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# Effect of chemical modification of fiber surface on natural fiber composites: A review

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## Abstract

The effect of different chemical modification of fiber surface on different mechanical properties of natural fibers composites are reviewed in this paper. Different fiber surface modifications like alkali, acetylation, potassium permanganate, peroxides, silane benzoylation etc. and the composition of the natural fibers components like cellulose, hemi-cellulose, lignin, pectin etc. are discussed. The main purpose of present study is to check the effect of the different fiber surface modification on natural composites. Different properties of the natural fiber composites are increases like the adhesion force between the reinforcement surface and matrix material at the surface contact, also it improve fiber strength. The water absorption properties of composites are reduced.

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**Keywords:** Natural fibers, mechanical properties, chemical treatment, composite material.

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## 1. Introduction

Natural fibers have the favorable properties like low cost, easy to available, low density, and recyclability etc. The disadvantages of natural reinforcement (fiber) are more absorption of moisture and the poor reinforcement (fiber) and matrix compatibility etc. Therefore, fiber surface treatments are used for modification of fiber surface and to improve addition between the matrix and fiber [1]. The natural fibers have better properties over man-made fibers include low cost, easy to available, low density, recyclable and bio-degradability [2]. Alkali solution and silane coupling agent treatments have been used to strengthen the fiber/matrix interactions in natural fiber polymer composites. Alkali treatments improves flexural properties of jute fiber reinforced unsaturated polymer composites [3- 4].

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The cylindrical natural fiber surface is treated with two percentage of alkali, it is a first surface treatment, the other surface modification are stearic acid, permanganate ( $\text{KMnO}_4$ ) and benzoyl peroxide etc. The good mechanical properties are achieved at 0.5 percentage  $\text{KMnO}_4$  surface treated natural fiber composite [5]. The polymer composites with natural fiber have some disadvantage like bad wettability and more moisture absorption and also incompatibility. The reason behind this is the bad adhesion forces between natural fiber and polymer composites. The adhesion forces between natural fiber and polymer composites can be improved by different surface fiber treatments with different concentration of chemicals [6]. The Alkali (5%) pre-treated sisal fiber is used in polyester composites for preparation of composites. The result of pre-treated sisal polyester composites is compared with other surface modification like silane, benzoylation and permanganate treatments. After the surface treatments the sisal fiber surface becomes rough, which produces good adhesion forces between sisal and polyester [7]. The 2 percentage alkali and 1 percentage oligomeric siloxane surface modified jute fiber composites show the good mechanical properties than the untreated fiber composites [8].

The different  $\text{KMnO}_4$  concentrations and urea surface treated fiber is used for preparation of jute poly-propylene composites at 45 percentage volume fraction of reinforcing fiber. The results show excellent mechanical properties at 0.05%  $\text{KMnO}_4$  surface modified jute fiber reinforcing composites, also it is found that they exhibit low water absorption properties than untreated natural fiber composite [9]. The natural sisal fiber composites consist of surface modifying agents like silane, benzoylation, permanganate, alkali, peroxide etc. The surface modified sisal composites have shown good mechanical properties than untreated sisal fiber composites [10]. The mechanical properties such as strength, stiffness and hardness etc. are improved after the surface treatment of the fiber. The different surface modification of the fiber is used like silane, benzoylation, permanganate and stearic acid [11]. The compatibility of celluloses, isocyanates, modified maleic anhydride poly-propylene, benzyl chloride and permanganates with the compatibility were studied by the sodium hydroxide treatment of cellulose fibers, and permanganates showed that the tensile effects were significantly improved in different treatments and vary with varying gradients [12].

## 2. Composition of natural fibers

The composition of cellulose fibers consists of cellulose microfibrils bound together by a lignin matrix in natural plant fibers. Lignin maintains fiber water; acts as a biological protection and a reinforcement agent to resist the gravity forces and the wind. A compatible agent between cellulose and lignin is believed to be hemicellulose found in the natural fibers [13]. The cell membrane is not a homogeneous membrane of a fiber/cell, which is shown in figure 1.

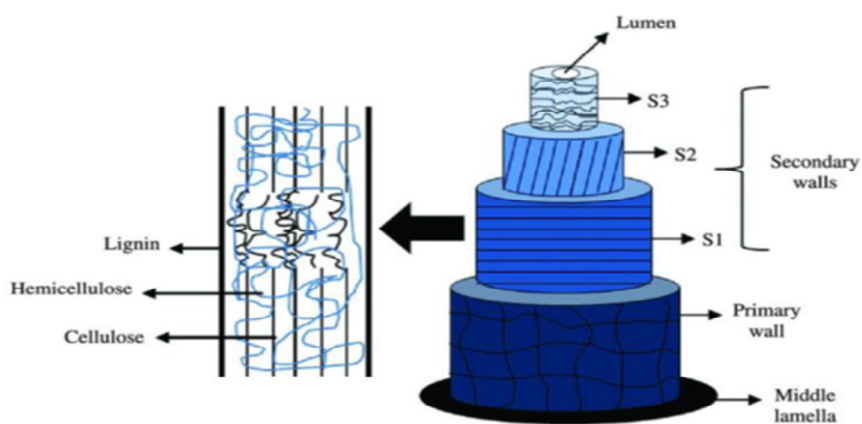


Figure 1. Composition of natural fibers [15].

Figure 1 shows that the fiber cell wall is divided into different layers like primary, secondary, and middle lamella etc. The secondary layer of the fiber is further also subdivided into external ( $S_1$ ), middle ( $S_2$ ), internal ( $S_3$ ). Secondary walls and the central one is called lumen that transports the minerals and water.

### 2.1. Cellulose

The main part of vegetal fibers are that the cellulose. The chemical structure of cellulose is shown in figure 2. It is chemical compound of  $\beta$ -D-Glucose destined within which  $-\text{CH}_2\text{OH}$  cluster is alternating on top and below the plane of the poly-saccharide molecule, therefore manufacturing long, branchless chains (figure 2) exists within the storage cell wall [16].

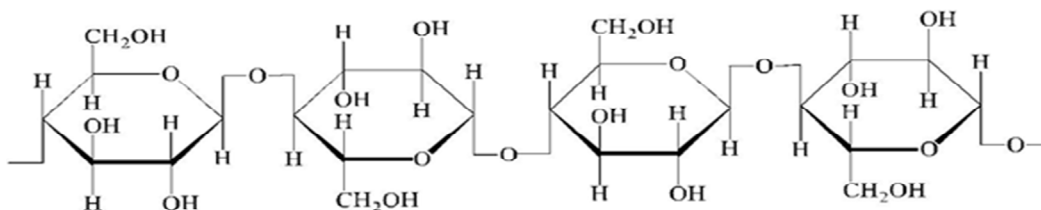


Figure 2. Cellulose chemical structure [17].

### 2.2. Hemicelluloses

Hemicellulose is one complex group of carbohydrates as shown in figure 3, surrounding the cellulose fibers of plant cells with other carbohydrates (e.g. pectin). The mostly hemicelluloses have xylans (many five-carbon sugar molecules combined), uranic acid (i.e. sugar acid), and arabinose. Xylan (Figure 3) is the pentosane example of a  $1\beta \rightarrow 4$  linkage D-xylose unit. Hemicellulose is high-hydrophilic, alkaline-soluble and acid-free to hydrolysed.

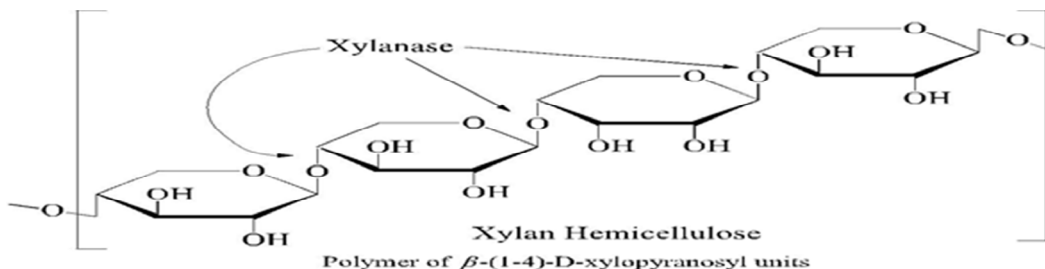


Figure 3. Hemi-Cellulose chemical structure [17].

### 2.3. Lignin

Lignin is indeed a strongly interlinked, amorphous-structured and molecular complex structure as shown in figure 4, it behaves as an agent for binding each cell to the fibers creating the membrane.

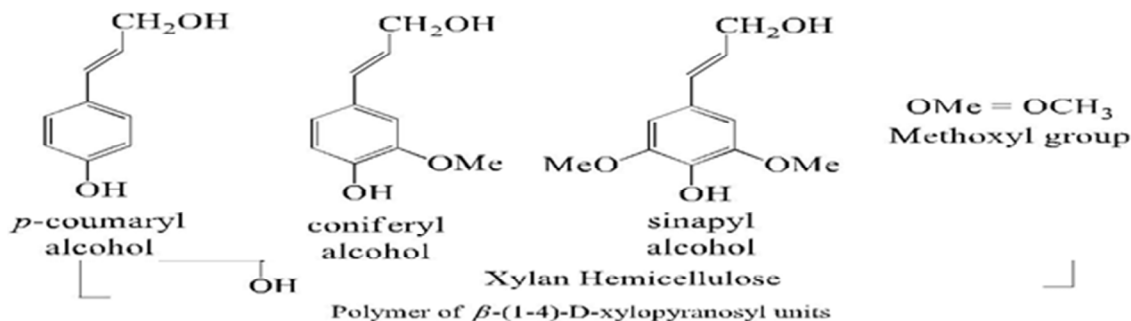


Figure 4. Lignin monomer chemical structure [17].

By joining the fibers together lignin increases the compressive strength of natural fibers to form a rigid structure [17].

## 2.4. Pectin

Pectin is indeed a complicated element of branches of acidic polysaccharides in the structure discovered in fruit and fairly fibres. The typical pectin structure is shown in Figure 5. The structure consists in large part of homopolymeric poly- $\alpha$ -(1-4)-D- galacturonic acid residues. Because of the carboxylic acid groups, pectin is the most hydrophilic compound in plant fibers and easily deteriorated by fungal deliberation [16]. In natural fibers, pectin along with lignin and hemicelluloses may be hydrolysed at high temperatures.

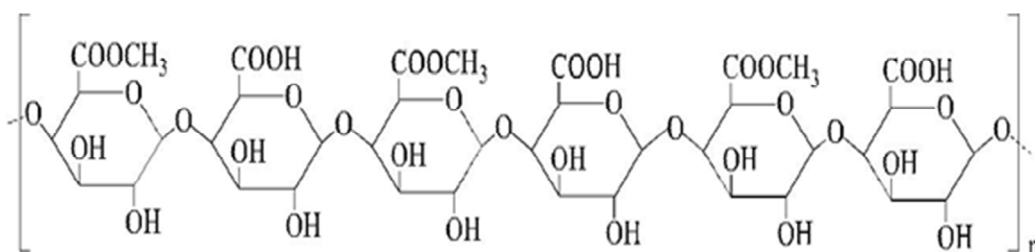


Figure 5. Pectin chemical structure [17]

## 3. Surface treatments of natural fiber

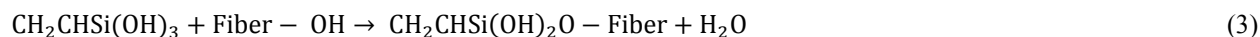
### 3.1. Alkaline treatment

Thermoplastics and thermosets are treated with alkaline as one of the most common surface modification for composites. Alkaline surface treatment is significantly modified to detach hydrogen attachment in the system structure which increases roughness of fiber surface. This surface modification of the natural composites removes the oils, wax and lignin, which is covering the outer surface of the cell membrane [18]. The addition of the sodium oxide (NaOH) in fiber by surface modification is facilitates the ionization of alcoholic body by hydroxyl, which can be written by the following chemical equation [19].



### 3.2. Silane Treatment

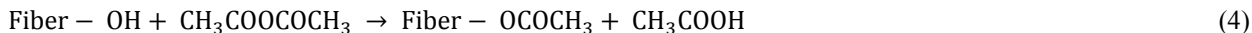
The chemical formula of Silane is  $\text{SiH}_4$ . Silanes are used to add polymer matrix and glass fibers to stabilize the composite material as coupling agents. The total number of cellulose hydroxyl groups at the fibre and matrix interface are removed by silane coupling agents. Hydroxyle alcohols lead to the formation of silanes in the presence of moisture. The silanol then reacts to the hydroxyle group in the fiber, forming stable covalent bonds to the fiber surface cell membrane. Thus, with the application of silanes, hydrocarbon chains reduce the fibers cramping by generating a cross-linking infrastructure, as the fiber matrix is attached by the covalent bonds [19]. Following are the reaction schemes for the silane treatment.



### 3.3. Acetylation

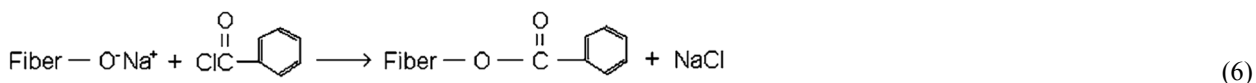
Acetylation surface modification is described a reaction of organic compound with acetyl ion  $\text{CH}_3\text{COO}^-$ . The plasticization of cellulosic fibers is causing esterification method. It is also known as acetylation of natural fibers. On the reaction of ethanoic anhydride and lingo-cellulose material, ethanoic anhydride reacts in side the hydroxyl

groups of cellulose. John et al. [20] prepare a flax reinforcement polymer composites and proved that flax fiber is chemical modifying agent. The significant enhancement in mechanical properties of flax fiber composites are occurred due to 18 percentage increase in acetylation modification.



### 3.4. Benzoylation Treatment

The transformation in benzoyl chloride and organic synthesis is a good example of benzoylation. It is used in fiber treatment. The water absorption properties of natural fibers are decrease by the benzoylation treatment and the progress in the interaction between the natural fiber and PS matrix. The reactions of the Benzoylation chemical modification can be written as mentioned below.

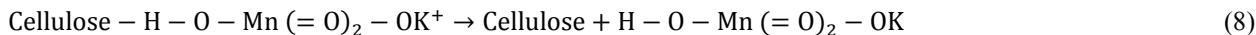
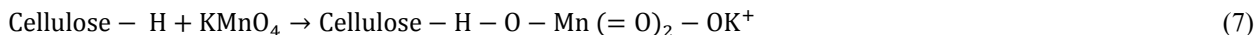


Joseph [21] treated sisal fiber with the benzoyl chlorite ( $\text{C}_6\text{H}_5\text{COCl}$ ) and sodium hydroxide solution. The hydroxyl compound of lignin and cellulose are activated by the alkaline pre-treated. Then fiber is put in deep solution for 15 minutes in 10 percentage benzoyl chloride and NaOH. After this process fibers are again deep in ethanol for escaping the benzoyl chloride and finally fibers are washed.

### 3.5. Permanganate Treatment

Permanganate group  $\text{MnO}_4^-$  belongs to the potassium permanganate. The ions  $\text{MnO}_3^-$  formed thru the radical cellulose by the potassium permanganate surface modification reaction. After this effectively charged  $\text{Mn}_3^+$  ion is culpable for co-polymerisation, as shown in the equations 7 and 8.

The alkali (5% concentrated) surface pre-treated fibers are deeper in 0.05 percentage concentrated solution of the potassium permanganate for 1 min with acetone. The fiber is drained out from the potassium permanganate solution and fiber is dried by air [22].



### 3.6. Peroxide Treatment

In chemistry, ROOR chemical group is member of the peroxide. The ROOR functional group contains the ion O–O. The ROOR functional group usually breaks easily to escape radicals (2RO). Then it is reacts with the matrix and cellulose fibers, which contains hydrogen. In peroxide treatment, alkali pre-treatment fibers are treated with one of those 6% dicumyl, peroxides in acetone solution for 30 minutes. Fibers are deep in solution for 30 min at 70°C, after this process fiber is washed in the distilled water. The free radical response between the PE matrix and cellulose fibers, for example, initiated by peroxide is shown in below equations [23- 24].



#### 4. Discussions

The mechanical properties such as strength, stiffness, impact strength etc. and percentage elongation of untreated and alkali surface modified natural Pattawia Leaf Pineapple Fiber (PLAF) composites are improved with increase in fiber percentage (highest at 20% wt) [25]. The various mechanical properties of the natural PLAF fiber reinforced composites are shown below as shown in below Table (1-3):

Table 1. The effect mechanical properties of Pattawia Leaf Pineapple Fiber.

Mechanical property	NaOH Concentration		
	0%	2%	4%
Tensile strength (MPa)	21.307	23.814	28.732
Tensile modulus (MPa)	793.568	1143.259	1233.768
Flexural strength (MPa)	29.651	31.265	37.961
Flexural modulus (MPa)	4138.325	4236.098	4326.28

The mechanical properties like tensile strength and modulus and % elongation of un-treated and alkali/silence or both of them surface modified natural roystonea regain fiber reinforced epoxy composites are improved with increase in fiber percentage (highest at 20% wt). Alkali surface modified fiber composite gives better properties then silence surface modified and also mixed (Alkali+ Silance) surface modified gives good properties then silence surface modified [26].

Table 2. Tensile Properties and % Elongation of un-treated and surface modified composites.

Treatments	Fiber in composites (10% wt.)		
	Tensile strength	Tensile Modulus	% Elongation
Untreated	19.47	1178.60	3.30
Alkali	21.29	1356.72	3.51
Silance	21.00	1201.44	3.50
Alkali+ Silance	21.59	1401.26	3.61

Natural fiber impurities as fats, lignin's and pectin's are removed by the surface modification of the natural fiber. The surface smoothness and water absorption properties of the areca fiber are decreased by the surface modification. Also the flexural properties of the areca reinforced epoxy composed are improved by the different surface modification of the areca fiber [27]. The flexural properties of the areca reinforced epoxy composed are shown below.

Table 3. Flexural properties of the areca fiber reinforce epoxy composites.

Treatments	Flexural properties in N/mm <sup>2</sup> at given fiber load (wt %)			
	40%	50%	60%	70%
Untreated	30.24	38.48	42.68	24.28
Alkali treated	52.54	61.28	84.86	26.84
P. P. T	54.38	64.96	88.98	27.26
Benzoyl Chloride	56.02	66.58	94.28	28.46
Acrylic Acid	57.54	68.52	96.84	28.98

The mechanical properties of sugar palm fiber reinforcement composites have shown good properties by the potassium permanganate surface modification. The highest tensile modulus gets at the 0.066 percentage of potassium permanganate solution. The highest tensile strength is achieved at the 0.125 percentage of potassium permanganate solution [28].

#### 5. Conclusions

Introduction to natural fiber reinforced composites, the composition of natural fiber, and surface modification of the natural fiber and the effect of chemical treatments on natural fiber composites are studied. Various treatments shows that mechanical properties of the natural fiber reinforced composites like tensile flexural (strength and modulus), flexural (strength and modulus), percentage elongation and water absorption etc. are significantly

improved. The different properties of un-treated and different surface modified natural fiber composites are compared. Results shows that alkali surface modified natural fiber composites gives better tensile/flexural strength than untreated composites.

The surface modified fibers are improved the adhesion force between natural fiber and matrix and also reducing the water absorption properties of the natural fiber reinforced composites. Composites with surface modified fibers had shown superior tensile properties than un-treated fibres. Mixed surface modified fiber gives better mechanical properties then single surface modified method except alkali method. The surface modified fiber composites with silane have shown good impact strength properties. Natural fiber impurities as fats, lignin's and pectin's can be removed by the surface modifications of the natural fibers.

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