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Opportunity of Non-Wood Forest Products in Biocomposites

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Abstract

In recent years industries are attempting to decrease their dependency on petroleum-based fuels and products due to increased environmental issues. The tremendous increase in production and use of plastics in every sector of life has led to huge plastic waste disposal problems and also an environmental threat. In order to prevail over the present scenario, the viable and cost-effective approaches are to prepare eco-friendly bio-composites based on non-wood forest products (NWFP), a part of forest wealth of the globe, especially natural fibres, agricultural wastes and extractives. Natural fibres and extractives have many advantages viz. low density, low cost, considerable toughness properties, nontoxicity, sustainability and biodegradability. NWFP based composites may be utilized to produce non-structural parts for diverse applications in various industries as high-performance materials with interesting properties for specific applications viz. furniture, thermal, acoustic insulations and automotive industries etc. In the present chapter, opportunities of extractives, cellulosic and lignocellulosic fibres from non-wood forest products in Bio-composites will be discussed.

Keywords: Non-wood forest products, Bio-composites, Tannins, Laccase, Fibres, Agriculture wastes

1. Introduction

Biocomposites are composites formed by the mixture of two or more than two constituents which are firmly stacked in a specific orientation in order to provide stability and toughness as per their requirement. Composites may be synthetic, biocomposites or natural composites. Natural composites are the wood, bamboo, silk, cellulose, and some animal products viz. feather, horn etc. Bio-composites are materials formed by reinforcement of natural fibres into adhesive or a matrix. The matrix may be a natural, synthetic material or an amalgamation of natural and synthetic materials. Environmental concerns over the synthetic matrix and further cost of synthetic fibres have led the encouragement of scientific community of using natural fibres as reinforcement material in polymeric composites.

2. Non wood forest products

The non wood forest products (nwfps) comprise all the forest products other than timber and fuelwood and are used by human beings since the time immemorial [1–3]. NWFPs include medicinal plants, essential oils, spices, edible wild

plants, gums, resins and oleoresins, fatty oils, tanning materials, natural organic colouring materials, katha and cutch, oxalic acid, fibres and flosses, beverages and narcotics, fodder and forage plants, saponins, fish poisons, insecticides, green manure, beads, rubber plants, plants useful for paper, basket and wicker work including canes, beedi leaf etc., miscellaneous materials including thatching and broom materials. Besides these plant products, animal products such as lac, honey, silk, horns, ivory and hides (of forest origin) are included among the nwfps [4–6]. Developing countries especially tropical region of the world more than three-fourths of the populations are dependent on nwfps for their nutrition, primary health care and livelihood subsistence. Therefore, nwfps play an important role in the daily lives of local population in particular rural and poor people dependency on nwfps for their daily needs of food, fodder, medicines, gums, construction material, etc. In addition to local consumption, nwfps are also traded in local, regional, national and international markets and the trade in nwfps not only generates employment opportunities but also contributes in the economic development of the country [7–9]. Among the nwfps fibres and flosses, bamboo and canes, tans and dyes, essential oils are important forest bio-products for livelihood support to marginal peoples residing in forest areas. After processing of the essential products (dyes, essential oils etc.), the left over biomass may be utilized for diverse industrial applications. The importance of these nwfps lies in the following facts.

2.1 Fibres and flosses

A wide range of plants yielding fibre occur in the forests wealth. Fibres are obtained from tissues of different parts of certain woody plants, which are used for various traditional applications such as making cloth, rope, mat and cordages etc. [10, 11].

2.2 Bamboo

Bamboo is abundantly found in most parts of the world, nearly 0.92 % of the total forest area, spread over 36 million hectares (MHa) [12]. Globally, bamboo has 111 genera with more than 1575 species. India is very rich in bamboo resources and the second major bamboo producing country having 16 MHa (22.46 %) of a total forest cover 71.2 MHa [13] comprising of 160 species after China. China is the richest in bamboo resources; it has more than 800 species [14, 15]. The bamboo is used for various industrial purposes [16–18]. Bamboo species thrives in almost all types of soil except in very dry soils. The bamboo is utilized for various purposes, viz. agriculture, handicraft, building industry (bamboo concrete, scaffoldings, house construction, etc.), interior decoration (Bamboo flooring board, mat, panelling, curtain, etc.), paper industry, textile industry, food, bamboo charcoal, and diverse range of daily use articles (toothpicks, chopsticks, incense sticks, etc.) [19–22]. Bamboo is a typical natural composite material with functionally gradient structure having multi-nodes, and the fibres are arranged compactly in the outer surface region in a definite fashion in comparison to inner surface region which provides fracture toughness. The fracture toughness of the bamboo culm depends on the volume fraction of fibres [23–28].

2.3 Essential oils

Essential oils from plants are widely used in pharmaceuticals, cosmetics, perfumery and specialty applications in various industries. The value of essential

oil bearing crops can be augmented by utilization of wastes using facile and economic methods. The major essential oil bearing crops are lemon grass, mentha, eucalyptus, lavender, rose, geranium, rosemary, basil, thyme, peppermint, chamomile, etc. [5].

2.4 Tans and dyes

A variety of vegetable tanning materials are produced in the forests. Important vegetable tanning materials are the myrobalan nuts and bark of wattle (*Acacia mearnsii*, *A. decurrens*, *A. nilotica* and *Cassia auriculata*, etc.). Other tanning materials include leaves of *Embllica officinalis* and *Anogeissus latifolia*, bark of *Cleistanthus collinus*, fruits of *Zizyphus xylocarpa*, bark of *Cassia fistula*, *Terminalia alata*, *T. arjuna*, etc. The term tannin was introduced by Seguin in the year 1796 to indicate various plant extracts, which have the capacity to convert hides and skins into leather [5, 29, 30]. Tans and dyes are simple chemical compounds made of carbon, hydrogen and oxygen. The structure and solubility of tannins are dependent upon the source and structure of tannins, however, vegetable tannins are water-soluble.

2.5 Wood tans

The important species yielding wood tans are Quebracho (*Quebracho Colorado*), this species is widely distributed in South America. The heart-wood contains 20-27 % tannin, which is obtained by cutting the wood into small chips and extracting the tannin with water. The cutch, a byproduct from Katha industry, obtained from khair (*Acacia catechu*) heart wood is used for tanning purposes.

2.6 Bark tans

The bark of various tree species is chipped off during the operation of timber or fuel-wood harvesting, some of the important species which yield bark tans are: *Acacia mearnsii*, *Acacia nilotica*, *Cassia auriculata*, *Shorea robusta*, *Terminalia arjuna*, *Cassia fistula*, *Cerriops roxburghiana*, *Rhizophora mucronata*, etc. Some other trees such as *Acacia leucophloea*, *Bridelia retusa*, *Lagerstroemia* spp., *Tamarix aphylla*, *Terminalia alata*, *Quercus* spp. and *Castanopsis* spp. also yield bark tans and are locally important.

2.7 Fruit tans

Fruits of some of the forest trees are utilized in tanning industries for extraction of different tannins. Some of the important species yielding fruit tans are as follows: *Acacia nilotica* (Babul), *Caesalpinia coriaria* (Divi-divi), *Zizyphus xylopyrus* (Kath bor), *Embllica officinalis* (Aonla), *Shorea robusta* (Sal), *Anacardium occidentale* (Cashew nut), *Tamarindus indica* (Tamarind) and *Terminalia chebula* (Myrobalan), etc.

2.8 Leaf tans

Leaves of some of plants provide tanning material however; they are not used on a large scale for commercial applications. Generally, village artisans and shoemakers use leaves for tanning leather on as a small scale. Important leaf tanning materials are obtained from leaves of *Anogeissus latifolia*, *Carissa spinarum*, *Embllica officinalis*, *Lawsonia inermis* and *Rhus cotinus*, etc.

2.9 Natural dyes

Natural dyes are broadly classified as plant, animal, mineral, and microbial dyes. They are obtained from the vegetable plant materials such as plant leaves, roots, bark, seeds, and from insect secretions and minerals. Dyes are used for various industrial applications including the coloring of textiles [31, 32].

3. Natural composites

Wood and bamboo are the natural composites, held together by the matrix as designed by the nature (**Figure 1**). Lignin is the largest biopolymer and principle cementing matrix which holds the components of natural composites together in a definite fashion. The awareness in the society globally and harmful effects of the synthetic materials on the environment has led to the progressive development of eco-friendly and sustainable materials. The scientific community have shown a lot of interest in developing sustainable bio-composites which are eco-friendly and may substitute partly or wholly the synthetic materials. Intriguingly, using natural fibres in development of biocomposites provides a reduction in greenhouse gas emissions and carbon footprint of composites [33, 34]. Due to environmental concern, demand for commercial raw material for utilization in composites increasing day by day. Therefore, after harvesting the important chemicals or fresh materials from the nwfps may be utilized on sustainable basis for making bio-composites for various industrial sectors. Among them, use of the natural fibres as reinforcement material, tannins and lignin as cementing material alone, in parts or in combination with synthetic matrix subsequent to proper modification, and further, valorisation

“What we need is ‘more imagination’ not more knowledge”: Albert Einstein

Figure 1.
Natural Wood Composite.

of residues from the nwfps is an important opportunity as raw materials for bio composites in a sustainable way.

4. Natural fibres and their utilization in bio-composites

A vast number of research papers and reviews are available for utilization of natural fibres in sustainable development of biocomposites. However, as mentioned, the fibres are sustainable raw materials and may be obtained from different sources from nwfps, further, low-cost, light-weight, availability, renewability, biodegradability; properties and strength are important factors for their utilization. The specific properties of the fibres are utmost important in developing the composites. Natural fibres comprise of cellulose, hemicelluloses, lignin, waxes and tannins etc. The percentage of these constituents varies with the source and processing of fibres. Further, the properties of biocomposites are also dependent upon the source of fibres and presence of these constituents. Natural fibres are obtained from plants or animals [35]. The plant fibres are commonly used for producing bio-composites and mostly sourced from nwfps or in some countries cultivation of these crops is being carried out for sustainable production. The commercial sources of fibres utilized in producing biocomposites worldwide due to their inherent properties. The classification of fibres based on source, their specific properties and utilization in biocomposites are summarised in **Tables 1-3**.

Natural fibres show a variation in properties. The fibre properties are dependent on the geographical location, process of isolation (ratting of fibres) and maturation period. However, some fibres exhibit highest tensile strength in a range from 300-1100 MPa (**Table 1**).

4.1 Merits and demerits of natural fibres

The inherent properties of the natural fibres of plants origin are important in developing the bio-composites. Natural fibres comprise of cellulose, hemicelluloses, lignin, waxes and tannins etc. The percentage of the cellulose, hemicelluloses, lignin etc., length and width of the fibres, varies with the source and processing of fibres. Further, natural fibres possess low density ($1.25\text{--}1.50\text{ g/cm}^3$), sufficient mechanical properties, sustainability, recyclability, biodegradability, availability and low-priced in comparison to synthetic fibres such as glass and carbon fibres [51, 52]. Intriguingly, these properties do not meet the requirements of biocomposites. The natural fibres are used for increasing the mechanical strength as reinforcement material in composites [53]. The synthetic matrix and natural fibres are not compatible to each other leading to poor mechanical properties. Further, fibres have also water absorption capacity of cellulose due the presence of numerous hydroxyl groups [54–56].

Natural fibres are used as reinforcement materials in composites. However, due to their susceptibility to moisture [56] mechanical properties of polymeric composites have a strong impact on the interface adhesion between the fiber and the polymer matrix [54]. The natural fibres are rich of cellulose, hemicelluloses, lignin, pectins, waxes and tannins etc, all of which are composed of hydroxyl groups. Thus, there are major challenges of suitability between the matrix and fiber that weakens interface region between matrices and natural fibres [55]. Generally, outer surface of the composite materials absorb water and decreases gradually into the bulk of the matrix. High water absorption capacity of the composite materials leads to decline in their mechanical strength and pressure on nearby structures due to absorption of water pertaining to the hygroscopic nature of the fibres and

Fibres Source	Common name	Part of the plant	Appearance	Diameter (µm)	Density (g/cm ³)	Tensile strength (MPa)	Young' modulus (GPa)
<i>Agave sislana</i>	Sisal	Leaf	Coarse-stiff; Creamy-White	50-200	1.45	468-640	9.4-22
<i>Corhorus capsularis</i>	Jute fibre	Bast	Fine Light brown	25-200	1.3-1.45	393-773	13-26.5
<i>Cocos nucifera</i>	Coconut fibre or Coir	Coconut fruit outer shell or husk	Course, white to brown	100-450	1.15	131-175	4-6
<i>Arenga pinnata</i>	Sugar-palm fibre	Bast, fruit, leaf	Coarse, brownish-black	50-800	1.29	190.29	3.69
<i>Cannabis sativa</i>	Hemp fibre	Bast	Silky-fine, white to light brown	26.5	1.48	514	24.8
Bamboo Species	Bamboo	Grass	Creamy white	10-40		503	35.91
<i>Linum usitatissimum</i>	Flax fibre	Bast	Creamy white	12-16	1.50	345-1100	27.6
<i>Hibiscus cannabinus</i>	Kneaf fibre	Stem	Pale	17.7-21.9	1.2-1.4		
<i>Boehmeria nivea</i>	Ramie fibre	Bast	White	25-30	1.5-1.55	400-1600	44
<i>Gossypium Sp.</i>	Cotton fibre	Seeds	Yellowish off-white	11-22	1.51	400	12
Conifers	Soft wood fibre	Soft wood tracheids	Variation in colour	20-35	1.5	1000	40
<i>Ananas comosus</i>	Pine apple	Leaf	White, smooth and glossy	8.66-63.43	1.44	413-1627	34.5-82.5

Table 1.
Plant fibres and properties [36–45].

subsequently can cause warping, buckling, bigger possibility of their microbial inhabitation, freeze, and unfreeze leading to destruction of mechanical characteristics of composite materials. Therefore, fibres are required to improve these limitations by physical and chemical modifications [57].

4.2 Alteration of properties of natural fibres

The compatibility of the natural plant fibres with the synthetic matrix is the main and foremost concern of developing bio-composites due to the different nature and properties of these two materials. The various methods have been studied and reviewed in the past in order to increase the functionality and compatibility of natural fibres. Fibres compatibility with the matrix and mechanical strength thereof may be increased by physical and chemical modification of the fibres.

Fibre	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Pectin (%)
Cotton	82–96	2–6	0.5–1	5–7
Pine apple	80–81	16–19	4.6–12	2–3
Hemp	70–92	18–22	3–5	0.9
Flax	72–84	16–18	0.6–5	1.5
Ramie	68–76	13–15	0.6–1	1.9–2
Abaca	61–64	21	12	0.8
Nettle	86	5.4	4	-
Banana	60–65	6–19	5–10	3–5
Jute	51–84	12–20	5–13	0.2
Kenaf	49–53 (alpha)	86.8–87.7 (Holocellulose)	14.7–21.2	-
Lemom grass	71.7	9.52	13.83	-
Coir	46	0.3	45	4
Sisal	43–78	10–13	4–12	0.8–2
Bagasse	32–48	21	19.9–24	10
Bamboo	26–43	15–26	21–33	-
Kapok	53.40–62.9	29.63	19.2–20.73	-
Henequen	77.6	13.1	4.8	-
Hard wood	43–47	16–24	25–35	-
Soft wood	40–44	25–31	25–29	-

Table 2.
Chemistries of important plant fibers [43, 46–50].

Type of Fibres	Source	Plant of fibres	Use	Properties
Bast fibres	Stem	Jute	Reinforcements	Long length high stiffness and strength
	Stem	Ramie	Reinforcements	Long length high stiffness and strength
Stalk	Bamboo	Bamboo species	Reinforcement	Short and long fibres
	Wood	Soft and hard wood	Reinforcement	Short fibres
Leaf	Leaf	Banana	Reinforcement	Long fibres
	Leaf	and sisal	Reinforcement	Long fibres
Seeds	Cotton	Cotton species	Reinforcement	Short fibres
	Agricultural wastes	Cereals etc.	Reinforcement	Short and long fibres

Table 3.
Plant based fibres, source and utilization in biocomposites.

4.2.1 Physical modification

The surface properties may be increased by physical treatments of the fibres. However, during extraction process, the journey of fibres to a final destination also involves the multi stepping process leading to stress and physical changes in the inherent properties of fibres. During the extraction process there are some fibres which involve simple process of extraction for example *Agave sisilana* fibres. In most of the cases, the processing of plant material containing raw material for bio-composites as fibres encompass the physical and mild chemical treatments leading to change in original properties of fibres. Therefore, extraction of fibres is also an important factor in considering the evaluation of properties of bio-composites. There are various processes developed and optimized for extraction of fibres and well documented.

The physical treatments of the isolated fibres change the structural and surface properties of the reinforcing fibres without altering the properties and disintegration of fibres. The physical treatments influence the mechanical properties resulting in proper bonding to the matrix and affects interfacial adhesion. The commonly used method for plant-based fibres is corona and cold plasma treatment, however other physical methods are also successfully used for surface activation such as thermotreatment [58, 59]; calendering [60], stretching [61] and hybrid yarns [62]. The corona treatment provides oxidation of the fibres, which changes the surface energy of the fibres and increases the number of aldehyde groups [63–65]. The corona and cold plasma treatment are called electric discharge methods and mostly used to activate cellulose fibres leading to increase in mechanical strength [63, 64, 66].

4.2.1.1 Corona treatment

Corona treatment is employed for treatment of fibres to increase the morphological and mechanical properties of lignocellulosic fibres resulting in an improvement of the interfacial compatibility between matrix and fillers. Homogeneity of composite materials, adhesion properties and mechanical properties (tensile strength, Young moduli) increase to a certain level (10–30%) with corona treatment [67, 68]. Recently, *Aloe vera* fibres [69] were treated with corona discharge during different time intervals and it was observed that rough surface morphology and degradation of fibres occurred due to etching mechanism caused by corona treatment.

4.2.1.2 Plasma treatment

Plasma treatment is an environmentally friendly green electric discharge method for treatment of fibres [70–72] and provides changes in surface energy, increase of the roughness and micro-cleaning of the treated fibres. The process causes surface crosslinking and can introduce reactive groups. Mostly low plasma treatment is being carried out in presence of gases to alter the surface properties of fibres. The base material is treated under atmospheric plasma glow discharge for various periods of time using helium, helium/nitrogen, and helium/acetylene, argon, oxygen, air etc. gas. The significance lies in the fact that sometimes desired properties obtained in seconds. Intriguingly, changes in surface roughness, tip-surface adhesion, and surface chemistry of the fibres and flexural strength, flexural modulus, and interlaminar shear stress, storage modulus and glass transition temperature increased significantly. The treatment is successfully employed to alter the surface properties of natural fibres used in composites as reinforcing material. The adhesion between sisal fibres and polypropylene matrix [73] increase the interfacial adhesion between flax fibre and matrix polyethylene and unsaturated polyester [74, 75]; improvement

in mechanical properties of ramie fibres [76, 77] polypropylene composites, increase in flexural strength and tensile strength of the composite prepared from jute fibre [78–81] were obtained by employing plasma treatments.

4.2.2 Chemical modification of fibres

Natural fibres possess high polarity in nature due to the presence of numerous hydroxyl groups on the fibre surface which makes them incompatible with the synthetic hydrophobic matrix resulting in poor interfacial bonding between the cellulosic fibres and the matrix producing bio-composites with lesser physical and mechanical strength. Chemical treatments of fibres are an important step for processing of bio-composites and enhancing the compatibility of fibres to the synthetic matrix. Bi-functional groups are introduced chemically into the fibres leading to activation of hydroxyl groups. The activated hydroxyl groups further react with the synthetic matrix thereby enhancing the interfacial adhesion and compatibility between the fibres and matrix [76, 82]. Reviews and chemical methods have been reported in the past to increase the functional behaviour of hydroxyl groups present in the polysaccharides. These methods have their own limitations for particular industrial aspects and are used for diverse industrial applications [83–94]. Mercerization, benzylation, acrylation, acrylonitrile grafting, permanganate treatment, peroxide treatment, and isocyanate treatment, bleaching, acetylation, silane and peroxide treatments, etherifications viz. cyanoethylation, quaternization, carboxymethylation and various coupling agents are commonly used for lignocellulosic fiber activation [76, 87]. Mercerization of fibres using alkali at different concentration and time period for activation and production of modified fibres with good adhesion properties have been applied for modification of fibres [95, 96]. Transverse strength of flax fibres may be increased sufficiently by the alkaline treatment which led to produce better adhesion properties between flax fibres and epoxy matrix [97]. Introduction of acetyl groups into the cellulosic fibres increases plasticity leading to hydrophobic character and mechanical strength to the reinforcing material [76, 98]. Coupling agents are frequently and successfully used to reduce the interfacial adhesion of fibres to the matrix. Various organosilanes mostly trialkoxysilanes are variably used as coupling agents and the process is referred as Silanization. The reactive alkoxy groups present in the silanes chemically bond with the hydroxyl groups and the formation of polysiloxane structures occurs [58, 99]. Maleic anhydride is another coupling reagent used to increase the interfacial adhesion of biocomposites [100]. Partial removal of lignin on the henequen fibres increases the adsorption of the silane couplings and interaction among the fibre and the matrix [101]. The mechanical properties including tensile, flexural, impact strengths and tensile modulus of the biocomposites were improved several times on Jute fibre polypropylene composites using *m*-isopropenyl- α - α -dimethylbenzyl-isocyanate (*m*-TMI) as the coupling agent using grafting process. Further, the tensile modulus of the composites prepared from virgin polypropylene increases manifold [102]. The use of the clay in the bio-composites formulation led to reduced mechanical properties. Intriguingly, techniques such as pre-coated fibres with nanoclay and maleated polyethylene mixture enhance the synergetic effect of the clay and bamboo fiber and further significantly increase the tensile strength, bending modulus and strength of the high density polyethylene bamboo composites [103].

Maleated coupling agents are widely used to strengthen composites containing fillers and fibre reinforcements. The maleated coupling provides efficient interaction of maleic anhydride with the functional surface of fibres and matrix. Agrofibre polypropylene composites were studied by introducing maleated coupler

that provides the flexural and tensile strengths by more than 60% with Epolene™ G-3015 increment in comparison to composites without coupler [89]. Maleic anhydride grafted rice husk [104], hemp fibres unsaturated polyester composites coupled with 3-isopropenyl-dimethylbenzyl isocyanate [105], maleic anhydride-grafted polypropylene jute fibre composites [106], coir fiber and m-isopropenyl- α - α -dimethylbenzyl isocyanate grafted polypropylene composites [107] may be implemented in production of superior biocomposites having high mechanical properties and strength.

5. Biocomposites from extractives

5.1 Biocomposites using tannins

Tannins are a group of polyhydroxy phenolic compounds and exhibit good alternatives to synthetic adhesives for green chemistry in developing composites. They are found abundantly in nature. Their functions are to protect the plants against predation and might help in regulating the plant growth. Tannins are heterogeneous in nature and chemically classified into two main groups viz. hydrolysable and condensed tannins. Hydrolysable tannins are small molecular weight (30-3000D) compounds, heterogeneous in nature and hydrolysed by water, acidic or alkaline conditions into smaller water soluble molecules such as gallic acid and ellagic acid (**Figure 2a** and **b**) constituting gallotannins and ellagitannins. The gallotannins and ellagitannins comprise of a central sugar unit esterified with several molecules of

Figure 2.

(a) Gallic acid (b) Ellagic acid (c) 5,7,3,4- tetrahydroxyflavan- 3- ol (d) 5,7,3,4- tetrahydroxyflavan- 3,4- diol (e) ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (f) HBT (1-hydroxybenzotriazole).

gallic acid and a dimer of gallic acid as the basic phenolic unit known as ellagic acid respectively. Gallotannins, or commonly tannic acid, is the acknowledged source of the hydrolyzable tannins produced by extraction with water or organic solvents from the galls of certain trees, *Quercus infectoria* and *Rhus chinensis*, and pods from *Caesalpinia spinosa*. The European chestnut tree (*Castanea sativa*) and the oak species especially *Quercus montana* also produce hydrolyzable tannins in sufficient amount which are used in leather manufacture. Ellagitannins, a class of hydrolyzable tannins produce ellagic acid on hydrolysis under acidic or alkaline conditions. Mostly these are present in angiosperms extractives. Ellagic acid and their derivatives have extensive applications as antioxidants, chelators, technical and biomedical applications. The possible applications viz. antibacterial, antifungal, antiviral, anti-inflammatory, hepato- and cardioprotective, chemopreventive, neuroprotective, anti-diabetic, gastroprotective, antihyperlipidemic, and antidepressant-like activities, among others have gained interest to researchers and reviewed for commercial exploitation [108, 109].

Condensed tannins (nonhydrolyzable tannin or proanthocyanidine) the larger polyphenol groups with high molecular weight upto 30000D compounds, form insoluble precipitates in aqueous solution and are the polymerization products of monomeric flavan-3-ol or flavan-3,4-diol precursors (**Figure 2c and d**) [110] which are joined through stable C-C bonds between C-4 and C-8 and between C-4 and C-6. Tannins are dynamically used in tanning of animal hides in the leather processing industry since 1960s, the beginning of the industry due to interaction and precipitation of the proteins [29], adhesive making (especially wood adhesives), fisheries, beverages manufacturing, animal feed, biosourced foams, wood preservatives, corrosion inhibitors, polyurethane surface coatings, epoxy adhesives, binders for Teflon coatings, as mineral absorption and protein, as iron gall ink production, adhesive production in wood-based industry, anti-corrosive chemical production, uranium recovering from seawater, and removal of mercury and methylmercury from solution. In continuum, tannins are also used as bioactive molecules in nutrition science, 3D printing and biomedical devices [109, 111]. Their presence in natural vegetable material has prompted scientific community for their industrial applications in many different ways. Since historical times their traditional use has allowed their further use after diverse chemical modification for various end use functionalized properties. The main inherent feature of the tannins is due to the presence of phenolic structure similar to synthetic phenols. Mostly the condensed tannins are polymers composed of flavan-3-ol monomers and are mainly extracted from bark and wood for commercial purposes. Structural diversity and functions of varied range of tannins are very well described elsewhere in the literature [112–116]. Tannins are extracted from plant material by simple methods. Nevertheless, there are various extraction processes were developed to isolate the tannins for diverse applications. However, the extraction process remains a challenge due to their heterogeneity character and compositions. Recently, various extraction processes, technological applications and their pros and cons were reviewed and appeared in leading scientific reports [117–119]. Due to similar tannin structural properties as that of synthetic phenols, the basis of wood adhesives was started in the middle of 1940s. The world first commercial wood adhesive credit goes to Australia in the 1960s using *Acacia mearnsii* (black wattle) bark tannins. The successes stories of producing tannin wood adhesive are continued till date with the advancements. The other species used in producing commercial tannins are *Pinus radiata* (radiata pine) bark [120].

Condensed tannins have been in industrial use for nearly 60 years as replacement for phenolic resins for wood based panels with high resistance against moisture and water as well as for boards with very low subsequent formaldehyde

emission. Mimosa tannins, obtained from mimosa bark are usually well appreciated for its functional properties for wood adhesives. A wider industrial usage of tannins suffers from the limited availability of raw materials and high transportation costs. Only South Africa is the only actual producer of mimosa tannins on industrial scale [121]. Tannins react with formaldehyde the main crosslinker, and form hardened and crosslinked structures, similar to synthetic phenolic resins. The methylene bridges are formed between two tannin molecules. These methylene bridges are resistant to environmental factors against hydrolysis due to the strong stability of C-C bonds. Tannin-phenolic resin (tannin wt 40%) and sisal fibres (50 wt%) thermoset adhesives were successfully prepared and met all the required standards viz. Izod impact strength increased significantly. Further, it was also observed that sisal fibres and the tannin-phenolic thermosets have close values of the dispersive component and compatible interaction between the sisal fibres and the tannin-phenolic matrix at the interface [122]. A new source of tannin was also reported as a by product during catechin extraction process from a plant leaves (*Uncaria gambier*) extract and the tannin-phenol-formaldehyde wood adhesive was successfully prepared which met all the international standards [110]. Further, a new source of fibres, obtained from *Pinus roxburghii* needles, was also utilized in preparation of composites using phenolic resin adhesives [101]. Since, the early 1990s there are several scientific reports and reviews pertaining to natural fibres and tannin extracts from a natural sources viz. plants, agriculture wastes are available in the literature [122–131].

5.2 Biocomposites from fibres using enzyme and lignin

The study of enzymatic systems to activate the cellulosic fibres is a green alternative approach to other modifications for preparation of biocomposites and very well scientifically studied in last four decades to improve the surface, chemical, morphological and thermal properties of natural fibres as reinforcement materials. The enzymes offer an inexpensive and ecofriendly attractive option to improve the surfaces of natural fibres for composites.

Laccases (EC1.10.3.1) are multinuclear copper oxidases often called ‘blue’ oxidases that catalyze the oxidation of a wide range of substrates including phenols. Fungal laccases (benzenediol:oxygen oxidoreductase, EC1.10.3.2) are obtained from extractives of various fungal strains as an extracellular product. This enzyme is produced extensively in higher plants and fungi. The enzyme is produced by different genera of ascomycetes [132–134]; deuteromycetes [135, 136] and mainly from basidiomycetes [137]. The production and purification of biotechnological enzymes have been reviewed extensively [138–145] due to its overwhelming response. The first laccase was obtained from a Japanese lacquer tree (*Rhus vernicifera*), since then new fungal laccases from *Trametes versicolor*, *Polyporus pinsitus*, *Rhizocotonia solani* and from Ascomycetes *Myceliophthora thermophila* and *Sccytalidium thermophilum* etc. were obtained and studied extensively [142, 143, 145–159].

Commercially, laccases have been used for delignification of wood, production of ethyl alcohol and identification of morphine and codeine etc. among the various applications [142, 160–170]. Various delignification processes using fungi have been developed by the scientific community successfully. These enzymes were considered to be capable of C α -C β cleavage of the side chain of lignin models and it was suggested that the enzymes participate in lignin degradation [171, 172]. The white rot fungi especially basidiomycetes degrade lignin in natural system more robustly than other organisms. They completely degrade lignin to carbon dioxide and water. The lignin degradation by white rot fungi was extensively studied earlier on *Phanerochaete chrysosporium* and *Sporotrichum pulverulentum* [173, 174]. The

enzymes lignin peroxidase and manganese peroxidase were the first isolated from the *Phanerochaete chrysosporium* fungus culture. Lignin peroxidase is capable of ionizing non-phenolic aromatic substrates as an oxidizing peroxidase and produce aryl cation radicals [175, 176], whereas, manganese peroxidase does not degrade the non-phenolic parts of lignin in wood [177]. Further, it was observed that laccases exhibit strong catalytic activity and biotechnological applications in the bleaching of kraft pulp by depolymerising and solubilising lignin in the presence of mediator compounds [168, 178–182]. These mediator compounds were called laccase mediator systems (LMS). A number of possible mediator compounds have been searched and described for enhancing the activity of enzymes but mostly the ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) and HBT (1-hydroxybenzotriazole) (**Figure 2e** and **f**), a derivative of benzotriazole have been used as the mediator systems [173, 183]. The oxidation of benzyl alcohols with ABTS^{2+} (**Figures 3** and **4**) have been experimentally proved by [182–184]. The reaction mechanism of lignin degradation with LMS is complex due to the complex nature of LMS and various reactive centres on the lignin molecule. The simple reaction mechanism was postulated by Freudenberg [185] on the non-phenolic lignin model compound, veratryl alcohol and suggested a possible mechanism of delignification of residual lignin. The scientific kinetic studies of veratryl alcohol and benzyl alcohols have also been studied in laccase mediator systems [178, 184, 186, 187].

Laccases have been found to possess catalytic ability not only to degrade lignin and in delignification process for applications in biobleaching process but also observed as their involvement in the *in vivo* lignin biosynthesis and possibly in lignification woody tissues in higher plants [188–196]. The approach of oxidation and polymerisation of lignin by the enzymes [161, 162, 197] was advanced to another biotechnological application for compounded materials using wood fibres, lignin and enzyme laccase. The high tensile strength of the woody system or biocomposites is produced by the cellulose fibres and the pressure strength is produced by the lignin matrix which is a cementing material polymerised *in situ* and held cellulose fibres together resulting in high strength to the natural composites. Cellulose and hemicelluloses (**Figure 5a**) are macromolecules composed of sugar molecules. Cellulose is composed of only glucose molecules having β -1-4 linkage (**Figure 5b**), whereas hemicelluloses composed of different sugar monomers aligned in a definite fashion. Cellulose formation by a single glucose molecule in plant cell requires four enzymes and biosynthesis of lignin composed of phenol units utilizes peroxidases and phenoloxidases (Laccases) [198–201]. The monomeric units of lignin comprised of coumaryl alcohol (H-lignin) present in grasses and agriculture crops, coniferyl alcohol (G-lignin) present in all species, dominant in conifers and syringyl alcohol (S-lignin) present in hard wood species up to 40% (**Figure 6**).

The production of composites emanates the same basic principle as the formation of natural wood: wood is processed and fragmented into fibres and small pieces as per need of the required composites. Fibres, isolated from soft or hardwood, fibre bearing species or agriculture wastes, are embedded into a matrix. The matrix or binder may be a urea-formaldehyde, phenol-formaldehyde, resorcinol-formaldehyde, isocyanates or in a combination as per requirement of the composites.

Figure 3.
 Laccase-catalyzed oxidation of veratryl alcohol in the presence of a mediator.

Figure 4.
Oxidation of ABTS by Laccase enzyme (blue colour, $\lambda_{\text{max}} 753\text{nm}$).

The postulated theories of delignification of lignin, lignifications of woody tissues, activation of the surface of fibres possessing lignin, by the peroxidases enzymes have been successfully applied to prepare green biocomposites. The use of enzyme for bonding in the wood was first suggested by Nimz [202]. In continuum, several scientific communities have been engaged in producing biocomposites using laccase peroxidase enzyme. Wood fibres are incubated for a certain time with phenoloxidas laccase enzyme and lignin crust on the fibre surface gets activated and oxidized. Activated fibres are compressed by operating standard operating conditions of pressure, temperature etc, and binderless fibre boards may be prepared as per standards [170, 200, 201, 203–207]. The utilization of peroxidases in production of biocomposites was also applied to fibres in last two decades [208]. Cellulose fiber enzyme

Figure 5.
 (a) Schematic diagram of cellulose and hemicelluloses in cellulose microfibrils arrangement, blue lines: cellulose; red line: hemicelluloses (b) Chemical Structure of cellulose.

composites [207], hemp fibre reinforced composites using enzyme and chelators [209], polypropylene composites using abaca fibre [210], sisal fibre/phenolic resin composites [211], laccase-treated kenaf fibre reinforced composites with polypropylene and maleic anhydride grafted polypropylene as coupling agents [212], rubber wood fibreboards [205], laccase-mediated grafting dodecyl gallate (DG) on the jute fiber composites [213], banana/polypropylene composites [214, 215], coconut fibre composites [216], natural fiber medium density fibreboard [217], jute polypropylene composites [218, 219], flax fibre epoxy Composites [220, 221] were successfully prepared and studied for increasing mechanical properties and interfacial adhesion of the biocomposites. These all studies indicated that enzymes have the potential ability to modify the surface properties of fibres as being utilized in production of biocomposites. The formation of biocomposites has been shown in graphical representation (Figure 7) [163, 165, 200, 201, 203, 204, 222–225].

6. Opportunities and future perspectives

In this chapter, we have underlined and discussed the different sources of natural fibres, their properties and the effect of treatments on natural fibres, etc. and further their effective use as reinforcement for polymer composite materials. Natural fibres are lucrative and worthwhile option for biocomposites. However, limitations such as poor thermal stability, moisture absorption and poor compatibility with polymeric matrices are challenges that need to be resolved.

There are a large number of fibres obtained from the natural resources; intriguingly only few of these fibres have been studied in detail for reinforcement of bio-composite materials and other industrial and traditional applications. In the present chapter popular natural fibres have been discussed as reinforced composites materials with combination of synthetic and natural polymers as modified matrix. Among the most popular natural fibres; flax, jute, hemp, sisal, ramie, and kenaf fibres were extensively studied and employed in different applications as reinforced

Figure 6.

Monomeric units of Lignin (a) Coumaryl alcohol (H-lignin) (b) Coniferyl alcohol (G-lignin) (c) Syringyl alcohol (S-lignin).

materials. But due to environmental and economic concern other fibres from natural resources such as pine, bagasse, pineapple leaf, coir, oil palm, banana, and agriculture residues are acquiring interest for various value added applications due to their inherent and diverse physical properties. Merits and demerits of the natural fibres and their inherent properties mainly influence the mechanical properties of bio-composites due to interfacial adhesion between the fibre and synthetic matrix.

Variability in natural fibres such as processing conditions, fibre diameter and length, lumen diameter, presence of other compounds such as amount of lignin and hemicelluloses needs to be standardising for the processing of particular fibres. High qualities of fibres are required to increase the potential of fibres as reinforcement materials. Maleated coupling agents are extensively used to enhance the composites strength using fibre as reinforcement material. These agents are used as

Figure 7.
 Graphical representation of Biocomposites.

couplers and bind synthetic matrix and functional surface of fibres and economical in processing. Further, using couplers the strength of fibres increased which lead to increase interfacial adhesion between two dissimilar components. However, maleated couplers illustrate superior performances with polypropylenes, polylactic acid and other polyolefins etc. Further, scientific inputs are required to improve the strength of biocomposites using maleated couplings by incorporating varied fibres.

The diverse ranges of fibres are required to investigate the quantification of residual lignin on the fiber surface and optimization of fiber isolation parameters since during the processing of fibres the amount of residual lignin may be different to the fibres isolated from the same resource. Further, the constituents and structure of lignin is also different in the fibres sourced material viz. soft and hard woods and vegetable crops and agriculture residues. Therefore, proper attention is required to investigate the activation of fibre surface and binder in the biocomposites similar to natural composites. In continuum, diverse range of appropriate laccase mediator systems (LMS) needs attention for biocomposites.

Green composites may be a suitable alternative for petroleum-based synthetic non-environment friendly materials by using enzymes especially 'laccases' one of the most ancient and efficient enzymes with promising future applications. The high reduction potential of laccases has led the vast industrial applicability, despite this, laccase potentialities are not fully exploited due to large-scale production, cost and efficiency. Systemetic progress has been made over the last three decades to enhance the utilization of laccase enzyme for various biotechnological applications and it is expected that laccases will be able to compete with other processes of bio-composites. Thus, scientific efforts are need of the hour in order to achieve the economical production of the biocatalyst, development of optimum production conditions like pH, temperature, medium composition and efficient mediator systems and further utilization in lignin activation of fibres.

In view of the above discussion, the following activities may be expedient in bio-composites development from natural resources.

- Identification and search of new fibres with better inherent properties and compatibility to the synthetic matrices.

- Agriculture residues consisting of sufficient amount of celluloses.
- Utilization of tannins and non toxic small aldehydes for making wood adhesives.
- Search of coupling agents and other bonding agents.
- Efficient production of laccases and other biotechnological economical enzymes from various fungal resources.
- Utilization of waste lignin from the paper industry and activation thereof using enzymes for lignin celluloses complexes.
- Activation of lignin on the fibre surface to act as binder and enzyme mediator systems to form efficient lignin cellulose complexes.
- Utilization of long and short fibres simultaneously to avoid voids for increasing the compactness and stiffness of bio-composites.
- Lignin starch/celluloses complexes for biodegradable plastics.
- Fire and water proof green bio-composites using natural fibres for interior design of automotive, aerospace and applications in construction industry.
- Utilization of laccases, celluloses, starches and lignin for various food grade composites as an alternative to plastic.

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Conflicts of interest

The author declares no conflict of interest.

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