

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.

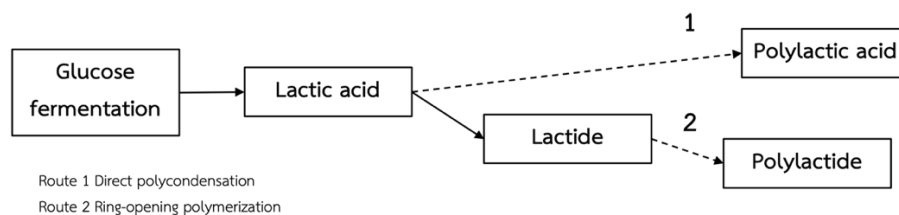


Figure 2.1 General routes of poly(lactic acid) production (Sin and Bee, 2019).

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 acid 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).

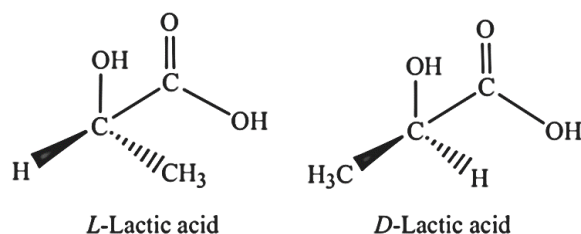


Figure 2.2 The stereoisomers of L-lactic acid and D-lactic acid (Xiao, Wang, Yang, and Gauthier, 2012).

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 (CO₂) 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 alkanates) (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).

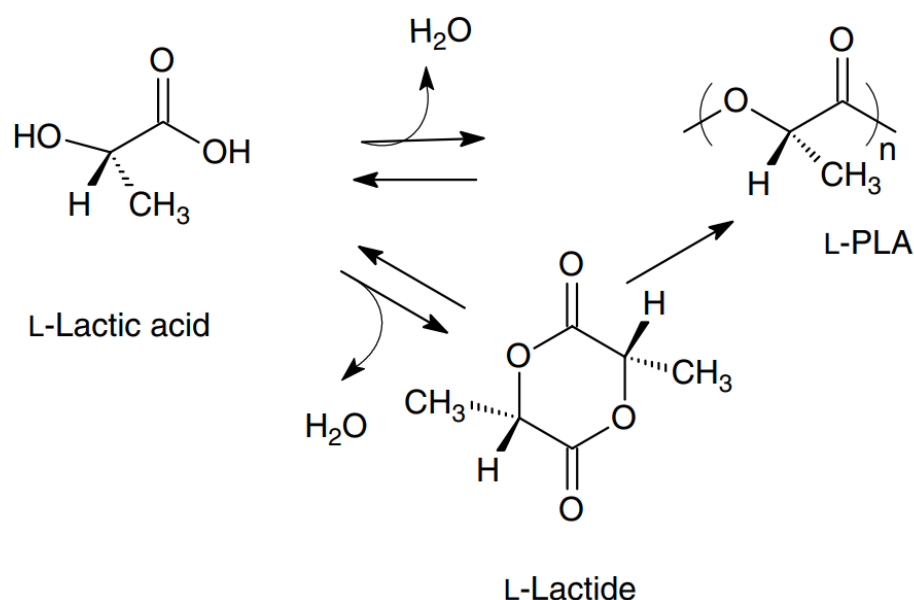


Figure 2.3 Polymerization degradation routes for polylactic acid (Elsawy, Kim, Park and Deep, 2017).

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 T_g. 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 C_5H_8 (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).

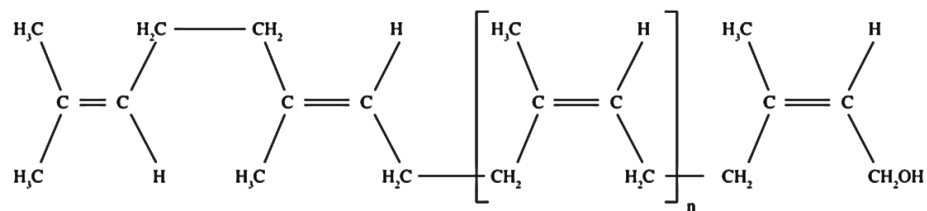


Figure 2.4 The chemical structure of natural rubber's cis-1,4-polyisoprene (Herculano et al., 2011).

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 (T_g), but it did have the potential to initiate cold crystallization (T_c) and subsequently increase the plastic's crystallinity. This resulted in a modification in the melting temperatures (T_m) of PLA. Remarkably, the heating process at temperatures higher than the T_m 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 compatibilizers dramatically reduced the T_g to a level like that of neat PLA. This improvement in compatibility between PLA and NR polymer blends was attributed to the presence of compatibilizers. 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 T_g of NR and at 65°C , which is the T_g 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 T_m and T_g in samples of PLA/NR blends of all compositions exhibit a tendency to decrease, whereas in neat PLA, they show an increase. Typically, the T_g 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 T_g. 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 T_g. 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 as sulfur oxides, CO₂, 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 μm) and PM 10 (particles with a size of 10 μm), 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 T_g and T_m 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, Drózd, and Pudętko, 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.

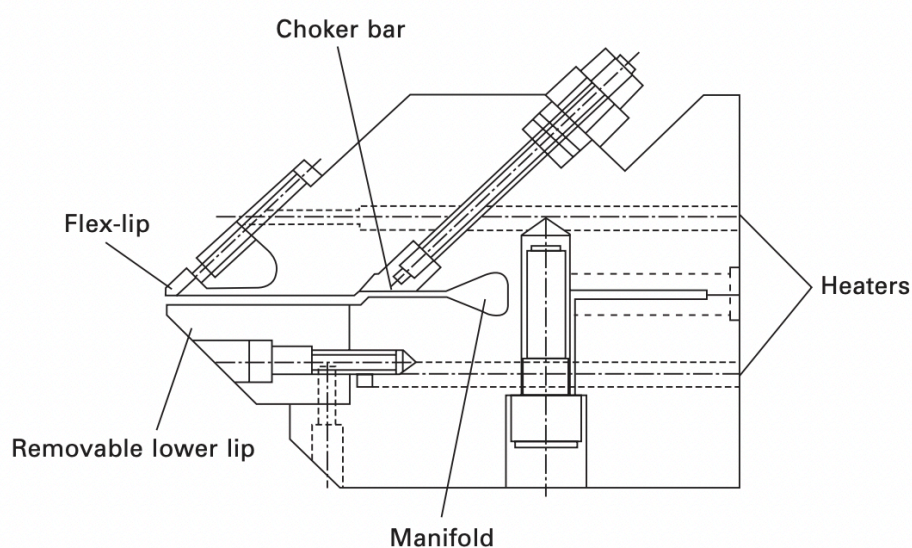


Figure 2.5 Slit die for cast film (Casalini and Perale, 2016).

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 $\pm 5\%$ 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(ϵ -caprolactone) (PCL), indicating a potential alternative, despite the inherent immiscibility of many polymers with PLA. This work utilised high-pressure carbon dioxide (CO₂) 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 CO₂-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 CO₂ 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.