



A Short Review of Polylactic Acid Blends Properties for Improvement and Innovation

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ABSTRACT

Advanced technology in petrochemical-based polymer has brought many benefits to mankind. However, the use of nonbiodegradable plastics materials for disposable application such as food packaging and house whole appliances are significantly disturbing and damaging the earth ecosystem. Polylactic acid (PLA) is a biodegradable plastic that is brittle. Because of this nature, PLA has a limitation in its usage. The common way to improve the toughness of PLA is via adding plasticizer. This review will provide brief account on recent developments in the synthesis of lactic acid (monomer of PLA) through biological route, PLA synthesis, unique material properties of PLA and modification of those by making copolymers and composites PLA absorption and degradation.

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Introduction

Advanced technology in petrochemical-based polymer has brought many benefits to mankind. However, the use of nonbiodegradable plastics materials for disposable application such as food packaging, house whole appliance and cookware are significantly disturbing and damaging the earth ecosystem (Nofar et al., 2019). Conventional plastics are resistant to biodegradation. The environmental impact of persistent plastics waste is of increasing global concern and alternative disposal methods are limited. Incineration of these plastic wastes always produces a large amount of carbon dioxide that contributes to global warming. In some cases, toxic gases such as dioxins, furans, mercury and polychlorinated biphenyls are also produced, which contributes to global pollution (Verma et al., 2016). On the other hand, satisfactory landfill sites are also limited.

For these reasons, there is an urgent need to develop renewable, source-based, environmentally benign polymeric materials (biopolymer), especially for use in short-term packaging and disposable application. Such materials would not involve the use of toxic or noxious component in their manufacturing and could allow for composting into naturally occurring biodegradation products (Fig. 1).

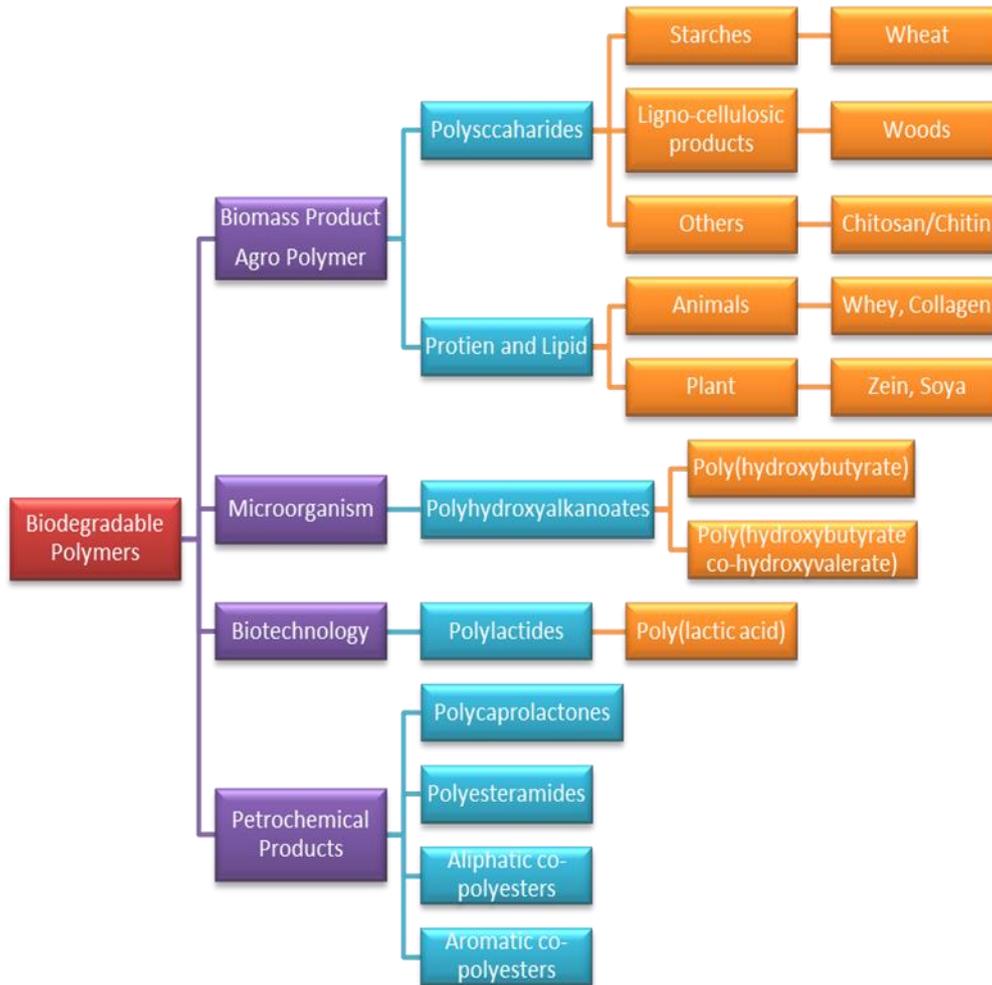


Fig. 1: Classification of biodegradable polymer (Avérous, 2004)

Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization. Biodegradable polymer may not produce from bio-source only, but it can also be derived from petroleum source (Nakajima, 2017). The biodegradation may be due to aerobic or anaerobic microorganisms, biologically active processes (enzyme reactions) or passive hydrolytic cleavage (Shah, et al., 2008). Examples of the biodegradable polymers include polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polylactic acid (PLA), polycaprolactone (PCL) and polybutylene adipate co-terephthalate (PBAT).

Lactic acid – An overview

PLA consists of hydroxyl and a carboxyl group which easily converted to polyester through polycondensation reaction. PLA can be synthesised and varied in its molecular weight depending on its application. PLA with high molecular weight is used in the packaging industry (Jamshidian et al., 2010) whereas PLA with low molecular weight PLA is generally used in biomedical applications, where fast degradation into the human body is required (Palacio et al., 2011). Conventional condensation polymerization of lactic acid was a popular method to synthesised PLA. However, an organic solvent is used for azeotropic distillation of condensation water and the polymerization period extended will produces PLA with higher molecular weight.

Polymerization of a racemic (Fig. 2) mixture of L- and D-lactides usually leads to the synthesis of poly-DL-lactide (PDLLA) which is not crystalline but amorphous. Subsequently, polycondensation of aqueous DL-lactic acid will give Mn's up to 6500 which reported for pure L-lactide (Mehta et al., 2006; Song & Murphy, 2018).

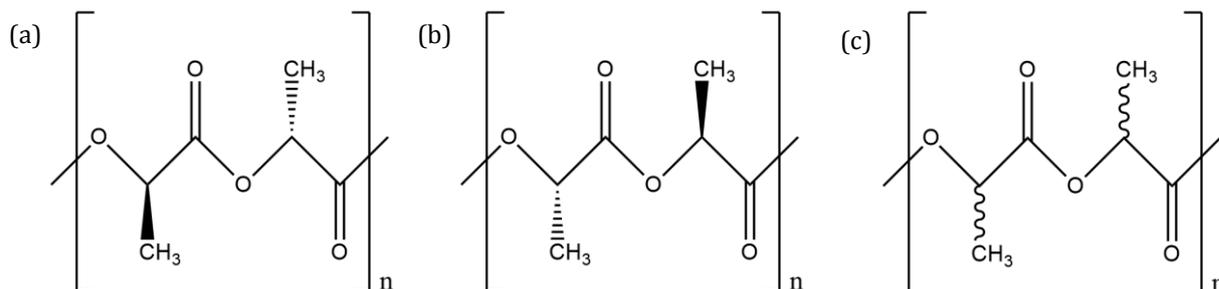


Fig. 2: Chemical structure of stereoisomer; (a) L-PLA, (b) D-PLA and (c) D,L-PLA

The commonly used catalysts for PLA synthesis are shown in Table 1. As mentioned, the use of stereospecific catalysts can lead to heterotactic PLA which will show different crystallinity property. As a result, many PLA important properties, are determined by the ratio of D to L enantiomers that exist. Different type of organic monocarboxylic iron complexes that used in the ring-opening polymerization of L-lactide were also been reported. The acetate anion as well as the iron partly, is chemically attached to the polymer chain, and the proposed polymerization mechanism is an anionic type of coordination insertion.

Table 1: Different catalysts used for the production of PLA (Gupta & Kumar, 2007)

Polymer	Catalyst	Solvent	Molecular weight
D, L PLA / L-PLA	Aluminium Isopropoxide	Toluene	Mn. 90,000
D-L PLA	Stannous octoate	Alcohols	Mw < 3,50,000
L-PLA,	Stannous octoate	Alcohols carboxylic acid	Mn, 250,000
L-PLA	Stannous octoate and compounds of titanium and zirconium	Toluene	Mn = 40,000– 100,000
D-PLA, L-PLA D-L PLA	Stannous trifluoromethane sulfonate, scandium(III) trifluoromethane sulfonate	Ethanol	-
L-PLA	Mg, Al, Zn, Titanium alkoxides	Methylene chloride	-
L-PLA	Yttrium tris(2,6-di-tert butyl phenolate) (in toluene)	ethanol 2-propanol, butanol,	Mn < 25,000
D-LPLA	Zn lactate	No solvent	Mn = 212,000
D-L PLA L-PLA	Butylmagnesium, Grignard reagent	Ethers	Mn < 300,000
L-PLA,	Potassium naphthalenide	THF toluene	Mn < 16,000
L-PLA	Complexes of iron with acetic, butyric, siobutyric and dichloroacetic acid	No solvent	Mw = 150,000

PLA - Monomer and Properties

PLA is linear aliphatic polyester synthesized by ring-opening polymerization of lactides and which are typically derived from corn starch fermentation (Fig. 3). PLA also can be produced by chemical synthesis. There are two possible routes (Fig. 4). First was the hydrolysis of lactonitrile by strong acids, which provide the racemic mixture of D-and L-lactic acid. Second was the catalyzed degradation of sugars; oxidation of propylene glycol; reaction of acetaldehyde, carbon monoxide, and water at elevated temperatures and pressures; hydrolysis of chloropropionic acid and nitric acid oxidation of propylene. The awareness to fermentative production of lactic acid has increased due to two prospects which environmental friendliness and of using renewable resources instead of petrochemicals. Fermentation able to produce high product specificity, as it produces a desired optically pure L-(+)- or D-(-)-lactic acid. Fermentation also offers several advantages compared to chemical synthesis like low cost of substrates, low production temperature, and low energy consumption (Komesu et al., 2017).

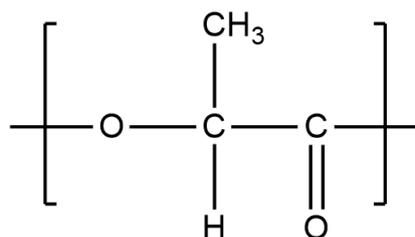


Fig. 3: PLA repeating unit

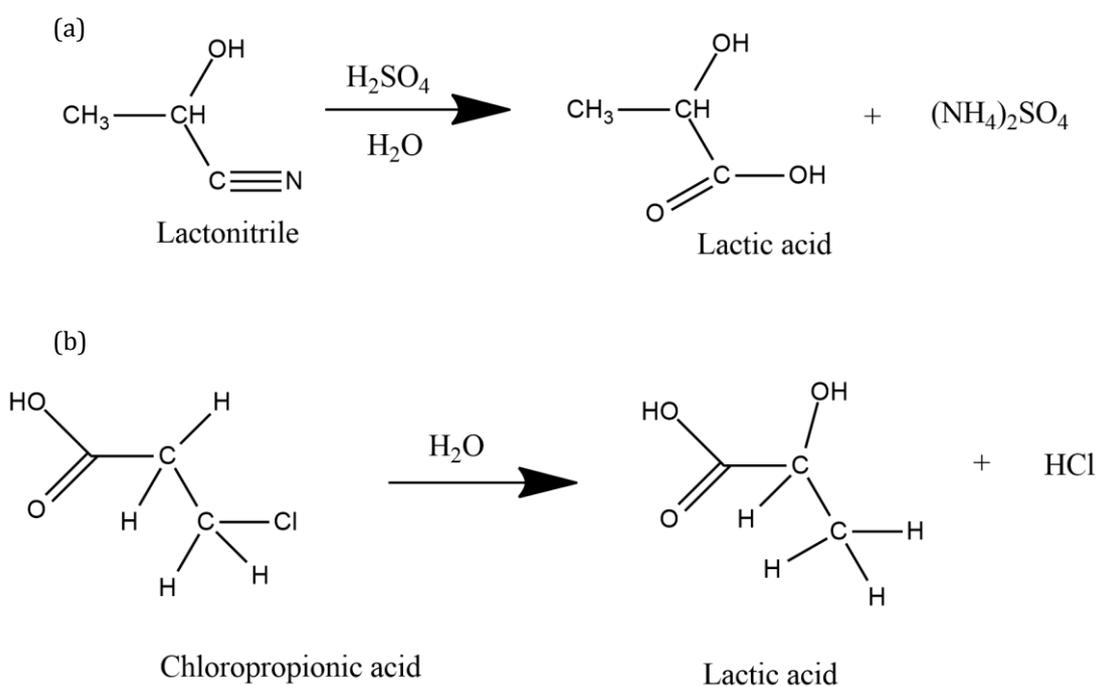


Fig. 4: Chemical synthesis of lactic acid by (a) hydrolysis of lactonitrile by strong acid and (b) catalyzed degradation of sugar.

PLA has been found to be environmentally biodegradable. Lactic acid bacteria (LAB) and some filamentous fungi are the chief microbial sources of lactic acid. The organisms that predominantly yield the L isomer are *Lactobacilli amylophilus*, *Lactobacilli bavaricus*, *Lactobacilli casei*, *Lactobacilli maltaromicus*, and *Lactobacilli salivarius*. Strains such as *Lactobacilli delbrueckii*, *Lactobacilli jensenii*, or *Lactobacilli acidophilus* yield the D-isomer or mixtures of both (Nampoothiri et al., 2010). Biodegradation of PLA occur through two step processes that begin with the high molecular weight polyester chain hydrolysed to lower molecular weight oligomers under an appropriate temperature and moisture environment. In the second step, microorganisms convert these low molecular weight components to carbon dioxide, water and humus (Jiang et al., 2006).

Some of factors affecting PLA properties are molecular weight, annealing time, component isomers and processing temperature. Poly-L-lactide (PLLA) is the product resulting from polymerization of L-lactide. The glass transition temperature and melting temperature for PLLA were recorded between 50-80 °C and 173-178 °C respectively. PLLA has a crystallinity of around 37%. The crystallization ability of polylactides decreases with chain stereoregularity and below 43% of optical purity crystallization is no longer possible (Sarasua et al., 1998). Because of that, polylactides and its isomers PLLA and poly D-lactide) (PDLA) show semi crystalline manners. Nevertheless, diverse polymerization methods were reported to rearrange lactyl structural unit chain to modifies the properties of polylactides. There's no positive result as both amorphous and crystalline polylactides used to show brittle behavior at room temperatures (Farah, Anderson, & Langer, 2016). Brittle mechanical behavior of polylactides was led from crystallization in the form of stereo complex (Zhang et al., 2018).

The reason can be reflected to picture PLA density. An amorphous PLLA has a density and crystalline value of 1.248 g ml⁻¹ and 1.290 g ml⁻¹ respectively (Farah et al., 2016). The amorphous PLA is soluble in organic solvents such as tetrahydrofuran (THF), chlorinated solvents, benzene, acetonitrile, and dioxane. This is different from crystalline PLA which is only soluble in chlorinated solvents and benzene at elevated temperatures (Garlotta, 2002).

In general, standard grade PLA has high modulus (3 GPa) and strength (50-70 MPa) which are comparable to that many petroleum-based plastics. Table 2 listed the common properties of PLA. As mentioned earlier, PLA is brittle and has a low toughness as well as physical aging problem that limits its application. The brittleness of PLA can be modified by copolymerization of lactides with another monomer such as caprolactone (Sangeetha et al., 2018). Increasing the caprolactone units by a few percent decreased the modulus but substantially increased the elongation.

Table 2: Physical properties of PLA

Physical properties	Value
Mechanical properties Tensile strength at yield (Mpa)	53
Elongation at yield (%)	10-100
Flexular modulus (Mpa)	350-450
Melting point	120-1704
Melt flow rate (g/10 min)	4.3-2.4
Density (g/cm ³)	1.25
Yellowness index	20-60
Haze	2.2

PLA - Improvement and consequences

Polymer blending (Fig. 5) is a convenient route for the development of new polymeric materials, and able to yield materials with property profiles superior to those of the individual components (Müller et al., 2017). This method is usually cheaper and less time-consuming for the creation of polymeric materials with new properties than the development of new monomers and/or new polymerization routes. An additional advantage of polymer blends is that the properties of the materials can be tailored by combining component polymers and changing the blend composition. The hard and brittle mechanical properties of PLA limit its development and practical application; therefore, several modifications have been proposed to improve processing and mechanical properties, such as copolymerization, plasticization, and polymer blending (Farah et al., 2016).

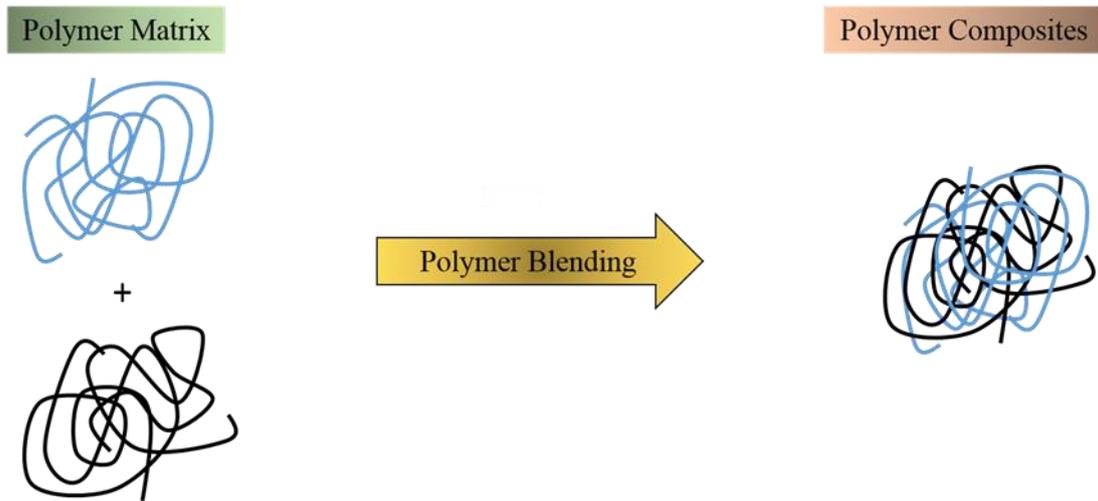


Fig. 5: Schematic pathway for polymer blending

There are three methods for blending polymer. Firstly, is the solution/precipitation, second is the solution/casting and lastly is the reactive blending (melt blending) (Fig. 6). However, the blends that have been prepared by different processing methods exhibited different properties (Imre & Pukánszky, 2015). For example, miscibility and phase behaviour of PLA/poly methyl methacrylate (PMMA) blends prepared by solution/precipitation has resulted in phase separation blends. Nevertheless, samples (PLA/PMMA) prepared by solution/casting did not exhibit phase separation (Zhang et al., 2003). Solution casting and melt blending was the most popular ways in producing polymer blends. From these three methods of blending, the blends can be distinguished into three different types: completely miscible blends, partially miscible blends and fully immiscible blends (Aid et al., 2017).

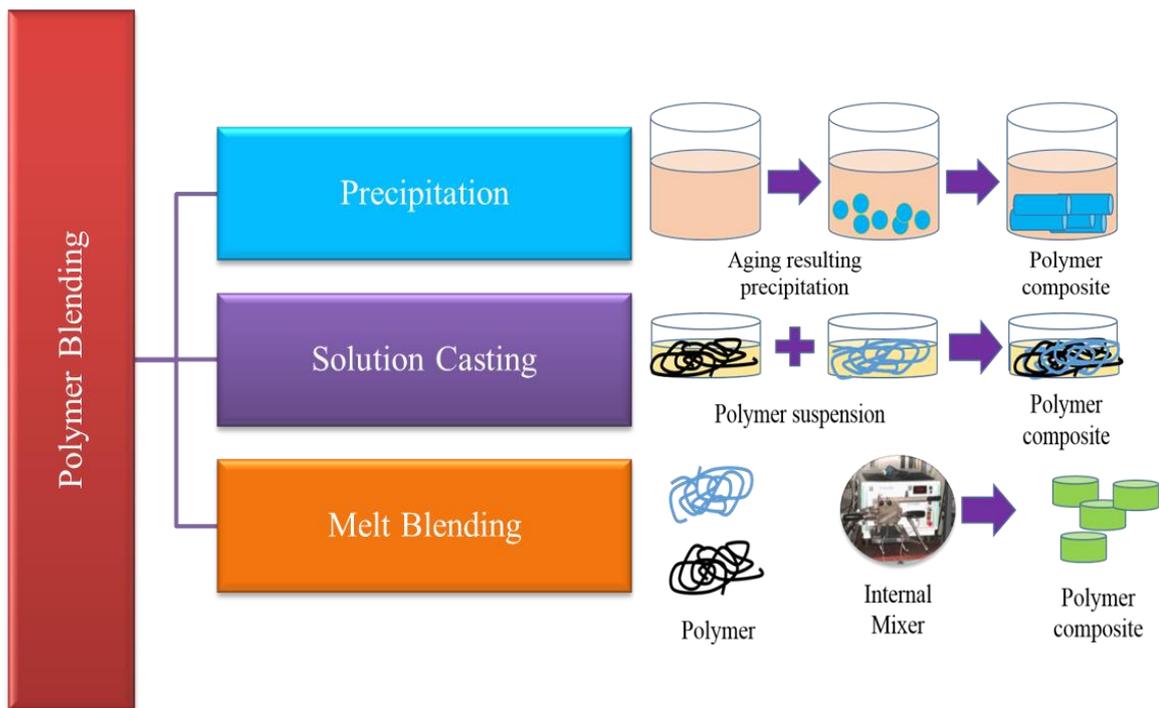


Fig. 6: Methods for polymer blending

Blending PLA with the presence of other polymers may be more practical and economical to obtain products with properties that are not currently attainable. All these years, only a few miscible blends have been identified. Most polymer mixtures form immiscible blends since adhesion between the polymer components is poor in certain blends. These blends are usually useless unless they can be compatibilized.

A common method to compatibilized and increase the processability and lower the initial tensile modulus (a decrease in stiffness) of a polymer is by using plasticizers during processing operations (Davallo & Pasdar, 2012; Mekonnen et al., 2013; Verbeek & Berg, 2010). Polymers are in principle can be used as polymeric plasticizers to change the physical properties of PLA (Immergut & Herman, 1965; Yasin & Tighe, 1992). Blending PLA with other polymers can modify the properties of PLA to the desire properties. For example, blending PLA with a rubbery type polymer formed non-brittle and tough blends (Nagarajan et al., 2016). It is often to get immiscible blends after two polymers were blended (Pivsa-art et al., 2016).

Many types of chemicals are studied to act as a plasticizer for PLA. Citrate esters (Martin & Ave, 2001) poly(ethylene glycol) (PEG), glucose monoesters and partial fatty acid esters (Hoffman, 2012), poly(vinyl alcohol) (PVA) (Chumeka & Tanrattanakul, 2013), polyethylene (PE) (Anderson & Hillmyer, 2004), polycaprolactone (PCL) (Liao & Wu, 2009), poly(butylene adipate-co-terephthalate) PBAT (Jiang et al., 2006) and polybutylene succinate adipate (PBSA) (Lee & Lee, 2005) were used to improve the flexibility and impact resistance of PLA.

Mechanical studies indicate that incorporated plasticizer changed the PLA nature from rigid to ductile (Marina et al., 2017), however will reduced the tensile strength (stress needed to break the sample, (Nikiforov et al., 2017) and tensile modulus (relative stiffness of a material, (Liao & Wu, 2009)) as compared with the origin PLA. This indicated incompatibility between the constituent polymers in the blend system which resulted in phase separation and poor interfacial adhesion between polymers (Abay et al., 2016; Broz et al., 2003).

Dynamic mechanical analysis (DMA) measure the response of a given material to cyclic deformation as a function of temperature. Storage modulus (G'), is corresponding to elastic response to the deformation, (measurement of the ability of material to store energy) whereas the loss modulus (G''), is corresponding to the plastics response to the deformation (ability of material to dissipate energy by flow) (Sinha et al., 2003). The storage modulus measures the stiffness of polymeric materials under the dynamic stress and strain condition while the loss modulus indicates the viscous behavior of the polymeric materials (Aziz & Ansell, 2004). G' is measured by quantifying the resistance to deformation phase with applied stress whereas G'' is determined from the components of the resistance that is out of phase.

A direct proof of polymer miscibility can be obtained by observing the behavior of the T_g with the blend's composition. One unusual property of immiscible blends is that one made from two amorphous polymers has two glass transition temperatures or T_{gs} (Thirtha, Lehman, & Nosker, 2006). Since the two components are phase separated, they retain their separate T_{gs} . If two T_{gs} are found, then the blend is immiscible. If only one T_g is observed, then the blend is likely to be miscible (Shi et al., 2013). The mechanical properties of this immiscible blend are going to depend on those of polymers that were major component, because the polymer phase is absorbing all the stress and energy when the material is under load (Deleo & Velankar, 2008; Yang et al., 2013). In addition, the immiscible blend is going to be weaker than its sample of pure polymer (Liu et al., 2018). The miscibility of a polymer blends is confirmed using SEM.

The SEM morphological studies of immiscible blend will indicate the existence of two-phase structure. Neat PLA had no necking in the tensile test showed a smooth longitudinal fractured surface without visible plastic deformation (Fig. 7). The observation is the same as several other researches (Jiang et al., 2006).

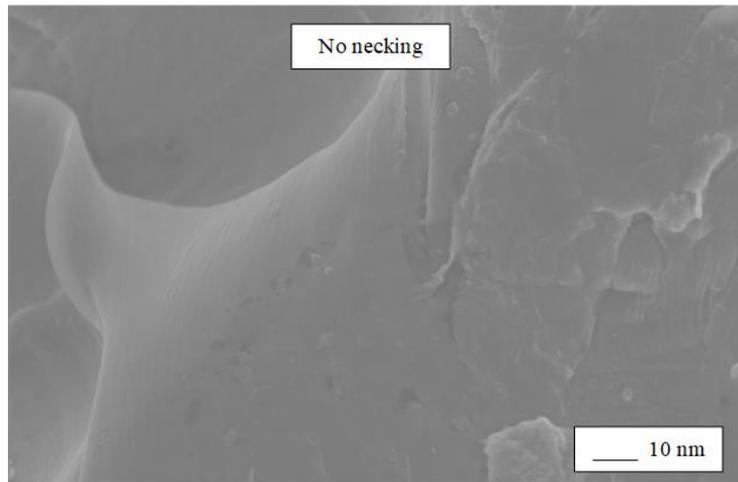


Fig. 7: PLA surface morphology

For immiscible blend, the debonding of the round particles from the PLA matrix under tensile stress is clearly observed (Osman et al., 2017). Note that the PLA samples are pulled apart as the appearances of cavities indicating the low adhesive properties between polymers (Fig. 8). These cavities were formed during tension when the stress was higher than the bonding strength at the interface between the polymer inclusions and because there was no sufficient interfacial adhesion (weak interaction) between polymers (Jiang et al., 2006; Osman et al., 2017).

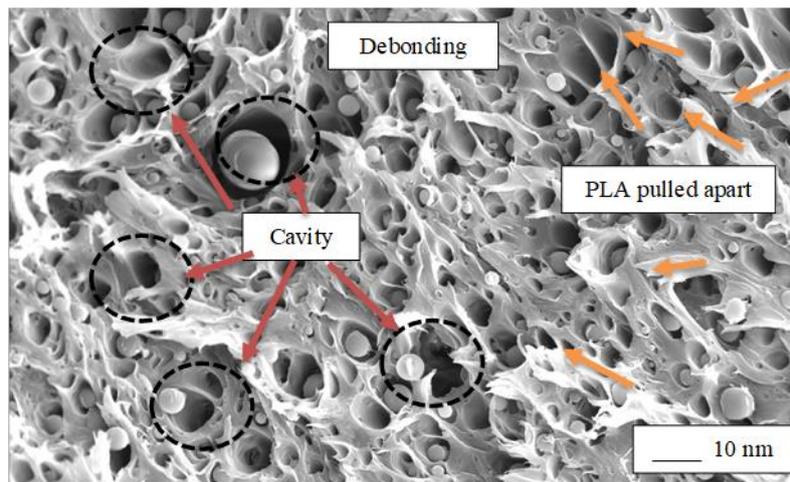


Fig. 8: PLA composite morphology (PLA was pulled apart) (Osman et al., 2017)

Thermal behavior of blends can be referred to cold crystallization temperature (T_c), melting temperature (T_m) and glass transition temperature (T_g). Crystallinity of blends is calculated as follows: (Ting et al., 2010).

$$X_c = (\Delta H_m / (\phi_{PLA}) / \Delta H_m^* \times 100\% \quad (1)$$

Where,

f = the weight fraction of the dispersed phase in the blends,
 ΔH_m = the melting enthalpy
 (J/g) that was calculated from the fusion peak in the DSC curve and
 ΔH_m^* is the heat of fusion for completely crystallized PLA (93.1 J/g).

The increased crystallinity might be caused by plasticizer nucleation and degradation of PLA polymer chains. It has been reported that plasticizer can act as nucleating agent for crystallization and molecular weight affects the crystallization of polymers. Generally, low molecular weight polymers have high crystallinity and high crystallization rate. In this pure blend case, both factors, that is, nucleation and lower molecular weight might be the cause of increased crystallinity. This result suggests the presence of

moisture decreased the molecular weight of PLA due to hydrolysis resulting in lower mechanical properties (Restrepo et al., 2018).

The water uptake of polymer may affect their mechanical properties, degradability, and dimensional stability. Water exposure and uptake may decrease the life of a polymer due to hydrolysis and micro crack formation (Correlo et al., 2007). In industry, one must know about the water absorption of polymer before determining their applications. In certain applications, some degree of water resistance may be desirable. Therefore, the water absorption of polymer was determined. Polymer matrix containing more polar group tends to absorb more moisture (hydrophilic character) (Kushwaha & Kumar, 2009). Higher water absorption property was observed in polymer blend consists of polymer that has low crystallinity (amorphous polymer) property than PLA (Kun & Marossy, 2013). This is an indication that the blend has the increased difficulty in forming polymer chain arrangements and causing poor adhesion with the hydrophobic PLA (Wu & Liao, 2007).

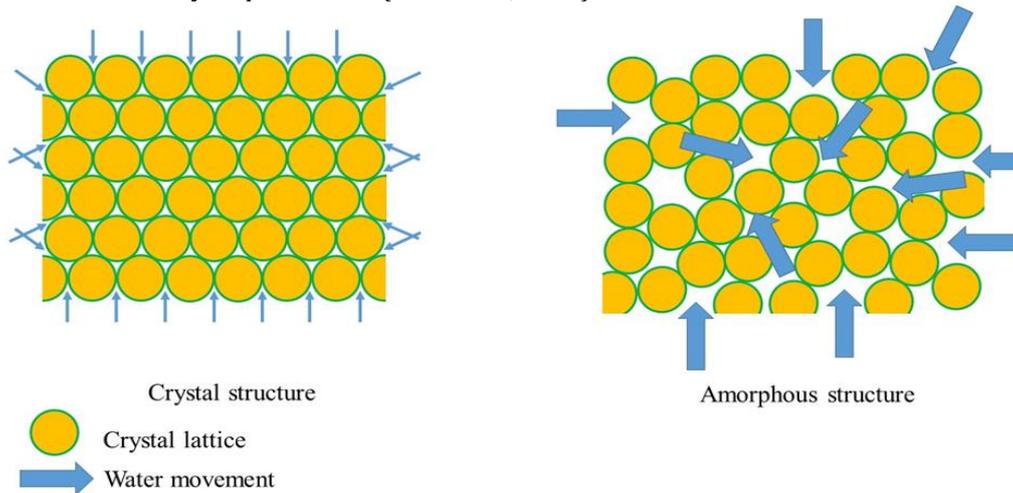


Fig. 9: Comparison of crystal and amorphous structures in water uptake process

Biodegradability can be determined by weight loss of the samples after contact with compost and/or soil. Generally, fungus biodegradation of biopolymers produces carbon dioxide, water and other harmless materials (Wu & Liao, 2005). The biodegradation of PLA has been investigated mostly in compost or soil environments (Qi et al., 2017). PLA is also ingested by animals and humans. Its application in medicine is widely studied and extensively developed. During the period of biodegradation test, the diffused water in polymer sample, will cause swelling and enhancing biodegradation (Liao & Wu, 2009). Furthermore, the hydrophilic-hydrophobic character of synthetic polymers greatly affects their biodegradability. A polymer containing both hydrophobic and hydrophilic segments seems to have a higher biodegradability than those polymers containing either hydrophobic or hydrophilic structures only (Ning et al., 2018)

Innovation

PLA meets many requirements as a packaging thermoplastic and is suggested as a commodity resin for general packaging applications. When plasticized with its own monomers, PLA becomes increasingly flexible (Ljungberg et al., 2005; Martin & Ave, 2001) so that a continuous series of products that can mimic PVC, LDPE, LLDPE, PP, and PS can be prepared. Degradation is increased with increasing plasticizer (Bhasney et al., 2017; Li et al., 2018), and shelf life is favoured by decreasing plasticizer content and/or orientation (Sinclair, 1996; Tawakkal et al., 2014). Because it is biodegradable, it can also be employed in the preparation of bioplastic, useful for producing loose-fill packaging, compost bags, food packaging, and disposable cutlery (Nofar et al., 2019). In the form of fibres and nonwoven textiles, PLA also has many potential uses, for examples upholstery, disposable garments, awnings, feminine hygiene products, and nappies (Adomavičiūtė et al., 2015; Avinc & Khoddami, 2009; Gürcüm & Üner, 2015). PLA has been used as the hydrophobic block of amphiphilic synthetic block copolymers that is used to form the vesicle membrane of polymerases (Noack et al., 2018; Oh, 2011).

PLA has been suggested to produce horticultural materials to reduce the environmental problem as a large quantity of plastic is used in this sector (Oliveira et al., 2014). PLA is also used as a matrix for

controlled release of herbicides (Roy et al., 2014; Šopík et al., 2019). Earlier, a study was conducted to evaluate the impact of PLA in growth stimulation and yield improvement (Bidyarani et al., 2016; Nampoothiri et al., 2010). Previous greenhouse study confirmed that both lactide and PLA have increased the soybean leaf area, pod number, bean number and bean and plant dry weight (Chang et al., 1996). This study suggests that the use of PLA as an encapsulation matrix for herbicides could reduce environmental impact and improve weed control and at the same time increase the yield of soybeans through releasing of plant growth stimulants in the form of oligomeric or monomeric lactic acid.

An application of PLA film precursor by using isothermal polarization method was used to made eletret (Galikhanov et al., 2016; Guzhova et al., 2016b; Guzhova & Galikhanov, 2015). PLA eletret demonstrate charge storage capability (Gao et al., 2016; Guzhova, et al., 2016a) and forbid charge absence through the volume (Nakagawa et al., 2004; Zeng et al., 2015). PLA are widely used in variety of application such as transistor, filter and transducer (Urbaniak-Domagala 2013).

Conclusion

Research on a recyclable and degradable polymer is very important to environment. PLA offers a possible material which can replaced nonbiodegradable polymers. This is because of its promising property such as did not produces toxic fume if incinerated, composable in soil and comparable physical properties with another petroleum-based polymer. Even though PLA devours many limitations on processing due to its material properties, researchers have worked tirelessly to find a method that can overcome these problems. Some of the methods that have been discovered to overcome PLA limitations are through blending PLA with other polymers, making micro and nanocomposites of PLA, coating with high barrier materials, and with polymer modification.

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