Interfaces in Green Composites: A Critical Review

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Abstract: This manuscript reviews various aspects of fiber/resin interface in fiber reinforced composites, with special emphasis on green composites that use plant based fibers and sustainable resins. In this chapter we describe the importance of fiber/resin interface, factors affecting it, various modifications of fiber and resin that can be employed to improve the interfacial property and the experimental techniques to characterize the interface. The nature of the bonding between the fiber and resin and the mechanism of fiber/resin interaction are also discussed. Improving the fiber/resin interface is critical in the case of green composites since the hydrophilic plant fibers and some of the hydrophobic resins have very poor bonding. Strong adhesion at the fiber/resin interface is desirable for effective transfer of stress from broken fibers to intact fibers and, thus, to obtain good mechanical properties of the composites. However, weak bonding can provide energy absorbing modes through interface failure, making the composites tough. Thus, from the same set of fibers and resin it is possible to obtain composites with different properties simply through the control of fiber/resin interface.

Keywords: Interface, Interphase, Composite, Resin, IFSS, Biobased, Green

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1 Introduction

Green composites derived from renewable resources, mostly from plants, have great potential to provide environmental as well as economic benefits to industries and end-users in the face of dwindling petroleum resources. Environmental concerns about large amounts of wastes generated from petroleum based polymers and composites that end up in landfills have stimulated increased research in the development of new and greener materials for construction, furniture, packaging, automotive and many other industries [1]. Fiber reinforced composite technology is based on taking advantage of the strength and stiffness of the high-performance fibers by incorporating them in a resin, which acts as a binder and also transfers load from broken fibers to the intact fibers through the fiber/resin interface.

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Particularly attractive are the new composite materials in which majority of the constituents are based on yearly renewable resources that prevent further stresses on the environment created by depleting already dwindling wood resources from forests [2]. Examples of such raw material sources include annually grown native crops and fibers which are abundantly available in all regions of the world. Plant derived fibers have been used for hundreds of years for diverse applications such as apparel, ropes, beds, bags, linen and many others. If new uses for fast growing, native plants can be developed locally for high value materials such as fully sustainable and environment-friendly 'green' composites, even the pollution due to transportation can be reduced. These renewable materials based green composites could reduce the use of traditional materials such as wood, minerals and plastics in many applications. In recent years there has been increasing interest to replace fiberglass in fiber reinforced composites by natural plant fibers such as flax, hemp, sisal and ramie which have good tensile properties [3–5]. Natural fiber reinforced composites play an important role as alternate materials especially to wood and wood based products such as plywood, medium density fiber boards (MDFs), oriented strand boards (OSBs) and particle boards [6]. While green composites have several industrial applications, some challenges such as low processability and fiber/resin adhesion need to be addressed. The use of adhesion promoters such as coupling agents, additives or chemical modification of the fillers can help in overcoming many of these limitations. These composites can be even more environment-friendly when the polymeric resin is biodegradable and derived from renewable sources as well. While such 'green' composites have special relevance, in particular, to developing countries because of their low cost, indigenous availability of raw materials, savings in energy as well as applications as wood substitute, they are also preferred in developed countries for their non-toxicity and easy disposability. Challenges related to natural fibers such as inconsistencies in the product performance due to natural variability in the fibers' origin, only seasonal availability, non-availability in the desired forms of reinforcements (roving, long fiber strands, prepeg, chopped strand mats, etc.,) improper processing of fiber, poor fiber/resin interface, etc., need to be carefully addressed for industrial exploitation.

As mentioned earlier, in recent years, significant efforts have been directed towards investigating the use of natural fibers as reinforcement in a broad range of polymeric resins including thermoplastics. Natural fibers, such as wood fiber, wheat straw, jute, bagasse, etc., offer several benefits: low cost, low density, high toughness, acceptable specific strength properties and biodegradability [7–9]. The use of natural fibers to reinforce resins has many benefits, such as low volumetric cost, increased heat deflection temperature, increased stiffness of thermoplastics and improvements in wood surface appearance. Natural wood fiber filled non-degradable plastics such as wood-polymer composites (WPCs), have been commonly used in decking, furniture components, door and window moldings, packaging pallets, and interior panels of automobiles [10–12].

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Polymer based composites have been widely used for several decades and their market share has seen continuous double digit growth as their applications have expanded in diverse fields. It is widely known that most polymers when incorporated with solid fillers can undergo significant property enhancement. Many fillers including calcium carbonate, glass fibers, talc, kaolin, mica, wollastonite, silica, graphite, synthetic fillers (e.g. poly(ethylene terephthalate) (PET)- or poly(vinyl alcohol) (PVA)-based fibers), high-performance fibers (carbon, aramid, glass, etc.), have been commonly used [13]. However, combining two dissimilar components in the form of composites with specific shapes makes the reuse and recycling of composites nearly impossible. This is particularly true for thermoset composites where the crosslinking of the resin cannot be reversed. As a result, over 94% of the composites are discarded in landfills [1]. While landfilling is expensive due to landfill fees and transportation costs, it also has significant negative environmental impact as the composites do not degrade for several decades or even centuries in the anaerobic environment of landfills. Furthermore, most plastics, fibers and composites are produced using petroleum as the raw material, which is a non-renewable resource. These problems have become particularly acute in the past 10–15 years with increased use of composites and have led to scientific research for the development of sustainable alternatives that can replace traditional composites having little or no environmental impact, often referred to as ‘green’ composites. This task can be made easier by the fact that many of the typical applications of these composites do not require high mechanical properties of advanced composites made using high strength fibers such as carbon, aramid and glass. Such applications include secondary and tertiary structures, panels, packaging, gardening items, housing panels, etc. [1, 14].

The most widely known and used natural organic fillers are wood flour and fibers. Wood flour can be easily and inexpensively obtained from sawmill wastes and is usually used after sieving to obtain the proper size. Wood fibers are produced by subjecting wood waste to thermo-mechanical processes. While wood fiber/flour addition does not enhance the properties significantly, natural plant based fibers have been used to take advantage of their good mechanical properties and high aspect ratio. Among these, fibers such as cotton, flax, sisal, kenaf, jute, hemp, ramie, etc., have been very common. Further environment-friendliness can be achieved upon using post-consumer recycled plastics in place of virgin polymeric resins. Wood flour and short fibers are of great interest because of their low cost, dimensional stability and high elastic modulus. While tensile properties do not improve with wood flour, the main shortcomings are poor filler particle/polymeric resin adhesion, low impact strength and high thermal decomposition at temperatures over 200 °C [1, 14]. Flax, sisal, hemp and kenaf fibers are relatively similar and are available in long lengths extracted from the stem (bast) of the plants; they can be used as fillers by cutting them into short (staple) fibers. Alternatively, they can be used as long fibers, in various forms such as nonwovens or woven fabrics, as reinforcing fillers.

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Bio-based composites are the combination of natural (bio-based) fibers such as wood fibers (both hard- and soft-wood) or nonwood fibers (e.g., rice straw, hemp, banana, pineapple, sugarcane, oil palm, jute, sisal and flax) with polymer resins from both renewable and non-renewable resources. The term 'bio-based composites' broadly covers composites where at least one constituent is bio-based: (i) bio-based fiber reinforced petroleum derived polymers which are nonbiodegradable e.g., polyolefins polyester, epoxy, vinyl ester, phenolics, etc., (ii) bio-based polymers reinforced with synthetic fibers such as aramid, glass or carbon, and (iii) bio-derived polymers (e.g. poly(lactic acid) (PLA) reinforced by bio-based fibers (e.g. jute, kenaf, etc.) [15]. Bio-based polymers reinforced with bio-based fibers are commonly called 'green' composites whereas the other two categories are referred to as 'greener' composites [1]. Most green composites tend to be biodegradable and compostable and, hence, need not go into landfills. A variety of plant based resins e.g., starch, proteins, etc., and fibers e.g., flax, ramie, kenaf, jute, hemp, sisal, etc., have been used to fabricate bio-based composites for many applications [1, 15].

Fiber reinforced composite properties depend on the constituent material properties i.e. the fibers and the resins used. The strength and stiffness of the composites are directly a function of the reinforcing fiber properties, which carry most of the load, and their volume content. The resin helps to maintain the relative position of the fibers within the composite and, more importantly, transfers the load from the broken fibers to the intact fibers [16]. As a result, fiber/resin interfacial properties are important and have a significant effect on composite properties including toughness, fracture stress in both longitudinal and transverse directions. To obtain high strength composites, all three factors, namely, fiber properties, resin properties and the fiber/resin interfacial characteristics are important and need to be considered.

2 Fiber/Resin Interface

The fiber/resin interface can be defined as the 2-dimensional boundary between the fiber and the resin surfaces [17]. Fiber/resin interface is critical to controlling composite properties because all fiber/resin interactions occur through the interface. These interactions can occur through three mechanisms: 1) mechanical coupling or micromechanical interlocking of the two materials, 2) surface energetics and secondary bonds such as van der Waals or electrostatic interaction or hydrogen bonding, and 3) covalent bonding between the fiber and the resin [12, 16, 18, 19]. Some of these interactions as well as the fibers acting as heat sink during thermoset resin curing, i.e., exothermic crosslinking reaction, can create an interphase region, which is a thin, 3-dimensional region surrounding the fiber with properties different from the bulk resin. In addition, in thermosets, the interphase can form due to preferential adsorption of either the curing agent or the resin at the fiber surface, leading to a region of higher or lower crosslinking [17]. In thermoplastic

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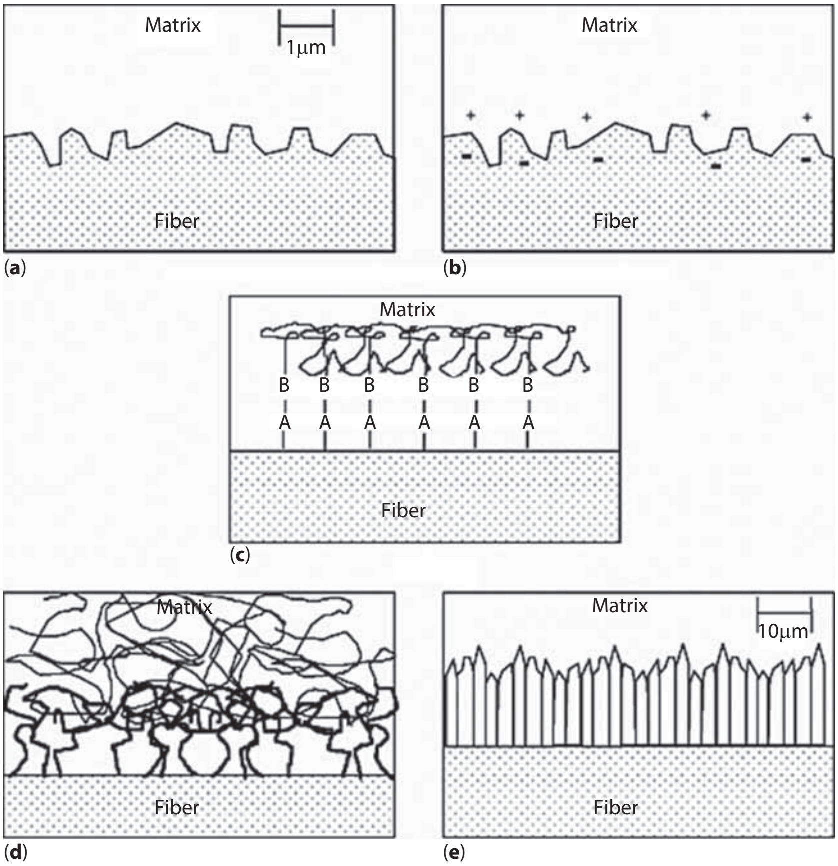

Figure 1 Schematic depiction of various interactions at the fiber/resin interface: (**a**) micromechanical interlocking, (**b**) permanent or induced dipole interactions, (**c**) chemical bonding, (**d**) chain entanglement, and (**e**) transcrystallinity [17].

resins, on the other hand, the interphase can be a region of transcrystallinity on the fiber surface that develops during cooling [17]. Figure 1 shows the schematic depiction of various interactions at the fiber/resin interface.

In the current context the interface may be described as the boundary between the two layers of different chemistry and/or microstructure, e.g., fiber and resin. However, such boundaries are rarely without any chemical interactions and, therefore, we can also define a region having a certain thickness, called the interphase, being the volume of material affected by the interactions at the interface. The term interphase, a three-dimensional zone, as distinct from a two-dimensional interface, is now widely used in the adhesion community to indicate the presence of a chemically or mechanically altered zone adjacent to the two main phases. The

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implication is clear, such an interphase zone will lead to a gradation of properties from one phase to another, rather than the abrupt change created by the two-dimensional interface.

2.1 *Importance of Fiber/Resin Interface*

The important role the fiber/resin interface plays was recognized in the mid-1960s in the case of advanced composites used as structural materials [20]. Since then, the subject of interface has grown to occupy a larger share of research on composite materials. Generally, studies of the fiber/resin interface have been divided into two main categories. In the first category, theoretical modeling of the stress profile along the fiber has been advanced recently by the availability of new experimental techniques based on Raman microscopy on micro-composites or single-fiber model materials [21]. In the second category, a variety of experimental methods are now available including single fiber composite (fragmentation) test and fiber pull-out or push-through, which allow direct measurements of the fiber/resin bond strength and of the fracture toughness of the composite [16, 22–25]. In addition to the two classical categories of fiber/resin interface studies, another category of interfacial control, whereby the chemical and physical properties of the original constituents and surface topography of fibers are modified as desired, has been introduced. Such changes result from chemical and/or physical processes, namely crosslinking, immobilization and crystallization, and it applies to a range of composites from advanced fiber reinforced composites to nanocomposites. The properties of the interfacial region or interphase dominate the properties of the composite to the extent that justifies the recently coined new name of ‘interface composites’ [22].

Fiber/resin interface is perhaps the most important yet least understood component of the composite material, simply because of its complexity [26]. In particular, there is a lack of understanding of processes occurring at the atomic level of interfaces and how these processes influence the global composite behavior. There is, however, a close relationship between the processes that occur at atomic, microscopic, and macroscopic levels. In fact, knowledge of the sequences of events occurring at these different levels is extremely important in understanding the nature of interfacial phenomenon. Interfaces in composites, often considered as 2-dimensional entities, are, in fact, zones of compositional, structural, and property gradients, typically varying in width from a single atom layer to micrometers [26]. Characterization of the fiber/resin interfacial characteristics is necessary to understand and predict the composite mechanical behavior. Among the many factors that govern the characteristics of composites involving fibrous materials, such as carbon, glass or ceramic, and a polymeric resin, it is certain that the fiber/resin adhesion plays a dominant role. The stress transfer at the interface requires an efficient coupling between the fiber and the resin. Hence, it is important to optimize the fiber/resin interfacial bonding depending on the composite

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properties required. A strong fiber/resin bond gives rise to a rigid, brittle and low impact resistant composite. On the other hand, a weak fiber/resin bond provides energy absorbing mechanism, through interfacial failure, making composites much tougher [16, 20, 26]. The tensile strength of the composite, in particular, is affected by the efficiency of load transfer from the resin to fiber via shearing at the interface. While interface failure is a common failure mode observed in reinforced composites, catastrophic failure of composites is due to the aggregation or combination of elementary processes, such as fiber breakage, resin cracking and interface failure. While both resin and fiber/resin interface transmit stresses from broken fibers to the intact fibers in composites, resin also protects the fibers from the environment. In addition, the resin also maintains the individual fiber positions within the composite [27].

2.2 Role of the Components of the Fiber Reinforced Composite

In general, fibers play a dominant role in determining the stiffness and strength of a composite and the choice of the resin determines properties such as maximum service temperature, viable processing approaches and long-term durability [17]. Resin materials can be divided into two broad categories: thermosetting and thermoplastic. Thermosetting resins are characterized by having a low-viscosity and reactive monomers or oligomers that cure (crosslink) by reacting with curing (crosslinking) agents to form an insoluble and infusible 3-D network structure. The cure temperature and time together control the extent of curing which influences many resin properties. A fully crosslinked (fully cured) resin shows increased mechanical properties and reduced swelling in solvents and lower moisture susceptibility. On the other hand, an incomplete cure may impart higher flexibility and toughness to the resin. Thermoplastics are linear or slightly branched polymers of relatively high molecular weight. They are of significant interest because they can be melted, remelted and fused, thus easing their repair in the field. Thermoplastic polymer morphology may be either amorphous or semicrystalline. The semicrystalline and even liquid crystalline morphologies can impart superior solvent resistance to the resin. Semicrystalline polymers display a melting temperature (T_m) for the crystalline part and processing must be performed above their T_m. Amorphous thermoplastics, on the other hand, are processed well above their glass transition temperature. A possible limitation for some applications of semicrystalline polymers may be because of the morphological changes that can occur during their processing or during the service, particularly due to the application of heat or exposure to solvents while under stress [28]. These changes in the crystalline structure and/or content may cause changes in the overall composite properties that can be highly undesirable (epoxies, vinyl esters, etc.). Likewise, control of morphology during processing is critical to achieving the desired resin properties such as toughness and chemical resistance [17]. A large number of resins are commercially available and provide a wide range of service temperatures.

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The role of the resin in the long-term durability of a composite is a critical issue. Durability is affected not only by the state of the resin, which may undergo physical aging or environmental degradation, but also due to changes in its interaction with the fiber at the interface. In addition, the stresses existing within the resin due to processing, thermal and fatigue cycling, and other mechanical loads during use are critical to the long term performance of the composite. Microcracking is one of the first damage modes observed in the resin phase. Microcracking can initiate fiber fracture, interfacial debonding and/or delamination that can limit the lifetime of the composite [29]. An even more severe case occurs when microcracks provide pathways for accelerated environmental degradation. For example, moisture ingress into the composite such as honeycomb structures followed by freeze-thaw or elevated temperature thermal oxidation can damage the structure and dramatically reduce mechanical properties [17].

Since the fibers are the reinforcing component, the mechanical properties such as tensile strength and Young's modulus of the composites are mainly controlled by the fiber tensile properties as well as fiber volume fraction, orientation and length [30, 31]. The main function of the resin when the composite is loaded is to transfer load from broken fibers, at break points, to intact (surviving) fibers through the shearing of the resin at the interface when the composite is under stress [16, 20, 32]. Efficient shear stress transfer can only occur when the fiber/resin bond is intact which results in superior mechanical performance of the composites. Indeed, it is known that higher fiber/resin interfacial bond strength increases the strength and stiffness of the composite, while the impact strength, toughness, and flexural modulus tend to decrease [20, 32]. Alternately, weak interfacial bonding encourages energy absorbing modes of crack propagation along the fiber/resin interface and, thereby, increases the fracture toughness of the composite [33]. However, at the same time the strength and stiffness of the composite decrease. The transverse strength and modulus of the unidirectional composites as well as the interlaminar shear strength (ILSS) and transverse flexural strength of fiber reinforced composites are also governed by the fiber/resin interfacial characteristics, with weaker interface resulting in lower property values. Interphase can also have a profound effect and interphase formation and design to control the fiber reinforced composite properties has been presented by Jones [34]. In a fiber reinforced composite containing 50% fiber volume fraction that is made up of fibers having 7.6 μm diameter, just 1 cm^3 of composite volume consists of 2570 cm^2 of interface [20]. This large amount of interface indicates that a small change in the interfacial characteristics can have a significant impact on the composite properties. In recent years, the diameters of the fibers have steadily become smaller and smaller and at present carbon nanotubes [CNTs] are being used to improve the resin properties and, in turn, the composite properties. In the case of CNT-based composites, particularly those that use single-wall CNTs, most part of the composite is simply CNT/resin interface and

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interphase [35]. This makes the interface and interphase characteristics all the more important [36, 37].

The incorporation of hydrophilic natural fibers in hydrophobic polymers, e.g., in greener composites, leads to heterogeneous systems whose properties tend to be inferior due to lack of fiber/resin adhesion. In such cases, treatment of fiber surfaces to improve its adhesion to resin can be critical in developing composites with good mechanical properties. Many fiber treatments such as bleaching, grafting of monomers, acetylation, etc. have been used and/or proposed [38–40]. In addition to the surface treatment of fibers, use of compatibilizers or coupling agents that can bond to both fibers and resin has also been explored. A schematic diagram of a coupling agent's functioning is shown in Figure 2. The compatibilizers can be polymers with functional groups grafted onto the backbone or side chains. The coupling agents are generally multifunctional organometallic compounds based on silicon, titanium, and zirconium and are commonly known as silane, titanate, or zirconate coupling agents, respectively. Table 1 presents the structures, functional groups, and applications of a few commercial coupling agents [41].

The failure mechanism of the interface in a carbon fiber/epoxy resin system has been studied, for six different epoxy blends, using the single filament composite technique [16]. The epoxy blends were formulated to yield a wide range of stiffness values, and their effect on interfacial failure was examined. Their results clearly showed that for stiff resins, debonding occurs at every fiber break. With increasing strain, the debond region increases, reducing the stress on the fiber. For rubbery resins, on the other hand, there is no debonding at the fiber break. Instead, the resin, being weak, cracks. Debonding and resin cracking result in different fiber/resin interfacial shear strength (IFSS) values. In summary, the resin mechanical properties, particularly the modulus, also affect the fiber/resin IFSS.

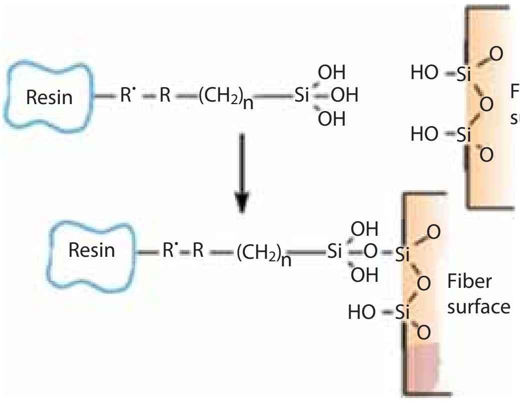

Figure 2 Schematic diagram of a coupling agent's functioning [42].

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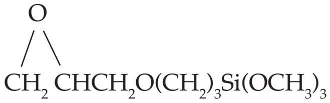
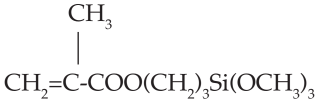
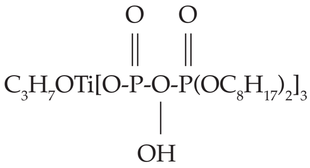
Table 1 Some Typical Representative Commercial Coupling Agents (Information collected from Kenrich company datasheets [41]).

	Functional Group	**Chemical structure**	**Applicable polymer(s)**
1	Vinyl	$CH_2{=}CHSiCl_3$ $CH_2{=}CHSi(OC_2H_5)_3$	Elastomers, polyethylene, silicone elastomers, unsaturated polyester, polypropylene, ethylene propylene diene monomer, ethylene-propylene copolymer.
2	Chloropropyl	$ClCH_2CH_2CH_2Si(OCH_3)_3$	Epoxy, epoxide
3	Epoxy	 $\overset{\overset{O}{/\ \backslash}}{CH_2\ CH}CH_2O(CH_2)_3Si(OCH_3)_3$	Elastomers, specially butyl elastomers, epoxy, phenolic and melamine, polycarbonate, poly(vinyl chloride), urethane
4	Methacryl	 $CH_2{=}\overset{\overset{CH_3}{\mid}}{C}{-}COO(CH_2)_3Si(OCH_3)_3$	Unsaturated polyesters, polyethylene, polypropylene, ethylene-propylene-diene plastics, ethylene-propylene copolymer
5	Amine	$H_2N(CH_2)_3Si(OC_2H_5)_3$ $HN(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	Unsaturated polyesters, nylon, polycarbonate, polyurethane, melamine-formaldehyde resin, phenol-formaldehyde, polyimide, melamine/phenol-formaldehyde
6	Cationic styryl	$CH_2CHC_6H_4CH_2H^+H_2(CH_2)_3$ $Si(OCH_3)_3Cl^-$	All polymers
7	Phenyl	$C_6H_5Si(OCH_3)_3$	Polystyrene
8	Mercapto	$HS(CH_2)_3Si(OCH_3)_3$ $HS(CH_2)_3Si(OC_2H_5)_3$	Epoxy, epoxide, polyurethane, urethane, styrene-butadiene plastic, ethylene propylene diene monomer
9	Phosphate (titanate)	 $C_3H_7OTi[O{-}\overset{\overset{O}{\|}}{P}{-}\underset{\underset{OH}{\mid}}{O}{-}\overset{\overset{O}{\|}}{P}(OC_8H_{17})_2]_3$	Polyolefins, acrylonitrile-butadiene-styrene, phenolics, polyesters, poly(vinyl chloride), polyurethane, styrenics

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2.3 Improving the Fiber/Resin Interface

From the above discussion it is clear that improvement in fiber/resin compatibility is a key to obtaining good mechanical properties. In order to incorporate natural cellulosic fibers which are hydrophilic into hydrophobic thermoplastics, such as high density polyethylene (HDPE), polypropylene (PP), poly(vinyl chloride) (PVC), etc., a fiber surface pretreatment or some other way of interface modification such as incorporation of compatibilizer is generally required. In order to improve the compatibility of the wood plant based fibers with the polymers, several chemical and other treatment methods have been developed. These include different treatments of the polymeric resins [43, 44], use of coupling agents [45–47], interface compatibilizers, e.g., silanes and isocyanates [47–50] and resin modifiers, e.g., maleic anhydride grafted polyolefins or elastomers. Other studies involving the use of organic carboxylic acids, e.g., stearic acid, acetic anhydride, maleic anhydride and phthalic anhydride have also been reported. These studies have indicated the effectiveness of these organic compounds in improving adhesion between natural fibers and thermoplastic resins [51–53]. According to the principles of interface coupling, the hydrophilic carboxyl group of an organic acid as the modifier can be expected to react with the hydroxyl groups on the natural fiber surface and the hydrophobic group would react with resin, providing a covalent bond, or have relatively high compatibility with the polymer resin. The combined effects of these interactions can effectively improve both the fiber dispersion and the resultant interfacial coupling.

The poor resistance to moisture absorption makes using natural fiber based composites less attractive for exterior applications. While several types of polymers have been used as resins for natural fiber reinforced composites, the most commonly used ones are thermoset polymers such as unsaturated polyesters, epoxies and phenolics that form ‘greener composites’ [54–60]. Thermoplastic polymers such as PE, polystyrene (PS) and PP have also been used [54–56]**.** While these polymers can restrict water absorption, they have different surface energies depending on their chemical structure which result in different affinities towards the fibers. It was reported that sisal/LDPE composites showed a better reinforcing effect because of high resin ductility and high strength of sisal as compared to that of LDPE resin [56]. Nair and Thomas [54] have reported on the tensile properties of polystyrene (PS) reinforced with short sisal fiber and surface treated (benzoylated) sisal fiber. The benzoylation of sisal fiber was achieved simply by agitating fiber in benzoyl chloride. They found this treatment enhanced the tensile properties of the composites. The improvement in the tensile properties (from 21.3 to 29.14 MPa) of treated fiber composite was attributed to the presence of phenyl structure in treated fiber similar to that of polystyrene, which improves the thermodynamic compatibility between benzoylated fiber and polystyrene. Another contributing factor to the improved properties was the reduction in the hydrophilicity of the

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fiber as a result of benzoylation, which reduces the surface energy of the fiber and makes it more compatible with the hydrophobic PS. The incorporation of sisal fiber, however, was reported to considerably reduce the glass transition temperature (T_g) of PS.

Joseph *et al*. [56] reported that among polyester, epoxy and phenol-formaldehyde resin based composites that used sisal fibers, the phenolic resin performed the best with respect to tensile and flexural properties owing to its high interfacial bonding in phenolic composites. They postulated that the higher fiber/resin bond strength for phenolic resin was due to the possible reaction between the methylol group of the resin with the hydroxyl group of cellulose. The strong adhesion between phenol-formaldehyde resin and lignocellulose has been shown to arise, at least partially, from chemical bonding between the phenol-formaldehyde prepolymer and the guaiacyl group of lignocelluloses. Joseph *et al*. [56] found that the reinforcing ability of sisal fiber in PP resin was less than that in low density polyethylene (LDPE). Since PP is more crystalline compared to LDPE, the increase in tensile strength by the addition of sisal fiber was less in the case of PP compared to LDPE [56].

Nanoparticle dispersion is known to enhance the mechanical properties, particularly stiffness, of polymers and resins [61]. As discussed earlier, resin stiffness has a significant effect on the fiber/resin IFSS. Effects of silica (SiO_2) nanoparticle loading (0–2 wt%) and ammonia/ethylene plasma-treated fibers on carbon fiber/epoxy interfacial properties as well as epoxy resin properties were studied by Lew *et al*. [62]. Single fiber composite (SFC) tests were performed to determine the fiber/resin interfacial shear strength (IFSS) while tensile tests on epoxy resin specimens were performed to quantify mechanical property changes as a function of silica content. The results indicated that up to 2% SiO_2 nanoparticle loading had only a little effect on the mechanical properties. For untreated fibers, the IFSS was comparable for all epoxy resins. With ethylene/ammonia plasma treated fibers, specimens exhibited a substantial increase in IFSS by 2 to 3 times, independent of SiO_2 loading. The highest IFSS value obtained was 146 MPa for plasma-treated fibers. Interaction between the fiber sizing and plasma treatment may be a critical factor in this IFSS increase. The results suggest that the fiber/epoxy interface is not affected by the incorporation of up to 2% SiO_2 nanoparticles. Furthermore, the fiber surface modification through plasma treatment is an effective method to improve and control adhesion between fiber and resin. Though these results are not for green composites the same strategy can be easily adopted to improve IFSS in green composites.

3 Measurement of Interface Properties

As mentioned earlier, good interfacial bonding to ensure load transfer from resin to the reinforcing fibers is a primary requirement for effective use of the fiber properties. Thus, a fundamental understanding of interfacial properties and a

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quantitative characterization of interfacial bond strength is critical in evaluating the mechanical behavior and capabilities of composite materials. A large number of analytical and experimental techniques have been developed for understanding fiber/resin interfacial adhesion in composites. Common tests for characterizing adhesion include contact angle measurements, tension or compression of specially shaped resin specimens containing a single fiber, the single fiber pullout test, single fiber fragmentation or composite (SFF/SFC) test, short beam shear and transverse tensile tests and the vibration damping test. A number of experimental techniques have also been devised to measure the mechanical properties of the fiber/resin and laminar interfaces in composites. These techniques can be classified into two different categories depending on the nature of the specimens employed and the scale of testing: first one involves the testing of single fiber microcomposites in which individual fibers are embedded in specially constructed resin specimens of various shapes and sizes; and the other uses laminated (stacked-layers) composites to measure the interlaminar/intralaminar properties. One important requirement of these tests is that the mechanics model developed for data reduction must be consistent with the real-life failure mechanisms. Table 2 presents the common fiber surface and fiber/resin interface characterization techniques that are being currently used [33].

A number of mechanical tests have been developed to measure the capacity of the interface to transfer stress from the resin to the fiber in a composite. The interfacial properties were first measured with an indirect compression method suggested by Broutman [63]. With the improvement in techniques as well as understanding of the interface, in the following years, many test methods were

Table 2 Common fiber surface and fiber/resin interface characterization techniques [33].

Fiber Surface Characterization Techniques	**Common Fiber/Resin IFSS Determination Techniques**
Infrared (IR) and attenuated total reflectance IR (FTIR-ATR)	Micromechanical tests
Raman spectroscopy	Single fiber composite test
X-ray photoelectron spectroscopy (XPS)	Single fiber pullout test
Surface roughness	Microbead test
Atomic force microscopy (AFM)	Single fiber pullout from microcomposite test
Scanning electron microscopy (SEM)	Microindentation test
Optical microscopy	Tests on composites
Surface energetics and wettability (Wilhelmy and sessile drop methods)	Short beam shear test
Electron spin resonance (ESR)	Interlaminar shear test
Ellipsometry (for coating thickness)	Transverse tensile test

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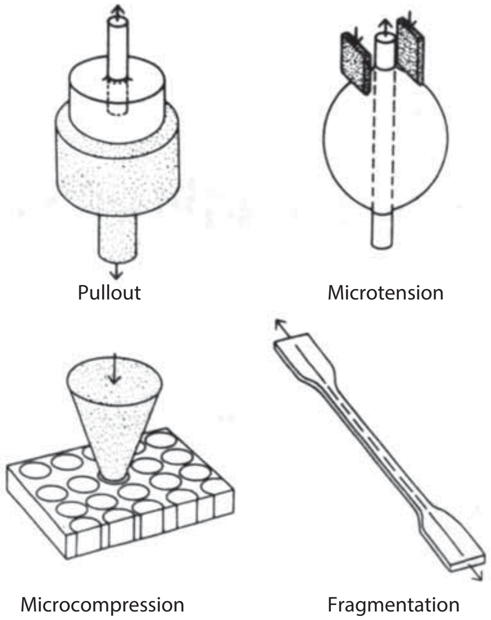

Figure 3 Four methods currently used for measuring interfacial properties [18].

developed. Currently, four techniques suitable for evaluating actual reinforcing fiber/resin adhesion strength have been widely used. These mechanical tests have been summarized by Piggott [18] and are illustrated in Figure 3. The single fiber pullout [64] and microtension (commonly called microbead test) [65] methods are basically equivalent in concept but differ in specimen geometry. In the single fiber pullout method, the fiber is embedded in a solid resin material and pulled with an increasing force.

The single fiber pullout test was originally applied to glass fiber-reinforced concrete and carbon filament-reinforced aluminum, and has been adapted by Favre and Perrin for use with fiber reinforced polymer/plastic (FRP) composites [66]. As demonstrated with many systems, it has been shown that the pullout test is relatively easy to carry out with rod-like or larger diameter fibers. However, when fiber/resin interfacial adhesion is strong and fiber diameter is small (< 10 μm, for example), the embedded fiber length must be very small. Otherwise, it will result in fiber breakage instead of pulling the fiber out of the resin. The microbead test was developed to prepare pullout samples with very small embedded fiber length [65]. In this method, the fiber is embedded in a small axisymmertrical drop of resin and pulled out. The microcompression or microindentation test was reported first by Mandell *et al*. [67]. This technique uses a small indenter to debond a fiber [16, 68, 69]. A composite specimen is sectioned perpendicular to the fiber axis, the end of a single fiber is compressively loaded with a very fine spheroconical

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diamond tip, and the fiber is pushed out from the composite. From the load versus displacement curve, the IFSS can be calculated. Further, finite element analysis can be used to understand the stresses at the interface and estimate the shear stress at the instant of debonding. In the single fiber fragmentation test, a single fiber is embedded in a polymer resin that forms a dogbone shaped tensile specimen. When the dogbone specimen is stretched in the fiber axial direction, the fiber breaks into small fragments, until finally the fiber lengths are all less than a critical length [16]. SFC technique coupled with acoustic emission can provide a reliable means for determining the number of breaks, and hence the average value of critical length [70]. The IFSS can then be estimated from the average critical length [71]. The acoustic emission technique can also be used for opaque resins.

As mentioned earlier, several commonly used techniques have been developed to determine the interfacial adhesion in composite materials [26]. They are briefly described below.

1. Single fiber pullout test or microbead technique - In the case of the microbead test, a very small amount of resin in the form of a microdroplet is deposited on a single filament [65]. The microdroplet forms a microbead when the thermoplastic resin is cooled or the thermoset resin is crosslinked. The force required to displace/debond the microbead is recorded and used to compute the interfacial shear strength (IFSS). In the case of single fiber pullout test, the shear strength of the fiber/resin interface in the composite is usually determined by measuring the force needed to pull the fiber axially out of the solid resin. This involves embedding part of the fiber in a pool of liquid resin with the fiber axis perpendicular to the surface, and allowing the resin to harden, either by crosslinking reaction in thermoset resin or by cooling in the case of thermoplastic resin. The fiber is pulled out using an Instron universal tester or similar equipment. The fiber diameter (D) and embedded length (L) are measured using an optical microscope. The microbead test is also performed using an Instron universal tester having a special microvise. The microvise plates are placed above the microbead and brought closer until they barely touch the fiber surface, with no pressure exerted. The fiber is then pulled out from the microbead at a steady crosshead speed until the microbead is debonded. Figure 4 (left) shows the schematic of the microbead test. The interfacial shear strength (IFSS), τ, in both single fiber pullout as well as in microbead test, is calculated using the following equation:

   $$\text{Interfacial shear strength } (\tau) = \frac{F}{\pi \times D \times L}$$

   where F is the force required to debond the microbead from the fiber.
2. Single fiber composite (SFC) test - In this test, the test specimen consists of a single fiber embedded in a dogbone shaped polymeric resin specimen [16, 72]. When the dogbone specimen is stretched in the fiber axial

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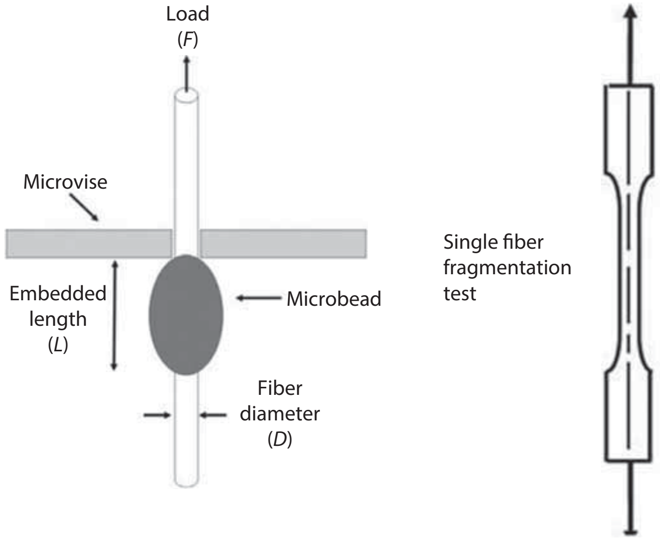

Figure 4 Schematics of the microbead (left) [24] and single fiber fragmentation (right) tests.

direction, the fiber starts to break into small fragments. With increasing strain, the fiber breaks incrementally into smaller fragments at locations where the fiber stress reaches the local fracture strength. The fiber fracture process continues until a point when no more breaks occur with additional specimen strain. At that time the test is complete and the fiber fragment lengths are measured. From the average fragment length (critical length) the IFSS is calculated using the following equation.

$$\text{Interfacial shear strength } (\tau) = \frac{\sigma_f\left(l_c\right)d}{2l_c}$$

where, σ_f is the fiber strength at the critical fragment length, l_c, and d is the fiber diameter. As can be seen from the equation above the fiber strength at critical fragment length, σ_f, is needed to obtain τ. This value is derived from tensile tests carried out on fibers at different gauge lengths and extrapolating the data to critical length using the weak link theory [72]. The principle behind this test is that the fiber will continue to fragment into shorter and shorter lengths until they are too short to develop tensile stresses via shear transfer from the matrix sufficiently to further fracture the fiber [16].

An issue with all these IFSS tests is that different tests performed on the same fiber/resin system are unable to provide similar quantitative answers. This is because of the differences in the specimen geometry and the way the test is conducted which results in different stresses and different failure modes and, hence, give different interfacial strength values. Further, the stresses in actual use may be complex and not represented in these tests. These issues with existing characterization techniques for the adhesion in composites have been one of the factors prompting continued development of new characterization methods.

One of the recent advances in this area has been the establishment of in-situ monitoring methods. These techniques allow for the measurement of the composite properties during the fabrication process as well as during their actual use providing real-time feedback on the composite status or in a sense, its 'health'. Among the approaches which are being developed in this regard are the use of ultrasonic and fiber optic sensors which monitor the events occurring at the fiber/resin interface when loaded [73]. In earlier conventional test methods it was necessary to remove the load from the structure, place a transducer on the structure and then inspect the unloaded structure.

Another area in composite interfaces which has been receiving a great deal of attention is the development of mathematical models to better explain the features of interfaces [26]. A number of studies that have been published use finite element analysis to understand the effect of different resin and filler materials on the interface properties [74–76]. The mathematical details of these approaches are quite complex in nature but realistic simulation results are being produced in many cases [77].

Koyanagi and coworkers [78] studied the interfacial adhesion between carbon fibers and epoxy resin. Their paper described the methods for evaluating interface mechanical properties using SFC specimens. In particular, they have discussed the test-type dependence on the obtained IFSS and suggested that the cruciform specimen technique was a more appropriate test method. Moreover, the time and temperature dependences of the interface strength and the interface failure envelope under a combined stress state were also described.

Another approach to interface strength characterization in fiber reinforced composites by means of micromechanical tests has been discussed by Zhandarov and Maeder [25]. They focused on single fiber pullout and microbead techniques and discussed the advantages and disadvantages of stress-based and energy-based models of interfacial debonding and corresponding adhesion parameters (local interfacial shear strength, critical energy release rate, and adhesion pressure). Following analytical models were developed in their study to measure the adhesion parameters as well as to determine the interfacial frictional stress: 1) the use of the debond or 'kink' force from the force-displacement curves, 2) two-parameter fit of experimentally measured maximum pullout force as a function of embedded length, and 3) models assuming two-stage debonding with imperfect interface at the second stage.

Each of the methods mentioned above has inherent problems and limitations that restrict its applicability as a universal test method for characterization of interfacial adhesion strength [79]. Also, all of these techniques deal with individual fibers but not multiple fibers as in the case of real composites and, hence, may not reflect the true interfacial property in composites. Due to the complex behavior of the interface, it is not clear at the present time if a correlation exists between the

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results obtained among the above described test methods. As a result, when the interfacial strength or characteristics are mentioned, these are usually referenced to a specific test method.

Besides the destructive methods described above, some nondestructive evaluation (NDE) techniques [80] such as radiography, acoustic emission, thermal NDE methods, optical methods, vibration damping techniques, chemical spectroscopy, etc., have also been applied to study the fiber reinforced composites. Among these techniques, the vibration damping method, which is based on energy dissipation theory, has been increasingly used for measuring interfacial adhesion. The principle of the method is based on the theory of energy dissipation. Accordingly, the quality of interfacial adhesion in composites can be evaluated by measuring the part of energy dissipation contributed by the interface, assuming that the interface part can be obtained by separating those of resin and fiber from the total composite. The energy dissipation of a material can be evaluated by the damping of the material. Nowick and Berry [81] summarized the techniques currently used for measuring vibration damping of materials and structures. The techniques for the measurement of damping often deal with natural frequency or resonance frequency of a system. In general, the investigation of vibration can be categorized as free vibration (or free decay) or forced vibration. Free vibration is executed by a system in the absence of any external input except the inputs of initial displacement and velocity. For example, it is possible to have a wire sample gripped at the top, and have a large weight hanging freely at the bottom; this system can be set either into longitudinal or torsional oscillation. The latter represents the well-known 'torsion pendulum', developed by Ke [82] in which the strain at any point can be expressed in terms of the angular twist of the inertia member.

Typical forced vibration techniques include the free-free beam technique [83] and the piezoelectric ultrasonic composite oscillator technique (PUCOT) [84–86]. These techniques have been applied to dynamic mechanical analysis (DMA) which is a widely used technique in polymer studies, and has attracted even more attention for interface characterization. However, the instrument is relatively expensive and cannot be operated at a high frequency which can provide more information from the tested materials. Vibration damping is increasingly being applied to characterize interfacial adhesion for composites which may see vibrations and damping during their use.

National Physical Laboratory (UK's National Measurement Institute) research has focused on developing measurement methods and predictive analysis for characterizing interfacial properties of fiber reinforced plastics and the role of the interface and interphase on thermal and mechanical performance of these materials. The aim is to provide more accurate methods and models for measuring and predicting interface and interphase properties to enable materials developers and users to tailor and optimize their performance. Measurement techniques based on instrumented nanoindentation and atomic force microscopy have been employed to obtain high-resolution maps of the elastic modulus and topographic images for

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transitions between fiber and interphase, and interphase and resin in composite materials. The measurement techniques being developed are considered relevant to conventional continuous and discontinuous fiber reinforced polymeric materials (including nanocomposites) and are expected to contribute to the improvement in multifunctionality of nanocomposites.

Most methods described above are primarily used for fiber/resin systems based on petroleum. However, they can be used for green composites as well.

4 Interfaces in Thermoplastic Green Resins

Many studies have been conducted on composite materials that combine natural cellulosic fibers with green thermoplastic polymers such as poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHAs) including poly(hydroxybutyrate) (PHB) and their copolymers such as poly(3-hydroxy butyrate-co-3-hydroxyl valerate) (PHBV), poly(caprolactone) (PCL), etc. [87–89]. These composites are slowly finding their way in commodity and non-structural applications such as casings of electronic products, interior parts of automobiles, etc. [15].

Research on biodegradable polymers as composite resins has been limited in comparison with research on petroleum based thermoplastic and thermoset polymers simply because of their relatively poor availability and high price. Most of the composites developed, however, have tensile and flexural strengths lower than 100 MPa which restricts their use in applications where higher strength is required.

PLA is a biodegradable thermoplastic polymer and its basic component is lactic acid which is derived from corn starch. Lactic acid is either polymerized to poly(lactic acid) by condensation polymerization reaction or via ring opening polymerization of a di-lactide intermediate [90–93]. Numerous tests have shown that PLA is a suitable resin for reinforcing with fibers to form composites [94–100]. It can form green composites when reinforced with plant based fibers. However, being hydrophobic PLA does not bond well to plant based fibers. Several research papers have dealt with the optimization of the process parameters and properties of the fiber reinforced PLA composites. Yamashita *et al.* [101] modified PLA resin with micro-fibrillated cellulose (MFC) and found significant increase in toughness of the resin and composite reinforced with bamboo fibers. Adding just 10% MFC to PLA was sufficient to increase the fracture toughness of the composite by about 90%. While MFC has high strength and helps reinforce the resin, the large amount of interface provided by the incorporation of MFC and poor MFC/PLA bonding combine to provide sufficient debonding energy to improve the toughness. Kimura *et al.* [102] examined compression molded ramie fiber reinforced PLA composites with respect to their tensile and bending strengths as well as stiffness by varying the fiber volume between 45% and 65%. Apparently, the compression molding pressure provides better fiber/resin bonding through mechanical means as the resin is forced in between the fibers and also to occupy the valleys created

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by fiber roughness. Ochi [103] investigated kenaf fiber/PLA composites where tensile strength and flexural strength as well as Young's modulus increased linearly up to a fiber content of 50%. The unidirectional biodegradable composite materials were fabricated from kenaf fibers and PLA which showed tensile and flexural strengths of 223 MPa and 254 MPa, respectively. Pan *et al*. [104] produced kenaf fiber/PLA composites by melt mixing and injection molding with fiber content up to 30%. Their results indicated that the tensile strength steadily improved with fiber content up to 30%. In this case also the molten resin was forced between the fibers occupying the valleys created by fiber roughness providing mechanical contribution to the kenaf/PLA interface. Bax and Muessig [105] studied injection molded flax and cordenka fiber reinforced hybrid PLA composites. Cordenka fibers are high strength rayon fibers that are commonly used for reinforcing in tires, hoses and composites. While the impact strength of pure PLA could be significantly improved by adding cordenka fibers, the flax fiber/PLA composites showed inferior properties. Cordenka fibers have high surface energy and rough surface. While high surface energy does not allow bonding with PLA, the rough surface provides means for mechanical bonding. Mittal [106] discussed the role of the interface in strength of adhesive joints. The interfacial tension between the substrate and the adhesive is the most important criterion: the lower the interfacial tension, the higher the joint strength. Ganster and Fink [107] investigated injection molded cordenka fiber reinforced PLA with a fiber weight content of 25%. Stiffness and strength values of the composites were approximately doubled compared to pure PLA while the impact strength was three times higher. Shibata *et al*. [108] fabricated compression molded lyocell fabric and PLA composites. Lyocell is a cellulosic fiber spun from its lyotropic solution. Tensile modulus and strength of lyocell/PLA composites improved with increasing fiber content and the impact strength was considerably higher than that of pure PLA. Fabrics, because of their weave and open spaces, provide significant possibilities for fiber/resin mechanical interaction. This, in turn, results in better mechanical properties. Oksman *et al*. [109] reported the work on flax/PLA composites and compared them to more commonly used flax/PP composites. Because of the brittle nature of PLA triacetin was used as plasticizer for PLA and flax/PLA composites in order to improve the toughness. Preliminary results showed that the mechanical properties of flax/PLA composites were about 50% stronger than the flax/PP composites. Again, this is due to better flax/PLA mechanical interaction. Van den Oever *et al.* [110] examined the different types of plant fibers such as ramie, flax and cotton as reinforcement for PLA to form composites. Their findings showed that the flexural stiffness of composites, which is a function of fiber properties, increased linearly with fiber content for all types of fibers while the impact strength reduced with increasing fiber content.

Huda *et al.* [88] studied the kenaf fiber reinforced poly(lactic acid) (PLA) laminated (layered) composites which were prepared by compression molding using

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the film-stacking method. The objective of this study was to evaluate the mechanical and thermal properties of these composites as a function of kenaf fiber modification using alkali and silane treatments. It was found that both silane treated and alkali treated fibers offered better interfacial bonding and thus reinforced composites showed superior mechanical properties compared to untreated fiber reinforced composites. The alkali followed by silane treated fiber reinforced composites also significantly improved mechanical properties. In this study, the processing method also played an important role in the impact property of the kenaf reinforced composites. It is well known that the impact response of fiber laminated composite materials is highly influenced by the interfacial bond strength as well as the resin and fiber properties [111, 112]. They stated that enhanced fiber/resin bonding coupled with weakened intercellular affinity, in the case of unidirectional laminates, serves as the prerequisite for an enhancement of impact strength. Improvement of kenaf/PLA interfacial adhesion alone, however, does not necessarily increase the impact performance [112, 113].

Luo and Netravali [114] studied the interfacial property in composite prepared using henequen fibers and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) resin. The interfacial shear strength was characterized by both SFC and microbead techniques. The henequen fiber/PHBV IFSS was 6.97 MPa, as measured using the SFC test, and 5.24 MPa, as measured by the microbead test. The low IFSS compared to most other fiber/resin systems was a result of the combination of hydrophobic PHBV and hydrophilic henequen fibers. No attempt was made to alter fiber surface or add a coupling agent to the resin to improve the henequen/PHBV IFSS. In another study Luo and Netravali [115] reported the mechanical and thermal properties of green composites made from pineapple fibers and the same PHBV resin. Tensile and flexural properties of the composites were found to be significantly higher in the longitudinal direction than the virgin resin after incorporating pineapple fibers. They also studied the average IFSS between the pineapple fiber and PHBV resin (8.23 MPa) as measured by the microbead technique [116]. Scanning electron microscopy (SEM) images of the microbead specimens revealed an interfacial failure. This was expected because of the noncompatible, hydrophobic/hydrophilic, chemistry between them. However, the higher IFSS compared to henequen/PLA was due to the fibrils on the fiber which got embedded in the resin providing strong mechanical interaction with the resin. As a result, green composites prepared by combining pineapple fibers and PHBV with 20 and 30% fiber weight content showed significantly higher tensile and flexural properties compared to virgin PHBV resin.

Poly(hydroxyalkanoates) (PHAs), a family of biodegradable aliphatic polyesters, differ from petroleum based synthetic polymers with regard to their being renewable resource and biodegradability [117]. Singh and Mohanty [118] developed green composites using natural bamboo fibers and PHBV. The fabrication of the green composites was carried out using injection molding following the

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extrusion compounding of PHBV and bamboo fiber with loadings of 30 or 40 wt%. It was found that tensile modulus of the PHBV composites increased with the fiber loading. At 30 wt% fiber loading the modulus increased by 67% and at 40 wt% the increase was 175%, while at the same time the tensile strength of PHBV decreased with further addition of bamboo fiber. They attributed this phenomenon to the lack of sufficient fiber/resin interfacial interaction, again due to incompatible chemistry between the two. The tensile and flexural moduli of PHBV based biocomposites reinforced with 40 wt% wood fiber was improved by 167% compared with neat PHBV. For the thermo-mechanical behavior, it was shown that the storage modulus of PHBV increased with the increase in fiber loading up to 40 wt% [117].

Lee and Wang [119] investigated the effects of lysine based di-isocyanate (LDI) as a coupling agent on the properties of biocomposites with poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) reinforced with bamboo fiber (BF). LDI was specifically added to improve the fiber/resin interfacial bonding and they did see improvements in the interfacial adhesion of both PLA/BF and PBS/BF composites because of crosslinking between the resin and the fiber. They also observed higher tensile properties and water resistance as a result of improved interfacial bonding.

Green composites composed of lyocell fabric and biodegradable polyesters, PHBV, poly(butylene succinate) (PBS) and poly(estercarbonate) (PEC), were prepared and studied by Shibata *et al*. [108]. The tensile modulus and strength of all the biodegradable lyocell/PHBV composites were found to increase with increasing fiber content. The effect of the surface treatment on the flexural modulus of the fiber reinforced composites was not so pronounced. This may be because the surface roughness of the fabric already provides good mechanical bonding. The flexural strength of PBS composites increased with fiber content, and esterification of the fiber by butyric anhydride gave the best result. While for the PEC/PLA resin based composites, flexural strength increased slightly with increased fiber content (0–20 wt%) in the case of using untreated fiber, and it increased significantly in the case of fibers esterified by butyric anhydride. Surface esterification using butyric or acetic anhydride was effective in increasing the flexural strength of PBS and PEC/PLA composites. For the PLA composite, flexural strength did not increase with the fiber reinforcement.

Among natural polymers, starch is one of the most promising materials because of its attractive combination of availability, low price and thermoplastic behavior, besides being biodegradable and renewable. Starch, made up of glucose molecules, also has the matching chemistry to bond well to cellulosic fibers through hydrogen bonding.

Alvarez and coworkers [120, 121] and Alvarez and Vazquez, [122] developed composites from thermoplastic starch based resins and sisal fibers. The thermal, melt rheological and creep properties were investigated extensively. It was reported that the shear rate was the most influential processing condition with respect to the material morphology. The intercalation effectiveness of the resin in the fibers is directly linked to the rheological behavior. The addition of sisal fibers

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to the starch resin promoted significant improvement in the composite creep resistance and thermal properties. Since sisal fibers do not creep much, good interfacial bonding with the starch, due to the chemical similarity and hydrogen bonding, was responsible to enhance the creep resistance of the composites.

Shibata *et al.* [123] investigated the effects of the volume fraction and fiber length on flexural properties of biodegradable composites. Kenaf and bagasse were mixed, individually, with corn starch based resin, and composite flexural specimens were fabricated by press forming. Bagasse was found to be more compressible than kenaf due to its hollow or cylindrical nature. For up to 60% volume fraction kenaf and 66% bagasse composites, the flexural modulus increased with increase in fiber volume fraction, and these results were in good agreement with the calculated values. Fiber/resin bonding for both kenaf and bagasse was expected to be good because of the chemical similarity. Decrease in flexural modulus was seen for fiber lengths of 2.8 mm kenaf and 3.2 mm bagasse, which could be assumed as below the critical fragment lengths. Beyond these fiber lengths, there was no change in the flexural modulus of the composite specimens.

Gomes *et al*. [124] fabricated green composites by reinforcing a corn starch based resin with curaua fibers. The fabrication process consisted of using stretched slivers of curaua fibers which resulted in unidirectional composites as stretching promoted parallel fiber arrangement. They further improved the fiber properties by alkali (NaOH) treatment, commonly known as mercerization which removes lignin and hemicellulose and leaves only cellulose. This increases the fiber/resin bonding through hydrogen bonding. Tensile test results showed that alkali-treated fiber composites had fracture strain two to three times that of untreated fiber composites, without a considerable decrease in strength. The tensile strength level achieved by untreated and alkali-treated fiber composites is not only attributable to fiber's tensile strength but rather to the factors such as improvement of interfacial bonding between fibers and matrix and decrease in the variability of alkali-treated fiber's strength. Alkali removes lignin and retains cellulose. This, in turn, improves the fiber wettability and the fiber/resin IFSS.

Rosa *et al.* [125] studied the tensile and thermal properties of treated coir fibers and starch/ethylene vinyl alcohol (EVOH) copolymer blend composites. They evaluated the mechanical and thermal properties of starch/EVOH/coir biocomposites. Coir fibers received three treatments: washing with water, alkali treatment (mercerization) and bleaching. All treatments modified the coir surface and resulted in improved thermal stability of the fibers and consequently of the composites. The best results were obtained for composites made using mercerized coir fibers where the tensile strength increased by about 53% compared to untreated coir fiber composites and about 33.3% compared to unreinforced starch/EVOH resin. As discussed earlier, mercerization improved fiber/resin adhesion, promoting good wettability and allowing an efficient stress transfer from the matrix to the fibers. Mercerization also reduced the coir fiber diameter and thereby increased the aspect ratio, improving composite properties.

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Liu *et al*. [126] prepared composites using bamboo cellulose crystals (BCCs), obtained by HNO_3–$KClO_3$ treatment and sulfuric acid hydrolysis, and glycerol plasticized starch. Results showed that tensile strength and Young's modulus of the starch/BCC composite films were enhanced by the incorporation of the crystals due to reinforcement of BCCs and reduction of water uptake. BCCs at the optimal 8% loading level exhibited a higher reinforcing efficiency for plasticized starch resin than any other loading level. Besides better BCC/starch interfacial bonding, decreased water uptake also accounted for the increased modulus and strength of the composites.

High strength composites were developed using Manila hemp fiber bundles and a starch-based emulsion-type biodegradable resin [127]. The tensile and flexural strengths of the composites increased with increasing fiber content up to 70%. These composites showed excellent tensile and flexural strengths of 365 MPa and 223 MPa, respectively. The fabrication with emulsion-type biodegradable resin contributed to reduction in voids and better fiber contact in the composites. As stated earlier, starch and cellulosic fibers have excellent chemical compatibility to form hydrogen bonds. Further, both the absence of voids and good fiber/resin contact contribute to good interfacial bonding, particularly mechanical bonding, because of the rough and fibrillar surface of the fibers. Takagi [128] also studied high strength and functional natural fiber reinforced composite materials using the same starch based resin but with Manila hemp fibers. Their results showed that the tensile strength of the cross-ply composites was maximum over 50 wt% due to the interaction between warp and weft during the hot-pressing. However, in the case of flexible weft such as cotton thread or resin fiber, the tensile strength of the cross-ply composites almost linearly increased with increasing fiber content.

Guimaraes *et al*. [129] studied the characterization of corn starch by X-ray powder diffraction and thermal analysis, as well as the processing and characterization of banana/sugarcane bagasse/starch fiber composites. Thermal analysis of corn starch showed good thermal stability for making composites. The composites of the same resin with banana and bagasse fibers prepared by compression molding showed more homogeneous composites with unpurified glycerin and structural changes in both resin composites, while their morphology was dictated by the properties of the fibers rather than by the resin. Improvements in tensile properties were observed in these composites over those of pure resin, which was explained based on fractographic observations. In the case of composites, tensile properties showed dependence on the processing method and temperature and applied pressure improved the properties of the composites with the same amount of fiber content.

5 Interfaces in Thermoset Green Composites

It is known that resins derived from natural oils (soybean, castor, linseed, etc.) can be used as substitutes for petroleum based thermosetting resins such as

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unsaturated polyesters, vinyl esters, and epoxy resins [130]. Natural oils are triglycerides of fatty acids, and they can polymerize when chemical functionalities are added on their active sites, particularly the double bonds. Epoxidation, ring opening reaction with haloacids or alcohols, ozonolysis, and hydration are some of the methods used to functionalize unsaturated plant oils [130]. Newly developed plant oil based resins are being tested by end-users and converters for high-volume composite applications in agricultural equipment, automotive components, civil infrastructure (bridges and highway components), marine structures (pipes and offshore equipment), rail infrastructure (carriages, box cars, and grain hoppers), and construction industry (particle board, ceilings, and engineered lumber). A broad range of fibers and fiber loadings (5–90%) have been investigated. The most common resins are epoxidized natural oils crosslinked with anhydrides, and polyurethanes made from natural polyols and di-isocyanates from petrochemical feedstock. Lee *et al.* [131] used a polyol from castor oil in a mixture with polycaprolactone diol to prepare castor oil-based polyurethanes with controlled mechanical properties. Hemp fibers modified with isocyanate were used to reinforce the polyurethane biocomposites [131]. In this study, castor oil converted to polyol was mixed with another polyol, polycaprolactone diol (PCL), to control the mechanical properties of castor oil based polyurethane. Hemp fiber was used to reinforce the polyurethane biocomposites. To improve the interfacial adhesion between the hemp fiber and the polyurethane matrix, the hemp fiber was reacted with isocyanate during polymerization of the castor oil/PCL polyurethane. A castor oil/PCL-based polyurethane (CPU) biocomposite reinforced with hemp fiber (HCPU) was also prepared. To improve interfacial adhesion between the hemp fiber and the CPU matrix, the hemp fiber was reacted with diphenylmethane di-isocyanate (MDI). Fourier transform infrared (FTIR) spectrum confirmed that urethane bonding had occurred at the fiber surface. With good fiber/resin bonding the Tg of the HCPU biocomposite was higher than that of pure CPU resin. However, in HCPU composites, as with CPU, the Tg decreased and the mechanical properties increased with increasing PCL content.

Epoxidized natural oils were reacted with acrylic acid to form acrylate epoxidized oil by Hong and Wool [132] and used for preparing composites with avian (chicken) feather fibers for use in modern high-speed microelectronics. This environmentally friendly, low cost composite can be a substitute for petroleum based composite materials. Keratin fibers are hollow, light, and are compatible with soybean (S) resins including acrylated epoxidized soybean oil (AESO). The incorporation of keratin fibers in the soy oil polymer enhanced the mechanical properties such as storage modulus, fracture toughness, and flexural properties. The fracture energy of a single keratin fiber in the composite was determined to be about 3 kJ/m^2 with a fracture stress of about 100–200 MPa. Considerable improvements in the keratin fiber (KF) and AESO composite properties should be possible by optimization of the resin structure and fiber selection. It was observed that the keratin fibers were broken without complete pullout during the fracture process

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indicating good adhesion between AESO resin and keratin fibers, as expected. The nodes and hooks on the feather fibers further increase the wetted surface area and mechanical bonding.

Nam and Netravali [133, 134] studied ramie fiber/soy protein concentrate (SPC) IFSS using the microbead technique. Soy resin has the ability to crosslink when hot-pressed because of the cysteine amino acid which forms -S-S- bonds. As mentioned earlier the cellulose/soy protein bonding is very good. The high IFSS values obtained for the ramie/SPC resin (22.8 MPa) indicated strong interfacial interaction between the two. This strong interfacial interaction is a result of a highly polar nature of both the ramie fiber and the SPC resin as well as the rough fiber surface. High IFSS can result in brittle, low toughness composites. They also studied the effect of glycerin, used as plasticizer, on the IFSS and found that glycerin was attracted to the fiber, disrupting the fiber/resin bond. With 60% glycerin (on SPC wt basis), the IFSS dropped to 13 MPa. Further, in their study, ethylene plasma polymerization was used to reduce the IFSS and, thus, improving its toughness. The plasma polymer imparted a polyethylene-like, non-polar polymer coating on the fiber surface. This also resulted in the fiber surface becoming smoother compared to the untreated fiber. Both fiber smoothness and non-polar nature of the coating reduced the ramie fiber/SPC resin IFSS. The ramie fiber/SPC resin IFSS reduced from 15 MPa for untreated fiber to about 11 MPa for fiber treated for 1 min and about 8 MPa for fiber treated with ethylene plasma polymer for 10 min. The load vs displacement plots for IFSS tests obtained for different fiber/resin combinations showed different failure modes. For plasma treated fibers with low IFSS, stick-slip type behavior was observed.

Lodha and Netravali [135] characterized the IFSS between ramie fiber and soy protein isolate (SPI) polymer using the microbond technique and found it to be in the range of 30 MPa. As stated earlier the high IFSS is because both ramie fiber and SPI polymer have polar groups which provide strong hydrogen bonding.

Mehta *et al*. [136] used unsaturated polyester resin and characterized the interface with hemp fibers. Alkali treatment and coupling agents including silane, unsaturated polyester and acrylonitrile were used to improve fiber/resin adhesion. They found improvement in tensile strength for most of the treatments indicating better fiber/resin adhesion but bending strength and impact strength were essentially unchanged. Cellulosic fibers were also treated with maleic anhydride, acrylic acid and silane coupling agent by Ganan and Mondragon [137] to increase compatibility between fibers and unsaturated polyester resin. Interfacial characteristics were evaluated using dynamic mechanical properties which showed significant improvements.

Biodegradable thermoset resins from cashew nut shells were reinforced with hemp fiber bundles by Mwaikambo and Ansell [138] to make composites and characterize their properties. Fibers were also mercerized with 4 and 6% NaOH solution. This treatment resulted in the highest Young's modulus and tensile strength of 65 GPa and 1064 MPa, respectively, of fibers as compared to the untreated fibers which had corresponding values of 38 GPa and 591 MPa, respectively. The treated

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fibers with the highest strength were used as reinforcement for cashew nut shell liquid resin. The unidirectional composites exhibited the best mechanical properties and composites with lowest porosity offered the highest mechanical properties. Increase in the molding pressure resulted in an increase in the mechanical properties for treated nonwoven hemp composites in which the presence of inherent binders in the fibers contributed to better fiber/resin contact. This is perhaps because of the pressure pushing the resin in between the fibers resulting in better fiber/resin contact and enhancing the mechanical bonding.

Silva and Frollini [139] emphasized the use of sugarcane bagasse to prepare composites with sodium lignosulphonate resin (product of natural and renewable sources with a high content of phenolic groups), which completely replaced phenol in a phenolic resin. Sugarcane bagasse fibers were sonicated in sodium lignosulphonate (NaLS) solution for 1 h and dried at 105 °C. Phenolic prepolymers and composites, reinforced with sugarcane bagasse fibers randomly distributed in the matrix (50 and 70 wt%, about 15 mm length), were prepared and characterized. Phenolic composites (PCs) and sodium lignosulphonate/formaldehyde composites (LSFCs) were prepared with sugarcane untreated and treated bagasse fibers as reinforcement. The impact strength of composites increased when the fibers were treated with sodium lignosulphonate (LSFCs), mainly at 50 wt% of fibers. These results indicate that the presence of moieties typical of lignin on the sugarcane fiber surface, due to the adsorption of sodium lignosulphonate (NaLS), improves the adhesion at the fiber/resin interface, as sugarcane bagasse has a high content of lignin (22.49%), that is, the fiber/resin affinity is intensified when the fiber is treated with NaLS due to increased compatibility.

Notwithstanding the intense research at the academic level, large-scale commercialization of green composites is still in its early stage compared to the large volume of biocomposites containing natural oil derived resins, mainly due to their higher costs.

Thermosetting green composites have not yet gained significant production volumes due to the scarcity of suitable biobased thermosets in the market. Among those available, green composites containing soybean oil based resin have recently appeared on the market [130]. Jakob Winter (Germany), for example, has developed Green LinE, a line of products made with flax and hemp fibers embedded in epoxidized natural oil based resins. The composites are manufactured by dipping natural fibers in desirable forms such as needlepunched nonwovens or woven/knitted fabrics in the resin followed by compression molding. According to the manufacturer, these biocomposites can be varnished and laminated. Environ Biocomposites Mfg. (Mankato, Minnesota) sells different composite product lines, where soybean based resin is combined with waste fibers such as recycled newsprint, wheat straw, and sunflower hulls. These biocomposites have been commercialized in the form of lightweight panels with colorful granite look for nonstructural indoor applications. Recently developed green composites based on natural oil derived thermoset resins are presented in Table 3 [140].

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Table 3 Recently developed green composites based on natural oil derived thermoset resins [140].

Composite manufacturing process	**Fiber**	**Resin**	**Fiber weight content**	**Reference**
Vacuum assisted resin transfer molding	Chicken feather	Acrylated epoxidized soybean oil + styrene	5–20%	130
Vacuum assisted resin transfer molding	Chicken feather	Soybean oil pentaerythritol glyceride maleate	5–20%	130
Resin transfer molding	Hemp	Castor oil + PCL + diphenylmethane di-isocyanate	5%	129
Sheet molding compound process	Luffa	Castor oil + diphenylmethane di-isocyanate	10%	139
Compression molding	Flax	Methacrylated soybean oil + styrene	60%	140
Compression molding	Jute	Polyurethane and epoxy resins from *Mesua ferrea* seed oil	50%	141
Compression molding	Hemp	Epoxidized linseed oil + methyl tetrahydrophthalic anhydride	0–65%	142
Compression molding	Wheat straw	Linseed oil, maleic anhydride and divinylbenzene	50–90%	143
Compression molding	Flax	Epoxidized soybean oil	0–15%	144
Compression molding	Coir, sisal	Castor oil + diphenylmethane di-isocyanate	14–30%	145
Resin transfer molding	Kenaf	Epoxidized soybean oil + maleic anhydride	10%	146
Resin transfer molding	Flax	Acrylated epoxidized soybean oil + styrene	20–40%	147

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6 Modification of Fiber/Resin Interface

Since different composites applications require different properties, it is critical to be able to manipulate the fiber/resin interfacial bonding to obtain the desired properties for the same fiber/resin combination. In fact, it is important to control the fiber/resin IFSS since most interfacial failures occur in shear mode rather than in tensile mode. This is particularly true for unidirectional composites when they could be loaded heavily during service. As mentioned earlier, it is generally accepted that fiber/resin IFSS is primarily controlled by three factors: *mechanical, chemical and fiber/resin surface energetics* [33]. The mechanical factors include thermal expansion mismatch between the fibers and the resin, surface roughness, post-debonding fiber/resin friction, specific surface area, and resin microvoid concentration adjacent to fibers. Most composites fabricated using thermoplastic or thermoset resins are processed at temperatures well above room temperature (RT). When the composites are cooled to RT, depending on the difference between the coefficients of thermal expansion (CTE) of the resin and the fiber, higher resin shrinkage can create circumferential compressive forces on the fiber, gripping it tightly [150]. This can result in significantly higher fiber/resin IFSS. However, at the same time, higher resin shrinkage, compared to fiber, can also create shear stresses at the fiber/resin interface as the resin shrinks in the longitudinal direction. This can reduce the IFSS if the resin shrinkage is significant [33]. In addition, if the fiber/resin bonding is strong, the resin shrinkage can also compress the fibers longitudinally and, thus, reduce the composite modulus. The fiber surface roughness provides interlocking between the fiber and the resin, thus increasing the mechanical bonding. Fiber surface roughness can also increase post-debonding fiber/resin friction which can enhance composite properties such as toughness. This, however, can only happen if the resin viscosity is sufficiently low and is able to flow into the valleys. Fiber surface roughness also increases the specific surface area of the fiber giving higher amount of interface area per unit weight or volume. Microvoids or bubbles around the fiber surface, created during processing or otherwise, reduce the fiber/resin interaction and, hence, reduce the IFSS. Fiber surface roughness can also contribute to the microvoids, particularly, if the fiber and resin surface energies differ significantly and the resin viscosity is high and is unable to fill the valleys. Chemical factors that influence fiber/resin IFSS include covalent bonding, hydrogen bonding such as acid–base interactions, and van der Waals interactions. Covalent bonding between the fiber and resin can provide strong interaction and can increase the IFSS significantly. Hydrogen bonding or acid–base interactions can also increase the interfacial interaction. However, hydrogen bonds and van der Waals interactions are weak (< 5 kcal/mol) compared to covalent bonding (~ 100 kcal/mol). While polar groups (e.g., $-NH_2$, -OH, -COOH, etc.) are required on both fibers and resin to form hydrogen bonds, the

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resin and fiber must also be in close proximity for van der Waals interactions or to form hydrogen bonds.

Most fibers, particularly the plant based ones, have a characteristic surface roughness or texture as a result of their fibrillary nature. This, in turn, imparts a roughness to the interface when the fibers are incorporated in a resin to fabricate a composite. Mechanical "lock and key" situation created by the hills and valleys of the fiber surface and how the resin negotiates them is an important but generally neglected aspect of the interface in the composites. It turns out that the mechanical bonding induced by the fiber roughness is quite important in all composites. Surface roughness can contribute to bonding only if the liquid resin is able to fully wet the fiber surface. If the liquid resin is unable to penetrate the asperities on the fiber surface, then the matrix resin can trap air in the valleys and leave interfacial voids on solidification. Interfaces in real composites are invariably rough, particularly those with natural fibers which tend to be fibrillar and not so smooth as the synthetic fibers, which allows for mechanical interlocking. The degree of interfacial roughness can be controlled to some extent, but there is always some mechanical bonding present. For example, during the fiber processing some fibrils may be separated and protrude out. These can get embedded in the resin while fabricating the composite providing additional mechanical bonding.

The stress transfer at the interface between two different phases, fiber and resin, is determined by the degree of adhesion. This situation calls for developmental strategies to modify surfaces of cellulosic fibers and thereby obtain an effective control over the fiber/resin interface. In order to improve the mechanical properties of composites, a coating can be applied on the fiber. The coating may consist of coupling agents or compatibilizing agents that can form covalent and/or hydrogen bonds with both fiber and the resin. Effects of coupling agents on cellulosic fibers containing reinforced thermoplastic composites and their influence on mechanical properties of composites have been reported by many researchers [151–153]. Raj *et al*. [151] studied the composite with linear low-density polyethylene (LLDPE) which was reinforced with chemithermomechanical pulp (CTMP) of aspen fiber, wood flour, and cellulose flour. Wood fibers were treated with isocyanate or a vinylsilane coupling agent to improve the adhesion between the fiber and polymer. Composites were made at different weight percentages of the fiber. Improvement in the tensile strength was seen when vinylsilane- or isocyanate-treated fibers were incorporated in the polymer. The tensile modulus remained relatively unaffected by the fiber treatment. The Izod-impact strength (un-notched) decreased at higher concentrations of the wood fiber in the composite.

Singh *et al*. [154] reported the effect of various chemical treatments such as organotitanate, zirconate, silane, N-substituted methacrylamide on the properties of sisal fiber reinforced polyester composites. Reinforcing fibers can be modified by physical and chemical methods. Many different approaches, reported in a number of reviews [9, 19, 155–160] have been explored to improve fiber/resin interface. These include fiber surface modification before composite fabrication via chemical

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esterification [161–166], etherification [161, 165, 166]), treatment with silane [9, 148, 157], or isocyanates [131, 167] or physical means (plasma [9, 158, 168–170] or corona treatments [168, 171] as well as modification of the polymeric resins [172, 173]. These treatments are briefly discussed in the following subsections.

6.1 Modifications of Green Resins

Yamamoto and coworkers [174] studied the interfacial properties between modified soy protein resin and kenaf fiber. In this case the soy protein isolate (SPI) was modified by adding a poly(carboxylic acid), Phytagel® (PG, Sigma-Aldrich Co., St Louis, MO), to make an interpenetrating network-like (IPN-like) structure of the resin. The effects of different PG wt% on the interfacial properties were characterized using SFC tests and optical microscopy. Since the kenaf fibers extracted from nonwoven mats for this study were short, length of each fiber was extended by gluing it to long polyethylene filaments on both sides. After drying the glue, dogbone shaped SFC specimens were prepared using pure and modified SPI resins. The dried SFC specimens were taken out from the mold and hot-pressed (cured) at 120 °C. The IFSS was calculated using the shear-lag analysis. Single fiber tensile tests at different gauge lengths were performed. The average stress values were used in calculating the IFSS. After the SFC tests, the specimens were observed under an optical microscope to characterize the fiber fracture modes and the region around the fiber fracture. The SFC test data showed that the IFSS was a function of the PG content. They found that the primary reason for this was the resin shrinkage which was controlled by PG. Interfacial failure mode was also found to be a function of the PG content. These findings were further confirmed by the microbead tests in which E-glass fibers were used with the modified SPI resins.

Mechanical properties of the SPC resin and hemp yarn/SPC were found to be significantly affected by the pH and protein content [24, 175]. This study showed that the fracture stress and Young's modulus of the SPC resin decreased with increasing pH values from 7 to 12 while their fracture strain and moisture content increased. Hemp yarn/SPC resin IFSS, however, increased with increasing alkaline condition and the maximum IFSS of 28 MPa was observed at pH 10. Unfolding of soy protein by addition of NaOH was thought to reduce its mechanical strength but increase the IFSS because of the exposure of the reactive groups forming hydrogen bonding and enhanced interaction with the fibers. The toughness of the composites increased up to pH of 10 and then decreased with further increase in the pH. Further, the IFSS increased with the protein content in the resins.

Jacob *et al*. [176] studied the interfacial and surface characterization aspects of natural fibers and their composites. Through different chemical modifications of natural fibers and characterization techniques they concluded that the fiber/resin adhesion was a major factor in determining the response of the interface and its integrity under stress. Both fiber surface and resin can be modified to obtain a strong interface. Various treatments being used for the lignocellulosic surfaces and

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the characterization techniques were illustrated in their study. The main interfacial characterization techniques used in this study were micromechanical techniques such as fiber pullout and SFC and were supported by spectroscopic, microscopic and swelling analyses.

Soy proteins have also been modified to improve the mechanical and thermal properties significantly and thus make the material more useful as resin [1, 115, 116, 133–135, 177–183]. Modified SPI by using stearic acid can improve the resistance to moisture absorption [115]. Modification of SPI with glutarldehyde and poly (vinyl alcohol) followed by fabrication of composites with flax yarns and fabrics can give good properties [179, 181].

6.2 *Modification of Fibers*

Fiber surface treatment is one of the important tools to improve the fiber/resin adhesion. Physical, chemical and morphological changes in fibers can be easily brought about through these surface treatments. These changes can lead to improved composite properties due to increased surface area of the fiber, chemical bonding and fiber/resin adhesion. Plant based hydrophilic fibers are incompatible with the hydrophobic polymer matrix and have a tendency to form aggregates. They also exhibit poor resistance to moisture. To eliminate the problems related to high moisture absorption, fiber treatments with hydrophobic aliphatic and cyclic chemicals containing reactive functional groups capable of bonding to the reactive groups in the resin have been tried. These modifications of natural fibers make the fiber hydrophobic and improve their interfacial adhesion with the hydrophobic resin. Chemical treatment of natural fibers such as de-waxing, de-lignification, bleaching, acetylation, cyanoethylation, chemical grafting, etc., have been used for modifying the surface properties of the fibers for enhancing its performance. Likewise, some physical methods have also been used to modify the fiber surface properties which ultimately improved the composite characteristics. Both methods are described below in details.

6.2.1 Physical Modifications of Fibers

Physical and high energy treatments can alter structural as well as surface properties of the fibers without the use of any chemical agent. These changes, in turn, influence the bonding between fiber and the resin. Four methods that can be classified as physical treatments include i) corona, ii) plasma, iii) heat treatment, and iv) steam pre-treatment. Corona treatments exploit the corona effect, i.e., the formation of high energy electromagnetic fields close to charged thin wires or points, with consequent ionization in their proximity even at atmospheric pressure and relatively low temperature [184]. It is one of the most interesting and easy techniques for surface activation by oxidation. In the ionized region, excited species (ions, radicals, etc.) are present and can actively modify fiber surfaces by introducing oxygen containing functional groups which increase the surface energy and,

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hence, the wettability by polar resins [106]. Polar groups also increase the possibility of fiber/resin hydrogen bonding. The corona method has been applied by various research groups on natural fiber reinforced composites [185]. Belgacem *et al.* [168] reported that the corona treatment of components remarkably improved the mechanical properties of the cellulose/polypropylene (PP) composites. A correlation was found between the mechanical properties of composites and the electrical conductance of aqueous suspensions of the corona treated cellulose fibers. The electrical conductance increased with the treatment level of cellulose fibers as a result of better interfacial contact.

Mechanical and rheological properties of cellulose/PE composites subjected to corona treatment were reported by Sapieha and coworkers [186, 187]. In their experiments corona treatments produced low molecular weight moieties on the surfaces of both PE and cellulose fibers. Corona treatment of one or both of the constituents resulted in decreased melt viscosities relative to compounds containing untreated materials. These treatments may act as lubricants at cellulose/PE interfaces. Corona treated fibers had higher apparent packing volumes in PE than untreated counterparts. This may have resulted from a reduction in their length when corona treated fibers were processed under high shear conditions. As a result of reduced length these fibers perturb the normal flow pattern in melt processing to a lesser degree than the longer fibers of untreated cellulose allowing better packing. Ragoubi and coworkers[188] used corona discharge to modify hemp fibers and found that the corona discharge modification of hemp cellulosic reinforcements rather than PP allowed greater improvements in the composite properties which resulted in an enhancement of 30% in Young's modulus and 32% in tensile strength.

Plasma treatment induces changes on the surface of the material where an ionized region is formed, depending on the gas used, which carries high energy photon, electrons, ions, radicals and excited species. Felix and Gatenholm [152] modified cellulosic fibers with cold oxygen plasma and characterized the interface in the system cellulose and LLDPE. Using SFC tests they showed that after only 15 s of treatment the IFSS was increased by 200%. They also measured the surface free energies of treated and untreated fibers and reported that the surface free energy of treated rayon fiber was increased. They also showed that the oxygen plasma increased the surface roughness as a possible explanation for the significant improvements in the IFSS. They suggested that hydroperoxide groups, which are assumed to be intermediates in the formation of different oxygen containing functional groups during oxygen plasma or corona treatment, may initiate grafting of the resin chains onto cellulose enhancing the interfacial interaction.

Physical treatments involve surface fibrillation, electric discharge, etc. [168, 189]. Surface modification by discharge treatment such as low temperature plasma, sputtering and corona discharge is of great interest in relation to the improvement in functional properties of plant fibers. Plasma technology has been widely used as an effective method for surface modifications of natural fibers such as

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flax [190, 191], sisal [192] keratin [193] and wood [194]. Low temperature plasma treatment, depending on the gas used, causes attachment of chemical/functional groups, surface etching (roughness), polymerization (coating), free radical formation, whereas sputter etching results primarily in physical changes such as surface roughness and this leads to increase in adhesion through mechanical interlocking [189]. Low temperature or cold plasma, such as radiofrequency plasma, has been a valuable technique to improve the surface characteristics of fibers and polymeric materials by utilizing the plasma components such as electrons, ions, radicals and excited molecules produced by the electrical discharge. Cold plasma generated under atmospheric pressure in the presence of inert helium can result in etching [189]. However, the radicals generated in the substrate can combine with oxygen in the atmosphere resulting in polar surface. The action of the plasma involves abstraction of protons and creation of unstable radicals that generate functional groups such as hydroxyl, aldehyde, ketone and carboxyl. Electrical discharge methods have been used for cellulose fiber modification to decrease the melt viscosity of cellulose-polyethylene composites [186] and to improve the mechanical properties of composites.

Heat treatment involves heating the fiber or processing the composite at temperatures close to those at which the components of natural fiber begin to degrade. When cellulose is heated, it undergoes both physical and chemical changes. Physical properties affected include weight, strength, crystallinity and color. Chemical changes include reduction of degree of polymerization (DP) brought about by bond scission, creation of free radicals, combination of radicals (crosslinking) and formation of carbonyl and/or carboxyl groups as a result of combining with oxygen. All these changes can enhance the fiber/resin interface and improve the mechanical properties of composites. Cao *et al*. (195) studied the improvement in mechanical properties of kenaf fibers by heat and alkali treatments before preparing composites. Compared with other heat treatment temperatures, the tensile strength of kenaf fiber at 140 °C exhibited maximum value, which was attributed to the increased crystallinity of fibers after heat treatment.

Steam stabilization, a process which controls the compressive deformation of lignocellulosic fiber through hydrothermal treatment has been employed for many fibers including bamboo [196, 197]. This can be accomplished by using steam generated from moisture within the compressed fiber at high temperature and thereby stabilizing the fibers in normal configuration. This treatment can achieve dimensional stability and, in some cases, fibrillation of fibers [196, 198]. In the study by Takagi *et al*. [197], three types of bamboo fibers were prepared as reinforcement to improve the mechanical properties of PLA at not only room temperature but also elevated temperatures. Bending, impact and thermal properties were evaluated for PLA and bamboo fiber (BF)/PLA composites. Annealing was applied to BF/PLA composites in order to improve their mechanical properties at elevated temperature. The experimental results showed that among the three bamboo fibers,

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steam-exploded filaments most significantly increased the bending strength of PLA matrix composites due to the highest interfacial strength between PLA and steam-exploded filament and addition of bamboo fibers promotes crystallinity of PLA in BF/PLA composites.

6.2.2 Chemical Modifications of Fibers

Natural cellulosic fibers are amenable to chemical modifications due to the presence of an abundance of hydroxyl groups that can be utilized. These hydroxyl groups form multiple hydrogen bonds between the cellulose molecules, thereby activating these groups that form effective interlocks within the system. Surface characteristics, such as wetting, adhesion, surface energy, or porosity of fibers, can be improved upon chemical modification. Further, the irregularities of the fiber surface play an important role in the mechanical interlocking at the interface. The interfacial properties can be improved through appropriate modifications which can result in changes in both physical and chemical interactions at the interface. A significant amount of work has been done in the field of chemical surface modification of natural fibers [199].

Chemical treatment of natural fibers that involves different processes such as de-waxing (de-fatting), de-lignification, bleaching, acetylation and chemical grafting have been used to modify the surface properties of the fibers for enhancing their performance. In particular, chemical modifications of the fiber surface through substitution of polar hydroxyl groups by nonpolar groups have been used as a successful route for improving mechanical properties of natural fiber composites [156, 198]. De-lignification/de-waxing is generally carried out by alcohol or benzene extraction or, more commonly, using caustic soda (NaOH) followed by alkali neutralization and drying at room temperature. This can improve the fiber/resin interface in the case of polar resins which can form hydrogen bonding. Caustic soda can also remove hemicellulose from the fibers increasing its cellulose content. This can increase the fiber tensile properties and help increase the composite properties. Many mild oxidative bleaching agents such as alkaline calcium or sodium hypochlorite and hydrogen peroxide are commercially used as well. Bleaching with hydrogen peroxide under alkaline conditions causes an increase in crystallinity index and surface roughness of the fiber due to the removal of lignin and hemicellulose. The increase in surface roughness of the fiber creates good interlocking with the resin, enhancing the interfacial adhesion between resin and fiber. As a result, the mechanical properties of bleached fiber composites are better [200]. Optimization of bleaching is important and if too strong, it can result in loss of fiber weight and tensile strength [201]. These losses are mainly attributed to the action of the bleaching agent or alkali or alkaline reagent on the noncellulosic constituents of fibers such as hemicellulose and lignin.

Coupling agents are known to enhance the fiber/resin bond and thus facilitate the stress transfer at the fiber/resin interface. Coupling agents are molecules that

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possess two chemical functional groups, one of which reacts with OH groups on the fiber and the other reacts with the resin, thus, covalently linking the fiber with the resin. As mentioned earlier, covalent bonding with 80–100 kcal/mole results in strong fiber/resin interface. However, in some cases covalent bond may be formed between the coupling agent and one of the constituents, fiber or resin, and secondary bonds such as hydrogen bonds with the other. The selection of the coupling agent that can combine both strength and toughness to a considerable degree to the composite can be critically important. This may be achieved by using longer coupling agents that covalently bond yet provide the needed flexibility at the interface for toughness. The most common coupling agents are silane, isocyanate and titanate based compounds [202]. Their chemical composition allows them to react with both fiber and the resin forming a covalent bridge between the two. In the case of cellulose fiber reinforced composites, isocyanates have been found to be reliable coupling agents with thermoplastic resins [19]. It is expected that the formation of primary (covalent) bonds between cellulose (OH groups) and isocyanate - and weak secondary bonds between thermoplastics and isocyanates improve the mechanical properties of wood fiber filled thermoplastics such as PP [203–205]. Pretreatment of fibers by coating with silanes or isocyanates, etc., provides better fiber dispersion by reducing the fiber-fiber interaction with the formation of a coating on the fiber surface [206]. These treatments are briefly described below.

6.2.2.1 Silane Treatments

Several theories have been proposed to explain the interfacial bonding mechanisms of silane coupling agents which are responsible for improved fiber/resin interactions and mechanical performance and hygrothermal stability of the composites [207–211]. Among these, the most widely accepted is chemical (covalent) bonding theory. In the chemical bonding theory, the bifunctional silane molecules act as a crosslink between the resin and the cellulose by forming a chemical bond with the surface of cellulose through a siloxane bridge while its organofunctional group bonds to the polymeric resin. This co-reactivity with both cellulose and resin via covalent bonds gives molecular continuity across the interface region in the composite. A number of factors affect the microstructure of the coupling agent, which in turn controls the mechanical and physical properties of the composites [210, 211]. These include the silane structure, its organo-functionality, acidity, drying conditions and homogeneity, the topology and the chemical composition of fiber surface. The general chemical formula of silane coupling agents is X_3-Si-R, which makes it a multifunctional molecule that can react at one end with the cellulose fiber surface and the other end with the resin phase. The 'R' group can react with the resin making a covalent bond while X group hydrolyzes to form a silanol group in aqueous solution. These groups react with the hydroxyl groups readily available on the cellulose fiber surface. While the 'R' groups may be vinyl, aminopropyl, glycidoxypropyl, etc., the 'X' groups can be chloro, methoxy or ethoxy. The

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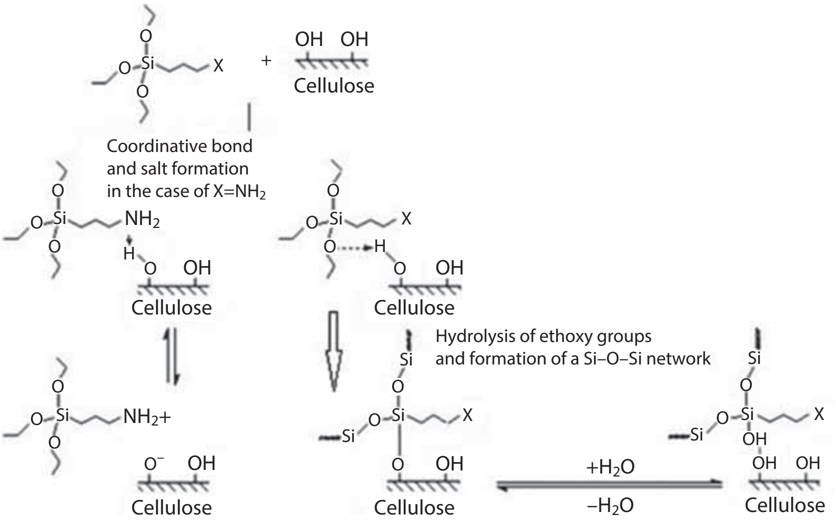

Figure 5 Schematic of silane coupling agent interactions with cellulosic fibers [212].

type of organofunctional group and pH of the solution dictate the composition of silane in the solution [212]. Figure 5 shows schematic of silane coupling agent interactions with cellulosic fibers [212]. It is, however, essential that both groups be chosen such that they can react with the functional groups in the resin under given curing conditions. Furthermore, the 'X' group must be chosen such that it can hydrolyze to allow reactions to take place between the silane and the OH groups on the cellulose surface. When the treated fibers are dried, a reversible condensation takes place between the silanol and –OH groups on the cellulose fiber surface, forming a polysiloxane layer, which is bonded to the cellulose surface [19]. When the silane coated cellulose surface is in contact with the resin, the 'R' groups on the fiber surface react with the functional groups present in the polymer resin, forming a stable covalent bond with the polymer. Apart from the chemical structure of silane, dispersion aids such as solvent and initiator (different organic peroxides) provide various chemical reactions as well as physical interactions at the interface. The coupling action of silanes can be accelerated by the presence of solvents and initiators which can reduce the treatment time. It is easy to see from the description above that the silane agents play an important role in improving fiber/resin interfacial characteristics which, in turn, improve the mechanical properties of the composites.

Kokta *et al*. [51] reported that composites with high density polyethylene (HDPE) and silane pretreated wood fibers showed greatly increased stiffness, but the elongation of the composites decreased with increase in filler concentration. They examined the influence of silane concentration, filler content and the nature

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of wood fiber on mechanical properties (tensile and impact strengths) of the composites. It was observed that the optimum tensile strength (at lower filler concentrations) can be achieved at 2 wt% concentration of silane [213]. Several other researchers who have worked with other fiber/resin systems have confirmed that treatment of fibers with silane coupling agents significantly improves the interfacial adhesion and, therefore, the mechanical properties of the composites [206, 213–215]. The performance of silane coupling agents in hardwood aspen fiber in different polymeric systems was reported by Raj *et al*. [216]. Treatment of wood fibers with silane coupling agent and polyisocyanate resulted in an increase in tensile strength as a result of better fiber/resin bonding. Lu *et al*. [202] studied corn stalk fibers (CSFs) modified chemically with alkali alone and a combination of alkali and silane coupling agents as reinforcements for PLA based composites to improve mechanical and thermal properties. It was observed that the treatment with a combination of alkali and silane was more effective in strengthening CSF/PLA bond and significantly improving the tensile and flexural strengths, crystallinity as well as heat deflection temperature of the CSF/PLA composites than the treatment with alkali alone.

6.2.2.2 Isocyanate Treatments

Isocyanates, in general, and poly(methylene) poly(pheny1) isocyanate (PMPPIC), in particular, are commonly used as wood binders in particle boards in Europe. Molecular structure of organic coupling agents normally has bi- or multi-functional groups. These functional groups isocyanates, maleic anhydrides, and dichlorotriazine derivatives interact with the polar groups, mainly hydroxyl groups of cellulose and lignin to form covalent or hydrogen bonding [46, 204, 216–218]. Alternately, organic coupling agents can modify the polymer matrix by graft copolymerization, thus resulting in strong adhesion, even crosslinking, at the interface. Isocyanates, however, are not considered to be environment-friendly or sustainable as they are derived from petroleum and tend to be toxic. Extensive experimental work on the application of isocyanates as coupling agents for different types of cellulose materials and polymers has been carried out by Kokta *et al.* [51]. They fabricated composites with cellulosic materials (cotton fiber, aspen wood fiber, saw dust), which were either pre-coated with an isocyanate polymer mixture or the isocyanate compound was added directly into the mixture of fiber and polymer. Various parameters concerning the performance of isocyanates as coupling agents were researched. Longer premixing time (e.g., 20 min) was shown to lead to improvement in mechanical properties of the composites. Moreover, the chemical structure of isocyanate, which provides a better interaction with thermoplastics, resulted in superior properties. Again, isocyanate can act as a promoter or as an inhibitor, depending on the concentration of the isocyanate used. For example, a moderate concentration promotes maximum mechanical properties, whereas a higher concentration deteriorates the mechanical properties. At a

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very high concentration level, one cannot rule out a greater probability of reaction among isocyanates which would lead to the formation of different by-products. In addition, the nature of the pulp (e.g., cotton, sawdust, etc.) and fiber loading percentage also play important roles in the mechanical properties of thermoplastic composites. Thomas and coworkers [54, 56] have reported on the mechanical properties of isocyanate treated fiber reinforced thermoplastic composites. Urethane derivatives of cardanol were used to treat sisal fibers to improve their compatibility with low density polyethylene (LDPE) resin. It was demonstrated that the CTDIC (cardanol derivative of toluene diisocyanate) treatment reduced the hydrophilic nature of the sisal fiber and thereby enhanced the tensile properties of the sisal-LDPE composites [167]. The synthesis of a urethane derivative of cardanol was carried out using cardanol (from cashew nut shell) and TDI (toluene diisocyanate). The long chain structure of CTDIC linked to the sisal fiber makes the fiber hydrophobic, compatible and highly dispersible in the thermoplastic resin. The PMPPIC treatment on sisal fiber has significant influence on the properties of composites such as increased thermal stability, reduced water absorption, etc. [206, 219, 220]. The isocyanate group of PMPPIC is highly reactive with the -OH group of cellulose and therefore a urethane linkage is formed, covalently linking the fiber with the resin. The urethane group results from the reaction of the isocyanate and the hydroxyl groups. This reaction can lead to crosslinked polyurethane when multifunctional reactants are used. However, when a diisocyanate and a diol react together, a linear polyurethane is obtained. In the absence of a catalyst, electron-withdrawing groups of the isocyanate molecule and electron-donating groups on the active hydroxyl group of cellulose increase the rate of reaction, so a smaller treatment time is required. Joly *et al*. [221] studied the effect of alkyl isocyanate treatment on the water absorption behavior of cotton fiber reinforced composites by varying the length of the alkyl chain. The results showed the importance of a critical length of the alkyl chain (between three and eight carbons) for reducing the amount of sorbed water by 25%. Ni and Frazier [222] have reported the synthesis of structurally isomeric ^{15}N-labeled polymeric methylenebis(phenylisocyanate) based adhesives. These were used with wood to make composites. They observed the formation of urethanes and polyureas in the wood composites through various characterization studies. They found that resin polymerization occurred via the reaction of isocyanate with wood moisture to form polyurea. Biuret formation and isocyanate dimerization were also detected. In the presence of traces of moisture, isocyanates will react preferably with water instead of hydroxyl groups of cellulose. This results in disubstituted ureas on the fiber surface and because of their basicity they can further react easily with isocyanates, which results in side chains that are bonded to the hydroxyl groups of cellulose. The main reaction of isocyanates, therefore, consists of reaction of alkyl or aryl ureas and their further reaction products with isocyanates. Rensch and Reidl [223] modified chemithermomechanical pulp (CTMP) with various isocyanates such as n-butyl isocyanate (BUI), phenyl isocyanate (PHI), hexamethylene di-isocyanate (HMDI)

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and polymethylene poly(phenyl) isocyanate (PMPPIC) in dimethylformide (DMF) in the absence of catalyst, and their effect on the thermoanalytical behavior of CTMP was investigated. The CTMP was composed of 45% spruce, 45% fir and 10% poplar as the cellulosic material. Aliphatic isocyanates such as BUI and HMDI showed a low potential for reaction with CTMP, compared to aromatic isocyanates with equal functionality like MDI and PHI. The use of MDI and its oligomeric modification PMPPIC as coupling agent resulted in an increased thermal stability of modified pulp compared to untreated pulp. FTIR studies of the isocyanate modified pulps showed urethane formation as being the main component of these chemical pulp modification processes. They also reported the presence of an endothermic peak in DSC thermograms when PHI was used at high concentrations. They explained this as a result of the secondary reaction between isocyanate and humidity, which yields urea, or to an isocyanate trimerization product, an isocyanurate. The presence of this secondary reaction component was linked with a high reduction in water uptake of modified pulp.

6.2.2.3 Graft Copolymerization

Chemical modification through graft copolymerization has also been an effective method of modifying the properties of natural fibers. The technique involves the grafting of various monomers onto the surface of cellulosic fibers [224, 225]. The reaction is usually initiated by free radicals of cellulose molecules. In the first step treatments with selected ions, transition metal ions, oxidative reagents as initiating agents generate free radicals on cellulose fiber surface [226]. The radical sites initiate grafting of alkyl acrylates (such as methyl, ethyl, butyl, and propyl), vinyl monomer (such as methyl methacrylate and acrylonitrile) onto cellulosic fiber surfaces. The altered chemistry at the fiber surface brings its surface energy closer to that of the resin and, hence, results in better interaction with the resin than before grafting. Pracella *et al*. [227] used polypropylene with modified hemp fibers by means of melt grafting reactions with glycidyl methacrylate (GMA) in order to improve the fiber/resin interactions. The improvement in fiber/resin interfacial adhesion caused by the grafting modification increased the tensile strength, modulus and stiffness of modified hemp fiber based composites significantly compared to composites without any fiber treatment. Escamilla *et al*. [228] reported the effect of methylmethacrylate [MMA] grafting on henequen fibers and its applications in composites. The grafting parameters such as monomer/cellulose ratio, initiator concentration and reaction time were varied in their experiments. The grafting of vinyl monomers onto cellulose and other cellulosic fibers has been studied extensively by many researchers [229–231]. While this reaction is initiated by free radicals of cellulose molecules, ionic initiated processes are also possible. Free radical sites may be formed on the cellulose molecules by dehydrogenation, depolymerization, oxidation or formation of unstable metal complexes, which may lead to an electron transfer

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to the metal, and cleavage of the glucopyranoside ring [19]. Ionic processes usually involve the formation of an alkoxide of cellulose with which copolymerization of vinyl monomers is initiated. The most commonly used methods of free radical initiation on cellulose are high-energy ionizing radiation, ceric ion redox systems and oxidative reagents [230]. Under these conditions the cellulose molecules undergo chain scission forming radicals. Grafting of polyacrylonitrile on jute fibers was carried out by aqueous polymerization of acrylonitrile in the presence of $NaIO_4$, or combination of $[IO_4]$ and Cu^{+2} ions as the initiator [231]. Ceric ion initiated grafting of alkyl arylates such as methyl, ethyl, propyl and butyl or methyl methacrylate onto cotton, paper or other hard cellulosic fibers has been reviewed by Mohanty and Misra [232]. Ghosh and Ganguly [233] reported the effect of grafting on the performance of jute fiber reinforced unsaturated polyester composites. Chemical modifications of jute fibers were achieved through graft copolymerization with acrylonitrile or methyl methacrylate. The polyacrylonitrile [PAN] grafting showed a higher improvement in the strength of the composite in comparison to poly(methyl methacrylate) [PMMA] grafting. Important factors in initiating graft copolymerization reaction of vinyl monomers with activated cellulose are the accessibility of free radical sites to the monomers, the lifetime of free radical sites and the interaction of the monomer solutions or vapors with activated cellulose to increase the accessibility of the free radical sites to monomer. After radical formation, the radical sites of the cellulose are treated with a suitable solution that is compatible with the resin chemistry, e.g., vinyl monomer [230] acrylonitrile [231] or polystyrene [204]. The resulting copolymer had characteristic of both fibrous cellulose and grafted polymer. One of the important factors to be remembered during the direct grafting onto the fiber is that the monomer cannot diffuse into ordered regions such as the crystallites, but only into the amorphous or disordered regions. Since the mechanical behavior of the fibers is largely determined by their internal morphology, grafting on the surface does not bring about any drastic changes in the properties of fibers [230].

The grafting of maleic anhydride (MA) onto PP occurs along the chain without modifying the length of the initial PP. The reaction of this comblike structure with cellulose may lead to a coating of fiber with several anchoring points. At higher temperatures, the scission of PP chain occurs with the formation of MA prepolymers at the scission ends. Reactions with cellulose then produce a brushlike grafting on the fiber, which is favorable for the entanglements with the resin chains. The maleic anhydride modified polypropylene (MAPP) chains of different lengths grafted onto cellulose surface have been explained in terms of the brush concept [234]. When a long chain polymer is attached to a surface or an interface, the mobility of the chains is restricted. The grafted chains adopt a random walk configuration in order to maximize their configurational entropy [235]. Under certain conditions, the grafted chains may stretch away from the surface and form a

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brushlike structure. Important factors that affect the stretching tendency are graft density, the molecular weight of grafted chains and the surrounding medium [236]. A high graft density allows neighboring grafted chains to overlap. In such cases the grafted chains tend to stretch away from the surface so as not to overfill the space. The adopted conformations lead to a brush height that grows faster than the typical chain dimension when the molecular weight increases. Joly *et al*. [221] also found that partial masking of cellulosic fiber with MA grafted PP (MAPP) reduced the water absorption in cellulose fiber reinforced composites. The effectiveness of MAPP copolymers as coupling agents in jute/PP composites was studied by Gassan and Bledzki [237]. They also found significant improvement in fiber/resin adhesion which resulted in composites with higher damage resistance under cyclic dynamic loading.

6.2.2.4 Impregnation Treatment of Fibers

A better combination of fiber and polymer is achieved by impregnation of the reinforcing fibers with polymeric resins compatible with the polymer, in effect matching their surface energies. In this method, fibers are impregnated by dipping the fibers in liquid monomers which are then polymerized *in-situ* using catalyst, heat or radiation [238]. A crosslinking agent may also be added during or after the impregnation. Because of their low viscosity, the monomers can go inside the fibers or the surface valleys easily. Once they are polymerized in those locations, the fiber/resin bonding can be significantly enhanced through the fiber/resin interaction as well as mechanical adhesion. Such treatment can also improve the dimensional stability of the composites because of strong fiber/resin interaction that restricts the movement with respect to each other. Improved dimensional stability of a wood-polymer composite (WPC) using solvent exchange technique of impregnation was reported by Manrich and Marcondes [238]. It is known that the elevated viscosity of the resin during processing of the composite hinders a complete impregnation of the fibers which results in a low mechanical interaction with the resin. Monomer solutions of low viscosity can be used for the purpose [239]. Franco *et al*. [240] reported improved interfacial properties of henequen/HDPE composites by the impregnation method. Composites consisting of HDPE, sand and short henequen fibers were developed and characterized. The flexural modulus was affected favorably by the fiber/resin interfacial adhesion. It was noticed that an increase of the sand content did not result in a proportional increase of the modulus for the untreated fibers. The improvement in the fiber/resin adhesion by both pre-impregnation and silane coupling agent did result in an increase of modulus with increasing fiber content for the lower sand content. For the higher sand content the fiber surface modification did not result in a noticeable increase in the mechanical properties of the composite. The higher mineral content, perhaps, was responsible for controlling the composite properties.

DOI: 10.7569/RAA.2015.097311

6.2.2.5 Alkali Swelling and Substitution Reactions

One of the old methods of cellulose fiber modification is mercerization, an alkali treatment that leads to fibrillation which causes breakdown of the composite fiber bundle into smaller fibrils. Alkali treatment depends on the type and concentration of alkali solution, time of treatment and temperature. It has been reported that when the oil palm fiber was immersed in NaOH solution for 48 h, the globular pultrusions present in the untreated fiber disappeared, leading to the formation of a larger number of voids [241]. While the alkali treatment slightly decreased the tensile strength, the Young's modulus of the fiber showed enhancement upon silane and alkali treatments. Loss of cuticles by the rupture of alkali sensitive bonds created a rough fiber surface promoting mechanical interlocking between fiber and resin. Effects of NaOH treatment and γ-irradiation on coconut fiber/phenol-formaldehyde composites were reported by Owolabi *et al.* [242]. Optimal conditions of mercerization ensure an improvement in tensile properties. The following reaction takes place as a result of alkali treatment:

$$\text{Fiber} - \text{OH} + \text{NaOH} \longrightarrow \text{Fiber} - \text{O}^{-}\text{Na}^{+} + \text{H}_2\text{O}$$

By impregnating fiber with alkaline swelling agents and by reacting with some chemical agents that can be substituted for the hydroxyl groups on cellulose molecules in the presence of alkali, highly decrystalized fibers can be obtained [243]. For example, OH group is substituted by Na in the chemical reaction shown above. The effective substitution reactions include acetylation by acetic anhydride and cyanoethylation. Richards [244] found that acetylation of wood increased the dimensional stability and reduced the susceptibility to decay. Increased strength, rot resistance and hydrophobicity of jute fiber after acetylation were reported by Anderson and Tillman [201]. Effect of alkali treatment time on the surface chemistry, morphology and bonding of kenaf fibers was studied by Williams *et al.* [245]. Through ATR-FTIR spectroscopy, XPS and SEM they showed that the most significant chemical changes on the surfaces occurred between 30 min and 4 h of treatment. However, fibers treated for 16 h showed the most significant increase in tensile strength. Of significant importance was that using this group of fibers in a composite ultimately resulted in poor properties. Since it was observed that longer treatment times resulted in fewer surface hydroxyl groups on the kenaf surfaces, the amount of sites needed for fiber/resin bonding was reduced which led to lower mechanical properties of the composites. It was believed that treating kenaf fibers for 2–4 h would work best as reinforcement in composites, because the mechanical properties of fibers were slightly higher, and more hydroxyl groups in cellulose were available to bond with compatible functional groups in resins. These results indicate that when treating natural fibers for use as composite reinforcement, it is essential to establish proper balance of fiber treatment that will increase mechanical properties of fibers as well as provide optimal bonding which will result in better composite properties.

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7 Summary

It is important to understand and fine-tune the fiber/resin interface since it controls several important mechanical properties of fiber reinforced composites. In light of this, several studies have been carried out in recent years to characterize and evaluate the influence of fiber/resin interface on the performance of composites. Both fiber surface and polymer resin properties can be modified to obtain desired interfacial characteristics. Various fiber/resin characterization techniques and treatments being used for the lignocellulosic surfaces as well as resin modifications have been discussed in this paper. Interfacial adhesion between natural fibers and resin will remain the key issue in terms of overall performance, since it dictates the final properties of the composites and currently there is great emphasis in using plant based fibers and sustainable resins to fabricate 'green' composites and move away from the petroleum based composites. Many studies have been examined and highlighted in this review that shows the importance of the interface, the influence of various types of surface modifications and their influence on the performance of composites. The main techniques for interfacial characterization are the micromechanical, spectroscopic, microscopic and swelling techniques. Properly understanding the behavior and modification of interfacial properties would enable researchers and composite manufacturers to develop composites with properties tuned for specific applications. Significant research is currently underway around the world to address and overcome the obstacles to develop fully functional green composites that can replace the currently used petroleum based composites.

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