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### RESEARCH ARTICLE

## IMPACT ON MORPHOLOGICAL, PHYSICOMECHANICAL AND THERMAL PROPERTIES OF POLYPROPYLENE COMPOSITES REINFORCED WITH CHEMICALLY MODIFIED BETEL NUT HUSK FIBER.

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#### Abstract

The betel nut husk fibers (BNHF) were extracted from waste betel nut fruit husks. These fibers were cut into 1 to 3 mm size and subjected to chemical treatment with hydrogen peroxide to enhance its compatibility with the Polypropylene (PP) matrix. These chemically treated fibers and untreated fibers were used as reinforcing materials to prepare Polypropylene composites. Different weight percentages (wt.%) (5, 10, 15, 20, 25 and 30%) of both treated and untreated betel nut husk fibers were used to prepare compression moulded PP composites to achieve better interfacial bonding and mechanical properties. Among them 10 wt% fibers and 90 wt.% PP matrix-based composites showed highest value. Tensile strength, elongation at break, FTIR, TGA-DSC, Scanning Electron Microscopy (SEM), water absorption properties were analyzed for all treated and untreated betel nut husk fibers reinforced PP composites. According to the FTIR spectroscopic results the chemical treatment removed an amount of lignin and other impurities, produced dialdehyde cellulose in BNHF. Water absorption tests and SEM observation results revealed that the composites with treated BNHF absorbed less water and good uniformity between fiber and matrix than composites with untreated BNHF. It was found that 10 wt.% treated fiber reinforced PP composites have higher tensile strength than all other composites.

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#### Introduction:-

Environmentally friendly new materials from natural fibers have been receiving considerable attention as substituted for synthetic fiber reinforcements. The uses of natural fibers in polymer composites as reinforcement have been increasing especially for producing cost-effective engineering materials (1-4). Natural fibers are mainly either plant or animal sourced. The first is essentially comprised of cellulose, whilst the latter is protein-based. Natural fibers have been utilized in several industries such as automotive, construction, energy and aerospace. Additional fields of applications of natural fiber composites are textiles, medicine, health care, pharmaceuticals, home and personal care, food and feed additives, construction and furniture, packaging, pulp and paper, bio-energy and bio-fuels (5). Over the past two decades ligno-cellulosic fibers have been receiving considerable attention as substitutes for synthetic fibers such as glass and carbon due to low density, high stiffness, low cost, renewability, biodegradability and high degree of flexibility during processing. Extensive studies carried out on ligno-cellulosic fibers such as sisal, jute,

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pineapple, banana and oil palm empty fruit bunch fiber has been shown that ligno-cellulosic fibers have the potential to be an effective reinforcement in thermoplastics and thermosetting materials (6). Among many natural fibers betel nut (*Areca catechu*) fruit husk appears to be a budding fiber, because it is cheap available in large quantities and very high potential recurrent crop (7). Although there have been numerous studies on mechanical behavior of ligno-cellulosic fiber reinforced composites, only a few references are available on betel nut fiber reinforced composites (8-10). The mechanical properties of fiber reinforced polymer composites are primarily affected by five main factors, namely tensile properties of the matrix and the fiber materials, fiber aspect ratio, fiber loading, fiber orientation and the interfacial bonding between the matrix and the fiber (11). To develop a composite material made from natural fibers with significantly improved strength stiffness, durability and reliability, it is important to have better fiber matrix interfacial bonding. Cellulose, hemicellulose and lignin are the main component of natural fiber and hence natural fibers are commonly termed as ligno-cellulosic fiber. These constituents make natural fibers hygroscopic and hydrophilic which hinders its bonding compatibility with hydrophobic polymer matrix in natural fiber reinforced polymer composites. Ligno-cellulosic fiber also has a high moisture absorption when in contact with water or kept in humid conditions. Therefore, chemical modification is needed to improve the bonding between the fiber and the matrix (12). Chemical treatment used as surface modification of ligno-cellulosic fiber have been studied by many researchers using alkali, permanganate, acetic anhydride, maleic anhydride, sodium chlorite and acrylic acid. Alkali Treatment improves the fiber matrix adhesion due to the removal of lignin and impurities. Permanganate treatment of natural fiber showed enhanced chemical interlocking at the interface and provided better adhesion with the matrix (13).

In Bangladesh, betel nut husk fiber is found everywhere as well as widely found in coastal area as waste materials. In the present study an attempt has therefore made to use these bio-wastes as reinforcing materials in polypropylene matrix at different wt. percentages. With this aim hydrogen peroxide was used for surface modification of BNHF to improve the properties of composites. The main target was to achieve mild oxidation by converting cellulose in BNHF to dialdehyde cellulose in BNHF. FTIR analysis was done for this investigation. Physico-mechanical, thermal and morphological properties were analyzed for all treated and untreated composites and reported in this paper.

#### **Experimental Part:-**

##### **Materials:-**

Betel nut fruit husks were collected from local betel nut plantation field and fibers were extracted from this husk by ratting process. Hydrogen peroxide (reagent grade) was used for fiber modification. Commercial grade Polypropylene from advance chemicals, Saudi Arabia was used as polymer matrix.

##### **Methods:-**

##### **Extraction of betel nut husk fiber (BNHF):-**

Betel nut husk fibers were extracted from collected betel nut husks. The fibers were cut into 1 to 3 mm pieces. Fibers were sieved and after washing fibers were then dried in sunlight for about three days. The extracted fibers were dried at 105°C in an oven for constant weight to the preparation of the composites.

##### **Treatment of betel nut fiber with hydrogen peroxide:-**

The oven dried raw betel nut fibers were cut into 1 to 3 mm length and immersed into 10% hydrogen peroxide solution prepared in distilled water. The pH of the solution was adjusted to 9. The oxidation reaction was carried out for 3 hours at 90°C temperature. These reaction parameters were optimized by following ATR-FTIR analyses. The reaction mixture was stirred by glass rod occasionally. After completion of the reaction, the mixture was then filtered to isolate the oxidized fiber. The fibers were thoroughly washed in tap water and finally washed with distilled water. The washed oxidized fibers were air dried and then in an oven at 105°C for constant weight. These oxidized fibers were used for composite fabrication.

##### **Composites preparation:-**

Before fabrication of composites treated and untreated betel nut husk fibers were dried in an oven at 105°C for 24 hours. Polypropylene was granulated in a grinder and dried at 80°C for 3 hours. The PP and BNHF were dry-blended in a blender for one minute. These mixers were then moulded in a compression moulding machine (Paul-Otto Weber Press Machine) at a molding temperature of 180°C. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table I.

The mixtures were hot pressed for 10 minutes and the applied pressure was 200 kN. The additional pressure of 50 kN was applied to get voids free compression moulded composite. The composite was allowed to cool and then completely cured composite was taken out from the mould. The same conditions of time, temperature, heating time, pressure and cooling time were maintained to prepare all composites. Finally, the compression moulded composites were cut to make specimens of suitable dimension to measure tensile and water absorption properties.

**Table 1:** -The composition of treated and untreated betel nut husk fibers (%) and PP polymer matrices (%) in composites.

Treated or untreated betel nut husk fibers (wt.%)	Polymer Matrixes PP (wt.%)
0	100
5	95
10	90
15	85
20	80
25	75
30	70

#### FTIR:-

FTIR spectrums were taken for untreated and treated BNHF samples. The treated and untreated betel nut husk fibers were used to make pellet with potassium bromide to take FT-IR. Approximately 0.5mg of dried and powdered BNHF was mixed with approximately 100mg of dried powdered potassium bromide in a small agate mortar pestle. The mixture was taken in a die to make pellets by applying vacuum pressure. The samples were then loaded into FTIR spectrometer (Forntier, PerkinElmer, USA) in 4000-700  $\text{cm}^{-1}$  wavelength range. IR spectra were obtained in the printed form.

#### Water absorption test of composite:-

The water absorption behavior of the developed composites of hydrogen peroxide treated and untreated betel nut husk fiber-polypropylene composites were carried out following ASTM D570-99 standard method. The dimension of each test specimens was 39 mm  $\times$  10mm  $\times$  4mm. The composite specimens were immersed in boiling distilled water for two hours. The initial weight ( $w_0$ ) of the specimens was measured after oven drying at 50 °C for 24 h. The specimens were immersed in boiling water for two hours. After the withdrawal of the specimens from the water tank, surface water was removed with absorbing paper and then weighed ( $w_1$ ) by a calibrated analytical balance. The water uptake percentage is represented as  $W$ , which is calculated by following the Eq. (1). Three specimens were taken to calculate average results and presented in the results and discussion section.

$$W = \left( \frac{W_1 - W_0}{W_0} \right) \times 100 \quad (1)$$

where,  $w_0$  is the dry initial weight,  $w_1$  is the weight after immersion in water.

#### Tensile properties of the composites:-

All the treated and untreated betel nut husk fiber-PP composites were used to measure the tensile properties of the composites using a universal tensile testing machine, model: 1410 Titans, capacity: 5kN, England. Tensile tests were conducted following ASTM D 3039/D 3039M-00 (2002) standard method and the crosshead speed of the test was 10 mm/min. Each test of the specimen was performed until tensile failure occurred except 100% PP composite. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values.

#### Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis:-

The thermo gravimetric analysis and differential scanning calorimetry of the 10 w.t% of treated, untreated BNHF-PP and 100% PP composites were recorded on a STA 449F3 NETZSCH thermal analysis instrument in the temperature range of 30-900 °C and the heating rate was set as 20°C  $\text{min}^{-1}$ .

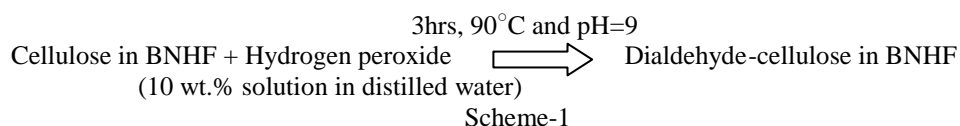
#### Scanning electron microscopy (SEM):-

The surface of the tensile test samples was observed under the field emission scanning electron microscope (JEOL JSM-7600F). The samples were mounted on the carbon tape, which were taped into aluminum plates and coated with ultrathin film of gold with a sputter coater. The images were taken to observe the morphology of the broken surface of the samples.

## Results and Discussion:-

### Surface modification of BNHF:-

Chemical treatment of BNHF with hydrogen peroxide was carried out and optimized the reaction parameters. It was presented in the scheme 1.



### FTIR analysis:-

The FTIR analysis was conducted to investigate the characteristic bands of the betel nut husk fiber, before and after chemical treatment with hydrogen peroxide which are depicted in figure 1 and figure 2 respectively. The reaction of hydrogen peroxide with cellulose in BNHF at  $90^{\circ}\text{C}$  yielded the oxidized product dialdehyde-cellulose in BNHF. In both figure 1 and 2, the broad peak at  $3393\text{ cm}^{-1}$  which appears in both spectra is attributed to O-H frequency. The FTIR spectra of treated fiber (fig-2) clearly shows the characteristic bands of aldehyde group at the region of  $2919\text{ cm}^{-1}$  and  $2849\text{ cm}^{-1}$  due to C-H stretching, another sharp peak at  $1645.61\text{ cm}^{-1}$  due to C=O stretching of aldehyde group in treated BNHF. In figure 1, a sharp peak at  $1738.37\text{ cm}^{-1}$  is due to C=O Stretching vibration of carboxylic acid and ester component of hemicelluloses in untreated BNHF. In treated BNHF the peak  $1738.37\text{ cm}^{-1}$  is corresponding to C=O Stretching vibration of hemicelluloses disappeared due to the removal of lignin and hemicelluloses (14).

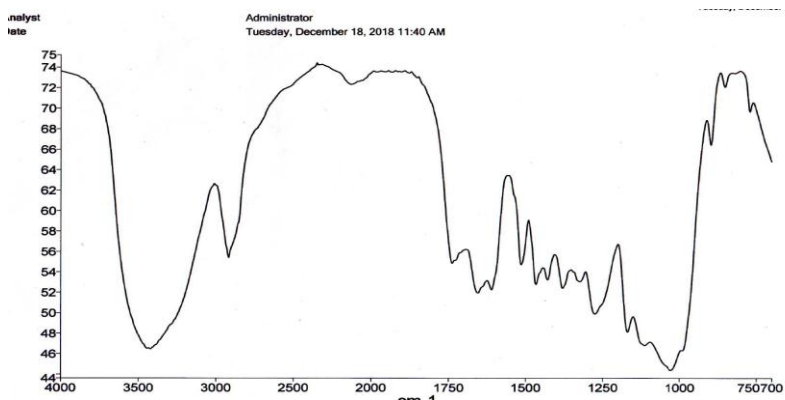
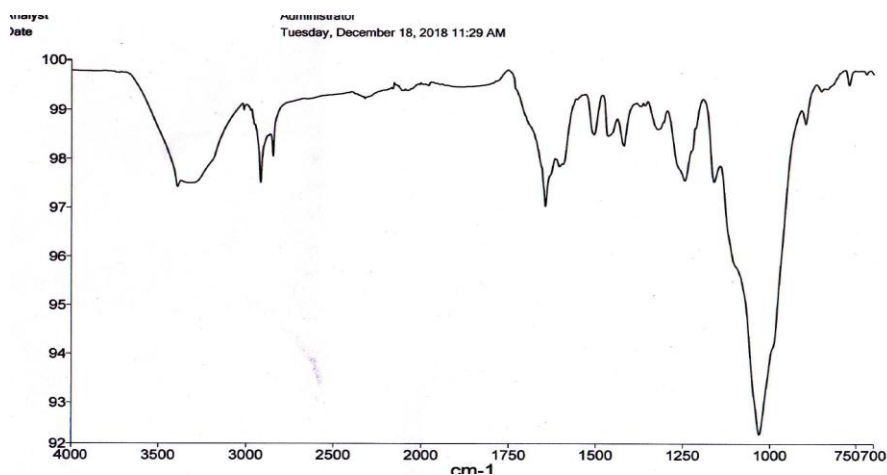


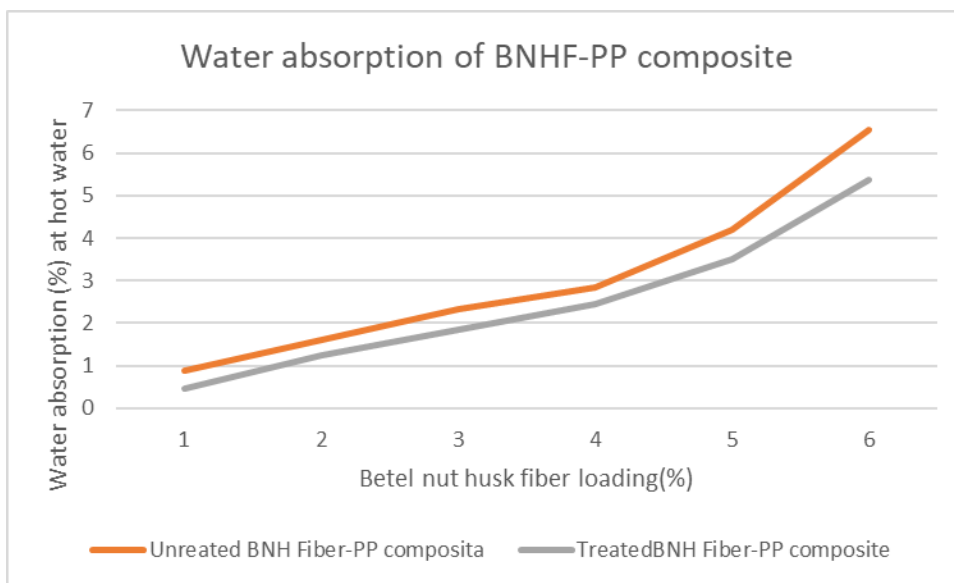
Figure 1:-FTIR of untreated BNHF



**Figure 2:-FTIR of hydrogen peroxide treated BNHF**

#### Water absorption:-

Water absorption test results of all treated and untreated betel nut husk fiber-PP composites are shown in Figure 3. It is clear from the figure that water absorption increases with increasing fiber loading for all composites but water absorption of untreated betel nut husk fiber-PP composites is higher than that of treated betel nut husk fiber-PP composites. This may be due to the hydrogen bonding formation of water molecules with the hydroxyl groups in the constituents of lignin, hemicellulose and cellulose of untreated betel nut husk fibers. Effective interfacial adhesion between fiber and matrix as well as improved hydrophobicity of fibers involved with the treatment lead to the reduction of water absorption. So, dimension stability will be higher for treated betel nut husk fiber-PP composites than untreated betel nut husk fiber-PP composites.

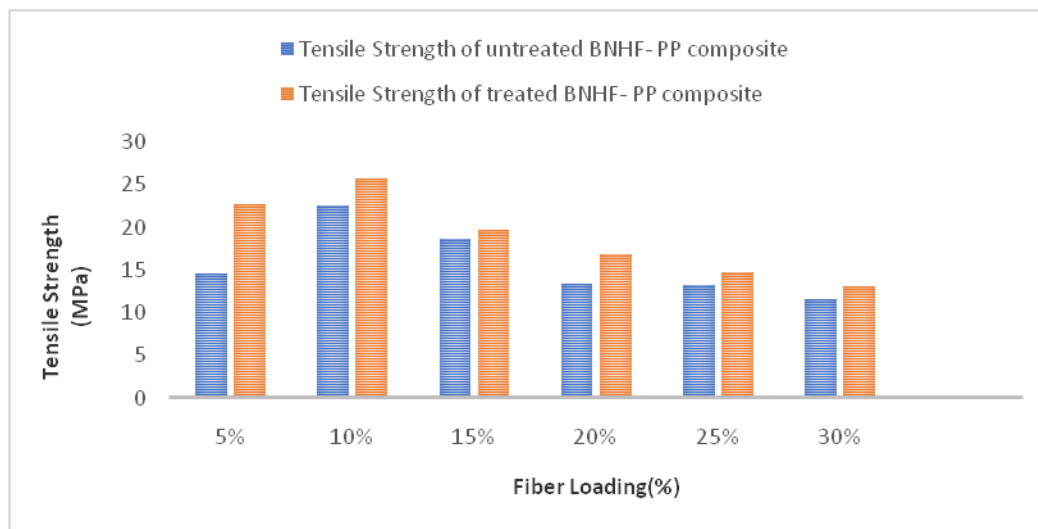


**Figure 3:-Water absorption of Treated and Untreated BNHF-PP Composites**

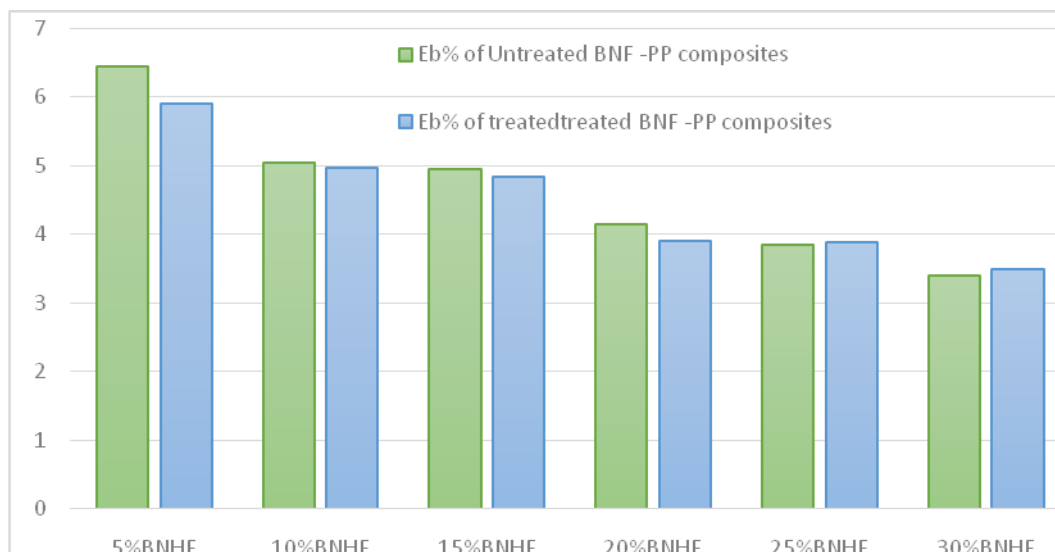
#### Tensile strength and elongation at break:-

The variation of tensile strength and elongation at break (%) of all untreated and chemically treated betel nut husk fiber reinforced polymer composites as function of fiber loading are represented in figure-4 and figure-5 respectively. The tensile strength of untreated and treated BNHF reinforced PP composites were increased linearly with the increases in fiber loading up to 10 %. These increases in the mechanical strength is primarily attributed to reinforcing effect acquaint by the fiber which allow a uniform stress sharing from continuous polymer matrix to dispersed phase (15). The noticeable decreases of tensile strength of the composite were observed as fiber loading was increased from 15% to 30%. Tensile properties of all treated BNHF-PP composites were higher than that of

untreated BNHF-PP composites. This may be due to the improvement of the fiber-matrix interfacial adhesion in composite made by hydrogen peroxide treatment. A decrease in the values of elongation at break was observed due to more brittle character of reinforced composites, especially for treated BNHF-PP composites.



**Figure 4:-**Tensile strength vs fiber loading (wt. %) of untreated and treated BNHF-PP composites.



**Figure 5:-**Elongation at break (%) vs fiber loading (wt. %) of untreated and treated BNHF - PP composites.

#### **Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis:-**

Thermogravimetric analysis and differential scanning calorimetry of the compression moulded PP, 10 wt. % untreated BNHF-PP composite and treated BNHF-PP composite were recorded and presented in figure-6, figure- 7 and figure-8 respectively. Degradation starts at 456.7°C and 99.98 % mass change is completed at 500°C for PP polymer whereas the mass change started at 434.6°C and 5.51% mass change is completed at 434.6°C and 89.57% degradation is done at 520°C for untreated for BNHF reinforced PP composites. In case of treated BNHF-PP composite, degradation started at 450°C and 95.43 % mass change is completed at 550°C. DSC is used to identify melting temperature and amount of energy absorbed or release by materials. Almost same thermal properties were found for treated and untreated BNHF-PP composites. But both treated and untreated BNHF enhanced the thermal properties of BNHF-PP composites then the virgin PP materials.

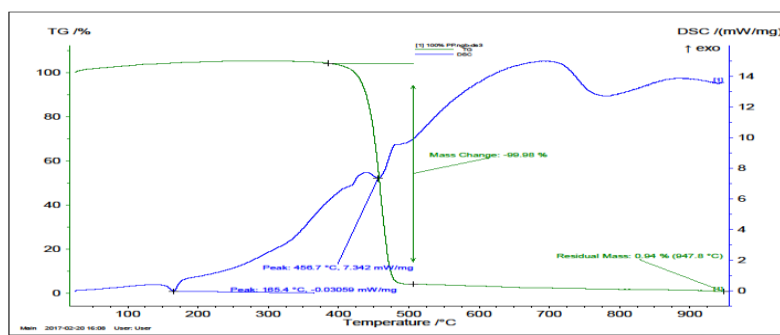


Figure 6:-TGA and DSC of 100% PP

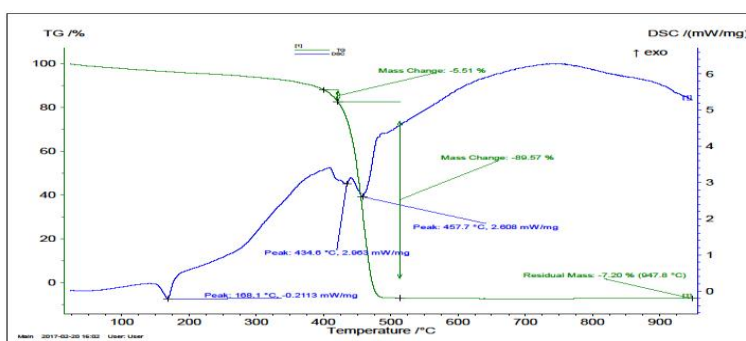


Figure 7:-TGA and DSC of untreated BNHF-PP composite

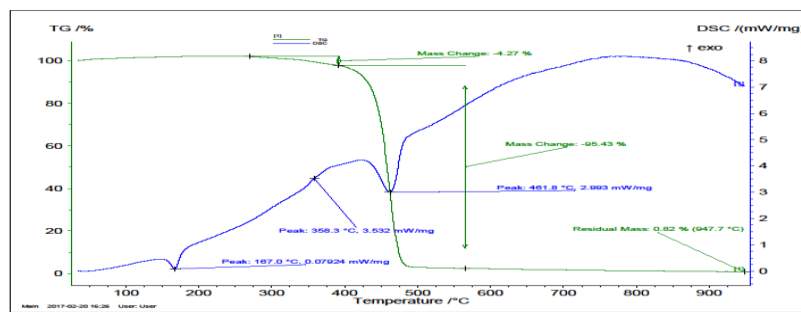
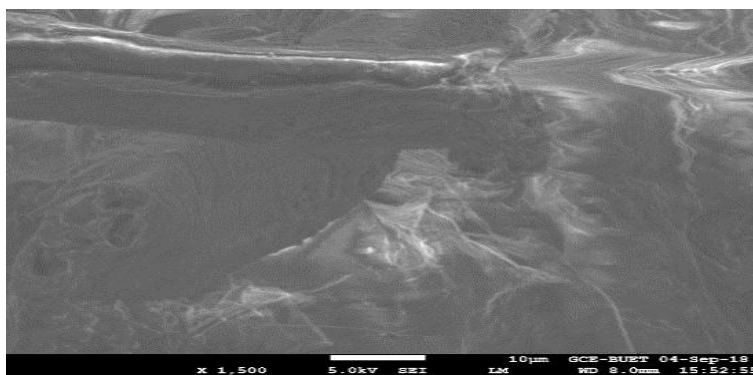


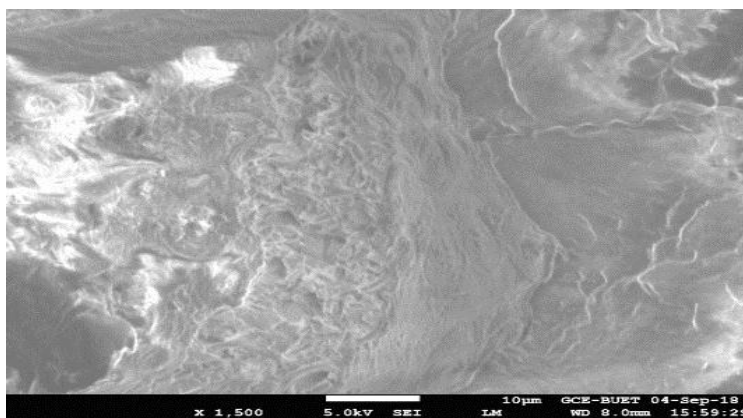
Figure 8:-TGA and DSC of treated BNHF- PP composite

#### Scanning electron microscopic (SEM) investigation:-

Scanning electron microscopy (SEM) is an important tool to the surface morphology study of materials. The fracture surface of tensile specimens 10 wt.% untreated BNHF-PP composite and treated BNHF-PP composite are examined using a field emission scanning electron microscope. From the analysis of SEM image of untreated and treated BNHF-PP composites (Figure-9, 10) it is found that treated BNHF is more fibrous than untreated BNHF. SEM image of treated BNHF-PP composite indicates the better interfacial adhesion between treated BNHF-PP composite as compared to untreated BNHF-PP composite. The improved fiber-matrix interaction is found in treated BNHF-PP composite. It exhibits better porous, surface morphology with very good uniformity.



**Figure-9:-SEM of untreated BNHF -PP composite**



**Figure-10:-SEM of treated BNHF-PP composite**

### **Conclusion:-**

The results of the present research works showed that the treatment of BNHF with hydrogen peroxide was very effective to improve the bonding at the fiber and polymer interface. Hydrogen peroxide treatment with BNHF converted the cellulose in BNHF to dialdehyde cellulose in BNHF. This treatment reduces the hydrophilic nature of treated BNHF and thereby enhanced the tensile properties of the treated BNHF-PP composites. Almost similar thermal properties exhibited in both treated and untreated BNHF-PP composites. All treated BNHF-PP composites showed better tensile properties than all untreated BNHF-PP composites. Both treated and untreated 10 wt. % BNHF-PP composites showed better tensile properties than other treated and untreated BNHF-PP composites respectively. SEM observation also revealed the better interfacial interaction between fiber and matrix in the treated BNHF-PP composites than untreated one. BNHF is an agricultural waste material and the production techniques of treated BNHF-PP composites are comparatively simple. So, the treated BNHF-PP composites will be competitive and cost-effective products.

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