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Tensile Properties of Coir Fiber Reinforced Polyvinyl Alcohol Composites: Effect of Chemical Modification

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***Abstract*- Composite of coir fiber reinforced polyvinyl alcohol (PVA) was prepared by solution casting method. Tensile properties of the resulting composite materials were studied in detail. Unmodified and chemically modified coir fibers were used for the preparation of composites. Glutaraldehyde (GA) and sodium hydroxide (NaOH) solutions were introduced to modify coir fibers. Studies revealed that the PVA reinforced with modified fibers exhibited higher tensile properties. Fatty acids and waxy residues removed from the coir fiber by reacting in the presence of strong sodium hydroxide enhance the tensile strength. Glutaraldehyde crosslinks cellulose and lignin present in the coir fiber increased the strength. Therefore, a better stability is expected for their composites compared to the composites prepared from unmodified coir fibers. Formation of pits on the surface of the fibers by the removal of impurities improved the interaction between fiber and matrix. Furthermore, a comparison study was also done on the crosslinking of polyvinyl alcohol with glutaraldehyde.**

***Index terms*- Coir fiber, Composites, Glutaraldehyde, Tensile strength**

I.INTRODUCTION

Due to the environmental concerns in recent years, the use of natural fibers as reinforcements in polymers and composites has attracted much attention. The development of new bio-based materials has been a great motivating factor for materials scientists as seen from the increasing trend of publications in the recent decade. It indicates the effective utilization of the renewable biomass waste commonly discarded but it can be used for eutrophication[1,2].

Polymers such as poly vinyl alcohol, chitosan, chitin, poly(lactic acid), polyurethane etc. are biodegradable and environmentally friendly materials. Sustainable green composites derived from nature such as bamboo, cotton, jute, sisal, coir, etc. have received increasing attention. The combination of both categories mentioned above can be used to develop eco-friendly materials with higher physical properties. Stability of such type of materials need to be studied interms of their mechanical, thermal and structural properties[3-6]. Natural and synthetic polymers are used as matrix including starch, poly(vinyl chloride) and waterborne epoxyetc. Most of the composites show significant improvement in their properties as compared to the pristine polymer [7-9].Pre-treatment, integral extrusion and drawing process are various methods to improve the mechanical property and the enhancement is essential to introduce them for practical applications [6, 10]. Coir fibers are extracted from the husks of coconut and it can be used to prepare green composites. Coconut trees are vastly grown in tropical countries such as India, Philippines, Malaysia, Thailand, Sri Lanka. Fibers extracted from coconut husk have higher tensile strength and modulus when compared to other natural fibers. Therefore, the composite prepared by incorporating coir fiber leads to improve the strength [11-13].

Majority of the coconut fibers are discarded or burnt and the residue affects the environment. Make use of such stuffs to develop eco-friendly material products can be termed as ‘waste to wealth approach’. The advantages of coir fibers are low-cost, light-weight, sustainable, easily available and outstanding mechanical properties[13,14]. Thus many attempts have been made to make composites using coir fibers as reinforcements such as coir/Polypropylene [15,16], coir/PBS[17,18], coir/Polyester[12] to improve the strength. But the strength of the coir composite was found to be not fully satisfactory. The enhancement in strength of composites is possible only on increasing the favourable interaction between fibers and matrix. To increase the interactions, fibers have been treated with alkali and aldehyde. Alkali treatment is an economical method to improve the adhesivity between fiber and matrix. The strength deterioration of coir fiber during alkali treatment is the main drawback [13]. Aldehydes bond easily to PVA though it exhibit some toxicity and high cost, which limits their further application [14]. But bi-functional aldehydes such as glutaraldehyde (GA) are the preferred cross-linking agents due to its low cost, commercial availability, good reactivity and very low toxicity. GA reacts with the hydroxyl functional groups of PVA chains, under acidic conditions forming acetal bonds [15]. Coir fibers treated with sodium hydroxide and glutaraldehyde were used as fillers for the preparation of composites.

II. MATERIALS AND METHODS

A. Materials

Coir fibers were collected from Central Institute of Coir technology, Bangalore, India. These fibers were extracted from coconut husk of matured fruit known as brown fiber extracted by decorticators process. The moisture content of the coir fiber was about 7.74%. NaOH pellets, 25% aqueous Glutaraldehyde, Phenolphthalein indicator and Polyvinyl alcohol were procured from Karnataka Fine Chem, Bangalore, India. The chemical composition of coir fiber is as depicted in Table 1.

B. Experimental

Alkyl and Aldehyde Treatment:

For alkali treatment, 500gm of NaOH dissolved in 500ml distilled water to prepare 50% (w/v) NaOH solution. Further, the coir sample was immersed in NaOH solution for 2 hours and washed with distilled water to remove NaOH completely from the fiber. Neutrality check was done by adding Phenolphthalein as an indicator into the drained water. The washing was continued till there was no change in colour of drained water. These fibers were dried in oven at 50°C for 2 hours and cut into small pieces of length less than 2cm and used for the preparation of composites. In addition to alkali treatment, the fibers were introduced for aldehyde treatment. An aqueous solution of Glutaraldehyde (25%) was used for the chemical modification of fiber. Coir fibers were immersed in 25% glutaraldehyde for one day and dried in oven at 50°C for 2 hours. Then the resulting samples were cut into small pieces of length less than 2cm and used as fillers in composites.

Table1. Chemical composition of coir fiber

Contents	Percentage (%)
Lignin	43.61
Cellulose	39.79
Hemicellulose	5.00
Pectin	0.95
Ash	3.90

Preparation of Composites:

Initially, 5g of PVA was homogeneously dissolved in 100 ml distilled water at 95ºC for half an hour. The solution was transferred to a petri dish and allowed to cool down to room temperature. Approximately 1g of coir fiber was weighed and dispersed in the PVA solution uniformly. This solution was dried at room temperature for 10 days. Transparent and flexible coir reinforced PVA composite films with average thickness of 1mm were obtained. Composite of coir fiber with crosslinked PVA was also prepared by adding 10ml of glutaraldehyde. These composites were kept in desiccator before characterisation to avoid moisture absorption.

Tensile Testing:

Tensile properties of the composites were studied by using universal testing Machine (Hounsfield, Model H10KS) at a crosshead speed of 100 mm/s and an applied load of 1kN. The measurement was carried out according to ASTM D412 method. Percentage of elongation, tensile strength and modulus were calculated from the stress-strain plots. The average test results of five samples were reported in the results.

Water absorption:

In order to find the water absorption of the composites, samples were subjected to swell in water. Composites of 1cm X 1cm were weighed (W_o)and immersed in a 20 mL distilled water at room temperature. For every interval the composites are removed from water, wiped to remove water and weighed (W_t). The same procedure was repeated until the water uptake reaches saturation. Water absorption was calculated by using the equation [17]:

$$M = \frac{W_t - W_o}{W_o} \text{ X } 100$$

where, $W_t$is the weight of swollen film at time t and W_o is the initial weight of the film.

Scanning Electron Microscope (SEM):

Scanning electron microscopy was performed to investigate the morphology of the coir fibers with a TESCAN VEGA 3 LMU instrument. The surface was sputter-coated with gold before scanning under microscope.

Fourier Transform Infrared Spectroscopy (FTIR):

Fourier transform infrared spectroscopy studies on pristine and chemically treated fibers were carried out by dispersing the powdered fiber samples on *KBr*pellets using a Thermo Nicolet, Avatar 370 FTIR spectrophotometer. All fiber samples were recorded in the 4000–400 cm^{-1} region with 32 scans in each case at a resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

Thin transparent composites of PVA and coir fibers are prepared. Stress-strain curves provide the information about the deformation and tensile properties of the composite materials. Universal testing machine was employed to evaluate the young's modulus, tensile strength and elongation at break. The mechanical properties of PVA/coir composites are shown in Table 2. Composite with higher tensile strength and elongation at break is observed for composites of cross linked PVA with glutaraldehyde treated coir fibers. This may be due to crosslinking of PVA and GA treated fibers. The scheme of crosslinking of PVA and Glutaraldehyde is shown in scheme 1 [17].By crosslinking, PVA penetrates into the cell wall between micro fibrils. Slow curing allows PVA to penetrate into the cell wall and develops interaction between cellulose and lignin present in the fiber. This enhances the tensile strength of cross linked PVA composites with GA treated fibers. Crosslinking mechanism of cellulose in the presence of glutaraldehyde is shown in scheme 2 [18].

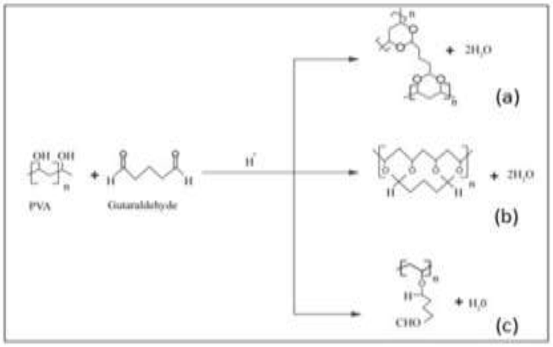
Tensile strength of cross linked PVA/NaOH treated fibers composite is better than the composites of cross linked PVA/uncured fibers. The treatment of coir fibers with NaOH removes impurities including small percentage of lignin on the surface of the fiber. Thus, crosslink density is reduced which declines the tensile strength when compared to the composite with GA treated fiber.

Table2.Mechanical Properties of PVA/coir composites

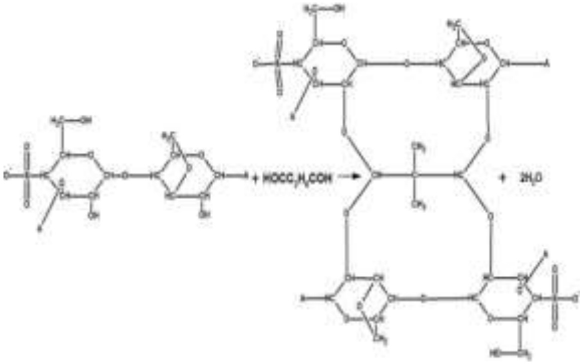
Sample Code	Tensile Strength (MPa)	Elongation at break (%)	Modulus (MPa)
PVA	45.31	825	19.41
Crosslinked PVA	46.55	450	14.71
Composite of crosslinked PVA with uncured coir	12.21	133	10.65
Composite of crosslinked PVA with NaOH treated coir fiber	16.68	116	12.71
Composite of crosslinked PVA with GA treated coir fiber	20.54	225	11.38

Fig 1 shows the stress-strain plot for different composites. The deformation behaviour of crosslinked PVA/untreated fiber composite is entirely different from the composites of fibers treated with NaOH and GA. Composite with treated fibers exhibit better tensile properties when compared to those with unmodified coir fiber. A reduction in elongation at break and enhancement in modulus as well as tensile strength are observed in case of composites with NaOH and GA treated coir fibers. Formation of pits on the surface of the fibers restricts the elongation of the resulting material.

Mechanical stability of the composite increases by crosslinking the matrix phase with GA. Composites prepared from GA treated coir fiber shows the superior elongation and stability in terms of modulus and ultimate tensile strength. Less interaction between fiber and matrix is the reason for higher value of elongation. Crosslinking of PVA and coir fiber leads to increase the tensile strength and modulus of PVA/GA treated coir fiber.



Scheme 1: Scheme showing the formation of crosslinks in PVA(a) intra-chain bonding (b) inter-chain bonding and incomplete intra chain bonding due to glutaraldehyde linking.



Scheme 2: Scheme showing the crosslinking of cellulose and Glutaraldehyde.

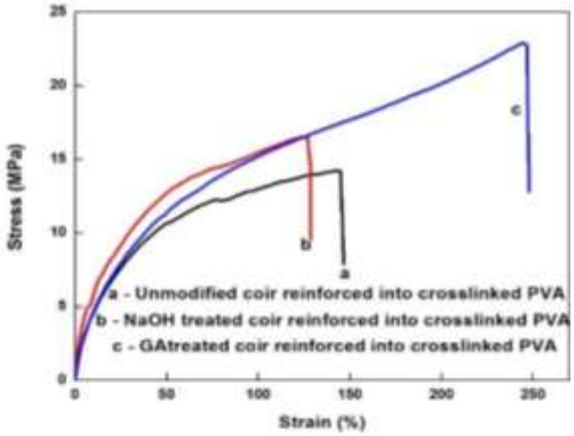


Fig 1: Stress- Strain curve for crosslinked PVA and modified coir fiber composites.

FTIR spectra of unmodified and chemically modified fibers are shown in Fig 2. The absorption bands at 2930cm^{-1}and 2860cm^{-1}are attributed to stretching of –CH$_2$and –CH- of cellulose and lignin present in the fibers. The intensity of peak at 3473cm^{-1}indicates the presence of hydroxyl groups in the fibers. The emergence of peak at 1251cm^{-1}in case of glutaraldehyde treated fibers can be attributed to the crosslinking of cellulose and lignin. The formation of shoulder at 2750cm^{-1} corresponds to C-H asymmetric stretching of methyl group in the aldehyde in case of glutaraldehyde treated fibers. The peak at 1450cm^{-1}corresponds to C-O associated with crosslinked PVA.

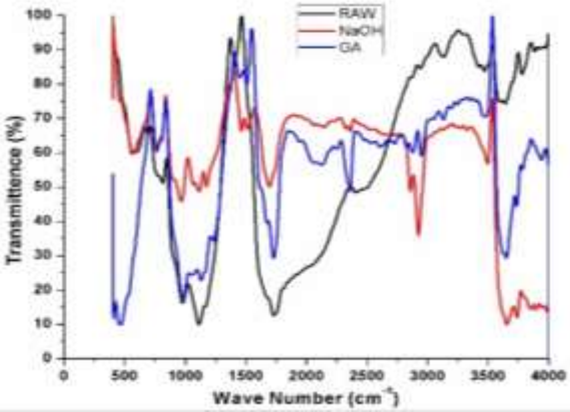


Fig 2:FTIR spectra of untreated, NaOH treated and glutaraldehyde treated coir fibers.

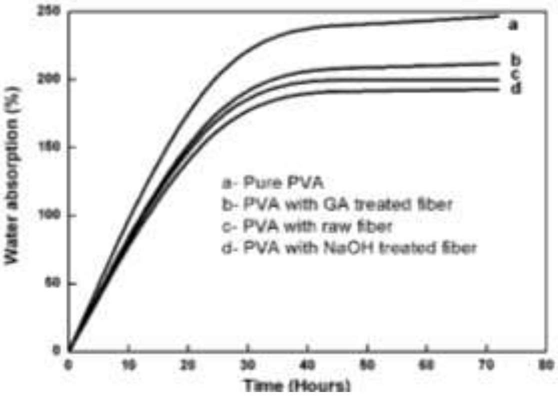
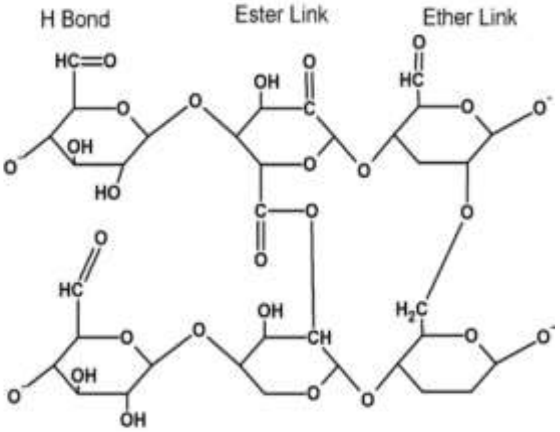


Fig 3. Water absorption behaviour of PVA/coir composites



Scheme 3: Ether and ester link.

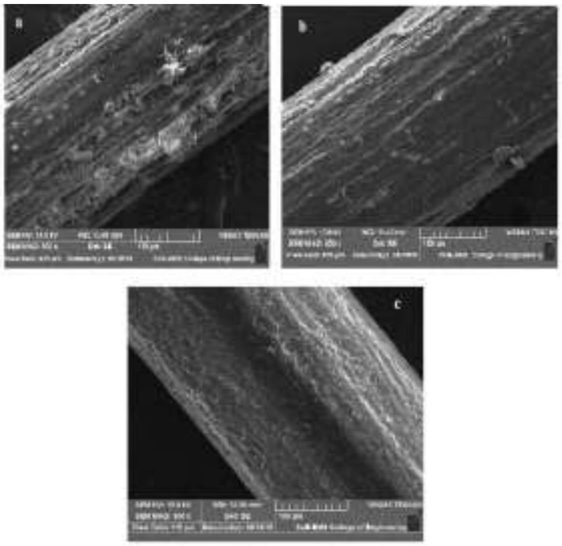


Fig 4:Sem Micrographs of (a) raw fibers (b) NaOH treated fibers and (c) GA treated fibers.

Composite of cross linked PVA with GA treated coir fiber shows higher amount of water absorption (Fig 3). Formation of pores and enhanced hydrophilic nature of GA treated fibers enhance the moisture absorption. The hydrophilic nature is enhanced due to the functional group present in the fiber. The polar cellulose, ether linkages and acetyl structure present in the fibers favours water absorption (scheme 3). PVA can be cross linked with GA because of the presence of hydroxyl group that forms acetal linkages with aldehyde group. Three type of crosslinking is formed viz., intermolecular, intra-molecular and incomplete intra-molecular crosslinking [17]. Crosslinking of GA treated fiber is clearly confirmed from the fine and continuous morphology as shown in the SEM micrographs (Fig 4c). The NaOH treated coir fiber composites showed reduced water absorption which may be due to the removal of impurities and waxy fatty acids during chemical treatment of coir fiber. Water absorption increases with increase in time until equilibrium condition is achieved. The water absorbing tendency of such composites can be eliminated by coating the surface with suitable coating materials.

IV. CONCLUSIONS

A biodegradable composite of PVA and coir fiber has been developed by solution casting technique. Coir fibers were reinforced into cross linked PVA after chemical treatment with NaOH and GA. A comparison study was conducted between the composites with untreated fiber and chemically treated fibers. Superior mechanical stability was observed for the composite with AG treated coir fibers. Composite of PVA with NaOH treated fiber shows higher tensile properties compared to the composite consists of untreated coir fibers. Crosslinking of PVA phase and introducing chemically treated coir fibers into PVA enhances the stability of resulting composite material.

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