Various Types of Natural Fibers Reinforced Poly-Lactic Acid Composites

Moussaoui Nafissa, Benhamadouche Lamia, Mohammad Jawaid, and Mohammad Asim

Abstract Advance composites are considered as the substitute of solid waste wood. By utilizing these waste materials with different type of polymers enhance the properties of material and also make efficient to use as product. Advance composites are also fulfilling the requirement of environment concerns. Polylactic acid (PLA) is one of the biopolymer, have been studied extensively, the basic studies such as structural and extraction process have been discussed. Many different type natural fibres and biopolymers are being used to prepare biodegradable materials. The properties of natural fibre have been studied on the basis of the chemical compositions that decide the properties of single fibre. There are several test have been conducted such as mechanical, thermal, physical, and weathering test on natural fibre reinforced PLA composites. In this chapter, PLA based natural fibre composites have been studied and their properties have been elaborated.

Keywords Polylactic acid · Natural fibre · Biocomposites · Thermal properties · Mechanical properties · Weathering properties

1 Introduction

The evolution of civilization has generally been influenced by man's need to find out new materials, enabling him to introduce the necessary properties to the increasingly more sophisticated tools of destruction. Companies that have gained experience in exploiting new materials, however, have enjoyed distinct advantages over their neighbors (Oksman et al. 2003). This has been widely illustrated in terms of key materials in which humankind has passed from the Stone Age to that of Bronze, the Iron Age,

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and steel. Bio composites are among the most popular materials of contemporary life or modern times which have transformed our lifestyle.

Nowadays, conception with a view to reconstruction or in a slightly broader perspective, eco-design is increasingly a philosophy that applies to products and materials. With the recent increase in environmental awareness, the use of natural fibers has become a major focus and important (Gassan and Bledzki 1999; Kalia et al. 2009). Natural fibers own many benefit, such as lightness, small density, availability and relatively lofty mechanical properties, like that as specific module and specific resistance (Asim et al. 2018; Gassan and Bledzki 1999; Omrani et al. 2016). Recently, natural cellulosic fibers are increasingly attractive to scientists as an alternative reinforcement in polymer composites (Begum and Islam 2013; Mohammed et al. 2015; Sepe et al. 2018; Thakur et al. 2014; Wambua et al. 2003). They are obtainable in large quantities and provide a new generation of reinforcements in polymeric materials. These eco-friendly fibers have been used as replacements for fiberglass, carbon, Kevlar, and other plastic polymer fibers in a variety of applications (Atiqah et al. 2014; Begum and Islam 2013; Wambua et al. 2003). Natural fiber composites aid in the conservation of non-renewable resources, which are the primary source of most materials used in today's applications.

Reinforcing building materials (concrete, mortar, and composite) with fibers is an increasingly popular technique. The introduction of nanocellulose and micro cellulose as reinforcements in polymer matrices (biodegradable or not) used in composites (such as glass fibers and carbons) (Chen et al. 2009; Frone et al. 2011; Liu et al. 2010; Lu et al. 2008; Sanjay et al. 2018).

Vegetable fibers can be associated with matrices of different natures. The use of plant fibers in a thermoplastic or thermosetting matrix (polypropylene polyethylene, epoxy or phenol–formaldehyde resins, polystyrene, and styrene) was the subject of many studies in the last few years (Frone et al. 2011; Liu et al. 2010; Lu et al. 2008; Nakagaito and Yano 2008). It is a technique already used and industrialized especially in the automobile (interior panels, floors of trucks, etc.), the construction (coating, profiles of doors and windows, closure) where is still domestic equipment (furniture of the garden) (Edhirej et al. 2017). They can replace glass fibers because of their mechanical performance.

The use of vegetable fibers (straw, flax, abaca, jute, banana, date palm, bamboo …), as a reinforcement of material, has aroused a keen interest during the last decade (Edhirej et al. 2017; Thakur 2013). Strengthening materials with these fibers reduces disposal problems because they are easier to recycle or burn than mineral fiber materials. When biodegradable materials are reinforced with plant fibers, these materials remain biodegradable and can be used in situations where they are subjected to loads. In recent decades, a great deal of works has been done to investigate the possibility of using natural fibers as a reinforcing element of thermoplastic and thermosetting materials, due to their environmental benefits and low cost (Thakur 2013). They offer further perspectives in waste collection because they are of biological origin and can hence give rise to vastly functional composite materials used in association with thermoplastic polymers (Wollerdorfer and Bader 1998).

The substitution of non-decomposable matrices by decomposable materials makes it possible to obtain entirely degradable and renewable composites (Atiqah et al. 2014; Begum and Islam 2013; Mohammed et al. 2015; Sepe et al. 2018; Thakur et al. 2014). Materials derived from renewable resources are receiving increasing interest from the academic and industrial worlds. They are very varied in nature and often have interesting characteristics. In the bioplastics market, there is a wide variety of polymers from renewable resources, including polyesters such as polylactide (PLA). The latter is without a doubt one of the most prospective competitor for future advancement as it is not only biodegradable but also made from renewable resources like corn starch (Garlotta 2001; Hartmann 1998; Jonoobi et al. 2010; Oksman et al. 2003). Poly-lactic acid have a high potential to replacement petroleum-based plastic due to its elevated mechanical properties and its process ability in comparison of other bio polymers, making it suitable with a variety applications such as automotive, medical and agriculture (Dorgan et al. 2005; Haafiz et al. 2013; Lim et al. 2008; Najafi et al. 2012; Oliveira et al. 2016). Poly lactic acid is a versatile polymer, completely degradable, produced from pure substances regenerative that ferment in acid. The ratio of the two acid molecules (D-lactic and L-lactic), that are composed of an amorphous to semi-crystalline or crystalline material, could alter the characteristic of PLA (Shen et al. 2009).

2 Natural Fibers

Natural cellulosic fibers have been utilized for 3000 years in composites, for example in antique Egypt, where clay and straw were blended to build walls. In the latest decade, natural fiber-reinforced polymer have attracted the attention from both academia and industry because of the advantages they over offer synthetic reinforcing fibers such as carbon and glass. The development of natural fibre composites has therefore been the subject of research over the last ten years. These natural cellulosic fibers are economical, very eco-friendly with specific properties, for example, they are non-abrasive and biodegradable (Li et al. 2007; Saheb and Jog 1999).

2.1 Natural Fibers Types'

Natural fibers, which are often cellulose fibers, are sorted according to their origin; they come from different areas of the plant: leaves (palm, banana, Alfa, pineapple, etc.), Seeds (Kapok, cotton, milkweed, etc.), Bast or stem (Kenaf, hemp, jute, ramie, bamboo, etc.), Fruit (coconut fiber, etc.) (Van Rijswijk et al. 2001).

As with all natural products, the mechanical and physical properties of natural fibers change significantly. These properties are governed by structure, chemical composition and depend on fiber types, age, plant organs and growing conditions.

Table 1 Classification and examples of natural fibers (Bismarck et al. 2005)

Origin	Provenance	Examples
Vegetal	Seeds	Cotton, kapok, milkweed
	Fruits	Coconut
	Bastor stem	Hemp, jute, ramie, kenaf
	Leaves	Sisal, henequen, abaca, pineapple
	Wood	Wheat, corn, barley, rye, oats, rice
	Stalk	Bamboo, bagasse, Alfa, reed
	Canes and reeds	
Animal	Wool/hair	Wool, hair, cashmere
	Silkworms	Mulberry silk, tussah silk
Mineral		Asbestos, Wollastonite

Table 2 Commercially important fiber sources(Salit et al. 2015)

Fibre source	Species	World production (10^3 tonnes)	Origin
Wood	(>10,000 species)	1,750,000	Stem
Bamboo	(>1250 species)	10,000	Stem
Cotton lint	Gossypiumsp	18,450	Stem
Jute	Corchorussp	2,300	Stem
Kenaf	Hibiscus cannabinus	970	Stem
Flax	Linumusitatissimum	830	Stem
Sisal	Agave sisilana	378	Stem
Roselle	Hibiscus sabdariffa	250	Stem
Hemp	Cannabis sativa	214	Stem
Coir	Cocos nucifera	100	Stem
Ramie	Boehmerianivea	100	Stem
Abaca	Musa textiles	70	Stem
Sunn hemp	Crorolariajuncea	70	Stem

The main component of all plant fibers is cellulose; it varies from one fiber to another (Tables 1 and 2).

2.2 *Chemical Composition of Natural Fibers*

Cellulosic fiber is a composite in itself. The reinforcement is constituted by layers of partially crystalline cellulose microfibrils. The latter is coated with an amorphous polysaccharide matrix (hemicelluloses and pectin) which is associated with hydrogen

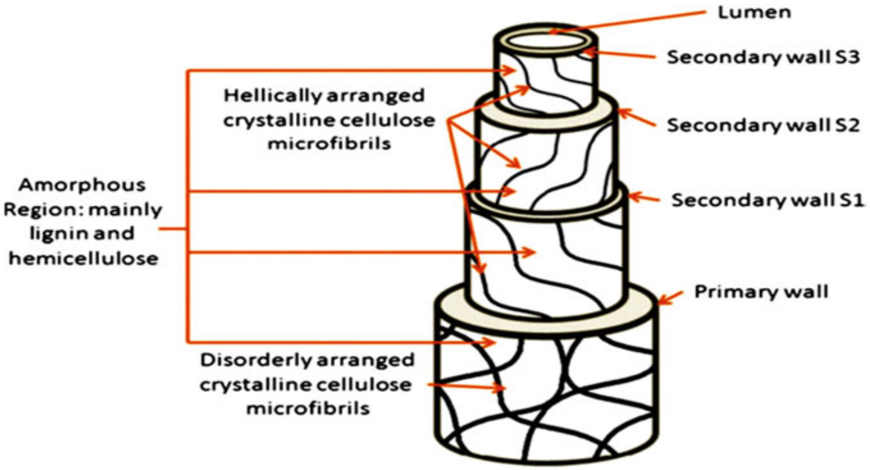

Fig. 1 Model for describing the structure of a plant fiber cell (Salit et al. 2015)

bonding and covalent lignin (Fig. 1) shows that the cellulose microfibrils are helically rolled up along the axis of the core fiber.

The orientation of the micro-fibril about the axis of the cell plays a large role on the mechanical properties of the fiber walls, more angle of the micro-fibril increases, the Young module decreases, while the extensibility of the walls increases (Dicker et al. 2014). The moreover, hemicellulose has a key role in the humidity absorption, bio decomposition, and thermal degradation of natural fibers. However, Lignin is responsible for the rigidity and hardness of wood and of plants. The proportions of theses constituents vary greatly according to the fibers and cellulose is the major constituent element. In general, natural fibre contains other organic components, in addition to cellulose, hemicelluloses and lignin. It contains about 2–6% starch, 2% deoxidized saccharine, 2–4% materials grasses, and 0.8–6% protein (Saheb and Jog 1999). The quantity of each constituent of a fiber depends in particular on the quality of the soil where the plant was grown, its level of maturity, the quality of the retting process, the conditions for measuring properties (humidity, temperature), etc. All these parameters explain the great differences between the values found in the literature (Beg 2007).

Cellulose is a natural polymer whose molecules, formed by long chains, consist of D-anhydro-glucopyranoses bound by β-(1,4)-glycosides bonds in positions C1 and C4 (Fig. 2). The degree of polymerization (DP) is about 10,000, it varies according to the plant species. The hydroxyl groups play a large role in the crystalline (Beg 2007; John and Anandjiwala 2008).

Unlike other fiber components that have an amorphous structure, cellulose has a large crystalline structure. Crystalline cellulose is one of the polymers with the highest modulus of elasticity, about 136 GPa compared to 75GPa of fiberglass (Beg 2007; John and Thomas 2010).

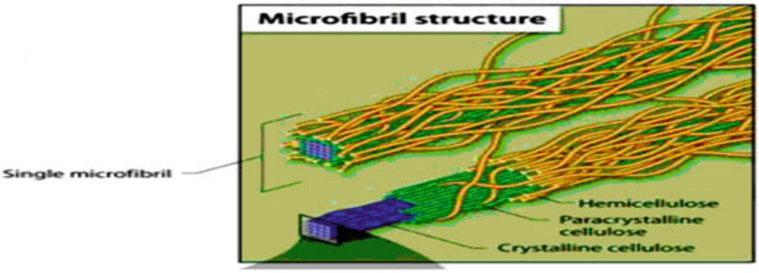

Fig. 2 Structure of the cellulose microfibrillar (Siqueira et al. 2010)

Lignin's an extremely heterogeneous macromolecule composed of aromatic polymers. It represents, after polysaccharides, the more abundant natural polymer in nature. It helps protect plants against the attack of pathogenic organisms and structural rigidity of cell walls. Lignin is made up of three-dimensional phenolic polymers, amorphous with three different penylopropane-type units: p-coumaryl, coniferyl, and sinapyl alcohols (Fig. 3). In the process of lignification, plant phenoloxidases as laccases are implicated and permit of the different elementary units to polymerize. After synthesis, lignin combines with various polysaccharides to form a matrix that forms the plant wall (Klyosov 2007).

Hemicellulose consists of a selection of polysaccharides (Dxylopyranose, D-glocopyranose, D-galactopyranose, etc.) which occur in short and highly branched chains. The degree of polymerization in this polymer is 20–300 times lower than

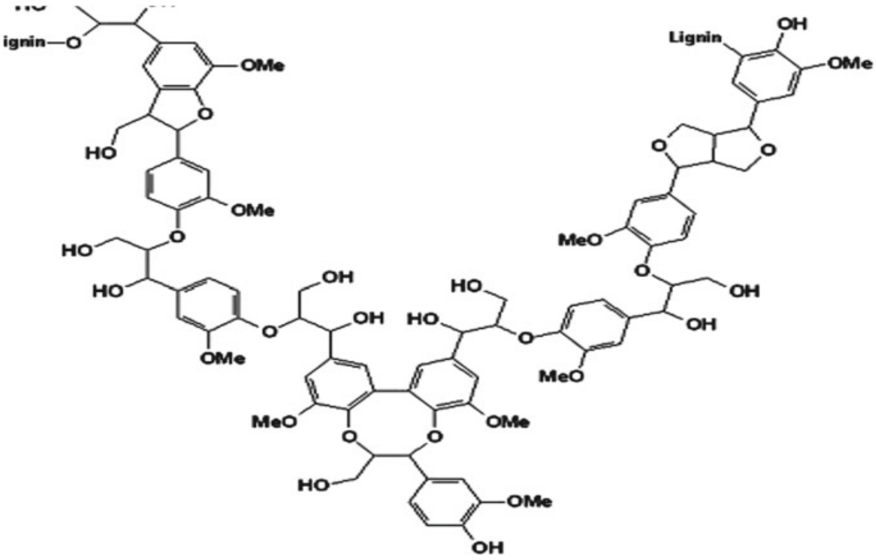

Fig. 3 Schematic representation of lignin (Klyosov 2007)

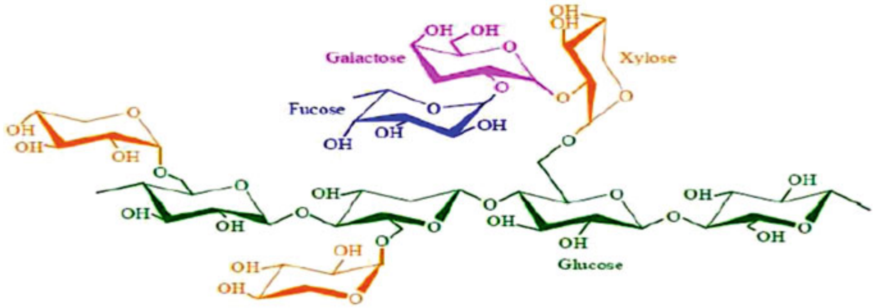

Fig. 4 Structure of a type of xyloglucan (Thygesen 2006)

in cellulose (Thygesen 2006). Hemicelluloses are different from celluloses by their multiple varieties of saccharides constituting the polymer that is different from one plant to another. Unlike cellulose, which is a linear polymer, hemicelluloses have a considerable degree of chain branching. Also, hemicellulose is rarely crystalline and is responsible for the sensitivity of the fibers to water through the interface (hydroxyl groups). This increases the risk of degradation due to external agents (bacteria, acids, etc.). One of the most studied hemicellulose classes corresponds to xyloglucans (Fig. 4).

A pectin is a group of complex heteropolysaccharides that typically represent about 35% of the primary walls in dicotyledons and 2–10% in monocotyledons. The structure of the pectin depends on the plant species and the proportions of the different types vary according to their position in the cell walls (Sakakibara 1980). Pectin's also the more hydrophilic compounds in plant fibers because of the existence of carboxylic acid groups.

3 Polylactic Acid

Polylactic acid (PLA) is aliphatic polyester; generally, it is based on α-hydroxy acids. These include polymandelic acid or polyglycolic acid. These acids are compostable and biodegradable. PLA is a thermoplastic polymer, with high mechanical characteristics (strength and modulus). Annually, it may be produced from renewable resources (Garlotta 2001).

Consequently, it has generated a lot of interest in potentially replacing petroleum-based polymers. Special qualities of PLA have been improved for biomedical uses even before its introduction as a packaging and base material. The commercial launch of biobased PLA in 2003 paved the way for more common applications. Its biocompatibility and bioresorbability made it an appropriate choice for applications including blood vessels, drug delivery systems, sutures etc.

In particular, PLA has found a significant number of applications in the packaging industry thanks to its excellent mechanical properties, transparency, and compostability (Saeidlou et al. 2012). The reinforcement of PLA with natural fibers appears to be an ideal choice to increase their mechanical characteristics and preserve the ecological character of the final product (Girones et al. 2012). In the majority of cases, the direct polycondensation method (Fig. 5) was used to prepare PLA from lactic acid. The resulting PLA had low molecular weight and poor mechanical properties. The performance of PLA has increased considerably following the evolution of production with open ring polymerization. This method requires a secondary substance such as lactide. Lactide is the periodic dimer of lactic acid, and it can be in the form of L-lactide, L, D-lactide (meso-lactide), and D-lactide stereo complex (Fig. 6). Currently, PLA synthesis rarely starts with chemically synthesized lactic acid. The lactic acid that is used is resulting from the transformation of carbohydrates like starch and cellulose. The majority of it comes from corn and cassava harvests. Fermentation created on microorganisms gives principally L-lactic acid (Ebnesajjad 2012).

For PLA to be produced on large-scale production lines in applications such as blow molding, injection molding, extrusion, and thermoforming, the polymer must have appropriate thermal stability to avoid degradation and retain its molecular weight and qualities. PLA is thermally degraded at temperatures exceeding 200 °C (392 °F) (Iwata 2015) by hydrolysis, lactide regeneration, dissociation of the main chain by oxidation, and by intra- or intermolecular transesterification processes.

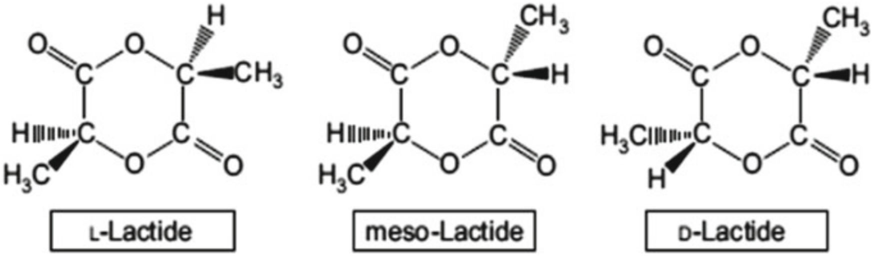

Fig. 5 D-Lactide stereo complex

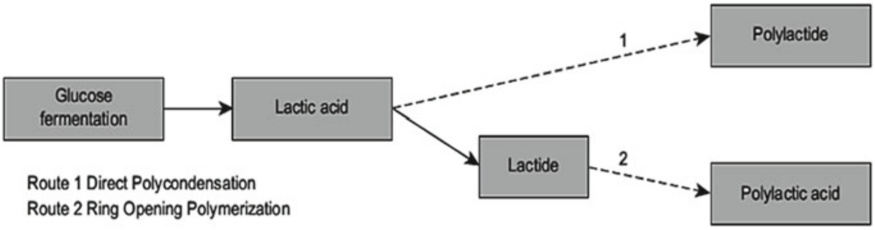

Fig. 6 General route of PLA production

The main reasons for PLA degradation are low molecular weight impurities, catalyst concentration, temperature, and time (Iwata 2015). Oligomers and catalysts increase the degree of degradation and reduce the degradation temperature of PLA. They can also cause changes in viscosity and rheology, fumes in the treatment process, and low mechanical characteristics.

Poly (lactic acid) homopolymers have a glass transition and melting temperature of approximately 175 °C and 55 °C respectively. They need processing temperatures between 185 and 190 °C (Spinu et al. 1996). At this stage, chain splitting and decompression reactions are known to occur, leading to a decrease in molecular weight and thermal degradation. Therefore, PLA homopolymers have a very short treatment period. The most common method to improve the transformability of PLA is based on the reduction of the melting point by random incorporation of small doses of lactic enantiomers of opposite form in the polymer (i.e. the addition of a small amount of D-lactide to L-lactide to get PDLLA). Unfortunately, the reduction in melting point leads to a significant decrease in crystallinity and crystallization rates (Spinu et al. 1996).

3.1 Synthesis of Polylactic Acid

The elemental component of PLA is lactic acid, which was first isolated in 1780 from sour milk by the Swedish chemist Scheele and produced for the first time in commerce in 1881 (Hartmann 1998). Food-related uses represent the main exploitation of lactic acid in the United States and account for approximately 85% of the product's market it is present in many processed foods as a buffer, acid flavoring agent, acidulant, and bacterial inhibitor. Lactic acid is formed either by chemical synthesis or by carbohydrate fermentation, which is the most predominant method (Benninga 1990; Frant 1981; Kharas et al. 1994).

Lactic acid (2-hydroxy propionic acid) is the most elemental of the hydroxy acids that have an asymmetric carbon atom and can be in two visually active compositions.

The L(+) isomer is produced in mammals including humans, while the D(−) and L(+) enantiomers are both derived from bacterial systems. Most of the lactic acid marketed worldwide is obtained by carbohydrates bacterial fermentation, from homolactic organisms such as various optimized or modified strains of the genus Lactobacilli, which constitute only lactic acid (Hartmann 1998). The Organisms producing mainly the L(+) isomer are L. bavaricus, Lactobacilli amylophilus, L. maltaromicus, L. casei, and L. salivarius. While isomer D or mixtures of both are given by strains such as L. delbrueckii, L. jensenii, or L. acidophilus (Hartmann 1998). The bacteria considered homofermentative produce lactic acid via Embden-Meyerhof and convert up to 1.8 mol of lactic acid per mole of hexose (i.e. more than 90% produce glucose-based lactic acid). From feedstocks, these strains produce high carbon conversions for animals under standard fermentation conditions, such as temperatures around 40 °C, relatively small to neutral pH, and low oxygen concentrations (Enomoto et al. 1994).

The different types of carbohydrates that can be used in fermentation processing are due to the specific strain of Lactobacillus. In principle, the majority of simple sugars extracted from agricultural by-products can be used. These sugars contain (1) sucrose from cane or beet sugar; (2) glucose, maltose, and dextrose from corn or potato starch; and (3) lactose from cheese whey. In addition to carbohydrates, organisms also require protein and other complex nutrients such as B vitamins, amino acids, and nucleotides, which must be obtained from corn liquor, yeast extract, cottonseed meal, or soy flour. These needs are highly dependent on the different species and it is common to create strains around existing nutrients, which can lead to considerable additional costs (Benninga 1990; Enomoto et al. 1994; Kharas et al. 1994).

Fiber reinforcement is a possibility to improve thermal stability. Polylactide polymers are rigid and brittle materials, so plasticizers are needed to improve stretching and impact resistance properties. The polylactide is completely biodegradable. Degradation is by hydrolysis to lactic acid, which is metabolized by microorganisms to water and carbon monoxide. By composting with other biomasses, biodegradation occurs in 15 days, and the material has completely disappeared in three or four weeks (Oksman et al. 2003).

4 The Properties of Natural Fiber/PLA Composites

4.1 Thermal Properties

Knowledge of the thermal properties of composites natural fiber/PLA is essential to develop the best methods for transforming these materials into useful products and to predict performance throughout the life of the products. It also provides essential information for troubleshooting when the material is not functioning as intended or when a product or process element needs to be modified, such as raw materials. The determination of principal characteristics of polymer systems, such as thermogravimetric analysis (TGA), glass-to-rubber transition temperature (Tg), and melting point (Tm), is essential using differential scanning calorimetry (DSC) experiments. In the latter case, Tg is usually determined as the inflection point of the specific heat increment at the glass–rubber transition. Dynamic mechanical analyses (DMA) can also be utilized to evaluate the Tg. However, a relaxation mechanism is demonstrated in the Tg temperature range by DMA analyses. Today, PLA is considered the most credible alternative to replace conventional polymers in composites, their thermal properties investigated for the potential use in load-bearing applications such as body-in-white and body structures in the automotive sector. The Tg of PLA depends on the molecular weight, optical purity (enantiomer), and thermal history of the polymer (Sarasua et al. 1998). The degree of crystalline is based on many parameters such as molar mass, temperature and annealing time, as well as on many key properties of a semi-crystalline polymer, including stiffness, fragility, toughness, etc. (Ahmed et al. 2009).

For example, Pan et al. (2007) observed that the addition of Kenaf (KF) considerably increased the crystallization rate and the tensile and storage modulus. The PLLA crystallization can be completed from the melt at 5 °C/min with the addition of 10% by weight of Kenaf during the cooling process. Also found that the size of the spherulite decreases in isothermal crystallization and the nucleation density increases considerably with the presence of Kenaf. Furthermore, with the addition of 30% by weight of Kenaf, the half times of isothermal crystallization were lowered to 46.5% and 28.1% of pure PLLA at 120 °C and 140 °C, respectively. Tawakkal et al. (2014) noted that thermo gravimetric analysis of the incorporation of 5% and 10% (w/w) thymol in pure PLA and PLA/kenaf composites shows that there is no significant change in decomposition temperature, while analysis by differential scanning calorimeter indicate a decrease in all key thermal transitions (Tg, Tcc, Tm and Hm). The test results for thermal properties suggest that thymol in these composite functions as a plasticizing agent. Tokoro et al. (2008) have incorporated three varieties of bamboo fibers into a PLA matrix to improve its impact strength and heat resistance. Their studies have led to the creation of good quality composite materials. The presence of bamboofibers considerably increases the impact resistance and thermal properties. Qin et al. (2011) confirmed that PLA/RSF (rice straw fiber) composites with PBA increased thermal stability. DSC data showed that RSF acted as a nucleating agent and that PBA made crystallization of PLA more difficult and incomplete. The available literature shows that thermo-mechanical analysis (TMA) should be performed in the future to improve the understanding of the influence of the addition of natural fibers in PLA composites.

4.2 Mechanical Properties

Recent research has indicated that PLA is a very suitable polymer matrix for natural fiber-filled composites. For example, Tokoro et al. (2008) have reinforced a PLA matrix with 3 kinds of bamboo fibers to increase its impact. Their studies are caused in good quality composite materials, with the presence of bamboo fibers significantly increasing impact performance. Ochi (2008) studied kenaf/PLA composites with diverse ratios of fibers. He showed that Young's modulus, tensile, and bending strength increased linearly up to 50% wt of the fiber content in the composite. The study found that unidirectional biodegradable composites made from emulsion-type PLA resin and kenaf fiber at 70% by weight had high bending and tensile strengths of respectively 254 MPa and 223 MPa. Shibata et al. (2004) have developed materials with PLA/lyocell fabric by compression molding. The tensile strength and modulus of the lyocell/PLA composites have been upgraded by increasing the fiber content. The impact resistance was significantly greater than that of pure PLA. Pan et al. (2007) as well developed PLA/kenaf composites by injection molding with kenaf fiber contents between 0 and 30%. At 30%, a 30% improvement in tensile strength was noted.

The extensive use of biocomposites in the manufacture of vehicle components would greatly benefit the industry, but to date, their low mechanical characteristics, associated mostly with thermal stability and the interactions between the matrix and the fibers, limit their usage. While studies mention the properties and potential improvements of biocomposites, the general mechanical behavior from a structural point of view is not fully understood and the mechanical performance is under target. Biocomposites are not yet adopted in mass-produced products in the automotive transport industry because their mechanical properties and performance in different environments and their effect under different loading conditions are not sufficiently taken into account. Biocomposites are not yet adopted in mass production in the automotive industry because their mechanical properties and performance in different environments and their effect under different loading conditions are not sufficiently taken into account (Nassiopoulos and Njuguna 2015).

The mechanical properties of fiber-reinforced composites are influenced by the length of fibers, the degree of filling, the aspect ratio of fibers or fiber bundles, the morphology of the fibers and the orientation of the fibers or bundles of fibers, and the degree of polymerization of the cellulose in the fiber. The mechanical characteristics of PLA-based composites also probably depend on the specific properties of the polylactide (e.g. residual lactide content, molar mass) as well as the processing conditions (e.g. catalyst, pre-drying, and processing temperatures) (Mohanty et al. 2005). Lanzillotta et al. (2002) found that the tensile strength of injection-molded PLA was not upgraded by adding 20–40% w/w of flax fiber. The authors justified this to poor adhesion between flax and PLA. The significant reduction in fiber length observed by these researchers may also partly justify the absence of an increase in the tensile strength of composites. Though, with increasing flax content, Young's modulus of these biocomposites increases linearly. After studying the chemical modification of fibers (for example, etherification, esterification) and reactive extrusion to modify PLA during treatment, the authors also concluded that improvements to the composite properties derived from the composite did not justify the associated costs.

The research group of the Structural Mechanics Institute of the German Aerospace Centre has developed and controlled PLA biocomposites reinforced with natural fiber mats. A composite Young's modulus of about 10 GPa and tensile strength of about 90 MPa were the results of their work (Riedel and Nickel 1999). The same authors cited in a later report that the bending modulus for PLA biocomposites was comparable to that for glass fiber reinforced polymers (Nickel and Riedel 2001).

The main objective of incorporating fibers into a polymer matrix is to significantly improve the modulus of the material, but this effect depends on the type and content of fiberin the matrix. It has been shown that the modulus of elasticity measured for PLA reinforced with 30% flax or cotton increases by 1.5–2.5 times that of crude PLA, depending on the type of fiber modification (Thakur and Thakur 2016).

4.3 Weathering Properties

It was found that the mechanical characteristics of PLA can be similar to those of traditional petroleum-based polymers. For this reason, PLA will be considered as an alternative polymer that can be exploited in other fields, particularly in the automotive sector. In this context, it is necessary to study the external properties of PLA, i.e. its resistance to weathering. In particular, the influences of UV and moisture exposure on the mechanical and other characteristics of PLA become critical (Kaynak and Kaygusuz 2016).

However, in the literature, there are not many studies (Copinet et al. 2004; Ikada 1997; Janorkar et al. 2007; Ndazi and Karlsson 2011; Shinzawa et al. 2012) on the consequences of weathering and their degradation processes. In general, the principal degradation process of ultraviolet (UV) irradiation observed is the random "main chain separation" in the chemical bonds of the PLA backbone by the absorption of a photon (Ikada 1997; Janorkar et al. 2007). The molecular weight of PLA is significantly reduced via "photolysis" of the C–O and C–C bonds, and/or the main "photo-oxidation" to produce carboxylic acid and ketones. The most important moisture degradation process described in the bibliography (Copinet et al. 2004; Ndazi and Karlsson 2011) after a decrease in molecular weight is the "hydrolysis" of the C–O bonds in the ester bonds of the PLA structure, which can also produce carboxylic acid and ketones. We have found other several works based on the study of the natural weathering and accelerated aging properties of composites PLA reinforced such as keratin (Spiridon et al. 2013), montmorillonite (Jandas et al. 2013; Zaidi et al. 2010), hempfiber(Islam et al. 2010), epoxy natural rubber and rice starch (Yew et al. 2009), cellulose whiskers (Grigsby et al. 2013) and condensed tannin (Bolio-López et al. 2013). In general, these studies have shown that the added fillers most often increase the level of deterioration without having an important influence on the processes.

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