

# PLA Based Biopolymer Reinforced with Natural Fibre: A Review

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**Abstract** In recent years renewed interest on the development of biopolymers, based on constituents obtained from natural resources is gaining much attention. Natural fibres such as kenaf, hemp, flax, jute, bamboo, elephant grass and sisal based polymer with thermoplastic and thermoset matrices offer reductions in weight, cost and carbon dioxide emission, less reliance on foreign oil resources and recyclability. Reinforced biopolymer with natural fibres is the future of “green composites” addressing many sustainability issues. Among the available biopolymer, PLA (polylactide) is the only natural resource polymer produced at a large scale of over 140,000 tonnes per year. Natural fibre reinforced PLA based biocomposites are widely investigated by the polymer scientists in the last decade to compete with non renewable petroleum based products. The type of fibre used plays an important role in fibre/matrix adhesion and thereby affects the mechanical performance of the biocomposites. The aim of this review is to investigate the effects of processing methods, fibre length, fibre orientation, fibre-volume fraction, and fibre-surface treatment on the fibre/matrix adhesion and mechanical properties of natural-fibre-reinforced PLA composites. Although much work has been performed to engineer the design of such superior biocomposites, the

information is scattered in nature. A comprehensive review on the major technical considerations undertaken to prepare such biocomposites over the last decade is investigated to address the feasibility of wide scale industrial acceptance to such biocomposites. A brief review on the available natural fibres and biopolymer is also given for a comparative study.

**Keywords** PLA · Natural fibres · Bio-based fibres · Fibres · Biopolymer

## Abbreviations

BRAF	Bleached red algae fibre
PLA	Poly(lactide)/poly(lactic acid)
PLLA	Poly-L-lactide
PDLA	Poly-D-lactide
sc-PLA	Stereocomplex PLA
PHA	Poly(hydroxyalkanoates)
PHB	Poly- $\beta$ -hydroxybutyrate
PHBV	Poly- $\beta$ -hydroxybutyrate-co-valerate
CA	Cellulose acetate
CAP	Cellulose acetate propionate
CAB	Cellulose acetate butyrate
WPC	Wood plastic composite

## Introduction

There is a growing urgency to convert agricultural by products and surpluses of the crops into new, profitable products [1–6]. The need to develop technology allied with environmental preservation has created a renewed interest in the scientific world to study the viability of using natural fibres as reinforcement agents in biopolymer matrices. Such fibre based composites normally show good mechanical properties and reduce the dependence on

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materials obtained from non renewable source (fossil based), leading to both economic and environmental benefits. The advantages of natural fibres over synthetic or man made fibres such as glass or carbon are low cost, low density, acceptable specific strength properties, eases of separation, carbon dioxide sequestration and biodegradability [7].

Natural fibres may be obtained either from plants or animals. Plant based fibres such as hemp, kenaf, flax, bamboo and sisal have gained much commercial successes in automotive applications [8–10]. Further research on the feasibility study to assess the potential application of natural fibres as reinforcing sheet moulding compounding materials for the use in building applications is also gaining much commercial interest [11].

Fibres obtained from animal sources like silk [12] and wool [13] are also used as reinforcing agents. A study by Sim et al. [14], on the dynamic mechanical and thermal properties of red algae fibre reinforced PLA (polylactide) biocomposite show improved mechanical strength with increasing fibre loading.

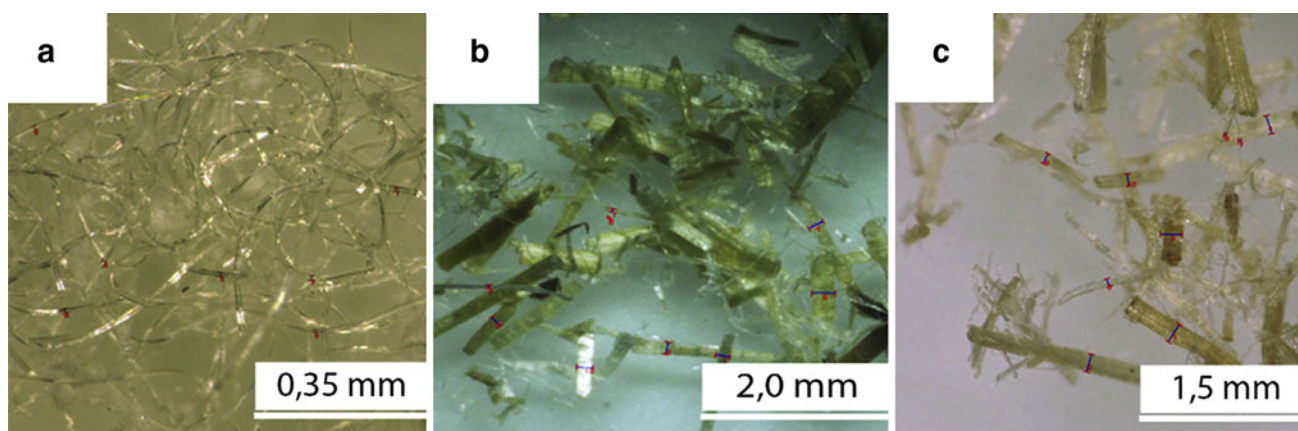
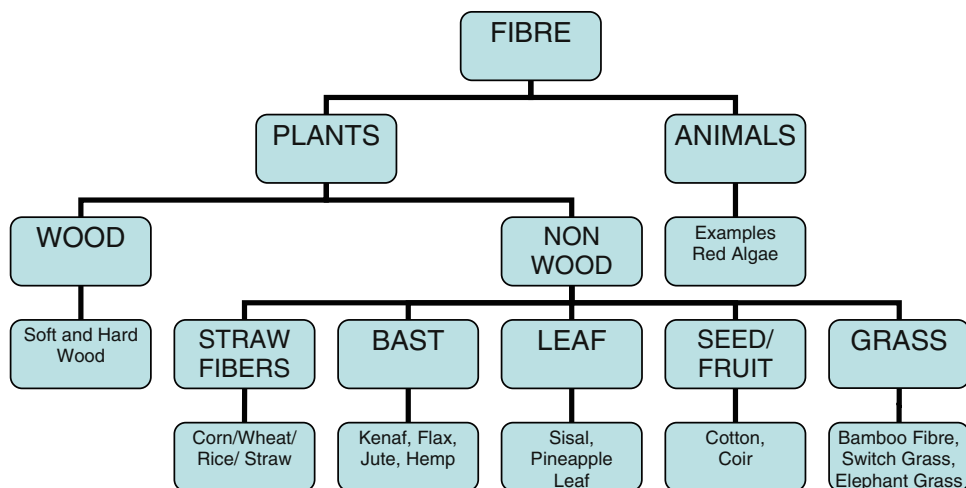
Biodegradable polymers like PLA, cellulose esters, polyhydroxyalkanoates (PHA) and starch polymers can be reinforced with these bio based fibres to produce environmentally beneficial “green composites” [15]. PLA is a natural resourced thermoplastic polymer which can be produced with a capacity of over 140,000 tonnes per year [16]. Increased availability of PLA and the competing petroleum costs are the key driving factors for the polymer scientists to produce novel PLA based biocomposites that can compete with petroleum based plastics available in the market.

Though such natural fibre reinforced biodegradable polymer composites offer many benefits, several major technical considerations must be addressed before the engineering, scientific and commercial communities gain the confidence to enable wide scale acceptance. Challenges include the homogenization of the fibre’s properties and a full understanding of the degree of polymerization and crystallization, adhesion between the fibre and the matrix, moisture repellence, and flame retardant properties to name a few [2, 3, 10]. The aim of this review is to investigate the effects of processing methods, fibre length, fibre orientation, fibre-volume fraction, and fibre-surface treatment on the fibre matrix adhesion, mechanical properties, degradation and stability of such natural-fibre-reinforced PLA based composites. This review is based on present state of the art research undertaken to engineer the design of such superior biocomposites over the last decade. A review on the available natural fibres and biopolymer is given in brief for a comparative study. Given the broad scope of this article, it will inevitably be incomplete, but will hopefully provide a sensible overview of the topic.

## Available Natural Fibres

Natural fibres can either be obtained from plants or animals. Figure 1 gives a brief understanding of the type of fibres available based on their sources. Fibres obtained from plants can either be from wood or non wood sources [7]. Wood plastic composites (WPC) are currently a rapidly growing market [17, 18]. They are commonly made by mixing wood flour or fibre and a virgin or recycled plastic to produce a composite product. Study on the effects of fibre length with the processing and properties revealed improved mechanical properties with increased fibre loading [19]. WPCs are extensively used in decking and railing systems, fenestration applications (e.g., window lineals, door stiles and rails), mouldings and exterior covering applications like siding and trimming. Non wood fibres can be resourced from plant straw, bast, leaf, seed, fruit or grass. Straw fibres are derived from resources like corn, wheat and rice hull and are characterized as having relatively high strength and stiffness, low density, renewability and carbon storage capacity [20, 21]. Composites from these fibres are used in residential construction materials, especially as deck boards. Bast fibres are derived from the outer cells of the stems of various plants. They have weight specific properties, superior to the corresponding properties of glass fibre reinforcements and perceived as an environmental friendly option [8, 9]. Examples of bast fibres include abaca [27], flax [2, 25], hemp [7], jute [11, 26] and kenaf [23, 24]. Figure 2 shows the micrograph image of man made cellulose fibre, abaca and jute. The type of fibres used plays an important role in adhesion to the matrix and thereby improving the mechanical parameters [2]. Flax, jute and hemp are used in the thermoplastic matrix composite panels for internal structures in the automotive industry [28]. Hemp is used to prepare sheet moulding compounds for building applications [11]. Identified primary sources of leaf based fibres are sisal [29], pineapple leaf [30], henequen [31], Vakka [32], palm [33, 34]. Compared to bast fibres, the fibres show superior impact properties [35]. The main drawback in using these fibres is their hydrophilic nature thereby causing difficulties in adhesion with the hydrophobic polymer matrix [30, 36, 37]. Examples of fibre derived from fruit and seed are those available from coir [1], coconut [4], date pits [38], etc., primarily used in non structural applications. Grass based fibre are those obtained from bamboo [5, 39], elephant grass [40] and similar resources. Several investigators have studied the fibre-surface treatment methods and the resultant effects on the physical and mechanical properties of this different fibre matrix composite system [5, 22, 39, 40, 41]. Sim et al. [41] studied the dynamic mechanical and thermal properties of bleached red algae fibre (BRAf) as derived from seaweed.

**Fig. 1** Classification of fibres  
(Courtesy: Mohanty et al. [7])



**Fig. 2** Micrographs of **a** Man Made Cellulose, **b** Abaca, **c** Jute (Courtesy: Bledzki and Jaszkiwicz [2])

The study showed improvement with increased fibre loading.

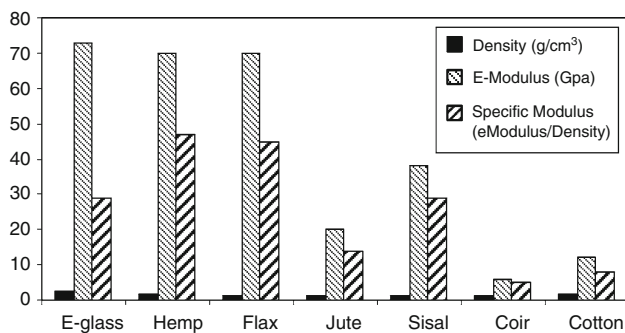
### Mechanical Properties of Different Natural Fibres

Natural fibres can be conceptualized as bundles of small reinforced fibre structures. The amount of cellulose and the angle of microfibrils are the two governing factors for the mechanical properties [42]. Table 1 compares the mechanical properties of various natural fibres with E-glass, as available in the literature. Figure 3 is a graphical representation to illustrate the modulus comparison of different natural fibres with E-glass. The tensile strength of E-glass is much higher than these fibres; however, the high density of E-glass is an advantage for the natural fibres, in competing with their specific strength with E-glass. The specific strength of hemp and glass is almost twice as much to that of E-glass for the same cause. Cellulose, hemicelluloses and lignin are the principal components of the fibre cell walls

along with pectin, which is considered to be the main binder [8]. Cellulose is the most important component in many natural fibres such as flax, jute, hemp, cotton, etc. and is estimated to have a modulus of 140 GPa when using X-ray diffraction to determine the strain [43]. A polysaccharide by nature, cellulose can be degraded to give glucose the smallest repeating unit being cellobiose as formed by the condensation of two glucose units and hence is also known as *anhydroglucose* (glucose minus water). Batra [44] states the principal components of raw hemp bast fibres with cellulose content as shown in Table 2. Vincent [43] reported values of 100 GPa for dry flax and close to 80 GPa for wet flax. Summerscales et al. [8, 9] reviewed the other parameters like effect of fibre orientation, presence of voids and fibre diameter on the mechanical properties of the composite. As depicted in his review, Fig. 4 presents reported elastic moduli against winding angle for several plant fibres. Krenchel [45] calculated the effectiveness of misaligned fibre reinforcements as a fibre orientation distribution factor, using the proportions of fibre at each angle

**Table 1** Mechanical properties of different natural fibres as compared to E-glass fibres (Courtesy: Bledzki and Jaszkiwicz [2], Bledzki et al. [3], Mohanty et al. [7])

Fibre type	Density (g/cm <sup>3</sup> )	E-Modulus (Gpa)	Specific modulus (eModulus/Density)
E-glass	2.55	73	29
Hemp	1.48	70	47
Flax	1.4	70	45
Jute	1.46	20	14
Sisal	1.33	38	29
Coir	1.25	6	5
Cotton	1.51	12	8



**Fig. 3** Modulus comparison of E-glass and some other natural fibres (Courtesy: Bledzki and Jaszkiwicz [2], Bledzki et al. [3], Mohanty et al. [7])

**Table 2** Proportions of the principal components of raw hemp bast-data (Courtesy: Batra [44])

Component	Min proportion (%)	Max proportion (%)
Cellulose	67.00	78.30
Hemicelluloses	5.50	16.10
Lignin	2.90	3.30
Pectin	0.80	2.50

and the fourth power of the cosine of the angle between the fibre and the reference direction. The  $\cos^4\theta$  line is forced through the data point for cotton (seed fibre) in Fig. 4 to indicate the applicability of this model to the molecular winding angle in the fibre for this limited data set regardless of the source of the fibre. In a similar study, the relationship between the fibre diameter and fibre strength at the corresponding fibre diameter is given by Virk et al. [46], taking jute fibres as the base of study. According to this study, the fibre strength is inversely proportional to the fibre diameter as shown in Fig. 5a. Figure 5b shows the relationship between the fibre length and the strength. The fibre strength

also decreases with increasing fibre gauge length. The relationship between the fibre strength and either fibre diameter or fibre length are both shown to have a logarithmic trend.

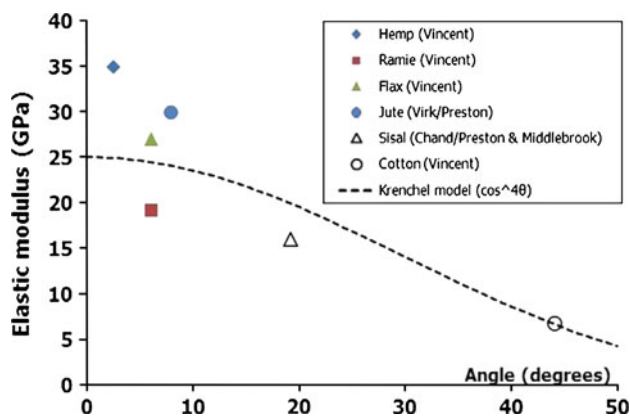
### Available Biopolymer and Their Benefits

Bio-based polymers are materials derived from renewable sources [47, 48]. As given in Fig. 6, bio-based polymers may be divided into three main categories based on their origin and production: Category 1: Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose, chitosan/chitin and proteins like casein and gluten [49]. Category 2: Polymers produced by classical chemical synthesis using renewable bio based monomers. A good example is PLA (polylactide) [50], bio polyester polymerised from lactic acid monomers. Category 3: Polymers produced by micro organisms or genetically modified bacteria. To date, this group of bio-based polymers consists mainly of the polyhydroxyalkanoates (PHA), but developments with bacterial cellulose are in progress [51].

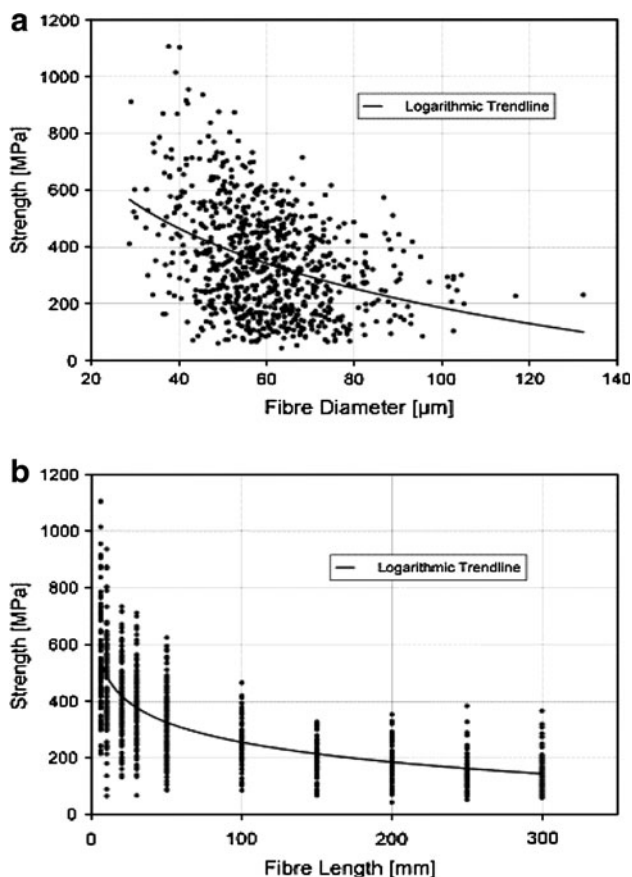
Researchers also have further categorized biopolymers based on the ability to be biodegradable [47]. It is important to note that while some bio-based packaging materials may be biodegradable, not all biodegradable materials are bio-based [48, 52]. Recent technological advances also have allowed biopolymers to be processed similarly to petroleum-based plastics, whether in sheets, by extrusion, spinning, injection moulding or thermoforming [47].

Figures 7 and 8 give a schematic diagram of the different varieties of biodegradable polymers, such as PLA, cellulose esters, and PHA. PLA is a naturally resourced thermoplastic polymer which can be produced from renewable agricultural sources like corn [53]. There are three possible isomeric forms of PLA. Poly (meso-lactide) or poly (DL-lactide) is amorphous grade of PLA (represented as A-PLA). They are transparent and do not have a melting point. The other two isomeric forms as shown in Fig. 9 are PLLA and PDLA. They are homo-crystalline in nature [54]. The majority of current commercial PLA is poly (meso-lactide), which is a mix of PLLA (>95%) and PDLA (<5%) [16]. Cellulose ester is considered potentially as a useful biodegradable polymer [55]. The structures of cellulose ester, including cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are represented in Fig. 8. Advances in cellulose ester applications include modern coating technologies, control release applications and in making biodegradable plastics [56].

PHA is produced from renewable resources like sugar and carbon dioxide and sunlight in the case of transgenic plants [57]. The copolymer of PHA polymer, i.e., poly- $\beta$ -



**Fig. 4** The dependence of the elastic modulus of plant fibres on the angle between the cellulose molecules and the fibre principle axis for bast fibres (*solid markers*), leaf fibres (*sisal*) and seed fibres (*cotton*) (Courtesy: Summerscales et al. [9]:part 1)



**Fig. 5** **a** Fibre strength against fibre diameter. **b** Fibre strength against mean fibre length (Courtesy: Virk et al. [46])

hydroxybutyrate (PHB) and poly- $\beta$ -hydroxybutyrate-co-valerate (PHBV) are successfully used as a matrix polymer in designing different varieties of fibre composites such as abaca [2], jute [42], flax [23], man made cellulose [2], bamboo [6, 39], wood fibre [18], cellulose [58] etc. to name a few.

There are many advantages of using biopolymer over petroleum based products.

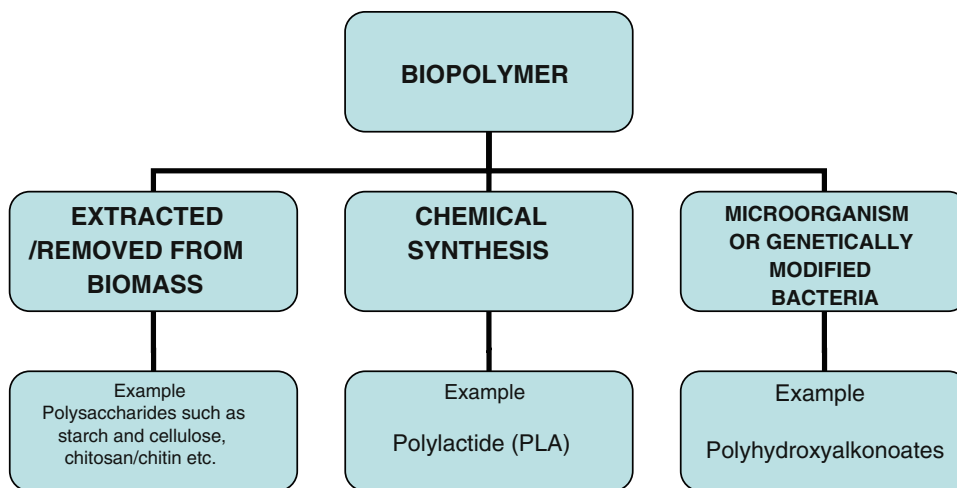
- It can be obtained from renewable agricultural resources [53].
- Its production consumes substantial quantities of carbon dioxide [59].
- It provides significant energy savings [60].
- It is recyclable and compostable [36].
- It can help farm economics [52].
- The physical and mechanical properties can be manipulated through the polymer architecture [2].

### Reinforced PLA Based Biopolymer with Natural Fibre

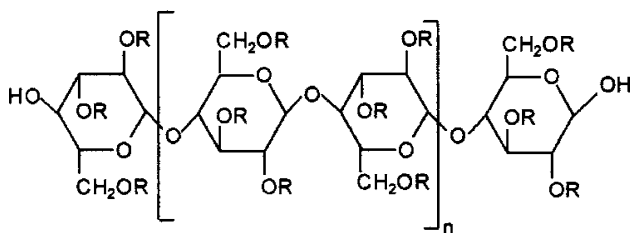
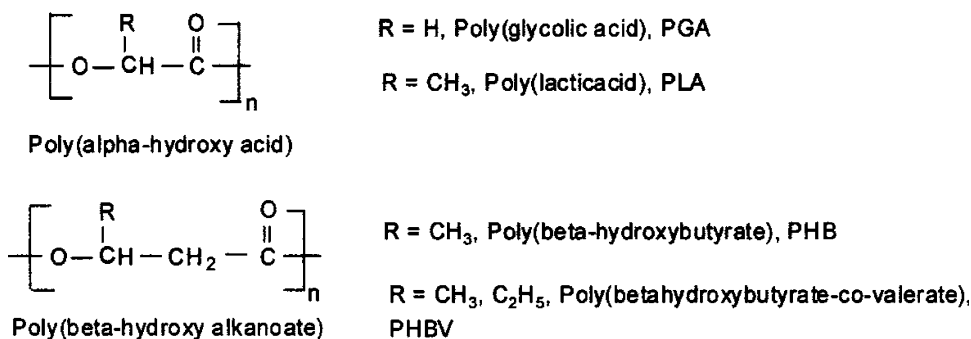
Among the available biopolymer, PLA is a naturally sourced thermoplastic polymer which can be produced with a capacity of over 140,000 tonnes per year [16]. The low emission of greenhouse gases and the low amount of energy used for PLA is promising [62]. The high price of PLA in comparison to other petroleum based products is the key factor to lower its competitiveness [63]. However, in the future increasing research and development achievements together with increasing demand of alternative petroleum based products is expected to reduce its price [53]. However, PLA is brittle in nature [61]. A possible strategy to further reinforce the mechanical properties of PLA with natural fibres has been developed by other researchers with different types of fibres, such as: kenaf [24], flax [25], Jute [26], abaca [27], and a cordenca rayon fibre [64] as reinforcement in order to replace synthetic fibre in polymer composites. A comparative study on the mechanical properties of PLA based composites with different reinforcement fibres is given in Table 3. Bax and Mussig [64] in their endeavour to prepare Cordenca reinforced PLA composite reached a maximum increase in impact strength of  $72 \text{ kJ/m}^2$  at a fibre mass ratio of 30 wt% which is approximately 4.5 times higher the value of pure PLA. Bledzki et al. [3] obtained better results as well when they used man made cellulose as reinforcements. A decrease in impact strength is observed in case of jute reinforcements with flax fibres by Plackett et al. [26]. Similar results were observed by Oksman et al. [25] and Bax and Mussig [64] when they tried to reinforce PLA based composites with flax. In a publication by Gangster et al. [65], the impact strength of a PLA/Cordenca composite with a fibre-mass proportion of 25% was examined with a value of approximately  $70 \text{ kJ/m}^2$ .

The impact strength of PLA/Cordenca composite is therefore more promising than all other biocomposites. Interestingly, when compared to the impact strength of flax/PP composite (which is  $32 \text{ kJ/m}^2$ ) as available in the

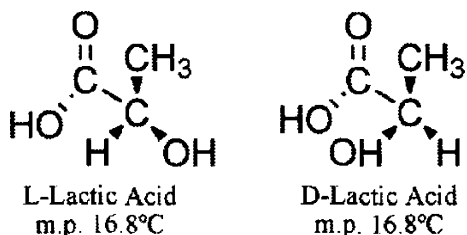
**Fig. 6** Classification of biopolymer according to origin and production



**Fig. 7** Structure of important biodegradable biopolymer (Courtesy: Mohanty et al. [7])



**Fig. 8** Structure of cellulose ester.  $n = 400\text{--}750$ ; R = H (Cellulose), acetyl (Cellulose Acetate) acetyl and propionyl (cellulose acetate propionate), or acetyl and butyryl (Cellulose Acetate Butyrate) (Courtesy: Mohanty et al. [7])



**Fig. 9** Chemical structure of L and D-lactic acid (m.p is melting point) (Courtesy: Auras et al. [53])

literature [66], the choice of PLA based Cordenka composites is more promising.

At impact the fibre is accompanied by three primary mechanisms, namely debonding, pull out and fracture. It has been assumed that the strain energy which is released by fibre debonding and fracture is proportional to the fibre length and diameter [46]. Thus, a much higher energy will be absorbed when there is a poor adhesion between the matrix and the fibre [3]. It may therefore be concluded that the better fibre/matrix adhesion in the PLA/flax composite is the cause for its worst impact strength as compared to PLA/Cordenka composite. From Table 3, it is reviewed that the reinforcing effect of the natural fibres and especially their influence on the elasticity of the composite are very high in comparison to unreinforced PLA. The variety of natural fibres has a fundamental influence on tensile strength. However, the reinforcement with man made cellulose clearly shows higher values as compared to other natural fibres. Bledzki and Jaszkiwicz [2] achieved 50% increase in tensile strength, while Bax and Mussig [64] obtained approx. 30% tensile strength improvement, which is similar to the values obtained by Gangster et al. [65]. Within the natural fibre group, jute seems to achieve the highest improvement in the study conducted by Bledzki and Jaszkiwicz [2] with a fibre loading of 30 wt% similar

**Table 3** Comparison of the mechanical properties of PLA composites with different reinforcement fibres

Sr No	Source	Fibre type	Fibre proportion in % wt	Charpy impact in %	Tensile strength in %	Young modulus in %
1	Bledzki and Jaszkiwicz [2]	Man Made Cellulose	30	260	175	1.5
2	Bledzki and Jaszkiwicz [2]	Jute	30	–	285	–
3	Shibata et al. [27]	Abaca	20	–	104*	170*
4	Gangster and Fink [65]	Cordenka	25	188*	157*	146*
5	Bax and Mussig [64]	Cordenka	30	447	130	155
6	Oksman et al. [25]	Flax	30/40	63*	106	244
7	Bax and Mussig [64]	Flax	30	69	121	202
8	Plackett et al. [26]	Jute	40	93	182	271
9	Nishino et al. [24]	Kenaf	70	–	286	492
10	Huda et al. [73]	Wood Flour	30	–	92*	196
11	Bledzki et al. [3]	Man Made Cellulose	30	360	145	175
12	Bledzki et al. [3]	Abaca	30	120	240	240

P.S > Because the values for mechanical properties for pure PLA presented in different papers differ significantly from each other percentage change values compared to the value for pure matrix material given in every particular work are presented. Values marked with an asterisk are calculated by using information which was not given in numeric values but in figures

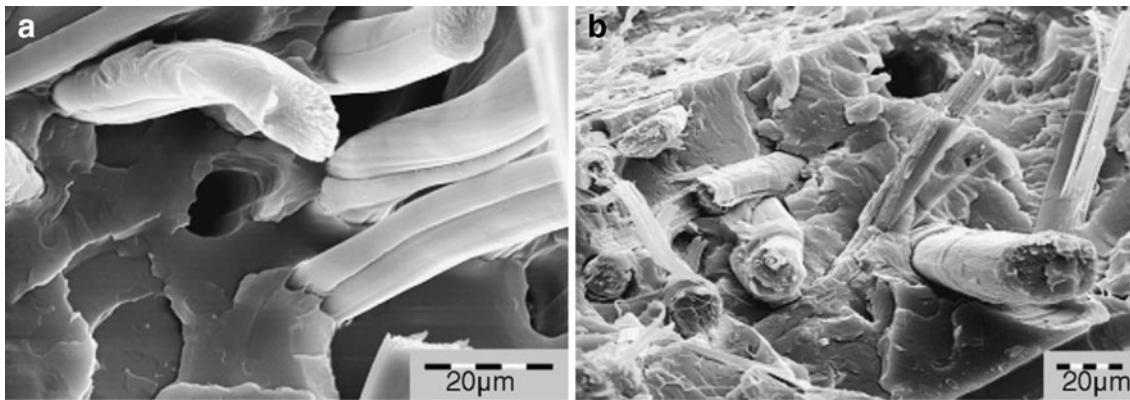
to the result obtained by Plackett et al. [26], after Kenaf, when Nishino [24] tried to further reinforce the kenaf based fibre by adding triacetin as a plasticizer.

Figure 10 shows the structure of “fibre bundles” where the cellulose is embedded in lignin, which functions as a kind of matrix. A natural fibre (fibre bundle) can be considered as a kind of naturally occurring composite. As stated earlier, the fibre strength can differ according to the orientation of the cellulose fibrils along the fibre axis. The other factors that affect the mechanical strength include fibre diameter, length and the aspect ratio. Natural fibre bundle diameter ranges considerably more than 50  $\mu\text{m}$ . Man made cellulose occurs in most cases as an elementary fibre with a diameter of only 12  $\mu\text{m}$ . Increasing fibre diameter affects the aspect ratio (fibre length/fibre diameter; L/D) and thus decreases the mechanical performance of the composites [2]. Bledzki and Jaskiewicz [3] pointed out that the highest aspect ratio of the man made cellulose fibre is the main cause for its enhanced mechanical properties. Similarly, jute fibre bundle undergo separation during processing, allowing a better distribution and a favourable diameter for improved mechanical properties.

### Fibre/Matrix Adhesion: Challenges

As shown in Fig. 9, PLA has slightly polar oxygen atoms which could form hydrogen bonds to the hydroxyl groups of the natural fibres. However, from literature review

[2, 3, 64], it can be assumed that these hydrogen bonds only have a small influence on the fibre/matrix adhesion. Approximation between the polar groups cannot occur during processing because of the macromolecular structure of cellulose, hemicellulose and lignin which are the main components of natural fibre. Scanned Electron Microscopy (SEM) images as taken by Bax and Mussig [64] of impact specimen are shown in Fig. 10. From this figure, it is evident that the fibre pull out is more distinct in case of PLA/Cordenka composite in comparison to PLA/flax composite. Longer fibre pull outs and cleaner fibre surfaces in case of PLA/Cordenka composites as shown in Fig. 10a is an indication for poor adhesion between PLA and Cordenka than between PLA and flax. in Fig. 10b. The authors concluded that the gaps between the PLA and the fibres could be possibly either due to debonding during mechanical testing or poor approximation during composite production. They compared their results with the composite of flax fibres in a MAPP (maleic anhydride-grafted polypropylene) matrix as an example of good matrix/fibre adhesion [66]. Similar result is observed by Plackett et al. [26] and in their Electron Microscopy Observation where jute fibres under tension show brittle failure. Moreover, void spaces between the fibre and polymer matrix indicates that the strength of the jute/PLA interface could be improved. Oksman et al. [25] in his study also found long fibre pull outs and clean fibre surfaces in the fractured surfaces of PLA/flax composites which proves a poor adhesion between the fibre and the matrix.



**Fig. 10** Detailed pictures of the fracture surface of composites with a mass proportion of 30% after impact testing **a** PLA/Cordenka composite, **b** PLA/flax composite (Courtesy: Bax and Mussig [64])

### Engineering Designing of Superior Biocomposites

Mohanty et al. [7] suggested a tri-corner approach of designing superior strength biocomposites, which include:

- Efficient (low cost but effective) bio fibre treatment.
- Matrix modification (functionalizing, blending)
- Selection of efficient processing condition

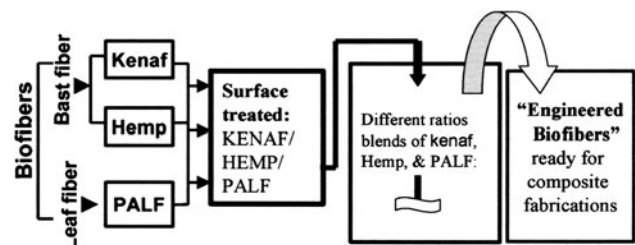
As discussed in the former section, natural fibres have a poor adhesion to hydrophobic matrices like PP because of their hydrophilic nature. Thus, there is a general assumption that hydrophilic nature of PLA will facilitate a better interaction between PLA and natural fibres. Nevertheless, long fibre pullouts and clean fibre surface of the PLA flax composites as observed by Oksman et al. [25] proves a poor adhesion between the fibre and the matrix. Bax and Mussig [64] concluded that these gaps observed could be possibly either by debonding during mechanical testing or poor approximation during composite production. Mohanty et al. [7] gave a schematic representation of the design of engineered natural fibre to prepare superior biocomposite as shown in Fig. 11, in context to the surface treatment of natural fibre to improve its adhesion to the matrix. The following paragraph gives a brief review on present state of the art approaches taken in relation to this tri corner approach to design such superior biocomposites.

#### Bio Fibre Surface Treatment

Surface treatment of fibre is designed to facilitate a better adhesion between the fibre and the matrix. Surface treatment can be accompanied by either adding compatibilizers or by chemically treating the fibre to alter the polymer architecture [22]. As PLA is a brittle material [61], Oksman et al. [25] tried to improve the adhesion of PLA/flax composite by using triacetin as a plasticizer. The addition of triacetin (12–15%) shows a positive effect on the

elongation at break for both pure PLA and PLA/flax composites. However, the highest addition of triacetin (15%) shows a negative impact on the stress and stiffness of the composite (Table 4). It is observed that addition of 5% triacetin in PLA shows the best impact strength. A close observation on the data presented in the table also reveals increasing standard deviation with increasing triacetin content. This phenomenon may be correlated to the residual moisture content in the flax which may have a negative effect on the triacetin/PLA fibre system. As expected, addition of 10 wt% triacetin decreased the thermal properties of PLA, owing to its plasticizing effect. Tan delta was increased from 55 to 70 °C, indicating some kind of interaction effect between the fibre and PLA due to triacetin. This study shows that triacetin can be used as a compatibilizer for the PLA flax system.

Shibata et al. [27] performed surface treatment of abaca fibre in preparing PLA based composites by esterification, alkali treatment and cyanoethylation to improve the interfacial adhesion between the matrix and lingocellulosic fibre. Esterification is accompanied by soaking chopped abaca fibres in acetic anhydride (or butyric anhydride/pyridine (molar ratio 1:1) solution at room temperature for approx 3 h. The filtered and washed fibres are subsequently treated with ethanol and dried at 70 °C. Alkali treatment is performed by soaking the chopped fibres in 2% sodium



**Fig. 11** Concept of design of engineered natural/bio fibre. PALF pineapple leaf fibre (Courtesy: Mohanty et al. [7])



**Table 4** Mechanical testing of plasticized PLA with triacetin with or without flax (Courtesy: Oksman et al. [25])

Materials	Elongation to break (%)	SD	Max stress (Mpa)	SD	E-Modulus	SD
PLA	2.0	0.2	50.3	2.4	3.4	0.1
PLA/5 5 Tri	2.2	0.2	41.7	3.4	3.0	0.2
PLA/10% Tri	1.8	0.2	43.6	1.6	3.4	0.2
PLA/15% Tri	2.6	0.1	37.2	1.6	2.6	0.2
PLA/40% Tri	0.9	0.2	44.1	7.2	7.3	0.5
PLA/5% Tri/40% flax	1.4	0.3	43.2	2.6	7.3	0.4
PLA/10% Tri/40% flax	1.1	0.5	29.5	4.0	5.4	1.0
PLA/15% Tri/40% flax	2.3	1.8	16.6	4.7	2.4	0.4

hydroxide aqueous solution for 2 h. Cyanoethylation is performed in three steps, soaking fibres in 4% sodium hydroxide aqueous solution for 1 h, followed by filtering and again soaking in acrylonitrile at room temperature for 1 h and subsequently washing it with 5% acetic acid before drying at 70 °C. Cyanoethylated abaca fibre slightly became wrinkled on the surface. Figure 12 represents the schematic structure of the surface modified fibre. The extent of surface modification by esterification and cyanoethylation is evaluated by the degree of substitution of average number of hydroxyl groups. No significant changes are observed in case of esterified or alkali treated fibre. However, cyanoethylated fibre shows wrinkled surface. The IR spectroscopic changes as reported due to the surface treatment shows an increased stretching vibration absorption of the C=O of ester group ( $1,750\text{ cm}^{-1}$ ) in esterified fibre, whereas for alkali treated fibre, this absorption energy decreased ( $1,750\text{ cm}^{-1}$ ). For cyanoethylated fibre a characteristic absorption of a cyano group ( $2,100\text{ cm}^{-1}$ ) is observed. Alkali treated fibre resulted in weight loss because of the leaching out of some of some fibre component. The effect of the surface treatment of the abaca fibre on the flexural modulus of the composite is not so pronounced. However, surface esterification using butyric anhydride or acetic anhydride is effective in increasing the flexural strength of PBS and PEC/PLA composites. The composites containing untreated fibre show the highest weight loss, indicating the highest biodegradability.

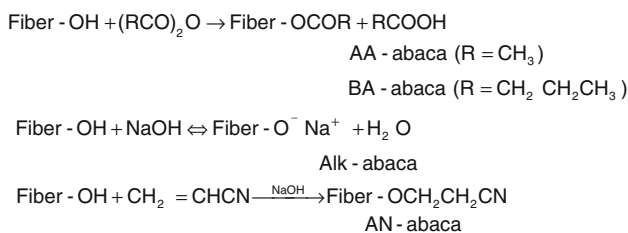
#### Matrix Modification

The recently announced heat-resistant PLA is based on stereocomplex technology. Stereocomplex formation between PLLA and PDLA occurs when L-lactide unit sequences and D-lactide unit sequences coexist in one system [54]. Stereocomplexation of PLA sometimes is also called stereocomplex (sc) crystallization or racemic crystallization. Melt blending PLLA and PDLA with a D/L ratio of 1:1 produces sc-PLA crystals with a melting temperature of 210–240 °C, which is about 30–60 °C higher

than the melting temperature of homo-crystalline PLLA [16]. Tsuji and Ikada [67] reported that stereocomplexation of PLA can improve the tensile properties of PLA films which was prepared by solvent casting. The blended sc-PLA films were reported to have better tensile properties compared to both non-blended PLLA and PDLA films. The improved tensile property was caused by the formation of stereocomplex macro-gel during solvent evaporation [67]. Moreover, the crystal growth rate of sc-PLA is reported to be comparable to that of PE [68]. Therefore, sc-PLA is potentially suitable for melt spun fibres and biaxially stretched films. Stereocomplex blends of PDLA and PLLA have a wide range of applications such as heat resistant automobile textiles [69], PLA foam as an insulation material [68], mobile phone housing [70] and many other applications.

#### Efficient Processing Condition

The mechanical properties of the fibre reinforced PLA composites depend on the fibre matrix adhesion, which may also be directly related to processing condition. Processing condition affects the degree of fibre wetting, crystallinity and composite porosity. Improved processing condition was obtained by Plackett et al. [26], when they prepared jute-PLA composite by compression moulding from 180 to 210–220 °C. The tensile strength and the modulus increased by 38 and 17%. Bledzki et al. [2] depicted a two step process extrusion followed by injection moulding to prepare fibre reinforced PLA based composites. This approach is similar to the former studies as conducted by Gatenholm and Mathiasson et al. [58, 59] when they tried to study the influence of the processing parameters on and fibrous reinforcement of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHBV). Bledzki et al. [3] compounded together PLA with endless fibres through a coating die and cooled to ambient temperature using a twin screw extruder, which was followed by injection moulding to prepare the final composite. Improved mechanical properties with a two step extrusion process were reported in comparison to agglomeration of



**Fig. 12** Schematic structure of surface treated abaca fibre. AA-abaca, acetic anhydride; BA, butyric anhydride; Alk-abaca, alkali treated abaca fibre; AN-abaca, Cyanoethylated abaca. Fibre-OH represents any hydroxyl group in the fibre cellulose component (Courtesy: Shibata et al. [27])

the compound with twin-rotary mixer, as performed by Shibata et al. [27]. A two step extrusion process facilitates in good dispersion of fibres in the matrix and thereby improves its mechanical properties. Oksman et al. [25] studied the reinforcement of PLA with flax fibre content of 30–40 wt%. The studied composite materials were manufactured with a twin-screw extruder and then compression moulded to test samples. The objective of the study was to test the processing and the material properties and compare it with more commonly used polypropylene flax fibre composites. It was found that addition of flax to the PLA matrix improved the mechanical properties; however there was no further improvement on addition of more loading of fibre possibly due to the same processing condition and fibre orientation.

#### Effect of Moisture Content on Degradation and Adhesion Mechanism

PLA is sensitive to hydrolytic degradation under melt processing condition in the presence of small amounts of moisture. Thus, the hygroscopic nature of the natural fibres has a negative effect on the adhesion mechanism as well as biodegradability of such composites. When Oksman et al. [25] tried to use triacetin as a plasticizer in PLA/flax composites, high addition of triacetin (around 15%) leads to increased residual moisture content in the flax and thereby has a negative impact on the adhesion of the fibre to the matrix system. Shibata et al. [27] performed surface treatment on abaca fibres by esterification, alkali treatment and cyanoethylation. They found that the composites containing the untreated fibres showed the highest weight loss, indicating the highest biodegradability. Very recently, van den Oever et al. [71] studied the effect of water content in undried and dried natural fibres. Van den Oever [72] discussed in brief about the effect of drying of the natural fibres on the composites flexural and impact properties. Further studies by him [71], to evaluate the effect of water content in undried and dried natural fibres on semi crystalline grade PLA revealed that different levels of moisture

in the fibres have a similar and small effect on PLA degradation and PLA hydrolysis appears rather affected by fibre diameter. The fibres evaluated were ramie, flax and cotton, containing 6–9 mass% moisture in the undried state and 0.2–0.4 mass% in the dried state.

#### Conclusion and Future Research

Natural fibre reinforced PLA composites are a 100% bio-based material with a promising mechanical properties profile in comparison to non renewable petroleum based products.

The mechanical properties of such composites depend on the type of fibre used and its homogenization to the matrix. Key governing factors that affect the mechanical properties are the content of cellulose in the fibre, fibre orientation, fibre length and diameter to name a few. Fibre diameter affects the aspect ratio and thus decreases the mechanical performance of such composites.

The impact strength of the composite depends on different grades of the fibres in use and is inversely proportional to its adhesion mechanism to the matrix. At impact the fibre is accompanied by three primary mechanisms, namely debonding, pull out and fracture. It may be assumed that the strain energy which is released by fibre debonding and fracture is proportional to the fibre length and diameter. It may thus be concluded better fibre/matrix adhesion results in its worst impact strength.

Both PLA and natural fibres are hydrophilic in nature and apparently is assumed that this property will facilitate a better adhesion. However, poor adhesion is obtained probably due to debonding during mechanical testing or poor approximation during composite production. Moreover PLA is also subjected to hydrolytic degradation under melt processing condition in the presence of small amounts of moisture. The recent evaluation on the effect of water content in dried and undried condition revealed that hydrolysis of PLA is dependant on fibre diameter leaving aside other factors.

Improved fibre matrix adhesion and thereby improved mechanical properties can be accomplished by engineering a superior processing condition in preparing the biocomposites, by altering the polymer architecture of the matrix or by the surface treatment of the fibre. In case of PLA/fibre matrix, this is achieved by a two step extrusion process resulting in good dispersion of fibres in the matrix. Surface treatment is accompanied by adding plasticizers like triacetin to PLA/flax matrix or by surface modification like esterification and cyanoethylation in case of PLA/abaca fibre composite. However, the surface modification in the latter case did not result in significant improvement in tensile strength.

In the present review, it seems as though not much work has been done on altering the polymer architecture of PLA matrix. Although matrix modification of the PLA on stereocomplexation technology is promising, not much work has been done to apply this technology to prepare fibre reinforced composites. Further research on the degree of polymerization and crystallization of PLA that leads to improve the adhesion mechanism between the fibre and the matrix is yet to be explored.

Earlier researchers have indicated that the fibre and the PLA in the matrix are inversely proportional to the energy absorption at impact. So a variety of natural fibres used has an influence on tensile strength. It will be interesting to study as well the effect of branching and copolymerization of PLA on the tensile strength of the matrix.

It is also concluded by early researchers while explaining the PLA/fibre matrix adhesion mechanism that poor adhesion is probably due to debonding during mechanical testing or poor approximation during composite production. Future research in this area is required to find out as to how the debonding during mechanical testing or poor approximation contribute to the gap between PLA and fibre matrix.

It is also observed from this review that some composites containing untreated fibre showed the highest weight loss, indicating the highest biodegradability. A technical balance to optimize the surface treatment that increases adhesion mechanism while compromising on biodegradability features is important to compete with sustainability issues. Further research is required to find this technical balance and answer the growing concerns such as littering and increase in crude oil prices.

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