Review:

Modifications of Poly(lactic Acid) with Blends and Plasticization for Tenacity and Toughness Improvement

Mohd Bijarimi Mat Piah[1*], Mohammad Norazmi Ahmad[2], Erna Normaya Abdullah[2], and Muhammad Zakir Muzakkar[3]

[1]*Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuh Persiaran Tun Khalil Yaakob, Kuantan 26300, Malaysia*

[2]*Experimental and Theoretical Research Laboratory, Department of Chemistry, Kulliyyah of Science, International Islamic University Malaysia, Kuantan 25200, Malaysia*

[3]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Jl. Kampus Hijau Bumi Tridharma, Anduonou, Kendari 93132, Indonesia*

Abstract: *This review focuses on the modification of the inherent brittleness of biodegradable poly(lactic acid) (PLA) to increase its toughness, as well as recent advances in this field. The most often utilized toughening methods are melt blending, plasticization, and rubber toughening. The process of selecting a toughening scheme is still difficult, although it directly affects the blend's mechanical properties. There has been a lot of development, but there is still a long way to go before we get easily processable, totally bio-based, 100% biodegradable PLA. The blends of PLA with other polymers, such as plasticizers or rubber, are often incompatible with one another, which causes the blend's individual components to behave in a manner consistent with phase separation. Polymer blending has been shown to be particularly effective in attaining high-impact strength. This review addresses the recent progress in improving the toughened PLA to gain properties necessary for the material's future engineering applications. As 3D and 4D printing becomes more accessible, PLA characteristics may be modified and treated utilizing more sophisticated production techniques.*

Keywords: *PLA; blend; rubber; plasticization; toughness*

■ INTRODUCTION

In our modern lives, polymer materials are commonplace and can be seen almost everywhere. Due to their low cost, lightweight, and high processability, commodity plastics may be used in a wide variety of products, from consumer items to technical applications. Two issues are associated with petroleum-based plastics, i.e., the rising production cost and the non-degradability of plastic products. Lately, oil prices have been increasing steadily annually, significantly affecting synthetic plastics' production costs. This development has driven the efforts to find a possible solution that does not rely on synthetic plastics. The need for replacement has become imperative

as there is mounting concern over the accumulation of petroleum-based disposal wastes worldwide. After the end of the life of plastic products, massive waste that is not biodegradable needs to be handled. Many initiatives have been launched to reduce the quantity of trash that ends up in landfills, and one clear target is plastic packaging. Despite implementing recycling and incineration efforts, this is insufficient, as we are dealing with mass disposal.

Poly(lactic acid) (PLA) and other biodegradable polymers have been developed, providing promise for a new waste management strategy. PLA, a biodegradable polyester manufactured from regenerative materials as

shown in Fig. 1-2, is pivotal in the bioplastic industry [1-5]. PLA has a limited crystallization rate, making it brittle and modest amounts of ductility, making it less than ideal for use in applications that need durability or engineering [6-10]. Prior to the last decade, PLA was only used in specialized biomedical applications such as resorbable sutures [11-12]. Due to its good biocompatibility, the PLA was used as sutures and dental, orthopedic, and drug delivery [13-15]. There is a lot of research and development going into plastics right now, and a lot of it is focused on finding ways to include biodegradable elements. Food packaging, bag and sack manufacture, loose-fill packaging, agricultural film, and a few specialized uses are only a few of the places where it has

been widely adopted, contributing to its rising profile.

PLA has the potential to replace traditional polymers, including polyethylene (PE), polypropylene (PP), and polystyrene (PS). However, PLA is too brittle to be used commercially, limiting the potential applications that require high-impact toughness [15,17-18]. As a result, several efforts have been made to alleviate the problem of toughness, particularly by melt mixing in the literatures [19-21]. However, this review focuses on PLA toughening mainly through melt mixing, plasticization, and toughening. In addition, it will bridge the brittleness gap in PLA by modifying its properties, particularly plasticization and rubber/elastomer toughening.
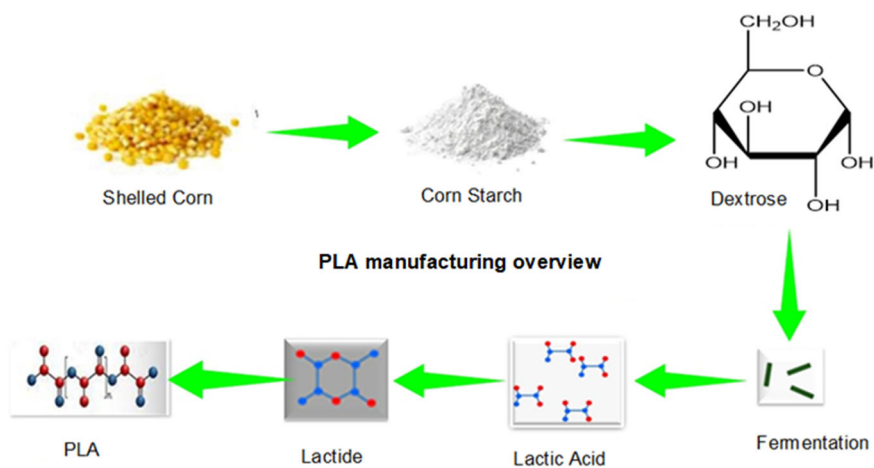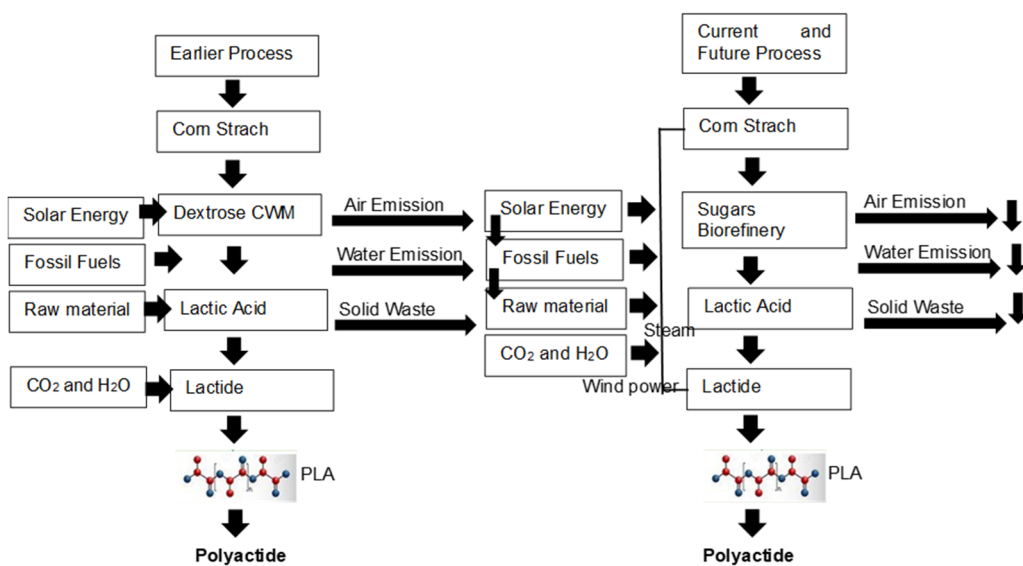

Fig 1. Overview of the production of PLA

Fig 2. Current and future PLA production technology. Adapted with permission from reference [16]

Indones. J. Chem., 2023, 23 (4), 1161 - 1180

1163

Properties of PLA

The stereochemistry of the PLA chain and crystallinity significantly affect the mechanical properties. In the chemistry of PLA, the two optical isomers are denoted by the letters D and L. In contrast to its naturally occurring isomer, D-lactide, the synthetic blend of D- and L-lactide is called L-lactide. Polarized light allows us to differentiate between the L and D forms [22]. Due to its random distribution of the two isomers of lactic acid, PDLA is an amorphous polymer that cannot crystallize. This material has weak tensile strength, poor elongation, and a short degradation time. PLLA is around 37% crystalline, with a melting point between 170 and 183 °C and a glass transition temperature between 55 and 65 °C [23]. Typical physical property values of PLA are given in Table 1.

Application of PLA

Resorbable sutures and other medical supplies are only two examples of how PLA is being put to use in specialized markets. Cups, bottles, and films are just a few of the many packaging uses for PLA. Typical product applications made from PLA are given in Table 2.

In the automotive sector, PLA has been mixed with kenaf fibers for car doors and dashboards due to its biodegradability compared to traditional plastics. For example, Toyota Motor Co. reported that a spare tire cover

Table 1. Physical properties of PLA [24]

Property	Units	Typical value
Density	g cm^{-3}	1.25
Melting temperature, T_m	°C	130–215
Glass transition temperature, T_g	°C	55–70
Degree of crystallinity, X_c	%	10–40
Melt flow rate	g/10 min	2–20
Tensile strength	MPa	44–66
Yield strength	MPa	53–70
Elongation at break	%	4–7
Tensile modulus	GPa	1.9–4.1
Notched Izod impact strength	J m^{-1}	18–66
Heat deflection temperature	°C	55
Flexural strength	MPa	88–119

Table 2. Typical product application made from PLA

Business division	Applications that are commercially accessible
Rigid thermoforms	• Clear clamshells for fresh fruits and vegetables • Trays of deli meat • Opaque dairy containers • Packaging and advertising for consumer electronics • Cold drink containers and other disposable items
Films with a biaxial orientation	• Wrap candy with a twirl and a flow • Display carton and envelope see-through panels • Film for lamination • Gift-basket exterior wrapping • Holding the fort
Bottles	• Low-storage milk • Food oils • Mineral water in bottles

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using 100% plant-derived kenaf/PLA composites was developed to replace kenaf/PP [25].

■ POLYMER BLENDS

Polymer blends have piqued the curiosity of polymer scientists for many years. *Trans* and *cis*-1,4-polyisoprene with gutta-percha (GP) blends were originally developed by Parkes in 1846. By varying the composition or adding fillers, the blends were formed into various rigid articles [26]. It has long been acknowledged that blending is the most flexible and cost-effective way to create novel materials that match the unique needs of polymer applications [27]. Many polymer resins are modified either by blending with other polymers or filling with fillers. It has been recognized that blending offers many advantages, such as improving the specific properties, e.g. toughening of brittle materials, and better procedure-friendliness thanks to a glass transition temperature-lowering miscible resin (T_g) or immiscible low viscosity resin. In addition, at the processing plant level, blending is more favorable as it increases the plant flexibility by reducing a number of grades, recycling and high productivity.

PLA Blends and Toughening

Materials made from polymer blends are anticipated to have improved characteristics compared to individual pure polymers [28-30]. It is, therefore, not surprising that PLA has been blended with several synthetics and biopolymers to enhance the properties of PLA and obtain novel materials. PLA has been blended with collagen, poly(butylenes succinate adipate), polyethylene glycol [31-42], poly(methyl methacrylate), polyethylene, poly(ethylene oxide) and poly(butylenes adipate-*co*-terephthalate) to produce materials with superior properties like as toughness, modulus, and impact strength, as well as thermal stability as compared to pure polymers [30].

The blending of PLA with other aliphatic polyesters is widely studied due to its biodegradable properties. Zhang et al. [43] developed new biodegradable materials by blending some available polyester. They investigated the property of multiphase containing poly(D, L-lactide) (PDLA), poly(ε-caprolactone) (PCL), poly(D,L-lactide-*co*-poly(ethylene glycol) (PELA), poly(ε-caprolactone)-*co*-poly(ethylene glycol) (PECL), and poly(β-hydroxybutyrate) (PHB), PLA/PCL, PELA/PECL, PHB/PLA, PHB/PELA, PHB/PCL, and PHB/PECL blends. The composition of blends was found to determine the morphology and hydrolytic behavior of immiscible PLA/PCL, PHB, and PHB/PLA and PHB/PCL blends. However, the addition of poly(ethylene glycol) (PEG) as a compatibilizer and PELA or PECL block copolymers have improved the miscibility of PELA/PECL, PHB/PELA, and PHB/PECL blends [43].

Surfactants made from a copolymer of ethylene oxide and propylene oxide might significantly improve the miscibility of PLLA and PDLLA. Chen et al. investigated the blends of biodegradable PLLA and poly-DL-lactic acid (PDLLA) or PCL, in addition to a third component, the surfactant - a copolymer of ethylene oxide and propylene oxide. They found that PLLA/PDLLA blends without surfactant had two T_g values, but with a surfactant, a linear shift of the single T_g as a function of composition occurred, with lower percentages of PLLA yielding lower glass transition temperatures, suggesting higher miscibility. The blend ratio of 40/60 PLLA/PDLLA is harder and tougher than PLLA but adding 2% surfactant increased the miscibility. Compared to PLLA/PDLLA blends, they found that PLLA/PCL blends had greater elongation and worse mechanical characteristics [44].

As discussed above, toughening of PLA remains the focus of researchers to enable PLA to be used in wider applications. Toughness is a measure of a sample's ability to absorb mechanical energy without breaking, typically defined as the area under a stress–strain curve. A tough material has a low brittleness but a high elongation to break and tensile strength. It is usually measured as the energy per unit volume to break material, proportional to the region covered by the stress-strain diagram. Nevertheless, the impact resistance test, such as Izod (ASTM D256), can be determined with a tensile test for toughness.

Plastic deformation at greater stresses is required for many uses, but its low toughness makes that impractical [45]. PLA has the processing properties of

polystyrene and the tensile strength and stiffness of polyethylene terephthalate (PET) [46]; it suffers low impact resistance [48]. It has been well established that plastics can be blended with elastomer in order to improve their toughness and impact resistance, as shown by previous researchers [22,48-51]. As a technique of enhancing mechanical characteristics and processability, blends are gaining prominence in the industrial sector. Modulus, yield stress, impact strength, and tensile strength are just some of the properties that may be enhanced by using the right polymer components in the right proportions.

Few researchers have addressed the problem of the poor toughness of PLA by blending it with other polymers to modify its properties [52-62]. Melt blending is the most common method for creating polymer blends, which are intimate mixes of polymers that are commercially accessible but do not share covalent connections. Properties of the resulting materials can be designed to meet application requirements and materials cost. In contrast to a single polymer, each component polymer in the polymer blends contributes to the final property of the material.

The combination of PLA with poly(butylene adipate-co-terephthalate) (PBAT) or another biodegradable polymer seems promising thus far, since both can be considered biodegradable. The toughening of PLA and PBAT by means of melt blending has been investigated by Jiang et al. In this immiscible blend, they found that PBAT was responsible for speeding up the PLA crystallization rate and little affected the ultimate crystallinity level. This approach obtained improved impact strength for blends containing 10% or higher PBAT. Furthermore, they concluded that the debonding-initiated shear yielding was responsible for the toughening mechanism in these PLA/PBAT blends. As for the failure mode, it has been shown that the PLA change from brittle to ductile fracture [63].

Schreck and Hillmyer [59] showed that *oligo*Nodax-*b*-poly(L-lactide) diblock copolymers might be added to a melted mix of poly(L-lactide) and NodaxH6 [poly(3-hydroxybutyrate-*co*-3hydroxyhexanoate)] to create a biodegradable composite. The notched impact resistance of the binary blends was found to be higher than that of the PLLA homopolymer after Nodax was added. However, in the ternary blends of *oligo*Nodax-*b*-poly(L-lactide) block copolymers, no additional improvement in the notched Izod impact resistance was observed. It was hypothesized that the brittleness of NodaxH6 particles and the reduced interfacial adhesion between particles and matrix may be responsible for this phenomenon [59].

Li and Shimizu [64] blended PLLA with acrylonitrile-butadiene-styrene copolymer (ABS) to increase its impact strength and elongation at the break, but they discovered that the melt mixture was immiscible and had poor mechanical qualities. PLLA/ABS was compatible when the reactive styrene/acrylonitrile/glycidyl methacrylate copolymer (SAN-GMA) was used together with ethyl triphenyl phosphonium bromide (ETPB) as a compatibilizer. As a result, the impact strength and elongation at break properties improve but with a slight loss in the modulus [64].

McDonald and co-workers [65] prepared a blend of poly(DL-lactide), poly(L-lactide-glycolide) and PCL by means of compression molding and solvent casting technique. The blend of PDLLA/PLGA was found to be miscible based on DSC analysis. However, an immiscible blend was obtained for the blend of PCL with PLGA or PDLLA; hence a strength reduction was noted. They have concluded that the blend of PCL with PLGA or PDLLA influenced the percentage of crystallinity [65].

Odent et al. [66] investigated the potential use of random aliphatic copolyesters as an impact modifier for PLA. Ring-opening polymerization synthesis between -valerolactone (VL) and -caprolactone (CL) yields amorphous poly(CL-*co*-VL) random aliphatic copolyesters (P[CL-*co*-VL]) (CL). Melt blending of PLA and random copolyesters (10 wt.%) was carried out using a DSM twin screw micro compounder at 200 °C at 60 rpm for 1 min. Injection molding and compression molding were then used to examine the impact of the copolyesters' composition and molar mass. They have found that using a higher molar mass with a molar composition of 45/55 mol% (CL/VL) improved the impact strength from neat PLA of 2.5 to 7.1 kJ m^{-2}. The

toughness improvement can be explained by the rubbery character of the dispersed phase and the blend morphology; amorphous or slightly crystalline microdomains give more impact strength as compared to high crystalline microdomains. Moreover, the samples prepared by compressing molding exhibited morphologies with larger microdomain sizes as compared to the injection molding [66].

Theryo et al. [67] prepared a rubber-toughened PLA hybrid synthesized using a polylactide graft copolymer. In this approach, a hybrid material containing 5 wt.% of rubber showed a remarkable improvement in tensile ductility and potential for optically transparent and impact-resistant PLA [67]. Meanwhile, Hashima et al. [68] developed a super-tough PLA by blending hydrogenated styrene-butadiene-styrene block copolymer (SEBS) with poly(ethylene-*co*-glycidyl methacrylate) reactive compatibilizer. A binary (PLA/SEBS) and ternary (PLA/PC/SEBS/EGMA) system were designed in this melt blend. It was found that Izod impact strength improved from 3 to 16 kJ m^{-2} for the system containing 70/30 PLA/SEBS. However, a super tough blend was obtained when ethylene-co-glycidyl methacrylate was added at 10% for the 70/20 PLA/SEBS system. In this system, they have successfully increased the impact strength to 92 kJ m^{-2} [68].

In another work, Ma et al. [69] reported the toughening of PLA by blending ethylene-*co*-vinyl acetate copolymer (EVA) with different vinyl acetate contents. It was found that the ratio of vinyl acetate and ethylene in random copolymers seems to control the compatibility and phase morphology. The optimum toughening, i.e., up to a factor of 30, was found at vinyl acetate content of approximately 50 wt.%. They concluded that there were no visible crazes following deformation and that the major toughening process for the PLA/EVA blend was internal rubber cavitation associated with matrix yielding [69].

A more comprehensive review of PLA toughening by other approaches can be found in the review by Anderson et al. [70] and Liu et al. [71]. Liu and Zhang [71] have also reviewed the progress of PLA toughening by focusing on plasticization, technology for copolymerization and more commercially viable melt-

blending [71]. The focus on PLA blending for toughening has been reviewed until to date [5,72-77].

PLA/Thermoplastic Elastomer Blends

PLA is one of the sustainable thermoplastics that can be chemically synthesized from renewable material and is an ideal candidate for biodegradable plastics in the market. Blending biodegradable PLA with natural rubber (NR)/epoxidized natural rubber (ENR) to obtain the desired properties at a lower cost and environmentally friendly would be seen as a potential option. Both PLA and NR are made from naturally occurring substances and may be processed using standard polymer processing equipment. In contrast to the ductile NR, the brittle thermoplastic PLA has high strength and modulus. Blending PLA with NR is an excellent option because of the materials' complimentary properties, which allow for the enhancement of PLA attributes like toughness and elongation at the break without compromising its biodegradability. It is expected that through the introduction of a rubbery component in the blend system, additional energy dissipation can be provided during the deformation process. Thus, this supplementary energy dissipation improves toughness. Natural rubber that has been epoxidized is a chemically modified version of *cis*-1,4-polyisoprene. By introducing epoxide groups into the polymer at various points, part of the unsaturation is eliminated. It is useful in processing since it helps make incompatible mixtures work together. ENR-50's addition to rubber blends enhances their ability to be processed, stiffness, resilience, oil resistance, air permeability reduction, superior damping, and wet grip performance [78]. It has been found that higher levels of polarity in ENR lead to greater compatibility with other polymers [51].

Rubber and plastic are combined to create thermoplastic elastomer (TPE), which is rapidly becoming the most lucrative segment of the polymer industry [79]. The primary benefits of these materials are the ease with which scrap and rejects may be recycled using thermoplastic technology, which eliminates the need for a factory or vulcanization. Impact strength and

ductility are both enhanced by the rubber component in rubber-modified thermoplastics. The combination of thermoplastic with NR results in a material known as thermoplastic natural rubber (TPNR). The processing additives have a role in determining whether or not the NR and thermoplastic pair are compatible. Impact characteristics are affected by phase size, the cohesive strength of the rubber phase, and adhesion between phases, whereas dynamic mechanical properties are dependent on mutual solubility.

TPNR combines the properties of hard and brittle plastic, and soft rubber offers a wide variety of applications where flexibility and softness are required. Compared to rubber, the processing of TPNR could be employed using conventional equipment such as injection molding, compression molding, and blow molding and extrusion process. A compatibilized blend will exhibit a single T_g between the two T_g values of the components, which may be used as an indicator of the blend's degree of homogeneity [80-81]. When the T_g is lower than the two-component T_g values, the extra component has a plasticizing effect. However, in NR-polyolefin blends, NR glass transition temperatures are lower($\sim -67\,°C$) and polyolefin ($\sim -60\,°C$) are close together; separation is less than 10 °C, and as such the movement of T_g in the blends will not be very indicative of the phase distribution [51].

Zhang et al. [82] investigated the mechanical properties of PLA, and biodegradable polyamide elastomer (PAE) blends to toughen the PLA. It was discovered that PAE, and PLA blends acquired a fair level of compatibility with one another. The tensile strength of the blend was comparable to that of clean PLA at 10% PAE concentration, but the elongation improved significantly [82].

Toughness was improved by the addition of other materials when PLA was mixed with ethylene-propylene copolymer, ethylene-acrylic rubber, acrylonitrile-butadiene rubber (NBR), and isoprene rubber by Ishida et al. According to the results of the Izod impact test, mixing PLA and NBR may result in a toughening effect because of the smaller particle size of the mixes. The morphology analysis also confirmed that interfacial tension between PLA phase and NBR was the lowest; hence according to

them; rubber with high polarity is more suitable for PLA toughening. NBR and isoprene rubber (IR), on the other hand, were able to produce plastic deformation and contribute to the material's high elongation capabilities when subjected to tensile stress. They also theorized that the rubber's inherent mobility plays a crucial role in the energy dissipation process during breaking [56].

Super toughened by melt blending at 240 °C, ternary blends of PLA, an epoxy-containing elastomer, and a zinc ionomer are reported by Liu et al. to exhibit intermediate strength and stiffness. It was shown that zinc ions might hasten the cross-linking of an epoxy-containing elastomer and cause reactive compatibilization between PLA and the elastomer's interface. It was hypothesized that the large boost in notched impact strength at high blending was due to the compatibilization effect [53].

PLA/natural rubber blend containing nucleating agents such as cyclodextrin, talc and calcium carbonate has been prepared by Suskut and Deeprasertkul [83] in an effort to enhance the toughness. Talc and calcium carbonate, but not cyclodextrin, were shown to boost the PLA crystallinity in the PLA/NR blends. The use of nucleating chemicals has greatly increased PLA's tensile and impact toughness [83]. In order to counter PLA's brittleness and poor crystallization, Bitinis et al. [84] created an NR/PLA blends by mixing the two materials together in a melt. By introducing 10 wt.% of NR, they were able to increase the elongation at break from 5% for plain PLA to 200%. The addition of NR was believed to increase the rate of crystallization as well as the crystallization ability of PLA [84].

Similar to Bitinis works, Jaratrotkamjorn et al. [85] prepared a rubber-toughened PLA via extrusion melt blending to investigate the effect of rubber polarity and viscosity and molecular weight on the mechanical properties of blends. In this study, they compared the toughening effects of NR, epoxidized natural rubber (ENR25 and ENR50), and natural rubber grafted with poly(methyl methacrylate) (NR-*g*-PMMA), concluding that NR had the greatest impact. Interestingly, they have found that the viscosity and molecular weight of NR decreased with increasing mastication, increasing the

impact strength of PLA/NR blends. This work indicated that the particle diameter was very important and probably more important than the rubber polarity. As such, the smaller particles of ENR and NR-*g*-PMMA were ineffective in promoting toughness compared to NR [85].

A study by Kowalczyk and Piorkowska [86] revealed that the immiscible blend of PLA/poly(1,4-*cis*-isoprene) was successfully prepared by melt blending in the Brabender batch mixer. The strain at the break of compression-molded film during uniaxial drawing was found to rise by as much as 80% when rubber at a weight fraction of 5 wt.% was included [86].

Petchwattana et al. [87] investigated the use of ultrafine acrylate particles as a toughening agent for PLA. With the addition of 10% of acrylate rubber, the tensile elongation at break increased from 3.5 to 200% or 50 times higher as compared to the neat PLA. Similar improvement was also observed for impact strength, where they recorded a fourfold improvement. The remarkable improvement was revealed to be related to the ultrafine acrylate rubber particle contribution in inducing crazes. The degree of crystallinity was increased at only 5% of acrylate rubber [87].

Liu et al. [88] reported in another investigation that PLA was toughened using a ternary blend of ethylene/*n*-butyl acrylate/glycidyl methacrylate terpolymer elastomer (EBA-GMA) and ethylene/methacrylate acid copolymer (EMAA-Zn). In this reactive blending approach, they noted that by increasing the reactive blending temperature, it favored the interfacial wetting and increasing the crosslinking of the EBA-GMA rubber phase and hence unfavorably enhanced its cavitation's resistance [88].

Bijarimi et al. explored the use of natural rubber to toughen the PLA via melt blending [3,28,89]. Using a range of rubber concentrations, they discovered that liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR) successfully toughened the brittle PLA. The summary of mechanical properties of PLA/rubber or elastomer based are given in Table 3.

Toughening Mechanism

The ductile development of all solid polymers belies their innate brittleness [90]. Combining stiff particles that may debond before plastic flow with rubbery particles that can cavitate. Massive crazing and shear yielding are two toughening processes of polymers that are well-recognized and understood. Commodities plastics such as polyamides, polystyrene and polypropylene have been toughened by the incorporation of the rubber phase [91].

Understanding the toughening mechanism associated with the polymer blend morphology in any blend systems is imperative. There exist few literature reports on the toughening mechanism of the toughened PLA. Whitening of a tensile specimen's elongated region has been linked to crazing development in certain investigations, suggesting that toughening improvements may be linked to crazing formation [92]. Multiple craze production at the fracture tip area, with elongated fibrils and voids constructing the crazes, was shown by Todo et al. [93] in PLLA/PCL blends. Furthermore, at the high tensile stress conditions present in the crack tip area, elongated PCL spherulites developed, giving rise to the stretched fibrils structure. They have concluded that the damage formations were the principal energy dissipation mechanisms for improving fracture energy.

Table 3. Mechanical properties of PLA/rubber or elastomer based

Blend Component	Composition	Stress at break (MPa)	Elongation at break (%)	Modulus (GPa)	Ref.
PLA/NR	90/10	40.10	200	2.00	[84]
PLA/NR	90/10	32.16	7.26	1.31	[85]
PLA/ENR25	90/10	19.30	2.31	1.38	[85]
PLA/ENR50	90/10	17.80	2.25	1.36	[85]
PLA/Acrylate rubber	90/10	48.98	198	2.00	[87]

Void development due to inadequate interfacial adhesion blending component was discovered to generate cavitation inside the rubber particles and debonding between the rubber particles and matrix in rubber-toughened polymers. It was found that good adhesion between components PLA/poly(1,4-*cis*-isoprene) was obtained, hence cavitation occurred inside the rubber particle. Accordingly, it was concluded that there were three fundamental processes at work: first, the rubbery particles induced crazing, and then cavitation inside the rubber particles boosted the shear yielding of PLA [86].

In another study, the blend of PLA/ultrafine acrylate induced a large number of crazes as the mechanism for energy absorption. Microdamage, void, and craze development, together with other fracture characteristics, including pull-out and scission of polymer fibrils, were proposed as the mechanisms responsible for energy dissipation at the crack tip area. It was concluded that the ultrafine acrylate rubber particles were dispersed and adhered well with the PLA, and hence crazing mechanism was responsible for major toughening [87].

It has also been found that crazing in PLA/EVA blends causes the formation of craze fibrils, which leads to significant dispersion along the tensile axis. However, cavitation happens first during deformation, and then the cavities and rubber particles stretch out. Some of the spaces even had a fibrillar structure, which helps with bridging and slows the voids from spreading. An essential part of the rubber phase's ability to absorb energy is its fibrillation. According to their findings, the PLA/EVA blend's primary toughening process is postulated to be internal rubber cavitation in conjunction with the matrix yielding [69].

Many studies have recently been done on PLA rubber/elastomer blends to change the characteristics of PLA for numerous technical applications that need demanding applications [9,15,27,94-99]. As for FDM 3D printing, PLA and NR were mixed with increasing toughness and investigated by Fekete et al. [100]. On the other hand, Musa et al. [101] have recently analyzed the potential of 3D fused deposition modeling employing filaments made of PLA-based thermoplastic elastomer. An understanding of the toughening mechanism that governs the toughness of PLA is crucial.

■ PLA/PLASTICIZATION

In the plastics and rubber sectors, plasticizers such as phthalates, benzoates, adipates, synthetic acid, and mineral oils are the most prevalent additions. However, it has always been challenging to determine which plasticizer is best for a specific use. Cost-benefit analysis is often used to determine which plasticizer is best for a certain application. The primary function of a plasticizer is to lower T_g, melting temperature (T_m), and modulus of a polymer without altering the chemical structure of the polymer, hence increasing the plasticity and flow of the polymer.

PEG plasticizers have been added to PLA-PEG blends to improve the toughness of PLA. PLA-PEG blends are more durable, flexible, and processable than PLA alone. PEG plasticizers increase the amorphous content and decrease the crystallinity of PLA, improving its toughness. Furthermore, PEG plasticizers reduce the viscosity of PLA in its molten state, increasing its processability. Furthermore, the addition of PEG plasticizers to PLA raises the glass transition temperature, making the blends more stable over a wider temperature range. The composition and chemical structure of PEG affects the characteristics in a major way of PLA-PEG blends. In general, higher PEG content and lower molecular weight PEGs improve toughness and flexibility while lowering the melting temperature and mechanical properties of the blends. In conclusion, PLA-PEG blends are a promising alternative to PLA in a variety of applications due to their increased toughness and flexibility. The properties of the blends can be altered by adjusting the PEG concentration and chemical structure of the PEG. This section reviews the usage of several types of plasticizers in an attempt to minimize PLA brittleness and thereby boost toughness.

The brittleness of PLA is a fundamental drawback to its usage in many applications. Therefore, plasticizers must be added to lower the glass transition temperature and increase toughness and processability, as commonly used in plastic industries for glassy polymer. Commonly, plasticizers being a non-volatile solvent and low molar mass added to the polymer for processability improvement by acting as a spacer at the molecular level

1170

Indones. J. Chem., 2023, 23 (4), 1161 - 1180

so that less energy is required to allow substantial rotation about the C–C bonds, and thus T_g is lowered [102]. An efficient plasticizer should reduce the glass transition temperature of the amorphous domains; if the T_g is near or lower than the ambient temperature, flexibility is achieved [103]. Therefore, a lot of attention is being given to improving the toughness of PLA by adding plasticizers.

Murariu et al. [14] investigated the toughening of PLA- Calcium sulfate anhydrite (CaSO$_4$) -anhydrite II composites utilizing bio-sourced tributyl citrate (TBC). With as low as 10% plasticizer, plasticized composites offer higher tensile and impact toughness. They found the PLA-β-anhydrite II (AII)-10%TBC sample under consideration for future development demonstrated fascinating properties such as tensile strength of 22–26 MPa, elongation at break of 160%, and high impact resistance (5.6 kJ/m^2). Mechanical tests of composites with higher TBC concentrations (15–20%) revealed typical elastomeric behavior, despite plasticizer migration, even after a short period of age [14].

Besides being eco-friendly and biocompatible, PLA also has better thermal processability compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), PEG, and PCL. Despite all the advantages, PLA is a very brittle material with less than 10% elongation at break [45,55]. This limitation has been overcome by introducing low molecular weight plasticizers such as glycerol, sorbitol and triethyl citrate.

The plasticization of PLA can be extensively found in the research literature. Plasticizers such as PEG, glucose monoesters, triethyl citrate (TC), acetyl triethyl citrate (ATC), fatty acid esters, oligomeric lactic acid and glycerol were used to improve the flexibility of PLA [104-106].

Labrecque and co-workers [106] investigated citrate esters plasticizer at 10, 20 and 30% by weight and found reduced T_g and improved elongation at break. Another researcher claimed that the increase of triacetin and tributyl citrate contents linearly reduces the glass transition temperature of PLA. At 25% of plasticizer content, miscibility with PLA was noted. Nevertheless, when the samples were heated at 35, 50 and 80 °C, phase separation was observed due to increased crystallinity during heat treatment. Phase separation occurs in

samples heated to 35, 50, and 80 °C, probably due to the crystallization of the substance [107].

The addition of different plasticizers with low molecular weights, like PEG and glycerol, has been studied by Martin and Averous [105]. The lowest glass temperature was achieved using PEG 400 plasticizer. However, glycerol was shown to be the least effective. T_g variation and mechanical characteristics were used for the analysis. Nevertheless, for the PLA melt-blended with thermoplastic starch, two different T_gs were observed in the blends, indicating limited compatibility [105].

Baiardo et al. investigated the acetyl tri-*n*-butyl citrate (ATBC) and PEGs plasticization of PLLA. The mechanical characteristics of plasticized PLA were discovered to vary as the plasticizer concentration increased; that is when the blend T_g was brought closer to room temperature, a gradual shift in the mechanical properties of the system was seen. Even though the tensile strength and modulus are both reduced, the elongation at break rises dramatically [108]. Incorporating monomeric plasticizers such tributyl citrate and bishydroxymethyl malonate has led to a reduction in PLA's T_g. Morphology stability and enhanced flexibility were found in the oligomeric plasticizer because of stronger polar interactions with PLA and a larger molecular weight [107].

Pillin et al. [109] analyzed the thermal and mechanical properties of PLA with PEG, poly(1,3-butanediol) (PBOH), acetyl glycerol monolaurate (AGM), and dibutyl sebacate (DBS) in an effort to enhance the material's mechanical properties for packaging applications. All plasticizers were melt blended with plasticizers at 10–30% w/w concentrations. PEGs were shown to be the most effective plasticizer, resulting in a change of the glass transition temperature T_g to a lower zone for all blends. But the modulus and stress at break were both lower in the PLA/PEG blends, principally because of the reduced cohesion induction, which was mirrored in the low stress at break. On the other hand, in this study, they have shown that the PBOH, AGM and DBS exhibited mechanical properties consistent with soft packaging applications [109].

Calcium sulfate derived from lactic acid production was blended with PLA and low molecular weight plasticizers (bis(2-ethylhexyl) adipate, glyceryl triacetate, and polymeric adipates) by Murariu et al. [110]. The works aimed at reducing the brittle behaviour of PLA-calcium sulfate composite. They have reported that adding up to 10 wt.%. of plasticizer increased the composition's impact strength by a factor of four without any modifier. Furthermore, the ternary blends were observed to have better processing and good filler dispersion [110].

Similarly to polyolefins and other thermoplastics, PLA can be treated, albeit its thermal stability may be improved [111-112]. Plasticizers are required to enhance the elongation and impact characteristics of PLA polymers, which are otherwise rigid and brittle. The processability of polymers is often enhanced by adding plasticizers such as partial fatty acid esters, glycerol esters, citrates, citrate oligoesters, and dicarboxylic esters [104]. Resistance to volatility, diffusion, extraction, and/or weathering, larger molecular weight plasticizers like PEG and poly(propylene glycol) and polyester plasticizers have also been studied for PLA plasticization [113-114].

Okammoto et al. [115] investigated the effect of molecular structures of polyester-diols (PED) such as poly(ethylene adipate) (PEA), poly(diethylene adipate) (PDEA) and poly(hexamethylene) (PHA) on miscibility, mechanical and thermal properties of plasticized PLA. In this work, they prepared various compositions of PLA/PED through melt blending and solvent casting. It was found that the blends of 80PLA/20PEA and 80PLA/20PDEA are miscible blends but only partially miscible for the 80PLA/20PHA blend. The large configurationally entropy caused by the chain flexibility of PDEA with the ether bond is responsible for the good miscibility between PLA/PDEA [115].

With the goal of creating biodegradable packaging made from PLA, Lemmouchi et al. [116] plasticized the PLA with blends of tributyl citrate (TBC) and low molecular (PLA-*b*-PEG) copolymers via a melt blending. In this study, the copolymer has been synthesized using potassium-based catalyst. The thermal and mechanical properties were investigated as a function of blend composition and copolymer structure/topology. They have found that for compositions containing 80 wt.%. PLA and 20 wt.%. Blend of plasticizers showed a T_g below 30 °C, high nominal strain at break and tensile strength. It was also found that this TBC and PLA-b-PEG blend has increased the impact strength of neat PLA. In terms of biodegradation, the test conducted in compost conditions showed that this plasticizer enhanced the degradation of PLA matrix [116].

Using a solvent casting method, Hughes et al. investigated the efficacy of methylene chloride/acetonitrile mixed solvent solutions with 10% plasticizer in increasing the flexibility of PLA films. In this approach, the compound with a solvent ratio of 70% methylene chloride and 30% acetonitrile was found to have less crystallinity and the highest flexibility, i.e., at 49.36% elongation. In addition, this compound had the same thermal behavior as the more crystalline films [117].

Hassouna et al. [118] introduced a novel technique for plasticizing PLA. Here, we use a co-rotating intermeshing twin-screw extruder to combine anhydride-grafted PLA (MAG-PLA) copolymer with PEG at 181 °C and 80 rpm. Melt blending compatibility between PLA and PEG was enhanced by grafting a small amount of PEG onto the anhydride-functionalized PLA chains. It was found that the molecular weight did not drop dramatically as a result of this melt blending and extrusion process. Furthermore, the glass transition temperature decreased as compared to the blends without grafting i.e., neat PLA blended with PEG. They have also concluded the addition of MAG-PLA did not significantly influence the behavior of this blend [118].

Another study by Bijarimi et al. [4] showed that PEG has the ability to strengthen PLA. It took 15 min to melt the blend PEG/PLA in an internal mixer heated to 180 °C with the speed set at 50 rpm. The blends were tested to determine their mechanical, thermal, and morphological characteristics. When PEG was added to the PLA matrix at concentrations between 2.5 and 10%, the tensile and flexural strength, stiffness, and notched Izod impact strength all reduced dramatically. As the PEG concentration increased, the glass transition and

melting temperatures (T_g and T_m) fell. In addition, the PLA/PEG mixes exhibited lower initial and peak degradation temperatures but greater final degradation temperatures than PLA alone. Morphological investigation revealed that the PEG was disseminated as droplets in the PLA matrix, with a clear demarcation between the PLA matrix and PEG phases [4].

Kim et al. explored plasticizing effect in poly(vinyl alcohol) blown film (butylene adipate-*co*-terephthalate). PLA/poly(butylene adipate-*co*-terephthalate (PBAT) mechanical characteristics and tear resistance were tested utilizing a blown film extrusion technique. Extreme brittleness, poor stiffness, and incompatibility restrict the utilization of PLA and PBAT packaging. Adipate, adipic acid, glycerol ester, and adipic acid ester were investigated for their effects on PLA plasticization and PLA/PBAT blown film manufacturing. Adipic acid ester improves PLA's flexibility and compatibility with PBAT. Plasticizer enhanced PLA matrix chain mobility. The plasticized PLA domain's adherence to the PBAT matrix was also improved. Plasticized PLA/PBAT blown film enhanced tear resistance in the machine direction from 4.63 to 8.67 N mm^{-1} and in the transverse direction from 13.19 to 16.16 N mm^{-1} [119].

The increased flexibility of biodegradable PLA/starch blends using epoxidized palm oil as a plasticizer was examined by Awale et al. [120], epoxidized palm oil (EPO) increased the PLA/PSt combination's flexibility. PLA/starch/EPO (PSE) combinations with a constant percentage of starch and a variable quantity of EPO were created via solution casting. EPO increases chain mobility by lowering the glass transition, melting, and crystallization temperatures of PSt. According to TGA, PSE is more heat-resistant than PSt. Mechanical testing showed that EPO at all concentrations enhanced impact strength and elongation-at-break. They demonstrated the greater adaptability of PLA-EPO combinations [120].

Ghari and Nazockdast [17] compared the morphological and mechanical properties of PLA/plasticized thermoplastic starches (TPS) blends and PLA/TPS+EVA blends. Combining PLA with thermoplastic starch was studied for its potential toughening effects. Similar studies were undertaken on molten ternary mixtures of PLA, dynamically cross-linked TPS, and EVA. In a viscoelastic melt study, citric acid (CA) reduced TPS viscosity and flexibility. They hypothesized that a dynamically cross-linked EVA produced the dispersed phase percolated network. Due to their unique construction, ternary blends are far more robust than binary blends [17].

Gzyra-Jagiela et al. [121] studied PLA modification through high-molecular compounds such as ethoxylated lauryl alcohol, ethylene oxide, and propylene oxide block copolymers combined with low-molecular substances such as di-2-ethylhexyl adipate, di-2-ethylhexyl sebacate, and triethyl citrate. Depending on the plasticizer employed, all of the adjusted samples showed lower glass transition temperatures than the untreated polymer. The most successful treatments were di-2-ethylhexyl adipate (ADO) and di-2-ethylhexyl sebacate (SDO). The elongation at the fracture site increased significantly with ADO, reaching around 21%. Despite having a higher glass temperature, SDO achieved the largest elongation (approximately 35%) [121].

Several factors, including nucleating agents, plasticizers, and molding conditions, were studied by Tabi et al. to see how they affected the qualities of injection-molded PLA products. Results showed that PLA treated with nucleating agents outperformed ABS in terms of heat deflection temperature, tensile strength, and Young's modulus. Even after being annealed or subjected to simultaneous nucleation and plasticization, the PLA compounds' elongation at break was much lower than ABS's. However, the brittleness of PLA was not alleviated by using plasticizers, nucleating agents, or varying the mold temperature. There was nevertheless a significant drop in PLA's elongation at break, which hovered between 1.7 and 2.5% throughout their studies [122]. A summary of the mechanical properties of plasticized PLA found in the literatures are given in Table 4.

In the realm of plastics manufacture, PLA blends are commonly utilized as a safe and environmentally acceptable alternative to standard synthetic polymers.

Table 4. Mechanical properties of plasticized PLA

Blend component	Weight %	Stress at break (MPa)	Elongation at break (%)	Modulus (GPa)	Ref.
PLA/PEG200	10	30.0	2.00	1.70	[109]
PLA/PEG400	10	-	26.0	1.49	[105]
PLA/PEG400	20	-	160	0.98	[105]
PLA/PEG400	10	39.0	2.40	1.92	[109]
PLA/PEG400	20	16.0	21.2	0.63	[109]
PLA/PEG1000	10	39.6	2.70	1.97	[109]
PLA/PEG1000	20	21.6	200	0.29	[109]
PLA/Oligomeric lactic acid	10	-	32.0	1.49	[105]
PLA/Oligomeric lactic acid	20	-	200	0.74	[105]
PLA/PEA	20	24.8	8.15	0.37	[115]
PLA/PBA	20	42.6	4.28	0.67	[115]
PLA/PHA	20	36.8	0.19	0.71	[115]
PLA/PDEA	20	17.7	7.05	0.26	[115]

The addition of plasticizers or low-molecular-weight polymers, both of which are polymers, can enhance the physical properties of PLA, such as its flexibility, tenacity, and heat stability. Glycerol is the most common type of plasticizer used in PLA, and it gives PLA a greater degree of flexibility. The inclusion of low-molecular-weight polymers, such as polyethylene glycol and polyvinyl alcohol, can increase the heat stability and brittleness of PLA. Additionally, the brittleness of PLA can be diminished. In addition, PLA blends containing these additives have the potential to improve the material's overall processability. In general, combining PLA with plasticizers or low molecular weight polymers can enhance the material's physical qualities, making it suitable for a broader range of applications. In addition, these mixes are harmless to humans and environmentally friendly, making them a good choice for a range of industries.

■ FUTURE OUTLOOK OF PLA

The immense potential uses of biodegradable polymers provide new avenues for lessening reliance on petroleum-based polymers. Despite the rise of PLA-based goods, there remains a poor view of product performance when compared to traditional plastics. Furthermore, the high cost of biobased polymers is a factor leading to inefficiency in the industrial sectors.

Despite significant drawbacks in characteristics, particularly brittleness and limited elongation, the future prospect for PLA is highly promising. It is not surprising, however, that much research is being conducted in an attempt to make PLA more suited for a wide variety of applications via property change. As previously discussed, mixing with other polymers and plasticization might address the intrinsic brittleness issue. However, greater efforts must be made to design a material with balanced stiffness and toughness qualities. All attempts so far have shown considerable promise, indicating that the future of PLA-based materials as a possible alternative for replacing commodity plastics is unquestionably bright. With updated technology in polymer processing, such as 3D and 4D printing, it is envisaged that PLA processing would be as efficient as processing mature commodities' plastics. As such, it serves as a catalyst for the commercialization of biodegradable polymers, especially for items with short life cycles and single-use applications.

■ CONCLUSION

PLA is utilized for a wide number of tasks across many different industries, including the packaging industry, engineering, and medicine. PLA is undergoing research and development to improve its toughness, property modification, and plasticizing capabilities,

which bode well for the material's future. Research has been focused on finding ways to make PLA materials more durable. One such method involves adding a very small amount of a compound similar to rubber that is compatible with PLA. This component, similar to rubber, is referred to as a rubber modifier, and it works to improve the tenacity of PLA. Modifications to the properties of PLA, such as the inclusion of UV stabilizers and antioxidants, are being investigated in other research with the intention of making the material more weatherproof and resistant to the effects of ultraviolet light. Plasticizing PLA is another option for those interested in increasing the material's flexibility. In order to produce plasticization in PLA, a low molecular weight plasticizer is added to the PLA. Because of this, the material becomes less rigid while simultaneously increasing its softness and flexibility. Plasticized PLA is frequently used in medical applications such as implants and prostheses. Examples of these uses include: In addition, PLA can be utilized in a wide variety of engineering applications. It is possible to generate prototypes as well as final things through the use of 3D printing. Both the construction and car industries use many components, such as interior panels and gaskets.

In conclusion, it is no doubt that PLA has a positive outlook. Through continued research and development, PLA can be improved to the point that it can meet the requirements of a variety of different applications. Because of its toughness, property modification capabilities, plasticizing capabilities, and engineering applications, this biodegradable thermoplastic material has a promising future.

■ **ACKNOWLEDGMENTS**

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