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Wear Behavior of Coir Reinforced Treated and Untreated Hybrid Composites

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Abstract:
The aim of this investigation is to study the three-body abrasive wear behavior of different weight percentage (wt%) filled organo-modified montmorillonite (oMMT) with constant wt% of treated and untreated coir sheath (CS) in unsaturated polyester (USP) resin. There-body abrasive wear of the hybrid composites were studied under different filler loading, treatment of the coir sheath, and abrading distance. The results of the abrasive wear test revealed that the wear volume increases with increase in abrading distance and specific wear rate is high for the untreated composites (UTCs) compared to alkali treated composites (ATCs) and silane treated composites (STCs). STCs with 1 wt% oMMT-filled USP hybrid composite exhibited better abrasive wear resistance compared to UTCs and ATCs. Different wear mechanisms were observed on the worn surfaces of the composites, including pitting, micro- and/or macro- cracks, as well as crack propagation of the matrix in the transverse direction.

Key words*: oMMT filled and CS reinforced USP composites, abrasive wear, Wear mechanisms*

1. Introduction

The need for the use of newer materials to combat wear situation has resulted in the emergence of polymer-base composites. Polymers and their composites are being used increasingly because of their good strength and low density. With their many advantages, polymers and their composites are now being used for numerous tribological purposes such as seals, gears, bearings, breaks, clutches, transmission belts, rollers, tank track pads, artificial joint, and office automation machinery. The inherent deficiency of polymer could be altered successfully by using varies special fillers namely short fibers, micro and nano-sized particulate filler [1]. The use of fillers, reinforcements and lubricants in the matrix, give raise to many combinations that provide increasing load withstanding capability, reduced co-efficient of frictions, improved wear resistance and thermal properties, higher mechanical strength etc. An internally lubricated composite with thermal stability and increased resistance to wear is an area wherein research is to be carried out [2].

Unsaturated polyester (USP) is a thermoset, capable of being cured from a liquid or solid state when subjected to a right condition. USP differs from saturated polyester, which cannot be cured in this way. In chemistry the reaction of a base with an acid produces a salt. Similarly, in organic chemistry the reaction of an alcohol with an organic acid produces an ester and Water. By using the special alcohols, such as glycol, in a reaction with di-basic acids, a polyester and water will be produced. Tayeb [3] explored the possibility of using sugar cane fibers reinforced polyester composites as a new candidate tribo-material for bearing applications. Yichenga et al. [4] fabricated composites with 4 types of pulp fibers and two types of thermoset polymers. 4 pulp fibers included hardwood and softwood high-yield pulp (HYP), kraft pulp, and whatman cellulose fibers and 2 polymers included unsaturated polyester (UPE) and vinylester (VE). FTIR and TGA tests were conducted and concluded that the two HYP fibers were more compatible to the UPE resin. Yousif et al. [5] developed polyester composites based on betelnut fibers and studied adhesive wear and frictional performance under deferent applied loads and sliding distances with dry-wet contact conditions they have used unsaturated polyester (Butanox M - 60) mixed with 1.5 % of methyl ethyl ketone peroxide (MEKP) as catalyst was selected as resin for their work. The results revealed that the fabricated composites had better wear and frictional performance under wet contact condition compared to dry. Raghu et al. [6] developed natural fiber composites of untreated and alkali -treated silk-sisal unsaturated polyester (USP)-based hybrid composites by using hand lay-up technique. Methyl Ethyl ketone peroxide and cobalt napthenate were used as a catalyst and accelerator. The effect of some acids, alkalis and solvents were used on the matrix and hybrid composites were studied according to ASTM standards and found that

silk-sisal hybrid composites are strongly resistant to almost all chemicals except carbon tetrachloride. They also suggested that these hybrid composites can be used for making water and chemical storage tasks.

Many researches have been done on the coconut tree parts like coconut coir and coconut shell due to their high potential for the mechanical and wear properties. With increasing emphasis on fuel efficiency, natural fibers such as coir based composites can be used in wide applications in automobiles and railway coaches and buses for public transport system [7]. Girish et al. [8], Sarawuth et al. [9], and Shiv Kumar and Kumar [10] developed composites reinforced with coconut coir and coconut shell particles and studied the mechanical properties of the composites and concluded that the composites reinforced with coconut parts yield good mechanical properties. Fiber surface treatment improves the tribological behavior.

Compared to inorganic fiber, natural fiber is a renewable and abundant resource. It has less negative impact on the environment owing to its ability of recycling and biodegradability. However, natural fiber possesses inherently complex structure, thermal degradation, and absorption properties. Therefore, studies have been examined the pre-treatments of the natural fibers and their effects on interfacial adhesive mechanism of natural fiber and polymer composites. Sudhakar et al. [11] developed a polymer matrix composites using modified and unmodified rise husk as reinforcement and studied their tribological properties by using pin on disk wear tester with abrasive paper of 400 grades, 120 mm diameter of rotating disc and by varying the applied loads. The modified rise husk composite is found to give better tribological properties compared to the other. Navin Chand and Dwivedi [12] studied the abrasive wear behavior of jute fiber-reinforced polypropylene composites. They followed 2 fiber treatment approaches. In 1st one they treated the jute fiber for 5min with 1% solution of maleic anhydride – grafted polypropylene dissolved in toluene solvent at 100º C. After treatment fibers were washed in toluene to remove extra MA-g-PP and then dried at 60º C in woven. In another approach 1 wt% MA-g-PP was added during the melt mixing of chopped jute fiber with PP at 170º C in a two roll mixture. It has been found that addition of MA-g-PP coupling agent during melt mixing gives better wear resistance as compare to the jute PP composites having MA-g-PP solution – treated jute fibers. Mansour et al. [13] focused the effect of chemical treatment of fibers by alkalization of alfa fiber reinforced polyester composite. Results showed that the bending behavior of composites made from alkali treated fibers are better compared to the UTCs for yielding better tribological properties.

Nano fillers have improved the wear resistance of the composites. In most of the cases, a polymer nanocomposite relies for its better wear resistance properties on the extremely high interface area between the filler and the matrix. High interface leads to a better bonding between the two phases and hence better strength and stiffness properties over unfilled polymer or traditional polymer composites. Many research has being carried out in the development of nano particles filled polymers composites through incorporation of nano-scaled materials such as ZrO_2, SiO_2, Si_3N_4, Al_2O_3, SiC, and ZnO [14-17]. One of the distinct advantages of nano fillers over micro fillers lies in that the performance improvement is often acquired at relatively low concentration of the nanofillers. Nanoclay is one of the most affordable material that has shown promising results in polymers. Nanoclay is made from montmorillonite mineral deposits with “platelet” structure with average dimension of 1nm thick and 70 – 150 nm wide. Nanomer 1.28E nanoclay is a modified montmorillonite mineral which is formulated for USP resin. When properly dispersed, nanomer 1.28Enanoclay creates a near-molecule blend commonly known as a nanocomposite. This new type of composite enhances strength. Nanomer 1.28E is supplied as a white powder which disperses to a particle so thin; they are nearly transparent in the resin system [18]. Xiaoling et al. [19] represented a better route to synthesize high-performance polymer MMT nanocomposites. They prepared two kinds of polymeric surfactant-modified MMTs by melt compounding. The experiment conducted by them proved that PMMA–H–MMT show better performance in increasing tribological and thermal stability of PVC-MMT composites. Suresha et al. [18] prepared organo-modified montmorillonite (oMMT)-filled epoxy nanocomposites with different wt% of oMMT. They studied three-body abrasive wear of the fabricated composites and revealed that the wear volume loss of all samples was increased with increase of load and abrading distance. The composite with 5 wt% oMMT filled epoxy nanocomposites exhibited better wear abrasive resistance as compared to that of neat epoxy and other oMMT filled epoxy nanocomposites.

Based on the above literature studies, till date no work was carried for the effect of treatment of coir sheath on three body abrasive wear behavior, and no work has been done in the combination of coir sheath and oMMT filled USP composites on the three-body abrasive wear behavior. In view of the above, this research of organo-modified montmorillonite-filled unsaturated polyester composites with different weight percentage of organo-modified montmorillonite reinforced with untreated, alkali treated, and silane treated coir sheaths.

2. Experimental details

2.1. Materials

General purpose unsaturated polyester (USP)of grade (KUP – 401) with density of 1.10g/cm^3 and hardener Methyl ethyl ketone peroxide (MEKP) were supplied by Rainbow Petro Chemical Industries Private Limited, New Delhi.

Coir sheath (CS), which is abundantly available in India, second highest in the world after Philippines,of density 0.19 g/cm^3, diameter of each fiber in the sheath of 0.5mm, tensile strength 22.1-88.64 MPa is taken as reinforcement. Table 1 shows the chemical composition of the CS. Because of high lignin content, coir is more durable compare to other natural fibers. The oMMT used was nanomer 1.26E supplied by M/s Sigma-Aldrich, India. This oMMT was surface-treated with octadecylamine surfactant for good dispersion in unsaturated polyester resin. The physical properties of the oMMT used in the present study are listed in the Table 2.

Items	Percentages (%)
Water soluble	5.25
Pectin and related compounds	3.00
Hemi-cellulose	0.25
Lignin	45.84
Cellulose	43.44

Table 1: Chemical composition of coir

Physical properties	Montmorillonite (nanomer 1.28E)
Color	Off white
$d_{(100)}$(nm)	2.34
Average particle size (μm)	8-10
Organic modifier	Octadecylamine
Bulk density (g/cm^3)	1.90
Cationic exchange capacity	130 meq/100g
Aspect ratio	200-500
Surface area (m^2/g)	750
Young's modulus (GPa)	175

Table 2: Physical properties of oMMT filler

3. Hybrid Composites Fabrication

Naturally woven coir sheaths were used as reinforcement. Three sets of composites were fabricated based on the treatment of the CS; untreated CS, alkali treated CS, and silane treated CS. In each set, filler was loaded as 0, 1, 2, 3, and 5 wt% in order to evaluate the optimum filler incorporation as CS wt% is maintained constant in all the sets of composites. In first set of five samples the untreated CS, in second set of five samples alkali treated CS, and in third set of five samples silane treated CS were taken along with varying matrix and filler content according to the calculated wt%. Table 3 shows the material composition of the fabricated composites.

Pre-calculated amount of USP, and oMMT, and were mixed using IKA high-shear mixer (T-T18 ULTRA TURRAX Basic) at an operating speed of 24,000 rpm for 15 min. the temperature during mixing was maintained at about 30ºC. After mixing, the mixture was degassed in a vacuum chamber for about 45 min. Then the curing agent was poured into mixture for developing the coir sheath reinforced laminates. The composite laminates were prepared by hand layup technique followed by compression molding. Naturally woven CSs were cut to the dimensions of 180*150 mm^2.

The resin was prepared by adding the catalyst and accelerator (2% of resin) used and stirred well for few min and a layer was applied on bottom half of the mold and the first layer of fabric was carefully placed over the resin coated surface and roller were used to thoroughly wet the reinforcement with the resin to enable good compaction and to remove entrapped air. The procedure was repeated

up to the number of fiber mats was laid. After applying the final layer of resin, layer of release film was applied and the top half of the mold was placed on it. An optimized pressure of 50kg/cm^2 load was applied for compression. After 12 hours of curing the specimens were taken out from the mold.

Alkali treatment: The second set of CSs was treated with 1 N alkali (sodium hydroxide) solution for 30 min at ambient temperature, maintaining a fiber-to-liquor ratio of 1:30 (w/v). The alkali treated fibers were washed several times with tap water to remove excess alkali and then with dilute acetic acid to remove any traces of alkali from the fiber surface and finally washed thoroughly with distilled water. Then the treated fibers were dried at room temperature for one week and finally kept in a hot air oven at 100^{o}C until it dries [20].

Silane treatment: A solution of 1% v/v 3-aminopropyltriethoxy silane was prepared in acetone. Acetone was used in preference to water to promote hydrolysis to take place with the moisture on the surface of the fibers rather than within the carrier. The pH of the solution was maintained at a value of 4 to bring about complete hydrolysis of the silane by the addition of acetic acid. The solution was then stirred continuously for 10 min. Then the third set of coir sheaths were immersed in the prepared solution for 30 min, and then washed thoroughly with distilled water. Then the treated fibers were dried at room temperature for one week and finally kept in a hot air oven at 100^{o}C until they dry [21].

4. Abrasive wear test

The modified dry sand-rubber wheel abrasion test set up (Make: Magnum Engineers, Bangalore) as per ASTM G-65 was used to conduct the three-body abrasive wear experiment and the test set up is as shown in Figure 1. The abrasive was fed at the contact face between the rotating rubber wheel and the test samples. The test was conducted at a rotation speed of 200 rpm and the rate of feeding the abrasive was 255 ± 5 g/min. The experiments were carried out under the load of 33N, abrading distance of 250m and 500m for different hybrid composites. The wear was measured by the loss in weight, which was then converted into wear volume using the measured density data. The specific wear rate (K_s) was calculated using wear volume using equation 1.

$$K_S = \frac{V}{L \times D} \quad [m^3/Nm] \qquad (1)$$

Where, V = volume loss, L = applied load, and D = abrading distance.

Figure 1: Dry sand rubber wheel abrasion tester

5. Scanning Electron Microscopy

After wear test, the worn surfaces were examined using a scanning electron microscope (SEM; JSM 840A model and JEOL make). Before taking micrographs, a thin gold film was deposited on the worn surfaces. Before the microscopic examination, a thin gold film was coated on the surfaces to enhance the conductivity of the samples and then photos were taken at specified magnification.

6. Results and Discussion

The three-body abrasive wear properties of hybrid composites were tested using the dry sand/rubber wheel abrasion test set up. Constant load of 33N, abrasive grain of grit size 218μm and sliding distances of 250 m and 500 m were considered as conditions for testing three groups of composites.

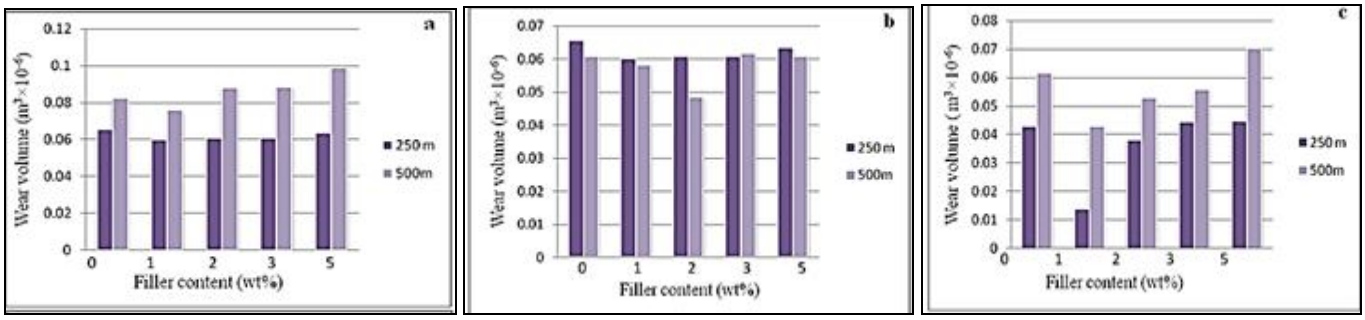

Figure 2: Wear volumes of (a) untreated, (b) alkali treated, and (c) silane treated composites under different abrading distances

The severity of abrasive wear depends upon the size abrasive particle size, shape and hardness, the magnitude of stress imposed by particle, and the frequency of contact wheel and composite. High contact pressure transferred to the abrasive has been shared by few sand particles, leading to maximum stresses at contact region. Hence, stress produced by an abrasive is sufficient to facilitate failure of matrix, leading to the matrix removal. Once the wear track is generated, with continuing wear, nano-surface layers are gradually exposed to the abrasive environment. Exposed nano-surfaces are then de-bonded from the surface as consequence of inadequate matrix support. More number of abrasive particles will come in contact rubber wheel, and load being shared by more number of abrasives leading to the decrease of stress at the contact regions.

7. Wear Volume

Figure 2a, 2b, and 2c shows the details of wear volume of the UTCs, ATCs, and STCs with respect to wt% of filler loading and abrading distances under 33N load. The data showed that the treated fiber reinforced composites showed better performance, because of the improved interaction between the polymer chains with the fiber and the matrix in the modified fiber reinforced composites. Lowest wear volume of 0.02209 cm^3 was found in STCs under 33N load, 1 wt% filler loading and 250 m abrading distance compared to low wear volume of 2 wt% filled ATCs with wear volume of 0.02479 cm^3 and a wear loss of 0.06005 cm^3 of 1 wt% nano clay filled UTCs. Wear volume mainly depends on the treatment of the CS and the abrading distance. As the abrading distance increased, wear volume was found high. Lowest wear volume was noted in STCs, whereas the highest wear loss was found in UTCs.

It was also observed that wear volume increases with increase in oMMT filler loading. This can be attributed to the fact that, at lower filler loading (<1 or 2 wt %) dispersion of oMMT in the matrix is good and hence its wetting with the USP is better consequently, particles resist from getting de-bonded from the reinforcement and the matrix. Whereas at higher filler loading (>1 or 2 wt%), oMMT particles get agglomerated due to hydrogen bonding between oMMT particles (strong filler-filler interaction), as a result the interaction between oMMT particles with matrix and reinforcement is reduced and oMMT particles can be easily de-bonded.

8. Specific wear rate

Figure 3(a), (b), and (c), the specific wear data display a sharp decrease at higher abrading distance in all the composites and increased with the increasing filler content after incorporating 1 or 2 wt% filler. Treatment of the CS showed a tremendous decrease in the specific wear rate. A low specific wear rate of 2.67798 (m^3/Nm) × 10^{-6}) was found in STCs with 1 wt% filler loading followed by the alkali treated composite with 2 wt% filler loading and untreated composite with 1 wt% filler incorporation. Low specific wear rate showed by the STCs is because of the reduced number of cellulose hydroxyl groups, which are available for moisture pick-up, reduced hydrophilicity of fiber's surface, and reduced swelling of the fiber, by creating a cross linked network due to covalent bonding, between matrix, fiber, and filler. After 1 wt% filler loading, specific wear rate started increasing as the filler content is increased.

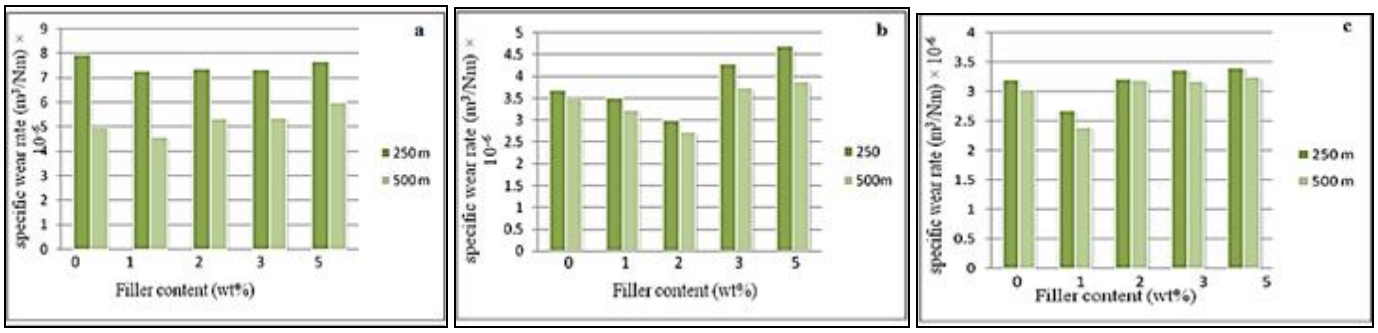

Figure 3: Specific wear rates of (a) untreated, (b) alkali treated, and (c) silane treated composites under different abrading distance

The damages in the filler rich regions are different at different abrading distances i.e., it is dependent on the distance and the treatment of the fiber. Inclusion of oMMT reduced the specific wear rate till 1 wt% incorporation in UTCs and STCs and 2 wt% in ATCs and then stated showing increasing wear rate trend. The data shown in Figure 2, clearly indicates that wear mechanisms depend strongly

upon the hardness of the composite. The wear rate was higher in higher wt% filled nano clay composites compared to lower wt% filled composites. This is attributed to brittle fracture of the composites.

9. SEM

To correlate the wear data effectively, scanning electron microscopy (SEM) was used. The scanning electron images were observed for the composites with low and high wear resistance of each set of composites under testing conditions of abrading distance of 250 m, applied load of 33 N, and abrasive grit size of 218μm. Three types of failure mechanisms have been identified in the literature for natural fiber-reinforced polymers: matrix failure, fiber fracture, fiber-matrix interfacial failure [22]. A wear interface or improper compatibility between fiber and matrix may lead to fiber pull out instead fracture, and may reduce the resulting wear properties. In this study, combination of these failures was observed depending on the composition of the composite.

In set of UTCs, composite with 0 wt% filler content showed very less wear resistance and 1wt% filled composite showed better wear resistance in the set of UTCs, which is shown in the SEM images (Figure 4(a) and (b)) of worn surfaces of the samples. 1 wt% nanoclay filled composite showed 8.8% less specific wear rate compared to the composite without filler.

Figure 4 (a) are representing the low wear resistance property because of the presence of cellulosic structure which is preventing the property of interfacial adhesion between the fiber and the matrix. Because of the improper adhesion, fiber breakage is seen in the image. Fibers were severely damaged and caused discontinuity and de-bonding. The Figure also shows the fracture of fiber bundle and incomplete distribution of the fiber and matrix by forming the cavities between them. Compare to the image a, images b is depicting good wear resistance due to loading of filler between the fiber and the matrix which intern reduces the cavities formation and increases the adhesion between them. Comparison between without filler and with filler in the composites reveals different wear mechanisms i.e., that is the addition of oMMT filler influenced the predominant wear mechanism. Micro-ploughing characterized by the formation of deep grooves is the dominant wear mechanism. Material removal on extruded edges was seen besides groves. Smooth grooves are seen with few surface cracks and debris concentrated in different regions.

Figure 5 shows the worn surfaces of the low and high wear resistances of the ATCs. Lot of improvement is seen in the worn surfaces of ATCs compared to UTCs. From data, it is clear that inclusion of filler in low amount has improved the wear resistance and higher amount of filler inclusion decreased the wear resistance.

Maximum wear resistance was found at 2 wt% nanoclay filled composite (Figure 5(b)), which can be decided as optimum wt%. The smooth, intact and well-bonded layers were formed at optimum filler loading. It confirms that, a considerable plastic deformation of particles from the matrix took place and developed a protective layer. This layer would provide a more uniform distribution of interface stresses with lower magnitude and thus became conductive to lower wear. Low wear resistance was found at the maximum filler contained composite i.e., at 5 wt% (Figure 5(a)). It may be due to improper distribution of filler, formation of debris and micro-crack propagation. Improper distribution of the filler increases the stress concentration, which intern reduces the mechanical interlocking between the constituents leading to propagation of micro-cracks. There may be other reason for the low wear resistance. Inclusion higher wt% of the oMMT makes the material brittle and degrades when it experiences the wear process. 2 wt% oMMT filled composite decreased the wear rate by 18.76 % whereas 5 wt% oMMT filled composite increased the specific wear rate by 33.04 %. It implies that 2 wt% nanoclay has the ability to have fairly good bonding with CS reinforced USP.

STCs have showed the better wear resistance properties like low wear volume and low specific wear rate due to surface modification of the fiber. Among the composites tested silane treated composite with 1wt% filler filled composite has showed the maximum wear resistance capacity. Same as those of other two sets of composites, higher filler loaded composite showed the minimum wear resistance which is analyzed using SEM images shown in Figure 6. 1 wt% filler filled composite showed 171.05 % low specific wear rate than UTC1 and 12.05 % low wear rate than the ATC2. In case of STCs no much of fiber breakages, cavities formation, and crack propagation were found due to well protection of the fiber by the matrix. Protection of the fiber could possible because of the good surface integrity of the fiber as it was made free from the waxy and cellulosic structures by coupling agents. However, damage to the composite is found at the 5 wt% filler incorporated composites because of the non-uniform distribution of the filler over the fibers and the matrix and brittle nature of the filler. A very less wear loss was found at the 1 wt% filler loaded composite due to its very good packing of polymer chains, inter-molecular forces, adhesion and interaction between the constitutes of the composite. Here damage of fiber was not found; hence it can be called as matrix damage dominating.

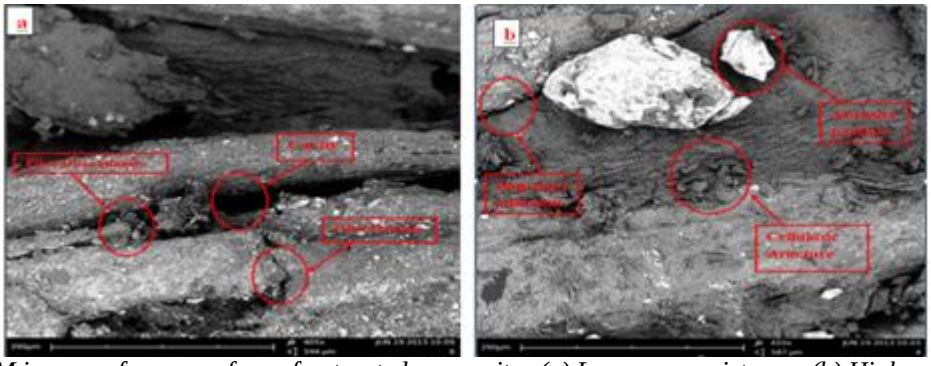

Figure 4: SEM images of worn surface of untreated composites (a) Low wear resistance, (b) High wear resistance

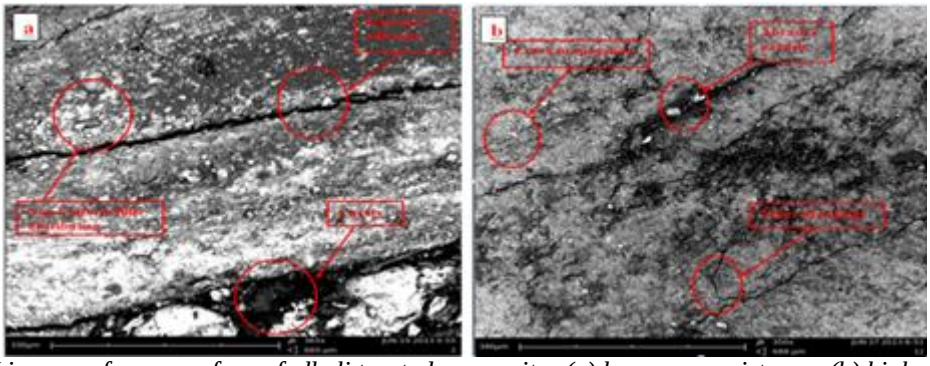

Figure 5: SEM images of worn surface of alkali treated composites (a) low wear resistance, (b) high wear resistance

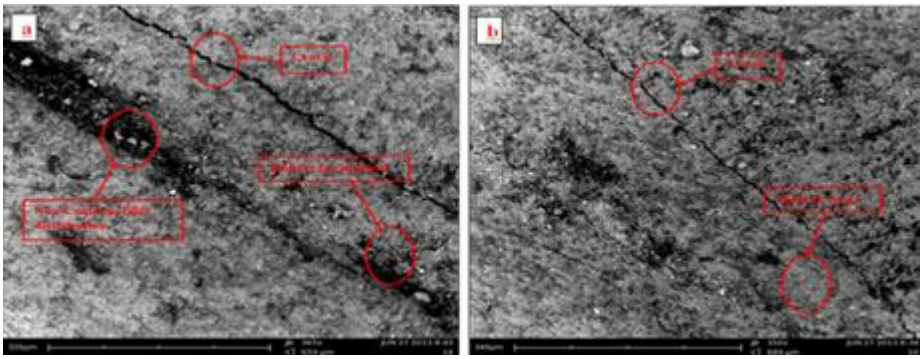

Figure 6: SEM images of worn surface of silane treated composites (a) low wear resistance, (b) high wear resistance

10. Conclusion

Following conclusions could be drawn from the abrasive wear results of USP hybrid composites with oMMT filler and untreated and treated CS.

- Wear volume and specific wear rate are high for the UTCs compare to ATCs and STCs. STCs show better wear resistance.
- Wear volume and specific wear rate of the composites show decreasing behavior till certain wt% of filler loading and starts increasing behavior.
- The wear volume losses increase with increase in abrading distance.
- A significant decrease in the specific wear rate with increasing abrading distance for oMMT filled and CS reinforced USP composites has been observed in STCs with 1 wt% filled composites.
- A maximum reduction of 59.73% and 171.05% in wear volume and specific wear rate respectively found in silane treated composite without filler content compare to untreated composites in absence of filler.
- Correlation between the experimental data and worn surfaces of the tested composites is found using SEM.

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