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Interface and bonding mechanisms of plant fibre composites: an overview

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Abstract: The development of plant fibre composite is on the rise for a wide range of applications. Probably a single most important aspect with respect to the formulation of plant fibre composites with superior mechanical performance is the optimisation of the interfacial bonding between the reinforcing plant fibre and polymer matrix. While the interface plays a pivotal role in determining the mechanical properties, e.g. transferring the stress and distributing the bond, it is among the least understood components of the composite. This paper presents an overview of the compatibility between the heterogeneous constituents of plant fibre composite, various modification approaches aiming at overcoming the incompatibility and refining the interfacial adhesion of the composite, interfacial bonding mechanisms, and the assessment of interface structure and bonding. It has been found that 1) the physical and chemical incompatibility between the fibre and matrix, leading to poor dispersion, weak interfacial adhesion and ultimately inferior composite quality, could be overcome through strategical modifications; 2) inter-diffusion, electrostatic adhesion, chemical reactions and mechanical interlocking are in general responsible for the interfacial bonding and adhesion of plant fibre composites; and

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3) a thorough knowledge of structure-property relationship of the composite could be established by conducting a set of direct and indirect interfacial assessments. This paper finishes with some critical suggestions and future perspectives, underscoring the roles of composite material researchers and engineers for the further in-depth studies and up-scale commercialisation of plant fibre composite.

Keywords: Plant fibre composite; compatibility; modification; bonding mechanism; interface structure.

1 Introduction

Plant fibre composite, as a significant branch of composite materials, has experienced a rapid expansion over the last decade. This speedy growth is largely due to the advantageous features that plant fibres provide over inorganic fillers and/or reinforcements, i.e. abundance, environmental friendliness, biodegradability, nontoxicity, low cost and density, flexibility during processing, and high tensile and flexural modulus[1-8]. Compared with wood materials, the plant fibre composite possesses better flexural and impact strength, higher moisture resistance, less shrinkage and improved weatherability. However, regardless these benchmarking characteristics, the optimization of the interfacial bonding between plant fibres and polymer matrix is one of the most indispensable procedures with respect to the optimal formulation of plant fibre composite[8].

The fibre-matrix interface is a reaction or diffusion zone in which two phases or components are physically, mechanically and/or chemically combined. Interfacial adhesion between the fibre and matrix plays a fundamental role in terms of the factors govern the mechanical characteristics of the composite[9]. The factors affecting the interfacial bonding between the fibre and matrix are the mechanical interlocking, the molecular attractive forces and the chemical bonds. However, the naturally hydrophilic plant fibres are not inherently compatible with hydrophobic polymers. In addition to the pectin and waxy substances in plant fibre acting as a barrier to interlock with nonpolar polymer matrix, the presence of plenty hydroxyl groups hinders its operative reaction with the matrix[10-13]. Therefore, the modification of the surface characteristics of plant fibre and hydrophobic polymer matrix is in particular essential in order to formulate a reasonable composite with superior interfacial bonding and effective inherent stress transfer throughout the interface. Various approaches, including physical treatments (i.e. solvent extraction, heat treatment, corona and plasma treatments), physic-chemical treatments (i.e. laser, γ-ray and UV bombardment)[14] and chemical modifications, have been attempted for improving the compatibility and bonding between the lignocellulosic molecules and hydrocarbon-based polymers[15-17].

The increasing environmental awareness has brought substantial research and industrial invest in another class of plant fibre composites, in which the matrices including starch, cellulose, chitin and chitosan, collagen, lignin, natural rubber, polyhydroxyalkanoate, polylactic acid (PLA) and soy-based resins, are fully biodegradable and sustainable biopolymers. Unlike synthetic polymer based composites, the similar polarities of both reinforcements and matrices impart the biodegradable composites better compatibility and interfacial adhesion[18]. However, some surface treatments of the fibres are specifically needed for the benefits of lowering down moisture sensitivity which generally leads to the dimensional instability due to the fibre swelling and hence loss of interface integrity.

This work primarily focuses on the interface and bonding mechanisms of plant fibre composites, which is organized into four main sections, i.e. the overview of the compatibility between the constituents of composites, the modifications aiming at improving the compatibility and interfacial bonding of the composites, the physical, mechanical and chemical bonding mechanisms, and the interface structure of the composites. The paper shall serve as a fundamental basis for further research and industrialization of plant fibre composites.

2 Compatibility between constituents of plant fibre composites

2.1 Compatibility between plant fibre and synthetic polymer

The main components of plant fibre include cellulose, hemicellulose, lignin, pectin, waxes and other low-molecule substances. Cellulose is the fundamental structural component found in the form of slender rod like crystalline microfibril, aligned along the length of fibre. It is a semicrystalline polysaccharide consisting of a linear chain of hundreds to thousands of β-(1-4)-glycosidic bonds linked D-glucopyranose with the presence of large amount of hydroxyl groups. Hemicellulose is a lower molecular weight polysaccharide that functions as a cementing matrix between cellulose microfibrils, presented along with cellulose in almost all plant cell walls. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. Furthermore, it is hydrophilic and can be easily hydrolysed by dilute acids and bases. Lignin is a class of complex hydrocarbon polymers (cross-linked phenol polymers) that gives rigidity to plant. It is relatively hydrophobic and aromatic in nature. Pectin is a structural heteropolysaccharide contained in the primary cell walls of plants giving the plants flexibility. Wax and water soluble substances are used to protect fibre on fibre surface[19-22]. The unique chemical structure makes the plant fibre hydrophilic in nature.

Although there are many advantages associated with the use of plant fibre as reinforcement in polymer composites, the incorporation of plant fibre in hydrophobic and non-polar polymers leads to indecent systems due to the lack of moderate compatibility and adhesion between the fibre and matrix. These would also cause some problems in the composite processing and material performance, including poor moisture resistance, inferior fire resistance, limited processing temperatures, the formation of hydrogen bonds within fibre itself, the tendency of fibre agglomerating into bundles and uneven distribution in a polar matrix during compound processing and insufficient wetting of fibre by the matrix which results in weak interfacial adhesion[19,23-25].

By this token, various physical and chemical modifications have been attempted for decreasing the hydrophilicity of plant fibre, enhancing the wettability of the fibre by polymers and also promoting the interfacial adhesion. These modification approaches are of different efficiency and mechanism for optimising the interfacial characteristics of the composite. Physical treatments, such as electric discharge, in general change the structural and surface properties of the fibre by introducing surface crosslinking, modifying the surface energy and/or generating reactive free radicals and groups, and thereby influence the mechanical bonding to the matrix. Chemical modification provides the means of permanently altering the nature of fibre cell walls by grafting polymers onto the fibres, crosslinking of the fibre cell walls, or by using coupling agents[26]. Such modification strategies tackling with the compatibility and interfacial bonding of plant fibre composite will be discussed in detail in the next section.

2.2 Compatibility between plant fibre and bioplastic polymer

The research of polymers obtained from different biorenewable resources generally referred as bio-based polymers and designed to be biodegradable has increased substantially recently. It is well known that renewable resources such as bioproducts (e.g.

cellulose or chitin, vegetable fats and oils, corn starch, etc.), bacteria as well as non-renewable petroleum (e.g. aliphatic/aliphatic-aromatic copolymer) are sources of a variety of polymeric materials[18,27-30]. Accordingly, the biodegradable polymers can be classified as naturally occurring or synthetic based on their origins. Natural polymers are available in large quantities from renewable sources, i.e. cellulose, pectin, lignin, collagens, chitin/chitosan, starch, proteins, lipids, etc. Microbially synthesized polymers include polyhydroxyalkanoates (PHA) and bacterial cellulose, while chemically synthesized polymers are produced from conventionally petroleum-based resource monomers including polyacids, poly(vinyl alcohols), polyesters, etc.[18,31-33]. Biodegradable bioplastics can break down in either anaerobic or aerobic environments, depending on how they are manufactured, and thus are being envisaged as prospective alternatives to their counterparts in olefin plastics. The incorporation of plant fibre into bioplastics to fabricate fully biodegradable composite materials has attracted attention for various purposes (Table 1), in particular for multifunctional applications, since many of these polymers, in addition to being biodegradable, also possess antimicrobial and antioxidant properties[34]. At this stage, the main impediment to the rampant use of bioplastic polymers is the high initial cost, currently cost three to five times of the extensively used resins such as PP, PVC, LDPE and HDPE[35].

Starch is not a true thermoplastic but it can be converted to thermoplastic starch (TPS) in the presence of plasticizers (i.e. water, glycerin, glycol, sorbitol, etc.) under high temperature and shear by forming hydrogen bonds with the starch[36]. Compared to the most synthetic plastics currently in use, the properties of TPS are unfortunately not satisfactory for its application as a thermoplastic especially the highly water-soluble character and poor mechanical and thermal properties[37,38]. A good approach to tackle with these drawbacks of TPS is the use of natural fibres as reinforcement for TPS, which including luffa fibre[36], sisal fibre[39], cotton fibre[40], sugarcane fibre[41], eucalyptus fibre[37], bagasse cellulose[42], and wheat straw fibre[43]. Starch is a naturally hydrophilic carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. The chemical structure similarities of TPS with plant fibre provide the resultant plant fibre/TPS composite with high compatibility and adhesion between the reinforcement and TPS matrix. As a result, the inclusion of plant fibre would not only lead to the improvement of the tensile strength and water and thermal resistance of the composite, but also hinder the re-crystallization of starch owing to the strong interaction between the fibre and starch[35-38].

Polylactic acid (PLA) is one of the most promising biodegradable polymers, derived from natural feedstock or agricultural products such as corn starch, rice, potatoes, sugar beet. It has attracted a great interest as a commodity polymer which is capable of replacing petrochemical polymers due to its similar mechanical properties to oil-derived plastics. However, the wider uptake of PLA is restricted by performance deficiencies, such as poor toughness arising from its inherent brittleness, and also the lower molecular weight and much higher production cost in comparison to conventional plastics[44,45]. Therefore, plant fibres have recently been incorporated into PLA matrix by researchers in order to overcome the brittle nature. Plant fibre/PLA composites containing less than 30 wt% fibre have shown an increased tensile modulus and reduced tensile strength compared with PLA, and this has been attributed to factors include the weak interfacial interaction between the hydrophobic PLA matrix and the hydrophilic cellulose fibres, and the lack of fibre dispersion due to a high degree of fibre agglomeration[46]. Various chemical methods of modifying the surface of the cellulosic fibres including esterification, acetylation, and cyanoethylation, along with coupling agents or compatibilisers have been explored in an effort to improve the interaction and adhesion occurring at the interface between the PLA matrix and the fibres by inducing chemical bonding and enhancing compatibilisation[5,46-49].

Polyhydroxyalkanoates (PHA) are a family of linear polyesters produced in nature by bacterial fermentation of sugar or lipids as intracellular carbon and energy storage granules. PHAs have a structure with the same three carbon backbones and distinct alkyl groups at the β or 3 positions. The main copolymers or homopolymers of the PHAs are poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(3-hydroxybutyrate-co-hydroxyoctanoate) and poly(3-hydroxybutyrate-co-hydroxyhexanoate)[50]. As one of the most studied and promising alternatives to the current mainstream petrochemical plastics, PHA bioplastics have two major drawbacks, i.e. low thermal stability (degrade at 200-250°C) and brittleness. The addition of plant fibre has been attempted to reinforce and toughen PHAs. Percentage crystallinity of the formulated plant fibre/PHA composite was found to increase with the increase of fibril loading. The composites also exhibited higher thermal stability, glass transition temperature and heat distortion temperature than pure PHA. Also, the composites could be developed further for various structural applications[51-53]. It has been reported that there existed a significant amount of interfacial interaction between the fibre and matrix in wood fibre/PHBV composite, which contributed to tensile and flexural capability[54]. The employment of compatibilisation techniques, including silane coupling agent, maleic anhydride and dicumyl peroxide, increased the fibre wettability and distribution, and enhanced the mechanical interlocking between the fibre and PHBV matrix[55].

Table 1 Plant fibre reinforced biodegradable polymer composites

Biopolymer matrix	Reinforcement	References

Pregelatinised cassava starch	Luffa fibre	[36]
Thermoplastic corn starch	Bleached *E. urograndis* pulp	[37]
Cellulose derivatives/starch blends	Sisal fibre	[39]
Thermoplastic rice starch	Cotton fibre	[40]
Thermoplastic corn starch	Sugarcane and banana fibres	[41]
Thermoplastic cassava starch	Cassava bagasse cellulose nanofibrils	[42]
Thermoplastic maize starch	Wheat straw cellulose nanofibrils	[43]
Thermoplastic cassava starch	Jute and kapok fibres	[56]
PLA	Wood fibre	[57][58]
PLA	Bamboo fibre and flour	[45][59][60]
PLA	Kenaf fibre	[61]
PLA	Flax fibre	[62]
PLA	Jute fibre	[63]
PLA	Banana fibre	[64]
PLA	Grewia optiva and nettle fibres	[65]
PLA	Nanocellulose fibre	[66]
PHB	Jute and lyocell fibres	[67]
PHB	Bamboo micro fabril	[53]
PHA	*Eucalyptus* pulp fibre	[68]
PHA	Tea plant fibre	[69]
PHA	Beer spent grain fibre	[70]
PHA	Wood flour	[51]
PHBV	Wood fibre	[54][55]

PHBV	Recycled cellulose fibre	[52]
PHBV	Cellulose nanowhisker	[71]

3 Modification of constituents of the composite

3.1 Physical treatments

Physical treatments of plant fibre alter the structure and surface properties of the fibres without using chemical agents, and thereby influence the mechanical bonding with the matrix in the composite. Radiation and discharge treatments such as UV radiation, gamma radiation, corona and plasma treatments are the most used physical techniques in plant fibre composite with regards to the improvement in the functional properties of plant fibre (Table 2), generally enabling significant physical and chemical changes as well as changes in the surface structure and surface energy of plant fibre[72-75].

A typical treatment of gamma radiation is known to deposit energy on the plant fibre in the composite and radicals were then produced on the cellulose chain by hydrogen and hydroxyl abstraction, ruptures of some carbon-carbon bonds and chain scission. Simultaneously, peroxide radicals are generated when matrix polymers are irradiated in the presence of oxygen. These active sites in both fibre and matrix produced by the gamma radiation result in the better bonding between the filler and polymer matrix, which consequently improves the mechanical strength of the composite[73,75,76].

Corona treatment is a surface modification technique that uses a low temperature corona discharge plasma to impart changes in the properties of a surface (e.g. surface energy). The corona plasma is generated by the application of high voltage to an electrode that has a sharp tip. The plasma forms at the tip. A linear array of electrodes is often used to create a curtain of corona plasma. The corona treatment of plant fibre causes the formation of high-energy electromagnetic fields close to the charged points, with consequent ionization in their proximity. In the ionized region, the excited species (i.e. ions, radicals, et al.) are present and the latter are active in surface modification, typically by the introduction of oxygen-containing groups in the molecular chain of plant fibre[77]. Plastic is a man-made synthetic material, which contains long homogeneous molecular chains that form a strong and uniform product. The chains of molecules are normally joined end to end forming even longer chains, leaving only a few open chain ends, thus providing only a small amount of bonding points at the surface. The small amount of bonding points cause the low adhesion and wettability, which is a problem in converting processes. A high frequency charge would provide both a more efficient and controllable method of increasing the adhesion and wettability of a plastic surface. During corona discharge treatment, electrons are accelerated into the surface of the plastic resulting in the long chains to rupture, producing a multiplicity of open ends and forming free valences. The ozone from the electrical discharge creates an oxygenation, which in turn forms new carbonyl groups with a higher surface energy. The result is an improvement of the chemical connection between the molecules in the plastic and the applied media/liquid. This surface treatment will not reduce or change the strength, neither will it change the appearance of the material. This corona treatment has been expansively applied in plant fibre composites especially in composites involving polyolefins as the matrix[72,78,79].

Plasma treatment is another useful physical technique to improve the surface properties of the plant fibre and polymeric materials by utilizing the ingredients such as high-energy photons, electrons, ions, radicals and excited species. Generally, the modification of plant fibre by the treatment in cold oxygen plasma obtained in a corona discharge under optimal operating conditions turns the fibre into a semi-active filler for the cellulosic compounds[80-82]. Thus, the adhesion at the fibre/matrix interface increases with the plasma treatment. The resulted impact is the improvement of the mechanical properties (i.e. flexural strength and modulus, tensile strength and modulus) of the composites. Nevertheless, the fibre may degrade at longer time of exposure due to the constant impact of particles on the surface, which inevitably weakens the interfacial adhesion[83-85]. UV radiation has also been employed to modify the surface characteristics of plant fibre composites[72,86,87]. The UV treatment of single jute fibre and jute yarn was found to result in higher gains in polarity in comparison with those observed in relation to corona-treated counterparts. The polarity and yarn tenacity could be adjusted by increasing treatment time at a constant bulb-sample distance or alternatively decreasing the distance. For the benefits of improving the overall mechanical properties of the plant fibre composites, an appropriate balance needs to be achieved between increased polarity of fibre surface and the decrease of fibre strength subsequent to excessive surface oxidation by UV radiation or corona discharge[72].

Table 2 Recent work on physical treatment of plant fibre composites

Composite	Treatment	Effect and outcome of the treatment	References
Basalt fibre/epoxy composite	Gamma irradiation	The irradiation induced the polymer chain scission and oxidation on the surface and inside resin matrix; the tensile property of irradiated composite maintained stable and the flexural performance had a low amplitude attenuation, while the interlaminar shear strength increased.	[73]
Jute	UV radiation	The tensile strength and bending strength of the	[87]

fibre/PE/PP composite		composite increased with the strengthening of UV radiation up to 50 radiation dose; compared to the untreated composite, the treated composite showed an increase of 18% tensile strength and 20% bending strength respectively.	
Miscanthus fibre/PP and miscanthus fibre/PLA composites	Corona treatment	The corona treatment of fibres resulted in a surface oxidation and an etching effect, leading to an improvement of the interfacial compatibility between fibre and matrices; hence, the mechanical and thermal properties (Young's modulus, stress at yield, glass transition temperature, and decomposition temperature) of the treated composites were greatly enhanced due to the better interaction between the constituents.	[78]
Flax fibre/polyester composite	Plasma treatment	After the air plasma treatment of flax fibre at a plasma power of 300 W, the tensile strength, flexural strength, flexural modulus and interlamilar shear strength of flax fibre-reinforced polyester composites increased by 34%, 31%, 66% and 39% respectively, primarily due to the improved adhesion between the treated fibre and polyester matrix.	[84]

3.2 Chemical treatments

3.2.1 Alkaline treatment or mercerization

The chemical treatments of plant fibre composites have been reported (Table 3). Alkali treatment is one of the most used chemical methods of modifying the cellulosic molecular structure of plant fibre when it is being used to reinforce thermoplastics and thermosets. This treatment, usually performed in NaOH aqueous solution, disrupts fibre clusters and forms amorphous at the expense of highly packed crystalline cellulose. The important modification occurring is the disruption of hydrogen bonding in the network structure. During the treatment, the sensitive hydroxyl groups (OH) are broken down, and thus react with water (H-OH) leaving the ionized reactive molecules to form alkoxide with NaOH (Scheme 1).

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

As a result, the hydrophilic OH groups are reduced and the surface roughness of the fibre is increased. It also removes a certain portion of hemicellulose, lignin, waxes, and oils covering the external surface of the fibre cell wall, depolymerizes cellulose and exposes the short-length crystallites[88-90]. Therefore, when the alkaline treated plant fibre is used to reinforce polar polymer composites, in comparison with the composite filled with untreated plant fibre, the enhanced surface roughness and increased reactive sites exposed on the surface would lead to a better mechanical interlocking and adhesion with the matrix, both of which are in charge of the interfacial strength of the composite[91,92]. However, it should be pointed out that the superfluous alkali concentration would result in excess delignification of plant fibre, thus weaken or damage the fibre being treated[89,93].

The alkali treatment of plant fibre can also be carried out in combination with other treatments. Fig. 1 shows the surface structures of untreated jute fibre, alkali treated jute fibre and alkali/organosilane/aqueous epoxy dispersions (ED) treated jute fibre[94]. The untreated jute fibre has rather smooth surface due to the cementing made up of fats, waxes, lignin, pectin, and hemicellulose forming on the fibre surface[95]. The alkali treatment provided the fibre with a flakey or grooved surface by partially removing the cementing. The NaOH/(APS+ED) treated fibre was covered by a sizing of varying thickness, forming a film on the fibre surface. In contrast, the NaOH/PAPS treated fibre showed a much rougher surface since the sizing was less uniform in thickness or rather varying on a much higher scale, and appeared more flakey and less attached[94].

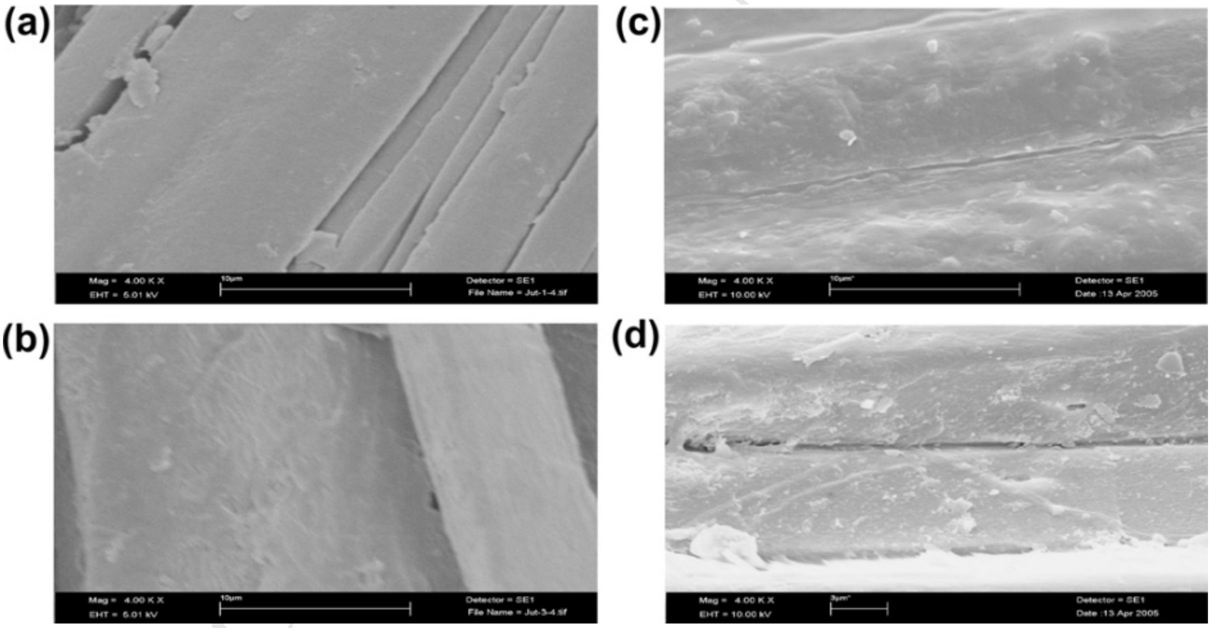


Fig. 1 SEM images of (a) untreated, (b) NaOH treated, (c) NaOH/(APS+ED), and (d) NaOH/PAPS treated fibres (APS: 3-aminopropyl-triethoxy-silane, PAPS: 3-phenyl-aminopropyl-trimethoxy-silane)[94]

3.2.2 Acetylation treatment

Acetylation of plant fibre is known as an esterification method causing plasticization of the fibre by introducing the acetyl functional group CH_3COO^-. The main principle of the reaction is to substitute hydrophilic hydroxyl groups (OH) of the cell wall with acetyl group CH_3COO^- from acetic anhydride ($CH_3COO-C=O-CH_3$), therefore rendering the fibre surface more hydrophobic (Scheme 2).

$$Fibre - OH + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow Fibre - O - COCH_3 + CH_3COOH \quad \text{(Scheme 2)}$$

The hydroxyl groups that react are those of the minor constituents of the fibre, i.e. hemicelluloses and lignin, and those of amorphous cellulose. This is because the hydroxyl groups in crystalline regions of the fibre are closely packed with strong interlock bonding, and are fairly inaccessible to chemical reagents[96].In order to accelerate the reaction and maximise the degree of acetylation, acid catalyst such as sulphuric acid and acetic acid are commonly used during the treatment[9,96]. The esterification reaction not only stabilizes the cell walls, with particular regards to moisture uptake and consequent dimensional variation of plant fibre, but also provides the fibre rough surface tomography with less void contents, thereby the adhesion of the fibre to the matrix can be improved[97-99]. It has been reported that the acetylation treatment of plant fibres resists up to 65% moisture absorption depending on the degree of acetylation[3,96]. More importantly, in comparison to the composite reinforced with untreated plant fibre, this esterification of plant fibre results in an improved stress transfer efficiency at the interface and the mechanical properties (tensile, flexural and impact properties) of its composites[100]. In addition, the enhanced hydrophobicity of the treated fibres was able to provide the composite with higher volume resistivity than that of untreated composites by reducing the dielectric constant of the composite[99].

3.2.3 Benzoylation treatment

Benzoylation treatment, an important transformation in organic synthesis, is another treatment aiming at decreasing the hydrophilicity of plant fibre. Prior to carrying out the reaction between the fibre and benzoyl groups ($C_6H_5C=O$), the plant fibre should be initially pretreated with NaOH aqueous solution in order to activate and expose the hydroxyl groups on the fibre surface. Thus, the fibre can be treated with benzoyl chloride, for which to be further substituted by benzoyl group, the reaction is given in Scheme 3[93,101,102]. This creates more hydrophobic nature of the fibre and improves fibre matrix adhesion, thereby considerably increases the strength and thermal stability of composite[103].

$$Fibre - O - Na + C_6H_5 - COCl \rightarrow Fibre - O - CO - C_6H_5 + NaCl \quad \text{(Scheme 3)}$$

3.2.4 Peroxide treatment

Interface property of plant fibre composite can also be improved by peroxide treatment. Peroxide is a chemical compound with the specific functional group ROOR containing the divalent ion bond O-O. In contrast to oxide ions, the oxygen atoms in the peroxide ion have an oxidation state of -1. Benzoyl peroxide and dicumyl peroxide are the most used chemicals for plant fibre surface modification in organic peroxides family. Both of these chemicals are highly reactive and are inclined to decompose to free radicals of the form $RO^{\cdot}$, and then the $RO^{\cdot}$ can be grafted onto cellulose macromolecules polymer chain by reacting with the hydrogen groups of plant fibre and polymer matrix (Scheme 4)[93,101,103]. As a result, good fibre matrix adhesion occurs along the interface of the composite[97,104].

$$RO - OR \rightarrow 2RO^{\cdot}, RO^{\cdot} + Polymer \rightarrow ROH + Polymer^{\cdot}$$

$$RO^{\cdot} + Cellulose \rightarrow ROH + Cellulose^{\cdot}$$

$$Polymer^{\cdot} + Cellulose^{\cdot} \rightarrow Polymer - Cellulose \qquad \text{(Scheme 4)}$$

3.2.5 Silane treatment

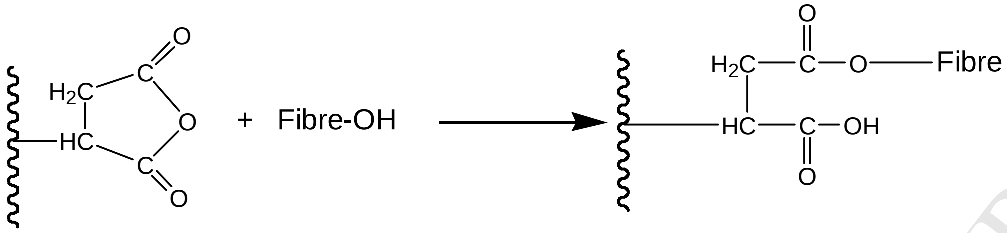
Silane is an inorganic chemical compound with chemical formula SiH4. Silanes are used as coupling agents to modify plant fibre surface. A typical silane coupling agent bears two reactive groups, one end of silane agent with alkoxysilane groups is capable of reacting with hydroxyl-rich surface, namely wood or other plant fibres, whereas the other end is left to interact with the polymer matrix. Specifically, in the presence of moisture, the silane (hydrolyzable alkoxy group) could react with water to form silanol, which would further react with the hydroxyl groups attached to the cellulose, hemicellulose and lignin molecules in the filler through an ether linkage with the removal of water[105]. The uptake of silane is very much dependent on a number of factors including temperature, pH, hydrolysis time and organofunctionality of silane[14]. The reaction scheme is given in Scheme 5.

$$Fibre - OH + R - Si(OH)_3 \rightarrow Fibre - O - Si(OH)_2 - R \qquad \text{(Scheme 5)}$$

On the other hand, the hydrophobic bonds in silane molecules were able to react with polymer matrix[105]. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fibre by creating an entangled/crosslinked network due to covalent bonding between the matrix and the fibre[89,106]. In addition, the introduced hydrocarbon chains were assumed to affect the wettability of the fibres and improve the chemical affinity of polymer matrix, thus the interfacial adhesion between fibre and matrix was enhanced[103,107].

3.2.6 Maleated coupling agents

The use of maleated coupling agents has proven to be an extremely efficient means of improving interfacial interactions between plant fibres and polymer matrices. The maleic anhydride groups react with the hydroxyl groups of plant fibres and remove them from the fibre cells reducing hydrophilic tendency. The reaction scheme is given in Scheme 6.



(Scheme 6)

Moreover, the maleated coupler forms C-C bond to the polymer chain with matrix[8]. The strongest adhesion can be achieved when the covalent bonds are formed at the interface between plant fibres and coupling agent as well as molecular entanglement between coupling agent and the polymer matrix[49]. The reaction mechanism of coupling agent with plant fibre and matrix can be explained as the activation of the copolymer by heating before the fibre treatment and then the esterification of cellulose fibre. This treatment increases the surface energy of plant fibre to a level much closer to that of the matrix, and thus results in better wettability and enhances interfacial adhesion between filler and matrix[89].

Table 3 Recent work on chemical treatment of plant fibre composites

Composite	Treatment	Effect and outcome of the treatment	References
Jute fibre/epoxy composite	Mercerization	The alkali treatment removed the cementing layer consisting of low molecular fats, lignin, pectin and hemicellulose in cellulose fibrils, leading to a cleaner and rougher fibre surface; thus, the resin wetting, and the interaction and mechanical interlocking between fibre and matrix were significantly improved, i.e. the	[94]

		interfacial shear strength of the composite was increased up to 40% after the treatment.	
Flax fibre/PP composite	Acetylation	The tensile and flexural strength of the treated composites increased with the increasing of acetylation up to 18% and then decreased; the increase was due to the removal of lignin and extractives, the increase in cellulose content, effective surface area and thus interfacial adhesion; the decrease was because of the degradation of cellulose and generation of internal crack and damage in the fibres.	[96]
Flax fibre/PE composite	Benzoylation Peroxide treatment	It was observed more uniform dispersion of the treated fibres within the polymer matrix, and also less agglomerated fibres with the presence of dissociated fibres in the matrix, which contributed to more efficient stress transfer from the matrix to the fibres upon stress solicitation, resulting in superior physical and mechanical properties.	[93]
Jute/polyester and jute/epoxy composites	Siloxane treatment	The bifunctional siloxane molecules created molecular continuity across the interface by covalently bonded with both cellulose surface and polymer resin of the composite; as a	[108]

		result, the tensile strength, flexural strength, and interlaminar shear strength of the composites were increased.	
Jute fibre/HDPE composite	Maleated coupling agents treatment	With respect to the untreated composite, the composites fabricated at 1% MAPE concentration suggested considerable enhancement in tensile, flexural and impact strength (38%, 45% and 67% respectively); the γ and a relaxation peaks shifted to higher temperature regions after the treatment due to the segmental immobilisation of the matrix chains at the fibre surface, indicating the enhanced interfacial adhesion.	[109,110]

4 Bonding mechanisms

In plant fibre composites, the main constituents are the reinforcing fibres and the polymer matrix phase. The properties and performance of the composites rely on three main parameters: matrix, reinforcement and interface. The interface region between the fibre and the matrix has been recognised to play a predominant role in governing the global material behaviour. The interface in composites, often considered as an intermediate region formed due to the bonding of the fibre and matrix, is in fact a zone of compositional, structural, and property gradients, typically varying in width from a single atom layer to micrometers. There is a close relationship between the processes occur on the atomic, microscopic and macroscopic levels at the interface. In fact, the knowledge of the sequences of events occurring on these different levels is extremely important in understanding the nature of interfacial phenomena. The interface region controls the stress transfer between the fibre and matrix, and is primarily dependent on the level of interfacial adhesion. A reasonable interfacial strength ensures the maximum stress level and can be maintained across the interface and from fibre to matrix without disruption. The efficiency of the load transfer is determined by the molecular interaction at the interface along with the thickness and strength of the interfacial region formed[111,112]. The fibre-matrix interfacial bonding mechanisms in general include inter-diffusion, electrostatic adhesion, chemical reactions and mechanical interlocking, which were presented in Fig. 2. Together these mechanisms are responsible for adhesion and usually one of them plays a dominant role.

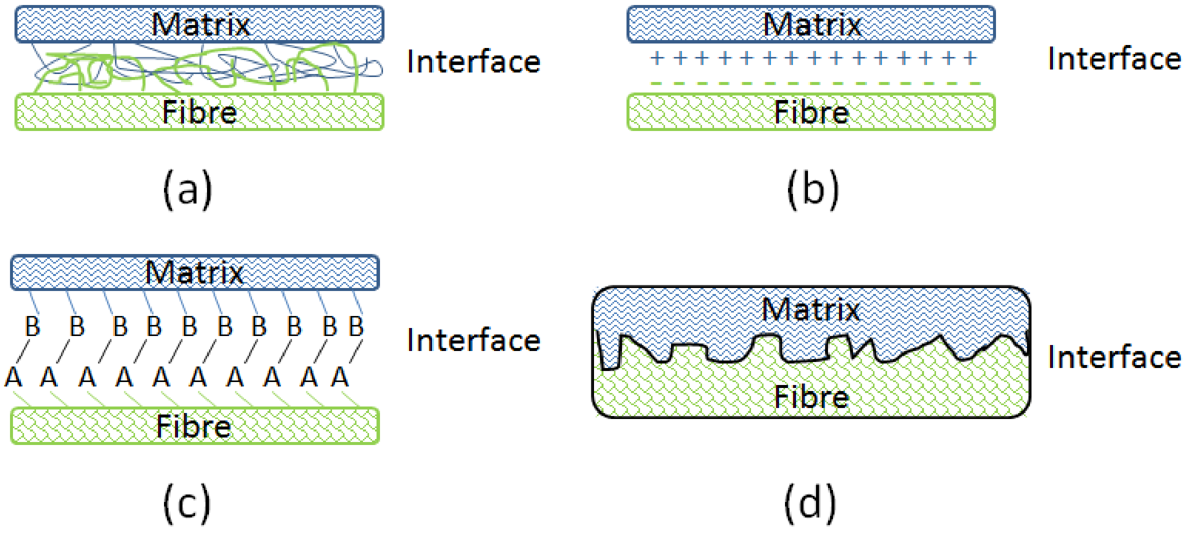


Fig. 2 Fibre-matrix interfacial bonding mechanisms: (a) molecular entanglement following interdiffusion, (b) electrostatic adhesion, (c) chemical bonding and (d) mechanical interlocking

Interdiffusion happens due to intimate intermolecular interactions between the molecules of the fibre substrate and the resin, which result from Van der Waals forces or hydrogen bonding[50]. In fact, there are two stages involved in this adhesion mechanism, i.e.

adsorption and diffusion. In the first stage, two constituents, fibre and matrix should have intimate contact which is in turn governed by two actions including spreading and penetration. Once good wetting occurs, permanent adhesion is developed through molecular attractions, e.g. covalent, electrostatic, and Van der Waals. On the other hand, good wetting between the substrates leads to the interdiffusion of molecules of both fibre and matrix. The extent and degree of diffusion depends primarily on the chemical compatibility of the two constituents and penetrability of the substrate[113]. Electrostatic adhesion is attributed to the creation of opposite charges (anionic and cationic) on the interacting surfaces of fibre and polymer matrix; thus, an interface consisting of two layers of opposites charges is formed, which accounts for the adhesion of the two constituents of composite. Chemisorption occurs when chemical bonds including atomic and ionic bonds are created between the substances as a result of chemical reactions[50]. Available physical and chemical bonds depend on the surface chemistry of the substrate and are sometimes collectively described as thermodynamic adhesion.

The mechanical interlocking phenomenon explains the adhesion when a matrix penetrates into the peaks, holes, valleys and crevices or other irregularities of the substrate, and mechanically locks to it[50]. It happens on a millimetre and micron length scale, and diffusion entanglement within the cell wall pores of fibre occurs on a nanoscale. The adhesion theories relying on mechanical interlocking can occur over larger length scale on the contact area. Adhesion, capillary forces, and other interaction factors can be ignored in most microscopic devices but they often dominate the behaviour of bonding quality at nanometre scales. Flow of polymer resin proceeds into the interconnected network of lumens and open pores of the natural fibre, with flow moving primarily in the path of least resistance. The adhesive occupies the free volume within the cell wall and therefore inhibits shrinking and swelling. The adhesive penetration of fibre occurs on two or more scales. There is micro-penetration, which occurs through the cell lumens and pits. Additionally, there is nano-penetration that occurs in the cell wall. Macro penetration of adhesive through process-induced cracks is also worth considering. Penetration of adhesive on any scale will impact bonding quality. The permeability is also a fibre related factor controlling the resin penetration. Permeability varies by surface characteristics and by direction e.g. tangential, radial and longitudinal. This mechanical interlocking mechanism is often used in polymer composites by etching the polymer surface to increase the surface roughness thereby increasing the contact area for adhesive penetration and mechanical interlocking of the substrate[113]. On the other hand, an increase in mechanical interlocking gives rise in enhancement of other bonding systems/mechanisms.

5 Interface structure

5.1 Morphology

SEM is the mostly used technique for investigating fibre-matrix interactions at fracture surfaces and polymer distributions in plant fibre composites. It allows the observation of monomer impregnated samples directly and after cured composites to yield information on the interaction of the polymer-fibre[8]. Migneault[114] investigated the variation in wetting at the fibre-matrix interface of composites among the different fibres employed, including aspen wood, spruce bark and spruce wood fibres by using SEM (Fig. 3). It was found that aspen fibres are completely wetted (noted A) whereas spruce and bark fibres are not in close contact with HDPE (noted C). The SEM micrographs also showed variation in interfacial adhesion and mechanical interlocking at the fibre-matrix interface. Aspen fibres presented macro-fibrils at the surface interlocking with the polymer matrix, thus increasing fibre reinforcement (noted B). The wetting and interlocking phenomena suggest a superior stress transfer in the case of aspen wood fibres, which explained the better performance of the aspen fibre reinforced composite than other fibres reinforced composites.

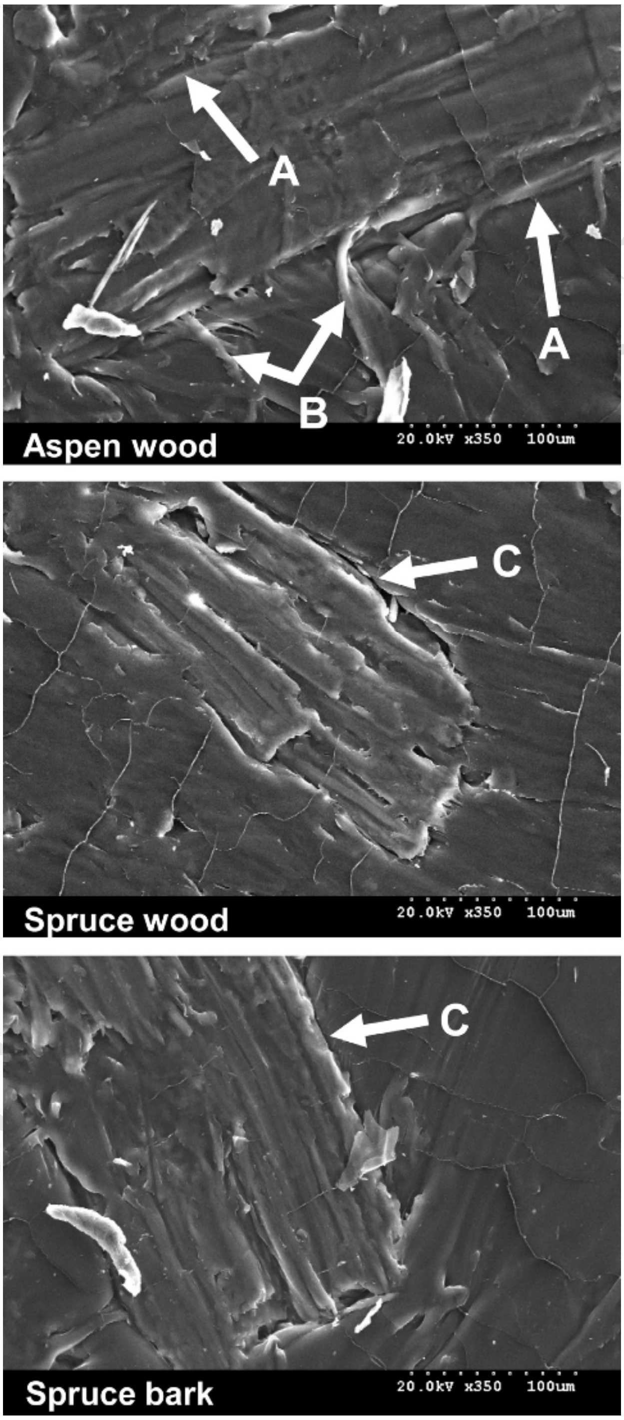
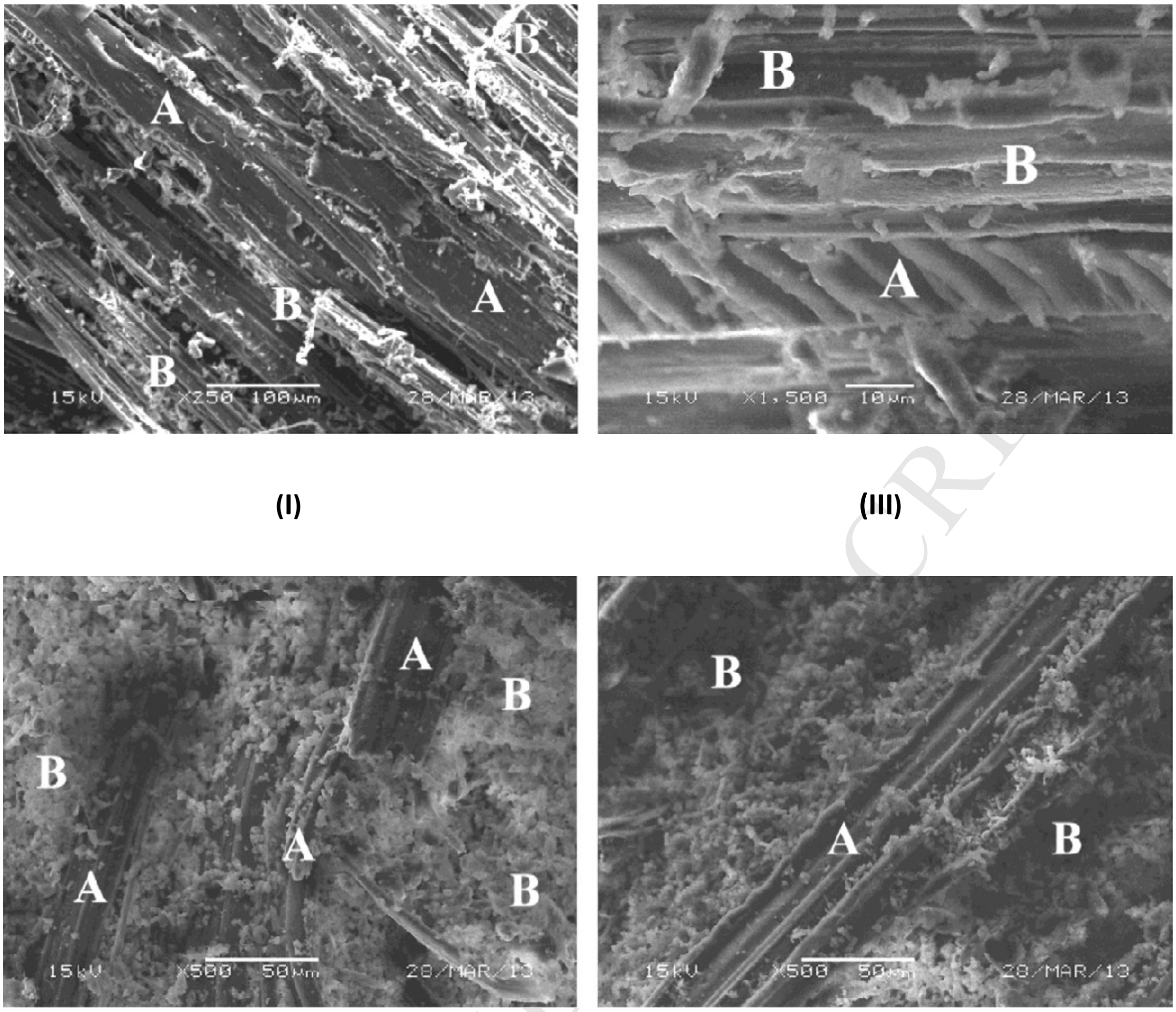


Fig. 3 Morphology of WPC made with selected fibres (legend: A = close contact/good wetting, B = macro-fibrils, C = no close contact)[114]

Pinto[115] examined the effect of silane treatment and Z-axis reinforcement on the morphological structure of jute-epoxy laminated composites by the use of SEM, the results were showed in Fig. 4. The fibres in the untreated plain weave sample (Fig. 4-I) appeared largely intact and undisturbed from their aligned position, denoting that the fibre/matrix interface failed before enough stress could be transferred to the fibres to break or pull them out. The untreated unidirectional sample (Fig. 4-III) showed similar fracture with the features (A) fracutred matrix and (B) intact and aligned fibres to the untreated plain weave sample. The difference in this case is the dominance of clean matrix fracture without any visible fibres suggesting the delamination resistance of this sample was primarily governed by matrix failure. Fig. 4-II showed the significant changes of the fracture surface of silane treated sample over that of untreated counterpart, i.e. (A) pulled-out and fractured fibres and (B) matrix fragments clinging to the surface. While the matrix fracture is still present, the fibre pull-out and breakage were seen to contribute to the sample's fracture resistance, implying the interface between fibre and matrix was strong enough to support the stress transfer to fibre to avoid the failure of the interface. The improved stress transfer from matrix to the fibre, which led the fibre to be pulled out prior to debonding, can also be seen on the surface of silane treated unidirectional composite with the presence of the more removed fibres from the epoxy matrix (A, Fig. 4-IV) and the great deal of matrix fragments attached to the surface (B, Fig. 4-IV).



(I) (III)

(II) (IV)

Fig. 4 Morphology the failure surfaces of (I) untreated and (II) silane treated plain weave jute-epoxy composites; and (III) untreated and (IV) silane treated unidirectional jute-epoxy composites[115]

5.2 Interfacial bonding capacity

5.2.1 Micromechanical measurements of interface shear capacity

The interpretation of the fibre/matrix adhesion is of special significance for the successful design and proper utilisation of plant fibre composites. There are several micromechanical testing methods for measuring the fibre/matrix interfacial adhesion, examples are single fibre fragmentation test (SFFT), single fibre pull-out test (SFPT), microbond test (MT), etc. The detailed summarisation of these tests can be found in the book of Kim & Mai[77].

The single fibre fragmentation test is originally developed from the early work of Kelly & Tyson[116], who investigated brittle tungsten fibres that broke into multiple segments in a metal matrix composite. In the fragmentation test (Fig. 5), a single fibre is totally encapsulated in a chosen polymer matrix, which in turn is loaded in tension. This experiment is done under a light microscope in order to in-situ observe the fragmentation process. The fibre inside the resin breaks into increasingly smaller fragments at locations where the fibre's axial stress reaches its tensile strength. This requires a resin system with a sufficiently higher strain-to-failure than that of the fibre. When the fibre breaks, the tensile stress at the fracture location reduces to zero. Due to the constant shear in the matrix, the tensile stress in the fibre increases roughly linearly from its ends to a plateau in longer fragments. The higher the axial strain, the more fractures will be caused in the fibre, but at some level the number of fragments will become constant as the fragment length is too short to transfer enough stresses into the fibre to cause further breakage. The shortest fibre length that can break on application of stress is defined as the critical fibre length, l_c. The average interfacial shear strength τ, with regards to the fibre strength σ, and the fibre diameter d, can be estimated from a simple force balance expression for a constant interfacial shear stress: $\tau = \sigma_f d/2l_c$.

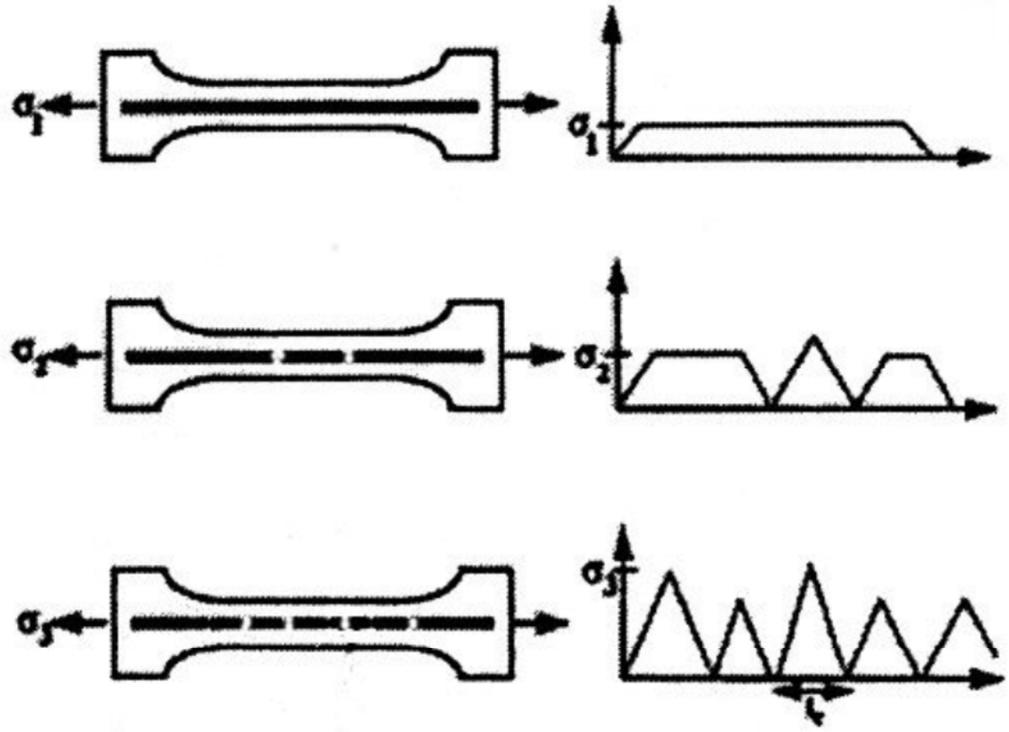


Fig. 5 Schematic of single fibre fragmentation test[117]

In the single fibre pull-out test (Fig. 6), the fibre is embedded in a block of matrix. The free end is gripped and an increasing load is applied as the fibre is pulled out of the matrix while the load and displacement are measured[118]. At the first stage of pull-out loading, the induced shear stresses along fibre do not exceed the bond strength between fibre and matrix. Once the force required to pull the fibre out of the block is determined, the corresponding interfacial shear strength can be calculated. The maximum load, *F*, measured before the detachment of the fibre from the matrix is related to the average value of the fibre-matrix shear strength, τ, through the equation $F = \tau \pi d l$, where πd is the fibre circumstance and *l* is the embedded fibre length[118].

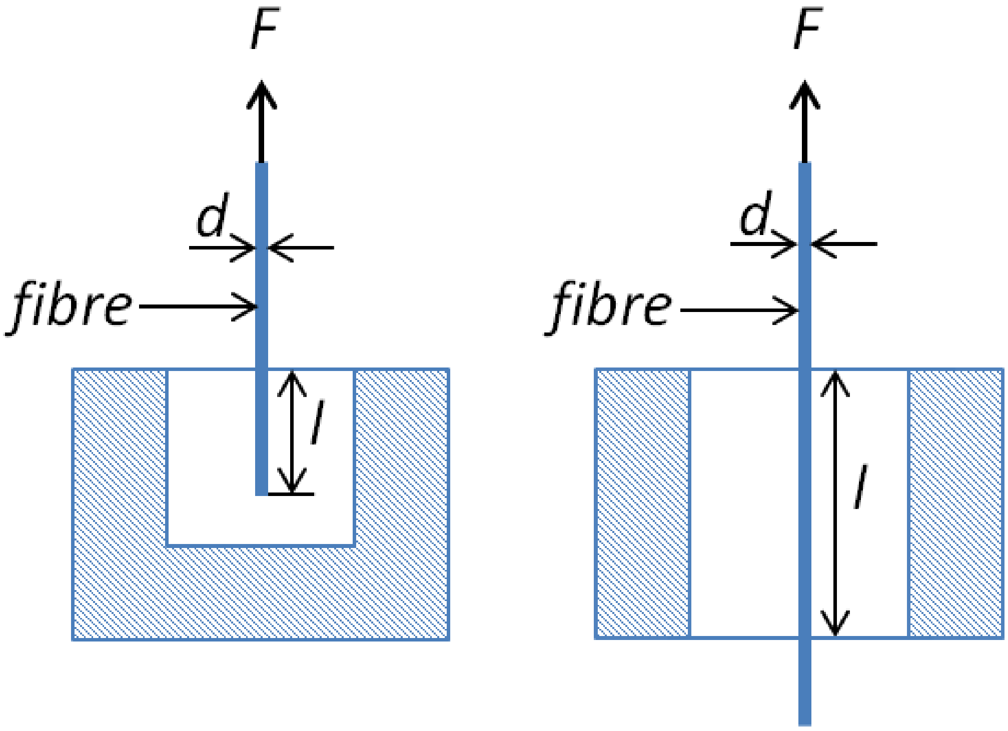


Fig. 6 Schematic of single fibre pull-out test

The other test method of interfacial shear strength, microbond test, is considered as a modified single fibre-pull out test. It consists of first applying small amount of resin onto the fibre surface in the form of a droplet that forms concentrically around the fibre in the shape of an ellipsoid, and then applying a shearing force to pull the fibre out of the droplet or vice-versa, thus the bead is restrained by opposing knife edges (Fig. 7) and stripped off, the applied load and the blade displacement are recorded. Assuming that the interface is in a uniform state of shear stress, the average of shear stress can be calculated by dividing the maximum measured force of debonding by the embedded area of fibre, i.e. $\tau = F/\pi dl$. The bond strength values can be used for investigating the dependence of composite performance on the energy absorbing characterisation of the interface and to establish the extent to which the fibre surface treatment can alter bonding[8].

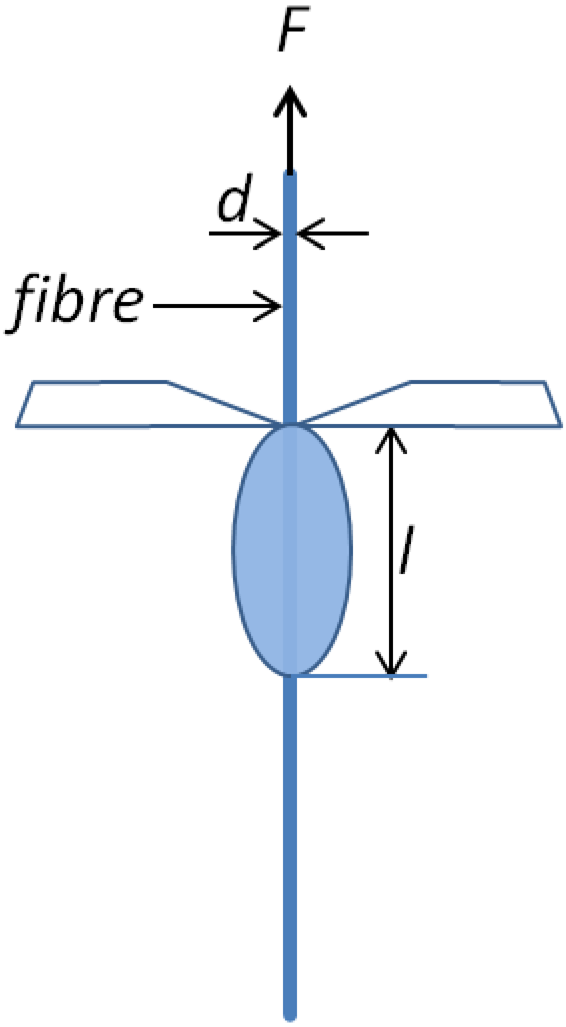


Fig. 7 Schematic of microbond test

5.2.2 Nanomechanical measurements of interface bonding capacity

Nanoindentation technique is an effective method in determining material surface properties at nanoscale, and has recently found its application feasible to plastics and natural fibres[119-128].This method is achieved by monitoring a probe penetrating into the specimen surface and synchronously recording the penetration load and penetration depth[128]. A schematic representation of a typical loading-displacement curve obtained during a full cycle of loading and unloading is presented in Fig. 8.

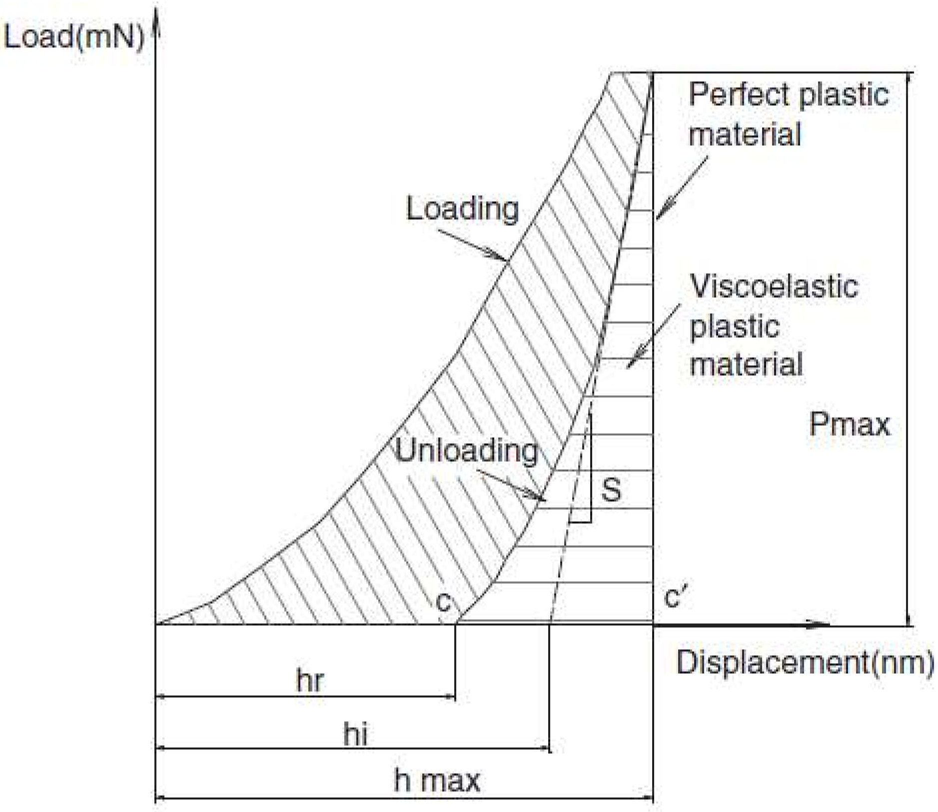


Fig.8 Typical loading-unloading curve of nanoindentation test[129]

In a typical test, a load in the range of 10 μN to 500 mN is applied to an indenter in contact with the specimen surface, an indent/impression is made (typically 10-500 nm) that consists of plastic and elastic deformation[129]. The maximum load P_{max}, the maximum depth h_{max}, the final depth after unloading h_r, and the slope of the upper portion of the unloading curve S are monitored in the loading-unloading cycle. The material properties, such as elastic modulus and hardness, can be extracted by analysing these data with the method developed by Oliver & Pharr[123]. The nanoindentation technique has been being established as the primary tool for investigating the mechanical properties of fibre/wood cell walls and polymers at nanoscale. However, extremely few studies have been performed on the interfacial properties of plant fibre composite by using this technique.

Lee[121] investigated the hardness and elastic modulus of cellulose fibre and polypropylene (PP) in a cellulose fibre-reinforced PP composite by the use of nanoindentation with a continuous stiff measurement technique. The hardness and elastic modulus in the interface region were measured with different indentation depth and spacing. It was assumed that the width of interface region (property transition zone) was less than 1 µm. However, 3D FEA-based (finite element analysis) results showed that even a perfect interface without property transition had almost same interface width as that measured by nanoindentation. Therefore, it would be difficult to calculate the exact mechanical properties using existing nanoindentation techniques without considering the effect of neighbouring material property in at least 8 times smaller region than indent size. Dhakal[129] studied the effect of water absorption on the nanohardness of woven fabric flax and jute fibre-reinforced bioresin-based epoxy biocomposites with the application of nanoindentation following the immersion at room temperature. The nanohardness decreased from 0.207 GPa for the flax dry sample to 0.135 GPa for the flax wet sample due to the weaker fibre interface resulted from the water immersion, whereas it seemed like the water absorption did not have adverse effect on the harness values of jute samples, which were 0.107 GPa and 0.112 GPa for dry and wet specimens respectively.

5.2.3 Spectroscopic measurements of interface bonding capacity

Fourier transform infrared spectroscopy (FTIR)

FTIR offers quantitative and qualitative analysis for organic and inorganic materials. It identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The resulting spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. This effective analytical instrument for detecting functional groups and characterizing chemical bonding information has been extensively used in composite materials.

Lu[130] investigated the effects of alkali soaking and silane coupling (KH560) modification of bamboo cellulose fibres (BCF) and maleic anhydride (MA) grafting of poly(L-lactic acid) (PLLA) on the improved interfacial property of cellulose/PLLA composites. The FTIR was applied to study the chemical structure of virgin cellulose and the changes after the pretreatments, and also the chemical structure of PLLA and cellulose/PLLA composites, with the results showing in Fig. 9. The OH stretching vibration peak of virgin cellulose at 3421 cm^{-1} was shifted to 3415 cm^{-1} after the alkali treatment, which was ascribed to the disturbing of hydrogen bond interaction that linked the cellulose and the impurities. The KH560 treated fibre demonstrated that new chemical bonds had been formed after the treatment by showing the peak at 1117 cm^{-1} corresponded with the Si-O-C stretching vibration and the peak at 802 cm^{-1} related to Si-C stretching in its FTIR spectrum. This was because the OH groups on silanol hydrolyzed from KH560 condensed with the OH groups on cellulose, thus the $CH_2CH(O)CH_2O(CH_2)_3SiO$- group had been grafted onto the cellulosic molecules. The improved interfacial adhesion between the cellulosic fibre and the matrix after the modifications can also be confirmed by the FTIR analysis of the composites, i.e. the filling of the untreated BCF in the composite did not lead to the changes of absorption peaks owing to the poor interaction between the fibre and the matrix, while after the three modifications, the OH stretching vibration at 3657 cm^{-1} had shifted to about 3650 cm^{-1}, indicating the superior interactions between the BCFs and PLLA.

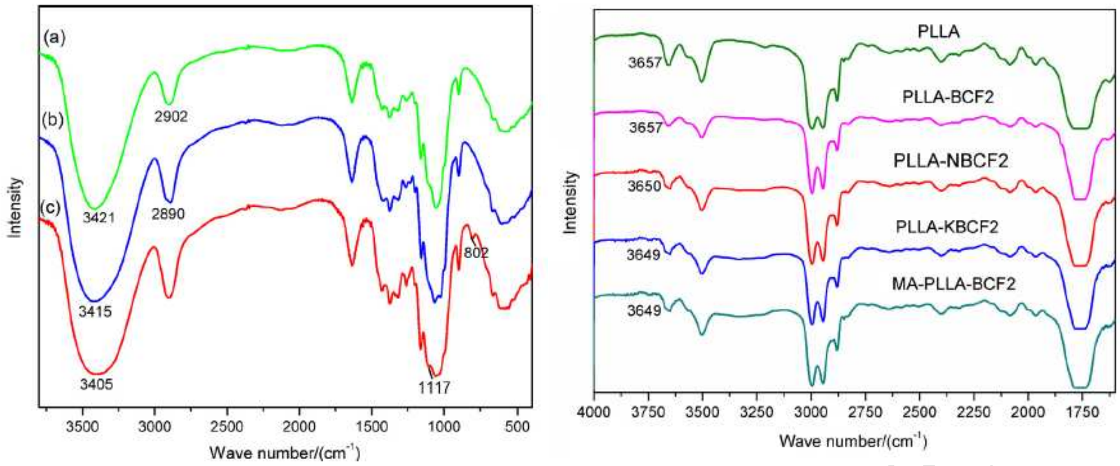


Fig. 9 FTIR spectra of a) BCF, b) NaOH treated BCF (NBCR), c) KH560 treated BCF (KBCF), PLLA and cellulose/PLLA composites[130]

Nuclear magnetic resonance spectroscopy (NMR)

NMR is an analytical chemistry technique used in quality control and research for determining the composition and purity of a sample as well as its molecular structure. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. An energy transfer from the base energy to a higher energy level (generally a single energy gap) happens when an external magnetic field is applied. The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.

NMR has become one of the significative techniques for surface characterization of plant fibre composites. Tavares[131] characterized the polyurethane/natural fibres (sisal fibre, and sugarcane waste fibre, SWF) composites focusing on interaction, homogeneity and compatibility between composite components by the use of solid-state NMR with the employed techniques magic angle spinning (MAS) and cross-polarization/magic angle spinning (CPMAS). Fig. 10 presented the comparison of CPMAS and MAS ^{13}C NMR spectra for PU/sisal and PU/SWF composites. In comparison to fibres, the PU/SCF and PU/sisal composites changed the chemical shifts of C anomeric to low frequency, and their proton values $T_1^H\rho$ were higher than those of fibres. In addition, the values determined for CH-OH and CH_2-OH were increased for PU/SCF compared with SCF and decreased for PU/sisal compared with sisal. These behaviours suggested that the PU/SCF had a better interaction between the matrix and the filler. Furthermore, since the relaxation parameter values increased, the modifications in the molecular packing and fibre chains ordination would lead the PU to be acting as a plasticizer as well.

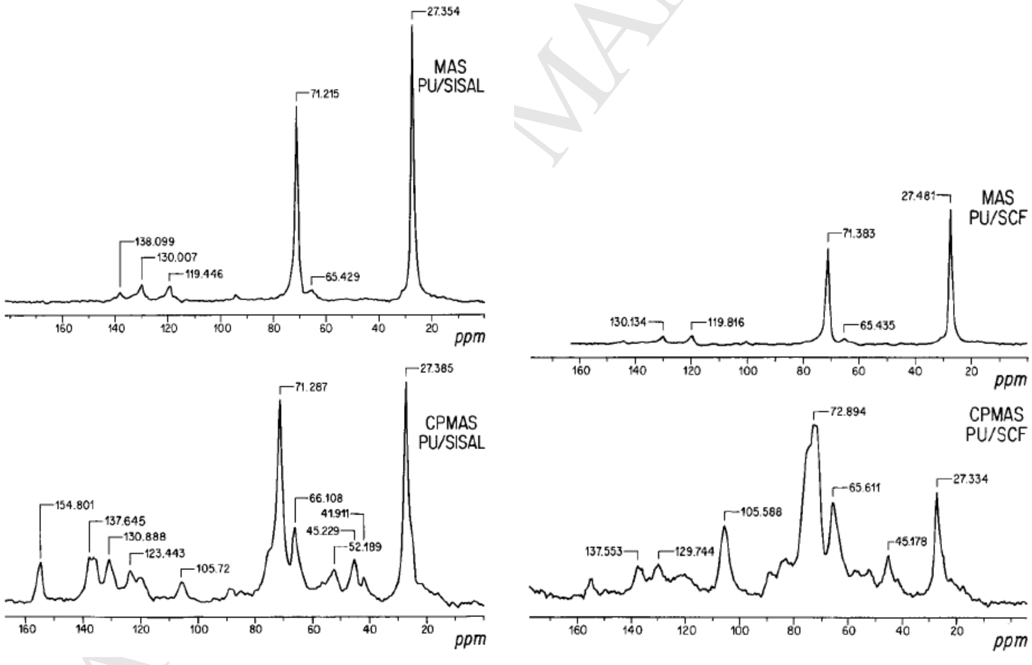


Fig. 10 Comparison of CPMAS and MAS ^{13}C NMR spectra for PU/sisal and PU/SWF composites[131]

X-ray photoelectron spectroscopy (XPS)

XPS is a well-established technique for analysing the surface chemistry of a material, which provides valuable quantitative and chemical state information from the surface of the material being studied. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while simultaneously measuring the kinetic energy and electrons that are emitted from the top 1-10 nm of the material being analysed. A photoelectron spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum from atoms which emit electrons of a particular characteristic energy. The energies and intensities of the photoelectron peaks enable the identification and quantification of all surface elements (except hydrogen). XPS has been used by researchers to qualitatively and quantitatively scrutinise the surface chemistry of treated and untreated plant fibres and their composites[132-134]. Apart from the information about the effect of surface treatments it offers, this technique might also indirectly help in establishing mechanisms of interfacial behaviour such as identifying boundary layers[118].

6 Conclusions and Future trends

Plant fibre composites have increasingly found their engineering applications in recent years especially in North America, Europe, China and Japan. The optimised interface of the composites governing the overall property has contributed to successful formulation and thus commercialization of the composites. Understanding the interface and bonding mechanisms of the composites is the key issue that requires significant research efforts in order to maximise the applications of the composites. The development and/or selection of efficient and cost effective surface modifiers or dispersion aids or coupling agents for both fibre and matrix are the first critical area to be considered for future development. The tendency is in favour of treatment that not only provides superb tailoring but also has minimal impact on economics. In addition, more attention should be paid to the nanoscale interfacial characterization of the composites in order to figure out the stress transfer, interfacial penetration, interaction or adhesion at nanoscale. Furthermore, although the application of nanoscience in plant fibre (e.g. nanocellulose reinforced composite) composites is currently at the infant state, nano-enhanced plant fibre composite will inevitably become important in the near future. The study of the interface and bonding of biobased nanocomposites would greatly benefit its development and help bridge the gap between scientific challenges and industrial productions.

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