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Surface Treatments Of Natural Fibres In Fibre Reinforced Composites: A Review

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Abstract

The use of natural fibres in fibre-reinforced composites comes with drawbacks. They are highly hydrophilic, leading to high moisture absorption and poor interfacial adhesion in matrix-reinforcement bonds. This affects the fibres' thermal stability as well as mechanical properties, hence limiting their wider application. This paper reviewed different ways in which natural fibres have been treated to improve hydrophobicity, reinforcement-matrix interfacial adhesion and thermal stability. It will investigate. among others, treatments like alkali, acetylation, bleaching, silane, benzoylation and plasma, which have been found to improve fibre hydrophobicity. The literature reviewed showed that these methods work to improve mechanical, chemical, and morphological properties of natural fibres by removing the amorphous surface, thus allowing for more efficient load transfer on the fibre-matrix surface. Studies in the literature found alkali treatment to be the most common surface modification treatment due to its simplicity and effectiveness. However, plasma treatment has emerged due to its lower processing time and chemical consumption. A comparative analysis of other improved properties was also investigated.

Keywords

hydrophilic, thermal stability, hydrophobic, amorphous, morphological property.

1. Introduction

In recent years, a proliferation of natural fibre usage in many industries like automotive, aerospace, construction, and packaging has occurred. This is because of natural fibres' advantages, which include low cost, a high strength-to-weight ratio, a high specific tensile and compressive strength, controllable electrical conductivity, a low coefficient of thermal expansion, corrosion, and fatigue resistance, and they are easy to form into complex shapes [1,2,3,4]. Owing to these advantages, automotive manufacturers like Bavarian Motor Works (BMW) have incorporated the use of natural fibres into various car parts like door panels, headliner panels and insulation panels in their vehicles [5]. However, natural fibres' hydrophilic nature, which is affinity to moisture absorption, leads to poor interfacial adhesion in fibre-reinforced composites [6]. The surface of a natural fibre is composed of oils, cellulose, hemicellulose, lignin, and a waxy layer, which impedes interfacial bonding. A good reinforcement-matrix bond is crucial because it ensures acceptable load transfer stress across the interface [7, 8]. Strong fibre-matrix adhesion is instrumental in improving the thermal and mechanical properties of the composite [5, 9].

To address poor interfacial adhesion in natural fibre reinforced composites caused by their hydrophilic nature, surface modification treatments like alkalisation, acetylation, bleaching benzoylation, and silane have been used to enhance reinforcement-matrix interfacial adhesion by eliminating the amorphous surface layer from the fibre and enhancing the physical strength of the fibres [10–12]. There is a need to review how different researchers have investigated the effect of these different surface modification techniques in natural fibres and the results they attained to enhance qualities like thermal stability, mechanical properties as well as natural fibre hydrophobicity.

The main constituents of natural fibres are cellulose, hemicellulose, lignin, wax, and pectin. Wax and pectin are a small part of the composition of fibres compared to the other three components. Table 1 shows the different compositions of natural fibre surfaces in different plant fibres

Cellulose is the major chemical constituent of natural fibres, which is found in their plant cells[13]. It is given by its chemical formula $(C_6H_{10}O_6)_n$ and is made up of glucose monomers $(C_6H_{10}O_6)$, where n represents the number of glucose monomers present in the polymer chain [14] . Surface modification methods are used to increase the cellulose content in natural fibres to improve their fibre tensile strength; but moderation of the surface modification is necessary to avoid the cellulose being damaged in the procedure [15]. Figure 1 shows the cellulose chemical structure.

Hemicellulose is a type of polymer found in natural fibres that is easily dissolved by an alkali, has high hydrophilicity, and can be easily hydrolysed by acid [14], [16]. This polymer consists of five different kinds of sugar units: glucose, mannose, arabinose, wylose, and glucuronic acid [14]. Its chemical structure is shown in Figure 2.

Lignin is a component of a natural fibre which links the hemicellulose and cellulose, providing rigidity to the plant cell wall, but not mechanical properties to the same extent as cellulose does [17]. Lignin is acid-soluble, but it cannot be hydrolysed by acids. Its chemical structure is displayed in Figure 3.

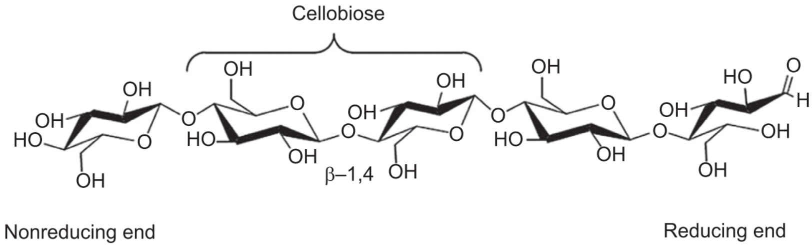


Fig. 1. Cellulose chain structure. Reprinted with permission from [14]

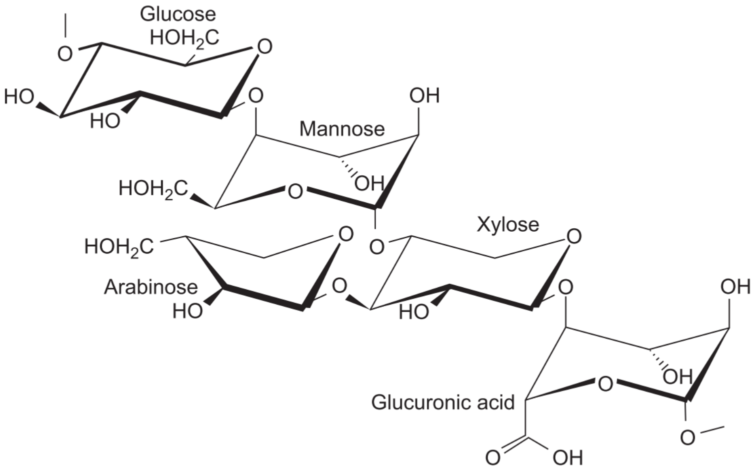


Fig. 2. Hemicellulose chemical structure. Reprinted with permission from [14]

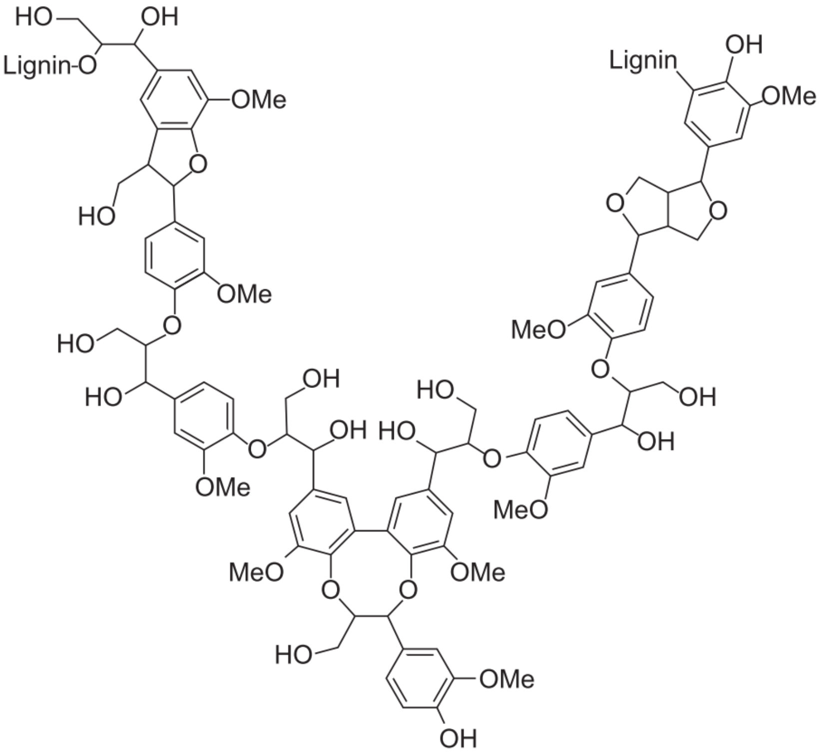


Fig. 3. Lignin chemical structure. Reprinted with permission from [14]

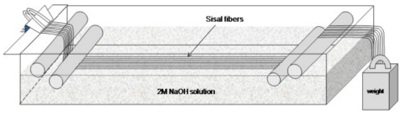
2. Surface modification methods in natural fibres

Treating natural fibres with various chemicals has been found to enhance thermal, morphological, and mechanical properties of natural fibres. The presence of chemical constituents hinders natural fibres' bonding ability to the matrix [18]. The type of chemical treatment used, its concentrations, and the treatment time are pivotal in optimising the final properties after treatment [19].

2.1. Alkaline treatment

Several studies have been conducted to evaluate the effect of the addition of an alkali to a fibre-reinforced composite. This method is also known as mercerisation, where a natural fibre is immersed in each concentration of aqueous sodium hydroxide (NaOH) at a given temperature for a given time. This procedure increases surface roughness, allowing for better mechanical interlocking, and exposes cellulose to the surface [20]. The chemical reaction for this treatment for this process is given by Equation (1) [21];

$$\text{Fibre -OH} + \text{NaOH} \rightarrow \text{Fibre -O -Na} + H_2O \qquad (1)$$



Alkaline Treatment setup of sisal fibre by J.T Kim et. al,2010 [22]

One specific study on alkalisation was by Oushabi et al. [9], who evaluated how it affects the morphological, mechanical, and thermal properties of date palm fibres. Sodium hydroxide (NaOH) of different concentrations; 0 wt%, 2 wt%, 5 wt%, and 10 wt% were used to treat the date palm fibres for an hour at 25 °C. They were then rinsed by purified water and oven-dried at 80°C for 24 hours. 5 wt% NaOH treatment was able to remove more surface impurities hemicellulose and lignin than 2 wt% NaOH treatment whilst not damaging the fibre surface, as would occur with 10 wt% NaOH. Furthermore, this treatment improved the tensile strength of the date palm fibre by 76%, with a reported value of 460 MPa at 5 wt% of NaOH. Thermogravimetric analysis showed decomposition of the treated date palm fibres at about 310℃, while raw date palm fibre showed decomposition of hemicellulose, cellulose, and pectin at 290℃ and secondary decomposition of lignin between 425℃ and 475℃. Secondary decomposition was not present when the date palm fibre had been treated, hence alkali treatment improved thermal stability.

In another report by Lassoued et al. [11], who also studied date palm fibres, particularly their thermochemical behavior before and after alkalisation, fibres were treated with NaOH of various concentrations 0.5%, 0.75%, 1%, 2%, and 5 % in time intervals of 2, 5, 7, and 24 hours. Residual sodium hydroxide was then removed from the fibres using distilled water, and then they were dried at room temperature and atmospheric pressure. Thermogravimetric analysis showed that untreated fibres underwent a mass loss of 48% from a temperature of 550 ℃, while treated fibres stabilised from 700 ℃ with a mass loss of 59%. The greater mass loss of the treated Tunisian palm fibres is postulated to be due to alkaline treatment improving their thermal stability. This is caused by the elimination of hemicellulose and lignin present in the outside layer of the date palm fibre. Alkali fibre treated with 2% sodium hydroxide for 2 hours had a tensile strength of 242.2MPa, which is an improvement from raw fibre, which had a tensile strength of 175 MPa. Treatment with 5% concentrations of NaOH and 2% of NaOH for 5-hour, 7-hour and 24-hour time periods had a tensile strength less than 175MPa, which showed that cellulose, which is important in giving the fibre better mechanical properties, gets damaged, thus inhibiting it from doing so. The improvement of tensile properties after NaOH treatment is consistent with researches performed by Ariawan et al, 2020 [23] on a *Salacca zalacca* fibre reinforced high density polyethylene (HDPE) composite and by Ganapathy et al. [24] on aerial roots of Banyan tree fibre used as reinforcement in fibre reinforced plastics.

2.2. Benzoylation treatment

This chemical treatment is performed after the fibre has been pre-treated with an alkali. It is usually performed using benzoyl chloride and benzoyl peroxide, which reduces moisture absorption and improves the thermal stability of a given fibre [14]. The chemical reactions below show these two-part treatments, where Equation (2) [25] shows the alkali pre-treatment and Equation (3) [26] the benzoylation treatment ;

$$\text{Fibre -OH} + \text{NaOH} \rightarrow \text{Fibre- O}^{-}\text{Na}^{+} + \text{H}_2\text{O} \qquad (2)$$

$$\text{Fibre- O}^{-}\ \text{Na}^{+} + \text{Cl-Cl(=O)} - \text{C}_6\text{H}_5 \rightarrow \text{Fibre} - \text{O-C (=O)} - \text{C}_6\text{H}_5 + \text{NaCl} \qquad (3)$$

This procedure was performed by Safri et al, [27] when they investigated how adding glass fibre and chemically treating sugar palm composites by means of benzoylation treatment affected their properties by performing a dynamic mechanical analysis of the composite. They reported that benzoylation treatment affected the loss modulus of the composite by reducing energy loss during material deformation. Furthermore, the storage modulus was increased in the benzoyl treated composites. Therefore, benzoylation treatment enhances fibre-matrix interfacial bonding.

In another benzoylation research by Izwan et al. [28], the effects of benzoyl treatment on sugar palm fibres that had been pre-treated using sodium hydroxide were studied. The sugar palm fibre specimen was immersed in a mixture of benzoyl chloride and 10% NaOH for three different immersion times of 10, 15, and 20 minutes. They observed a reduction in diameters in the treated sugar palm fibre, which pointed to the removal of the amorphous layer that is present in the fibre surface, and this subsequently enhanced the interfacial adhesion that would occur between the fibre and polymer. Optimum tensile strength was observed for the benzoyl treated specimen after 15 minutes, which had the highest tensile strength and modulus of 173.99 MPa and 6.64 GPa, respectively. This is because it had the highest cellulose content, due to more hemicellulose and lignin being removed in the chemical treatment. However, longer immersion time led to a reduced tensile strength because cellulose was damaged during the process. The increase in tensile strength of the benzoyl treated natural fibre reinforced composite from raw fibre is correlated to the study by P. Madhu et al. [6] performed on *Agave americana* fibre.

2.3. Bleaching Treatment

This treatment is used to remove lignin left on the surface of the fibre after it has gone through alkali treatment. This is done by immersing the natural fibre in a mixture of hydrogen peroxide and sodium hydroxide (H_2O_2 + NaOH) or a mixture of sodium chlorite ($NaClO_2$) and acetic acid (CH_3COOH) [14].

Kumneadklang [29] characterised cellulose fibre harvested from oil palm frond biomass. Sodium hydroxide pellets of 98% concentration were used in alkaline treatment. Two methods of cellulose fibre isolation were used: without pressure for 2 hours and at 90-100 ℃, and under a pressure of 7 bar and 150 ℃ for an hour. In both methods, fibres were immersed in various NaOH solutions of 5, 10, and 15 %wt. The fibres were cleansed in distilled water to get rid of residual lignin and hemicellulose, and then dried. The fibre was subsequently bleach treated with 10% hydrogen peroxide at 90-100 ℃ for an hour. The surface morphology of the treated fibres showed that the surface roughness was reduced because impurities had been removed during these treatments. Treated oil palm fibre under pressure had the highest crystallinity at 77.78% due to the elimination of hemicelluloses and lignin. Thermal analysis showed the thermal properties of the oil palm fibre specimens. Raw oil palm fibre had a residual mass of 12.12% from the onset temperature of 263.5℃ to a maximum of 365.3℃, Oil palm fibre treated with 15% NaOH without pressure had a residual temperature of 8.42 ℃ from the onset temperature of 265.8 ℃ to a maximum of 364.8 °C , and oil palm fibre treated with NaOH under pressure had a residual mass of 1.93 % from the onset temperature of 317.1 °C to a maximum of 366.8 °C. This study attributed the removal of hemicellulose and lignin from the samples to the improvement in thermal properties.

Improved thermal stability and higher cellulose content was confirmed by Johar [30] after treating industrial rice crops with the bleaching process. The chemical composition of the untreated rice husk fibres was found to be 35wt% cellulose, 33wt% hemicellulose, 23wt% lignin and 25wt% silica ash. Thermogravimetric analysis (TGA) was used to study the thermal stability of the rice husk fibres by observing the fibres' crystallinity index. This was done by the continuous heating of the fibre to 900 °C. The untreated rice husk fibre had a crystallinity index of 46.8%. The fibres were then pre-treated using alkali solution of 4wt% NaOH at the reflux temperature for 2 hours, and next rinsed with distilled water, which process was repeated two more times. The crystallinity index after alkali treatment was 50.2%. After this stage, the chemical composition of the rice husk fibres was found to be 57wt% cellulose, 12wt% hemicellulose and 21wt% lignin. The fibres were bleached using a buffer solution of acetic acid, 1.7wt% aqueous sodium chlorite and distilled water at a reflux temperature of 100-130 °C for 4 hours. The chemical composition after bleaching was found to be 96wt% of cellulose and a negligible composition of lignin, hemicellulose, and silica ash. The crystallinity index after bleaching was 56.5%. The improvement in the crystallinity of the fibres meant that the bleached fibres had the highest thermal stability as compared to the untreated fibres and those that had only been alkali treated. Colour changes observed on the rice husk fibres were consistent with the composition results. The untreated rice husk fibres were brownish and then changed to a brownish orange after alkali treatment. Bleaching treatment further changed their colour to completely white, which was due to the removal of non-cellulosic components from the fibre as well as the hemicellulose, lignin, and waxy layers from the rice husk fibres. Consistent with the results of Kumneadklang [29], the smoothness of the fibre surface after bleaching treatment was observed. This is postulated to be due to the removal of the protective layer of waxes and pectin which exist on the fibre surface.

2.4. Acetylation Treatment

This treatment is usually preceded by alkaline treatment or bleaching treatment for better results. Acetylation treatment is a chemical reaction that introduces the acetyl function into a natural fibre [14]. This is done by applying acetic anhydride and acetic acid to the fibres via the esterification method, where the hydroxyl group (-OH) present in the natural fibre is replaced by an acetyl group (CH_3CO) [31]. This reaction can be conveyed as Equation (4) [21];

$$\text{Cellulose-OH} + CH_3\text{-CO} - O - CO - CH_3 \rightarrow \text{Cellulose- O - CO} - CH_3 + CH_3COOH \quad (4)$$

Senthilraja [32] studied the effect of acetylation on the mechanical behaviour and durability of palm fibre vinyl-ester composites. The palm tree interior trunk part was crushed and used to prepare fibre specimens. The palm fibres were immersed in vinyl ester of: 2%, 4%, 6%, 8%, and 10% concentrations, and the composite was cured at 80 °C and 2.6 MPa. Results gathered from this study showed that the mechanical behaviour and durability of the composite improved due to the chemical treatment with acetyl chloride. This is because acetylation treatment reduces the moisture absorption of the fibres, thus improving interfacial adhesion between them and the matrices.

Fitch-Vargas et al. [33] studied the properties of an acetylated sugarcane fibre-reinforced starch-based bio-composite. The sugarcane fibre underewent alkaline and bleaching treatment before acetyl treatment with sodium hydroxide and hypochlorite sodium solution. Acetylation of the fibres was done by immersing them in a 4% acetic acid solution for an hour. The fibres were subsequently rinsed by distilled water and oven-dried at 60 °C for 24 hours. The treated fibres showed better mechanical properties, lower water affinity, and better thermal stability than untreated fibres. This was due to the presence of hydrophobic acetyl groups in the sugarcane fibres. Fourier Transform Infrared (FTIR) analysis corroborated this. These results are consistent with what Senthilraja [32] reported.

2.5. Silane Treatment

Silane treatment is a coupling agent that fills micropores present in the natural fibres' surface and in so doing strengthening interfacial adhesion [21]. A coupling agent forms links between the natural fibre reinforcement and matrix to improve interfacial adhesion [34]. The chemical reaction for silane treatment is shown in Equation 5 [35].

$$CH_2CHSi\,(OH) + \text{Fibre} - OH \rightarrow CH_2CHSi\,(OH)_2O\text{-Fibre} + H_2O \quad (5)$$

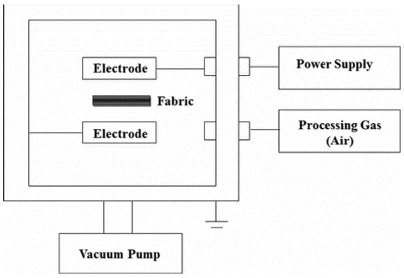
Mohammad Asim et al. [36] investigated the impact of using silane treatment on the fibre-matrix bond of kenaf and pineapple leaf fibres. Two treatments were prepared of 2% NaOH, 6% silane in distilled water and 6% NaOH, 2% silane to treat kenaf and pineapple leaf fibre. The scanning electron micrograph showed the existence of impurities on the surfaces of both the kenaf and pineapple leaf fibre. Treatment of these fibres made them smoother than untreated fibres. The smoothness of the surfaces is caused by the silane treatment, and the removal of lignin and hemicellulose from the fibre surface was caused by the alkali treatment. Smaller, uniform fibres were found in treated fibres, because of the fact that the chemicals used removed the amorphous outer layer present in the untreated fibres. Results showed that the 2% silane, 6% NaOH treatment gave better results. Asim concluded this investigation by saying that silane treatment improves the hydrophilicity of pineapple leaf fibre and kenaf fibre.

Orue et al. [37] studied how silane treatments affect poly(lactic acid)/sisal fibre composites. The fibre was pre-treated with alkali treatment before silane was applied. The alkali pre-treatment was done in 2 steps: firstly, immersing the raw sisal fibres in 2wt% NaOH solution for 12 hours at room temperature to swell them and then immersing the fibres in 7.5 wt% NaOH for 90 minutes at 100 °C. The fibres were then washed in distilled water and oven-dried at 100°C for 12 hours to prepare for the silane treatment. The sisal fibres were then soaked in water for 3 hours while being sonicated to enhance silane accessibility to cellulose hydroxyl groups. Results showed a decrease in the density of the fibres, caused by the removal of lignin, hemicellulose, and impurities that exist in the sisal fibre surface. Morphological analysis of the composites showed improved interfacial adhesion in the composite, which was caused by the removal of the amorphous layer.

Liu et al. [38] investigated the influence of silane treatment on corn stalk fibre reinforced polymer composites. Silane coupling agents in water and absolute ethyl alcohol of 1 wt%, 5 wt%, 9wt% and 13wt% concentrations were used to immerse the corn stalk fibre specimen . The silane-treated corn stalk fibres were then rinsed in distilled water to remove residual silane coupling before being oven-dried for 24 hours at 90 °C. The polymer matrix was dried in a heat-treatment tank at 80 °C for 24 hours, mixed with treated corn stalk fibre, and hot pressed to make a composite. The silane solution treatment was found to be effective in reducing the water absorption of the fibre. The removal of lignin and hemicellulose present in the fibre surface enhanced the corn stalk fibre's hydrophobicity and matrix-reinforcement bond.

2.6. Plasma Treatment

This technique is whereby plasma is produced from a vacuum chamber through ionisation of a gas and is used to modify a fibre surface [39]. As a result of this method, there is less chemical consumption and waste produced, and the production time is lower compared to the conventional chemical treatments discussed [40]. Plasma treatment leads to the etching of surface layers of the fibres, enhancing interlocking with the matrix [41].



2.7. Plasma Processing System [42]

Zhou et al. [43] was able to experiment on ramie fibres with polypropylene to find out how atmospheric pressure plasma affects their interfacial shear strength. The fibres were pre-treated by immersing them in ethanol for 10 minutes, and then plasma treatment was conducted using an atmospheric pressure plasma jet system at 20 °C and 65% relative humidity. The treatment times selected were 8, 16 and 24 s. The fibres that were plasma treated for 24 s gave an optimal interfacial shear strength improvement of 46%. The authors postulated that the plasma treatment duration must be sufficiently brief for maximum surface grafting and long enough to enhance interlocking of the fibre with the polypropylene matrix.

The effect of cold plasma treatment on polyethylene/kapok composite interfacial adhesion was investigated by M. Macedo et al. [44]. Kapok fibres were treated with a voltage in the range of 400-500V, oxygen gas flowrate of 10cm^3/min, a reactor pressure of 1.5 mbar, and an exposure time of an hour before the composite was fabricated. The tensile strength of the polypropylene was not significantly affected when the fibres were added. Morphological analysis showed a good adhesion between the polyethylene and kapok fibres. The authors conclude that the improvement was due to the plasma treatment.

3. Conclusions

Treatments of natural fibres are centred around modifying the fibre surface to remove the amorphous surface, which consists of hemicellulose and lignin. Removal of these components increases the composition of cellulose in the fibre surface which is responsible for giving strength to the fibre. This action reduces the fibre's moisture affinity and improves mechanical, morphological and thermal properties by ensuring that there is strong interfacial adhesion when the fibre is bonded to the matrix. Adequate treatment is important as insufficient treatment does not remove enough hemicellulose and lignin from the fibre surface, and over-treatment removes cellulose from the fibre surface, which is instrumental in giving stiffness to the natural fibre. Further research into various palm tree fibres is necessary to explore and find optimum results by utilising these chemical treatments. Research points to alkali treatment as the most used surface modification technique, highlighted by both the fact that there is abundant literature on its use and that methods like bleaching and silane treatment require natural fibres to be pre-treated by alkali before being applied. The future points to the incorporation of fibre-reinforced composites as a substitute to reduce the usage of metals in engineering industries. Physical treatment techniques like plasma treatment and corona treatment have gained attraction in the engineering community because of their lower production time and chemical production. The exploration of many more plant fibres is imperative to find better performing fibres to be used in composites. Currently, composites are used mostly in a non-structural capacity due to their lower fracture toughness. Future research should be focused on producing tough, thermally stable natural fibre reinforced composites that are still lightweight.

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No.	Fibre Matrix Composites	Applied treatment method	Resultant properties	Ref.
1.	Abaca fibre reinforced composites	Alkali treatment with 5 wt.% NaOH	Increase in tensile strength of ~8% and interfacial shear strength of 32%	[45]
2.	Coir-fibre reinforced polymer composites	5wt.% NaOH alkali treatment at 20℃ for 30 minutes	Increase in tensile strength and flexural strength of 17.8% and 16.7%, respectively	[46]
3.	Benzoxazine resin reinforced with alfa fibres	Alkali treatment with 5wt.% NaOH for 5 hours	Enhancement of microhardness, flexural strength, and modulus by 29, 37 and 10%, respectively.	[47]
4.	Oil palm/bagasse fibre reinforced phenolic hybrid composites	2% v/v silane treatment and 4% v/v hydrogen peroxide	Increase in tensile strength and flexural strength of ~56 and 120%, respectively	[48]
5.	*Acacia tortilis* fibre reinforced natural composite	Alkali treatment with 10 wt.% NaOH	Enhancement of tensile strength by 27.5%.	[49]
6.	Flax/banana/industrial waste tea leaf fibre reinforced hybrid polymer composite	5 wt.% NaOH treatment for 12 hours at 27℃.	Tensile and flexural strength were enhanced by ~7% and ~5% respectively.	[50]
7.	*Mutingia Calabura* bark fibre reinforced green-epoxy composite	2-hour alkali treatment with 5% NaOH. 2% silane treatment for 2 hours.	Crystallinity index enhancement of 41.01% with NaOH and 14.86% by silane treatment. Tensile strength improvement of 37.75% and 28.92% with NaOH and by silane treatment, respectively. Thermal stability improvement of 14.15% and 4.81% for NaOH and silane treatment, respectively	[51]
8.	Coir and oil palm empty fruit bunch	Acetylation with a mixture of toluene, methanol, and acetone (4:1:1 volume ratio) for 5 hours at 100℃	Increase of tensile strength by 8% and 10.8% for coir and oil palm fruit bunch respectively	[52]

Table 1.

Conflict of Interest

The authors would like to declare that they have no known competing financial interests or personal relationships that could have appeared to influence the publication of this paper.

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