



Chemical modifications of natural fiber for composite material

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ABSTRACT

Environmental awareness, increasing concern with the green house effect and bio-degradation have hastened the construction, automotive and packaging industries to look forward for sustainable materials with least impact on the existing surroundings. Natural fibers reinforced bio-degradable composites seem to be a good alternative because of their eco-friendly nature and renewability which make them eco-friendly attracting materials for their application in diversified fields. Because of excellent characteristics such as low weight, high strength and stiffness, natural fiber reinforced composite matrices have found a large dispersal in several areas of technical applications. In this paper different methods for chemical modification of natural fibers so as to incorporate water repellency, resistance towards chemicals and better mechanical properties, have been discussed.

INTRODUCTION

Composites have become an integral part of our day to day life and they can be found everywhere. In the olden time bricks which made from starw and mud are the classic examples of composites [1].Composites in the form of wood, teeth, bones, muscle tissue also has its own importance in the nature. Composites materials generally consist of a matrix reinforced with either particle or fibers.

Natural fibers were used for reinforcing the matrix until early in the mid 20th century. Since 1950 there was an increased demand for the stronger, stiffer, light weight composites in the field such as aerospace, transportation and construction. This leads to the incorporation of high performance fibers for reinforcement. Because there newer composites having low specific gravity, superior strength and modulus like metals [2, 3].Composite are those material made up from two or more distinct materials having different chemical and physical properties provide a well defined structure [4]. Other than fiber natural plant materials having its own importance in the form of medicine such as camellia sinesis and their leaves are used for making cigarettes and

its powder is used for relief of asthma [5]. Much of natural product obtained from plants having own medicinal values such as biologically active phytochemicals are normally present in leaves, roots, barks and flowers [6] and there are number of medicinal plants which possess anti fertility property [7]. Nanocomposites have its own importance such as ZnO is an ecofriendly material and non toxic for human bodies and also used in biomedical applications [8].

Fibers reinforced composites

Fiber reinforced composites consist of fiber as reinforcement and polymer or matrix. The matrices which are earlier reported such as (HDPE) high density polyethylene, LDPE (low density polyethylene), (PP) polypropylene and polyether ketone (PEEK) etc. [9-18]. Fibers reinforced composites earlier use various types of glass, carbon, aluminium oxide and many others such as flax, hemp, jute and henkeen and many others are used as fiber reinforcement for composites [9-14, 19-21]. Natural fibers are better than man made because of their low cost, low density, recyclability and biodegradability [22-24]. Natural fiber reinforced composites can be used in the plastics, automobile and packaging industries [25].

Natural fiber reinforced composites have attracted the attention of the research community it is because they are turning out to be an alternative solution to the ever depleting petroleum sources.

1. Chemical composition of natural fiber

Reinforcing efficiency of natural fiber is depends upon the nature of cellulose and its crystallinity. Components which are present in natural fibers are cellulose (α -cellulose) hemicelluloses, lignin, pectin and waxes. Cellulose is a natural polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by β -1,4- glucosidic linkage at C_1 and C_4 position [26].

Hemicellulose is different from a cellulose. It comprises a group of polysachrides compiled of a combination of five and six carbon ring sugars. It differs from cellulose in three aspects firstly it contain several sugar units secondly they exhibit a considerable degree of chain branching containing pendent side groups give rise to its ion crystalline nature. Third one is degree of polymerisation because in case of hemicelluloses it is 50-30 but in cellulose is 10-100 times more than that of hemicelluloses. Hemicellulose is very hydrophilic, soluble in alkali and easily hydrolyzed in acids.

Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents and it is totally insoluble in most of solvents and cant be broken down into monomeric units. Lignin is considered to be thermoplastic polymer having a glass transition temperature of around $90^{\circ}C$ and melting temperature of around $170^{\circ}C$ [27]. It is totally amorphous and hydrophobic in nature. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized and easily condensable with phenol [28].

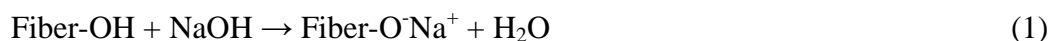
Pectin are a collective name for heteropolysachrides. They provide flexibility to plants. Waxes make up the last part of fibers and they consist of different types of alcohols.

2. Chemical modifications

1.1. Alkali treatment

Alkaline treatment or mercerization is one of the best used chemical treatment for natural fibers. Due to alkali treatment there is an increase in the amount of amorphous cellulose at the expense

of crystalline cellulose. By this treatment there is a removal of hydrogen bonding in the network structure. Reaction which takes place during this treatment is shown below.



1.2. Chemical composition of some natural fibers is shown in the table [29-31].

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Abaca	56-63	20-25	7-9	3
Alfa	45.4	38.5	14.9	2
Bagasse	55.2	16.8	25.3	-
Bamboo	26-43	30	21-31	-
Banana	63-64	19	5	-
Coir	32-43	0.15-0.25	40-45	-
Cotton	85-90	5.7	-	0.6
Caraua	73.6	9.9	7.5	-
Flax	71	18.6-20.6	2.2	1.5
Hemp	68	15	10	0.8
Henequen	60	28	8	0.5
Isora	74	-	23	1.09
Jute	61-71	14-20	12-13	0.5
Kenaf	72	20.3	9	-
Kudzu	33	11.6	14	-
Nettle	86	10	-	4
Oil Palm	65	-	29	-
Piassava	28.6	25.8	45	-
Pinapple	81	-	12.7	-
Ramie	68.6-76.2	13-16	0.6-0.7	0.3
Sisal	65	12	9.9	2
Sponge gourd	63	19.4	11.2	3
Straw (wheat)	38-45	15-31	12-20	-
Sun hemp	41-48	8.3-13	22.7	-

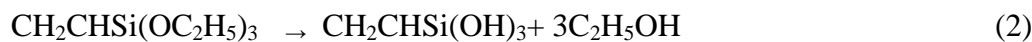
The type of alkali treatment such as KOH, LiOH, NaOH and its concentration will influence the degree of swelling and degree of lattice transformation into cellulose [32]. Alkali solution not only affects the cellulosic components inside the plant fiber but also affect the non cellulosic components such as hemicellulose, lignin and pectin [33].

Jacob et al., examined the effect of NaOH conc. (0.5, 1,2,4 and 10%) for treating sisal fiber reinforced and concluded that maximum tensile strength resulted from the 4% NaOH treatment at room temperature [34]. Mishra et al., reported that 5% treated NaOH fibre reinforced polyester composites having better tensile strength than 10% NaOH treated composites [35]. Because at high concentration there is delignification of natural fiber taking place and as a result damage of fiber surface. The tensile strength of composite decreased drastically after certain optimum NaOH concentration.

1.3. Silane treatment (SiH₄)

Silanes are used as coupling agents to let glass fibers adhere to a polymer matrix, stabilizing the composite materials. Silane coupling agents may reduce the number of hydroxyl groups in the fiber matrix interface. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanols reacts with hydroxyl group of the fiber, forming stable covlant

bonds to the cell wall that are chemisorbed on to the fiber surface. As a result the hydrocarbon chains provided by the application of silane restrain the swelling of the fiber by creating a crosslinked network due to covalent bonding between the matrix and the fiber. The reaction schemes are given as follows [36].



Silane treatment in surface modification of glass fiber composites have been applied by various researchers [37-40]. They have found that Silane coupling agents are effective in modifying natural fiber-polymer matrix interface and increasing the interfacial strength. Schemes of interaction of silane with cellulosic fiber is shown in the (Figure. 1).

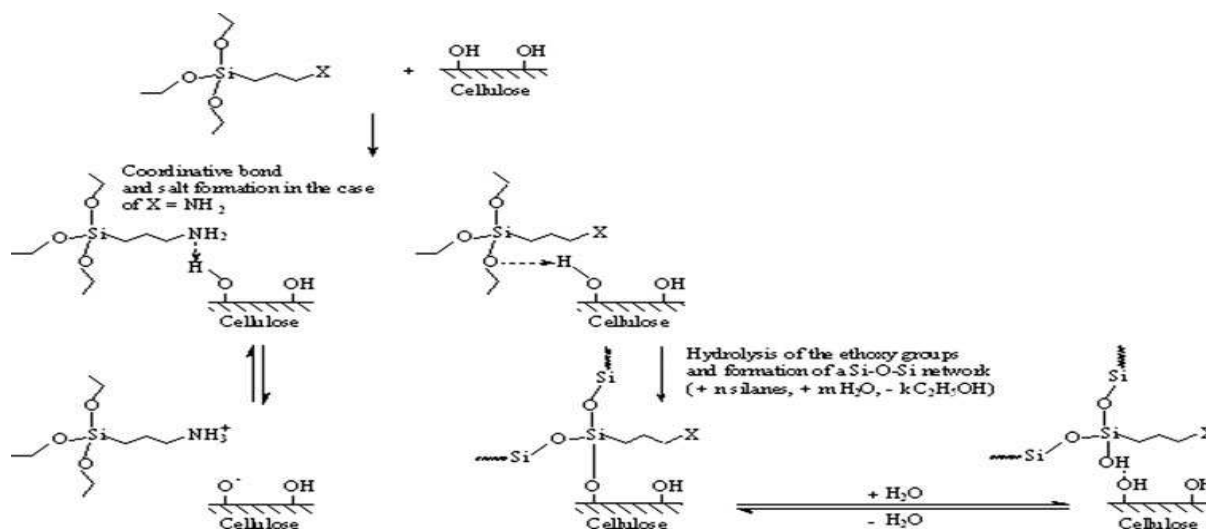
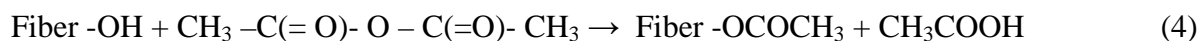


Fig. 1. Scheme of interaction of silanes with cellulosic fibers [41].

1.4. Acetylation of Natural Fibers

During Acetylation there is an introduction of an acetyl functional group (CH₃COO⁻) into an organic compound. Esterification is a well known method for acetylation of natural fibers and it causes plasticization of cellulosic fibers. The reaction which involves the generation of acetic acid (CH₃COOH) as by-product which must be removed from the lignocellulosic material before the fiber is used. Chemical modification with acetic anhydride (CH₃-C(=O)-O-C(=O)-CH₃) substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, modifying the properties of these polymers so that they become hydrophobic. The reaction of acetic anhydride with fiber is shown as [42].



Acetylation can reduce the hygroscopic nature of natural fibers and increases the dimensional stability of composites. Acetylation was used in surface treatments of fiber for use in fiber-reinforced composites [18,43,42, 44]. Acetylation treatment of sisal fiber was reported to improve the fiber-matrix adhesion. The procedure included an alkaline treatment initially, followed by acetylation. Mishra *et al.*, [35] have reported the acetylation of sisal fibers. Dewaxed sisal fiber was immersed in 5 and 10% NaOH solution for 1 h at 30⁰C; the alkaline-treated fiber was soaked in glacial acetic acid for 1 h at 300C; it was decanted and soaked in acetic anhydride

containing one drop of concentrated H_2SO_4 for 5 min. Nair et al., [45] treated raw sisal fiber in 18% NaOH solution, then in glacial acetic acid and finally in acetic anhydride containing two drops of concentrated H_2SO_4 for a period of 1 h. The treated surface of sisal fiber reportedly became very rough and had a number of voids that provided better mechanical interlocking with the polystyrene (PS) matrix. It was also reported that acetylated natural fiber-reinforced polyester composites exhibited higher bio-resistance and less tensile strength loss compared to composites with silane treated fiber in biological tests [46].

1.5. Peroxide Treatment

Peroxide is a molecule with the functional group ROOR which contain the divalent ion O–O. Organic peroxides tend to decompose easily to free radicals of the form RO^* ; RO^* then reacts with the hydrogen group of the matrix and cellulose fibers. For example, the peroxide initiated free radical reaction between PE matrix and cellulose fibers is shown by the following [18,47].



Benzoyl peroxide (BP, $((\text{C}_6\text{H}_5\text{CO})_2\text{O}_2)$) and dicumyl peroxide (DCP, $(\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O})_2$) are chemicals in the organic peroxide family that are used in natural fiber surface modifications. In peroxide treatment, fibers are coated with BP or DCP in acetone solution for about 30 min after alkali pre-treatment [18,48,49]. Sreekala et al., [48] observed that decomposition of the peroxide was favored at high temperature ; for the peroxide-treated oil palm fiber-reinforced PF composites could withstand tensile stress to a higher strain level. Joseph and Thomas [47] studied the BP and DCP treatment on short sisal fiberreinforced PE composites. The tensile strength values of composites increased with the increase in concentration of peroxide up to a certain level (4% for DCP and 6% for BP) and then remained constant. As a result of peroxide treatment, the hydrophilicity of the fibers decreased [18] and the tensile properties increased [47].

1.6. Other chemical treatments

Paul et al., [18] and Zafeiropoulos [50] have reported that treatment of natural fiber with Stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) in ethyl alcohol solution was investigated earlier. It was reported that this treatment removed non-crystalline constituents of the fibers, and change in the fiber surface topography occurs. Zafeiropoulos [50] also observed that treated flax fibers were more crystalline than the untreated ones and steatation decreased the fiber surface free energy. Sodium chlorite (NaClO_2) usually is used in bleaching fibers; however, it could delignify lignocellulosics. Studies have been conducted wherein it was used in fiber surface treatment for composites.

Mishra et al., dipped untreated sisal fiber, for use in sisal–PS biocomposites, in sodium chlorite solution with a liquor ratio of 25:1 at 75°C for 2 h. Tensile strength of bleached sisal fiber–PS composite was less than other chemical treated fiber composites which may be due to the fact that delignification of the fiber lowered its tensile strength [51]. But it was reported that flexural strength was better for bleached fiber composite because of lower stiffness and more flexible character of fibers after delignification. After delignification, the polymer replaces the role of lignin in fibers and makes composites more hydrophobic and tougher [51]. Similar result on

tensile strength of bleached composites using sodium chlorite was also reported by Li et al., [52] on flax fiber–PE composites.

1.7. Natural Fibre reinforced Composite

Natural fibers such as sisal, flax and jute possess good reinforcing capability with polymers. These fibers are relatively inexpensive originate from renewable resources and possess favourable value of specific strength and specific modulus. Natural fiber reinforced composites come from the renewable materials and can be mechanically recycled. Some of the recent studies on the natural fiber reinforced composites have been cited in this paper.

1.8. Banana fiber reinforced composites

Effect of chemical modifications on the dynamic mechanical properties of banana fiber reinforced polyester composites was studied by Pothan et al., [41]. A number of silane coupling agents were used to modify the banana fibers. Joseph et al., studied the environmental durability of chemically modified banana fiber reinforced phenol formaldehyde (PF) composites. They observed that silane, NaOH and acetylation treatments improved the resistance of the banana/PF composites on outdoor exposure and soil burial [53].

Idicula et al., investigated the thermo physical properties of banana sisal hybrid reinforced composites as a function of chemical modification. Sisal and banana fiber were subjected to mercerization and polystyrene maleic anhydride (MA) treatments. They observed that chemical modification resulted in an increase of 43% in the thermal conductivity when compared with untreated composites [54].

1.9. Flax fiber reinforced composites

Most of studies concerning the chemical modification of flax fiber has been reported earlier by many researchers. Weyenberg et al., [33] investigated the chemical modification of flax fiber by alkali treatment. The study concentrated on optimizing parameters, such as time and concentration of NaOH, to develop a continuous process for the treatment and fabrication of unidirectional flax fiber epoxy composites. The authors observed a specific improvement in the mechanical properties of the resulting material; treatment with 4% NaOH solution for 45 s increased the transverse strength of the composites by up to 30%.

Wang et al., [55] investigated the Effects of different chemical modifications on the properties of flax fiber-reinforced rotationally molded composites. The chemical modifications carried out were mercerization, peroxide treatment, benzylation, and peroxide treatment. The modified fibers were then extruded with the polymer matrix to form the composite and an improvement in interfacial adhesion was observed.

Zafeiropoulos et al., [56] investigated the effect of chemical modification on the tensile strength of flax fibers. The authors tried acetylation and stearamine and found that the tensile strength of flax fibers did not exhibit any drastic improvement. The SEM examination of the fractured surfaces revealed that acetylated fibers exhibited a different mode of failure from the other fibers, suggesting that the treatment altered the bulk properties along with the surface properties.

1.10. Hemp fiber reinforced composites

Bledzki et al., [57] have studied the influence of chemical treatment on the properties of hemp fiber-reinforced epoxy and PP composites. The effects of different mercerization parameters, such as concentration of alkali (NaOH), temperature, duration time, and tensile stress applied to

the fibers on the structure and properties of hemp fibers were studied and judged via the cellulose I-II lattice conversion. It was observed that the mechanical properties of the fibers can be controlled in a broad range using appropriate parameters during mercerization treatment.

Aziz and Ansell [58] investigated the effect of alkali treatment on the mechanical and thermal properties of hemp fiber-reinforced polyester composites. The SEM photomicrograph of the longitudinal surface of untreated fiber bundles in (Figure 2a) shows the presence of wax, oil, and surface impurities. Waxes and oils provide a protective layer to the surface of the fibers. The longitudinal view of the 6% NaOH-treated hemp fiber in (Figure 2b) shows a very clean surface. Its surface topography shows the absence of surface impurities, which were present in the untreated fiber. The individual ultimate fibers also show a slight separation which was not apparent in the untreated hemp fiber shown in (Figure 2a).

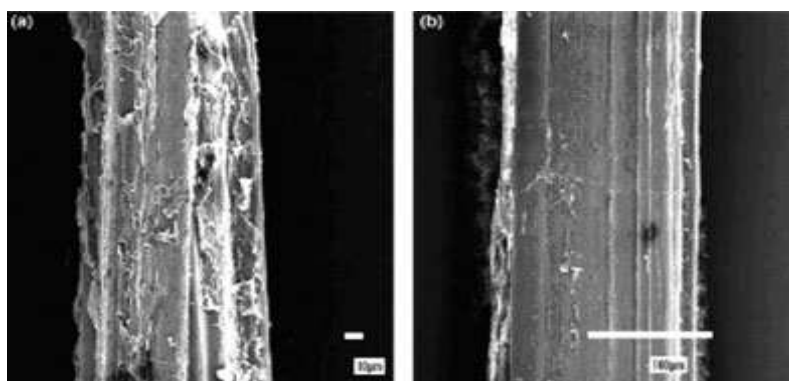


Fig. 2. SEM micrographs of longitudinal views of (a) untreated hemp fiber and (b) 6% NaOH-treated hemp fiber [58].

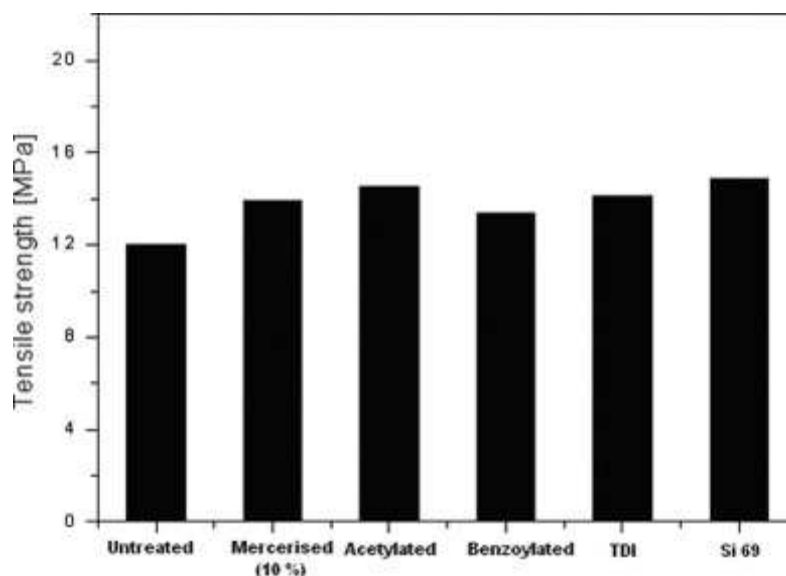


Fig. 3. Variation of tensile strength with different chemical modifications [59].

1.11. Isora Fiber Reinforced Composites

In an interesting study, researchers have used a novel fiber (isora fiber) in natural rubber [59]. Isora fiber resembles with jute in appearance but surpasses it in strength, durability, and luster. The effects of different chemical treatments, such as acetylation, benzoylation, treatment with

toluene diisocyanate (TDI) and silane coupling agents, on the mechanical properties of isora fibers and composites were analyzed. Isora fiber was seen to have immense potential as reinforcement in natural rubber. The variation in tensile strength with chemical modification is shown in (Fig. 3) and it can be observed that treatments with NaOH and TDI exhibited higher tensile strength among other chemical modifications.

1.12. Pineapple Fiber Reinforced Composites

Green composites were fabricated using pineapple leaf fibers and soy-based resin [60]. The addition of polyester amide grafted glycidyl methacrylate (PEA-g-GMA) as compatibilizer was seen to increase the mechanical properties of composites. Tensile and flexural strengths of composites containing treated fibers were found to be 35 and 50 MPa, respectively, whereas those of composites containing untreated fibers were found to be 30 and 45 MPa, respectively.

Lopattananon *et al.*, [61] investigated the chemical modification of pineapple leaf fibers in natural rubber. NaOH solutions (1, 3, 5, and 7%, w/v) and benzoyl peroxide (BPO) (1, 3, and 5 wt% of fiber) were used to treat the surface of fibers. It was found that all surface modifications enhanced adhesion and tensile properties. The treatments with 5% NaOH and 1% BPO provided the best improvement of strength (28 and 57%, respectively) of composites when compared with that of untreated fiber composites.

1.13. Sisal Fiber Reinforced Composites

Mwaikambo and Ansell [62] carried out the alkali treatment of sisal fibers and analyzed the changes with respect to the diameter and internal structure, such as cellulose content, crystallinity index, and micro-fibril angle. Alkalization was found to change the internal structure of sisal fibers which exhibited approximately same specific stiffness as that of steel. The crystalline nature of the treated fibers was also found to increase due to alkali treatment. Their results indicated that the structure of sisal fiber can be chemically modified to attain properties that will make the fiber useful as a replacement for synthetic fibers.

Martins *et al.*, [63] studied the effect of chemical modifications on the structure and morphology of sisal fibers by NMR spectroscopy. Mercerization, acetylation, and resorcinol/hexamethylenetetramine (R/H) treatments were applied to sisal fibers in order to improve their adhesion in composites materials. The results showed that the fibers/ acetylation of fibers prior to the treatment with 20/10 g/L R/H solution for 15 min was the best treatment since the fibers obtained exhibited the biggest effective surface area available for chemical interaction and mechanical interlocking with the matrix.

CONCLUSION

Chemical modification of natural fibers is necessary for increased adhesion between the hydrophilic fibers and hydrophobic matrix. The most promising approach seems to be one in which covalent bonds are formed between the fiber and matrix. As apparent from the above studies, one of the most common and efficient methods of chemical modification is alkali treatment of fibers and it has been used to treat almost all the natural fibers with successful results.

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