Journal of Computers, Mechanical and Management
Journal homepage: www.jcmm.co.in

Volume 1 Issue 1

Sustainable Green Composites: A Review of Mechanical Characterization, Morphological Studies, Chemical Treatments, and Their Processing Methods

Nithesh Naik[*][a], Nilakshman Sooriyaperakasam[b], Yashoda K. Abeykoon[c], Yomali S. Wijayarathna[d], G. Pranesh[a], Soumik Roy[a], Rovin Negi[e], Budnar Kunjibettu Aakif[f], Asela Kulatunga[g], and Jayakrishna Kandasamy[h]

[a]Department of Mechanical and Industrial Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India 576104
[b]Department of Mechanical Engineering, University of Moratuwa, Colombo, Sri Lanka 10400
[c]Department of Chemistry, Postgraduate Institute of Science, University of Peradeniya, Kandy, Sri Lanka 20400
[d]Department of Environmental and Industrial Sciences, Faculty of Science, University of Peradeniya, Kandy, Sri Lanka 20400
[e]Department of Aeronautics and Automobile Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India 576104
[f]Department of Chemical Enginering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India 576104
[g]Department of Manufacturing and Industrial Engineering, University of Peradeniya, Kandy, Sri Lanka 20400
[h]School of Mechanical Engineering ,Vellore Institute of Technology, Vellore, Tamil Nadu, India 632014

Abstract

Composites have a wide application in the modern world and have successfully replaced traditional engineering materials. Dependencies on composites are extensively increased due to the desire for material durability, high modulus, chemical inertness, flame retardance and thermal isolation. The emergence of new bio-based materials and technologies has taken on new dimensions, bringing with it the profound promise of sustainable development through green composites. Next-generation materials, such as green composites, offer users a wide range of benefits. Although several scholarly articles are available on green composites, the most common ones are not covered in a single paper in the currently available literature. As a result, this article aims to give an overview of bioresin-based green composites so the reader can better understand the mechanical properties, chemical treatment methods, and associated processing techniques.

Keywords: Green Composites; Green Fibers; Bioplastics; Mechanical Properties; Chemical Treatment

1 Introduction

Composites are versatile groups of compounds that can be seen in unexpected applications. Dependencies of composites are extensively increased due to the desire for material durability, high modulus, chemical inertness, flame retardance and thermal isolation. The composite materials are broadly classified into three major categories: polymer matrix, metal matrix, and ceramic matrix [1].

---

[*] Corresponding author: nithesh.naik@manipal.edu

Received: 14 September 2022; **Accepted:** 31 October 2022; **Published:** 31 October 2022

DOI: 10.57159/gadl.jcmm.2.3.23014.

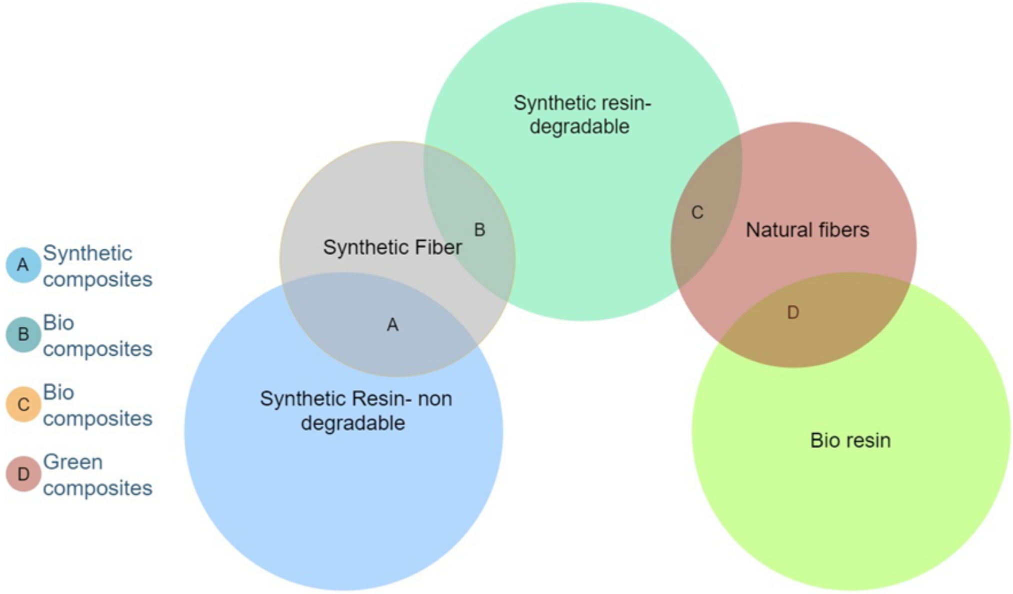


Figure 1: Classification of polymeric composites.

Among these composites, polymeric composites possess many benefits over the other two categories. Figure 1 depicts a broad classification of polymeric composites. These polymer matrices (both synthetic and biopolymers) are highly sought after due to their flexibility, lightweight and ease of production. Growing demand for sustainability has led to a surge for bio-based materials from non-renewable resources to replace synthetic materials. evolving decipherable information. Green composites (GC) show significant environmental friendliness and comparable attributes with synthetic polymers. GC prepared using natural fiber reinforcement demonstrates good mechanical properties such as tensile, compressive and flexural strengths and may be used for various applications [2–4]. Though the properties of GC predominantly depend on the properties of the matrix, fibers and reinforcement, the ultimate factor that dictates the properties of the composites is their intrinsic orientation of the constituents. Therefore, microscopic analyses are widely carried out to investigate the morphological properties of GC [5]. Finding new composite materials and improving the characteristic strength of composite materials remain the trend in the scientific community. Following that, the development of green materials is of serious interest soon after the realization of the environmental impacts caused by synthetic materials. Natural fiber production on the nanoscale is booming these days to incentivize the strength capacity of the reinforcement fibers in the composite elements [6, 7].

After all, the applications of biocomposites in automotive, building product applications, and aviation sectors, as well as biomedical, energy, and sports, have grown enormously [8, 9]. GC can either be formulated with natural fiber and biodegradable petroleum polymer matrices such as polycaprolactone (PCL), poly (butylene succinate) (PBS), co-polyester amide (PEA), poly butyrate adipate terephthalate (PBAT) and polyvinyl alcohol (PVA) or with natural fibers and bioresins [8, 10] such as cellulosic plastics, polylactides, soy-based plastics, starch plastics and microbially synthesized biopolymers. Several articles discuss green composites, but most often, they are only limited to a few fibers or resins or either limited to mechanical properties or chemical treatments of specific fiber/matrix combinations. In most cases, scholars overlook incorporating all aspects of green composites, including fiber and resin matrix processing methods. As a result, identifying gaps in all available relevant information and summarizing it in one place becomes an obvious requirement. Therefore, a potent researcher spends a great deal of time reading all the information from various sources, delaying the advancements that could contribute to creating a better world. Therefore, an effort has been made to synthesize all the relevant information related to the most common green fibers, bioresin & green composites in one place. Those interested in biofibers or bioresin can obtain most of the information from this article, as the authors have spent considerable time reviewing a vast body of literature and condensing it into a concise and informative paper. Composite manufacturers, young researchers, and those interested in GC can obtain as much information as possible from this single paper and expand their research, which may contribute to this field in the future.

In other words, the detailed study presented in this article aims to provide critical and clear insights into the commercially available/used bioresin-based green composites (BRGC), their biological classification, intrinsic properties, and surface preparation to achieve the optimal results desired for their respective applications. Through its various sections, this review discusses the biological classification of bioplastics and biofibers; the various mechanical characterization in terms of modulus, strength, flexibility, durability, micro macro-structural overviews; the chemical treatment methods; processing techniques of well-known GC; and challenges and future potentials of bioresin-based natural fiber reinforced green composites. Figure 2 provides a comprehensive overview of this review paper.

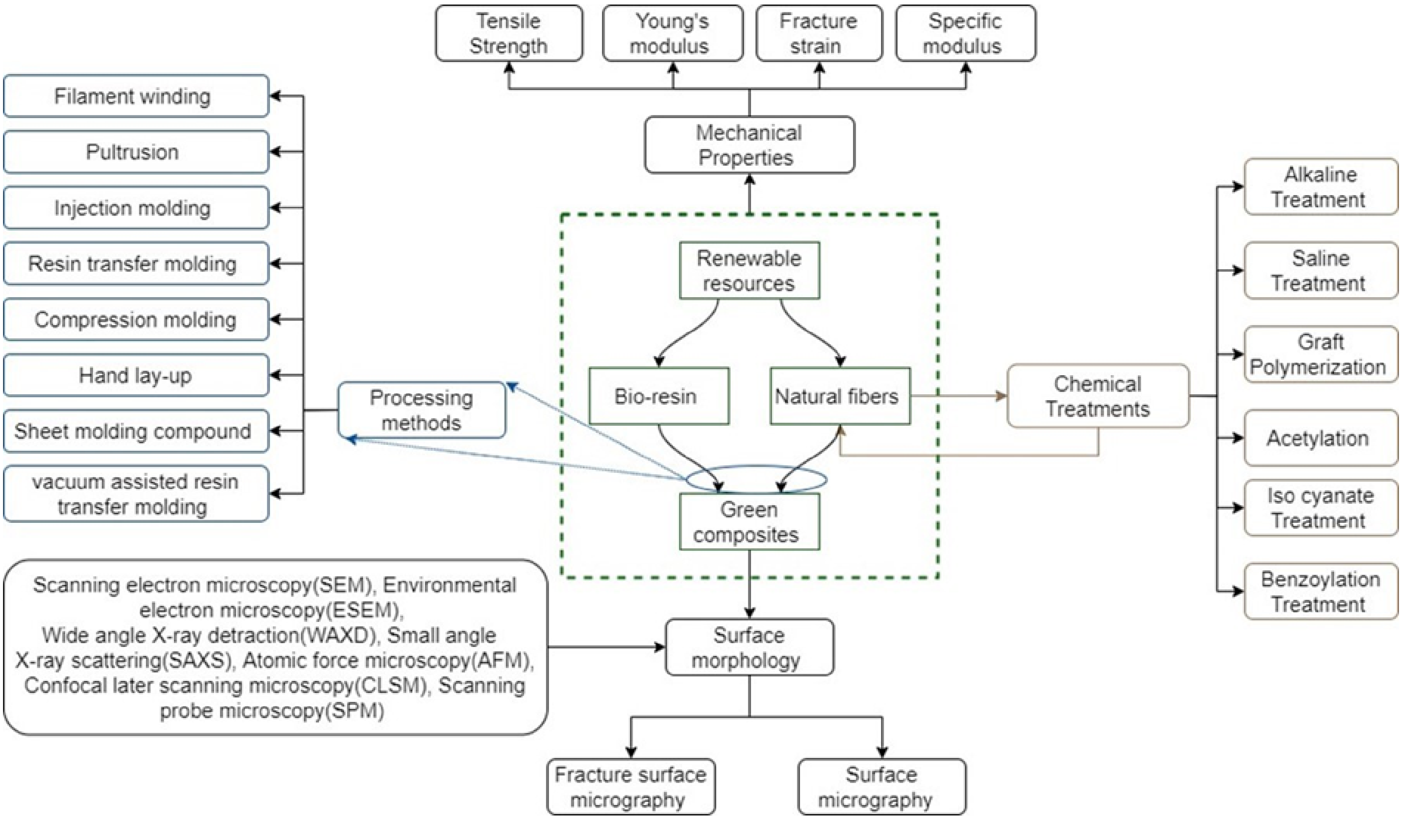


Figure 2: Overview.

2 Background

2.1 Search strategy

A non-systematic review of all published English-language material on green composites was done. The Google Scholar, SCOPUS, Research Gate, and Web of Science databases were scoured for academic articles for evaluation. The search was sequenced using numerous keyword combinations. The keywords employed were green composites, green fibers, bioplastics, mechanical properties, and chemical treatment. The permitted search terms included review articles, original research articles, case studies and data sets.

2.2 Selection strategy

The review includes all the articles that deal with the mechanical properties of green fiber/bioresin combinations, green fibers, chemical treatment of the green fibers, morphological analysis of fiber /matrix composites and green fibers. Apart from the inclusion and exclusion strategy, articles about all the relevant topics were manually searched to screen the work of interest and included if they matched the scope of the study.

2.3 Inclusion criteria

- Articles on green composites, green fibers and bioresin.
- Review articles and experimental studies on biocomposites.
- Full-text articles, experimental studies of different fibers/matrix combinations concerning the chemical treatment methods and morphological studies.

2.4 Exclusion criteria

- All the articles without full texts
- Studies that do not deal with the mechanical characterization, chemical treatment, and surface morphology of the green fibers, bioresins and their combinations

3 Biological Classification of Green Composites

The GC can be manufactured by combining natural fibers and biodegradable polymers, where biodegradable polymers can be derived from microbial synthesis, petrochemical synthesis, or natural resins. The constituents of green composites are summarized in Figure 3.

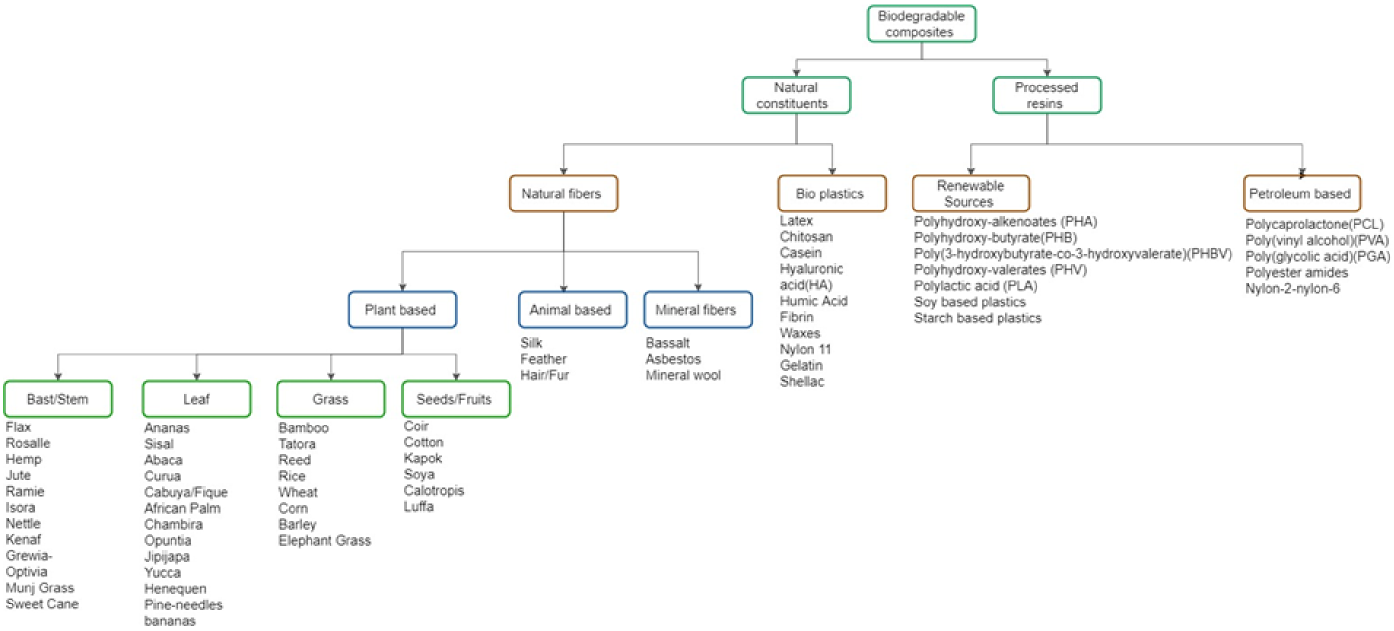


Figure 3: Classification of green composites.

3.1 Natural fibers

Almost all fibers are possible candidates for composite reinforcements. However, the cost, environmental requirements and performance standards are the factors that need to be satisfied before their deployment. Plant-based fibers, primarily lignocellulosic fibers, can meet these requirements. However, before employing fibers as a constituent for composites, they should be isolated from other constituents like lignin, hemicellulose, wax and proteins [8]. Natural fibers can be subdivided into fibers derived from plants, animals, and minerals. Plant-derived fibers can further be classified into wood feedstock or non-wood feedstock. Non-wood fibers are again subdivided into the grass, stem/bast, leaf or seed hair/fruit fibers, depending on their origin [11]. The reinforcement fibers' main objective is to improve the mechanical properties of the final composite. However, natural fibers extend the potential to deliver greater added value, sustainability, renewability and lower costs, especially in the automotive industry. Table 1 shows the annual production of commercially available natural fibers [11–13].

Fibers from agricultural residue

It is abundantly clear that the annual accumulation of agricultural residues, which ultimately leads to burning such biomass in open fields, will contribute to global warming [14]. As an alternative, researchers and environmental activists have started focusing on utilizing bio-waste while minimizing feedstock costs and negative environmental impacts [15]. The most abundant agro-residues are cereal straws, primarily utilized for energy generation and animal feed. According to the Cambridge University Press, the world's energy intake from cereal grains is around 60%. So, the opportunity to utilize the agricultural residue fibers is workable. Generally, the main fiber extracted from agricultural remaining is called cellulose fiber (CF). Bio-based residuals can be used as a reinforcement in many instances, such as bagasse, sunflower stalk, corn stalk, rice husk, soy stalk, wheat straw, corn husk [16–20]. Several studies deal with producing green composites from agricultural residues. Crop residues are excellent alternative substitute resources for natural fibers as they are bulkily available at low cost and widespread on a greater scale.

3.2 Bioplastics (Bioresins)

The matrix governs the composites' shapes, environmental tolerances, surface mien, and durability. Composite matrix/resin contributes the largest towards the environmental impact for most composite syntheses. Therefore, implementing a bioplastic (bioresin) would help achieve a positive impact on the sustainability of the outcome. Table 2 lists the commercially available/emerging bioplastics used in the different industrial arenas. Bioresins are generally derived as artificial or man-processed macromolecule constituents produced by biological sources. In other words, bioresins bind the fibrous material together and disperse the stress element throughout the composites, also known as the disperse phase. Crop-based bioplastics can either be thermosetting or thermoplastics. However, some studies reveal that non-biodegradable biopolymers can be seen in a few durability-demanding applications.

Table 1: Commercial natural fiber production [12, 13]

Fiber Source	World Production (10^3 tons)
Sugar cane Bagasse	102000
Bamboo	30000
Jute	2850
Kenaf	970
Flax	830
Grass	700
Sisal	378
Hemp	214
Coir	650
Ramie	100
Abaca	91
Banana	200
Cotton	19010
Kapok	123

These discoveries may contradict the paradigm that all natural polymers are biodegradable. Due to the desire for persistent polymers, which can be an alternative to synthetic polymers, non-degradable bioplastics were synthesized in a way that may degrade at very low rates / in the presence of specialized microorganisms. Polythioesters (PTE) [21] drop-in bioplastics such as bio-based polyethylene terephthalate (PET), bio-based Polyethylene Furanoate (Bio-PEF) [22], bio-based polyethylene (PE), bio-polycarbonate, bio-polyamide (PA 4,10/ PA 6,10) are few examples of biopolymers whose degradation rates are low. Biopolymers can either be hydrophilic or hydrophobic. Generally, bio-based polymers are the different constituent classes of hydrocolloids and lipids. These hydrocolloids are hydrophilic in nature. Lipids are hydrophobic in nature. Polysaccharides are hydrocolloids. Usually, they are carbohydrates formulated with carbon, hydrogen and oxygen in a 1:2:1 ratio. Polypeptides are generally proteins, a formation of long-chain amino acids. Figure 4 illustrates how conventional bioplastics fall under polysaccharides and polypeptides.

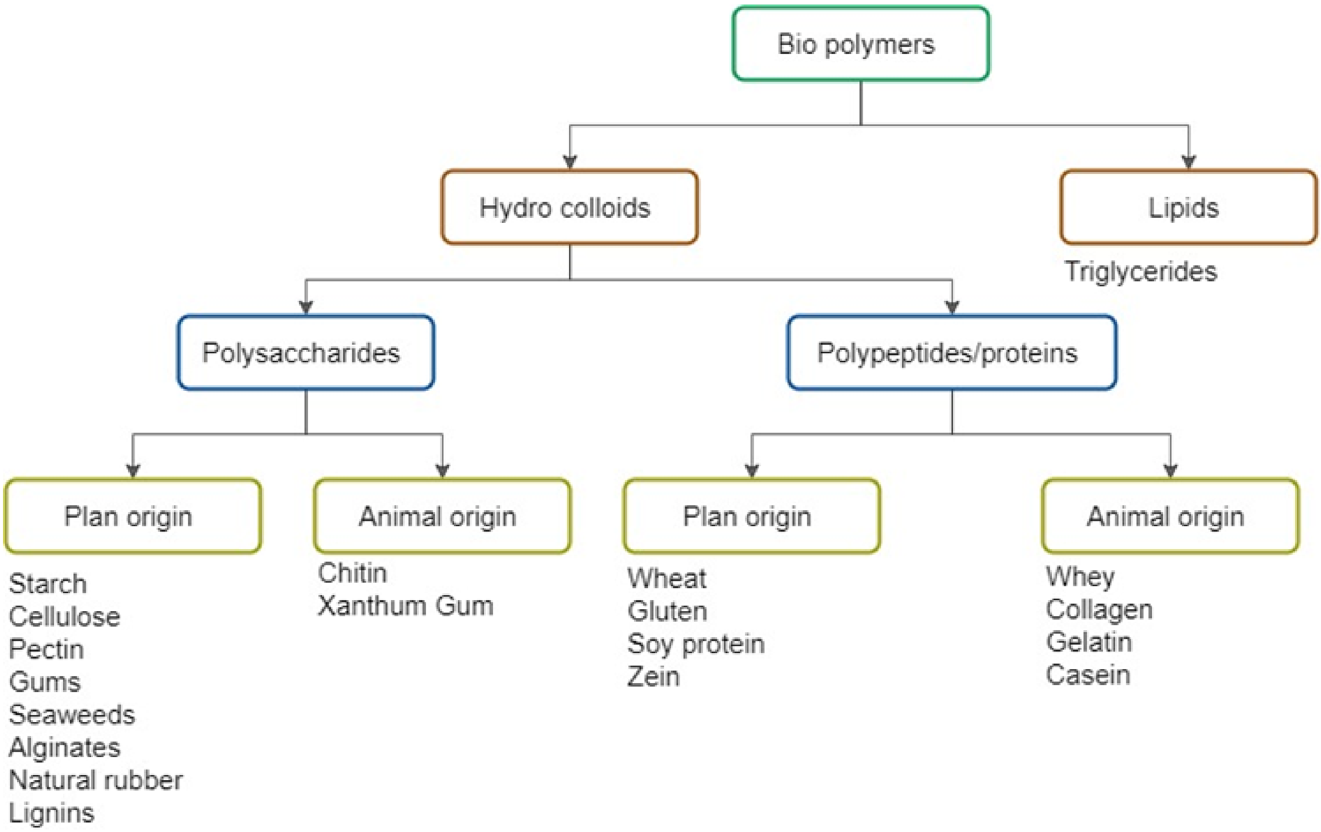


Figure 4: Types of biopolymers [23].

Table 2: Commercially available biopolymers.

Polymer	Feedstock, Method of process
Polyhydroxy Alkenoates (PHAs)	Direct synthesis from sugar, Microorganism/bacterial fermentation
Polylactic acid (PLA)	L-Lactic Acid, D-Lactic acid, Chemical and biological synthesis
Poly (Acrylic acid) (PAA)	3-Hydroxypropionic acid, Radical polymerization
Polyethylene (PE)	Ethanol, Dehydration and polymerization
Polyvinylchloride (PVC)	Ethanol, Dehydration and polymerization
Polyamide 11 (PA11)	Ricin oleic acid, Condensation reaction
Polyisoprene (Natural Rubber)	Isoprene, Mini-emulsion polymerization
Polyacrylic acid	3-hydroxy propionic acid, Dehydration, purification and Crystallization
Cellulosic	Cellulose, Dissolving, Extrusion and Precipitation
Thermoplastic starch (TPS)	Starch, Twin screw extrusion, mixing method
Aliphatic Polyester	1,3-propanediol, succinic acid, fatty acids, Copolymerization
Polyether	1,3-propanediol, fatty acids, Super acid-catalyzed condensation
Furan resins	Xylose, Polycondensation under the presence of weak acids
Epoxy resins	Triglycerides, Epoxidation
Bio-based Polyethylene Terephthalate (PET)	Sugarcane -Sugar, Fermented and distilled to ethanol, Monoethylene glycol (MEG) from bioethanol, MEG is combined with purified Terephthalic acid (PTA)
Bio-based Polyethylene (PE)	Sugarcane -Sugar, Fermented and distilled to ethanol, Dehydrated to ethylene, Polymerization
Bio-Polycarbonate (PC)	Corn-Isosorbide, Hydrogenation of Glucose to produce sorbitol, Isosorbide is obtained from double dehydration of sorbitol
Bio-Polyamide (PA 4,10/ PA 6,10)	Castor oil -Sebacic acid, The Dicarboxylic acid (Sebacic acid) part of Polyamide is produced from a renewable resource (Castor oil)

The scientific identification of green materials

ASTM D6866 is a standard test method for determining bio-based/biogenic carbon content or the percentage of bio-based contents of the given substances using radiocarbon analysis. The analysis is the percentage calculation of the relative amount of 14C in the carbon content of the material. In general, fossil-based carbon does not contain a 14C isotope, whereas materials that belong entirely or particularly to renewable resources have a significant amount of carbon isotope material. The tests reveal the results with a maximum total error of ±3% (absolute). This method does not elaborate on environmental impact, product performance, functionality or geological origin and is only applicable to compostable material which can produce CO_2 by-products. The major limitations of plant fibers compared to synthetic fibers are their non-uniformity, dimensional variations and variant mechanical property due to the variations between two fibers (though from the same cultivation), and the majority of composites comprised of natural materials are susceptible to performance and dimension changes when they come into contact with water.

4 Mechanical Characterization of Green Composites

Composites are the mixture of different constituents to form a single substance which is often intended to produce superior material performance compared to its sole materials. It is the mixture of substances wherein physical bond makes it compact. Those constituents are namely the continuous phase (matrix), dispersed phase (reinforcement) and interfacing phase (contagious coatings). As the fibers in a GC are hollow and lignocellulosic substances, they have very good thermal and acoustic insulation properties compared to synthetic fibers. But still, the mechanical properties of natural fibers are lagging compared to synthetic fibers. Studies report that chemical and mechanical surface treatments can overcome mechanical performance deficiencies of natural fibers and enhance the surface roughness of the subjective fiber material. However, due to the low-density factors and the specific mechanical modulus, the gravity is comparable to or even better with synthetic fibers. Table 3 tabulates green fibers' mechanical and physical properties that reinforce the green composites. Nevertheless, a study on hemp fiber elaborated on the changes in the mechanical properties with fiber separation wherein the hemp fiber separated with the 'steam explosion separation' method showed superior tensile properties compared to the fibers separated using the 'biological separation' method for the same fiber [10]. Material elongation is one of the critical considerations when choosing the right materials. As the materials are usually subjected to high strain and harsh environmental conditions, the fracture strain of the green composites increases larger than that of room temperatures. Generally, these composites demonstrate high elasticity with high temperatures [24]. The fiber aspect ratio is majorly dependent on how the fibers are extracted and processed, and both fiber orientation and the aspect ratio strongly influence the composite formulation. In a nutshell, it affects the mechanical properties of overall composite performance in return. The impact performance of the composites ensures the degree of usability of composites in the harsh environment, which is the primary sake for the usage. Yet, the crucial element of green composites is fiber/matrix adhesion which promotes good stress transfer. In general, cellulose in the fibers has a strong hydrophilic character due to three hydroxyl groups per monomeric unit, but biopolymers like PLA and poly (hydroxybutyrate) are generally hydrophobic [26, 25].

Table 3: Mechanical and physical properties of natural fiber [13, 24, 25]

Natural fiber	Tensile Strength (MPa)	Young's modulus (GPa)	Specific modulus (GPa)	Failure strain (%)	Length, l (mm)	Diameter, d (µm)	Density (kg/m3)	Microfiber angle (J)
Cotton	300-700	6-10	4-6.5	6-8	20-64	11.5-17	1550	20-30
Kapok	93.3	4	12.9	1.2	8-32	15-35	311-384	-
Bamboo	575	27	18	-	2.7	10-40	1500	-
Flax	500-900	50-70	34-48	1.3-3.3	27-36	17.8-21.6	1400-1500	5
Hemp	310-750	30-60	20-41	2-4	8.3-14	17-23	1400-1500	6.2
Jute	200-450	20-55	14-39	2-3	1.9-3.2	15.9-20.7	1300-1500	8.1
Kenal	295-1191	22-60	-	-	2-61	17.7-21.9	1220-1400	-
Ramie	915	23	15	3.7	60-250	28.1-35	1550	-
Abaca	12-400	41	-	3.4	4.6-5.2	17-21.4	1500	-
Banana	529-914	27-32	20-24	1-3	2-3.8	-	1300-1350	11-12
Pineapple	413-1627	60-82	42-57	0-1.6	-	20-80	1440-1560	6-14
Sisal	80-840	9-22	6-15	2-14	1.8-3.1	18.3-23.7	1300-1500	10-22
Coir	106-175	6	5.2	15-40	0.9-1.2	16.2-19.5	1150-1250	39-49
Oil palm	248	3.2	-	25	-	-	0.7-1.55	-

So, the material adhesion properties are to be ensured to the better stress transfers among the fiber & matrix.Mechanical characterization is one of the prevalent methods to predict the mechanical performance of any composites. It enables researchers to classify the composites according to their tensile strength, young's modulus, flexural strength, compressive strength, flexural modulus and impact strength. Mechanical property measurements of composites and fibers must adhere to a standard testing procedure, preferably the one prescribed by the American Society of Testing Materials (ASTM). The mechanical properties of green composites depend upon various parameters such as fiber aspect ratio, percentage of fiber content, surface treatment of fibers, coupling agents to increase the bonding between fiber and matrix and fabrication techniques [27–30]. It is to be noted that the mechanical performances of the composite materials also largely rely on the fabrication process. The materials' tensile moduli and tensile strength show slight increments with the compression pressures applied during the molding process. Table 4 summarizes the mechanical properties of the most common green composites.

5 Morphological Study of Bioresin-based Composites

The physicochemical orientation of the intrinsic constituent governs and differentiates composites' properties. Fiber reinforcements in the composites have two different forms, (a) woven and (b) non-woven (bulk fiber /fiber bundle). Different techniques can categorize the physio-chemical properties. Structural properties are analyzed by spectroscopic and microscopic techniques such as scanning electron microscopy (SEM), environmental electron microscope (ESEM), confocal laser scanning microscopy (CLSM), small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), and wide-angle X-ray diffraction (WAXD) [27–29]. On the other hand, the measurement of other properties of the composite films is very extensive and depends on the individual applications [30]. The surface morphology micrograph analysis widely varies with the purpose of the subject content. The fractured surface morphology is one of the popular usages of micrographs for observing the intrinsic behavior of composites during tensile/impact/fracture and toughness testing, [16, 29–34]. The next significant importance following the fractured surface morphology is given to fiber surface pre-treatments morphology to confirm the level of roughness, smoothness, cavity and voids on the surface [35, 36]. Also, water absorption testing measurement practices outlined with standard ASTM D570-81 have often been seen to use micrograph analysis Liu2005,Lee2006. In some instances, surface micrographs were used to examine the soil burial test of biodegradability [29].

6 Chemical Treatment

The primary disadvantage of using natural fibers as reinforcement in GC is their incompatibility with the matrix due to their surface impurities and affinity for water absorption. Thus, modification of the fibers into a compatible structure becomes essential. Generally, chemical modification is a process that utilizes chemicals to refurbish the surface of the fibers to perform better. Cellulose-based fibers are compacted with lignin, wax, pectin or crystalline constituents that rush the chemical penetration/matrix to fiber interfacial adhesion. So natural fibers undergo some modification, making them feasible for composite production. The chemical modifications can be classified into five methods: mercerization/alkaline treatment, oxidation, crosslink, grafting and coupling agent treatment [1].

Table 4: Mechanical and physical properties of green composites.

Constituents(Fiber /matrix)	Molding Pressure (MPa)	Fiber content (%)	Tensile strength (MPa)	Fracture strain (%)	Young Modulus (GPa)	Reference
Curaua/cornstarch-based	-	30.1	327	1.16	36	[33]
Abaca/PLA	-	30	74.0 ± 0.7	1.44 ± 0.1	8.0 ± 0.34	[13]
Jute/PLA	-	30	81.9 ± 2.9	1.8	9.6 ± 0.36	[13]
Lyocell/PBS	5	60	117.4	9.9	3.16	[28]
Abaca/(PHBV/Eco-flex)	-	30	28.0 ± 1.3	0.9 ± 0.1	4.4 ± 0.06	[13]
Ramie/Eco flex	9.8	44-52	75.9	8	1.67	[24]
Lyocell/PHBV	10	63.2	108.8	10.6	2.46	[28]
Lyocell/PLA	10	62.1	100.5	6.4	5.55	[28]
Hemp/PHBV	2.03	32	27	1.1	-	[9]
Coir dust/PHB	-	30	7.4	2.2	0.4712	[37]
Wood/PHBV	0.551	30	18.08	-	1.94	[34]
Bamboo/PHBV	0.551	30	18.9	-	1.71	[34]
Flax/Soy-protein	8	-	18.6	16.4	0.448	[38]
Hemp/Cashew nutshell	6	-	43.82 ± 6.36	0.89 ± 0.12	8.7 ± 1.46	[39]

Hydrophobicity and hydrophilicity are the two concerns regarding the chemical treatment of fibers or the fiber's compatibility preparation. In particular, hydrophile fibers do not promote adhesion compared to hydrophobic polymers; thus, they are called dispersed matrix. So, the poor wetting of fibers causes the non-uniform distribution of fibers and the void formation, leading to crack initiation and moisture penetration to the composites, resulting in anisotropy eventually. As a result of their hydrophilic nature, natural fibers also absorb moisture from the surrounding air and thus can be a serious problem, particularly for the thermosetting resins, as it inhibits the curing processes when the manufacturing process is being done, leading to the low mechanical performance of the entire composite materials. The chemical treatment of the natural fibers is one of the effective ways to compromise the interfacial bond impairments between the fibers and the resin matrix as it holds on to reduce the OH (Hydroxy) functional group from the fiber surface (ionic hydroxy groups have the thirsts of water) and improves the surface roughness that enhances the interfacial interaction. Numerous treatment methods were reported to improve fiber/matrix compatibility. Nevertheless, the adhesion between two materials is the function of several factors, including surface polarity and roughness. A study with Curaua fiber green composites held an experiment with untreated and 10% alkali-treated fibers, which showed considerable changes in the mechanical properties of the compact material [33]. In yet another study, the chemical treatment of jute fiber with pyridine showed an improvement in the surface structure, and complementary scanning electron microscope images of treated jute fibers proved the modification of natural fiber using chemical agents. Table 5 lists numerous chemical treatment methods used to enhance the properties of the fibers by altering the chemical groups, surface morphology, inherent wettability, and tensile strength. In a study, the mechanical treatment of wheat straw fibers was compared with the chemical treatment [40]. The authors concluded that chemical treatment provides way better results than mechanical treatment. As per the SEM photomicrographs, as depicted in Figure 5, wheat straw fibers processed by mechanical and chemical means, chemically treated fibers show a homogeneous, uniform surface texture while comparing mechanically processed fibers in which surface irregularities are more prevalent even after the treatment.

Table 5: Chemical treatment of different natural fibers.

Natural fiber	Chemical reactants	Reference
Pineapple leaf	c-aminopropyl trimethoxy silane (Z-6011) and c-methacrylate propyl trimethoxy silane (Z-6030)	[41]
Green coconut	NaOCl, NaOCl/NaOH, or H2O2	[41]
Sisal	NaOH	[42]
Bamboo	NaOH	[43]
Alfa	NaOH	[44]
Carica Papaya	NaOH	[45]
Kenaf	NaOH	[46]
Hemp	(3-glycidyloxypropyl) trimethoxy silane	[47]
Ramie	NaOH, NaOH-Saline, Silane	[48]
Pineapple leaf	NaOH and KOH	[49]
Sisal	Stearic acid	[50]
Sisal	NaOH	[42]
Okra bas	NaClO2	[51]

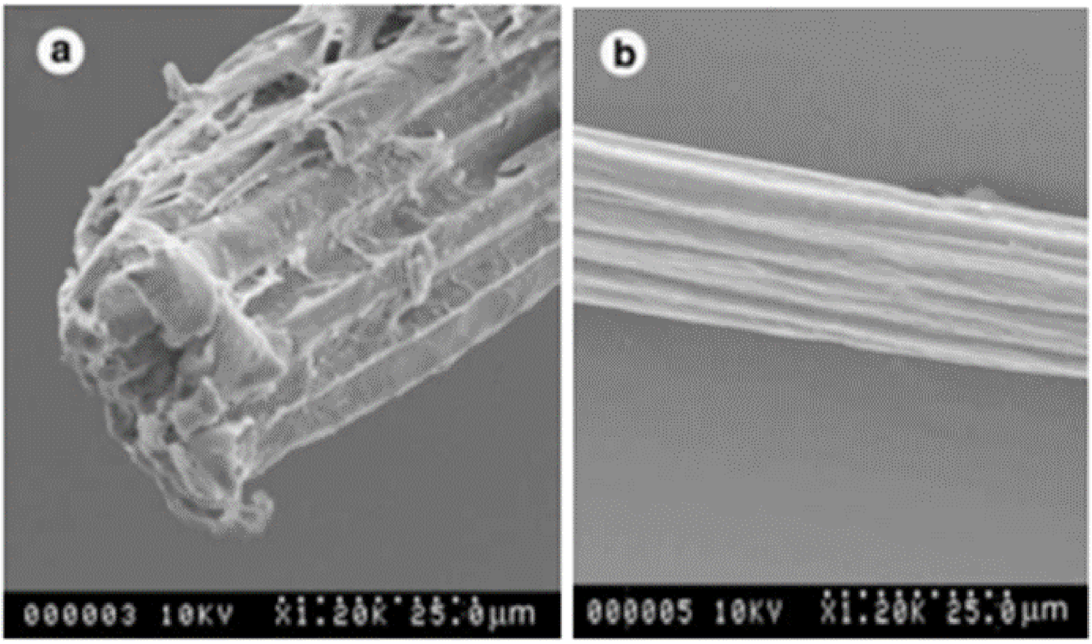


Figure 5: Surface of wheat straw fibers after (a)mechanical processing (b) chemical processing [40].

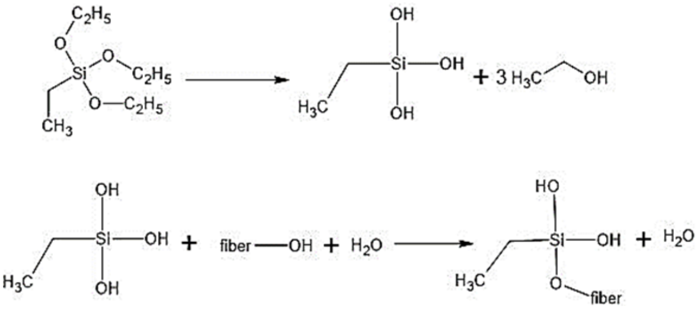
6.1 Alkaline treatment

As it removes a certain amount of lignin, wax, and vegetable oils from the surface of natural fibers, mercerization or alkaline treatment is one of the most common chemical treatments and the least expensive method of treating natural fibers [18]. It is a process in which natural fibers are immersed in an aqueous solution of sodium hydroxide (NaOH) over a period of time and at a specific temperature. The treatment time plays a significant role in the degree of modification [35]. As the concentration of NaOH(aq) increases, the fiber's color turns yellow despite disrupting hydrogen bonds and improving surface roughness[20]. As the treatment varnish the lignin, pectin and hemicellulose from the fiber, the density of the fiber matrix increases [52]. Usually, alkali treatment of the natural fibers changes its crystallinity, orientation of fibrils and unit cell structure [53]. The sophisticated alkaline treatment requires optimized treatment parameters; if not, it deviates the final results through fiber embrittlement, pore formation and fiber defibrillation [54]. In one study, the impact of alkali treatment on pineapple leaf fiber for pineapple leaf fiber/PLA composites has shown that alkali-treated fiber-reinforced composites offered superior mechanical performance [26, 46] as the treatment increased the crystallinity of the cellulose and thereby the mechanical performance of the composites. In addition, the alkalized fiber composites have a high storage modulus corresponding to their high flexural modulus.

$$\text{Cellulose}—\text{OH} + \text{NaOH} \longrightarrow \left[\text{Cellulose}—\text{O}^{-}\ \text{Na}^{+}\right] + H_2O + \text{Impurities}$$

6.2 Saline treatment

The hydrophilic fibers and hydrophobic matrix often show incompatibility while combining. So, one option would be coupling the fibers and resin matrix through the coupling agents. At a rough glance, silane is a chemical compound with the referring chemical formula of SiH4. Saline molecules with bi-functional groups are the choices in this context that link the fibers and resins through the siloxane bridge, which gives molecular continuity across the interfacial region of the composite. These coupling agents are of the general chemical structure, R(4-n)-Si-(R1X)n, where R is alkoxy, R1 is an alkyl bridge connecting silicon atoms, and X represents organofunctionality [55]. These organofunctionalities of silanes are typically amino, mercapto, glycidoxy, vinyl, or methacryloxy groups. For instance, the reaction of saline treatment can be referred to as follows:

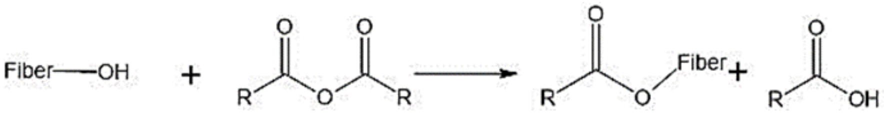


6.3 Graft polymerization

The graft polymerization onto lignocellulosic fibers is important in the physio-chemical modification of the natural fibers [56, 57]. This reaction is usually carried out in desirable temperatures while maintaining the standard. The cellulose is treated with an aqueous solution with selected ions and is exposed to high-energy radiation. In a study, redox activation was done to graft the copolymers into the natural fibers used in the composites at the end [58]. Redox catalysis is an effective method for generating free radicals under mild conditions. Grafting copolymerization of biofibers for biocomposites can be done in three ways: (a) grafting with a single monomer, (b) grafting with two or more monomers, and (c) grafting with the polymer directly [59]. There are plenty of techniques being used as a redox catalytic [41–43, 50, 56–65]. Among other graft copolymerization techniques, CuSO4-NaIO4-based treatment is quite popular as no acidic agents are used during graft copolymerization, as the use of acidic substances diminishes the quality of the outcomes. However, some researchers addressed the suitability of ceric-ion-induced redox initiation for the starch-based substrates validating that ceric-ions can effectively oxidize starch. As graft yield is a function of temperature, increasing temperature increases graft yield. [57, 60].

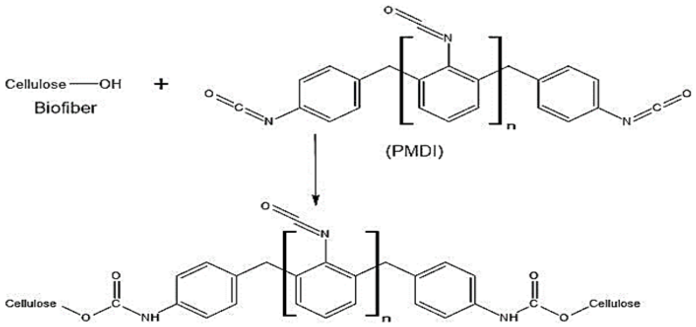
6.4 Acetylation

Acetylation is one of the chemical treatments in which fibers are exposed to the Acetyl function groups (CH3COO-) to replace the hydrogen bond held points into the hydrophobic Acetyl group (CH3CO), which improves properties such as dimensional stability, biological inertness, and UV-induced degradation [55]. Usually, before the treatment with glacial acetic acid (CH3COOH), the natural fibers are alkali-treated/bleached. The treated fibers are immersed in glacial acetic acid for 1h and later soaked in acetic anhydride for 2-5 minutes, containing two drops of H2SO4(conc). Hydrophobic acetyl groups trigger the hydrophobic nature of the fibers. Acetylation facilitates the removal of non-crystalline constituents, improves surface topography, changes surface free energy and improves the stress transfer efficiency in the fibers.



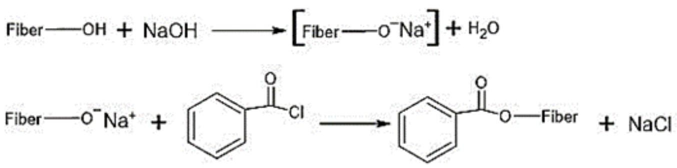
6.5 Isocyanate treatment

The Isocyanate group can react with the hydroxyl groups on the fiber surface, which improves the interfacial adhesion with the polymer matrix. The process is usually held in intermediate temperature ranges. The functional group of Isocyanates, –N=C=O, actively reacts with the fibers' hydroxyl group and produces strong covalent bonds. The reaction of natural fiber with isocyanate groups of polymeric di-Phenyl methane diisocyanate (PMDI) is as follows [61].



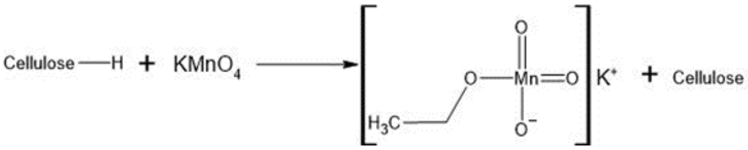
6.6 Benzoylation treatment

Benzoyl chloride is most often used in fiber treatment. Benzyl ($C_6H_5C=O$) in the benzyl chloride is designated to eliminate the hydrophilic nature of the natural fibers that improve the adhesion with the hydrophobic resin matrix. The fiber is usually pretreated with alkali to activate the fiber's cellulose and lignin hydroxyl groups. Later, it is left to the reaction with benzyl chloride (15 minutes usually). Then the fiber is isolated and treated with ethanol (around 1 min), then oven dried. An example reaction of a cellulosic hydroxyl group of fiber with benzyl chloride is as follows [55].



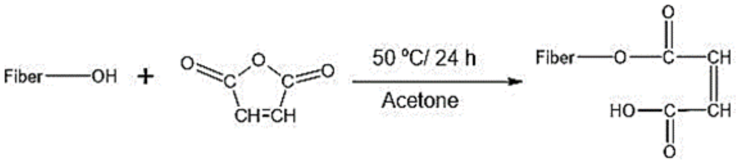
6.7 Permanganate treatment

Most permanganate treatments are conducted (1-3 minutes) with potassium permanganate ($KMnO_4$) resolved in acetone in different concentrations (typical concentrations in the range of 0.005%- 0.205%) [62] after alkaline pre-treatment [50, 63, 64]. Permanganate treatment tends to form a cellulose free radical through the MnO3- ion formation. The highly reactive Mn3+ irons are later responsible for graft copolymerization as follows:



6.8 Maleic anhydride treatment (coupling agents)

Maleic anhydride agents are widely used to strengthen the interfacial impairments in fillers and reinforced fibers. The process also proceeds after following alkalization treatment. The use of maleic anhydride treatment as a coupling agent reduces the ability of moisture absorption and improves hydrophobicity. The weight percentage of fiber determines the amount of maleic anhydride required. An example treatment is as follows [65]. Table 5 below tabulates all the possible chemical reaction techniques in common for natural fibers



7 Processing of green composites

Several composite fabrication methods are being practiced producing the desired composite material performance, such as injection molding, compression molding, pultrusion, resin transfer molding, extrusion and thermoforming. Generally, the selection of processing technique depends on materials to be processed, quality of desired outcome, complexity of parts, cost of production and capital investments [7]. The resin transfer molding (RTM) technique is used in complex components with large surface areas. Composites having vinyl ester and unsaturated polyester resins are usually processed with RTM. The main drawback of RTM is that fiber to resin ratio is hard to be controlled. Pultrusion techniques are used in the fabrication of long fat sheets and channels. The process material is usually polyurethane (PU). Injection molding is a more prevalent process of fabricating one-piece objects and storage containers. Usually, polybutylene succinate (PBS), polypropylene (PP) and polybutylene adipate terephthalate (PBAT) are the fabrication materials. On the other hand, material wastage is high, and the production rate is low in compression molding. Thermoforming is for fabricating and disposing of polypropylene cups, containers, and blister trays. The production rate is high in the thermoforming process. Table 6 synthesizes the processing methods of the most common, commercially available fiber matrixes. Generally, the processing techniques are constituent-specific with the materials as discussed above.

8 Conclusion

Composites are tailored-made materials that show unique qualities in pursuing sophisticated material production. Synthetic composites have been boasted as cradle-to-grave lightweight materials used ever since. However, widespread environmental concerns in conceiving sustainability and ecological friendliness have increased significantly recently. Thus, the production of environmentally friendly materials emerged. Among the most viable solutions, green materials stood alone among the crowd while showing the greatest responses in automotive, aviation, building materials, household appliance and biomedical applications after the abundant advantages perceived from bio-based materials. A subject's life cycle assessment (LCA) reveals the overall potential environmental impacts on the surroundings. Substituting natural fibers for synthetic fibers has been seen as a prevalent method for improving the sustainability of the composites, as the energy consumption associated with natural fiber production is around half that of synthetic fiber production's carbon dioxide emissions. Although the product is said to be biodegradable, it doesn't mean that it can be thrown straight into the environment. Generally, any products at their end life, particularly industrial wastes, need to be gone through the right treatments with specific conditions before it is swept away. Green materials cannot be the solution for littering and should be regulated with standard practices. Thus, biodegradability or composability barely means the product will degrade in any environment. Degradation demands certain factors such as humidity, temperature, time and bacterium/fungi in a specific environment. Industrial composting facilities avail these triggered degradability and specific conditions. Besides environmental concerns, green composites are rich with some user, and industry-friendly advantages, encompass good electrical resistance, friendly processing, no wear of tools, eliminated skin irritation, low specific weight, higher specific strength, good thermal & acoustic insulations and low

Table 6: Processing methods of different natural fiber biocomposites.

Fiber	Matrix	Fiber content(%)	Processing method	Reference
Flax yarn	Vinyl ester	24	Resin transfer molding	[66]
Flax silver	Unsaturated polyester	58	Compression molding	[67]
Flax yarn	Unsaturated polyester	34	Resin transfer molding	[66]
Kenaf	PLA	80	Compression molding	[68]
kenaf	PHB	40	Compression molding	[69]
Hemp	PLA	30	Compression molding	[70]
Flax	Poly (l-lactic acid)	30	Film stacking	[71, 72]
Flax (Uni-directional)	Soy protein	-	Resin transfer molding	[38]
Chicken feather	Acrylated epoxidized soybean oil + styrene	5-20	Vacuum-assisted resin transfer molding	[72]
Luffa Cylindrica	Castor oil + dihenylmethane diisocyanate	10	Sheet molding compound	[73]
Wheat straw	Linseed oil, maleic anhydride, and divinylbenzene	50–90	Compression molding	[74]
Coconut, sisal	Castor oil + diphenylmethane diisocyanate	14–30	Compression molding	[75]
Jute	Polylactide	30	Injection molding	[76]

initial investments. These favorable likings of green materials upsurge their application throughout various manufacturing sectors. Numerous fibers and bioresins are available abundantly without any cost or at low cost showing different mechanical and impact performances, and they can be combined to alter the varying reinforcement/matrix combinations. The main disadvantage of using green fiber is that it is fond of water/moisture. Thus, it must be modified to a standard structure to retard the ability to absorb water and moisture. Therefore, for the green composites' desired performance, the ingredients, especially natural fibers, must be pretreated to yield their best performances. Among those alkalis, treatments have been seen frequently with most natural fibers. The main objective of this research study was to reduce the time potent researchers surf scholarly articles to get data and information for future studies. This review paper is believed to reach its zenith in comprehending the aspects of each constituent of various & most common bioresin-based composites and elucidating the research community in a single paper. Thus, a researcher can find all necessary information in one place and further developments and contributions to field can be done without further delays.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding Declaration

This research did not receive any grants from governmental, private, or nonprofit funding bodies.

Author Contribution

Nithesh Naik: Conceptualization and Writing- Reviewing and Editing; **Nilakshman Sooriyaperakasam**, **Yashoda K. Abeykoon**, **Yomali S.Wijayarathna**, **Pranesh G**, **Soumik Roy**, **Rovin Negi** and **Aakif Budnar Kunjibettu**: Data curation, Writing–original draft preparation **Asela Kulatunga** and **Jayakrishna Kandasamy**: Writing- reviewing and editing.

References

[1] H. S. Shekar and M. Ramachandra, "Green Composites: A Review," *Materials Today: Proceedings*, vol. 5, no. 1, pp. 2518–2526, 2018.

[2] M. Mariano, F. Pilate, F. B. De Oliveira, F. Khelifa, P. Dubois, J. M. Raquez, and A. Dufresne, "Preparation of Cellulose Nanocrystal-Reinforced Poly(lactic acid) Nanocomposites through Noncovalent Modification with PLLA-Based Surfactants," *ACS Omega*, vol. 2, pp. 2678–2688, jun 2017.

[3] M. Nagalakshmaiah, N. El Kissi, and A. Dufresne, “Ionic Compatibilization of Cellulose Nanocrystals with Quaternary Ammonium Salt and Their Melt Extrusion with Polypropylene,” *ACS Applied Materials and Interfaces*, vol. 8, pp. 8755–8764, apr 2016.

[4] M. A. Anwer, H. E. Naguib, A. Celzard, and V. Fierro, “Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin particulate green composites,” *Composites Part B: Engineering*, vol. 82, pp. 92–99, dec 2015.

[5] A. Keller, “Compounding and mechanical properties of biodegradable hemp fibre composites,” *Composites Science and Technology*, vol. 63, pp. 1307–1316, jul 2003.

[6] R. U. Halden, “Plastics and health risks,” in *Annual Review of Public Health*, vol. 31, pp. 179–194, Palo Alto: Annual Reviews, 2010.

[7] A. Ashori, “Wood-plastic composites as promising green-composites for automotive industries!,” *Bioresource Technology*, vol. 99, pp. 4661–4667, jul 2008.

[8] G. S. Mann, L. P. Singh, P. Kumar, and S. Singh, “Green composites: A review of processing technologies and recent applications,” *Journal of Thermoplastic Composite Materials*, vol. 33, pp. 1145–1171, aug 2020.

[9] M. McNutt, “Climate change impacts,” *Science*, vol. 341, p. 435, aug 2013.

[10] D. Salarbashi, J. Bazeli, and E. Fahmideh-Rad, “Fenugreek seed gum: Biological properties, chemical modifications, and structural analysis– A review,” *International Journal of Biological Macromolecules*, vol. 138, pp. 386–393, oct 2019.

[11] S. Raghavendra, T. Aravinda, and S. Sarapure, “Nano green composites-an overview,” *International Journal of Applied Engineering Research*, vol. 13, no. 1, pp. 115–116, 2018.

[12] M. Nagalakshmaiah, S. Afrin, R. P. Malladi, S. Elkoun, M. Robert, M. A. Ansari, A. Svedberg, and Z. Karim, “Biocomposites: Present trends and challenges for the future,” in *Green Composites for Automotive Applications*, pp. 197–215, Elsevier, 2018.

[13] O. Faruk, A. K. Bledzki, H. P. Fink, and M. Sain, “Biocomposites reinforced with natural fibers: 2000-2010,” *Progress in Polymer Science*, vol. 37, pp. 1552–1596, nov 2012.

[14] S. Prasad, A. Singh, N. E. Korres, D. Rathore, S. Sevda, and D. Pant, “Sustainable utilization of crop residues for energy generation: A life cycle assessment (LCA) perspective,” *Bioresource Technology*, vol. 303, p. 122964, may 2020.

[15] D. B. Pal, A. Singh, and A. Bhatnagar, “A review on biomass based hydrogen production technologies,” *International Journal of Hydrogen Energy*, vol. 47, pp. 1461–1480, jan 2022.

[16] A. Ashori and A. Nourbakhsh, “Bio-based composites from waste agricultural residues,” *Waste Management*, vol. 30, pp. 680–684, apr 2010.

[17] S. L. Fávaro, M. S. Lopes, A. G. Vieira de Carvalho Neto, R. Rogério de Santana, and E. Radovanovic, “Chemical, morphological, and mechanical analysis of rice husk/post-consumer polyethylene composites,” *Composites Part A: Applied Science and Manufacturing*, vol. 41, pp. 154–160, jan 2010.

[18] R. Prithivirajan, S. Jayabal, and G. Bharathiraja, “Bio-based composites from waste agricultural residues: Mechanical and morphological properties,” *Cellulose Chemistry and Technology*, vol. 49, no. 1, pp. 65–68, 2015.

[19] C. Nyambo, A. K. Mohanty, and M. Misra, “Polylactide-based renewable green composites from agricultural residues and their hybrids,” *Biomacromolecules*, vol. 11, pp. 1654–1660, jun 2010.

[20] N. Reddy and Y. Yang, “Properties and potential applications of natural cellulose fibers from cornhusks,” *Green Chemistry*, vol. 7, no. 4, pp. 190–195, 2005.

[21] D. Y. Kim, T. Lütke-Eversloh, K. Elbanna, N. Thakor, and A. Steinbüchel, “Poly(3-mercaptopropionate): An nonbiodegradable biopolymer?,” *Biomacromolecules*, vol. 6, pp. 897–901, mar 2005.

[22] L. Zimmermann, A. Dombrowski, C. Völker, and M. Wagner, “Are bioplastics and plant-based materials safer than conventional plastics? In vitro toxicity and chemical composition,” *Environment International*, vol. 145, sep 2020.

[23] P. C. Srinivasa and R. N. Tharanathan, “Chitin/chitosan - Safe, ecofriendly packaging materials with multiple potential uses,” *Food Reviews International*, vol. 23, pp. 53–72, jan 2007.

[24] R. Nakamura, K. Goda, J. Noda, and J. Ohgi, “High temperature tensile properties and deep drawing of fully green composites,” *Express Polymer Letters*, vol. 3, no. 1, pp. 19–24, 2009.

[25] G. Cicala, G. Cristaldi, G. Recca, and A. Latteri, “Composites Based on Natural Fibre Fabrics,” in *Woven Fabric Engineering* (P. D. Dubrovski, ed.), pp. 317–342, editor. books.google.com. IntechOpen; 2010 [cited 2021 Aug 25]. p. Available from: Sciyo, aug 2010.

[26] M. S. Huda, L. T. Drzal, A. K. Mohanty, and M. Misra, “Effect of chemical modifications of the pineapple leaf fiber surfaces on the interfacial and mechanical properties of laminated biocomposites,” *Composite Interfaces*, vol. 15, pp. 169–191, jan 2008.

[27] I. Živković, C. Fragassa, A. Pavlović, and T. Brugo, “Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites,” *Composites Part B: Engineering*, vol. 111, pp. 148–164, feb 2017.

[28] M. Shibata, S. Oyamada, S. I. Kobayashi, and D. Yaginuma, “Mechanical properties and biodegradability of green composites based on biodegradable polyesters and lyocell fabric,” *Journal of Applied Polymer Science*, vol. 92, pp. 3857–3863, jun 2004.

[29] W. Liu, M. Misra, P. Askeland, L. T. Drzal, and A. K. Mohanty, “’Green’ composites from soy based plastic and pineapple leaf fiber: Fabrication and properties evaluation,” *Polymer*, vol. 46, pp. 2710–2721, mar 2005.

[30] P. J. P. Espitia, N. d. F. F. Soares, J. S. d. R. Coimbra, N. J. de Andrade, R. S. Cruz, and E. A. A. Medeiros, “Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications,” *Food and Bioprocess Technology*, vol. 5, pp. 1447–1464, jul 2012.

[31] H. Takagi and Y. Ichihara, “Effect of fiber length on mechanical properties of ”green” composites using a starch-based resin and short bamboo fibers,” *JSME International Journal, Series A: Solid Mechanics and Material Engineering*, vol. 47, no. 4, pp. 551–555, 2004.

[32] M. A. Sawpan, K. L. Pickering, and A. Fernyhough, “Improvement of mechanical performance of industrial hemp fibre reinforced polylactide biocomposites,” *Composites Part A: Applied Science and Manufacturing*, vol. 42, pp. 310–319, mar 2011.

[33] A. Gomes, T. Matsuo, K. Goda, and J. Ohgi, “Development and effect of alkali treatment on tensile properties of curaua fiber green composites,” *Composites Part A: Applied Science and Manufacturing*, vol. 38, pp. 1811–1820, aug 2007.

[34] S. Singh, A. K. Mohanty, T. Sugie, Y. Takai, and H. Hamada, “Renewable resource based biocomposites from natural fiber and polyhydroxybutyrate-co-valerate (PHBV) bioplastic,” *Composites Part A: Applied Science and Manufacturing*, vol. 39, pp. 875–886, may 2008.

[35] F. Corrales, F. Vilaseca, M. Llop, J. Gironès, J. A. Méndez, and P. Mutjè, “Chemical modification of jute fibers for the production of green-composites,” *Journal of Hazardous Materials*, vol. 144, pp. 730–735, jun 2007.

[36] C. Asasutjarit, S. Charoenvai, J. Hirunlabh, and J. Khedari, “Materials and mechanical properties of pretreated coir-based green composites,” *Composites Part B: Engineering*, vol. 40, pp. 633–637, oct 2009.

[37] J. D. S. Macedo, M. F. Costa, M. I. Tavares, and R. M. Thiré, “Preparation and characterization of composites based on polyhydroxybutyrate and waste powder from coconut fibers processing,” *Polymer Engineering and Science*, vol. 50, no. 7, pp. 1466–1475, 2010.

[38] X. Huang and A. Netravali, “Characterization of flax fiber reinforced soy protein resin based green composites modified with nano-clay particles,” *Composites Science and Technology*, vol. 67, pp. 2005–2014, aug 2007.

[39] L. Y. Mwaikambo and M. P. Ansell, “Hemp fibre reinforced cashew nut shell liquid composites,” *Composites Science and Technology*, vol. 63, pp. 1297–1305, jul 2003.

[40] S. Panthapulakkal, A. Zereshkian, and M. Sain, “Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites,” *Bioresource Technology*, vol. 97, pp. 265–272, jan 2006.

[41] P. Threepopnatkul, N. Kaerkitcha, and N. Athipongarporn, “Effect of surface treatment on performance of pineapple leaf fiber-polycarbonate composites,” *Composites Part B: Engineering*, vol. 40, pp. 628–632, oct 2009.

[42] G. L. Prasad, B. S. Gowda, and R. Velmurugan, “Comparative Study of Impact Strength Characteristics of Treated and Untreated Sisal Polyester Composites,” *Procedia Engineering*, vol. 173, pp. 778–785, 2017.

[43] X. Zhang, F. Wang, and L. M. Keer, “Influence of surface modification on the microstructure and thermo-mechanical properties of bamboo fibers,” *Materials*, vol. 8, pp. 6597–6608, sep 2015.

[44] M. Rokbi, H. Osmani, A. Imad, and N. Benseddiq, “Effect of chemical treatment on flexure properties of natural fiber-reinforced polyester composite,” *Procedia Engineering*, vol. 10, pp. 2092–2097, 2011.

[45] A. Saravanakumaar, A. Senthilkumar, S. S. Saravanakumar, M. R. Sanjay, and A. Khan, “Impact of alkali treatment on physico-chemical, thermal, structural and tensile properties of Carica papaya bark fibers,” *International Journal of Polymer Analysis and Characterization*, vol. 23, pp. 529–536, aug 2018.

[46] O. M. Asumani, R. G. Reid, and R. Paskaramoorthy, “The effects of alkali-silane treatment on the tensile and flexural properties of short fibre non-woven kenaf reinforced polypropylene composites,” *Composites Part A: Applied Science and Manufacturing*, vol. 43, pp. 1431–1440, sep 2012.

[47] R. Sepe, F. Bollino, L. Boccarusso, and F. Caputo, “Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites,” *Composites Part B: Engineering*, vol. 133, pp. 210–217, jan 2018.

[48] D. K. Debeli, Z. Qin, and J. Guo, "Study on the Pre-Treatment, Physical and Chemical Properties of Ramie Fibers Reinforced Poly (Lactic Acid) (PLA) Biocomposite," *Journal of Natural Fibers*, vol. 15, pp. 596–610, jul 2018.

[49] K. Senthilkumar, N. Rajini, N. Saba, M. Chandrasekar, M. Jawaid, and S. Siengchin, "Effect of Alkali Treatment on Mechanical and Morphological Properties of Pineapple Leaf Fibre/Polyester Composites," *Journal of Polymers and the Environment*, vol. 27, pp. 1191–1201, jun 2019.

[50] A. Paul, K. Joseph, and S. Thomas, "Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers," *Composites Science and Technology*, vol. 57, pp. 67–79, jan 1997.

[51] G. M. Arifuzzaman Khan, M. Shaheruzzaman, M. H. Rahman, S. M. Abdur Razzaque, M. S. Islam, and M. S. Alam, "Surface modification of okra bast fiber and its physico-chemical characteristics," *Fibers and Polymers*, vol. 10, pp. 65–70, feb 2009.

[52] K. J. Vardhini, R. Murugan, C. T. Selvi, and R. Surjit, "Optimisation of alkali treatment of banana fibres on lignin removal," *Indian Journal of Fibre and Textile Research*, vol. 41, pp. 156–160, aug 2016.

[53] X. Colom and F. Carrillo, "Crystallinity changes in lyocell and viscose-type fibres by caustic treatment," *European Polymer Journal*, vol. 38, pp. 2225–2230, nov 2002.

[54] S. K. Ramamoorthy, *Properties and Performance of Regenerated Cellulose Thermoset*. PhD thesis, 2015.

[55] R. M. Rowell, "Acetylation of natural fibers to improve performance," *Molecular Crystals and Liquid Crystals*, vol. 418, pp. 153–164, jan 2004.

[56] A. K. Mohanty, P. C. Tripathy, M. Misra, S. Parija, and S. Sahoo, "Chemical modification of pineapple leaf fiber: graft copolymerization of acrylonitrile onto defatted pineapple leaf fibers," *Journal of Applied Polymer Science*, vol. 77, pp. 3035–3043, sep 2000.

[57] P. C. Tripathy, M. Misra, S. Parija, S. Mishra, and A. K. Mohanty, "Studies of Cu(II)-IQ-4 initiated graft copolymerization of methyl methacrylate from defatted pineapple leaf fibres," *Polymer International*, vol. 48, pp. 868–872, sep 1999.

[58] J. Rout, M. Misra, and A. K. Mohanty, "Surface modification of coir fibers I: Studies on graft copolymerization of methyl methacrylate on to chemically modified coir fibers," *Polymers for Advanced Technologies*, vol. 10, pp. 336–344, jun 1999.

[59] L. Wei and A. G. McDonald, "A review on grafting of biofibers for biocomposites," *Materials*, vol. 9, p. 303, apr 2016.

[60] M. E. Carr, "Preparation and Application of Starch Graft Poly(vinyl) Copolymers as Paper Coating Adhesives," *Starch - Stärke*, vol. 44, no. 6, pp. 219–223, 1992.

[61] A. K. Mohanty, M. Misra, and L. T. Drzal, "Surface modifications of natural fibers and performance of the resulting biocomposites: An overview," *Composite Interfaces*, vol. 8, pp. 313–343, jan 2001.

[62] E. Zini and M. Scandola, "Green composites: An overview," *Polymer Composites*, vol. 32, pp. 1905–1915, dec 2011.

[63] K. Joseph, S. Thomas, and C. Pavithran, "Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites," *Polymer*, vol. 37, pp. 5139–5149, nov 1996.

[64] M. S. Sreekala, M. G. Kumaran, and S. Thomas, "Water sorption in oil palm fiber reinforced phenol formaldehyde composites," *Composites - Part A: Applied Science and Manufacturing*, vol. 33, pp. 763–777, jun 2002.

[65] A. Bessadok, S. Marais, F. Gouanvé, L. Colasse, I. Zimmerlin, S. Roudesli, and M. Métayer, "Effect of chemical treatments of Alfa (Stipa tenacissima) fibres on water-sorption properties," *Composites Science and Technology*, vol. 67, pp. 685–697, mar 2007.

[66] S. Goutianos, T. Peijs, B. Nystrom, and M. Skrifvars, "Development of flax fibre based textile reinforcements for composite applications," *Applied Composite Materials*, vol. 13, pp. 199–215, jul 2006.

[67] M. Hughes, J. Carpenter, and C. Hill, "Deformation and fracture behaviour of flax fibre reinforced thermosetting polymer matrix composites," *Journal of Materials Science*, vol. 42, pp. 2499–2511, apr 2007.

[68] S. Ochi, "Mechanical properties of kenaf fibers and kenaf/PLA composites," *Mechanics of Materials*, vol. 40, pp. 446–452, apr 2008.

[69] S. Phillips and L. Lessard, "Application of natural fiber composites to musical instrument top plates," *Journal of Composite Materials*, vol. 46, pp. 145–154, jan 2012.

[70] M. S. Islam, K. L. Pickering, and N. J. Foreman, "Influence of alkali treatment on the interfacial and physico-mechanical properties of industrial hemp fibre reinforced polylactic acid composites," *Composites Part A: Applied Science and Manufacturing*, vol. 41, pp. 596–603, may 2010.

[71] E. Bodros, I. Pillin, N. Montrelay, and C. Baley, "Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications?," *Composites Science and Technology*, vol. 67, pp. 462–470, mar 2007.

[72] C. K. Hong and R. F. Wool, “Development of a bio-based composite material from soybean oil and keratin fibers,” *Journal of Applied Polymer Science*, vol. 95, pp. 1524–1538, mar 2005.

[73] B. N. Melo, C. G. Dos-Santos, V. R. Botaro, and V. M. Pasa, “Eco-composites of polyurethane and Luffa aegyptiaca modified by mercerisation and benzylation,” *Polymers and Polymer Composites*, vol. 16, pp. 249–256, may 2008.

[74] D. P. Pfister and R. C. Larock, “Green composites from a conjugated linseed oil-based resin and wheat straw,” *Composites Part A: Applied Science and Manufacturing*, vol. 41, pp. 1279–1288, sep 2010.

[75] R. V. Silva, D. Spinelli, W. W. Bose Filho, S. Claro Neto, G. O. Chierice, and J. R. Tarpani, “Fracture toughness of natural fibers/castor oil polyurethane composites,” *Composites Science and Technology*, vol. 66, pp. 1328–1335, aug 2006.

[76] A. K. Bledzki and A. Jaszkiewicz, “Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres - A comparative study to PP,” *Composites Science and Technology*, vol. 70, pp. 1687–1696, oct 2010.