

PLA based biocomposites for sustainable products: A review

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ABSTRACT

In recent decades, demand for sustainable materials in place of low cost and high strength materials has been triggered globally, which has motivated researchers towards biocomposites/green composites. The PLA has been the most promising matrix material for sustainable biocomposites owing to its biodegradability, good availability, eco-friendliness, antibacterial property, and good mechanical and thermal properties. The PLA-based biocomposites are economical, full/partial biodegradable depends upon types of reinforcement, light in weight, and also offer good thermal and mechanical properties. A number of research works have been performed on PLA and its biocomposites to explore their potential for sustainable products. However, no comprehensive review with up-to-date research data on PLA and its biocomposites are reported so far. This fact motivated to summarize the reported studies on PLA and its biocomposites. The aim of present review is to highlight the current and past trends in the research of PLA and its biocomposites. This review article covers current and past efforts reported by researchers on the synthesis and sustainability of PLA, processing, characterization, applications and future scope of its biocomposites. This study observed that PLA-based composites are the most emerging materials that can replace existing non-biodegradable and non-renewable synthetic materials. The PLA-based biocomposites could be considered as the best source of sustainable products. PLA's mechanical and thermal properties can be enhanced by reinforcing the nano and micro sizes of natural fibers and cellulose.

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1. Introduction

Most of the commonly used plastics, such as polypropylene (PP), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), etc., are synthetic polymers manufactured from petroleum and its allied components [1]. Petroleum-based products are globally concerned due to their non-biodegradable and non-biocompatible nature, and petroleum reserves are depleting expeditious due to massive consumption worldwide [2,3]. These global environmental concerns and regulations have triggered researchers to develop biodegradable and biocompatible materials which could replace conventional petroleum based products [1]. Biocomposites are considered the best alternative materials to address these issues and ensure an eco-friendly and sustainable environment [4,5]. In biocomposites, matrix materials are derived from agricultural waste and reinforcement materials are natural fibers derived from biomass and agricultural waste. The natural fibers are composed of cellulose,

hemicellulose and lignin [6]. The first partially biodegradable composites were prepared in the 1890s using thermoplastic resin and cellulose fibers [7]. The advantageous characteristics of biocomposites (i.e., biodegradability, no toxicity, renewability, low density, good mechanical properties, economical, etc.) have drawn the attention of researchers and scientists as potential alternatives for petroleum based products [8–10]. In addition, they also have acoustic and thermal insulation properties. These excellent properties make them suitable to be used in a wide range of applications in various fields: automobile industry (door panels, boot linings, wheel boxes, storage panels and noise insulation panels, etc.), packaging (food packaging, laptop and mobile casing and its covers, bottles) and electronic and goods packaging, etc., Sports (bicycle frame, rackets, helmets and surfing boards, etc.) and construction (door panels, window frames, railings and furniture, etc.) [11–13].

There are numerous natural and synthetic biodegradable polymers available such as poly-lactic acid (PLA), poly-lactic-co-glycolic acid (PLGA), polyethylene glycol (PEG), poly-hydroxy butyrate (PHB), polycaprolactone (PCL), etc. That can be used as matrix materials for the development of biocomposites. Among these, PLA is the most suitable and promising candidate to replace petroleum

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based plastics, because it is renewable. This biodegradable polymer is obtained from agricultural products such as corn, sugar beet, starch, soy protein, etc. It possesses good mechanical properties, thermal properties and good transparency. Its properties can be extensively improved by manufacturing biocomposites with the reinforcement of different natural fibers in the PLA matrix, as reported in the literature [5,14,15].

The research works carried out in the field of PLA biocomposites is systematically discussed in this review paper. This study provides a better understanding of the PLA and its biocomposites in terms of their development, advantages, disadvantages, recent trends and possible opportunities for the future. This review work could be very useful to new researchers who wish to start work on the development of sustainable products using biocomposites/green composites.

2. Poly-lactic acid (PLA)

According to history, Wallace et al. [16] first attempted to develop PLA in 1932 using the polymerization and depolymerization of oligomeric lactides and the later patent was filed by Du Pont in 1954 [17]. Around the 1960s, the high molecular weight PLA was prepared by modifying the techniques, which have comparable properties to petroleum-derived plastics. But this method of production was not economical. The commercial production of PLA was started in 1997, after the development of the process by Cargill Dow Corporation [17]. In this technique, the melting technique synthesized PLA rather than the solution. The first continuous production of PLA was started in 2002 in Blair, Nebraska, with a capacity of 300 lbs annually. The production of PLA on a large scale ultimately reduced the cost of PLA production drastically. PLA is bio-based material and has the property of inherent biodegradability. It is widely used for food packaging applications. The body can easily observe it; therefore, PLA was the first polymer used for biomedical applications [18]. According to Jem's law, the market of PLA is increasing globally and demand doubles every 3–4 years [8,19].

PLA is a trendy aliphatic thermoplastic polymer derived from renewable resources such as sugarcane, maize, cassava, corn, etc. It is a fully biodegradable and biocompatible biopolymer. It requires low energy consumption and produces minimum greenhouse gases during its production. The many advantageous properties of PLA (i.e., biodegradability, good availability, eco-friendliness, antibacterial property, and good mechanical and thermal properties) make it a promising polymer for sustainable products. Some demerits of PLA are also reported such as low toughness, low barrier properties, low thermal resistance, low glass transition temperature, etc.

The mechanical properties of PLA are compared with some other polymers such as polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS) and nylon as depicted in Table 1. The tensile modulus of PLA was the highest among all the polymers. At the same time, it has higher tensile and flexural strength than PVC and PP. PLA is a thermoplastic polymer that can be cast and molded into various complex shapes and reshaped for different applications. In

addition to these properties, it has good thermal stability, and oil and grease resistance properties at low temperatures. Its appearance makes it appropriate for domestic appliances like bottles, cups, trays, etc. [20].

PLA is produced from monomer - Lactic acid (2 hydroxy propionic acid), which Swedish chemist Scheele discovered in 1780. The chemical structure of monomer lactic acid is shown in Fig. 1. It has two different stereo-isomers, dextrorotatory form L (+) isomer and levorotatory form D (−) isomer. Both isomers are mirror images of each other and the sign signifies the direction of rotation of plane polarized light, L (+) isomer rotates the plane of polarized light clockwise and D (−) isomer rotates in anticlockwise direction [21]. These isomers can also be referred as l -lactic acid (L-LA) and d -lactic acid (D-LA).

The chemical structure of PLA can be modified by changing the arrangement of l -lactic acid (L-LA) and d -lactic acid (D-LA) monomers in the polymerization process with the help of suitable catalysts and reactions condition. Generally, pure PLA has a semi-crystalline structure, but amorphous and crystalline structure polymers can be obtained by modifying the stereochemical composition of monomers [9]. The properties of a polymer depend on the chemical composition of the monomer present in the polymer. The standard physical properties of the PLA are shown in Table 2. Apart from this, PLA's physical and mechanical properties can be improved by varying D-LA and molecular weight, as suggested in the literature [9]. The PLA shows hydrophobic behaviour due to the presence of CH_3 in the chemical structure [23,24].

2.1. PLA synthesis

PLA is a thermoplastic polymer that can be obtained from lactic acid monomer through different processes such as; Ring-opening polymerization (ROP), poly-condensation, azeotropic dehydration and enzymatic polymerization. The conventional techniques for producing high molecular weight PLA require high temperatures of 180–200 °C, low pressure of 5 mm Hg and are also time-consuming. With the advancement of technology, high molecular weight PLA can be produced in less time with mild reaction conditions. Among these processes, ROP and poly-condensation of lactic acid are the most commonly used methods for making PLA.

The lactic acid monomer is produced by extracting sugar or starch in vegetable sources such as corn, sugar beet, starch, soy protein, etc, through either fermentation or petrochemical routes.

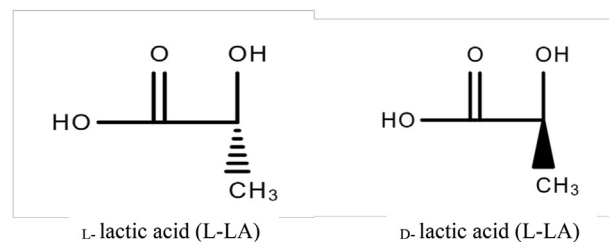


Fig. 1. Stereo-isomers of lactic acid.

Table 1
Comparison of mechanical properties of PLA with different polymers [22].

Polymer	Tensile modulus (MPa)	Tensile strength (MPa)	Flexural strength (MPa)	Elongation (%)
PLA	3.2	49	70	2.5
PVC	2.6	35.35	90	3.0
PP	1.4	49	49	10
PS	3.4	49	80	2.5
Nylon	2.9	71	95	5

Table 2
Physical properties of PLA [25].

Physical property	Range
Specific gravity	1–1.5
Melting temperature	140–210 °C
Molecular weight	Approximate 1.6×10^5 Daltons
Melt flow index	4–22 (g/10 min)
Crystallinity	5–35%
Glass transition temperature	50–75 °C
Solubility parameters	$21 \text{ J}^{0.5}/\text{cm}^{1.5}$

The petrochemical process is not widely used because lactic acid produced by this process has an optically inactive mixture of L and D lactic acid isomers [21]. The fermentation process developed in the 1990s was an efficient and eco-friendly approach to producing lactic acid monomers [12]. The *Lactobacillus* bacteria convert corn starch into lactic acid through fermentation. The steps involved in preparing PLA from agricultural waste are shown in Fig. 2. The preparation of PLA begins with the fermentation of starch in the medium of ammonia and bacteria in the reactor, which produces

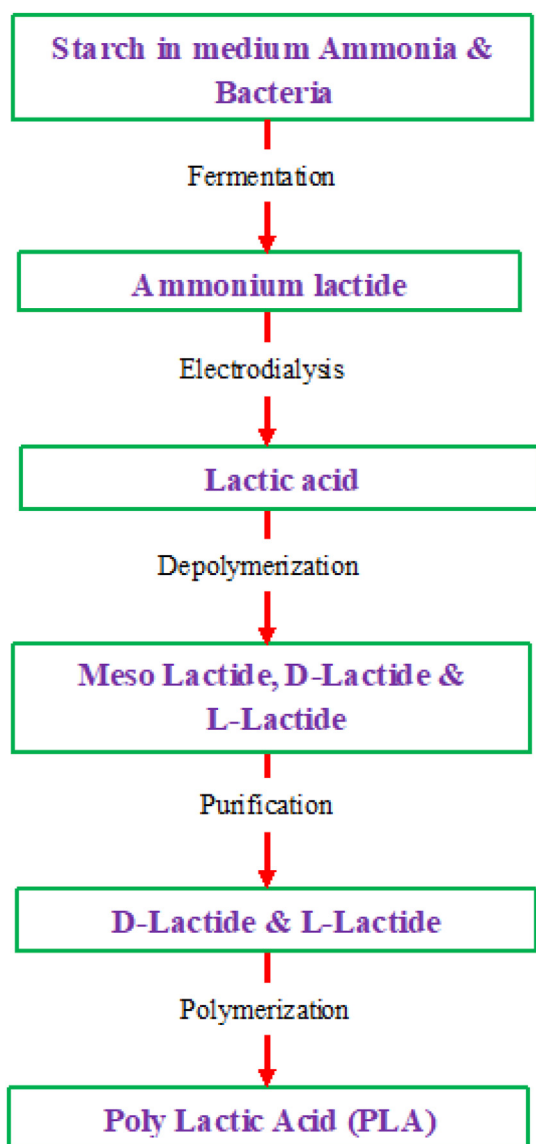


Fig. 2. Synthesis of PLA

ammonium lactate [26]. In subsequent steps, ammonium is separated by the electrodialysis process and produces lactide when ammonium lactate is passed through the water splitting chamber. The water is removed from the lactide and forms a prepolymer, depolymerization of lactide causes its breakdown into three subgroups, namely, L-lactide, D-lactide and meso lactide. The meso-lactide is removed by purification with the help of heat [27]. Then, this L-lactide, D-lactide is used as a monomer in the polymerization reaction that produces polylactic acid (PLA). Some catalysts are also used to increase the reaction rate and make an efficient polymerization process. The most commonly used catalyst is Tin stannous octotatate $\text{Sn}(\text{Oct})_2$ [28]. The lactic acids formed by fermentation have 99.5% L-lactic acid isomer and 0.5% D-lactic acid isomer. The polymerization of lactic acid monomers can produce PLA through poly-condensation and ROP.

This process produces low molecular weight PLA in the range of 2–10 kDa due to the presence of water and impurities. Ring-opening polymerization process is a solvent free process. In this process, catalysts and initiators such as tin (II) bis (2-ethyl hexanoate), commonly called $\text{Sn}(\text{Oct})_2$, in the presence of an alcohol (ROH) are used to convert cyclic lactide monomers into PLA [29], as shown in Fig. 3. This process provides high molecular weight PLA. Therefore, the Ring-opening polymerization technique produces PLA on an industrial scale [30].

2.2. Sustainability of PLA

PLA is a sustainable polymer from renewable resources that is fully biodegradable and eco-friendly. When PLA products complete their life and decompose in the environment, it produces carbon dioxide (CO_2) and water (H_2O), which are utilized for the production of vegetable products by the photosynthesis process. These agricultural products are again utilized for the production of PLA. The steps involved from PLA production to its complete decay are represented by the life cycle of PLA, as shown in Fig. 4. These important factors ensure the sustainability of PLA polymer [31]. The emission of CO_2 gas in the biodegradation of PLA is approximately 1600 kg per metric ton, which is relatively less as compared to other polymers such as polypropylene (PP) – 1850, polyethylene terephthalate (PET) – 4150, polystyrene (PS) – 2740 and nylon – 7150 kg per metric ton. The CO_2 emitted by the biodegradation of PLA is used to grow agricultural products, ultimately reducing greenhouse gas emissions. Therefore, the production of PLA from agricultural products on a large scale can also cause a significant reduction in the emission of greenhouse gases. The energy required for the production of PLA, from the growth of corn to PLA pellets, is 75.4 MJ/kg, including renewable energy – 24.6 MJ/kg and fossil energy – 50.8 MJ/kg. This amount of fossil energy required for producing PLA is 25–55% less than the fossil energy required for producing petroleum-derived plastics [30,32].

2.3. Advantages and limitations of PLA

In recent decades, biocomposites are gaining the attention of researchers and scientists to extend their applications in many sectors and make them more suitable and promising candidates to replace existing petroleum-derived products due to global awareness of sustainable products and the rapid growth depletion of petroleum reserves. PLA is the most suitable emerging biopolymer to be used in place of petroleum-derived products due to its availability, biodegradability, biocompatibility, and low density. These advantageous properties make it appropriate use for biomedical, food packaging and many other commodity purposes. Some inherent properties of PLA, such as low impact strength, poor ductility, low elongation at break, low thermal resistance, slow

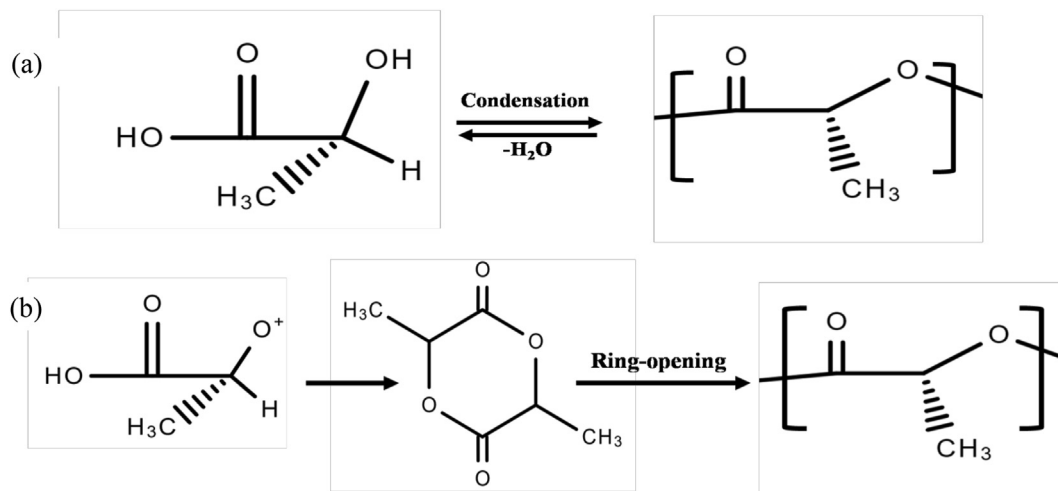


Fig. 3. Polymerization of PLA: (a) direct condensation and (b) ring-opening polymerization.

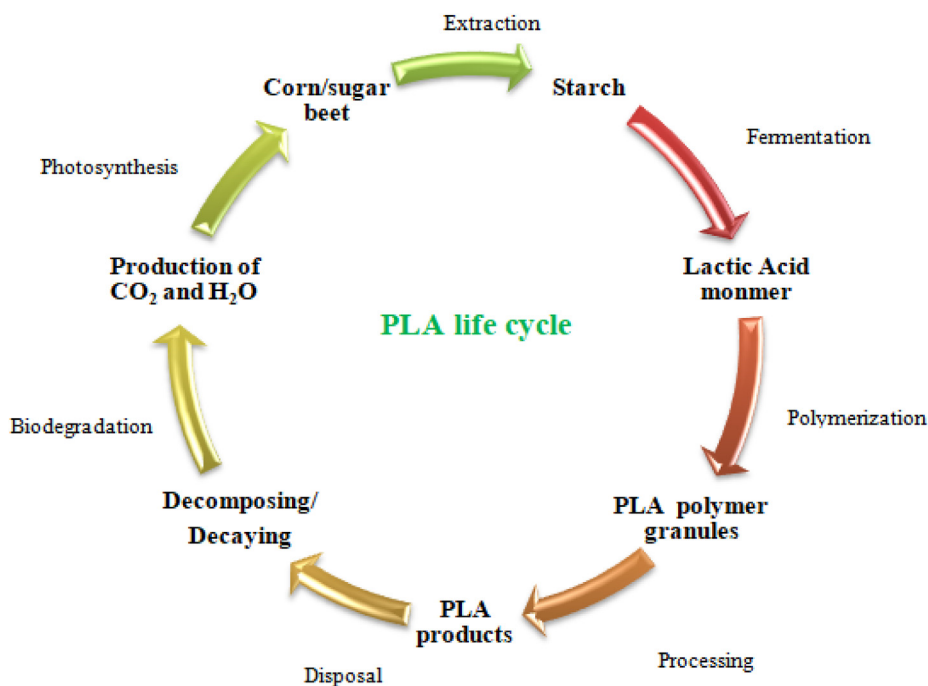


Fig. 4. PLA life cycle in nature.

crystallization rate, brittleness, and moisture sensitivity, limit the applications in many engineering sectors [5,33–35]. Adding PEG can significantly improve the brittle nature of PLA but also reduces the modulus of elasticity [5]. Few researchers suggested the addition of nano clay to the PLA can enhance its performance. These nanoparticles are easily mixed with PLA due to hydrogen bonding which links the carbonyl group of PLA to ammonium group of clay. Literature shows that the properties of PLA can be improved with the reinforcement of natural fibers, cellulose and nanocellulose [36].

3. Biocomposites/natural fibers reinforced polymer composites

Environmental concerns and the high cost of products prepared by synthetic fibers and petrochemical polymers have led to using

natural fiber as reinforcement in biocomposites. Biocomposites are the special type of composite materials formed by polymers matrix and a reinforcement of different https://en.wikipedia.org/wiki/Natural_fibers. The biocomposites can be divided into non-wood fibers and wood fibers based on reinforcement. Natural fibers are relatively long and have a high percentage of cellulose, which offers high tensile strength and crystallinity. On the other hand, these fibers have some disadvantages also due to the presence of hydroxyl groups (OH) that can attract water molecules. Thus, the fibers might swell, creating voids at the interface of the composite, thereby decreasing the mechanical properties and dimensional stability.

Biocomposites are used as an alternative to synthetic materials that may be non-renewable, non-biodegradable or manufactured by the pollution emitting process [37]. Biocomposites have recently

received more attention because of raising environmental awareness and the drive toward sustainable technologies [38]. Biocomposites are environmentally friendly and their applications are growing in various fields: transportation, building and construction industries, packaging, consumer products, etc. [39]. The following reasons are given as such for using biocomposites: (i) to maintain the environmental and ecological balance, (ii) to minimize the depletion of petroleum resources, (iii) to provide value addition to the agricultural waste, (iv) to enhance the health and wealth of the human, (v) to offer a high strength to weight ratio and (vi) to impart good corrosion resistance. The advantages and disadvantages of biocomposites are listed in Table 3.

3.1. Natural fiber as reinforcement

Over the last three decades, natural fibres have been gaining much more attention as a substitute for synthetic fibres reinforcement. The advantages and disadvantages of natural fibers are tabulated in Table 4, whereas a comparison of the properties of natural fibers over synthetic fibers is given in Table 5. Unlike the traditionally artificial fibres like glass and carbon, these lignocelluloses fibres can offer certain advantages to the composites such as renewability, biodegradability, low density, high stiffness, low cost, and a high degree of flexibility during processing.

The main elements of natural fiber are cellulose, hemicelluloses, lignin, and pectin. The main component of natural fiber is cellulose which resists alkali but is hydrolyzed in acid. The work of hemicelluloses is to support matrix agents of cellulose. Hemicelluloses are naturally hydrophilic, soluble in alkali, and easily hydrolyzed in acids. The nature of lignin is amorphous and hydrophobic. The physical and mechanical performances of natural fibers are provided in Table 6. Further, the chemical compositions of these fibers are provided in Table 7.

3.2. Applications of biocomposites

The biocomposites are proposed to be used/are being used in many applications due to their superb performances over polymers composites prepared using artificial fibers. The major fields of applications of biocomposites are as such: automotive parts, building & construction, electrical and electronics industries, parts of agricultural equipment, packaging materials, biomedical, and structural part [51–54].

4. PLA-based composites

The demand for composite materials is increasing every day and gaining the attention of researchers due to their excellent properties, which increase the range of applications. The advantageous feature of composite materials as compared to conventional bulk materials is the high strength to weight ratio. Traditional composites are generally made from synthetic polymers, which are derived from petroleum-based products. These polymers are not

Table 4

Advantages and disadvantages of natural fibers [39,43].

Advantages	Disadvantage
<ul style="list-style-type: none"> • Biodegradable, renewable and sustainable. • Zero impact on the environment. • Low cost and abundantly available in nature • Low energy requirement for processing • Non-toxic and recyclable • High specific strength 	<ul style="list-style-type: none"> • High moisture uptake • Tendency to form agglomerate with resins • Poor compatibility with matrix • Properties vary with their origin • Moderate strength • Poor wettability with resin

Table 5

Comparison of natural fibers with synthetic fibers.

Properties	Natural fibers	Synthetic fiber
Origin	Natural	Man-made
Density	Low	More
Specific strength and modulus	High	Moderate
Strength	Moderate	High
Thermal sensitivity	High	Low
Energy consumption during processing	Low	High
Moisture sensitivity	High	Low
Eco-friendly	Yes	No
Recyclability	Good	Moderate
Biodegradable	Yes	No
Resource	Infinite	Limited
CO ₂ emission	No	Yes
Health risk	Low	High
Cost	Low	High
Use	Moderate	More

widely accepted due to environmental concerns as they are not biodegradable, not sustainable and pollute the environment during decomposition. Apart from these, petroleum resources are depleting very fast and might be completely exhausted due to massive consumption. PLA-based biocomposites are one of the best potential alternatives to replace non-biodegradable and non-sustainable composites [55]. As discussed in the earlier section, PLA is a fully biodegradable and sustainable polymer that does not create any adverse effects on the environment as well as economical. In biocomposites, biopolymers that are derived from renewable resources, such as; PLA, starch, etc., are used as matrix and natural fibers such as; sisal, hemp, wheat straw, coir, flax, etc., are used as reinforcement materials. The applications of composite materials have been extended to many fields and still increasing, such as aerospace, automotive, sports, furniture, medical and food packaging [56].

4.1. Processing techniques

Generally, green biocomposites are fabricated using conventional methods for manufacturing synthetic fibers reinforced polymer (FRP) composites. Here, biocomposites manufacturing

Table 3

Advantages and disadvantages of biocomposites [40–42].

Advantages	Disadvantage
<ul style="list-style-type: none"> • Biodegradable and recyclable • Less pollution • Low cost • Low energy requirement for their development • Resistance to fungal attack • Require less maintenance • Minimal health hazards and less toxic • Abrasion resistance to machines 	<ul style="list-style-type: none"> • High moisture uptake • Low thermal stability • Poor compatibility • Poor wettability of reinforcements (hydrophilic) with the polymer matrix (hydrophobic) • Non-uniform properties • Moderate strength

Table 6
Physical and mechanical properties of natural fibers.

Origin	Fiber	Diameter (μm)	Density (g/cm^3)	Tensile strength (MPa)	Tensile Modulus (GPa)	Elongation (%)	Ref.
Bast	Jute	25–250	1.3–1.49	393–800	13–26.5	1.16–1.50	[44]
	Flax	25	1.50	500–1500	27.60	2.70–3.20	[45]
	Hemp	25–600	1.47	690	70	2.0–4.0	[46]
	Kenaf	40–90	1.22–1.40	295–930	22–53	3.70–6.90	[47]
	Ramie	22–80	1.50	400–938	61.4–128	3.6–3.8	[46]
	Okra	61–93	—	184–557	8.9–11.8	4–8	[47]
	Alfa	—	0.89	350	22	5.80	[47]
	Rosella	—	—	147–184	2.76	5–8	[47]
	Sisal	100–300	1.30–1.50	507–955	9–28	2.0–2.90	[48]
	Banana	100–250	0.80	161.80	8.5	2.0	[45]
Leaf	Pineapple	50	1.53	170–1627	60–82	2.40	[47]
	Abaca	10–30	1.50	430–813	31.1–33.6	2.90	[47]
	Date	155–250	0.99	309	11.32	2.73	[47]
	Curaua	170	1.40	158–729	—	5	[47]
	Coconut tree leaf sheath	140–490	—	46.40	2.30	2.84	[47]
	Senseviera cylindrical	230–280	0.92	585–676	0.20–11.20	11–14	[47]
	Kapok	22–65	1.47	45–64	1.73–2.55	2–4	[47]
	Cotton	—	1.50–1.60	287–597	5.50–12.60	7–8	[44]
	Oil palm	—	1.55	248	3.20	2.50	[47]
	Coir	150–250	1.20	175	4–6	3.0	[44]
Grass	Bamboo	240–330	0.91	441	35.90	2.50	[44]
	Elephant grass	70–400	0.87	185	7.40	2.50	[47]
	Sea grass	5	1.50	453–692	3.10–3.70	13–26.60	[47]
	Baggase	200–400	1.25	96.24	6.42	4.03	[44]

Table 7
Chemical compositions of natural fibers.

Fiber	Cellulose (%)	Hemi- cellulose (%)	Lignin (%)	Pectin (%)	Moisture (%)	Wax (%)	Ref.
Jute	61–71.50	12–20.40	11.8–13	0.2	12.5–13.70	0.50	[49]
Flax	64.10–71.90	16.70–20.60	2.0–2.2	1.8–2.30	8–12	1.70	[49]
Hemp	70.20–74.40	17.90–22.40	3.70–5.70	0.90	6.20–12	0.80	[50]
Kenaf	31–39	21.50	15–19	—	11	—	[49]
Ramie	68.60–76.20	13.10–16.70	0.60–0.70	1.90	7.50–17	0.30	[50]
Okra	67.50	15.40	7.10	3.40	—	3.90	[47]
Alfa	45.40	38.50	14.90	—	—	2	[47]
Sisal	67–78	10–14.20	8–11	10	—	2	[44]
Banana	63–64	10–19	5	—	10–12	—	[50]
Pineapple	70–82	—	5–12	—	11.80	—	[50]
Abaca	56–63	15–17	7–9	7–9	—	3	[47]
Areca	53.20	35–64.80	13–24.80	—	—	—	[49]
Coconut tree leaf sheath	27	14	27.70	—	4.70	—	[47]
Senseviera cylindrical	79.70	10.13	3.80	—	3.08	0.09	[47]
Kapok	64	23	13	23	—	—	[47]
Cotton	82.70–90	5.70	—	0–1	7.85–8.50	0.60	[49]
Oil palm	65	10.12	17.50	—	—	4	[47]
Coir	32–43	0.15–0.25	40–45	3–4	8	—	[49]
Bamboo	24–43	30	21–31	—	—	—	[44]
Wheat straw	51	26	16	—	—	—	[47]
Rice husk	38–45	12–20	—	—	—	—	[47]
Bagasse	52.20	18.80	25.30	—	—	—	[47]
Sea grass	57	38	5	10	—	—	[44]

techniques are broadly classified into three groups, first one is open molding processes and the second is closed molding processes and the third is an additive manufacturing process, as shown in Fig. 5. The open molding processes can be further classified as hand layup, spray layup, filament winding and autoclave. The closed molding processes can be further classified as compression molding, injection molding, Extrusion injection molding and resin transfer molding.

4.1.1. Injection molding and extrusion injection molding

The injection molding process is one of the most popular methods for fabricating composite materials. In this method, the mixture of thermoplastic polymer and fibers in the molten state (above melting point) is forced to fill the shape of the cavity of the mold. After the solidification of the material, the component is

removed from the mold. This method is the most popular method among researchers for fabricating PLA biocomposites. The injection molding method is an efficient and economical process for the commercial production of complex components on a large scale, such as automobile parts, consumer goods, etc. While in the extrusion injection molding process, the PLA pellets and filler materials are fed to the barrel through a hopper. The schematic view of the extrusion injection molding machine is shown in Fig. 6. The heater mounted on the surface of the barrel causes the melting of PLA. It is mixed with filler materials with the help of a rotating screw. Then, this homogeneous mixture of PLA and filler is forced to inject the mold of the desired shape through the converging nozzle to reduce the chances of air entrapment [57]. Generally, mold is made up of two parts one is stationary and the other is movable. After the solidification of materials in the mold, the product is

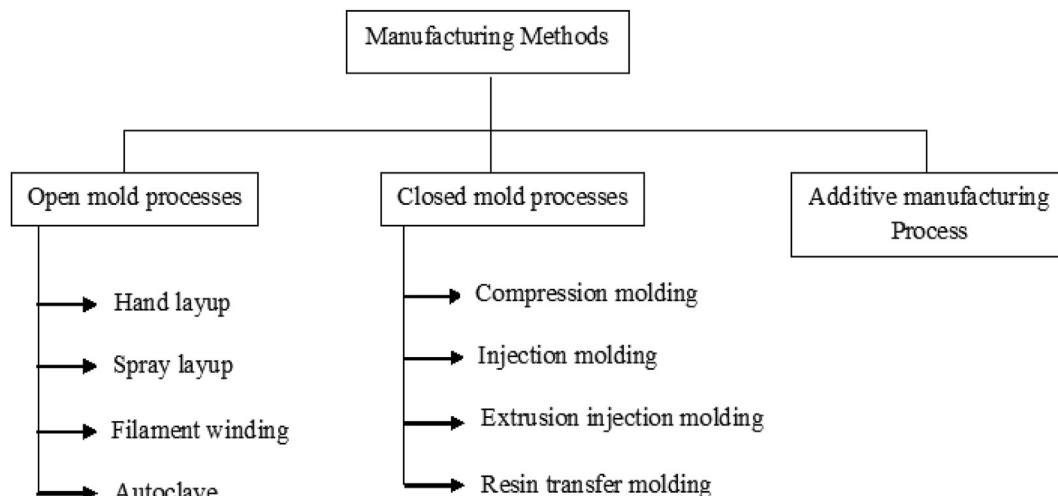


Fig. 5. Manufacturing techniques used to fabricate PLA-based biocomposites.

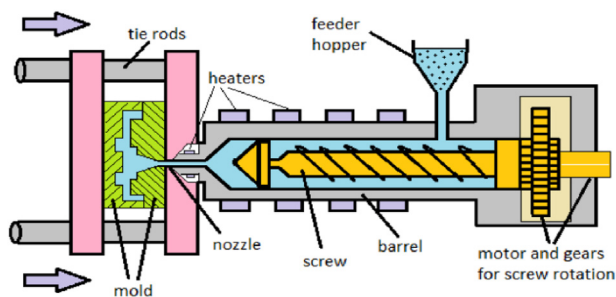


Fig. 6. Extrusion injection molding for the fabrication of PLA biocomposites [62].

removed by separating the movable part from the mold's stationary part. Many literatures have reported the fabrication of PLA-based fibers reinforced biocomposites using injection molding as well as extrusion injection molding methods. Orue et al. [58] prepared the PLA-based sisal reinforced biocomposites and investigated the effect of fiber's chemical treatment on the mechanical properties. Similarly, Komal et al. [59] fabricated banana fibers that reinforced PLA biocomposite using injection molding, extrusion injection molding and compression molding. This investigation revealed that biocomposites' fabrication methods do not significantly impact the thermal properties, glass transition temperature, hardness and chemical composition. On the other side, fibers' orientation and distribution produce variations in crystallinity, mechanical properties and dynamic properties.

From the literature survey, it was observed that obtaining uniform mixing of PLA and filler is challenging. Due to low density of filler materials, it gets concentrated or agglomerated at the center of the extruder [60]. These issues can be overcome up to a certain amount by mixing some compatibilizers, stabilizers and solvents in appropriate proportion. A twin screw extruder is mostly used because it provides better mixing of fibers in the polymer melt. This mixture of polymer and fibers is forced to extrude through the die and solidify in the atmosphere. These composite pellets are used as input material for injection molding [61].

4.1.2. Compression molding

Compression molding is another known method to fabricate PLA-based composites. This method is most popular for both thermoplastic and thermosets materials. This method supplies PLA and reinforced or filler materials to the lower mold. The

reinforcement material is placed in the form of a fiber's mat. The mold is heated to high temperature so that PLA can melt and uniformly mixed over the fibers mat. Then high pressure of approximately 20 kPa is applied to the mold to obtain the final shape of composite product [63]. This method is used for high rate production, good dimensional accuracy and high strength products. Komal et al. [59] prepared PLA reinforced banana fibers composite using this method. The molten mixture of PLA pellets and banana fibers was supplied to the mold, heated at a temperature of 170 °C and pressed with high pressure of 40 bar. The composite material was removed from the mold and solidified in the open atmosphere when the temperature reached 50 °C. Many researchers have reported this method for the fabrication of PLA biocomposites. Bax and Mussing [56] fabricated PLA based biocomposite with the reinforcement of 11% flax by compression molding. With the fibers reinforcement, mechanical properties such as tensile modulus and tensile strength increased by 61% and 26%, respectively. Dong et al. [64] fabricated coir reinforced (5–30 wt%) PLA biocomposites. They reported that tensile and flexural modulus increased considerably, but tensile and flexural strength decreased. Similarly, Faludi et al. [65] also prepared PLA biocomposites with the reinforcement of corn cub and wood fibers by compression molding and reported the improvement of mechanical properties with the reinforcement.

4.1.3. Hand layup

Hand layup is the simplest and oldest open mold process to fabricate the PLA based biocomposites. In this process, dried fibers were manually placed in the mold and matrix resin is applied over the fibers and pressed through the rollers. The mold was sprayed with a reagent for easy removal of the composites from the mold. This method is applicable for short fibers, fibers mats and fabric. This method is generally used for low volume production rates [66,67].

4.1.4. Filament winding

The filament winding process is an open mold conventional method to fabricate biocomposites. In this process, firstly fibers are passed through a resin and thermoplastic matrix bath. This impregnated composite material is rolled over the rotating mandrel till the desired thickness is achieved. The filament winding process is used to fabricate the hollow composite part. The fabricated composite part's mechanical properties depend on the deposited fibers' stacking sequence over the mandrel. The lower angle of

filament deposition produces high tensile strength, while the higher angle provides higher crushing strength [68,69].

4.1.5. Additive manufacturing process

Additive Manufacturing (AM) or 3D printing process is a more recent technique used to manufacture biocomposites. Among the different AM processes, particularly the Fused deposition modeling (FDM) Process is the simplest and cost effective technique used for thermoplastic polymers such as; PLA and ABS, etc., and its fibers reinforced biocomposites. Many literatures reported the fabrication of fibers reinforced PLA Biocomposites [70–73]. In this method, fibers reinforced PLA biocomposite filament is prepared by the extrusion process using a twin screw extruder. The filament is fed to the liquefier through the roller mechanism. Filament gets melted when it reaches the contact of the heating block and is extruded in the form of thread, deposited on the moving substrate in a controlled manner. In this process, fibers are used in the form of nano size; nanocellulose is primarily used as reinforcement for the fabrication of PLA biocomposites. The research on the fabrication of biocomposites using the FDM process is less than the conventional methods but it has been trendy in recent time. From the literature, it can be observed that the part fabricated by 3D printing showed significantly inferior mechanical strength compared to injection molding/compression molding due to the porous structure of the FDM fabricated part. The properties of the 3D-printed part depend on the FDM process parameters [74–77].

4.2. Characterization of PLA-based composites

4.2.1. Mechanical property

The mechanical properties of the biocomposites depend on several factors like a method of fabrication, properties of fibers and matrix, the content of constituent materials, shape and size of fibers, temperature, interfacial bonding, etc. The properties of fibers depend on the source of fibers and the area of cultivation, which eventually affects the mechanical properties of the biocomposites [78–81]. Many investigations have been carried out to analyze the effect of fibre reinforcement in the PLA matrix [78,82–84]. Bajpai et al. [8] prepared PLA based biocomposite with reinforcement of 20 wt% sisal fibers. It was observed that mechanical properties such as tensile, flexural and impact properties were significantly improved up to 80.6 MPa, 249.8 MPa and 106.06 kJ/m², respectively with the reinforcement of fibers. It was noted with the increase of reinforcement from 20 to 40 wt %. Tensile strength increased

remarkably up to 352 MPa and modulus to 13.9 GPa [58]. Yu et al., 2009 [81] observed in their study that tensile, flexural and impact properties of PLA biocomposites were enhanced by adding 30 wt% ramie fiber up to 55.3 MPa, 105.2 MPa and 10.2 kJ/m², respectively. Further, the effect of adding the same percentage of ramie fiber (30 wt%) on the impact and flexural strength was investigated by Yu and Li, 2014 [80]. It was observed that impact strength was increased to 11.3 kJ/m² and flexural strength was increased to 132.5 MPa. The addition of 20 wt% flax fibers in the PLA matrix observed the maximum tensile strength of 76.2 MPa and impact strength of 21.6 kJ/m². While with 30 wt% flax fibers reinforced, PLA composite showed a maximum tensile modulus of 8.1 GPa. Similarly, the reinforcement of other fibers, such as kenaf, hemp, bamboo and jute fibers in the PLA matrix, significantly enhanced the mechanical properties of the biocomposites [55,85–87]. Table 8 shows the influence of different fibre reinforcements on the mechanical properties of PLA matrix.

The mechanical properties of the biocomposites can be improved with the surface modification of the fibers. The surface modifications of fibers provide better adhesion bonding with the polymer matrix. In the surface modification, fibers are chemically treated with alkali, acetylation, silane coupling agent, and potassium permanganate [88]. Manral et al. [89] investigated the effect of chemical treatments on the mechanical properties of PLA-based composites. The tensile strength, flexural strength and viscoelastic properties were significantly increased and the maximum value was observed at 20% w/v reinforcement. The surface modification of the fibers by chemical treatment causes non cellulosic component removal and enhances composites' strength. But at the same time the impact strength was decreased with the treatment because chemical treatment causes brittleness of the fibers results in decreasing the impact strength of the composites. Ramesh et al. [90] also fabricated PLA hybrid biocomposite with the reinforcement of alkali treated kenaf fibers by 30 wt% (6% NaOH) and montmorillonite clay in different proportions (1%, 2% and 3%). The best mechanical property was observed with the reinforcement of 1% montmorillonite clay. The flexural strength was increased by 46.41% and tensile strength increased by 5.87%. Boubekeur et al. [91] fabricated waste wood flour reinforced (0–40 wt %) PLA biocomposites and stated that the young modulus increased with the addition of wood flour, but impact strength and elongation at break decreased.

Thermal annealing of the biocomposites had remarkable change in the mechanical properties. Fonseca et al. [92] fabricated PLA biocomposites with the reinforcement of three cellulosic fibers

Table 8
Mechanical properties of natural fiber reinforced PLA biocomposites.

Sr. No.	Fiber	Manufacturing Methods	Fibers wt%	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Ref.
1.	Kenaf	Injection molding	20			115	7.6	[93]
2.	Banana	Extrusion injection molding	20	57	1.61	104	5.6	[59]
3.	Banana	Injection molding	20	52	1.43	104	4.8	[59]
4.	Sisal	Compression molding	20	80.6	5.3	249.8	9.75	[94]
5.	Rice straw	Solvent casting	30	22.27	2.59	26		[95,96]
6.	Rice husk	Extrusion compression molding	20			90	4.5	[97]
7.	Hemp	Compression molding	40 (vol%)	54.6	8.5	112.7		[86]
8.	Jute	Compression molding	30 (vol%)	64.13	3.39	97.74	7.36	[85]
9.	Jute	Compression molding	50	32.3	2.11	41.8		[98]
10.	Banana and sisal	Injection molding	30	79	4.1	125	–	[99]
11.	Pine wood flour	Twin screw extruder	50 wt%	66.2	5.4	98		[100]
12.	Okra	Twin screw extruder	30 wt%	58.4	4.6			[101]
13.	Coir	Twin screw extruder	10 wt%	57.9	4.0	107.1		[102]
14.	Flax	Compression molding	50 wt%	151	18.5	215		[103]
15.	Ramie	Compression molding	30 wt%	53	4.3	104		[80]
16.	Oil seed filler	Twin screw extruder	8 wt%	62.6	1.43			[104]
17.	PBAT & office waste paper	Injection molding	20 wt% & 10 wt%	49	2.9	73		[105,106]

agave, coir and pine. In his investigation, they concluded that the reinforcement and annealed treatment significantly enhanced the mechanical properties of biocomposites. The mechanical properties of PLA-based biocomposites are comparable to petroleum-based plastics. Therefore non-biodegradable petroleum based products can be replaced with fibers reinforced PLA composites.

4.2.2. Thermal property

Generally, the thermal degradation temperature of fibers starts at a lower temperature of 200–210 °C while PLA degrades at 300 °C [107]. The reduction in thermal stability of PLA biocomposites is mainly due to the degradation of natural fibers because it starts to degrade at a lower temperature [107]. Therefore, it is crucial to investigate fibers-reinforced PLA biocomposites' thermal properties. The thermal stability of biocomposites and their constituents PLA and fibers are analyzed by the TGA and DTG characterization [102,108]. The thermal decomposition of PLA biocomposites majorly takes place in three distinct regions. The first region of thermal degradation occurs around 100 °C. This slight reduction in weight loss of about 5–10% is due to the evaporation of the moisture content in the fibers of the biocomposites. The second region of thermal degradation is due to the fibers' breakdown of hemicellulose and cellulose. Thermal degradation of PLA matrix also takes place in this region. Among the cellulose, hemicellulose and lignin, hemicellulose degrades first because it has the lowest thermal stability then, followed by cellulose and lignin. Lignin degradation occurs at higher temperatures due to high thermal stability. Lignin and other noncellulosic components are degraded in the last region due to high temperature. Fonseca et al. [92] revealed that the thermal stability of the PLA biocomposites could be substantially improved by the annealing process, which modifies the materials' crystallinity.

From the literature, it was observed that the thermal degradation of pineapple fibers reinforced (30 wt%) PLA biocomposites began at 325 °C and reached maximum degradation at 415 °C with weight loss of 80% and residue of 18% [109]. For hemp fibers reinforced (20 wt %) PLA biocomposites, starting degradation temperature was observed at 303 °C and maximum degradation at 398 °C with 95% weight loss and 1.2 residues [110]. Boubekour et al. [91] concluded in their investigation, that the addition of waste wood flour in the PLA biocomposites does not have a significant impact on the thermal properties. While the crystallinity of the biocomposites increased with the reinforcement, indicating that wood flour acts as a nucleating agent. The details of thermal analysis of various fibers reinforced PLA biocomposites are shown in Table 9.

4.2.3. PLA-based nanocomposites

Manufacturing PLA-based bionanocomposites with the reinforcement of nanocellulose is a more interesting and trendy way to improve the properties of PLA considerably. Nanocellulose is the

natural fiber that is extracted from lignocellulosic biomass. For nanocellulose, at least one dimension must be less than 10 nm, and others might be in several micrometers. The nanocellulose can be extracted from various natural resources such as plants and agricultural products [112–117]. Generally, nanocellulose are categorized into two groups based on their extraction method and dimensions: cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF), as depicted in Table 10. The acid hydrolysis of cellulose produces CNC, while CNF is obtained by mechanical processing like ball milling, etc. Cruz et al. [118] prepared PLA based composites with the reinforcement of microfibers cellulose (MFC) and a combination of microfibers and nanocrystals cellulose (CNC). They observed that the replacement of MFC with CNC by 1–5%, the mechanical and thermal properties were significantly enhanced. The flexural strength was increased by 40% and storage modulus by 35% at room temperature.

The PLA based bionanocomposites are completely biodegradable because both PLA and nanocellulose are derived from renewable resources. PLA composites reinforced with nanocellulose offer enhanced mechanical and thermal properties owing to excellent properties of nanocellulose such as low density, high aspect ratio, high specific modulus, high stiffness, low coefficient of thermal expansion and non toxic. The compatibility of the nanocellulose in the PLA matrix is a little bit challenging due to the hydrophobic and hydrophilic nature of PLA and nanocellulose. To obtain a better interaction between nanocellulose and PLA and uniform dispersion of nanocellulose in the matrix, compatibilizers, coupling reagents and surface treatment of nanocellulose have been carried out [119–121]. In their study, Sung et al. [119] observed that the tensile modulus increases with the addition of CNC – 1, 3, and 5 wt%, whereas the elongation percentage decreases. Fabrication and mechanical properties of PLA bionanocomposites with the reinforcement of nanocellulose have been reported in several literatures [122–127]. From the results reported in the literature, it can be concluded that the addition of nanocellulose significantly improved the mechanical properties, as shown in Table 11.

4.2.4. PLA based films biocomposites

The PLA based film is another method of fabricating PLA film biocomposites with bio-fillers' reinforcement. Gond and Gupta

Table 10
Comparison between CNC and CNF [118].

Parameters	CNC	CNF
Shape	Needle like	Long fiber network
Diameter	5–70 nm	5–60
Length	100–250 nm	> 1000 nm
Crystallinity	High	Low
Extraction method	Acid hydrolysis	Mechanical treatment

Table 9
Thermal properties of PLA biocomposites.

Sr. No.	Natural fibre	Reinforcement wt%	Thermal degradation				Ref.
			Initial temp. (T _i)	Wt% loss	Initial temp. (T _f)	Wt% loss	
1.	Kenaf	20	321	10	367	75	[94]
2.	Rice husk	20	305	10	340	75	[94]
3.	Sisal	20	304	5	370	90	[104]
4.	Bamboo	40	250	5	350	84	[108]
5.	Hemp	20	303	10	398	95	[107]
6.	Pineapple	30	325	10	415	80	[106]
7.	Jute	50	310	9	378	93	[88]
8.	Olive husk flour	20	260	7	324	86	[109]
9.	Flax	34	310	5	380	90	[110]
10.	Coir	10	336	10	385	82	[111]

Table 11
The mechanical properties of PLA bionanocomposites.

Types of nanocellulose	Source	Reinforcement Wt %	Manufacturing methods	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation %	Ref.
CNC	Bamboo pulp	1	Extrusion	51	22.5	1.9	[123]
		1	Extrusion	56.2	1.3	6.4	[122]
		3		56.2	1.4	5.5	
	Coffee silverskin	5		54.9	1.4	4.9	
		1	Solution casting	52	2.5	13	[124]
		3		49	2.7	10	
		5		63.1	3.3	2.8	[125]
CNF	Kenaf	1	Solvent casting	28.8	0.8	31.1	[126]
	Banana waste	1	Melt Extrusion	27.04	1.23	3	[127]
	Linter pulp	3		34.8	1.27	3	
		5					

[128] prepared PLA bionanocomposites films with the reinforcement of varying nanocellulose weight percentages by solvent casting. The nanocellulose was extracted from the sugarcane bagasse by chemical treatment. The crystallinity and barrier properties of PLA bionanocomposite films were improved by the addition of nanocellulose. Dhar et al. [129] manufactured CNC reinforced PLA biocomposite films using dicumyl peroxide (DCP) cross-linking agent by extrusion process. The tensile strength and modulus were enhanced by 40% and 490%, respectively. They observed that the thermal stability of PLA/CNC biocomposite film fabricated using cross-linking agent DCP was higher [110]. The crystallinity was also improved because the grafting of PLA on the CNC acts as a nucleating agent. Finkenstadt and Tisserat et al. [130] prepared biodegradable biocomposite mulch film by reinforcement of osage orange wood fibers of different length 140 nm, 200 nm and 400 nm with different reinforcement of 10 & 25 wt%. They investigated the effect of reinforcement on the mechanical properties and observed that with the addition of osage orange wood fibers the tensile strength decreased, but the tensile modulus were increased. With the 25 wt% reinforcement of osage orange wood fibers of length 140 nm and 200 nm, the tensile modulus of PLA bionanocomposites films increased as compared to neat PLA films. The tensile modulus of films with the reinforcement of 140 nm fibers size was 0.610 ± 0.028 GPa and for 200 nm fibers size, 0.643 ± 0.024 was observed, which were higher than the neat PLA film of 0.575 GPa. Similarly, Panicker et al. [131] fabricated PLA bionanocomposite films using solvent casting by adding nanocellulose from sugarcane bagasse. The mechanical and thermal properties of the PLA bionanocomposites films were compared with the pure PLA film. It was noticed that the tensile strength and tensile modulus were increased with the addition of nanocellulose up to 0.3 wt%. The addition of CNC improved the interaction between the PLA matrix and CNC, which restricted crack growth and resulting increased strength and modulus. But further addition beyond 0.3 wt% strength and modulus decreases might be due to the agglomeration of nanocellulose in the matrix. Liu et al. [132] fabricated bagasse hemicellulose based films with the addition of chitosan and glycerol using the solvent casting method and investigated mechanical and barrier properties. They reported that mechanical properties increase with hemicellulose percentage (1.6–4 wt%), maximum tensile strength and elongation percentage of 22 MPa and 65% were observed at 4 wt%, respectively. The further increase of hemicellulose percentage decreases mechanical properties due to low compatibility between the molecular chains. Chitosan is added in the fabrication of films because it has high molecular weight and provides good film forming competence. Similarly, the addition of glycerol in the solution improves flexibility in the film fabrication process.

4.2.5. 3D/4D printed PLA biocomposites

3D printing of PLA biocomposites and nanocomposites has been very popular technique among the scientists and researchers. The FDM (fused deposition modeling) is one of the 3D printing techniques that has been used for printing of thermoplastic materials. There are several investigations have been carried out on 3D printing of PLA biocomposites reinforced with natural fibers extracted from various biomass in multiscale such as microcrystalline cellulose (MCC), nanocrystalline cellulose (CNC) and cellulose nanofibrils (CNF) [133–136]. It was observed that the mechanical and thermal properties of PLA biocomposites were significantly improved with these reinforcement. Murphy et al. [137] fabricated PLA biocomposite filament with the reinforcement of MCC for 3D printing. They observed that biocomposite fabricated with the addition of 3 wt% MCC have the highest storage modulus below glass transition temperature and addition of 5 wt% MCC have the highest storage modulus above the glass transition temperature. The crystallinity of the biocomposites was also enhanced with the reinforcement of MCC because these filler particles acts as nucleating agent. It has been suggested by the researchers that PLA is a good biodegradable polymer that can be utilized for 4D printing due to its shape memory effects [138–141]. The shape memory effects means the ability of material to regain its original shape.

Hong et al. [142] prepared lignin reinforced PLA biocomposites and analyzed their performance of 3D printed parts. It was observed that the mechanical properties can be significantly improved with the surface modification of lignin. The tensile strength of PLA biocomposite reinforced with surface modified lignin by carboxyl functional groups showed better performance than the pristine lignin reinforced PLA biocomposites. Duigou et al. [143] suggested that the rheological behaviour of the materials has a significant impact on the deposition characteristics. The material should have low viscosity at high shear rates to facilitate the extrusion process and also should have high zero-shear viscosity to retain its shape after the extrusion from the nozzle and deposition. 3D printed PLA biocomposites are suggested for the advanced applications in the field of biomedical due to its biocompatibility and biodegradability. It can be used for the applications of drug delivery, tissue engineering and cellular structure. It can also be used for the preparation of some organs and cellular structures [144,145].

4.2.6. Applications of PLA based biocomposites

Natural fiber reinforced PLA composites are extensively used for several applications [52,146] such as; automobiles, furniture, food packaging, infrastructure and many more. Jute reinforced and sisal reinforced polymer composites are used for the fabrication of different components of automobiles, such as door panels, seat backs and dashboards, etc. Building components include window frames, sliding, wall partitions, floor, etc. Bax and Mussing [56] in

his work proposed the potential use of cordenka reinforced PLA composites for the automobile sector and electronic industry. The PLA composites use agricultural waste, reducing environmental pollution and adding value to agricultural activity.

5. Conclusions and future scope

With increasing awareness by utilizing the environmental friendly materials in engineering applications, the use of PLA-based biocomposites/green composites has progressively increased. The PLA based biocomposites are one of the best alternatives to replace non-biodegradable petroleum-derived products globally due to environmental concerns. These composites offer acceptable mechanical and thermal properties leads to be considered a suitable replacement for the existing non-biodegradable petroleum based products. This review article offers a comprehensive review on the PLA and its biocomposites in various aspects such as processing, advantages, limitations, characterization, challenges, applicataions and future scopes to accomplish the demand of present and future generations. It was observed that the properties of PLA-based biocomposites significantly depend on the method of manufacturing processes, source of natural fibers, content of reinforcement, chemical treatments and interfacial bonding. The PLA based biocomposites exhibit possibilities for a wide range of high performance applications including automotive, domestic appliances, textiles, biomedical, etc. These sustainable biocomposites have tremendous potential to fabricate durable products and could be the centerpiece of the market.

PLA-based biocomposites are utilizing in many applications, but further research and development is required to minimize the processing cost, to improve the performance and for increasaed utilization in industrial applications. PLA and its biocomposites are the most used materials worldwide in 3D printing, but one of the main challenges is achieving the performance comparable to commonly used conventional processes (i.e. compression molding and injection molding). The 4D printing gives the benifits of complex design manufacturing and ability to create self-actuating objects. PLA biocomposites could be very useful for 4D printing as PLA displays a shape memory effect and other advantageous characteristics.

Declaration of competing interest

The authors declare that they have no competing interests.

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References

- [1] N. Raddadi, F. Fava, Biodegradation of oil-based plastics in the environment : existing knowledge and needs of research and innovation, *Sci. Total Environ.* 679 (2019) 148–158, <https://doi.org/10.1016/j.scitotenv.2019.04.419>.
- [2] T.A. Hottle, M.M. Bilec, A.E. Landis, Sustainability assessments of bio-based polymers, *Polym. Degrad. Stabil.* 98 (9) (2013) 1898–1907, <https://doi.org/10.1016/j.polymdegradstab.2013.06.016>.
- [3] S. Sid, R.S. Mor, A. Kishore, V.S. Sharanagat, Bio-sourced polymers as alternatives to conventional food packaging materials: a review, *Trends Food Sci. Technol.* 115 (2021) 87–104, <https://doi.org/10.1016/j.tifs.2021.06.026>.
- [4] V. Nagarajan, A.K. Mohanty, M. Misra, Perspective on polylactic acid (PLA) based sustainable materials for durable applications: focus on toughness and heat resistance, *ACS Sustain. Chem. Eng.* 4 (6) (2016) 2899–2916, <https://doi.org/10.1021/acssuschemeng.6b00321>.
- [5] N. Tripathi, M. Misra, A.K. Mohanty, Durable polylactic acid (PLA)-Based sustainable engineered blends and biocomposites: recent developments, challenges, and opportunities, *ACS Eng. Au* 1 (2021) 7–38, <https://doi.org/10.1021/acseengineeringau.1c00011>.
- [6] J. Trifol, C. Sillard, D. Plackett, Chemically extracted nanocellulose from sisal fibers by a simple and industrially relevant process, *Cellulose* 24 (1) (2017) 107–118, <https://doi.org/10.1007/s10570-016-1097-5>.
- [7] K. Oksman, M. Skrifvars, J.F. Selin, Natural fibers as reinforcement in polylactic acid (PLA) composites, *Compos. Sci. Technol.* 63 (9) (2003) 1317–1324, [https://doi.org/10.1016/S0266-3538\(03\)00103-9](https://doi.org/10.1016/S0266-3538(03)00103-9).
- [8] P.K. Bajpai, I. Singh, J. Madaan, Development and characterization of PLA-based green composites: a review, *J. Thermoplast. Compos. Mater.* (2013) 1–30, <https://doi.org/10.1177/0892705712439571>.
- [9] G. Rajeshkumar, et al., Environment friendly , renewable and sustainable poly lactic acid (PLA) based natural fiber reinforced composites – a comprehensive review, *J. Clean. Prod.* 310 (127483) (2021) 1–26, <https://doi.org/10.1016/j.jclepro.2021.127483>.
- [10] T. Need, B. Polymers, Review sustainability of biobased and biodegradable plastics 1 introduction : the need for biobased and production of biobased and biodegradable, *Clean* 36 (5–6) (2008) 433–442, <https://doi.org/10.1002/clean.200700183>.
- [11] R. Jonas, L.F. Farah, Production and application of microbial cellulose, *Polym. Degrad. Stabil.* 59 (1–3) (1998) 101–106, [https://doi.org/10.1016/S0141-3910\(97\)00197-3](https://doi.org/10.1016/S0141-3910(97)00197-3).
- [12] O. Akampumzu, P.M. Wambua, A. Ahmed, W. Li, X. Qin, Review of the applications of biocomposites in the automotive industry, *Polym. Polym. Compos.* 38 (11) (2016) 1–17, <https://doi.org/10.1002/pc>.
- [13] K.N. Bharath, S. Basavarajappa, Applications of biocomposite materials based on natural fibers from renewable resources: a review, *Sci. Eng. Compos. Mater.* 23 (2) (2016) 123–133, <https://doi.org/10.1515/secm-2014-0088>.
- [14] U.K. Sanivada, G. Mármol, F.P. Brito, R. Fanguero, PLA composites reinforced with flax and jute fibers - a review of recent trends, processing parameters and mechanical properties, *Polymers (Basel)* 12 (2020) 1–29.
- [15] R. Siakeng, M. Jawaid, H. Ariffin, S.M. Sapuan, M. Asim, N. Saba, Natural fiber reinforced polylactic acid composites : a review, *Polym. Compos.* 40 (2) (2018) 446–463, <https://doi.org/10.1002/pc.24747>.
- [16] W.H. Carothers, G.L. Borough, F.J. Natta, Studies of polymerization and ring formation. X. The reversible polymerization of six-membered cyclic esters, *J. Am. Chem. Soc.* 54 (2) (1932) 761–772, <https://doi.org/10.1021/ja01341a046>.
- [17] J.R. Dorgan, B. Braun, J.R. Wegner, D.M. Knauss, Poly(lactic acids): a brief review, *ACS Symp. Ser.* 939 (2006) 102–125, <https://doi.org/10.1021/bk-2006-0939.ch007>.
- [18] R.K. Kulkarni, K.C. Pani, C. Neuman, F. Leonard, Polylactic acid for surgical implants, *Arch. Surg.* 93 (5) (1966) 839–843 [Online]. Available: <http://archsurg.jamanetwork.com/>.
- [19] K.J. Jem, B. Tan, The development and challenges of poly (lactic acid) and poly (glycolic acid), *Adv. Ind. Eng. Polym. Res.* 3 (2) (2020) 60–70, <https://doi.org/10.1016/j.aiepr.2020.01.002>.
- [20] L. Ranakoti, et al., Critical review on polylactic acid: properties, structure, processing, biocomposites, and nanocomposites, *Materials* 15 (12) (2022) 1–30, <https://doi.org/10.3390/ma15124312>.
- [21] R.M. Rasal, A.V. Janorkar, D.E. Hirt, Poly(lactic acid) modifications, *Prog. Polym. Sci.* 35 (3) (2010) 338–356, <https://doi.org/10.1016/j.progpolymsci.2009.12.003>.
- [22] I. Kühnert, Y. Spörner, H. Brünig, N.H.A. Tran, N. Rudolph, Processing of poly(lactic acid), *Adv. Polym. Sci.* 282 (2018) 1–33, https://doi.org/10.1007/12_2017_30.
- [23] M.J. John, S. Thomas, Biofibers and biocomposites, *Carbohydr. Polym.* 71 (3) (2008) 343–364, <https://doi.org/10.1016/j.carbpol.2007.05.040>.
- [24] G.-Q. Chen, Microbial lactic acid, its polymer poly(lactic acid), and their industrial applications, *Chen, GQ, Plast. from Bact. Microbiol. Monogr.* 14 (2010) 121–132, https://doi.org/10.1007/978-3-642-03287-5_6.
- [25] R. Pantani, V. Volpe, G. Titomanlio, Foam injection molding of poly(lactic acid) with environmentally friendly physical blowing agents, *J. Mater. Process. Technol.* 214 (12) (2014) 3098–3107, <https://doi.org/10.1016/j.jmatprotec.2014.07.002>.
- [26] Y. Zhou, Y. Cui, X. Qu, Exopolysaccharides of lactic acid bacteria: structure, bioactivity and associations: a review, *Carbohydr. Polym.* 207 (2019) 317–332, <https://doi.org/10.1016/j.carbpol.2018.11.093>. September 2018.
- [27] A. Djukić-Vuković, D. Mladenović, J. Ivanović, J. Pejčin, L. Mojović, Towards sustainability of lactic acid and poly-lactic acid polymers production, *Renew. Sustain. Energy Rev.* 108 (2019) 238–252, <https://doi.org/10.1016/j.rser.2019.03.050>.
- [28] M.N. Kumar, et al., Lactic acid fermentation by cells immobilised on various porous cellulosic materials and their alginate/poly-lactic acid composites, *Bioresour. Technol.* 165 (2014) 332–335, <https://doi.org/10.1016/j.biortech.2014.02.110>.
- [29] J.L. Robert, K.B. Aubrecht, Ring-opening polymerization of lactide to form a biodegradable polymer, *J. Chem. Educ.* 85 (2) (2008) 258–260, <https://doi.org/10.1021/ed085p258>.
- [30] E.T.H. Vink, K.R. Rábago, D.A. Glassner, P.R. Gruber, Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production, *Polym. Degrad. Stabil.* 80 (3) (2003) 403–419, [https://doi.org/10.1016/S0141-3910\(02\)00372-5](https://doi.org/10.1016/S0141-3910(02)00372-5).
- [31] R. Scaffaro, A. Maio, E.F. Gulino, B. Megna, Structure-property relationship of PLA-Opuntia Ficus Indica biocomposites, *Compos. B Eng.* 167 (2019) 199–206, <https://doi.org/10.1016/j.compositesb.2018.12.025>.
- [32] E.T.H. Vink, D.A. Glassner, J.J. Kolstad, R.J. Wooley, R.P. O'Connor, The eco-profiles for current and near-future NatureWorks® polylactide (PLA) production, *Ind. Biotechnol.* 58 (2007) 58–81.

- [33] K. Zhang, V. Nagarajan, M. Misra, A.K. Mohanty, Supertoughened renewable PLA reactive multiphase blends system: phase morphology and performance, *ACS Appl. Mater. Interfaces* 6 (15) (2014) 12436–12448, <https://doi.org/10.1021/am502337u>.
- [34] H. Balakrishnan, A. Hassan, M. Imran, M.U. Wahit, Toughening of polylactic acid nanocomposites: a short review, *Polym. Plast. Technol. Eng.* 51 (2) (2012) 175–192, <https://doi.org/10.1080/03602559.2011.618329>.
- [35] V.A. Yiga, M. Lubwama, S. Pagel, J. Benz, P.W. Olupot, C. Bonten, Flame retardancy and thermal stability of agricultural residue fiber-reinforced polylactic acid: a Review, *Polym. Compos.* 42 (1) (2021) 15–44, <https://doi.org/10.1002/pc.25835>.
- [36] J. Nagarjun, J. Kanchana, G. RajeshKumar, S. Manimaran, M. Krishnaprakash, Enhancement of mechanical behavior of PLA matrix using tamarind and date seed micro fillers, *J. Nat. Fibers* 19 (12) (2022) 4662–4674, <https://doi.org/10.1080/15440478.2020.1870616>.
- [37] S.J. Christian, *Natural Fibre-Reinforced Noncementitious Composites (Biocomposites)*, Elsevier, 2019.
- [38] D. Ray, S. Sain, *Plant Fibre Reinforcements*, Elsevier, 2017.
- [39] S.K. Ramamoorthy, M. Skrifvars, A. Persson, A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers, *Polym. Rev.* 55 (1) (2015) 107–162, <https://doi.org/10.1080/15583724.2014.971124>.
- [40] H. Kargarzadeh, et al., Recent developments on nanocellulose reinforced polymer nanocomposites: a review, *Polymer* 132 (2017) 368–393, <https://doi.org/10.1016/j.polymer.2017.09.043>.
- [41] P. Asokan, M. Firdous, W. Sonal, Properties and potential of bio fibers, bio binders, and bio composites, *Rev. Adv. Mater. Sci.* 30 (3) (2012) 254–261.
- [42] M. Jawaid, S.M. Sapuan, O.Y. Alotman, Sustainable biocomposites: challenges, potential and barriers for development, *Green Biocomposites*, Green Energy Technol. (2017) 409, <https://doi.org/10.1007/978-3-319-46610-1>.
- [43] Z. Sydow, K. Bińczak, The overview on the use of natural fibers reinforced composites for food packaging, *J. Nat. Fibers* 16 (8) (2019) 1189–1200, <https://doi.org/10.1080/15440478.2018.1455621>.
- [44] P. Sahu, M.K. Gupta, Sisal (Agave sisalana) fibre and its polymer-based composites: a review on current developments, *J. Reinforc. Plast. Compos.* 36 (24) (2017) 1759–1780, <https://doi.org/10.1177/0731684417725584>.
- [45] L. Yan, N. Chouh, K. Jayaraman, Flax fiber and its composites - a review, *Composer Part B* 56 (2014) 296–317, <https://doi.org/10.1016/j.compositesb.2013.08.014>.
- [46] M.A. Al-Maadeed, S. Labidi, *Recycled Polymers in Natural Fibre-Reinforced Polymer Composites*, Woodhead Publishing Limited, 2013.
- [47] T.P. Sathishkumar, P. Navaneethakrishnan, S. Shankar, R. Rajasekar, N. Rajini, Characterization of natural fiber and composites - a review, *J. Reinforc. Plast. Compos.* 32 (19) (2013) 1457–1476, <https://doi.org/10.1177/0731684413495322>.
- [48] M. Saxena, A. Pappu, R. Haque, A. Sharma, *Sisal Fiber Based Polymer Composites and Their Applications*, 2011.
- [49] Y. Tong, et al., Improving cracking and drying shrinkage properties of cement mortar by adding chemically treated luffa fibers, *Comput. Chem. Eng.* 71 (2014) 327–333, <https://doi.org/10.1016/j.conbuildmat.2014.08.077>.
- [50] I.M. De Rosa, C. Santulli, F. Sarasini, Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated Phormium tenax leaf fibers, *Mater. Des.* 31 (5) (2010) 2397–2405, <https://doi.org/10.1016/j.matdes.2009.11.059>.
- [51] H. Dahy, Natural fibre-reinforced polymer composites (NFRP) fabricated from lignocellulosic fibers for future sustainable architectural applications, case studies: segmented-shell construction, acoustic panels, and furniture, *Sensors* 19 (3) (2019), <https://doi.org/10.3390/s19030738>.
- [52] M.R. Nurul Fazita, et al., Green composites made of bamboo fabric and poly (lactic) acid for packaging applications-a review, *Materials* 9 (6) (2016) 1–29, <https://doi.org/10.3390/ma9060435>.
- [53] F.V. Ferreira, I.F. Pinheiro, S.F. De Souza, L.H.I. Mei, L.M.F. Lona, Polymer composites reinforced with natural fibers and nanocellulose in the automotive industry : a short review, *J. Compos. Sci.* 3 (51) (2019) 1–17.
- [54] E. Castro-Aguirre, F. Iniguez-Franco, H. Samsudin, X. Fang, R. Auras, Poly(lactic acid)—mass production, processing, industrial applications, and end of life, *Adv. Drug Deliv. Rev.* 107 (2016) 333–366, <https://doi.org/10.1016/j.addr.2016.03.010>.
- [55] M.R. Sanjay, P. Madhu, M. Jawaid, P. Sentharamakannan, S. Senthil, S. Pradeep, Characterization and properties of natural fiber polymer composites: a comprehensive review, *J. Clean. Prod.* 172 (2018) 566–581, <https://doi.org/10.1016/j.jclepro.2017.10.101>.
- [56] B. Bax, J. Müssig, Impact and tensile properties of PLA/Cordenka and PLA/flax composites, *Compos. Sci. Technol.* 68 (2008) 1601–1607, <https://doi.org/10.1016/j.compscitech.2008.01.004>.
- [57] M.R. Thompson, J. Sun, Wet granulation in a twin-screw extruder : implications of screw design, *J. Pharmacol. Sci.* 99 (4) (2010) 2090–2103, <https://doi.org/10.1002/jps>.
- [58] A. Orue, A. Jauregi, U. Unsuaín, J. Labidi, A. Eceiza, A. Arbelaiz, Composites : Part A the effect of alkaline and silane treatments on mechanical properties and breakage of sisal fibers and poly (lactic acid)/sisal fiber composites, *Composer Part A* 84 (2016) 186–195, <https://doi.org/10.1016/j.compositesa.2016.01.021>.
- [59] U.K. Komal, M.K. Lila, I. Singh, PLA/banana fiber based sustainable biocomposites : a manufacturing perspective, *Composer Part B* 180 (107535) (2020) 1–11, <https://doi.org/10.1016/j.compositesb.2019.107535>.
- [60] W. Lertwimolnun, B. Vergnes, Effect of processing conditions on the formation of polypropylene/organoclay nanocomposites in a twin screw extruder, *Polym. Eng. Sci.* 46 (3) (2006) 314–323, <https://doi.org/10.1002/pen>.
- [61] K.L. Pickering, M.G.A. Efendy, T.M. Le, A review of recent developments in natural fiber composites and their mechanical performance, *Composer Part A* 83 (2016) 98–112, <https://doi.org/10.1016/j.compositesa.2015.08.038>.
- [62] M. Uluskan, Six Sigma in plastic injection molding: reuse defective parts in new article production as raw material input or not? *J. Ind. Eng.* 32 (2) (2021) 341–363.
- [63] D. Shumigin, E. Tarasova, A. Krumme, P. Meier, Rheological and mechanical properties of poly (lactic) acid/cellulose and LDPE/cellulose composites, *Mater. Sci.* 17 (1) (2011) 32–37.
- [64] Y. Dong, A. Ghataura, H. Takagi, H.J. Haroosh, A.N. Nakagaito, K. Lau, Composites : Part A Polylactic acid (PLA) biocomposites reinforced with coir fibers : evaluation of mechanical performance and multifunctional properties, *Composer Part A* 63 (2014) 76–84, <https://doi.org/10.1016/j.compositesa.2014.04.003>.
- [65] G. Faludi, G. Dora, K. Renner, J. Móczó, B. Pukánszky, Biocomposite from polylactic acid and lignocellulosic fibers : structure – property correlations, *Carbohydr. Polym.* 92 (2) (2013) 1767–1775, <https://doi.org/10.1016/j.carbpol.2012.11.006>.
- [66] S. Milenkovic, V. Slavkovic, C. Fragassa, N. Grujovic, N. Palic, F. Zivic, Effect of the raster orientation on strength of the continuous fiber reinforced PVDF/PLA composites, fabricated by hand-layup and fused deposition modeling, *Compos. Struct.* 270 (2021), 114063, <https://doi.org/10.1016/j.compstruct.2021.114063>, February.
- [67] M.M. Billah, M.S. Rabbi, A. Hasan, A review on developments in manufacturing process and mechanical properties of natural fiber composites, *J. Eng. Adv.* 2 (1) (2021) 13–23, <https://doi.org/10.38032/jea.2021.01.003>.
- [68] L.K. Cardon, K.J. Ragaert, R. De Santis, A. Gloria, *Design and Fabrication Methods for Biocomposites*, second ed., Elsevier, 2017.
- [69] J. Preethikaharshini, K. Naresh, G. Rajeshkumar, V. Arumugaprabu, M.A. Khan, K.A. Khan, Review of advanced techniques for manufacturing biocomposites: non-destructive evaluation and artificial intelligence-assisted modeling, *J. Mater. Sci.* 57 (34) (2022) 16091–16146, <https://doi.org/10.1007/s10853-022-07558-1>.
- [70] T. Ambone, A. Torris, K. Shanmuganathan, Enhancing the mechanical properties of 3D printed polylactic acid using nanocellulose, *Polym. Eng. Sci.* (2020) 1–14, <https://doi.org/10.1002/pen.25421>.
- [71] Y. Tao, H. Wang, Z. Li, P. Li, S.Q. Shi, Development and application of wood flour-filled polylactic acid composite filament for 3d printing, *Materials* 10 (4) (2017) 1–6, <https://doi.org/10.3390/ma10040339>.
- [72] C. Aumate, N. Soatthyanon, T. Makmoon, P. Potiyaraj, Polylactic acid/kenaf cellulose biocomposite filaments for melt extrusion based-3D printing, *Cellulose* 28 (2021) 8509–8525.
- [73] M.T. Alturkestany, V. Panchal, M.R. Thompson, Improved Part Strength for the fused deposition 3D printing technique by chemical modification of polylactic acid, *Polym. Eng. Sci.* (2018) 1–6, <https://doi.org/10.1002/pen.24955>.
- [74] M. Roxas, S. Ju, P.E. Sullivan, Fluid dynamics analysis of desktop-based fused deposition modeling rapid prototyping, Thesis of Bachelor of Applied Science, Department of Mechanical and Industrial Engineering, University of Toronto, 2008.
- [75] H.K. Dave, et al., Compressive strength of PLA based scaffolds: effect of layer height, infill density and print speed, *Int. J. Mod. Manuf. Technol.* XI (1) (2019) 21–27.
- [76] M.F. Afrose, S.H. Masood, P. Iovenitti, M. Nikzad, I. Sbarski, Effects of part build orientations on fatigue behaviour of FDM-processed PLA material, *Prog. Addit. Manuf.* 1 (2016) 21–28, <https://doi.org/10.1007/s40964-015-0002-3>.
- [77] A. Dey, N. Yodo, A systematic survey of FDM process parameter optimization and their influence on Part Characteristics, *J. Manufacturing Mater. Process.* 3 (64) (2019) 1–30.
- [78] T. Yu, J. Ren, S. Li, H. Yuan, Y. Li, Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites, *Composer Part A* 41 (4) (2010) 499–505, <https://doi.org/10.1016/j.compositesa.2009.12.006>.
- [79] Z.H. Zhu, B.H. Mo, M.Y. Hao, Study of contents ratio of cellulose, hemicellulose and lignin on the mechanical properties of sisal fibers reinforced polylactic acid (PLA) composites, *IOP Conf. Ser. Mater. Sci. Eng.* 544 (1) (2019) 1–7, <https://doi.org/10.1088/1757-899X/544/1/012012>.
- [80] T. Yu, N. Jiang, Y. Li, Study on short ramie fiber/poly(lactic acid) composites compatibilized by maleic anhydride, *Composer Part A Appl. Sci. Manuf.* 64 (2014) 139–146, <https://doi.org/10.1016/j.compositesa.2014.05.008>.
- [81] T. Yu, Y. Li, J. Ren, Preparation and properties of short natural fiber reinforced poly(lactic acid) composites, *Trans. Nonferrous Met. Soc. China (English Ed.)* 19 (SUPPL. 3) (2009) s651, [https://doi.org/10.1016/S1016-6326\(10\)60126-4](https://doi.org/10.1016/S1016-6326(10)60126-4).
- [82] M.A. Sawpan, K.L. Pickering, A. Fernyhough, Improvement of mechanical performance of industrial hemp fibre reinforced polylactide biocomposites, *Composer Part A Appl. Sci. Manuf.* 42 (3) (2011) 310–319, <https://doi.org/10.1016/j.compositesa.2010.12.004>.
- [83] M. Asim, M. Jawaid, K. Abdan, M. Nasir, Effect of Alkali treatments on physical and Mechanical strength of Pineapple leaf fibers, *IOP Conf. Ser.*

- Mater. Sci. Eng. 290 (1) (2018), <https://doi.org/10.1088/1757-899X/290/1/012030>.
- [84] Z. Yang, H. Peng, W. Wang, T. Liu, Crystallization behavior of poly(ϵ -caprolactone)/layered double hydroxide nanocomposites, *J. Appl. Polym. Sci.* 116 (5) (2010) 2658–2667, <https://doi.org/10.1002/app>.
- [85] J.I.P. Singh, S. Singh, V. Dhawan, Influence of fiber volume fraction and curing temperature on mechanical properties of jute/PLA green composites, *Polym. Polym. Compos.* 28 (4) (2020) 273–284, <https://doi.org/10.1177/0967391119872875>.
- [86] R. Hu, J.K. Lim, Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites, *J. Compos. Mater.* 41 (13) (2007) 1655–1669, <https://doi.org/10.1177/0021998306069878>.
- [87] A.K.M. Moshiul Alam, M.D.H. Beg, D.M. Reddy Prasad, M.R. Khan, M.F. Mina, Structures and performances of simultaneous ultrasound and alkali treated oil palm empty fruit bunch fiber reinforced poly(lactic acid) composites, *Compos. Part A Appl. Sci. Manuf.* 43 (11) (2012) 1921–1929, <https://doi.org/10.1016/j.compositesa.2012.06.012>.
- [88] B.K. Goriparthi, K.N.S. Suman, N. Mohan Rao, Effect of fiber surface treatments on mechanical and abrasive wear performance of polylactide/jute composites, *Compos. Part A Appl. Sci. Manuf.* 43 (10) (2012) 1800–1808, <https://doi.org/10.1016/j.compositesa.2012.05.007>.
- [89] A. Manral, P.K. Bajpai, Effect of non-acidic chemical treatment of kenaf fiber on physico mechanical properties of PLA based composites, *J. Nat. Fibers* (2021) 1–19, <https://doi.org/10.1080/15440478.2021.1889435>.
- [90] P. Ramesh, B.D. Prasad, K.L. Narayana, Morphological and mechanical properties of treated kenaf fiber/MMT clay reinforced PLA hybrid biocomposites, *AIP Conf. Proc.* 2057 (2019) 1–7, <https://doi.org/10.1063/1.5085606>, 020035.
- [91] B. Boubekeur, V. Massardier, M. Polymères, Low-density polyethylene/poly (lactic acid) blends reinforced by waste wood flour, *Soc. Plast. Eng.* (2020) 1–9, <https://doi.org/10.1002/vnl.21759>.
- [92] A.A. Pérez-Fonseca, J.R. Robledo-Ortiz, R. González-Núñez, D. Rodrigue, Effect of thermal annealing on the mechanical and thermal properties of polylactic acid–cellulosic fiber biocomposites, *J. Appl. Polym. Sci.* 133 (31) (2016) 1–10, <https://doi.org/10.1002/app.43750>.
- [93] S. Serizawa, K. Inoue, M. Iji, Kenaf-fiber-reinforced poly(lactic acid) used for electronic products, *J. Appl. Polym. Sci.* 100 (1) (2006) 618–624, <https://doi.org/10.1002/app.23377>.
- [94] P.K. Bajpai, I. Singh, J. Madaan, Comparative studies of mechanical and morphological properties of polylactic acid and polypropylene based natural fiber composites, *J. Reinforc. Plast. Compos.* 31 (24) (2012) 1712–1724, <https://doi.org/10.1177/0731684412447992>.
- [95] M. Ghorbani, C. Jamshid, M. Rovshanideh, F. Hemmati, Poly (lactic acid)/thermoplasticized rice straw biocomposites : effects of benzylated ligno-cellulosic filler and nanoclay, *Iran. Polym. J. (Engl. Ed.)* 28 (9) (2019) 777–788, <https://doi.org/10.1007/s13726-019-00743-1>.
- [96] M.A. Saidi, A. Gorin, K.H. Soon, E. Jayamani, The optimum sodium hydroxide concentration for high strength pla-rice straw composites, *J. Mech. Eng. Sci.* 12 (1) (2018) 3472–3478.
- [97] A.A. Yussuf, I. Massoumi, A. Hassan, Comparison of polylactic Acid/Kenaf and polylactic Acid/Rise husk composites: the influence of the natural fibers on the mechanical, thermal and biodegradability properties, *J. Polym. Environ.* 18 (3) (2010) 422–429, <https://doi.org/10.1007/s10924-010-0185-0>.
- [98] J.I.P. Singh, S. Singh, V. Dhawan, Effect of curing temperature on mechanical properties of natural fiber reinforced polymer composites, *J. Nat. Fibers* 15 (5) (2018) 687–696, <https://doi.org/10.1080/15440478.2017.1354744>.
- [99] B. Asaithambi, G. Ganesan, S. Ananda Kumar, Bio-composites: development and mechanical characterization of banana/sisal fibre reinforced poly lactic acid (PLA) hybrid composites, *Fibers Polym.* 15 (4) (2014) 847–854, <https://doi.org/10.1007/s12221-014-0847-y>.
- [100] Y. Altun, M. Doğan, E. Bayramlı, Effect of alkaline treatment and pre-impregnation on mechanical and water absorption properties of pine wood flour containing poly (lactic acid) based green-composites, *J. Polym. Environ.* 21 (3) (2013) 850–856, <https://doi.org/10.1007/s10924-012-0563-x>.
- [101] E. Fortunati, et al., Okra (abelmoschus esculentus) fibre based PLA composites: mechanical behaviour and biodegradation, *J. Polym. Environ.* 21 (3) (2013) 726–737, <https://doi.org/10.1007/s10924-013-0571-5>.
- [102] Z. Sun, L. Zhang, D. Liang, W. Xiao, J. Lin, Mechanical and thermal properties of PLA biocomposites reinforced by cor fibers, *Int. J. Polym. Sci.* (2017) 1–9, <https://doi.org/10.1155/2017/2178329>, 2017.
- [103] M. Akonda, S. Alimuzzaman, D.U. Shah, A.N.M.M. Rahman, Physico-mechanical, thermal and biodegradation performance of random flax/polylactic acid and unidirectional flax/polylactic acid biocomposites, *Fibers* 6 (4) (2018), <https://doi.org/10.3390/fib6040098>.
- [104] V.L. Finkenstadt, et al., Poly(lactic acid) green composites using oilseed co-products as fillers, *Ind. Crop. Prod.* 26 (1) (2007) 36–43, <https://doi.org/10.1016/j.indcrop.2007.01.003>.
- [105] C. Xu, X. Zhang, X. Jin, S. Nie, R. Yang, Study on mechanical and thermal properties of poly(lactic acid)/poly(butylene adipate-co-terephthalate)/Office wastepaper fiber biodegradable composites, *J. Polym. Environ.* 27 (6) (2019) 1273–1284, <https://doi.org/10.1007/s10924-019-01428-9>.
- [106] D. Battagazzore, A. Noori, A. Frache, Natural wastes as particle filler for poly(lactic acid)-based composites, *J. Compos. Mater.* 53 (6) (2019) 783–797, <https://doi.org/10.1177/0021998318791316>.
- [107] C. Ngaowthong, et al., Recycling of sisal fiber reinforced polypropylene and polylactic acid composites: thermo-mechanical properties, morphology, and water absorption behavior, *Waste Manag.* 97 (2019) 71–81, <https://doi.org/10.1016/j.wasman.2019.07.038>.
- [108] R.K. Gond, M.K. Gupta, A novel approach for isolation of nanofibers from sugarcane bagasse and its characterization for packaging applications, *Polym. Compos.* 41 (12) (2020) 1–11, <https://doi.org/10.1002/pc.25788>.
- [109] S. Kaewpirom, C. Worarat, Preparation and properties of pineapple leaf fiber reinforced poly(lactic acid) green composites, *Fibers Polym.* 15 (7) (2014) 1469–1477, <https://doi.org/10.1007/s12221-014-1469-0>.
- [110] R. Masirek, Z. Kulinski, D. Chionna, E. Piorkowska, M. Pracella, Composites of poly(L-lactide) with hemp fibers: morphology and thermal and mechanical properties, *J. Appl. Polym. Sci.* 105 (2007) 255–268, <https://doi.org/10.1002/app>.
- [111] J. Lin, Z. Yang, X. Hu, G. Hong, S. Zhang, W. Song, The effect of alkali treatment on properties of dopamine modification of bamboo fiber/polylactic acid composites, *Polymers* 10 (4) (2018), <https://doi.org/10.3390/polym10040403>.
- [112] D. Hammiche, A. Boukerrou, B. Azzeddine, N. Guermazi, T. Budtova, Characterization of polylactic acid green composites and its biodegradation in a bacterial environment, *Int. J. Polym. Anal. Char.* 24 (3) (2019) 236–244, <https://doi.org/10.1080/1023666X.2019.1567083>.
- [113] Mr Foruzanmehr, P.Y. Vuillaume, S. Elkoun, M. Robert, Physical and mechanical properties of PLA composites reinforced by TiO₂ grafted flax fibers, *Mater. Des.* 106 (2016) 295–304, <https://doi.org/10.1016/j.matdes.2016.05.103>.
- [114] S. Kobayashi, A. Tanaka, Resin impregnation behavior in processing of unidirectional carbon fiber reinforced thermoplastic composites, *Adv. Compos. Mater.* 21 (1) (2012) 91–102, <https://doi.org/10.1163/156855112X629540>.
- [115] H. Kargarzadeh, M. Ioelovich, I. Ahmad, S. Thomas, A. Dufresne, Chapter: Methods for extraction of nanocellulose from various sources, In book: Handbook of Nanocellulose and Cellulose Nanocomposites. (2017) First Ed. Publisher: John Wiley and Sons, DOI: 10.1002/9783527689972.ch2
- [116] M. Mahardika, H. Abrial, A. Kasim, Production of nanocellulose from pineapple leaf fibers via high-shear homogenization and ultrasonication, *Fibers* 6 (2) (2018) 1–12, <https://doi.org/10.3390/fib6020028>.
- [117] R.K. Gond, M.K. Gupta, M. Jawaid, Extraction of nanocellulose from sugarcane bagasse and its characterization for potential applications, *Polym. Compos.* 42 (10) (2021) 1–13, <https://doi.org/10.1002/pc.26232>.
- [118] M.A. Ruz-cruz, P.J. Herrera-franco, E.A. Flores-johnson, Thermal and mechanical properties of PLA-based multiscale cellulosic biocomposites, *J. Mater. Res. Technol.* 18 (2022) 485–495, <https://doi.org/10.1016/j.jmrt.2022.02.072>.
- [119] N.F. Zaaba, M. Jaafar, H. Ismail, Tensile and morphological properties of nanocrystalline cellulose and nanofibrillated cellulose reinforced PLA biocomposites: a review, *Polym. Eng. Sci.* 61 (1) (2021) 22–38, <https://doi.org/10.1002/pen.25560>.
- [120] M. Ghasemlou, F. Daver, E.P. Ivanova, Y. Habibi, B. Adhikari, Surface modifications of nanocellulose: from synthesis to high-performance nanocomposites, *Prog. Polym. Sci.* 119 (2021), 101418, <https://doi.org/10.1016/j.progpolymsci.2021.101418>.
- [121] D.Y.S. Low, et al., Recent developments in nanocellulose-reinforced rubber matrix composites: a review, *Polymers* 13 (4) (2021) 1–35, <https://doi.org/10.3390/polym13040550>.
- [122] S.H. Sung, Y. Chang, J. Han, Development of polylactic acid nanocomposite films reinforced with cellulose nanocrystals derived from coffee silverskin, *Carbohydr. Polym.* 169 (2017) 495–503, <https://doi.org/10.1016/j.carbpol.2017.04.037>.
- [123] P. Dhar Monika, V. Katiyar, Thermal degradation kinetics of polylactic acid/acid fabricated cellulose nanocrystal based bionanocomposites, *Int. J. Biol. Macromol.* 104 (2017) 827–836, <https://doi.org/10.1016/j.ijbiomac.2017.06.039>.
- [124] M.J. John, R. Anandjiwala, K. Oksman, A.P. Mathew, Melt-spun polylactic acid fibers: effect of cellulose nanowhiskers on processing and properties, *J. Appl. Polym. Sci.* 127 (1) (2013) 274–281, <https://doi.org/10.1002/app.37884>.
- [125] M. Jonoobi, J. Harun, A.P. Mathew, K. Oksman, Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion, *Compos. Sci. Technol.* 70 (12) (2010) 1742–1747, <https://doi.org/10.1016/j.compscitech.2010.07.005>.
- [126] N. Herrera, A.P. Mathew, K. Oksman, Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: mechanical, thermal and optical properties, *Compos. Sci. Technol.* 106 (2015) 149–155, <https://doi.org/10.1016/j.compscitech.2014.11.012>.
- [127] S. Ghasemi, R. Behrooz, I. Ghasemi, R.S. Yassar, F. Long, Development of nanocellulose-reinforced PLA nanocomposite by using maleated PLA (PLA-g-MA), *J. Thermoplast. Compos. Mater.* 31 (8) (2018) 1090–1101, <https://doi.org/10.1177/0892705717734600>.
- [128] R. K. G. M.K. Gupta, Development and characterization of PLA based green nanocomposites films for sustainable packaging applications, *J. Nat. Fibers* 19 (17) (2022) 15738–15750.
- [129] P. Dhar, D. Tarafder, A. Kumar, V. Katiyar, Thermally recyclable polylactic acid/cellulose nanocrystal films through reactive extrusion process, *Polymer* 87 (2016) 268–282, <https://doi.org/10.1016/j.polymer.2016.02.004>.

- [130] V.L. Finkenzstadt, B. Tisserat, Poly(lactic acid) and Osage Orange wood fiber composites for agricultural mulch films, *Ind. Crop. Prod.* 31 (2) (2010) 316–320, <https://doi.org/10.1016/j.indcrop.2009.11.012>.
- [131] A.M. Panicker, K.A.R.T.O. Varghese, Mixed morphology nanocrystalline cellulose from sugarcane bagasse fibers/poly (lactic acid) nanocomposite films : synthesis , fabrication and characterization, *Iran. Polym. J. (Engl. Ed.)* 26 (2) (2017) 125–136, <https://doi.org/10.1007/s13726-017-0504-6>.
- [132] Y. Liu, B. Sun, Z. Wang, Y. Ni, Mechanical and water vapor barrier properties of bagasse hemicellulose-based films, *Bioresources* 11 (2) (2016) 4226–4236, <https://doi.org/10.15376/biores.11.2.4226-4236>.
- [133] T. Ambone, A. Torris, K. Shanmuganathan, Enhancing the mechanical properties of 3D printed polylactic acid using nanocellulose, *Polym. Eng. Sci.* (2020) 1–14, <https://doi.org/10.1002/pen.25421>.
- [134] M.T. Alturkestany, V. Panchal, M.R. Thompson, Improved Part Strength for the fused deposition 3D printing technique by chemical modification of polylactic acid, *Polym. Eng. Sci.* (2018) 1–6, <https://doi.org/10.1002/pen.24955>.
- [135] Z. Wang, J. Xu, Y. Lu, L. Hu, Y. Fan, J. Ma, Industrial Crops & Products Preparation of 3D printable micro/nanocellulose-poly(lactic acid) (MNC/PLA) composite wire rods with high MNC constitution, *Ind. Crop. Prod.* 109 (2017) 889–896, <https://doi.org/10.1016/j.indcrop.2017.09.061>.
- [136] L. Li, Y. Chen, T. Yu, N. Wang, C. Wang, H. Wang, Preparation of polylactic acid/Tempo-oxidized bacterial cellulose nanocomposites for 3D printing via Pickering emulsion approach, *Compos. Commun.* 16 (2019) 162–167, <https://doi.org/10.1016/j.coco.2019.10.004>.
- [137] C.A. Murphy, M.N. Collins, Microcrystalline cellulose reinforced polylactic acid biocomposite filaments for 3D printing, *Pymer Compos* (2016) 1–10, <https://doi.org/10.1002/pc>.
- [138] C. Yang, B. Wang, D. Li, X. Tian, Modelling and characterisation for the responsive performance of CF/PLA and CF/PEEK smart materials fabricated by 4D printing, *Virtual Phys. Prototyp.* 12 (1) (2017) 69–76, <https://doi.org/10.1080/17452759.2016.1265992>.
- [139] K.K. Laali, et al., Novel fluorinated curcuminoids and their pyrazole and isoxazole derivatives : synthesis , structural studies , Computational/Docking and in- vitro bioassay, *J. Fluor. Chem.* 206 (2018) 82–98, <https://doi.org/10.1016/j.jfluchem.2017.11.013>.
- [140] S.K. Leist, D. Gao, R. Chiou, J. Zhou, Investigating the shape memory properties of 4D printed polylactic acid (PLA) and the concept of 4D printing onto nylon fabrics for the creation of smart textiles, *Virtual Phys. Prototyp.* 12 (4) (2017) 290–300, <https://doi.org/10.1080/17452759.2017.1341815>.
- [141] D. Mohan, T.Z. Khai, M.S. Sajab, H. Kaco, Well-dispersed cellulose-graphene in 4D printing biopolymer, *Mater. Lett.* 303 (130522) (2021) 1–4.
- [142] S. Hong, J.H. Park, O.Y. Kim, S. Hwang, Preparation of chemically modified lignin-reinforced PLA biocomposites and their 3D printing performance, *Polymers* 13 (667) (2021) 1–10.
- [143] A. Le, D. Correa, M. Ueda, R. Matsuzaki, M. Castro, A review of 3D and 4D printing of natural fibre biocomposites, *Mater. Des.* 194 (108911) (2020) 1–26, <https://doi.org/10.1016/j.matdes.2020.108911>.
- [144] S. Liu, S. Qin, M. He, D. Zhou, Q. Qin, H. Wang, Current applications of poly (lactic acid) composites in tissue engineering and drug delivery, *Compos. Part B* 199 (108238) (2020) 1–25, <https://doi.org/10.1016/j.compositesb.2020.108238>.
- [145] F.P.W. Melchels, M.A.N. Domingos, T.J. Klein, J. Malda, P.J. Bartolo, D.W. Huttmacher, Progress in polymer science additive manufacturing of tissues and organs, *Prog. Polym. Sci.* 37 (8) (2012) 1079–1104, <https://doi.org/10.1016/j.progpolymsci.2011.11.007>.
- [146] M.R. Sanjay, G.R. Arpitha, L.L. Naik, K. Gopalakrishna, B. Yogesha, Applications of natural fibers and its composites: an overview, *Nat. Resour.* 7 (3) (2016) 108–114, <https://doi.org/10.4236/nr.2016.73011>.