/10.1007/s11356-021-14163-3

Singla, R. K., Zafar, M.T., Maiti, S.N., and Ghosh, A.K. (2017). Physical blends of PLA with high vinyl acetate containing EVA and their rheological, 119longat-mechanical and morphological responses. *Polymer Testing, 63*, 398-406. https://doi.org/10.1016/j.polymertesting.2017.08.042

Sirichalarmkul, A., and Kaewpirom, S. (2021). Enhanced biodegradation and processability of biodegradable package from poly(lactic acid)/poly(butylene succinate)/rice-husk green composites. *Journal of Applied Polymer Science, 138*(27), 1-14. https://doi.org/10.1002/app.50652

Sookprasert, P. (2014). *Compatibilization of poly(lactic acid)/natural rubber blends using natural rubber-graft-poly(lactic acid).* (Master's Degree). Chulalongkorn University, Bangkok.

Sookprasert, P. And Hinchiranan, N. (2017). Morphology, mechanical and thermal properties of poly(lactic acid) (PLA)/natural rubber (NR) blends compatibilized by NR-graft-PLA. *Journal of Materials Research, 32*(4), 788-800. https://doi.org/10.1557/jmr.2017.9

Sriyapai, P., Chansiri, K., and Sriyapai, T. (2018). Isolation and Characterization of Polyester-Based Plastics-Degrading Bacteria from Compost Soils. *Microbiology, 87*(2), 290-300. https://doi.org/10.1134/S0026261718020157

Stachowiak, T., Postawa, P., Malinska, K., Drózdz, D., and Pudełko, A. (2022). Comparison of Physical and Thermal Properties of Mulching Films Made of Different Polymeric Materials. *Materials 15*(7610), 1-13. https://doi.org/10.3390/ma15217610

Suaduang, N., Ross, S., Ross, G.M., Pratumshat, S., and Mahasaranon, S. (2019). *Effect of spent coffee grounds filler on the physical and mechanical properties of poly(lactic acid) bio-composite films* Paper presented at the Materials Today: Proceeding, Thailand. https://doi.org/10.1016/j.matpr.2019.06.260

Suebpongsang, P., Ekasingh, B. And Cramb, R. (2020). Commercialisation of Rice Farming in Northeast Thailand. In R. Cramb (Ed.), *White Gold: The Commercialisation of Rice Farming in the Lower Mekong Basin* (pp. 39-68). Singapore: Springer Nature. https://doi.org/10.1007/978-981-15-0998-8_2

Suksut, B., and Deeprasertkul, C. (2011). Effect of Nucleating Agents on Physical Properties of Poly(lactic acid) and Its Blend with Natural Rubber. *Journal of Polymers and the Environment, 19*(1), 288–296. https://doi.org/10.1007/s10924-010-0278-9

Taiatele, I., Dal Bosco, T.C., Faria-Tischer, P.C.S., Bilck, A.P., Yamashita, F., Bertozzi, J. Michels, R.N., and Mali, S. (2019). Abiotic Hydrolysis and Compostability of Blends Based on Cassava Starch and Biodegradable Polymers. *Journal of Polymers and the Environment, 27*(11), 2577-2587. https://doi.org/10.1007/s10924-019-01541-9

Taib, N.A.A.B., Rahman, M.R., Huda, D., Kuok, K.K., Hamdan, S., Bakri, M.K.B., Julaihi, M.R.M.B., and Khan, A. (2023). A review on poly lactic acid (PLA) as a biodegradable polymer. *Polymer Bulletin, 80*, 1179-1213. https://doi.org/10.1007/s00289-022-04160-y

Tan, Z., Yi, Y., Wang, H., Zhou, W., Yang, Y, and Wang, C. (2016). Physical and Degradable Properties of Mulching Films Prepared from Natural Fibers and Biodegradable Polymers. *Applied Sciences, 6*(147), 1-11. https://doi.org/10.3390/app6050147

Tang, Z., Zhang, C., Liu, X. And Zhu, J. (2012). The crystallization behavior and mechanical properties of polylactic acid in the presence of a crystal nucleating agent. *Journal of Applied Polymer Science, 125*(2), 1108-1115. https://doi.org/10.1002/app.34799

Teixeira, S., Eblagon, K.M., Miranda, F., Pereira, M.F.R. and Figueiredo, J.L. (2021). Towards Controlled Degradation of Poly(lactic) Acid in Technical Applications. *Carbon Research, 7*(2), 1-43. https://doi.org/10.3390/c7020042

Tertyshnaya, Y. V., Karpova, S.G., Podzorova, M.V., Khvatov, A.V., and Moskovskiy, M.N. (2022). Thermal Properties and Dynamic Characteristics of Electrospun Polylactide/Natural Rubber Fibers during Disintegration in Soil. *Polymers, 14*(5), 1-16. https://doi.org/10.3390/polym14051058

Tessanan, W., Chanthateyanonth, R., Yamaguchi, M., and Phinyocheep, P. (2020). Improvement of mechanical and impact performance of poly(lactic acid) by renewable modified natural rubber. *Journal of Cleaner Production, 276*(123800), 1-14. https://doi.org/10.1016/j.jclepro.2020.123800

Thai Rice Exporters Association. (2022). *2017-2022 Rice Production Forecast*. Retrieved 30 November 2022, from http://www.thairiceexporters.or.th/production.htm.

Tham, C.Y., Abdul Hamid, Z.A., Ahmad, Z. And Ismail, H. (2014). Surface Modification of Poly(lactic acid) (PLA) via Alkaline Hydrolysis Degradation. *Advanced Materials Research, 970*, 324-327. https://doi.org/10.4028/www.scientific.net/AMR.970.324

Thongpin, C., Klatsuwan, S., Borkchaiyapoom, P. And Thongkamwong, S. (2013). Crystallization Behavior of PLA in PLA/NR Compared with Dynamic Vulcanized PLA/NR. *Journal of Metals, Materials and Minerals, 23*(1), 53-59.

Tisserat, B., Joshee, N., Mahapatra, A.K., Selling, G.W., and Finkenstadt, V.L. (2013). Physical and mechanical properties of extruded poly(lactic acid)-based Paulownia 122longate biocomposites. *Industrial Crops and Products, 44*, 88-96. http://dx.doi.org/10.1016/j.indcrop.2012.10.030

Van Cong, D., Hoang, T., Giang, N.V., Ha, N. T., Lam, T.D., and Sumita, M. (2012). A novel enzymatic biodegradable route for PLA/EVA blends under agricultural soil of Vietnam. *Materials Science and Engineering C, 32*(3), 558-563. https://doi.org/10.1016/j.msec.2011.12.012

Van Krevelen, D. W., and Te Nijenhuis, K. (2009). Processing Properties. *Properties of Polymers*, 799-818. https://doi.org/10.1016/B978-0-08-054819-7.00024-8

Vasile, C., Stoleru, E., Darie-Nita, R. N., Dumitriu, R. P., Pamfil, D. And Tartau, L. (2019). Biocompatible Materials Based on Plasticized Poly(lactic acid), Chitosan and Rosemary Ethanolic Extract I. Effect of Chitosan on the Properties of Plasticized Poly(lactic acid) Materials. *Polymers*, *11*(6), 1-28. https://doi.org/10.3390/polym11060941

Velghe, I., Buffel, B. Vandeginste, V., Thielemans, W., and Desplentere, F. (2023). Review on the Degradation of Poly(lactic acid) during Melt Processing. *Polymers 15*(2047), 1-33. https://doi.org/10.3390/polym15092047

Vink, E.T.H., Rabago, K.R., Glassner, D.A. and Gruber, P.R. (2003). Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. *Polymer Degradation and Stability, 80*(3), 403-419. https://doi.org/10.1016/S0141-3910(02)00372-5

Voznyak, Y., Morawiec, J., and Galeski, A. (2016). Ductility of polylactide composites reinforced with poly(butylene succinate) nanofibers. *Composites Part A: Applied*

Science and Manufacturing, 90, 218-224. https://doi.org/10.1016/j.compositesa.2016.07.011

Voznyak, Y., Morawiec, J., and Galeski, A. (2018). Ductility of polylactide composites reinforced with polyhydroxyalkanoates nanofibers. *AIP Conference Proceedings, 020078*, 1-5. https://doi.org/10.1063/1.5045940

Wang, X., Pan, H., Jia, S., Lu, Z., Han, L., and Zhang, H. (2022). Mechanical properties, thermal behavior, miscibility and light stability of the poly(butylene adipate-co-terephthalate)/poly(propylene carbonate)/polylactide mulch flms. *Polymer Bulletin, 80*, 2485–2501. https://doi.org/10.1007/s00289-022-04173-7

Wufuer, R., Li, W, Wang, S., and Duo, J. (2022). Isolation and Degradation Characteristics of PBAT Film Degrading Bacteria. *International Journal of Environmental Research and Public Health, 19*(17087), 1-12. https://doi.org/10.3390/ijerph192417087

Xiao, L., Wang, B., Yang, G. And Gauthier, M. (2012). Poly(Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications. In D. N. Ghista (Ed.), *Biomedical Science, Engineering and Technology* (pp. 247-282). New York: InTech. https://doi.org/10.5772/23927

Xie, H., Cui, B., Hao, S., Li, S., Jia, X., Wang, W. (2022). Exploring the macroscopic and microscopic characteristics of rice stalk for utilization in bio-composites. *Composites Science and Technology, 230*(109728), 1-8. https://doi.org/10.1016/j.compscitech.2022.109728

Xie, L., Xu, H., Niu, B., Ji, X., Chen, J., Li, Z.M., Hsiao, B.S., and Zhong, G.J. (2014). Unprecedented Access to Strong and Ductile Poly(lactic acid) by Introducing In Situ Nanofibrillar Poly(butylene succinate) for Green Packaging. *Biomacromolecules, 15*(11), 4054-4064. https://doi.org/10.1021/bm5010993

Xu, C., Sun, C., Wan, H., Tan, H., Zhao, J., and Zhang, Y. (2022). Microstructure and physical properties of poly(lactic acid)/ polycaprolactone/rice straw lightweight bio-composite foams for wall insulation. *Construction and Building Materials, 354*(129216), 1-6. https://doi.org/10.1016/j.conbuildmat.2022.129216

Xu, C., Yuan, D., Fu, L., and 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/10.1016/j.polymertesting.2014.05.005

Yaacob, N.D., Ismail, H., and Ting, S.S. (2016). Soil Burial of Polylactic Acid/Paddy Straw Powder Biocomposite. *Bioresources, 11*(1), 1255-1269. https://doi.org/10.15376/biores.11.1.1255-1269

Yadav, S., and Kumar, P. (2023). Effect of neem leaves and stock density of earthworm (Eisenia fetida) on quality of rice straw vermicompost. *Advances in Environmental Research, 12*(1), 51-64. https://doi.org/10.12989/aer.2023.12.1.051

Yaisun, S., and Trongsatitkul, T. (2023). PLA-Based Hybrid Biocomposites: Effects of Fiber Type, Fiber Content, and Annealing on Thermal and Mechanical Properties. *Polymers, 15*(4106), 1-14. https://doi.org/10.3390/polym15204106

Yussuf, A. A., Massoumi, I. And Hassan, A. (2010). Comparison of Polylactic Acid/Kenaf and Polylactic Acid/Rise Husk Composites: The Influence of the Natural Fibers on the Mechanical, Thermal and Biodegradability Properties. *Journal of Polymers and the Environment, 18*(3), 422-429. https://doi.org/10.1007/s10924-010-0185-0

Zaaba, N.F. and Jaafar, M. (2020). A review on degradation mechanisms of polylactic acid: Hydrolytic, photodegradative, microbial, and enzymatic degradation. *Polymer Engineering and Science, 60*(9), 2061-2075. https://doi.org/10.1002/pen.25511

Zandi, A., Zanganeh, A., Hemmati, F., and Mohammadi-Roshandeh, J. (2019). Thermal and biodegradation properties of poly(lactic acid)/rice straw composites: effects of modified pulping products. *Iranian Polymer Journal*, 1-13. https://doi.org/10.1007/s13726-019-00709-3

Zhang, C., Huang, Y., Luo, C., Jiang, L., and Dan, Y. (2013). Enhanced ductility of polylactide materials: Reactive blending with pre-hot sheared natural rubber. *Journal of Polymer Research, 20*(121), 1-9. https://doi.org/10.1007/s10965-013-0121-9

Zhang, Z., Cao, B., and Jiang, N. (2023). The Mechanical Properties and Degradation Behavior of 3D-Printed Cellulose Nanofiber/Polylactic Acid Composites. *Materials, 16*(6197), 1-15. https://doi.org/10.3390/ma16186197

Zhang, Z., Lyu, M., Guo, P., Xu, Y., Niu, H., Zhang, S., and Zhu, G. (2023). Natural weathering behavior and photo stability improvement of poly (butylene succinate-co-butylene terephthalate)-based mulch films under two typical climatic conditions. *Environmental Technology & Innovation, 30*(103055), 1-14. https://doi.org/10.1016/j.eti.2023.103055

Zhao, X., Hu, H., Wang, X., Yu, X., Zhou, W. And Peng, S. (2020). Super tough poly(lactic acid) blends: a comprehensive review. *Royal Society of Chemistry Advances, 10*(22), 13316-13368. https://doi.org/10.1039/D0RA01801E

Zhao, X., Pelfrey, A., Pellicciotti, A., Koelling, K., and Vodovotz, Y. (2023). Synergistic effects of chain extenders and natural rubber on PLA thermal, rheological, mechanical and barrier properties. *Polymer, 269*(125712). https://doi.org/10.1016/j.polymer.2023.125712

Zhou, Q. And Butchosa, N. (2016). Nanocellulose-based Green-Nanocomposite materials. In S. Kalia (Ed.), BiodegradaBle green Composites (1 ed., pp. 118-148). New Jersey: John Wiley & Sons. https://doi.org/10.1002/9781118911068.ch5

Zhu, L., Qiu, J., Liu, W., and Sakai, E. (2019). Mechanical and thermal properties of rice Straw/PLA modified by nano Attapulgite/PLA interfacial layer. *Composites Communications, 13*, 18-21. https://doi.org/10.1016/j.coco.2019.02.001

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).

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

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.

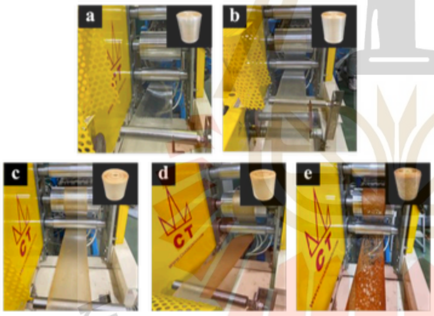

Figure 1. Physical characteristics of (a) neat PLA, (b) PLA/NR, and PLA/NR/RS biocomposite films; (c) 3%, (d) 5%, and (e) 10%.

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.

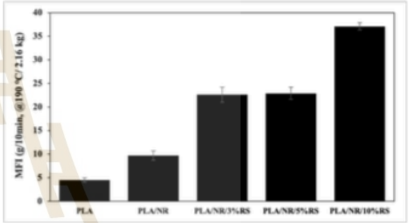

Figure 2. Melt flow index (MFI) of neat PLA, PLA/NR, and PLA/NR/RS biocomposites.

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

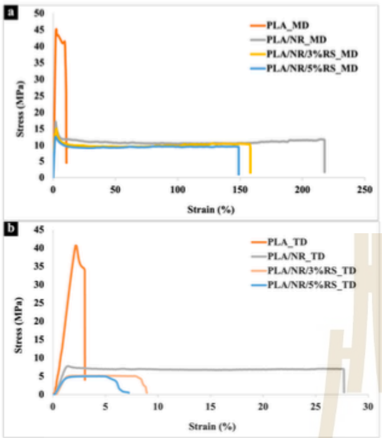

Figure 3. Stress-strain curve of neat PLA, PLA/NR, and PLA/NR/RS biocomposite films; (a) machine direction (MD) and (b) transverse direction (TD).

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.

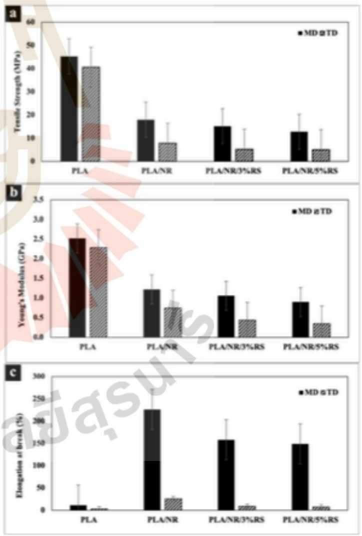

Figure 4. Average tensile properties of neat PLA, PLA/NR, and PLA/NR/RS biocomposite film; (a) Tensile strength, (b) Young's Modulus, and (c) Elongation at break.

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.

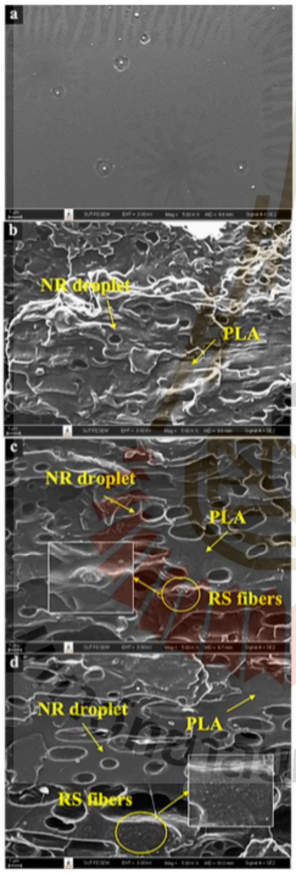

Figure 5. FE-SEM micrographs at 5000×magnification of tensile fracture surface of (a) neat PLA, (b) PLA/ NR, and PLA/NR/RS biocomposite films at RS contents of; (c) 3%, and (d) 5%.

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.

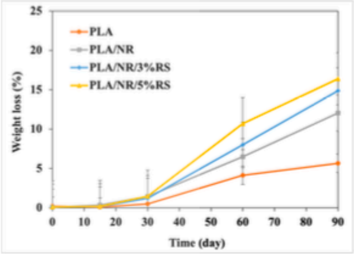

Figure 6. Weight loss percentage of PLA, PLA/NR, and PLA/NR/RS biocomposite films.

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.

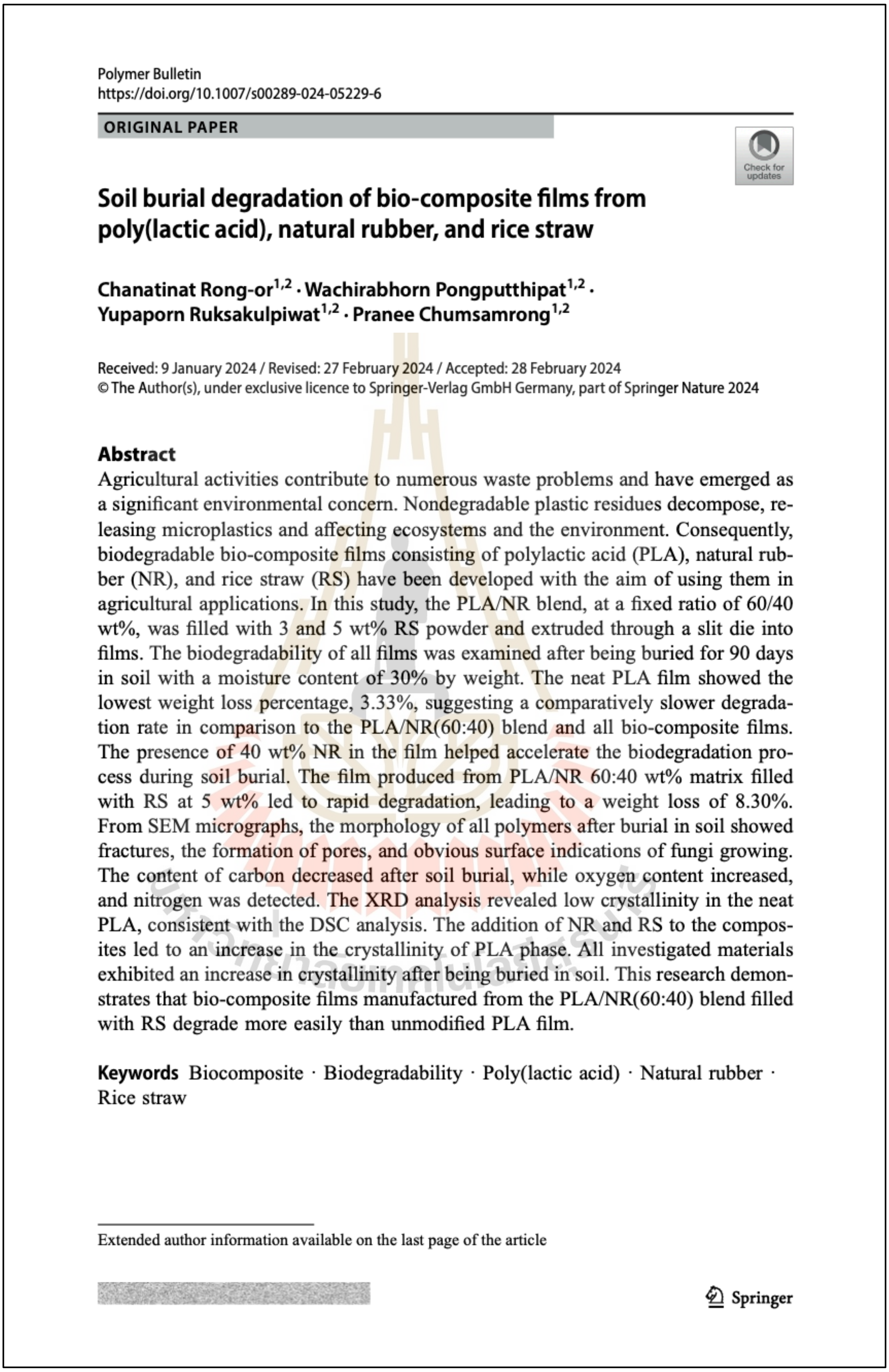
11 Pongputthipat, W.; Ruksakulpiwat, Y.; Chumsamrong, P. *Polym. Bull.*, 2022; 1-19.

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

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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).

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

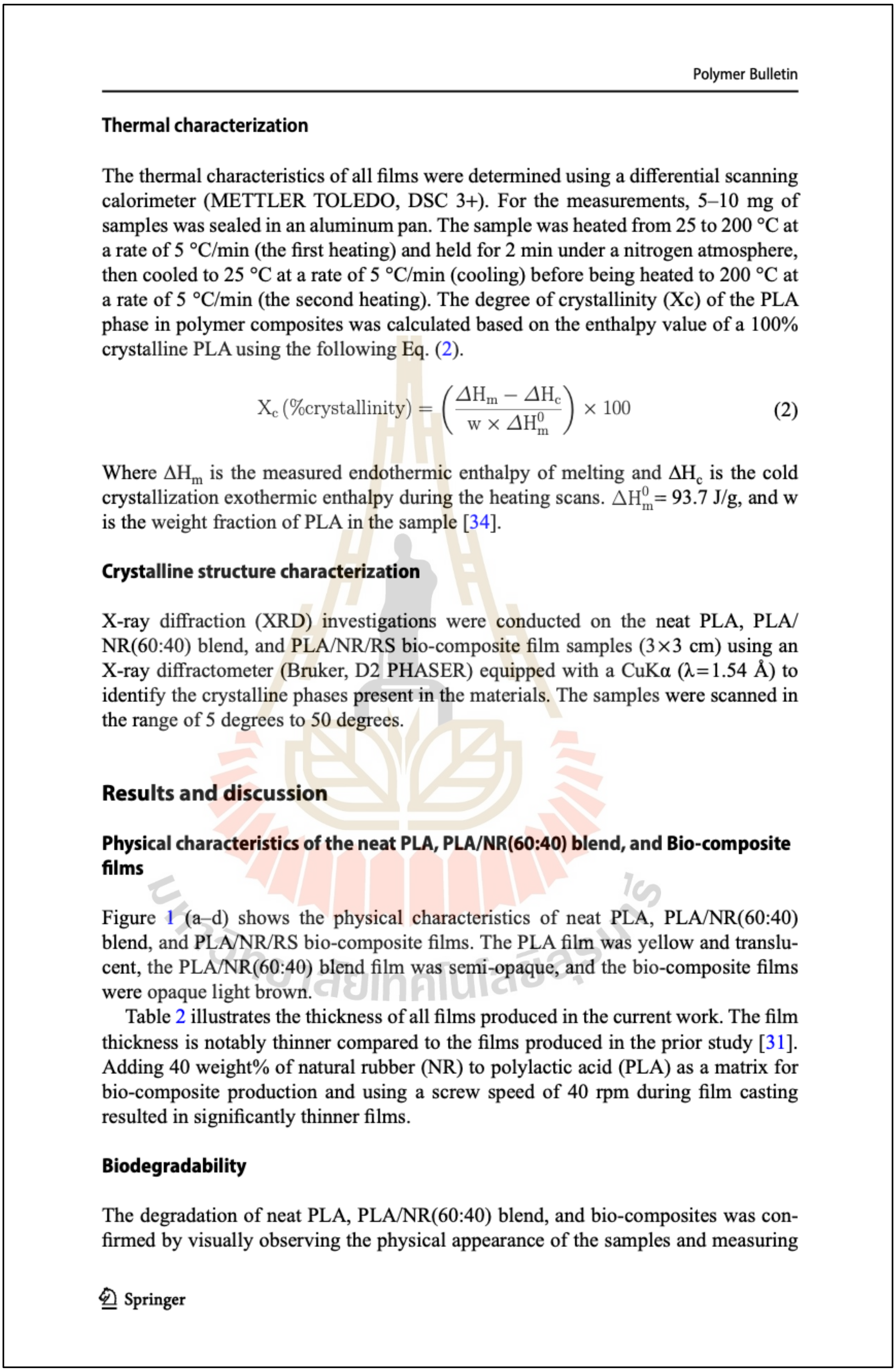
Where w_i represents the initial dry weight of the samples, while w_t represents the dry weight of the sample retrieved after being buried in soil for a determined time [33].

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

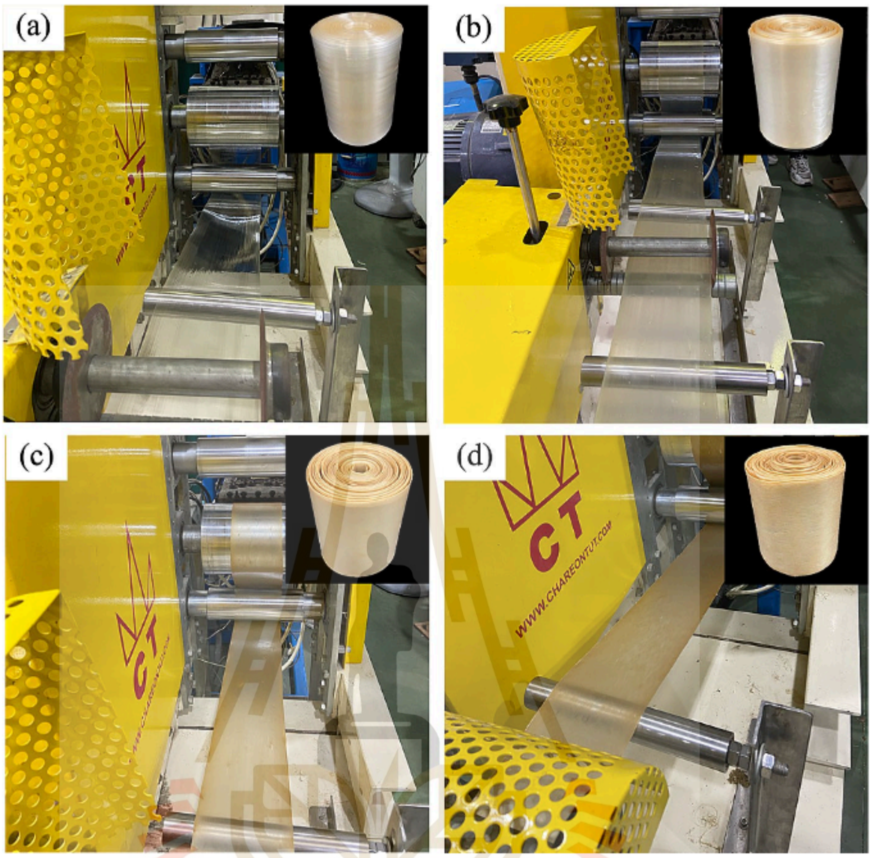


Fig. 1 Photographs of the cast films: neat PLA (**a**), PLA/NR(60:40) blend (**b**), and PLA/NR/RS biocomposite at RS contents of 3 wt% (**c**) and 5 wt% (**d**)

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

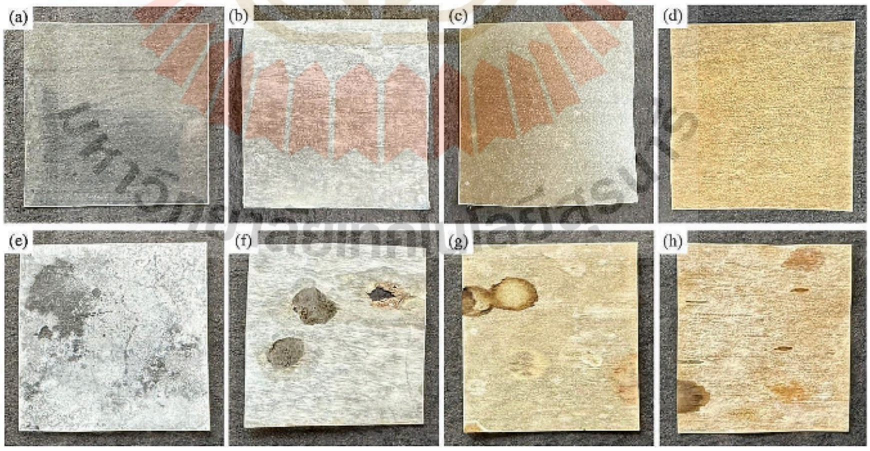


Fig. 2 Physical appearance of neat PLA (**a**), PLA/NR(60:40) blend (**b**), PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**) before soil burial test and neat PLA (**e**), PLA/NR(60:40) blend (**f**), and PLA/NR/RS bio-composite films at RS contents of 3 wt% (**g**) and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

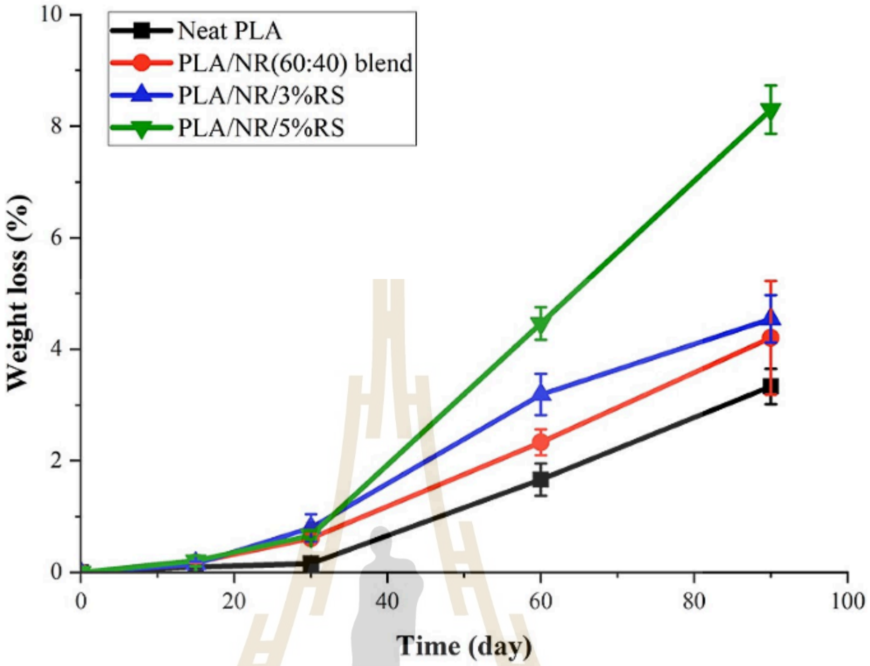


Fig. 3 Weight loss percentage of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films

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	

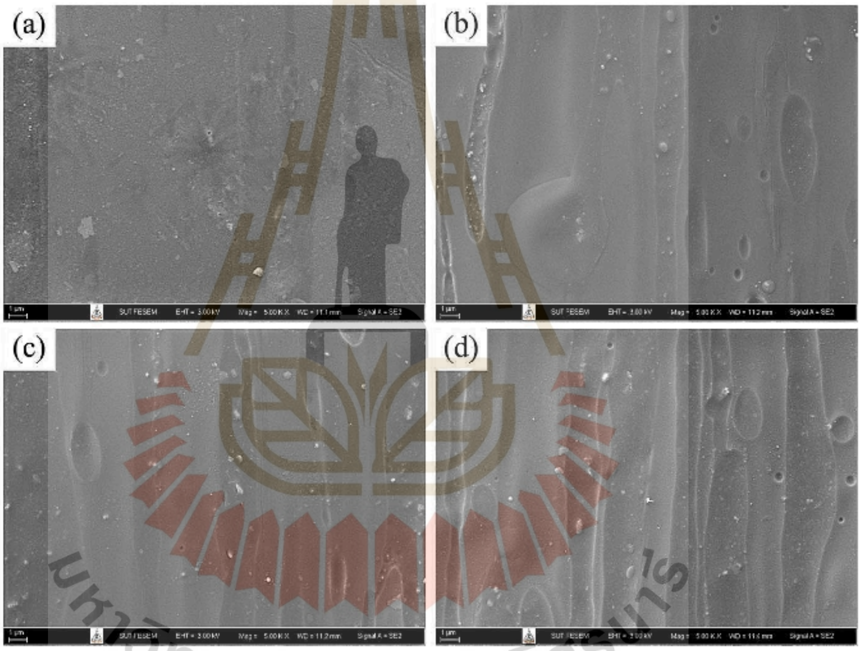


Fig. 4 FE-SEM micrographs at 5000x magnification of film surface of neat PLA (**a**) PLA/NR(60:40) blend (**b**), and PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**)

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-

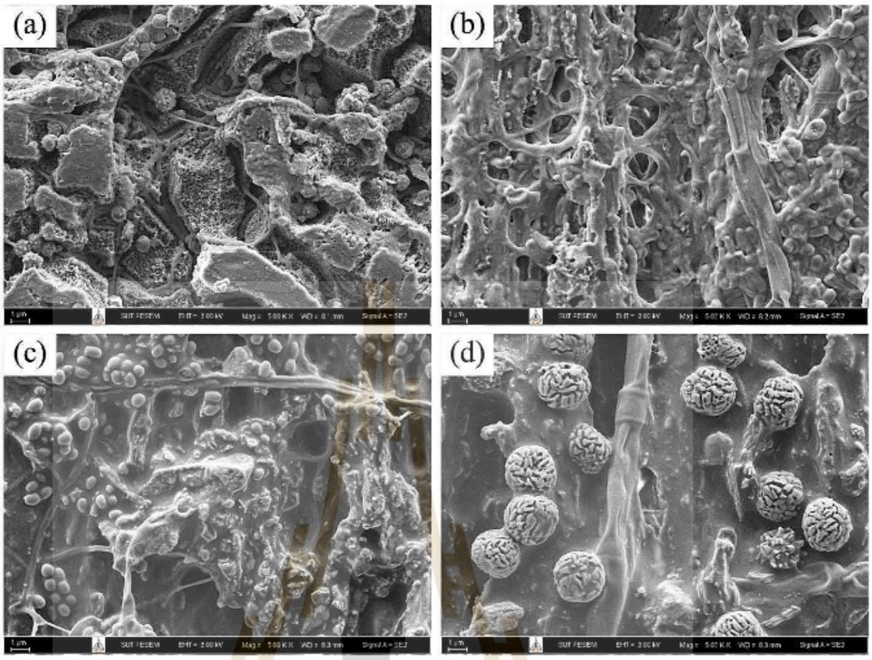


Fig. 5 FE-SEM micrographs at 5000x magnification of film surface after soil burial for 90 days of neat PLA (**a**) PLA/NR(60:40) blend (**b**), and PLA/NR/RS bio-composite films at RS contents of; 3 wt% (**c**), and 5 wt% (**d**)

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

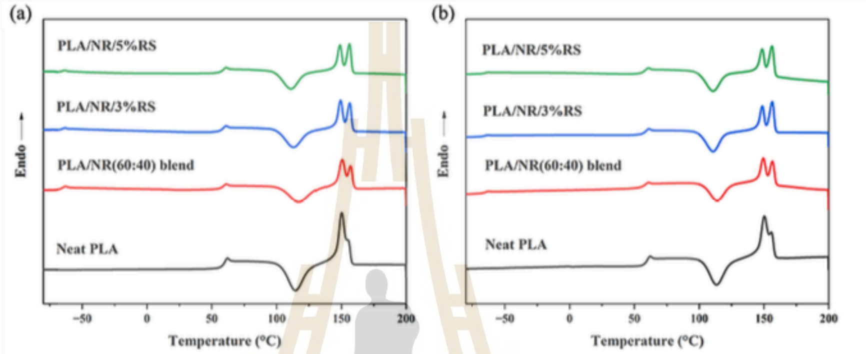


Fig. 6 DSC thermograms of neat PLA, PLA/NR(60:40) blend, PLA/NR/3%RS, and PLA/NR/5%RS bio-composite films before (**a**) and after (**b**) burial in soil for 90 days

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.

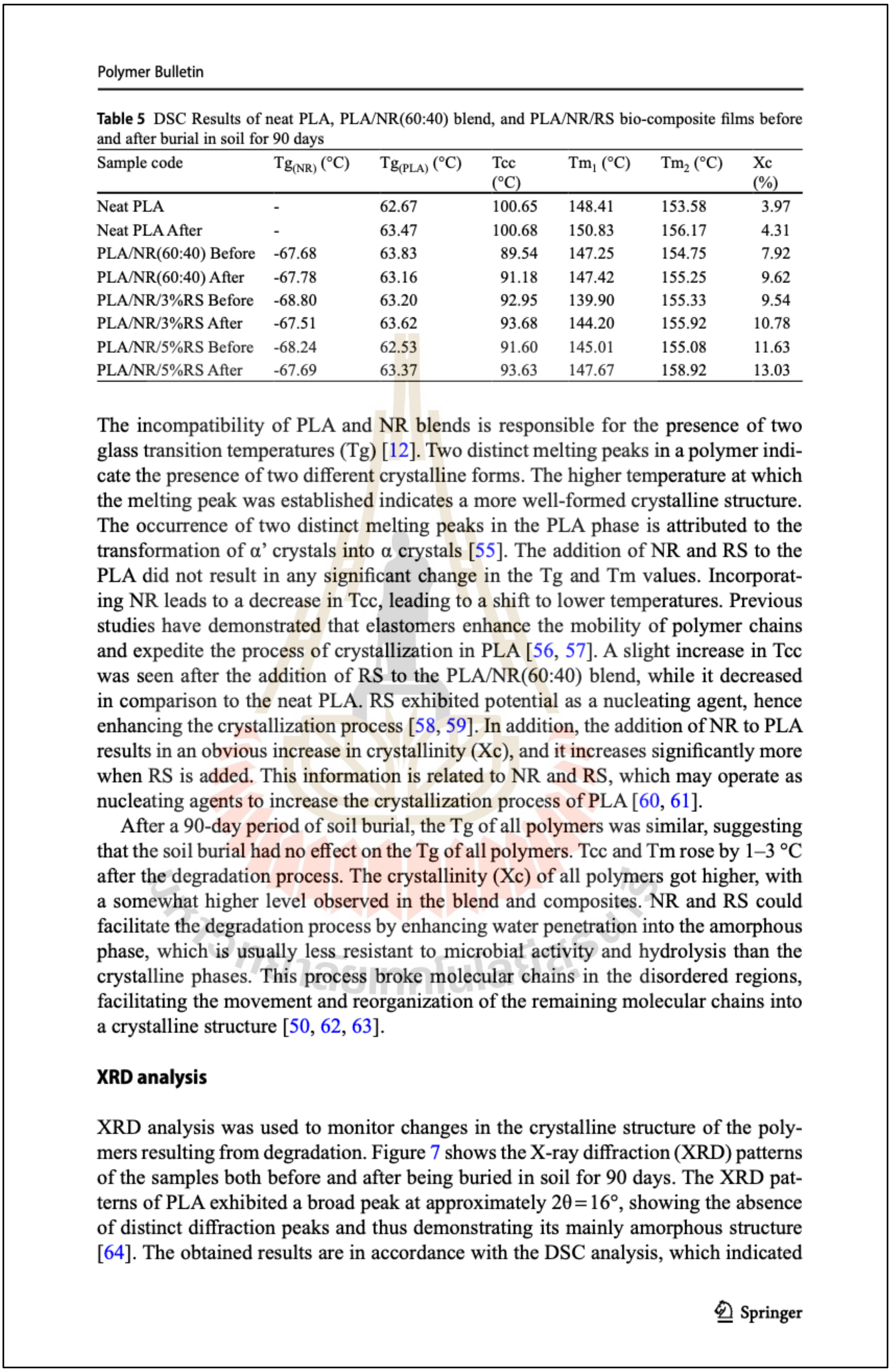


Table 5 DSC Results of neat PLA, PLA/NR(60:40) blend, and PLA/NR/RS bio-composite films before and after burial in soil for 90 days

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 2θ = 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

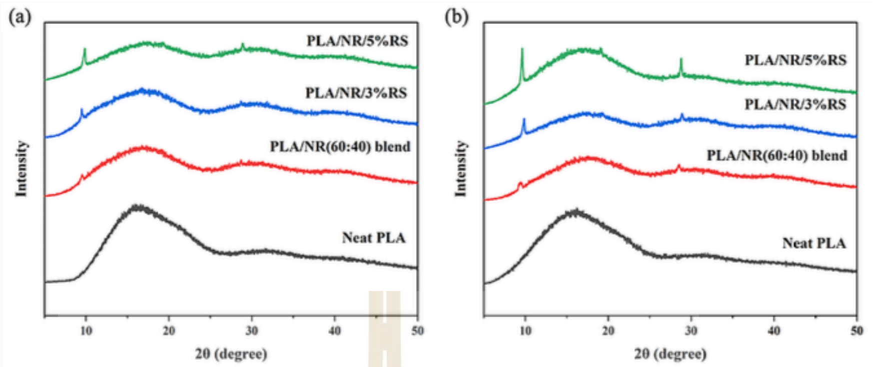


Fig. 7 XRD patterns of neat PLA, PLA/NR(60:40) blend, PLA/NR/3%RS, and PLA/NR/5%RS bio-composite films before (**a**) and after (**b**) burial in soil for 90 days

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

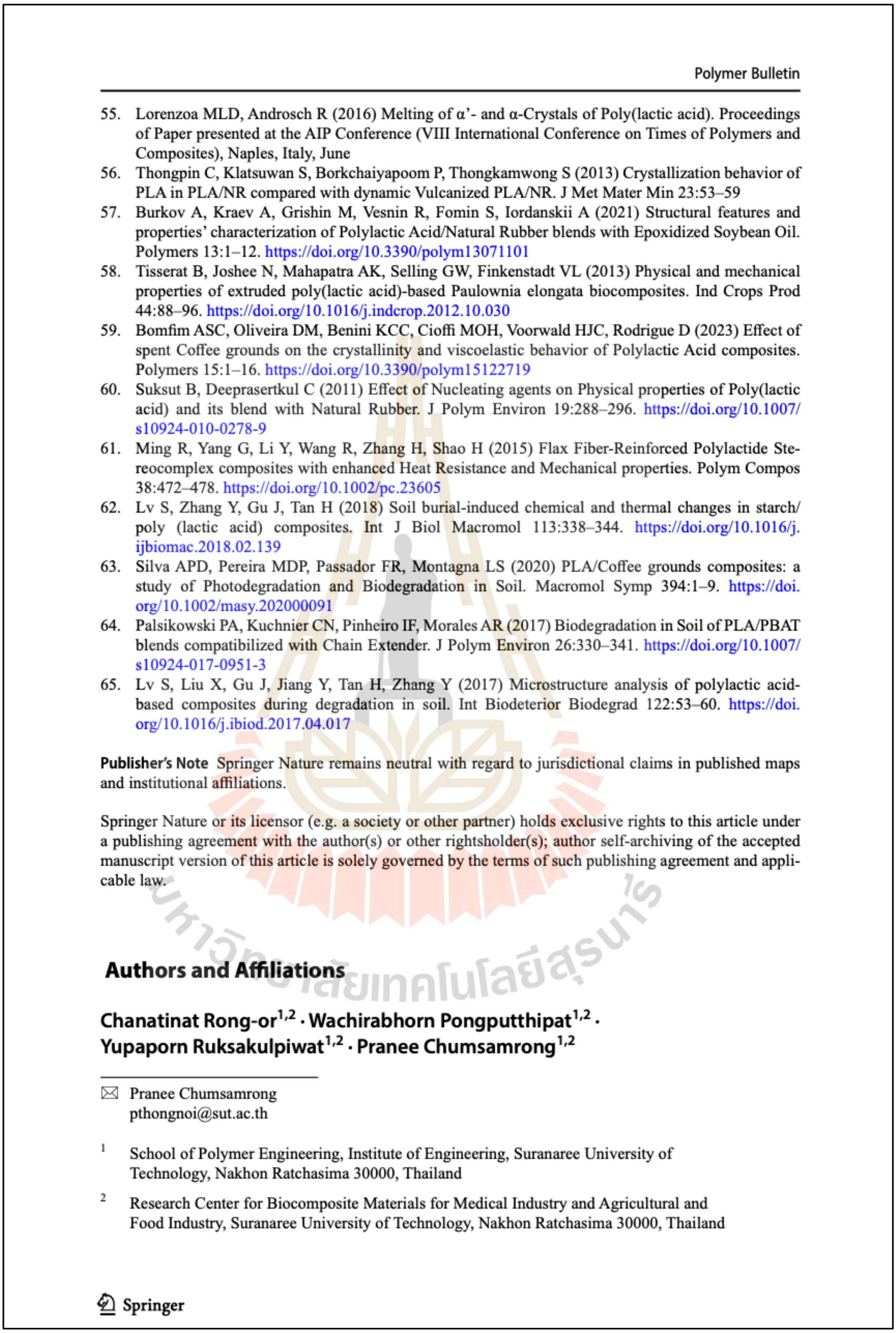
Competing interests The authors declare no competing interests.

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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Miss Chanatinat Rong-or was born on August 15, 1997, in Phayao, Thailand. In 2016, she completed her high school education at Samakkhiwitthayakhom School in Chiang Rai. In 2020, she acquired a Bachelor's Degree in Polymer Engineering from Suranaree University of Technology. After completion, she obtained the position of foreman at First Rubber Co., Ltd. Subsequently, she studied her Master's degree in the Materials Engineering Program at the School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology. During studying her master's degree at SUT, she presented her research on "Poly(Lactic acid)/ Natural Rubber/ Rice straw Bio-composite films for Agricultural application" at the 13th International Polymer Conference of Thailand (PCT 13 Conference) in Bangkok, Thailand. The publication of this work can be found in the PCT-13 Proceedings Book. Her research on "Soil burial degradation of bio-composite films from poly(lactic acid), natural rubber, and rice straw" was published in the Polymer Bulletin.