

ALKALI TREATMENT AND ITS EFFECT ON TRIBOLOGICAL PROPERTIES OF NATURALLY WOVEN COCONUT SHEATH POLYESTER COMPOSITE

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Abstract: In the recent years natural fibres have drawn great interest for its bio-degradability, low cost and its availability in nature. Among different types of natural fibres, naturally woven coconut sheath fibres are one of the recently explored alternatives for synthetic fibres. These fibres are generally treated with alkali for enhancing mechanical properties and reinforcing characteristics. Tribological applications like gears, cams, bearings, etc. can be benefited from such composites. In most cases chemical treatment are done favouring the structural properties however, their influence on tribological properties are rather not considered. In the current research, hybrid composites (polyester resin with naturally woven coconut sheath (N) and glass fibres (G)) were tested against hardened steel counterface in a pin on disc configuration. Tests were performed at 40 N normal force and 3.5 m/s sliding velocity. From the results all hybrid combinations except (NNN) shows degrading wear properties with the alkaline treatment. The friction properties are modified by having low friction coefficients for all combinations except NGN and GGG hybrids. From the observed SEM images the surface morphology of NNN hybrid significantly differs from the rest of the combinations in both treated and untreated specimens. The partial removal of individual phase (resin) prevails in untreated specimen for which the fibres are highly visible. However, such phenomenon is not dominant in the alkali treated material showing better reinforcing behaviour complimenting low friction properties. The alkali treated specimen has reduced fibre size comparing the untreated specimen which results in low wear resistance. Compromise between friction and wear properties between each other the untreated fibres are best suited for tribological applications. Furthermore, investigations on treatment process and other treatments might have some influence in tribological behaviour.

Keywords: coconut sheath; glass fibre; hybrid; composite; wear.

1 INTRODUCTION

Polymer composites, used in versatile for tribological applications have changed its course from synthetic fibres to natural fibres in the last few decades. The most commonly used fibres in the composites are carbon fibres, aramid fibres and glass fibres. Cost is one of the driving factors on the selection of fibers in polymer composites for which the natural fibres has an effective role. In the recent years, explorations on the capabilities of natural fibres for engineering applications are being done [1]. The natural fibre which is freely available in nature and a renewable source are utilized based on the resources available from different demography. Some of the natural fibres which are being investigated in the recent years are banana fibres, jute, coir and sisal [2-5]. All these fibres are available in loose form however in few engineering application woven fibres are used for gaining structural integrity and modifying tribological properties in accordance with design aspect. Such a natural fibre is readily available from coconut tree in form of leaf sheath. Already the coir from the fibrous coat of the coconut were used as a filler material, nevertheless, the naturally woven fibres in form of leaf sheath in form of mats are neglected. This can be used as naturally woven fibers with polymer matrix. Studies on structural properties of the coconut leaf sheath demonstrate its use as a laminate in polymer composites [6 & 7]. Only limited research was done on composites from these materials to identify its mechanical and tribological capabilities [8, 9].

Natural fibres as such cannot be used due to inhomogeneity and binding properties of the fibres with the matrix. Such incompatibilities makes difficult for using them as a filler material in polymer composites. Goud *et al* briefs that this incompatibility is a consequence of mismatch in the polar group and the water absorption properties between the matrix and the filler. Studies reveal that alkaline treatments are being done to increase the binding strength, wettability and the compatibility between fibre and the matrix [7-15]. The hydrophilic nature of fibres was converted to hydrophobic by alkali treatment for enhancing the wettability and to increase the interface strength between the fibre and the matrix. Reddy *et al* reported that the elimination of amorphous hemicellulose was evident on using alkali treatment, moreover the crystal nature of the fibres were improved [6]. Ray *et al* also reported the removal of hemicellulose which resulted in weight loss for jute fibres. In a study conducted by Goud *et al* on palm fibres epoxy composites the tensile and the flexural properties improved however, the impact strength has decreased due to the reduction in fibre pull-out mechanism. Thamane *et al* also reported better results on the mechanical properties in Agave Americana with HDPE [14]. Apart from the improvement in structural properties the alkali treatment also improved the thermal stability of the fibres Liu *et al* observed positive thermal behaviour in alkali treated Indian grass fibre. Thus based on literature it is interesting to investigate the alkali treated naturally woven coconut fibres for its structural and tribological properties. Since these surface modification of these fibres can potentially affects the tribological properties a thorough study on the alkali treated fibres are required. Subsequent to the alkali treatment silane treatment further enhances the mechanical properties of the material. In our earlier research on coconut sheath-reinforced composite has improved its tensile, flexural and impact strength by 85%, 110% and 75% respectively. The waxy substances are being removed in the paves way for silane deposition on the fibre surface [9].

These treatment methods are based on enhancing the structural properties and the mechanical behaviour, however the effect of the treatment on tribological behaviour and the material responses to surface interaction are not been well understood. The fibre pull out mechanism in impact strength observed by Goud *et al* reveals that the individual phase removal in composites could be avoided on alkali treated specimen. Considering wear, phase removal is critical in applications where contaminations of debris are disregarded. The modification of the tribological properties depends on phase that is dominant on the individual phase removal. Debris of fibre will have negative impact on friction properties but the resin removed as an individual phase can act as a protective layer in improving friction and wear. Since there is a regular pattern involved in the woven fabric the influence of fibre orientation will also significantly affect the frictional properties in tribological applications. Our earlier wear tests with pin-on disc configuration on silane treated (trichlorovinyl silane in 1 L acidified water with 3.5 pH.) composites shows excellent results on comparing with glass fibre reinforced polyester composite. Fibre pull-out was also eliminated in the silane treated naturally woven hybrid composites.

In the current research, naturally woven coconut sheath on an unsaturated polyester resin in combination with glass fibre is used to study the tribological behaviour. The arrangement of the fibre to the tribological behaviour is also studied. The difference in friction and wear characteristics between untreated and alkali treated composites and its influence on wear mechanism is investigated. The overall objective is to enhance the tribological properties and cost reduction to create a friction map with respect to different material combinations and arrangements. The current investigation unveils the dependence of wear mechanisms on the treatment process which elucidates the usage of newly developed natural fibre composites for specific tribo-systems.

2 EXPERIMENTAL DETAILS

2.1 Materials

Unsaturated Polyester (USP) general purpose grade was used as matrix material. Methyl Ethyl Ketone Peroxide (MEKP) as catalyst and Cobalt-Naphthenate as accelerator were used. Commercially available E-Glass chopped strand mat (GL) was also used as reinforcement for comparison purpose. Figures 1 & 2 shows the photographs of coconut tree arrow marked with the coconut sheath (CS) which is processed further for enhancing the fibre properties. Table 1 shows the property comparison between most reported coir fibres with newly identified woven coconut sheath fibres. It can be noticed that, the crystalline member (i.e. cellulose) is more in the newly identified coconut sheath compared to the conventional coir fibres. In plant fibre, the cellulose is the primary load bearing member.



Figure 1: Coconut tree with sheath (arrow marked)



Figure 2: woven coconut sheath

In literatures (Table 1), the strength of the coir fibres is reported as weak while comparing with other natural plant based fibres. One of the reason for having weak strength is the the cellulose content, for which it is expected that the newly identified coconut sheath may differ from conventional coir fibres in all aspects. On the other hand, the presence of wax in coconut sheath may significantly influence the formation of the composite interface.

Table 1: Property comparison for novel coconut sheath with conventional coir fibres

Properties	Coir Fiber	Coconut Sheath
Wax content (%)	-	0.4062
Density at room temp. (g/cc)	1.15	1.3753
Cellulose content (%)	32	68.36
Lignin content (%)	29.23	20.63
Moisture content (%)	8	8.79
Ash content (%)	1.5	1.044

2.2 Surface Modification and fabrication

The naturally woven coconut sheath was initially battered with cold water and dried. The dried fibres were immersed in 1 N alkali solution for an hour. After thorough washing with distilled water, the woven mats were dried in room temperature for a day. Furthermore, the woven mat were cut into the required dimension and kept ready for moulding. The compositions of hybrid composites were described in Table 2. Compression moulding technique was used for the fabrication of composites. An optimized pressure of 50 kg/cm² load was applied for compression. After 12 hours curing, specimens were taken out from the mould and cut into the dimension according to the ASTM standards.

Table 2: Formulations of composite specimens

Composites	Specimen code	Unsaturated polyester (wt%)	Coconut sheath (wt%)	Glass fibre (wt%)
Coconut sheath fibre (CS) -USP	NNN	52	48	-
Glass fibre (GL) -USP	GGG	52	-	48
Coconut sheath + Glass fibre -USP	NNG	52	32	16
Coconut sheath + Glass fibre -USP	NGN	52	32	16
Coconut sheath + Glass fibre -USP	GGN	52	16	32
Coconut sheath + Glass fibre -USP	GNG	52	16	32

2.3 Wear testing

A pin-on-disc configuration as per ASTM G-99 standard was used for the sliding wear test. Composite pin with 10mm x 10mm x 3mm dimension against hardened alloy steel disc with hardness value of 62 HRC and arithmetic mean roughness (Ra) of 0.54 were used. The surfaces of both the sample and the disc were cleaned with a soft paper soaked in acetone and thoroughly dried before the test. The wear was measured by mass loss for which the pin assembly was initially weighed to an accuracy of 0.0001 g in an electronic balance (SHIMADZU AUX 220). A normal force of 30N was applied for a sliding distance of 2100 m at a sliding velocity of 3.0m/s. Prior to testing, the test samples were polished against a 600 grade SiC paper . The specific wear rate (Ks) was calculated from the equation:

$$K_s = \frac{\Delta V}{Lxd} \left(\frac{m^3}{Nm} \right)$$

Where, ΔV is the volume loss in m^3 , L is the load in Newton, and d is the abrading distance (Sliding distance) in meters.

3 RESULTS AND DISCUSSION

3.1 Surface Modification Effect

Fourier transform-Infrared spectroscopy was performed in both the treated and untreated specimen showing significant difference in wavelength between each other. Many of the FT-IR bands were shifted to higher wave number (by $3-6 \text{ cm}^{-1}$) in NaOH treated coconut sheath reinforced composites. However, only few bands were shifted to lower wave number (by $3-5 \text{ cm}^{-1}$). The absorbance measured at all the peaks were increased in the NaOH treated coconut fibre. The significant broadening of the band at around $3100-3700 \text{ cm}^{-1}$ in NaOH treated coconut sheath reinforced composite can be attributed to the increased NaOH treatment time and hydrogen bonded OH stretching vibrations from the chemically bonded OH groups of the cellulose structure. The overall trend from shifting in wave numbers, increasing absorbance and broadening of peaks supports the increase of crystallinity on NaOH treated coconut sheath on comparing with untreated coconut sheath fibre composite.

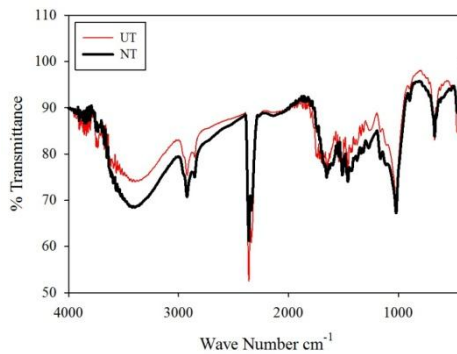
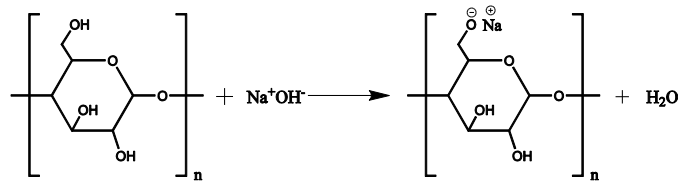


Figure 3: FTIR Spectra of treated, untreated coconut sheath composites

The possible chemical modification mechanism of natural fibre cellulose by NaOH treatment is explained here,



The physical properties of the coconut sheath fibre were evaluated after the alkali treatment. The Table 3 shows the modification in the physical and chemical properties of coconut sheath fibre treated with NaOH over the untreated fibres, where the percentage of cellulose and wax content have significantly reduced.

Table 3: Property comparison for untreated and treated coconut sheath fibres

Property	Untreated Coconut Sheath	NaOH Treated Coconut Sheath
Wax content %	0.4062	0.1224
Density g/cc	1.3753	0.9796
Cellulose content %	68.36	52.89
Lignin content %	20.63	33.29
Moisture content %	8.79	12.66
Ash content %	1.044	5.355

3.2 Dry Sliding Wear

The variation of the coefficient of friction as a function of sliding distance for coconut sheath and hybrid composites is shown in Figures 4 & 5.

The coefficient of friction can be understood in two different directions from the application point of view. For bearing application a relatively lesser or negligible CoF is expected and for braking application a high friction coefficient is required. Figures 4 & 5 clearly show the application direction for this novel reinforcement. CoF for glass fibre composite and its hybrid composite with high glass contents shows less CoF whereas coconut sheath and its hybrid with high coconut fiber contents shows relatively higher CoF. Irrespective of reinforcements, an increasing trend in CoF observed from onset to 1500m, besides steady state noted

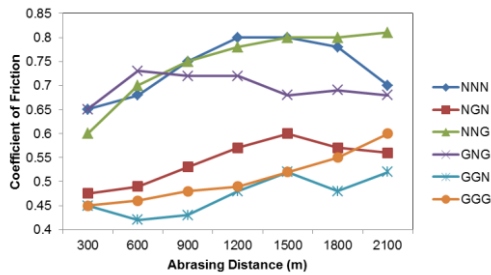


Figure 4: CoF for untreated composites

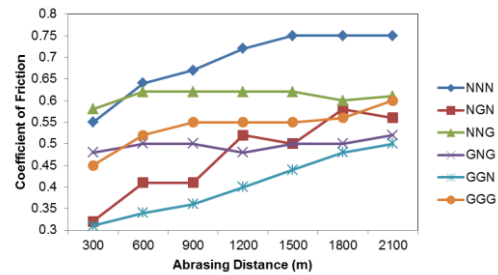


Figure 5: CoF for treated composites

In general with glass fibre reinforcement, wear debris cover the surface and a significant deposit of transfer film was observed on the counter material thus reducing friction characteristics for having lower CoF. However, coconut sheath fibre composites shows negative frictional characteristics on comparing with glass fibre reinforced composites. Moreover the alkali treatment specimen shows better frictional properties than the untreated specimen. However, this is with the hybrid group NGN with 32% of natural fibres shows a relatively low CoF for untreated specimen. Between the untreated and the treated specimen individual phase removal was evident as a consequence of poor binding property. Due to the inhomogeneity in the surface morphology a high CoF incurs for the untreated material.

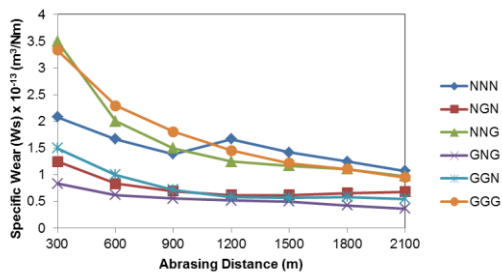


Figure 6: Specific Wear for untreated composites

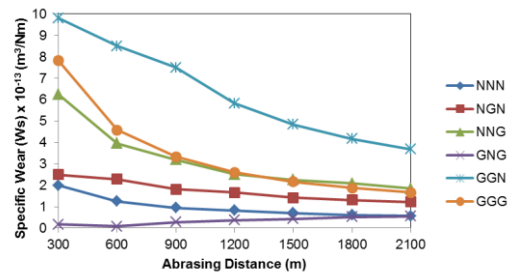


Figure 7: Specific Wear for treated composites

Figures 6 & 7 shows the specific wear rate as a function of abrading distance. The wear increased with increase in brittle nature. The glass fibre reinforced composites being more brittle shows higher wear rate. Loss of material is common in onset and upto 1200m running. NNN composites shows less wear compared to conventional glass fibre reinforced composites. Hybrid shows intermediate wear behaviour, surface modification through alkali treatment significantly modifies the wear loss. To have a better insight about the mechanisms contributing to wear and friction post-mortem analysis through SEM was done (figures 8 – 11). SEM imaging was done at different locations of the pin however; micrographs representing the dominant mechanism are presented in figure 8 - 11.

Figure 8 shows the micrograph of the worn untreated coconut fibre specimen where non-uniformity in the surface morphology in forms of craters and unevenly distributed resin is observed. Re-adhesion of the resin covering the fibres is apparent due to the poor wettability and binding property of the untreated specimen. The non-uniformity in the surface morphology contributes to have high frictional characteristics. But, in case of alkali treated specimen a homogeneous spread of resin is visible as seen in figure 10 moreover; partial removal of individual phase (resin) is also seen however it is not dominant.

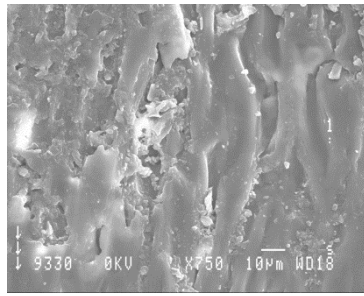


Figure 8: Worn surface of untreated CS/USP composite

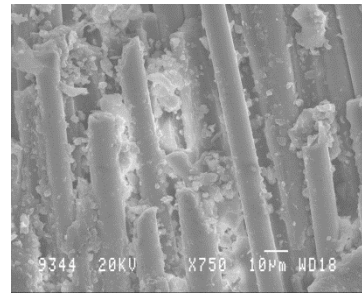


Figure 9: Worn surface of untreated GF/USP composite

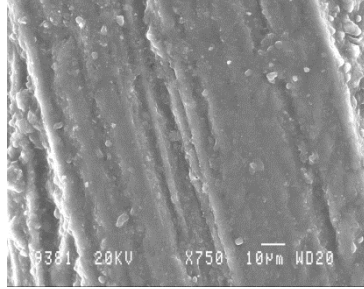


Figure 10: Worn surface of treated CS/USP composite

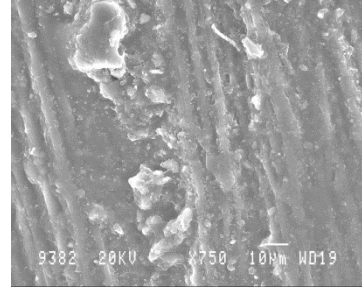


Figure 11: Worn surface of treated GF/USP composite

Comparing figure 8 and 10 the treated specimen has a relative smaller fibre. Considering figure 9 and 11 of the glass fibre reinforced composites there is also a significant different in the fibre size. Also removal of individual phase is the dominant mechanism in the untreated specimen. In both case the micrograph of the treated specimen shows a homogenous surface with partial exposure of thinned fibres. On the whole the treated specimen underwent a mild abrasion by means of micro-plowing between the fibres. In untreated specimen an adhesive nature is seen in figure 8 for the natural fibre composites. And for the untreated glass fibre composites broken fibres shows a form of multiple cycle deformation mechanism by resin removal and debonding of fibres. The protective transfer film by the phase removal of resin deposited on the counterface materials aids for better wear properties in untreated specimen.

4 CONCLUSION

The tribological properties of the coconut sheath and glass fibre reinforced USP matrix composites have been investigated. The effect of surface modified fibres using NaOH on the tribological behaviour is discussed. The following conclusions could be drawn:

- The novel coconut sheath reinforcement showed good wear resistance compared to conventionally used glass fibre reinforcement.
- Fibre surface modification through alkali bath increased the mechanical interlocking and forms thick interface.
- Composite made using surface treated coconut sheaths has high CoF than the glass fibre composites.
- The high adhesion bonding between the matrix and the coconut sheath fibre aids to a transition in mechanism from resin cratering to abrasion. Alkali treatment is effective in coconut fiber composites having high wear resistance however, treated glass fiber composites show poor wear characteristics and hybrid composites shows intermediate wear behaviour

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6 REFERENCES

- [1] Marino Xanthos, Polymers and Fillers, Functional Fillers for Plastics: Second, updated and enlarged edition., ISBN: 978-3-527-32361-6 John Wiley & Sons, 3-16, Jan-2010.

- [2] Sushree Sangita Mullick, Fabrication And Characterisation Of Alkali Treated Natural Fibre Reinforced Polymer Composites, Master thesis, Department of physics, Indian institute of technology-Rourkela, May 2012
- [3] Singh V. K, Gope P. C, Chauhan Sakshi, Bisht Deepak Singh, Mechanical Behavior of Banana Fiber Based Hybrid Bio Composites, *J. Mater. Environ. Sci.* 3 (1) (2012) 185-194
- [4] P. Asokan, M. Firdoous and W. Sonal, Properties And Potential Of Bio Fibres, Bio Binders, And Bio Composites, *Rev.Adv.Mater. Sci.* 30 (2012) 254-261
- [5] Sudhakar Majhi, S.P.Samantarai, S.K.AcharyaInternational, Tribological Behavior of Modified Rice Husk Filled Epoxy Composite, *Journal of Scientific & Engineering Research*, Volume 3, Issue 6, June-2012
- [6] K. G. Satyanarayana, C. K. S. Pillai, K. Sukumaran, s. G. K. Pillal, p. K. Rohatgi, kalyani vijayan, Structure property studies of fibres from various parts of the coconut tree, *Journal of materials science* 17 (1982) 2453- 2462
- [7] Obi Reddy K. Sivamohan Reddy G. Uma Maheswari C. Varada Rajulu A. Madhusudhana Rao K, Structural characterization of coconut tree leaf sheath fiber reinforcement, *Journal of Forestry Research* (2010) 21(1): 53-58
- [8] Irullappasamy Siva, Jebas Thangiah Winowlin Jappes, Bheemappa Suresha, Investigation on Mechanical and Tribological Behavior of Naturally Woven Coconut Sheath-Reinforced Polymer Composites, *Polymer Composites*, 723-731, 2012
- [9] J. T. Winowlin Jappes, I. Siva, Studies on the Influence of Silane Treatment on Mechanical Properties of Coconut Sheath-Reinforced Polyester Composite, *Polymer-Plastics Technology and Engineering*, 50: 1600–1605, 2011
- [10] Govardhan Goud and R N Rao, Effect of fibre content and alkali treatment on mechanical properties of Roystonea regia-reinforced epoxy partially biodegradable composites, *Bull. Mater. Sci.*, Vol. 34, No. 7, December 2011, pp. 1575–1581.
- [11] W. Liu, a. K. Mohanty, I. T. Drzal, p. Askel, m. Misra, Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites, *Journal Of Materials Science* 39 (2004) 1051 – 1054
- [12] V. Manikandan, J.T. Winowlin Jappes, S.M. Suresh Kumar, P. Amuthakkannan, Investigation of the effect of surface modifications on the mechanical properties of basalt fibre reinforced polymer composites, *Composites: Part B* 43 (2012) 812–818
- [13] Dipa Ray, B K Sarkar, A K Rana And N R Bose, Effect of alkali treated jute fibres on composite properties, *Bull. Mater. Sci.*, Vol. 24, No. 2, April 2001, pp. 129–135.
- [14] Timothy Thamae, Caroline Baillie, Influence of fibre extraction method, alkali and silane treatment on the interface of Agave americana waste HDPE composites as possible roof ceilings in Lesotho, *Composite Interfaces*, Vol. 14, No. 7–9, pp. 821–836 (2007)
- [15] M.Dedeepeya, T.Dharma Raju & T. Jayananda Kumar, Effect of Alkaline Treatment on Mechanical and Thermal Properties Oftypha Angustifolia Fiber Reinforced Composites, *International Journal of Mechanical and Industrial Engineering (IJMIE)*, ISSN No. 2231 –6477, Vol-1, Issue-4, 2012