Chapter 6
Greener Surface Treatments of Natural Fibres for the Production of Renewable Composite Materials

Koon-Yang Lee, Anne Delille, and Alexander Bismarck

Abstract Natural fibres have been the prime candidate to replace synthetic fibres for the production of composite materials. Major advantages associated with natural fibres include low cost, low density, high toughness and biodegradability. However, these intriguing properties of natural fibres do come at a price. The hydrophilic nature of natural fibres often results in poor compatibility with hydrophobic polymer matrices. Various surface treatments of natural fibres using chemicals have been developed to improve the compatibility between the fibres and the matrix, but large amounts of solvents are usually involved. In this chapter, greener surface treatments without the use of hazardous chemicals are reviewed. These include plasma treatments, the use of enzymes and fungi for the extraction and surface treatment of raw fibres or natural fibres and the deposition of bacterial cellulose onto natural fibres. These treatments are aimed at improving the interfacial adhesion between the fibres and the matrix, thereby improving the stress transfer efficiency from the matrix to the fibre. The effects of these treatments on the properties of natural fibres are discussed. In addition to this, the overall impact of these treatments on the mechanical properties of the resulting natural fibre reinforced composites is also addressed.

Keywords Bacterial cellulose · Hierarchical composites · Mechanical properties · Natural fibres · Surface modification

Contents

A. Bismarck (✉)
Department of Chemical Engineering, Imperial College London, Polymer and Composite Engineering (PaCE) Group, South Kensington Campus, London SW7 2AZ, UK
e-mail: a.bismarck@imperial.ac.uk

S. Kalia et al. (eds.), *Cellulose Fibers: Bio- and Nano-Polymer Composites*,
DOI 10.1007/978-3-642-17370-7_6, © Springer-Verlag Berlin Heidelberg 2011

6.1 Introduction

Public's growing demand for more environmentally friendlier products, the search for greener sustainable technology, the ever-growing problem of global waste, environmental legislative pressure such as the end-of-life vehicle [1], the landfill of waste products [2] and waste electrical and electronic equipment regulations [3], as well as the depletion of fossil resources (and corresponding increase in raw materials prices), have initiated the interest of using renewable resources in the polymer industry [4, 5]. Polymer manufacturers are forced to consider the life cycle of their products and evaluate the environmental impact of these products throughout the products' lifetime. These include the selection of raw materials, polymer processing, recycling and disposal. Combining all these factors and the worldwide availability of plant-based natural fibres [6], research interest of using natural fillers to reinforce polymers is re-emerging in the field of composites engineering over the last three decades. The use of natural fibres in the production of composite materials is well developed [7–17]. Such extensive use of natural fibres as reinforcement for polymers is not surprising as natural fibres offer several advantages over conventional reinforcing fibres, such as lower cost, low density, high toughness and biodegradability [18, 19]. A big step towards the application of natural fibre reinforced composites can be found in door panels of *Mercedes-Benz E-class* [20]. Daimler AG replaced the door panels of *Mercedes-Benz E-class* with flax/sisal fibre mat embedded epoxy resin. A remarkable weight reduction of 20% and an improvement in the mechanical properties of the door panels were achieved. This further improves the protection of the passengers in an event of an accident. In addition to this, Rieter Automotive won the JEC Composites Award 2005 for their development in natural fibre reinforced thermoplastic composites for an under-floor module with integrated aerodynamic, thermal and acoustic functions [21].

6.1.1 A Brief Introduction to Natural Fibres

Natural fibres can be derived either from plants (such as flax or hemp), produced by animals (such as silk or spider silk) or from minerals (such as asbestos). Table 6.1 shows the comparison of selected physical properties between natural fibres and synthetic fibres. Although the mechanical properties of natural fibres are very much lower than those of conventional synthetic fibres, such as glass or carbon fibres,

Table 6.1 A comparison between the physical properties of selected natural fibres and synthetic fibres

Fibre	Density ($g\ cm^{-3}$)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Flax	1.5	345–1,500	27.6	2.7–3.2
Hemp	1.47	690	70	1.6
Jute	1.3–1.49	393–800	13–26.5	1.16–1.5
Ramie	1.55	400–938	61.4–128	1.2–3.8
Sisal	1.45	468–700	9.4–22	3–7
Cotton	1.5–1.6	287–800	5.5–12.6	7–8
Silk[a]		600	10	20
Spider silk[b]		800–1,000	7.2–9.2	30–60
Basalt[c]	2.66	3,050	92.5	
Asbestos[c]		550–750	1.0–3.5	
E-glass	2.55	3,400	73	2.5
Kevlar	1.44	3,000	60	2.5–3.7
Carbon	1.78	3,400[d]–4,800[e]	240[e]–425[d]	1.4–1.8

Source: Adapted from Bismarck et al. [22]. Further developed with Craven et al. [23], Brant [24], Perez-Rigueiro et al. [25] and Martiny et al. [26]

[a] Natural fibre derived from animal sources (silkworm)

[b] Natural fibre derived from mineral sources

[c] Natural fibre derived from spider (*Argiope trifasciata*)

[d] Ultra high modulus carbon fibre

[e] Ultra high tenacity carbon fibre

significant research effort is still poured into the field of plant-based natural fibre reinforced composite materials due to its low cost and low environmental impact. On a "per weight" basis, flax, jute and hemp fibres have higher tensile moduli than E-glass fibres [27, 28] due to the low density of natural fibres (~1.4 $g\ cm^{-3}$) compared to E-glass (~2.5 $g\ cm^{-3}$). This is particularly important in applications where weight reduction is a priority. Therefore, it is not surprising that natural fibres are used as reinforcement for polymer matrices to replace conventional glass fibres.

6.1.2 Structure of Plant-Based Natural Fibres

Plant-based natural fibres are rigid and they are composed of cellulose, hemicellulose, lignin, pectin, waxes and water-soluble compounds, with cotton being the exception. Cotton is made up of nearly 90 wt% cellulose, 5.7 wt% hemicellulose, 1 wt% pectin and 0.6 wt% waxes [7]. Cellulose is the major constituent in plant-based natural fibres. It is a linear molecule consisting of repeating β-D-glucopyranose units linked together by 1 → 4 glycosidic bonds (Fig. 6.1). It has a degree of polymerisation of approximately 10,000 [29]. Strong hydrogen bonds exist between cellulose molecules due to the presence of hydroxyl groups, which governs the physical properties of cellulose. It has a semi-crystalline structure, consisting of crystalline and amorphous regions. Cellulose in natural fibres (such as cotton, flax and ramie) typically has a degree of crystallinity of between 65 and 70% [30].

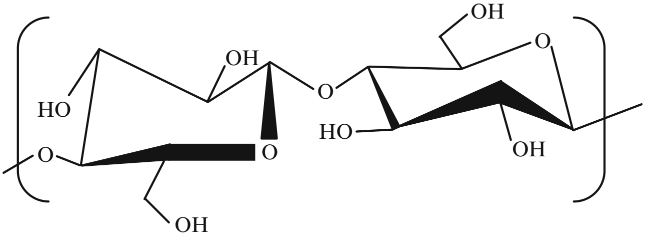

Fig. 6.1 Schematic diagram showing the structure of cellulose

The amorphous regions can be hydrolysed by acids to create short cellulose nanocrystals [31]. Nevertheless, cellulose is stable in most common organic solvents. It can only be dissolved in strong acidic solutions such as concentrated phosphoric acids and concentrated sulphuric acid [32] or ionic liquids such as *N*-ethylpyridinium [33] and lithium chloride/*N*,*N*-dimethylacetamide [34].

Hemicellulose is the other major constituent of plant-based natural fibres and it is made up of a combination of 5- and 6-ring carbon polysaccharides [22]. It is a branched polymer and has much shorter polymer chains (degree of polymerisation of between 50 and 300) compared to native cellulose. In addition to this, hemicellulose is very hydrophilic in nature [35], easily hydrolysed by acids and soluble in alkali. The role of hemicellulose in natural fibres is to form the supporting matrix for cellulose microfibrils.

Lignin is a phenolic compound that provides rigidity to the plant [22] and acts as a binder to consolidate the polysaccharide, holding cellulose and hemicellulose fibres together [36]. It was found that lignin has high carbon low hydrogen content and this implies that it is highly unsaturated or aromatic. Lignin can be produced by the dehydrogenation polymerisation of *p*-coumaryl, coniferyl and sinapyl alcohols [37]. It contains hydroxyl (–OH), methoxyl ($–O–CH_3$) and carbonyl (C=O) groups. Ethylenic and sulphur containing groups have also been identified in lignin [7]. Lignin is amorphous and hydrophobic in nature. It has been shown that lignin possesses a softening temperature of about 90°C and a melt temperature of 170°C [35].

6.2 Green Modifications of Plant-Based Natural Fibres

Although natural fibres are highly comparable to conventional glass fibres on a “per weight” basis, the major drawback arises from the inherent variability of natural fibres [22]. Natural fibres can vary in terms of their dimensions and mechanical properties, even within the same cultivation. This situation is different from synthetic fibres, which can be manufactured uniformly (e.g., Toray’s T700S carbon fibre has only a variability of ±10% in its tensile strength and modulus [Commercial documentation – No AQ.866-9 (September 2003), Personal communication], ±3% in its diameter). All natural fibres are hydrophilic in nature due to the presence of large amounts of hydroxyl groups; their absorbed moisture content can be as high as 30% at 95% relative humidity [38]. This extremely hydrophilic nature of natural fibres often results in poor compatibility between natural fibres and hydrophobic polymer matrices, such as polypropylene or polylactide [14]. Another factor that limits the use of natural fibres is its low thermal stability. To avoid degradation of natural fibres during thermal processing, the temperature at which natural fibres are exposed to is usually limited to 200°C (shorter processing time is preferable) [39]. This further limits the choices of polymers that can be used as potential matrix for natural fibre reinforced composites. Figure 6.2 shows the reduction in the tensile strength of natural fibres with increasing processing temperature and time of the natural fibres.

To improve the compatibility between natural fibres and hydrophobic polymer matrices, various methods have been explored to increase the hydrophobicity of natural fibres [40–42]. Most of the chemical surface treatments of natural fibres involve silylation [43–46], acetylation [47], benzoylation [48], maleated coupling agents [49], isocyanate treatment [50] and grafting polymers to natural fibres [51]. Although these methods alter the wettability of natural fibres, large quantities of hazardous chemicals were or are usually involved in the process of hydrophobising the natural fibres and the chemical waste must be handled and disposed of appropriately. This adds extra cost to the production of natural fibre reinforced composites, making the chemical treatments less attractive as a viable solution. Moreover, chemical treatments of natural fibres do not always result in improved composite performance. The main reason is the anisotropicity of natural fibres. The transverse modulus of natural fibres is orders of magnitude lower than its axial modulus [52, 53]. Cichocki Jr et al. [52] showed that the axial modulus of jute fibres is 38.4 GPa, but its transverse modulus is only 5.5 GPa. [53] also showed that the axial modulus

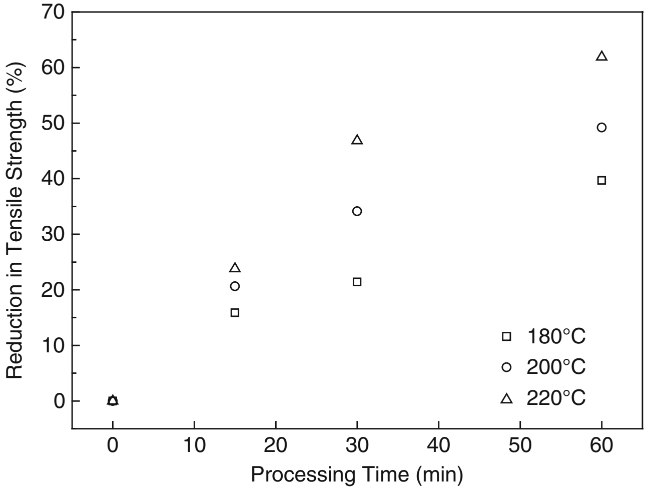

Fig. 6.2 Temperature and time dependency of natural fibre's tensile strength. Adapted from [39]

of flax fibres is seven times larger than its transverse modulus (axial modulus: 59 GPa, transverse modulus: 8 GPa). In addition to this, [54] also attributed the failure of natural fibres to deliver good performance in composites to the high linear thermal coefficient of expansion (LTCE) of natural fibres. The interfacial shear stress between the fibre and the matrix is the product of residual compressive stresses (σ_r) and the static friction coefficient at the fibre–matrix interface. Due to the high LTCE of natural fibres, σ_r will be lowered, leading to poor interfacial shear strength between the fibres and the matrix. Therefore, chemical modification of natural fibres might not be the next step forward. Instead, efforts should be focussed on environmental friendlier processes to increase the hydrophobicity of natural fibres and to avoid the shrinkage problem of natural fibres during thermal processing.

6.2.1 Plasma: A Brief Introduction

Plasma is known as the fourth state of matter. It is defined as a gaseous environment composed of charged and neutral species with an overall zero charge density. Plasma has been shown to modify the tribology of thermoplastics and synthetic fibres (such as carbon fibres) [55–58]. Further details regarding plasma treatments of various materials can be found in the literature [59–61]. Plasma treatments have the ability to change the surface properties of the fibres through the formation of free radicals, ions and electrons in the plasma stream [62]. During plasma treatment, the substrate is bombarded with high-energy particles travelling in the stream of plasma or vacuum UV (in low-pressure plasma). As a result, the surface properties such as the wettability, surface chemistry and surface roughness of the substrate can be altered without the need for any hazardous chemicals or solvents. Usually, plasma treatments modify the surface of natural fibres by [61] (1) removing weakly attached surface layers (i.e., cleaning and abrasion) and (2) forming new functional groups (functionalisation and cross-linking). The functional groups formed on the surface of natural fibres depend on the nature of the plasma feed gas. Therefore, plasma treatment minimises the environmental impact of natural fibre surface treatments. Different types of plasma sources are available [63] and they are summarised in Table 6.2.

6.2.1.1 Low-Pressure Plasma Treatment of Natural Fibres

The plasma discharge can be generated at atmospheric (see next section) or under vacuum conditions [42]. Essentially, the two types of plasmas generated are the same. The plasma produced can be used to modify the surface energy of natural fibres [64, 65], cross link the fibres [64], create free radicals to initiate polymerisation [51] or introduce functional groups onto the surface of the fibres [61]. A major advantage of employing low pressure plasma treatments is that such plasma can be generated at low power output. Atmospheric plasma treatments are usually carried out at a

Table 6.2 Comparison between different plasma sources

Plasma source	Gas temp (°C)	Electron temp (eV)	Applied voltage (kV)	Charge density (cm^{-3})
Arc and torches	7,000–65,000	2.5–6.8	10–50	10^{16}–10^{19}
Corona	50–400	4–6	10–50	10^{9}–10^{13}
Dielectric barriers	50–400	2–10	5–25	10^{12}–10^{15}
Low-pressure discharge	10–500	1–10	0.2–0.8	10^{8}–10^{13}
Atmospheric pressure discharge	25–200	1–2	0.05–0.2	10^{11}–10^{12}

Adapted from [63]

maximum power of 10 kW [64, 66]. Low pressure plasma treatments, on the other hand, are carried out at much lower power output of about 60–100 W [67, 68]. As aforementioned, the mechanical properties of natural fibres are highly dependent on the temperature at which the natural fibres are exposed to. By using a smaller power output, it is possible to minimise the thermal damage caused by plasma treatment on the natural fibres, thereby preserving the properties of natural fibres. However, there are disadvantages associated with low pressure plasma treatments. A well-designed plasma reactor system is required along with vacuum pumps and seals. In addition to this, low pressure plasma is also often used in small batch process only due to the limitation in the size of the vacuum chamber as a result of capital and operating costs.

Various researchers have investigated the use of low pressure plasmas to modify the surface of natural fibres [67–74]. Low pressure plasma has been used to treat wood fibres and sisal fibres, using argon and air as the plasma feed gas [67, 68]. Table 6.3 summarises the mechanical properties of untreated and plasma-treated natural fibre reinforced polypropylene (PP) composites. The plasma treatment of the fibres had a positive impact on the mechanical properties of the resulting wood fibre and sisal fibre reinforced PP composites when compared to the composites containing untreated natural fibres. The tensile strength was found to increase by as much as 16% for both wood fibres and sisal fibres reinforced PP composites. The tensile modulus improved by as much as 127% (wood fibre) and 93% (sisal fibre), respectively. When comparing neat PP to plasma-treated wood fibre or sisal fibre-reinforced PP composites, the tensile modulus improved by as much as 127% (wood fibre) and 113% (sisal fibre), respectively, and the tensile strength improved by as much as 17% (for both wood and sisal fibre). This is an indication of improved interfacial adhesion between the fibres and the matrix as a result of plasma treatment.

Jute fibres were treated in low pressure argon plasma [74]. The fibres were treated in argon plasma for 5 min, 10 min and 15 min, respectively. With longer plasma treatment, the fibres became rougher and the formation of pits on the fibre surface was observed when the fibres were plasma treated for 15 min. This is a result of plasma etching, which results in the degradation of the jute fibres [75]. The wettability of the plasma-treated jute fibres by water decreased with increasing treatment time (Table 6.4). This is also accompanied by an increase in the flexural strength of the plasma-treated jute fibre reinforced polyester composites. It was

Table 6.3 A comparison between untreated and plasma-treated wood fibre and sisal fibre reinforced PP composites. σ and E denote tensile strength and tensile modulus, respectively

Composites	Wood fibre		Sisal fibre	
	σ (MPa)	E (GPa)	σ (MPa)	E (GPa)
Neat PP	23	1.5	23	1.5
Untreated fibre	22	2.6	22	2.6
Argon plasma	25	3.0	24	3.2
Air plasma	27	3.4	27	2.9

All composites contain 20 wt% fibres. Adapted from [67, 68]

Table 6.4 A comparison between neat and plasma-treated jute fibres and the flexural strength of jute fibre reinforced polyester composites

Jute fibre treatment	Water/air contact angle	Polar surface energy (mJ m^{-2})	Flexural strength of polyester composites (MPa)
Neat jute fibres	81.6°	21.9	158.8
5 min plasma treated	84.1°	17.5	152.4
10 min plasma treated	86.9°	11.6	181.6
15 min plasma treated	90.0°	8.5	143.2

Adapted from [74]. The composites contain 15 wt% fibres loading fraction

found that the flexural strength of the composites improved by 14% (10 min plasma-treated jute fibres) compared to neat jute fibre reinforced polyester. This improvement was attributed to the increased roughness and hydrophobicity of the plasma-treated fibres, which results in better interfacial adhesion between the fibres and the matrix. However, composites reinforced with fibres treated in plasma for 15 min showed a 10% decrease in the flexural strength. This is a direct result of heavy degradation of the treated fibres during the prolonged plasma treatment [72].

6.2.1.2 Atmospheric Air Pressure Plasma Treatment of Natural Fibres

To improve the wettability and interfacial adhesion between natural fibres and a polymer matrix, atmospheric air pressure plasma (AAPP) treatment can be applied to natural fibres to remove non-cellulosic substances from the surface of these fibres. The advantages of using AAPP treatment for composite production are its low operating cost, short treatment time and greater flexibility, as no vacuum system is required [76–78]. It was reported that oxygen and nitrogen plasma led to a reduction of the critical surface tension[1] of lignocellulosic fibres as a result of etching effect [64]. Compressed air can be used as an alternative feed gas to overcome this negative impact generated by oxygen and nitrogen feed gases on lignocellulosic fibres.

As a general rule, good adhesion can be achieved when the surface tension of the substrate (natural fibres) is larger than that of the matrix. [64] have shown that the critical surface tension can be modified through AAPP treatment (Fig. 6.3). Different lignocellulosic fibres can be seen behaving differently if exposed to the same

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[1] The critical surface tension of a solid substrate corresponds to the surface tension of an imaginary liquid that will just wet the substrate completely.

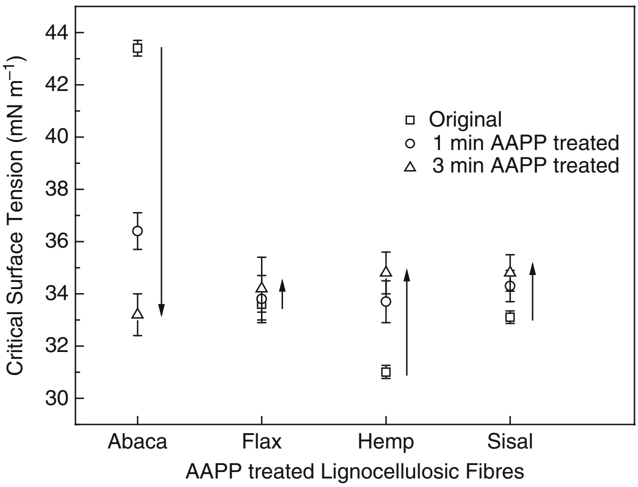

Fig. 6.3 Critical surface tension of lignocellulosic fibres after AAPP treatment at various times. Adapted from [64]

AAPP treatment. The critical surface tension of abaca fibres reduced with increasing treatment time. However, hemp and sisal fibres showed otherwise. With increasing AAPP treatment time, the critical surface tension increased. The authors hypothesised that longer treatment times of hemp and sisal fibres led to the cross-linking of the fibre surfaces (hemp fibres) and decomposition of hydrophobic groups. This might have led to the observed increase in the critical surface tension.

The effect of AAPP treatment on the properties of natural fibre reinforced cellulose acetate butyrate (CAB) composites was then further studied [66]. At a fibre loading fraction of 30 wt%, the storage modulus of the short fibre composites improved by as much as 370% (Fig. 6.4). This is due to the enhanced interfacial adhesion between the fibres and the matrix as a result of AAPP treatment (as measured by single fibre pull-out test) [79]. In addition to this, the increment in the mechanical glass transition temperature and a reduction in the height of tan δ showed better fibre–matrix bonding and fibre-in-matrix distribution. It is evident that AAPP treatment is able to improve the fibre–matrix interface, resulting in composites with improved mechanical properties.

6.2.2 *The Use of Enzymes for Natural Fibre Extraction and Surface Treatments*

Retting is a process of the separation or loosening of bast fibres from its non-fibrous components [80]. Water-retting is performed by immersing the stalks of the fibre crops in water for a certain period of time. Water penetrates the central

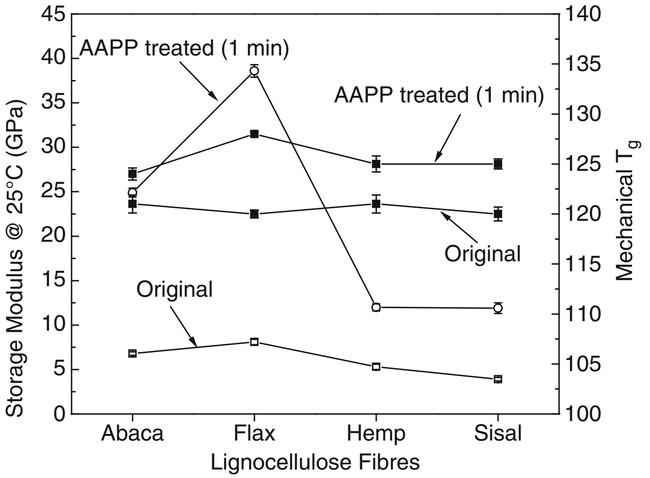

Fig. 6.4 Viscoelastic behaviour of AAPP-treated lignocellulosic fibre reinforced CAB composites. *Hollow icon* indicates storage modulus, *solid icon* indicates mechanical T_g. Adapted from [66]

stalk, swells the inner cells and bursts the outer most layers of the plant materials. This increases the absorption of moisture and decay-producing bacteria. Water-retting is able to produce high-quality fibres, but it also produces large amount of waste [81] and, therefore, this process was discontinued in many countries (apart from China and Hungary) [82]. Dew-retting, on the other hand, relies on fungi to colonise harvested fibre crop material in the fields. A combination of bacteria, air, sun and dew produces fermentation, which dissolves much of the stem materials surrounding the fibre bundles [80]. However, this method suffers from several disadvantages. Appropriate moisture and temperature conditions during dew-retting are needed [80]. This is a parameter that is very difficult to control as it is highly dependent on the region and the weather. In addition to this, the fibres extracted through dew-retting method have lower quality compared to water-retted fibres [80, 83].

Enzyme-retting is a natural fibre extraction method that refers to the separation of fibres from its non-fibre components through the use of enzymes [84]. This process generally uses pectin-degrading enzymes such as the commercially available Viscozyme L or Flaxzyme from Novozyme (Bagsvaerd, Denmark). The use of pectin-degrading enzymes promotes the selective degradation of pectinaceous substances [22]. Apart from this, the use of different types of enzymes such as cellulase, hemicellulase, laccase and peroxidase have also been reported [85, 86]. There are many advantages associated with enzyme-retting over conventional water-retting and dew-retting. Enzyme-retting is able to overcome the problems associated with dew- and water-retting as the fibres are treated in a well-controlled environment and the produced fibres possess the quality of water-retted fibres without large amount of fermentation waste. However, high cost associated with enzymes and equipment have limited this technology to pilot scale only [87].

Foulk et al. [88, 89] compared dew-retted flax fibre reinforced high-density polyethylene (HDPE) composites with enzyme-retted flax fibre reinforced HDPE composites. Flax fibres were extracted with commercially available Viscozyme L (Novozymes, Bagsvaerd, Denmark) and a chelator, Mayoquest 200 (Callaway Chemical Co. Smyrna, GA). Mayoquest 200 is a chelator that contains about 36–38% sodium EDTA and 40% total dissolved salts [80]. The chelator is often used to improve the efficiency of enzyme-retting by sequestering calcium from the solution [90]. Figure 6.5 shows the effect of different flax fibre extractions (dew-retted, enzyme-retted at different enzyme/chelator concentration) on the mechanical properties of the randomly oriented flax fibre reinforced HDPE composites. The flax fibres treated with enzymes and chelators showed significant improvements in terms of tensile properties compared to raw flax fibre reinforced composites. Enzyme and chelators modified the surface of flax fibres by removing pectin and calcium, therefore enhancing the interfacial adhesion between the fibres and the matrix. The composites reinforced with dew-retted flax fibres showed worse properties compared to enzyme-retted flax fibres. This is most probably due to poor surface properties of dew-retted fibres (containing high levels of calcium and the inability of dew-retting to remove specific components such as pectin) compared to enzyme-retted fibres.

In addition to using enzymes for the extraction of natural fibres, they can also be used to treat post-extracted natural fibres. Enzyme treatments of natural fibres also have advantages over conventional alkaline-treated natural fibres. [91]

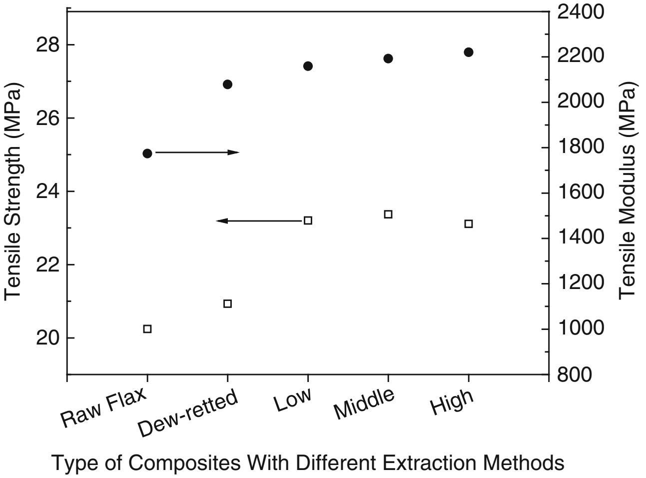

Fig. 6.5 A comparison between not-treated flax fibre, dew-retted flax fibre and enzyme-retted flax fibre reinforced HDPE composites. Adapted from [88]. Low indicates 0.05% enzyme and 5 mM chelator, medium indicates 0.1% enzyme and 10 mM chelator and high indicates 0.3% enzyme and 25 mM chelator

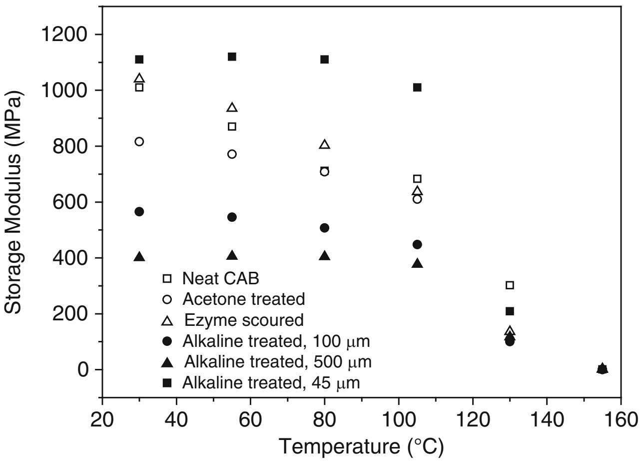

Fig. 6.6 Viscoelastic behaviour of flax fibre reinforced CAB composites. Adapted from [91]

compared the viscoelastic properties of neat, alkali-treated and enzyme-treated hemp fibre reinforced CAB composites. Hemp fibres were treated with Scourzyme L (Novozymes, Bagsvaerd, Denmark). Scourzyme is an alkaline pectinase that removes pectin without significant degradation of cellulose [92]. The enzyme-scoured hemp fibre reinforced CAB composites showed improvements over neat CAB, neat hemp fibre reinforced CAB and most of the alkaline-treated hemp fibre reinforced CAB. The composites reinforced with alkaline-treated hemp fibres (fibre length of 45 μm), however, possessed the highest storage modulus. Single fibre tensile tests indicated that the neat, alkaline-treated and enzyme-scoured hemp fibres possess Young's moduli of 42.8, 29.0, and 91.4 GPa, respectively [93, 94], with alkaline-treated fibres possessing the worst mechanical properties. Therefore, the observed better storage modulus of alkaline-treated hemp fibre reinforced composites (fibre length of 45 μm, Fig. 6.6) observed might be due to the greater control of fibre suspension in the polymer solvent prior to composite consolidation (solution casting method) [91]. Nonetheless, composites reinforced with enzyme-scoured hemp fibres possessed a toughness (area under the stress– strain curve) of 40% higher than that of untreated hemp fibre reinforced composites. This is an indication of the potential of enzyme treatment on natural fibre reinforced composites.

6.2.3 *The Use of Fungi for Surface Treatments and Extraction of Natural Fibres*

Enzyme-retting and treatments have been shown to be an effective method of treating natural fibres to improve the interface between the fibres and the matrix, leading to improved mechanical properties of the composites. However, it is expensive and limited to pilot scale only. Another underexplored method of natural fibre surface treatment involves the use of fungi. The use of fungi can provide low-cost, highly efficient and environmentally friendly alternatives to natural fibre surface treatment [95]. Unlike dew-retting, fungal treatment is performed in a more controlled environment. The controlled parameters include the type of fungi, the temperature and the period of treatment.

Fungi can be classified into four categories: basidiomycetes, ascomycetes, zygomycetes and deuteromycetes, respectively. White rot fungus (basidiomycetes) is the only fungus that has been shown to degrade lignin, exposing cellulose and hemicellulose [95]. It has also been shown that white rot fungus can degrade the hydrophobic constituents of natural fibres such as triglycerides and fatty acids. In addition to this, white rot fungus can also degrade sitosterol, sitosterol esters and resin acid [96]. These compounds are known to be resistant towards microbial degradation [97–99]. Therefore, it is not surprising that white rot fungus is used to remove non-cellulosic compounds from natural fibres in order to improve the mechanical properties of the resulting natural fibre reinforced composites.

The use of white rot fungus in the treatment of natural fibres can be found in the literature [95, 100–102]. White rot fungi treated hemp fibres have higher crystallinity index as measured by X-ray diffraction when compared to untreated fibres [95]. This is a direct result of the fungi's ability to remove non-cellulosic compounds such as amorphous lignin, thereby increasing the crystallinity index. Zeta-potential measurements have also shown that non-cellulosic compounds were removed by the fungal treatment. A more negative zeta potential was obtained and this was due to the exposed hydroxyl groups from cellulose as a result of fungal treatment.

Table 6.5 shows the tensile strengths of hemp fibres and randomly oriented hemp fibre reinforced polypropylene (PP) composites. The fibres were treated with white rot fungi and/or alkali. The tensile strength of the composites improved by as much as 32% (combination of alkali and white rot fungi treatments) when compared to neat hemp fibre reinforced composites. Fungi treatments can provide extra benefits in addition to alkali treatment alone. This improvement seen in the composites is a result of improved fibre morphology and mechanical interlocking between the fibre and the matrix.

Table 6.5 Tensile strength of hemp fibre and its PP composites treated with white rot fungi

Treatment type	Lignin removal	Single fibre tensile strength (MPa)	Composites tensile strength (MPa)
Control	–	683	36.7
Phanerochaete sordida	Yes	576	41.5
Pycnoporus sp.	Yes	470	44.6
Schizophyllum Commune	Yes	354	45.0
Alkali	Yes	621	43.3
Alkali + *Phanerochaete sordida*	Yes	579	48.3

Adapted from [95]

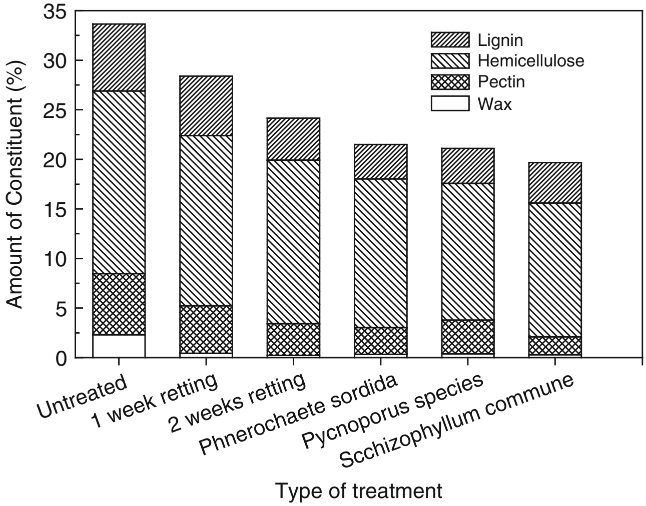

Fig. 6.7 A comparison between natural retting and white rot fungi treatment on the amount of non-cellulosic compound in hemp fibres. Adapted from [100]

White rot fungi have also been used to extract natural fibres [100]. Clarke et al. [103] reported a method for natural retting in which the hemp fibre bundles are separated from the plant by sealing the fibres in a bag for a fixed period of time. The microorganism present in the fibres will produce enzymes to remove non-cellulosic compounds. In a study by [100], natural retting was conducted by sealing non-retted hemp fibres in a bag under a controlled condition of 60% relative humidity for certain periods of time at room temperature. In another separate experiment, the authors treated non-retted hemp fibres with white rot fungi. It can be seen that fungal treatments removed more lignin compared to natural retting treatments (Fig. 6.7). The crystallinity index of the fibres increased from 66% to approximately 85%, due to the removal of non-cellulosic compounds from the fibres, which are generally amorphous. Figure 6.8 shows the tensile properties of single hemp fibres and randomly oriented hemp fibre reinforced polypropylene (PP) composites as a function of different types of treatments. Although the tensile strength of the fibres decreased when compared to neat hemp fibres, the composite strength improved by as much as 30% as a result of fungal treatment. This suggests improved fibre properties (crystallinity index) and interfacial adhesion (surface roughness) between fibres and the matrix, which was confirmed by scanning electron micrographs. Natural retted fibres does improve the composite's tensile strength (due to the removal of non-cellulosic compounds) when compared to unretted fibre reinforced composites but the increment in the observed tensile strength is less than that of white rot fungi treated hemp fibre reinforced PP composites. This might be a direct result of poor single fibre tensile strength due to long retting time.

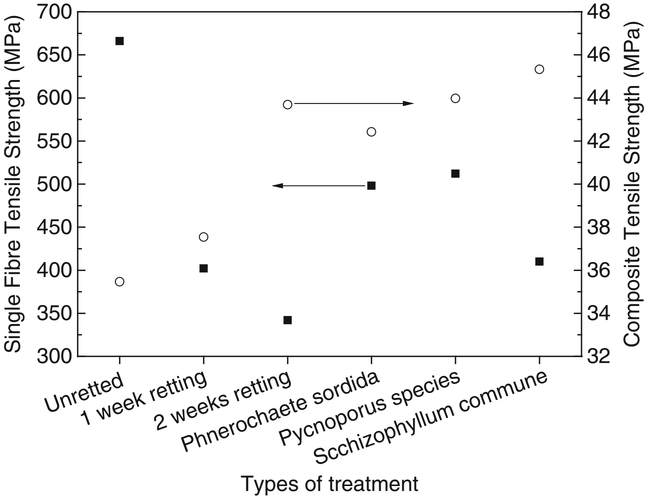

Fig. 6.8 Tensile properties of hemp fibres and hemp fibre reinforced PP composites treated with different methods. Adapted from [100]

6.2.4 Coating Natural Fibres with Nanocellulose

The previous three sections involved the treatment of natural fibres by removing substances from the natural fibres. This section, however, describes a new modification that does not involve the removal but the *addition* of new material onto the surface of natural fibres. This type of modification involves the deposition of nanosized cellulosic materials onto the surface of natural fibres to enhance the interfacial adhesion between the fibres and the matrix [9, 10, 14, 104]. By doing so, a hierarchical structure can be created. These works were inspired by nature. Nature maximises the efficiency of structural materials by creating hierarchical structures: the arrangement of the constituents at every level, from the molecular level to the macroscopic level. By applying this concept, composites that possess a hierarchical structure with improved mechanical properties can be manufactured.

In addition to plant-derived cellulose, cellulose can also be synthesised by bacteria such as from the *Acetobacter* species. By culturing cellulose-producing bacteria in the presence of natural fibres in an appropriate culture medium, bacterial cellulose is preferentially deposited in situ onto the surface of natural fibres. The introduction of bacterial cellulose onto natural fibres provides new means of controlling the interaction between natural fibres and polymer matrices. Coating of natural fibres with bacterial cellulose not only facilitates good distribution of bacterial cellulose within the matrix, but also results in an improved interfacial adhesion between the fibres and the matrix. This enhances the interaction between the natural fibres and the polymer matrix through mechanical interlocking.

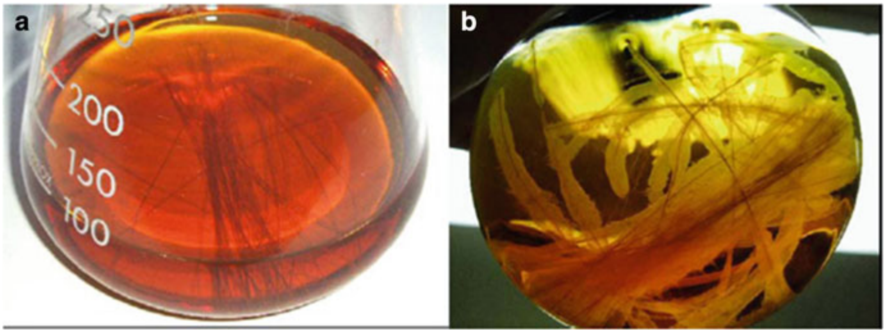

Fig. 6.9 Images showing (**a**) natural fibres immersed in a culture medium of *Gluconacetobacter xylinum* before bacteria culturing (**b**) the culture medium after 2 days. Reprinted from Pommet et al. [14] with permission from ACS publication

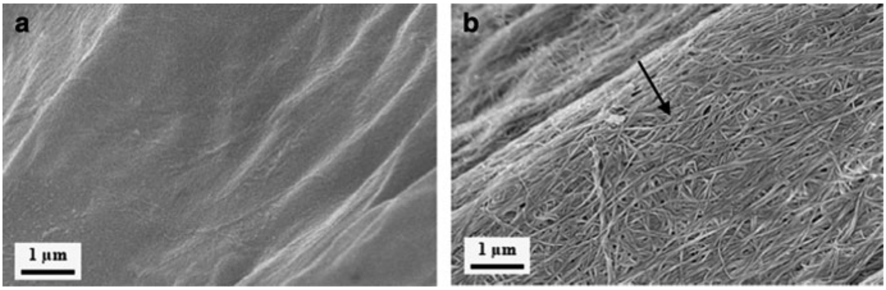

Fig. 6.10 SEM images showing (**a**) neat sisal fibre (**b**) sisal fibre coated with bacterial cellulose. Reprinted from Pommet et al. [14] with permission from ACS publication

Bacterial cellulose-coated natural fibres introduced nanocellulose at the interface between the fibres and the matrix, leading to increased stiffness of the matrix around the natural fibres. Figure 6.9 shows the images of the culture medium and natural fibres immersed in the culture medium before and 2 days after culturing. A layer of bacterial cellulose (BC) pellicles can be seen growing away from the surface of the natural fibres. Scanning electron micrographs of the BC-coated sisal fibres are shown in Fig. 6.10. A layer of bacterial cellulose nanofibrils can be seen attached onto the surface of sisal fibres (Fig. 6.10b). The coating of natural fibres with BC could also be a potential solution to the aforementioned shrinkage of natural fibres during thermal processing of the composites. Due to the low thermal expansion of BC ($0.1 \times 10^{-6}\ \mathrm{K}^{-1}$) [105], the BC coating could potentially bridge the gap that exists between the fibres and the matrix due to the high LCTE of natural fibres.

Simple weight gain measurements showed that approximately 5–6 wt% of BC was deposited onto the surface of these natural fibres. However, the mechanical properties of the natural fibres after bacterial cellulose modification depend on the

Table 6.6 The mechanical properties of natural fibres modified with bacterial cellulose nanofibrils

Natural fibres	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Neat sisal fibre	15.0 ± 1.2	342 ± 33	2.9 ± 0.1
Bacterial cellulose-modified sisal fibre	12.5 ± 1.0	324 ± 33	4.5 ± 0.4
Bacterial cellulose-modified sisal fibre with purification[a]	12.0 ± 0.9	310 ± 32	4.1 ± 0.5
Neat hemp fibre	21.4 ± 2.0	286 ± 31	2.0 ± 0.2
Bacterial cellulose-modified hemp fibre	8.8 ± 0.7	171 ± 11	2.9 ± 0.2
Bacterial cellulose-modified hemp fibre with purification[a]	8.0 ± 0.6	130 ± 12	2.9 ± 0.2

Adapted from [14]

[a] Purification indicates the extraction of post-bacterial cellulose-modified sisal fibres with NaOH at 80°C

Table 6.7 Interfacial shear strengths between modified natural fibres and CAB or PLLA

Natural fibres	Interfacial shear strength to CAB (MPa)	Interfacial shear strength to PLLA (MPa)
Neat sisal fibre	1.02 ± 0.06	12.1 ± 0.5
Bacterial cellulose-modified sisal fibre	1.49 ± 0.03	14.6 ± 1.2
Neat hemp fibre	0.76 ± 0.06	–
Bacterial cellulose-modified hemp fibre	1.83 ± 0.12	–

Adapted from [10] and [14]

type of natural fibres used. The modification process did not change the mechanical properties of sisal fibres, but the properties of hemp fibres were affected (see Table 6.6). The exposure of the hemp fibres to BC caused a drastic loss of fibre strength and Young's modulus. This might be due to a further separation of the bast fibres into smaller individual fibres making up the technical fibre as a result of the intrinsically non-cohesive structure of bast fibres. The interfacial shear strengths between sisal fibres and CAB and PLLA increased by 46 and 21%, respectively, and the interfacial shear strength between hemp fibres and CAB increased by as much as 140% (Table 6.7). It should be noted that the increment seen in the interfacial shear strength between hemp fibres and CAB could also be due to the combined effect of BC coating and the disintegration of the fibres. This improvement seen in the interfacial shear strengths indicates enhanced stress transfer between the fibres and the matrix, which is a direct result of improved interfacial adhesion due to the bacterial cellulose coating applied to natural fibres.

Bacterial cellulose-modified sisal and hemp fibres have also been used to produce unidirectional natural fibre reinforced CAB and polylactide (PLLA) model composites [9]. The mechanical properties of bacterial cellulose-coated sisal fibre reinforced polymers showed significant improvements over neat polymers (Table 6.8). The tensile strength and modulus for sisal/PLLA composites improved by as much as 68 and 49%, respectively. However, improvements were

Table 6.8 Mechanical properties of bacterial cellulose modified hemp and sisal fibres reinforced CAB and PLLA composites

Composites	Neat fibre		Modified fibre		Improvements	
	σ (MPa)	*E* (GPa)	σ (MPa)	*E* (GPa)	σ (%)	*E* (%)
CAB/Hemp[a]	98.1 ± 12.7	8.5 ± 1.3	86.7 ± 13.6	5.8 ± 0.5	−12	−35
PLLA/Hemp[a]	110.5 ± 27.2	11.8 ± 4.2	104.8 ± 9.1	7.9 ± 1.2	−5	−33
CAB/Sisal[a]	92.9 ± 9.3	5.5 ± 0.5	100.4 ± 7.0	8.8 ± 1.4	8	59
PLLA/Sisal[a]	78.9 ± 14.7	7.9 ± 1.3	113.8 ± 14.0	11.2 ± 1.2	44	42
CAB/Hemp[b]	15.8 ± 2.2	1.9 ± 0.1	13.4 ± 1.4	0.6 ± 0.2	−15	−69
PLLA/Hemp[b]	13.4 ± 3.6	3.2 ± 0.2	13.3 ± 2.5	2.3 ± 0.3	−1	−28
CAB/Sisal[b]	10.9 ± 1.7	1.6 ± 0.1	14.4 ± 3.7	1.8 ± 0.3	32	15
PLLA/Sisal[b]	10.0 ± 3.1	2.1 ± 0.1	16.8 ± 4.1	3.1 ± 0.2	68	49

Adapted from [9]

[a] The loading direction is parallel (0°) to the fibres

[b] The loading direction is perpendicular (90°) to the fibres

not observed for composites containing BC-coated hemp fibres. The tensile strength and modulus decreased by as much as 15 and 69%, respectively, for hemp/CAB composites. One should note that the fibres were damaged during bacteria culture and their tensile strength were only one third of that of the original fibres. The use of BC-coated sisal fibres has also led to some improvements in short fibre reinforced PLLA composites [104]. It was shown that the crystallinity of the matrix and the tensile and flexural properties improved through the addition of bacterial cellulose-coated sisal fibres to PLLA. The tensile and flexural properties of these composites were found to be higher than that of commercial polypropylene used in the automotive industry. This indicates the potential of hierarchical composites for applications in the automotive industry.

6.3 Conclusion

Natural fibres have significant advantages over conventional glass fibres. These include low cost, low density, high specific strength and, most importantly, biodegradability (this might, however, result in problems if the fibres degrade within inside the matrix). They are the prime candidates for the manufacturing of truly green composites. However, the extremely hydrophilic nature of these natural fibres often leads to poor compatibility between conventional thermoplastics, such as polylactide. Modification to the matrix is one of the possible solutions to this problem. Surface treatments of natural fibres to enhance the interface between the fibres and the matrix might be a viable solution. Chemical treatments have been explored extensively in this context but it is not the most desirable method; hazardous chemicals are often involved in the chemical treatment of natural fibres. Solvent waste disposal after chemical treatment is another problem associated with surface chemical treatment of natural fibres.

New and greener methods of surface treatment are emerging. Plasma treatments have been shown to be effective in increasing the critical surface tension of natural fibres, thereby improving the wettability between the fibres and the matrix. Enzyme-retting and treatments are also other emerging methods to extract or treat natural fibres. Non-cellulosic compounds such as pectin, lignin and hemicellulose can be removed by specific enzymes, exposing the main cellulose backbone of natural fibres, which was shown to result in increased surface tension. Enzyme-retting is favourable when compared to conventional water-retting and dew-retting methods. Water-retting produces vast amounts of fermentation waste, while dew-retting has the disadvantage of producing fibres that possess lower quality compared to enzyme-retting due to the inherent difficulties in controlling the retting parameters. However, enzyme-retting is limited to pilot scale only due to its high operating and capital cost when compared to water- and dew-retting methods.

White rot fungi have been shown to be effective in lignin removal. It has been used to remove non-cellulosic compounds from natural fibres, exposing the underlying cellulose and hemicellulose. A combination of alkali and fungal treatments showed the most improvement in the composites' mechanical properties. The surface of natural fibres can also be modified by coating them with a layer of (bacterial) cellulose nanofibrils, which allows the production of hierarchical composites. This can be done by immersing natural fibres in a culture medium containing cellulose-producing bacteria, such as the *Acetobacter* species. By using natural fibres as a substrate for cellulose-producing bacteria, the bacteria will deposit their cellulose preferentially onto the surface of natural fibres. This increases the effective area of the interface, enhances the interfacial adhesion through mechanical interlocking and improves the wettability of the fibres by the matrix, as bacterial cellulose possesses higher surface tension than natural fibres [106, 107]. The resulting polymers reinforced with bacterial cellulose-coated natural fibres have comparable properties with commercial polypropylene used in the automotive industry, indicating the potential of such surface treatment.

Public's demand for more environmentally friendly products and environmental legislations should motivate the composites industry (at least in parts) to move away from conventional synthetic materials such as synthetic glass fibres and polypropylene to greener materials such as natural fibres and biobased polymers. A combination of natural fibres as the reinforcing agent and greener surface treatments to enhance the interface and biobased polymers as the matrix should enable the production of truly green composite materials. The *ideal* truly green composite materials should be as follows: When the material is not at the end of its lifetime, it should be recyclable without significant loss of mechanical properties. When the material is at the end of its life cycle, it can be triggered to biodegrade in composting condition. Therefore, the next challenge in green composites would be the production of green composites with triggered biodegradability and good recyclability.

Acknowledgements The authors would like to thank the UK Engineering and Physical Science Research Council (EPSRC) for funding (EP/F032005/1).

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