Studies on Biodegradable and Non-biodegradable Polymer Composites with Chemically Modified Betel Nut Micro to Nano fiber

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Dedicated

To

My Parents

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ABSTRACT

This thesis is composed with the aim of use of resources and management of waste betel nut husk fiber (BNHF) in a more sustainable way. In this research work betel nut *(Areca catechu)* husk fiber reinforced thermoplastics were prepared by compression moulding technique. BNHF were extracted from betel nut fruit and the chemical composition of BNHF was analyzed. To improve the properties of BNHF reinforced thermoplastic composites different types of chemical treatment with BNHF were carried out. The effects of this treatment on physico- mechanical and thermal properties of the composites were studied. Different types of non-biodegradable polymer such as low density polyethylene (LDPE), high density polyethylene (HDPE), Polypropylene (PP) and polystyrene (PS) were used as matrix materials. BNHF were treated with sodium hydroxide to improve their adhesion to LDPE matrix. The change in the functional group of treated BNHF was studied by FT-IR spectroscopic analyses. Compression molded BNHF-LDPE composites were prepared using different weight percent of treated and untreated BNHF with compositions 5, 15, 20, 25 and 30 wt% in LDPE. BNHF were used as reinforcing materials to prepare HDPE matrix based composites. Extracted BNHF were chemically treated with sodium *meta*-periodate to enhance its compatibility with the HDPE matrix in treated BNHF-HDPE composites. Another chemical treatment of BNHF with hydrogen peroxide was done to achieve mild oxidation by converting cellulose in BNHF to dialdehyde cellulose in BNHF. These chemically treated fibers and untreated fibers were used as reinforcing material to prepare PP-BNHF composites. The reinforcing effect of BNHF in polystyrene (PS) matrix was also studied. BNH fibers were chemically modified with sodium hypochlorite. The sodium hypochlorite treated and untreated BNHF were used for composite fabrication as reinforcing material with polystyrene in different weight fraction of fiber loading. An improved new extraction procedure of cellulose has been developed and the nano-cellulose was successfully isolated by chemical and mechanical treatment. The reinforcing effects of these cellulose and nano cellulose with biodegradable polymer polyvinyl alcohol and poly-acrylic acid have been studied. The composites were characterized by FT-IR and SEM analysis and their physico-mechanical and thermal properties were analyzed by tensile test, TGA and DSC analysis. According to the FTIR spectroscopic results the positive chemical treatment removed an amount of lignin and other impurities and produced dialdehyde cellulose in BNHF. Mechanical properties such as tensile strength, elongation at break, impact strength were measured. Improved mechanical properties were obtained for all the treated fiber reinforced composites over untreated BNHF reinforced plastics composites. Morphological analyses showed the evidence of stronger interfacial adhesion between the fiber and matrix in the all treated BNHF-polymer composites than the untreated BNHF-polymer composites. Almost same thermal properties were obtained for all treated and untreated BNHF reinforced polymer composites. Water absorption test were carried out for all composite to investigate the effect of chemical treatment on the moisture absorption properties which have direct effect on dimensional stability of the composites. Water absorption tests and SEM observation results revealed that the composites with treated BNHF absorbed the less water and good uniformity between fiber and matrix than composites with untreated BNHF. It was found that 10 wt % treated fiber reinforced composites have higher tensile strength than all other composites. It was also found that nano cellulose fiber reinforced polymer nano composites have higher tensile strength than cellulose fiber reinforced polymer composites.

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Elaboration	:	Abbreviation
Betel Nut Husk Fiber	:	BNHF
Low Density Polyethylene	:	LDPE
High Density Polyethylene	:	HDPE
Polypropylene	:	PP
Polystyrene	:	PS
Attenuated Total Reflection	:	ATR
Fourier Transform Infrared	:	FTIR
Scanning Electron Microscope	:	SEM
Thermo Gravimetric Analysis	:	TGA
Differential Scanning Calorimetric Analysis	:	DSC
Centimeter	:	cm
Gram	:	g
Milligram	:	mg
Milliliter	:	mL
Excreta	:	etc.
Equation	:	Eq.
Percentage	:	%
Nano meter	:	nm
Weight percentage	:	wt %
Molarity	:	M
Normality	:	N

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The growing environmental awareness about greenhouse gas emissions and environmental pollution, manufacturers and scientists are keen to study novel environmentally friendly sustainable materials. Intensive research and developments have been carried out by many researchers, engineers and scientists to develop biodegradable and sustainable composites using natural fibers [1]. Today green composites are widely researched because of the need for inventions of advanced materials, conservation of environment and reduction of carbon dioxide release into the atmosphere. Additionally, the fiber reinforced composites have received potential applications in automotive, structural and packaging. Moreover, biodegradable lignocellulosic fibers can give sound thermal and insulating performances and even they are easily recyclable also. Logically, these benefits of lignocellulosic fibers attract the automotive industry people. For instance, Daimler Chrysler used the composite of flax–sisal fiber mat with epoxy matrix as door panels of the Mercedes Benz E-class model. Coconut fibers bonded with natural rubber latex are being used in seats of the Mercedes Benz A-Class model [2]. Composites are materials consisting of two or more chemically distinct constituents, on a macro-scale, having a distinct interface separating them. One or more discontinuous phase therefore, is embedded in a continuous phase to form a polymer composite. The discontinuous phase which is useally harder and stronger then continuous phase is called reinforcement and the continuous phase is termed as matrix [3]. Reinforcement is the part of the composite that provides strength, stiffness, and the ability to carry a load. The matrix can be classified as thermoplastic or as thermosetting. Thermoplastics polymer can generally be processed several times by melting and shaping the melt and the final product is obtained by cooling. Thermoplastics are generally either linear or branched polymer. Thermosetting polymers undergo irreversible reaction (cure) on heating and this is usually accompanied by formation of covalent bonds between polymer chains and changing into a substantially infusible insoluble material [4].

Most of synthetic polymers are produced from petrochemicals and are not biodegradable. Synthetic fibers such as glass graphite (carbon), boron, organic metallic and ceramic are commonly used in composite fabrication owing to their good mechanical properties [5]. These materials are expensive and harmful to the environment. The use of natural fiber as reinforcement in polymer composites has been increasing especially for cost-effective materials over the past few years due to environmental awareness, depletion of non-renewable petroleum resource and growing demand on sustainable product development. Natural fibers give competent potential to be used as an alternate for glass or other's manmade synthetic fiber reinforcement materials in composites [6]. Enhancing the natural fiber polymers will form a new class of materials that have a good potential in future as a substitute for wood-based materials in many structural applications. Composite materials in which at least one of the constituents is derived from natural resources are defined as bio-composite materials [7]. These includes composites materials made from the combination of natural fiber reinforced petroleum derived polymer which are non-biodegradable, and biopolymers reinforced synthetic fibers such as glass and carbon these two categories are not fully environmentally friendly [8]. The third categories which is, bio-polymers reinforced by natural fibers which commonly termed as "green bio-composites" are more environmentally friendly [9].

Natural fibers are classified into three categories. These are plant fibers, animal fibers and mineral fiber. Plant fibers are generally comprised mainly of cellulose, hemi-cellulose, lignin, pectin. Prominent natural fibers are cotton, jute, flax, ramie, sisal and hemp. Cellulose fibers are mainly used in manufacturing of paper and cloth. This fiber is categorized into seed fibers, leaf fibers, bast fiber/ stem fiber, fruit fiber, stalk fiber [10].

These eco friendly materials have various interesting properties, which make it an attractive and comparable to traditional synthetic reinforced material. Some advantages of natural fiber are abundantly available, inexpensive, low density, high specific stiffness and strength, lightweight, desirable fiber aspect ratio, minimal health hazards, non-abrasive; outstanding insulation properties enhanced energy recovery, renewability and biodegradability [7, 9]

These materials are rapidly emerging as prospective substituted to the metal and ceramic based materials. Natural fiber-based composites have been utilized as door panels, seat backs, head liners, dash boards, and interior parts of automobiles [11]. The usage of composites is not only limited to automobile parts but it also extends to current generation military aircraft. These advanced materials have the potential to contribute to aircraft development, since one-third of the structural mass (such as wing, fin, control surfaces and radome) of an aircraft is made from fiber reinforced polymer composites [12].

Any substance that contains both cellulose and lignin is a lignocellulosic material. Hard wood saw dusts, jute fibers, palm fibers, coconut fibers and rice straw fibers are used as reinforcements in polymer composites [13-17]. The use of lignocellulosic fiber as reinforced materials in thermoplastics has received a lot of interest due to their low cost, low density and non-abrasive nature. As renewable material cellulose is most abundant biomass in nature and posses some promising properties, such as good mechanical properties, low density, thermal stability, bio-compatibility and biodegradability [18]. Cellulose nano fibers extracted from natural jute fiber by chemical and mechanical technique have potential for use as reinforcing fiber in bio-composites application [19]. From different research work and application in various fields it has been proved that natural fiber reinforced and thermoplastic polymer matrix-based composites are much more applicable. Composite fabricated from thermoplastics material have longer shelf life, higher strain to failure, faster to consolidate and retain the ability to be repaired reshape and reused as need arises. To prepare thermoplastic composites various matrix materials like HDPE, polypropylene (PP) [20-22], poly(vinyl chloride) (PVC) [23, 24], polyethylene (PE) [25–28], poly(lactic acid) (PLA) [29, 30] and polystyrene (PS) [31] used with reinforcing agent such as betel nut fiber, kenaf, wood, flax, cotton, hemp, Kraft pulp, pineapple leaf, coconut husk, areca fruit, oil palm, abaca, sisal, henequen leaf, jute, banana, ovine leather, and straw etc. 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. A better understanding of the chemical composition and surface adhesive bonding of natural fiber is necessary for developing natural fiber-reinforced composites. The components of natural fibers include cellulose, hemicelluloses, lignin, pectin, waxes and water-soluble substances. Composition may differ with the growing condition and test methods even for the same kind of fiber. Cellulose is a semi crystalline polysaccharide made up of D-glucopyranose units linked together by β-(1-4) - glucosidic bonds [32]. And the large amount of hydroxyl group in cellulose gives natural fiber hydrophilic properties when used to reinforce hydrophobic matrices; the result is a very poor interface and poor resistance to moisture absorption [33]. Hemicellulose is strongly bound to cellulose fibrils presumably by hydrogen bonds. Hemi-cellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is partly soluble in water and hygroscopic [34]. Lignins are amorphous, highly complex, mainly aromatic, polymers of phenyl propane units [32] but have the least water absorption of the natural fiber components [34]. Because the low interfacial properties between fiber and polymer matrix often reduce their potential as reinforcing agents due to the hydrophilic nature of natural fibers, chemical modifications are considered to optimize the interface of fibers.

Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. The development of a definitive theory for the mechanism of bonding by chemicals in composites is a complex problem. Generally, chemical coupling agents are molecules possessing two functions. The first function is to react with hydroxyl groups of cellulose and the second is to react with functional groups of the matrix. Many researchers have analyzed that the chemical modification of the natural fibers optimizes the interface locking between the fiber and the matrix and improving the other properties. During this process, hydroxyl groups which are on the natural fibers were activated or some new functional groups will be introduced, which will create effective interlock bonding with the matrix. It is very difficult to have a particular mechanism theory of bonding by chemical treatment in composites and to achieve it is very much complex in nature. In general, chemical modification/treatment or coupling agent will process two functions. The first most function is to react with the hydroxyl group of the fiber cellulose and the second to react with functional groups of the matrix. Several mechanisms of coupling in material were outlined by Bledzki and Gassan namely: (a) elimination of weak boundary layers; (b) production of a tough and flexible layer; (c) development of a highly cross linked inter-phase region with a modulus intermediate between that of substrate and of the polymer; (d) improvement of the wetting between polymer and substrate; (e) formation of covalent bonds with both materials; and (f) alteration of acidity of substrate surface. Improved sufficient Mechanical properties and resistance to moisture absorption of natural fibers have been achieved by various surface treatments. Chemical modifications of natural fibers aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers [36–39].

The usage of natural fibers as reinforcement in composites is not new; numerous surveys and studies on properties and behavior of natural fiber-reinforced composites have been carried out to a great extent. However, not much study on using the betel nut husk fiber as a reinforcing material has been done, very few references are available. Betel nut husk fiber is being a very high potential perennial crop, abundantly available and also inexpensive among all the natural fiber reinforcing materials. Details about the species, origination, cultivation, and constitution are noted [40]. The husk produces approximately 2.50-2.75 g of betel nut husk fiber can be produced from each husk [41]. Some of the authors noted that, areca fiber possesses a very good fiber surface roughness, this will intern help in achieving better interfacial bonding between fiber and matrix, which will lead to high mechanical properties for the composites [42]. In present days, these betel nut husk fiber being widely used as fuel in the processing of areca nut. The unmanaged green areca husk left in the plantation causes terrible odor and other decay-related problems [43]. Therefore, an extensive planning for the disposal of husk is necessary. Thus, the use of this unmanaged and underutilized husk as reinforcement to structural material has been thought and some amount work has been done.

Betel nut husk fibers are generally lignocelluloses, consisting of helically wound cellulose micro-fibrils in an amorphous matrix of lignin and hemi-cellulose. A chemical composition plays a significant role in defining the properties of fiber and its composites. The primary composition of areca husk is the varying proportions of α-cellulose, hemi-cellulose, lignin, pectin, wax, and moisture. It is noted here that, areca fibers consists of alpha cellulose 53.20%, hemi-cellulose 30-64.8%, lignin 7-24.8%, 4.4-4.8% of ash, 11.7% of moisture, and very negligible percentage of the pectin and wax [44-48].

Betel nut husk fiber being short in nature and its SR [aspect ratio (AR)] is very less. SR is the ratio of the length of fiber to the diameter of the fiber. This is derived value from the dimensions of the fiber. Fiber length and fiber diameter are among the important parameters to determine the strength of natural fiber. The variation of the length and diameter and the standard for densities are discussed elsewhere [47]. Betel nut husk fiber being very short measuring around 30-60 mm in length and 28-90 mm in diameter. Natural fiber with high SR is more favorable as it possesses high tensile strength. In addition, it has a significant effect on the flexibility and rupture behavior of natural fiber. Strength of betel nut husk fiber has noted that E = 2.54 ± 0.5GPa, and the elongation at breaking 15±3% [49].

Adhesion/anchoring or bonding between the betel nut husk fiber and the matrix is an extremely important factor, which will affect the mechanical properties of its composite. Bonding guarantees the good stress transfer from matrix to fiber. This type of bonding can result from a chemical cross linking or from physical origin [50]. Like any other natural fiber, betel nut husk fiber also has disadvantages in the preparation of the composites like; the compounding difficulty; because of inherently polar and the hydrophilic nature of the fiber and the non-polar characteristics of the matrix leading non-uniform distribution [51]. This will significantly weaken the properties of the composites. Similarly, restriction in the processing temperature will be another constraint of fiber because the natural fibers will degrade at higher processing temperature; this internally restricts the selection of the matrix material, i.e., restricted to 180-230°C. Wet ability of the fiber plays an important role in deciding the compatibility of the fiber with matrix. The wet ability of the fiber mainly depends on the viscosity of the matrix and surface tension of the both the materials. It should be noticed that surface tension of the fiber should always more than the matrix. Low microbial resistance and susceptibility to rotting will be other constraints to the successful utilization of natural fibers for long lasting composites application. These properties create severe difficulty during storage, shipping, and composite processing. Apart from, the above mentioned serious problem, the non uniformity, variation of dimensions and of their mechanical properties will also lead to other problems in developing the composites. The presence of a natural waxy substance on the fiber surface and hydroxyl groups lead to ineffective fiber-matrix bonding and poor surface wetting [52].

Literature study reveals that the advantages of the betel nut husk fiber and natural fiber are more when compared with disadvantages. The deficiency has a corrective measure in terms of surface treatment. To get the desired properties, surface modification of the betel nut husk fiber surface plays a key role.

It has been very well-understood and established by many researchers that the mechanical, thermal and acoustical performances of the composites depend not only on the properties of the principle components but also on the nature and strength of the interface. The interface plays a significant role necessitating a study on modification of the fiber surface. In general, the surface treatment/ modification of natural fibers will not only enhance the bonding between the fiber and matrix but also improve many specific aspects such as reducing the moisture absorption sensitivity and providing better and greater adhesion. The similar polarity between the two materials will add/ improve adhesion strength between the matrix and natural fiber. Hence, the surface modification/treatment will be major criteria to enhance the properties of the fiber [53-54]. Different surface modification processes are involved, majorly four are extensively and exhaustively used to improve the properties; chemical, physical, physico-chemical, and mechanical. The above-mentioned treatments are helpful in improving the adhesion property between the fiber and the matrix, by improving the surface roughness on the fiber, which will lead to the significant increase in the strength or other properties of composites. Additional information on different surface treatment/modification of natural fibers may be referred in many references [55-59].

Cellulose is one of the most abundant, renewable and biodegradable polymer resources produced by nature in the biosphere. For the past few years, the preparation of cellulose nano-crystals (CNCs) and their application in nano composite materials have gained increasing attention because of their inherent properties like elastic modulus (130-150 GPa), high specific area (up to several hundreds of m^2/g), high length to width ratio (up to several hundred) combined with low density ($1.6g/cm^2$), low thermal expansion (0.1 $ppmK^{-1}$), biodegradability and renewability [60].

CNCs are mostly produced from various cellulosic materials, such as bleached pulp, cotton, micro crystalline cellulose (MMC) or plants [61]. Due to special intrinsic nano structure and excellent properties, nano cellulose have wide application potentials such as aero gels, biomedical materials, packing materials, optical or electro conductive materials and several mechanically reinforced nano composites [62-65].

Bangladesh is basically an agricultural country. Bangladesh produces huge amount of betel nut and it is categorized as an important economic crop. Betel nut husk fiber are obtained from the husk of betel nut fruits Among all the natural fiber-reinforcing materials, betel nut husk fiber appears to be a promising material because it is inexpensive, abundant in nature and a very high potential perennial crop . It belongs to the species *Areca catechu L.*, under the family palmecea and originated in the Malaya peninsular, East India. The husk of the betel nut is a hard fibrous portion covering the endosperm ant constitutes about 60- 80% of total weight and volume of the fresh fruit [66]. The average filament length (4 cm) of the betel nut husk fiber is very short compared to other bio-fibers. Mainly two types of filaments are present, one very coarse and the other very fine. The coarse ones are about ten times as thick as jute fibers and the fine are similar to jute fiber. The fiber could be used for making value added items such as thick boards, fluffy cushions and non-woven fabrics, and thermal insulators [67]. The present use of this highly cellulosic material is as a fuel in betel nut processing. Unmanaged betel nut husk left in the plantation causes bad odor and other decay-related problems. Therefore, extensive planning for the disposal of husk is required. Thus, the use of this unmanaged husk as structural material required a detailed study of physical, chemical and thermal characteristics. Currently Therefore, this study seeks to determine the physical and mechanical properties of betel nut husk fiber reinforced composites. Chemical modification of betel nut husk fiber (BNHF) with sodium hydroxide, sodium meta-periodate, hydrogen peroxide and sodium hypochlorite were carried out in aqueous medium in this work. Reinforcing effect of treated and untreated BNHF in non-biodegradable and biodegradable polymer composite has been studied. A novel and improved extraction procedure of cellulose from BNHF have been developed in this study. An improved new method of preparation of nano-cellulose and the physicochemical and physico-mechanical properties of synthesized nano-cellulose fiber reinforced composites has also been developed. A better understanding will help to develop productive uses of betel nut husk fiber for developing an alternative material to wood and also minimizing environmental problem of waste biomass.

1.2 Objective

The aim and objectives of this research work are to use bio-waste betel nut husk fibers as sustainable reinforcements in thermoplastic based composites. The objectives are given below:

- To prepare novel and improved biodegradable and non-biodegradable fiber reinforced composites with thermoplastics. With this aim fiber will be modified with different oxidizing agents.
- To develop nano-cellulose fiber reinforced composite with PVA, PAA and different polymers. With this aim, it is also necessary to synthesize nano-cellulose fiber from betel nut fiber
- To study the physicochemical properties of synthesized nano-cellulose fiber reinforced composites especially the composite properties with the crystalline quantities of the nano-cellulose fiber.
- To optimized the Fiber loading of nano-cellulose fibers for making a composite with minimum biodegradability and maximum mechanical performance.

CHAPTER 2

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED LOW DENSITY POLYETHYLENE COMPOSITE

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED LOW DENSITY POLYETHYLENE COMPOSITE

2.1 Introduction

Over the last few years, as a result of the growing environmental awareness about greenhouse gas emissions and environmental pollution, manufacturers and scientists are keen to study novel environmental friendly materials. Intensive research and developments have been carried out by many researchers, engineers and scientists to develop biodegradable and sustainable composites using natural fibers [68] . Synthetic fibers like carbon and glass though exhibits excellent mechanical, thermal properties and durability but difficulties in disposal processing which produce lot of black smoke and bad odors. In order to overcome this problem, necessity of natural fibers based composites is demanding to make the world ‘green’. The composites referred to as bio-composites which are combine natural fibers such as kenaf, jute, hemp and sisal with biodegradable or non-biodegradable polymers [69]. Natural fibers are cheaper and substitute for synthetic fibers. Compared with synthetic fibers, natural fibers have many advantages like low density, cheaper, high strength and high stiffness, no harm to environment, renewable sources and biodegradable properties [70].

In this research work, betel nut husk fibers were used as reinforcing materials with thermoplastics to make composites. Betel/ Areca nut is the seed of Areca palm and *Areca catechu* is a species of palm which grows mainly in the Southeast Asia and South Asia region. It is abundantly available in Bangladesh as waste fibers of betel nut fruits. Composites made with natural fibers offers use in various applications such as aerospace, leisure, construction, households, sport, packaging, automotive industries by replacing metallic components due to their inherent light weight and immune to corrosion [69, 71]. However due to hydrophilic nature of natural fibers give rise to incompatibility between fiber and polymer in composites. This leads to undesirable properties of the composites. Hence fiber surface is modified with coupling agent in order to have interfacial adhesion between fiber and matrix [69]. Natural fibers are composed of cellulose, hemicelluloses, lignin, pectin, wax, and ash. Chemical treatment of the natural fibers can overcome the limitations due to hydrophilic nature by cleaning the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness [70]. Swain *et al.* worked on abrasive wear behavior of surface modified jute fiber reinforced epoxy composite [72]. They reported that benzoyl chloride treated based composite notably gave better abrasive wear resistance than the untreated and alkali treated based composite. This was due to the high-interfacial adhesion and low-composite porosity. Siregar *et al.* investigated and reported on effect of the alkali (NaOH) treatment on the mechanical properties of pineapple leaf fiber (PALF) reinforced high impact polystyrene (HIPS) composites [73]. They obtained highest mechanical properties value for the short PALF treatment with NaOH concentration of 4%. Prasad *et al.* investigated on effect of the alkali (NaOH) treatment followed by bleaching with H_2O_2 on tensile properties of short jute fiber reinforced polypropylene and reported about small increase in the strength of composite with treated fibers compared to composite with untreated fibers [74]. In a review by Ram *et al.*, it is shown that some works were done in the field of replacing existing industrial safety helmet material acrylonitrile butadiene styrene (ABS), with variety of polymer composites [75]. The study shows that hybrid polymer composites have good potential to replace ABS in safety helmets. Desai *et al.* also reported in a review on effectiveness of Areca (betel) fiber as a reinforcing material in eco-friendly composites [76]. The review report states that in the recent past, it has been noticed that not much appreciable research been carried out on the optimized surface treatment, manufacturing techniques, and product application using the areca fibers. Hence, there are more opportunities to develop economical and ecologically superior engineered material by utilizing these areca fibers and its composites.

In this piece of research work, betel nut *(Areca catechu)* husk (BNHF) fibers were treated with sodium hydroxide to improve its adhesion with LDPE. Betel nut husk fibers (BNHF) were used to prepare sodium hydroxide treated and untreated BNHF reinforced low density polyethylene (LDPE) composites. Extracted and washed BNHF were treated with sodium hydroxide to improve their adhesion to LDPE matrixes. Chemical treatment BNHF of betel nut husk fibers with sodium hydroxide was carried out and the change in the functional group of treated BNHF was studied by FT-IR spectroscopic analyses. The aim of this research is to find out the effects of treated and untreated BNHF loading on the physico-mechanical properties of betel nut husk fiber-LDPE composites.

2.2 Materials

2.2.1 Matrix polymer

A commercial grade low density polyethylene (LDPE) was purchased from Polyolefin Company Pvt. Ltd., Singapore. Melting point of this LDPE was measured and found to be 105-109°C.It is mentioned in literature that the malting point of commercial grade LDPE lies in the range 105-115°C

2.2.2 Reinforcing material

Betel nut husk fibers were used as reinforcing material in this research work. Betel nut is the fruit of Areca palm tree (Areca catechu). Matured betel nuts were collected from local betel nut plantation field, Barisal, Bangladesh. The betel nut husk is the fibrous part of the fruit. Betel nut husk fibers were extracted from collected betel nuts.

2.2.3 Chemicals

The analytical grade sodium meta-periodate, sodium hydroxide and hydrogen peroxide were used for surface modification of fiber. The chemicals used in this study are listed below.

Chemicals/ Reagents	**Name of suppliers**
Sodium hydroxide [NaOH]	Merck, Germany
Sodium metaperiodate [$NaIO_4$]	Merck, Germany
Hydrogen peroxide [H_2O_2]	BDH, England
Sodium chlorite 80%[$NaClO_2$]	BDH, England
Sulfuric acid (H_2SO_4)	Merck, India
Polyvinyl alcohol (PVA**)**	Merck, Germany
Poly-acrylic acid (PAA**)**	Merck, Germany
Sodium hypochlorite (NaOCl)	BDH, England

2.3 Experimental

2.3.1 Betel nut husk fiber (BNHF) Extraction

Betel nut husk fibers were collected from matured betel nut fruits by retting process. Matured betel nut fruits were soaked in water at room temperature for 15 days for retting. The retted fibers were separated manually by hand stripping methods. The fibers were brushed and cleaned with agitated water, and washed thoroughly with distilled water. Fibers were then dried in sunlight for about three days. The extracted fibers were dried at 105°C in an oven for constant weight. The fibers were chopped into 1 to 3 mm. Fibers were sieved and dried after washing with distilled water.

2.3.2 Surface modification of BNHF by sodium hydroxide

Aqueous solution of sodium hydroxide 6% (w/v) was prepared to conduct reaction with dried betel nut husk fibers (BNHF). Dried betel nut husk fibers were immersed in that solution for one hour at room temperature approximately 25°C and the fibers were stirred occasionally with a glass rod. Fiber to liquor ratio was 1:20 (w/v). After completion of the reaction, the alkali treated BNHF were thoroughly washed in tap water and then immersed in distilled water for 24 hrs. Finally, fibers were washed with distilled water to remove the alkali completely and the pH was measured until it was found neutral. The alkali treated BNHF were dried in air first then further dried in an oven to get a constant weight.

2.3.3 Fabrication of BNHF reinforced LDPE composite

Treated and untreated betel nut husk fibers and betel nut micro fiber were dried in an oven at 80°C for 24 hours. LDPE was granulated in a grinder and dried at 80°C for 3 hours before fabrication of composites. The LDPE 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).The compressing moulding process is very widely used to produce articles from polymer materials. In this research work we use a type of mould which has the upper and lower part having completely plane with smooth surface. It can act as heater and cooler simultaneously. In this moulding process one have to make a die for casting with his desired size. We made dies, having a rectangular cavity about (15 cm x 12 cm), and the thickness of dies are 2 mm and 4 mm. The materials were placed into the die so as to fill the die. The mold were placed into the machine and closed down under pressure, the materials were compressed between the two halves and compacted to shape inside the die. The excess materials expelled out of the mold as thin film are known as "flash". The compact mass get cured and hardener to shape under the influence of heat. The mixtures were hot pressed for 10 minutes at 150^{o}C temperature 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 demoulded by hand or any other suitable device. 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 properties. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table 2.I.

Table 2.1: Different weight fraction of untreated and NaOH treated betel nut fiber reinforced LDPE composites.

Sample Number	Reinforcing material (wt%)	Polymer matrix (wt%)	Composites
No. 1	BNHF : 05	LDPE : 95	05:95 (wt %) BNHF: LDPE
No. 2	BNHF : 10	LDPE : 90	10:90 (wt %) BNHF: LDPE
No. 3	BNHF : 15	LDPE : 85	15:90 (wt %) BNHF: LDPE
No. 4	BNHF : 20	LDPE : 80	20:85 (wt %) BNHF: LDPE
No. 5	BNHF : 25	LDPE : 75	25:75 (wt %) BNHF: LDPE
No. 6	BNHF :30	LDPE : 70	30:70 (wt %) BNHF: LDPE
No. 7	BNHF : 00	LDPE : 100	100 (wt %) LDPE
No. 8	Treated BNHF : 05	LDPE : 95	05:95 (wt %) treated BNHF: LDPE
No. 9	Treated BNHF : 10	LDPE : 90	10:90 (wt %) treated BNHF: LDPE
No. 10	Treated BNHF : 15	LDPE : 85	15:90 (wt %) treated BNHF: LDPE
No. 11	Treated BNHF : 20	LDPE : 80	20:85 (wt %) treated BNHF: LDPE
No. 12	Treated BNHF : 25	LDPE : 75	25:75 (wt %) treated BNHF: LDPE
No. 13	Treated BNHF :30	LDPE : 70	30:70 (wt %) treated BNHF: LDPE

Figure 2.1: Betel nut

Figure 2.2: Extracted betel nut husk fiber

Figure 2.3: Treated betel nut husk fiber

Figure 2.4: Compression Molding Machine

Figure 2.5: Image of Composite

2.3.4 Characterization of BNHF reinforced LDPE composites

The untreated and treated betel nut husk fiber and their reinforced LDPE composite materials were characterized by FT-IR Spectroscopy and Scanning Electron Microscopy (SEM) as stated below.

2.3.4.1 FTIR spectroscopy

FTIR spectrums were taken for untreated and NaOH treated BNHF samples. The treated and untreated betel nut husk fibers were used to make pellet with potassium bromide to take FT-IR. Approximately 0.5 mg of dried and powdered BNHF was mixed with approximately 100 mg 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, Perkin Elmer, USA) in 4000-700 cm^{-1} wavelength range. IR spectra were obtained in the printed form.

2.3.4.2 Scanning electron microscopy (SEM)

The fractured surfaces of tensile test samples were 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 ultra thin film of gold with a sputter coater. The images were taken to observe the morphology of untreated BNHF, treated BNHF and the broken surface of the composites samples. The photographs are presented in the result and discussion section.

2.3.5 Mechanical properties of composites

Tensile test and Impact test of all prepared composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods. Specification and picture of the used machines, operating condition and dimension of test specimens are given below.

2.3.5.1 Tensile properties of the composites

The tensile test of all treated and untreated betel nut husk fiber reinforced polymer composites were measured 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 and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves were obtained by the instrument. The maximum load values were also recorded by the instrument which could be recalled after the completion of the test. The highest load in the tensile test gave the ultimate strength.

Figure 2.6: Tensile test specimen

2.3.5.2 Impact test

The Izod impact test of prepared BNHF- LDPE composite samples were performed according to Izod impact test methods include ASTM D256-02. QPI-IC-21 J universal Charpy / Izod Analog Impact tester machine from Qualitest North America were used to perform Izod impact test for all samples. The length, width and thickness of the specimen were 64 mm, 12.7mm and 3.2 mm respectively. V-shaped notched specimens were used. A total of ten samples were tested and the mean values of the absorbed energy were taken. The impact strength (J/m^2) was calculated by dividing the recorded absorbed impact energy with the cross-sectional area of the specimens. The dimension of test specimen and design of notch cut on it is shown below.

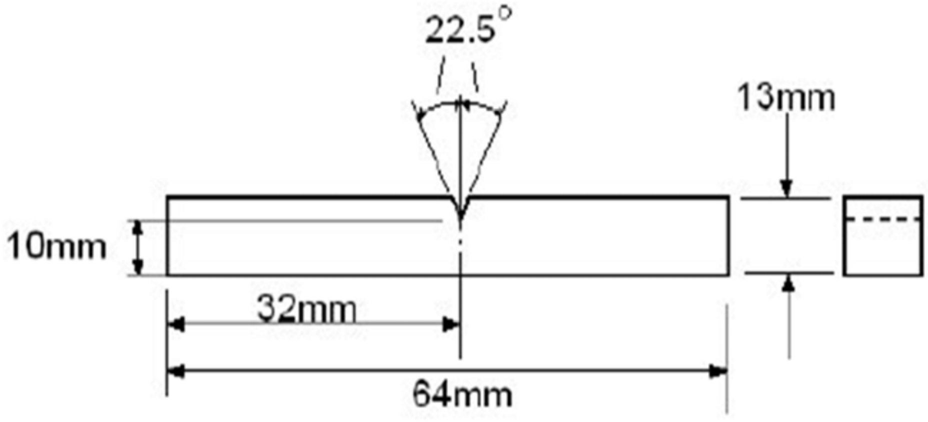


Figure 2.7: Dimension of Izod Type Test specimen

2.3.6 Thermal properties of composites:

Thermo gravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC)

The thermo gravimetric analysis and differential scanning calorimetric analysis of the 10 wt% of treated, untreated and 100% LDPE 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 min^{-1} in a nitrogen atmosphere. Ten mg of the sample was heated in the sample pan.

2.3.7 Water absorption test of composite

The water absorption behavior of the developed composites of sodium hydroxide treated and untreated betel nut husk fiber- LDPE composites were carried out following ASTM D570-99 standard method. 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.

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

Where, W_0 is the dry initial weight, W_1 is the weight after immersion in water.

2.3.8 Biodegradability of Composites

Biodegradability (BD) of composite was determined by measuring the weight loss of the specimens which were buried in soil. The test was done by using the gardening soil collected from local market. The selected each specimen was buried in the soil at temperature (25–30 °C). At two days intervals, water was poured so that the soil was kept in humid condition. After burial of particular time the specimens were exposed from the soil, where the burial duration was 90 days. Thereafter, the specimens were washed with water and dried at 40 °C in a vacuum oven up to a constant weight. Due to biodegradation the weight loss (%) was calculated according to the following formula (Eq. 2):

$$BD(\%) = \frac{(w_{bb} - w_{ab})}{w_{ab}} \times 100 \qquad (2)$$

Where w_{bb} and w_{bb} are the dry weights of composites before and after the burial, respectively.

2.4 Results and discussions

In this work, the physico-mechanical, thermal and morphological properties of different types of betel nut husk fiber reinforced low density polyethylene composites have been investigated. The effects of fiber surface modification with NaOH on Mechanical, thermal and Morphological properties of prepared composite have also been studied. The interpretations of the results are presented in the following sections.

2.4.1 FTIR spectroscopic analysis of untreated and NaOH treated betel nut husk fiber

The FTIR spectra of untreated and alkali treated BNHF are shown in figure 2.8. Sodium hydroxide treatment was done to improve the adhesion between fiber and matrix in the composites. The characteristic bands of untreated and alkali treated BNHF are summarized in table 2.2 and table 2.3 respectively. It is clear from the figures that the absorption band at 1738.37 cm^{-1}of untreated BNHF have disappeared completely in the treated BNHF. This indicates that the alkali treatment of betel nut husk fibers had removed the impurities, hemicelluloses and part of lignin. Through surface modifications, substantial improvement of fiber properties could be possible. In this context, chemical treatments may increase the hydrophobic nature of the fiber as well as remarkable enhancement of wettability of the matrix also be possible The similar FT-IR results were also reported by Oushabi *et al* in the case of alkali treated date palm fibers [77].

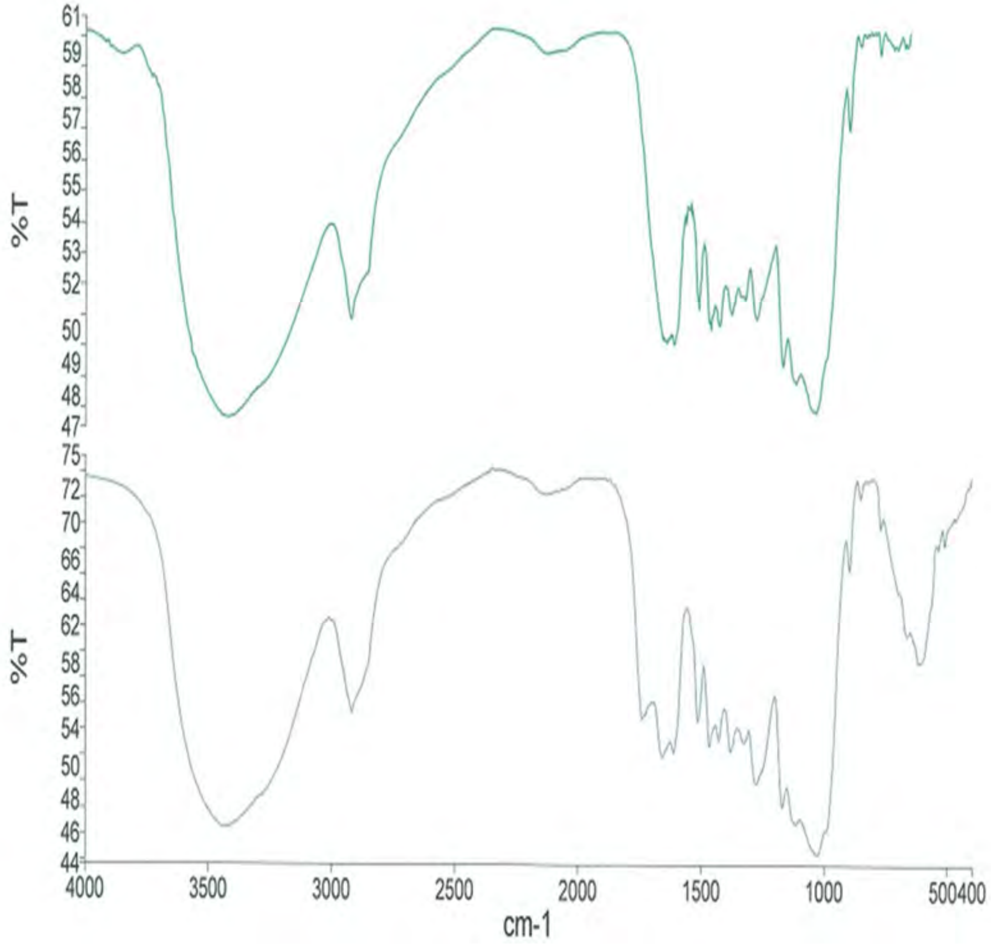


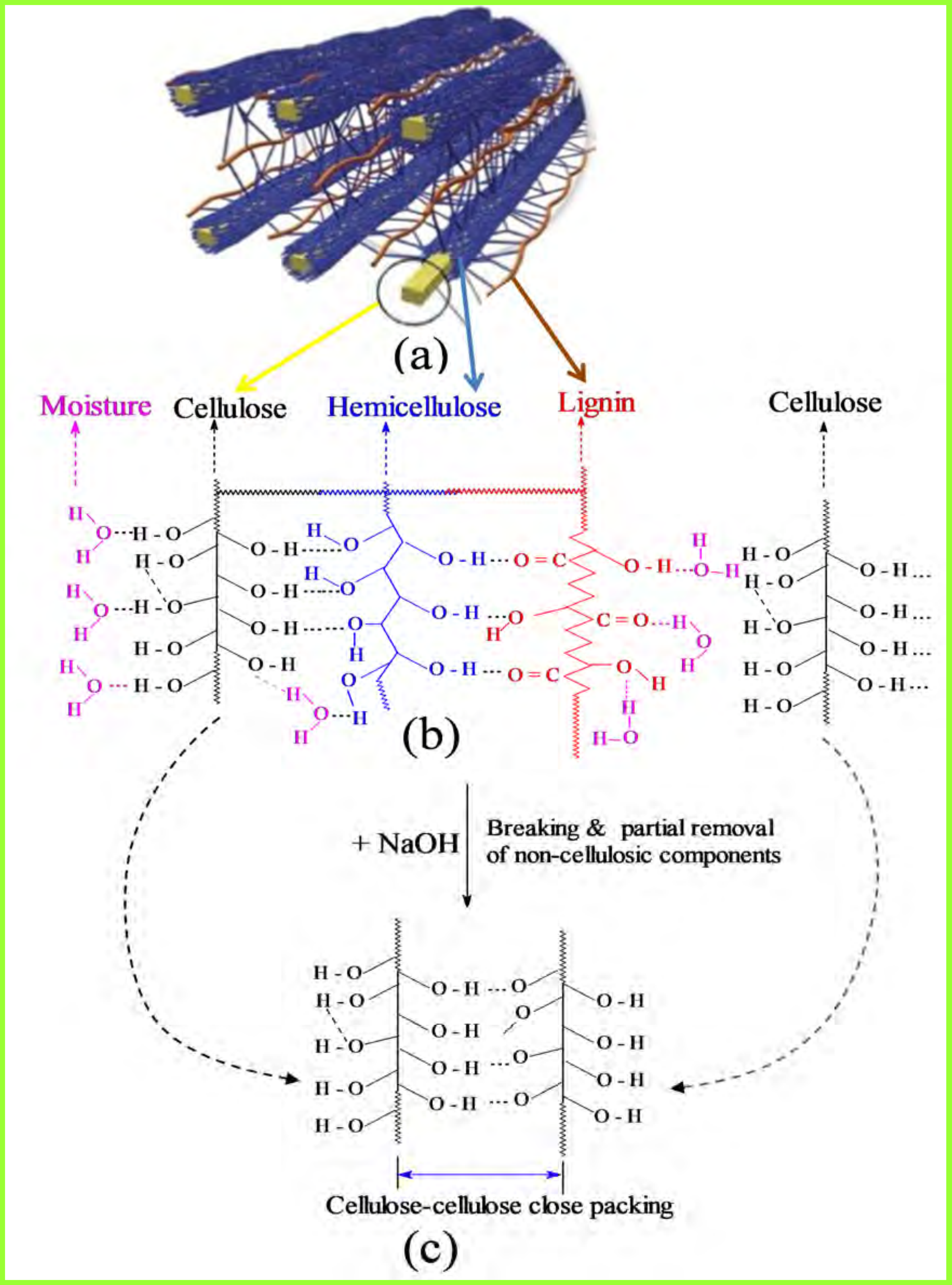
Figure 2.8: FTIR spectra of untreated betel nut husk fiber (lower) and sodium hydroxide treated betel nut husk fiber (upper)

Table 2.2: FTIR spectral data of untreated betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3422.40	-OH stretching from the cellulose, hemicellulose and lignin
~ 2919.57	C-H vibration in aromatic ring and alkanes
~1738.37	C=O stretching from the lignin and hemicelluloses
~ 1610.31	C=C stretching from aromatic in-plane
~ 1513.87	C=C stretching in aromatic skeletal ring due to lignin
~ 1428.43	C-C stretching from aromatic ring

Table 2.3: FTIR spectral data of sodium hydroxide treated betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3423.26	-OH stretching from the cellulose, hemicellulose and lignin
~ 2922.18	C-H vibration in aromatic ring and alkanes
~ 1609.86	C=C stretching from aromatic in-plane
~ 1509.06	C=C stretching in aromatic skeletal ring due to lignin
~ 1425.39	C-C stretching from aromatic ring



Scheme 2.1: Effect of alkali treatment in BNHF (Image adopted from [78]

2.4.2 Morphological investigation of BNHF-LDPE composites

The Scanning electron microscopy (SEM) images of treated and untreated betel nut husk fiber-LDPE composites are shown in figure 2.9 and figure 2.10 respectively. The SEM Micrograph of fracture surfaces of 25 wt % alkali treated BNHF-LDPE composite shows uniform dispersion and better interfacial adhesion between the fiber and matrix in figure 2.10. The weak interfacial adhesion between the fiber and matrix is observed in figure 2.9 which represents the fracture surface of 25 wt % untreated BNHF-LDPE composites. So it may be concluded that alkali treated fibers are able to improve the compatibility between the fiber and matrix in the composites.

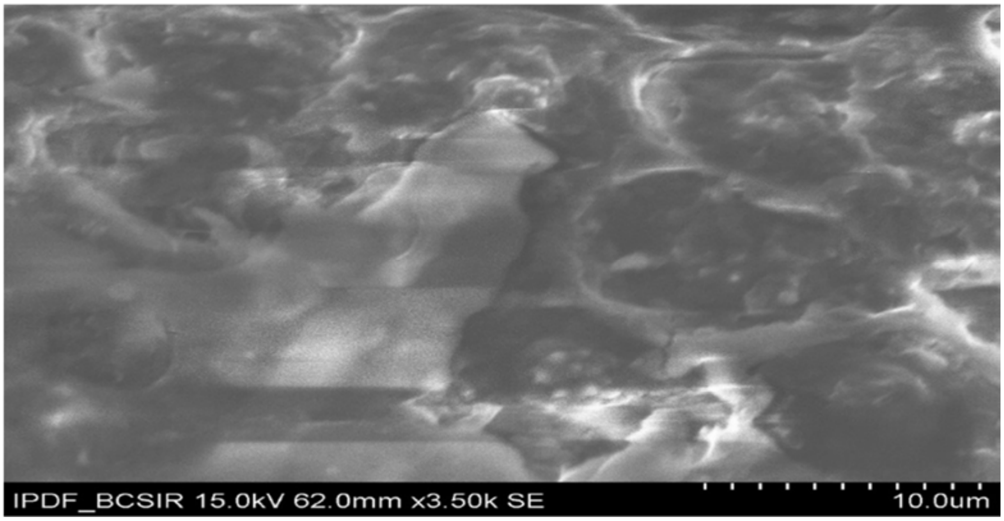


Fig 2.9: SEM image of untreated 25 wt % betel nut husk fiber-LDPE composite

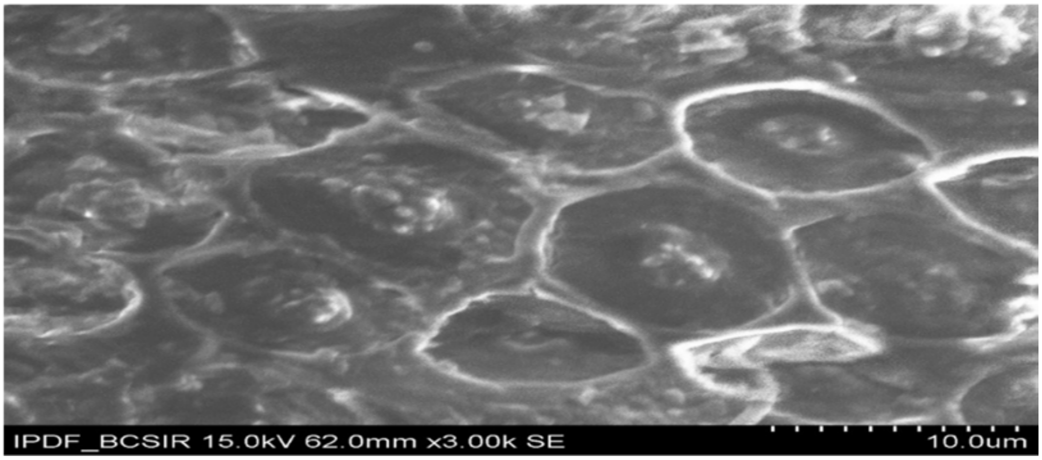


Fig 2.10: SEM image of alkali treated 25 wt % betel nut husk fiber-LDPE composite

2.4.3 Tensile strength and elongation at break of untreated and treated BNHF reinforced -LDPE composites

The tensile strengths of the untreated and treated BNHF-LDPE composites are shown in figure 2.11. It is observed from the figure that the tensile strengths of the composites increased up to 10 wt. % fibers loading & then decreased. The elongations at break of untreated and treated BNHF-LDPE composites are shown in figure 2.12. Elongation at break of all composites decreases with increasing fiber loading .This reduction is due to the lack of stress transfer from the LDPE matrix to betel nut fibers, the similar results were found for kenaf- PP composites [79]. Tensile properties of all treated BNHF-LDPE composites are higher than that of untreated BNHF-LDPE composites. The tensile strength and ductility were better in the case of treated BNHF-LDPE composites than that of untreated BNHF-LDPE composites. This may be the reason for the improvement of the fiber-matrix interfacial adhesion in composites made by alkali treatment.

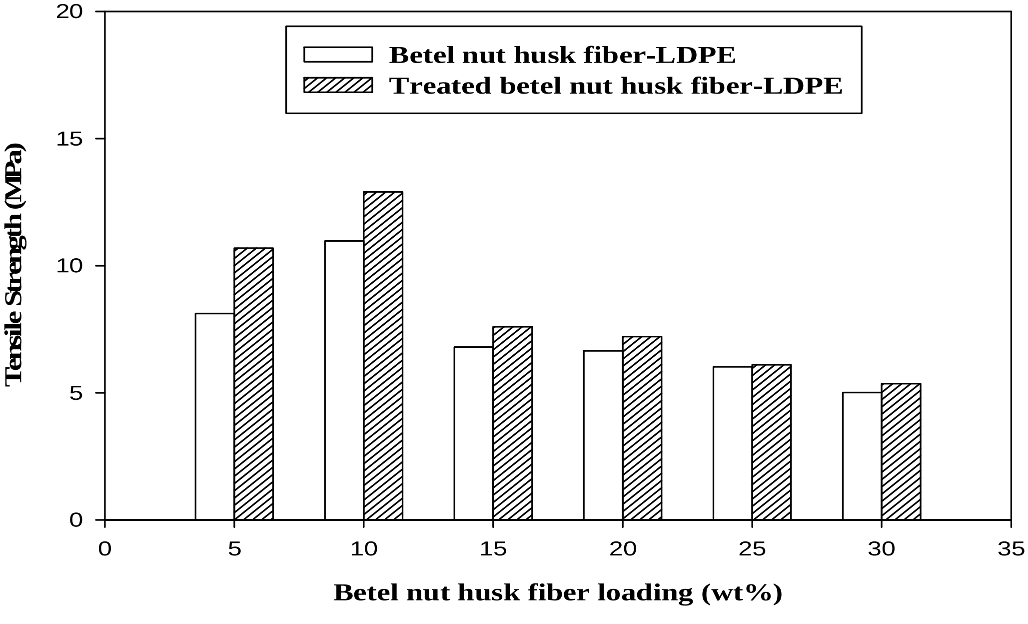


Fig 2.11:- Tensile strength (MPa) vs betel nut husk fiber (wt%) curves for raw & treated betel nut husk fiber-LDPE composites

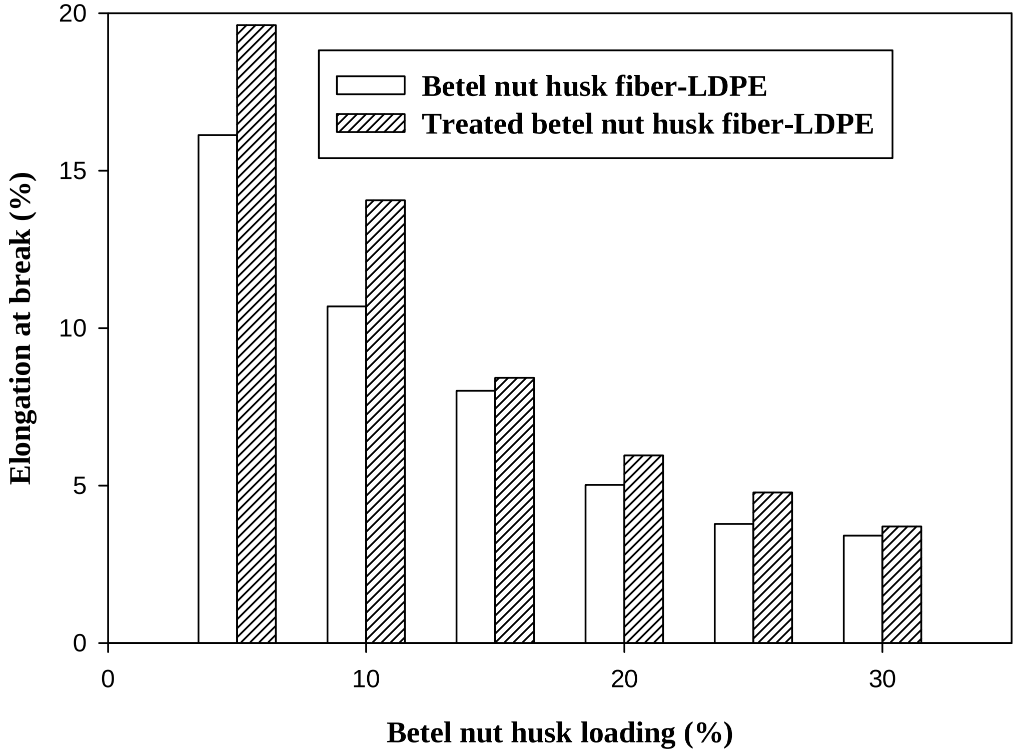


Fig 2.12:- Elongation at break(%) vs betel nut husk loading (%) curves for raw & treated betel nut husk-LDPE composites

2.4.4 Impact Strength

The Izod impact test of prepared BNHF- LDPE composite samples were performed according to Izod impact test methods include ASTM D256-02. The impact strength of the untreated BNHF-LDPE composite and NaOH treated BNHF-LDPE composites are shown in figure-2.13. Impact strength of prepared composite decrease with increasing the fiber loading percentage of all composites, but chemical treatment enhanced the impact strength of BNHF-LDPE composites.

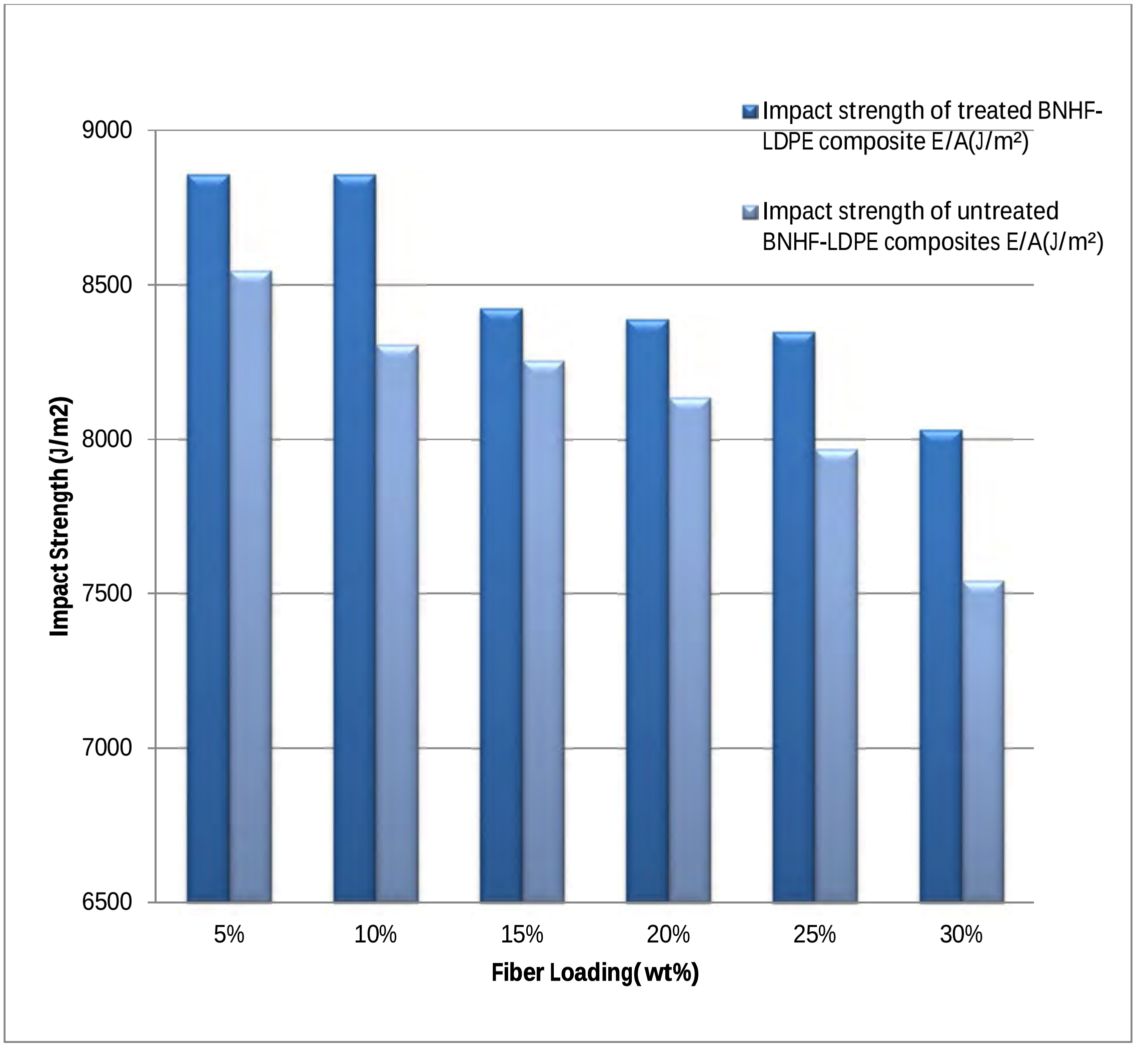


Figure-2.13 Effect of fiber loading (wt. %) on Impact strength of treated and untreated BNHF-LDPE composite

2.4.5 Thermal properties of Untreated and treated Betel Nut Fiber Reinforced LDPE Composites

The thermo grams of LDPE and 5% treated BNHF fiber loading LDPE composites presented in the figure 2.14 and figure 2.15. It was observed in the thermo grams of LDPE that degradation start at 446.8°C and 99.97 % mass change was completed at 515°C and the melting temperature of LDPE was found at 109.4 °C whereas for treated BNHF-LDPE composite the mass change started at 373.9°C and 4.34% mass change was completed at about 450°C, another degradation was found at 484.1°C and 93.38% degradation was done at 515°C for BNHF reinforced LDPE composite, the melting temperature of polymer matrix in treated BNHF-LDPE composite was found 114.2 °C.

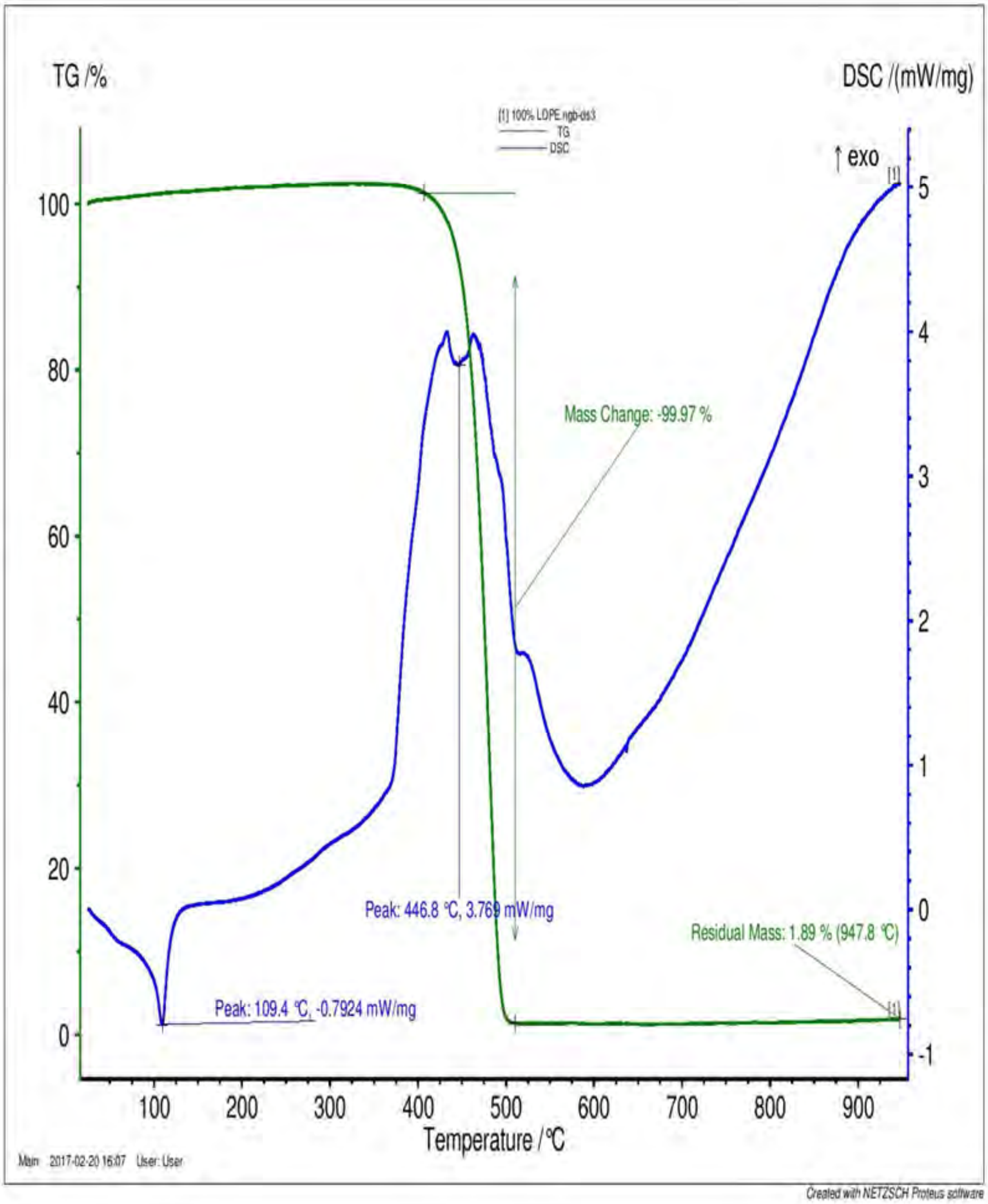


Figure 2.14: TGA and DSC of LDPE

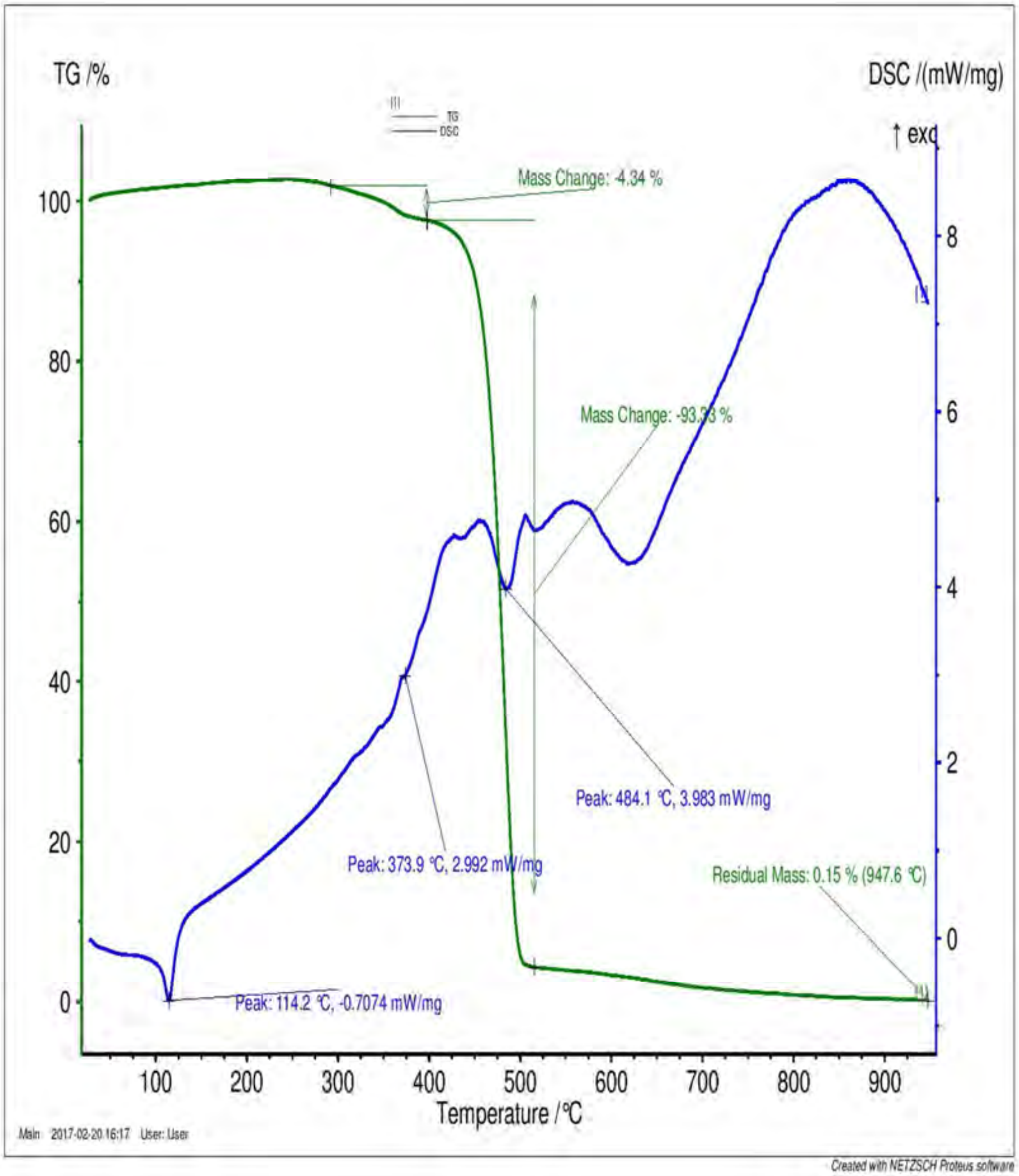


Figure 2.15: TGA and DSC of treated BNHF- LDPE composite

2.4.6 Water absorption of BNHF-LDPE composites

Water absorption in ligno-cellulosic based composites is an important characteristic which determine its applications of these materials. Water absorption test results of all treated and untreated BNHF-LDPE composites are shown in figure 2.16. It is clear from the figure that water absorption increases with increasing fiber loading for all composites but water absorption of untreated BNHF-LDPE composites is higher than that of treated betel nut husk fiber-LDPE composites. This may be due to the hydrogen bonding formation of water molecules with the hydroxyl groups in the constituents of lignin, hemicelluloses and cellulose of untreated BNHF. Alkali treatment of BNHF removes their hemicelluloses completely and reduces the lignin part. So treated betel nut husk fiber-LDPE composites show less water absorption than untreated BNHF-LDPE composites. So dimension stability will be higher for treated betel nut husk fiber-LDPE composites than untreated BNHF-LDPE composites.

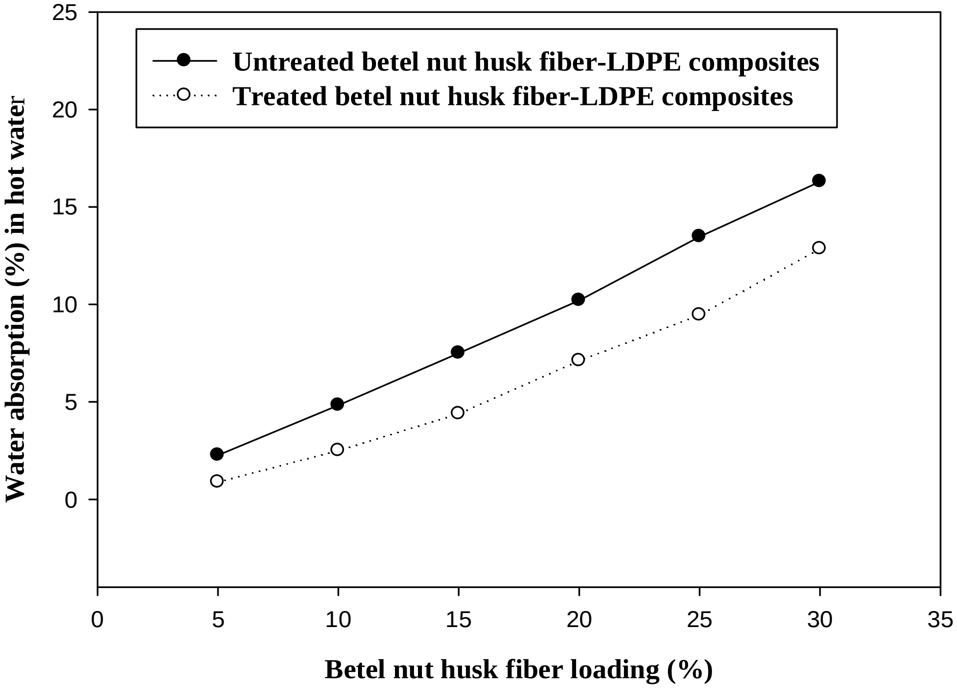


Fig 2.16:- Hot water absorption (%) vs fiber loading (%) curves for untreated and treated betel nut husk fiber-LDPE composites

2.4.7 Biodegradability of Composites

The biodegradability of prepared BNHF-LDPE composites had been studied and test results are shown in figure 2.17. Composites biodegradability was determined by measuring the weight loss of the specimens which are buried in soil. The test was done by using the gardening soil at average spring temperature (25–30 °C). The weight of all selected specimen were recorded. The selected each specimen was buried in the soil. After burial of 90 days the specimens were exposed from the soil. All specimens were washed and dried in an oven for constant weight. The weights of dried specimens were recorded and the biodegradation (%) was calculated according to formula (Eq-2). From this figure (2.17) it is clear that biodegradation increases with increasing fiber loading (%) for all composites but untreated BNHF-LDPE composites were more biodegradable than that of treated betel nut husk fiber-LDPE composites.

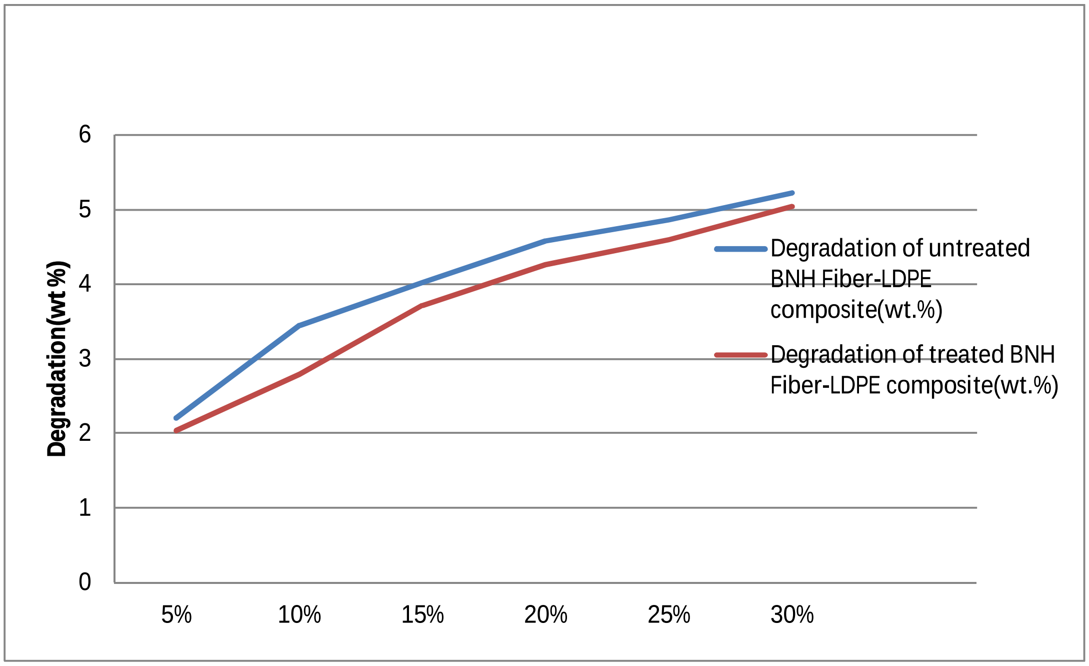


Figure 2.17: Biodegradation (%) of different fiber loaded (wt %) of treated and untreated BNHF-LDPE composites

2.5 Conclusion

The treatment of betel nut husk fibers with NaOH (6%) removes the impurities and hemicelluloses and reduces the lignin content of fibers. FT-IR spectroscopic analyses also supported the evidence of removal of hemicelluloses. The absorption band 1738.37 cm^{-1} of untreated BNHF was disappeared in the FTIR spectrum of alkali treated BNHF which indicate the removal of lignin from fiber. Alkali treatment of BNHF reduces the moisture absorption property and improves the interfacial adhesion between fibers and matrices in composites. The enhancement of the hydrophobicity in BNHF due to alkali treatment results the better compatibility between the fibers and matrices of the LDPE composites. The tensile properties of treated BNHF -LDPE composites are higher than that of untreated betel nut husk fiber-LDPE composites. The tensile strength of LDPE-BNHF increased with increasing fiber loading (wt %) of composites up to 10 wt% of fiber loading then decreases with increasing the fiber loading (wt %). 10 wt% of treated fiber loaded composite showed the highest tensile strength. The reduction of water absorption in the alkali treated betel nut husk fiber-LDPE composites will increase their dimensional stability. Uniform dispersion and better interfacial adhesion between fibers and matrixes were observed SEM image of treated BNHF-LDPE composite. The morphological observation also proves the strong interfacial bonding between fibers and matrixes in the alkali treated BNHF-LDPE composites. Alkali treated BNHF-LDPE composites are less biodegradable then untreated BNHF-LDPE composites. So this research may provide valuable contributions to developing betel nut husk fibers as sustainable reinforcements in thermoplastic based composites.

CHAPTER - 3

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED HIGH DENSITY POLYETHYLENE COMPOSITE

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED HIGH DENSITY POLYETHYLENE COMPOSITE

3.1 Introduction

Environmental friendly greener materials like natural fibers are promising alternative materials to traditional glass fibers due to their good specific strength, low cost, renewability and market appeal, fully biodegradable nature and non-abrasive character [80]. Natural fiber used as reinforcement can be classified into many categories i.e. baste, seed, straw fiber, leaf, and grass fiber. Hardwood saw dusts, jute fibers, palm fibers, coconut fibers, rice straw fibers are used as reinforcements in polymer composites due to low cost, low density and biodegradability [81-85]. In the past agro based waste products have been used as natural sources to collect natural fibers suitable for agro-tech protective clothing [86]. Instead of glass or carbon fiber and inorganic fillers, natural fibers from natural sources are more potential as biodegradable reinforcing materials. From different research work and application in various fields it has been proved that natural fiber reinforced and thermoplastic polymer matrix based composites are much more applicable. A wide range of agro-based fibers is being utilized as the main structural components or as reinforcing agents in the fiber-matrix based composite materials which are used from decorative, interior design and automotive interior components. Uses of different natural fibers which are work as reinforcing agent is also described elsewhere [82-84]. In addition, natural fibers are now being widely used as fillers in the different industries like plastic industry to acquire expected results as well as to reduce the price of the finished product [87]. 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, hemi-cellulose and lignin are the main component of natural fiber and hence natural fibers are commonly termed as lingo-cellulosic materials. These constituents make natural fibers hygroscopic and hydrophilic which they have poor compatibility with hydrophobic polymer matrix in natural fiber reinforced polymer composites. Better fiber matrix interfacial bonding can be achieved by the surface treatment of natural fiber. Many Researchers have analyzed that the chemical modification of the natural fibers optimizes the interfacial locking between the fiber and the matrix and improving the other properties. During this process hydroxyl groups which are on natural fibers were activated or some new functional groups will be introduce, which will create effective interlock bonding with the matrix. Chemical treatments used as surface treatments are such as alkaline, permanganate, acetic anhydride, stearic acid, silane, malicanhydride, and benzoylation have been studied by many researchers [88-97].

Betel nut is the fruit of *Areca catechu* tree is found everywhere in Bangladesh as well as widely found in the coastal area. Betel nut husk fiber which is extracted from the betel nut fruit is generally unusable. This biodegradable fiber is cheap and easily used to prepare composite materials. The aim of this work is to use it as a reinforcing material with HDPE matrix at different wt. percentages. Another aim of this research work is to treat the extracted fibers chemically, which could improve the properties of the composites. Sodium *meta*-periodate was used for treatment with betel nut husk fibers. The novelty of this work is the chemical modification of betel nut husk fibers with sodium *meta*-periodate. Different types of properties such as tensile strength, elongation at break, water uptake, TGA-DSC analysis, soil degradation test as well as scanning electron microscopy (SEM) etc were analyzed for all treated and untreated BNHF reinforced HDPE composites and reported in this chapter. These composites can be used in automobile sector, interior design, aircraft sector and making furniture etc.

3.2 Materials

3.2.1 Polymer matrix

A commercial grade high density polyethylene (HDPE) from PTT Global Chemical Public Company, Thailand, was used as polymer matrix. Melting point of this HDPE was measured and found to be 130-135°C. It is mentioned in literature that the melting point of commercial grad HDPE lies in the range 130-135°C.

3.2.2 Reinforcing materials

Betel nut husk fiber is, the outer part of betel nut fruits (Areca catechu) was used as reinforcing material in this work. Matured betel nuts were collected from local betel nut plantation field. The betel nut husk fibers were extracted from collected betel nuts as mentioned in previous chapter.

3.2.3 Chemicals

The analytical grade sodium meta-periodate and other reagents were used from Merck, Germany.

3.3 Experimental

3.3.1 Chemical treatment of betel nut husk fiber with sodium *meta*-periodate

The washed and air dried raw BNHF fibers were oven dried at 105 °C for 5 hours. Sodium *meta*-periodate solution (0.06 M) was prepared in distilled water and the dried BNHF fibers were immersed in sodium *meta*-periodate solution. Fiber to liquor ratio was 1:16 (w/v). The pH of the solution adjusted to 5 by adding sulfuric acid. The reaction was carried out for 4 hours at 90°C. The reaction mixture was stirred occasionally. The mixture was cooled and filtered to isolate the oxidized BNHF fibers. The oxidized BNHF fibers were thoroughly washed in tap water and finally washed with distilled water. The washed oxidized fibers were air dried. The air dried fiber was dried in a vacuum oven at 105 °C for constant weight. These oxidized BNHF fibers were used for composite fabrication.

3.3.2. Fabrication of BNHF reinforced HDPE polymer Composite

The fabrication of untreated and sodium *meta* periodate treated betel nut husk fiber reinforced HDPE composites were carried out by compression molding technique. The mould (12×15 cm^2) was cleaned and filled with dry blended mixture of betel nut husk fibers and HDPE powders to prepare composites. Weight fraction 5%, 10%, 15%, 20%, 25%, 30% of BNHF and treated BNHF was carefully controlled during the mixing of two ingredients. The composites were hot pressed under 160°C temperature and 200 N pressures. These procedures were followed for all the composites fabricated in the ratio of composition shown in the table 3.1. 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.

Table 3.1 Different weight fraction of betel nut fiber reinforced HDPE composites

Sample Number	Reinforcing material (wt %)	Polymer matrix (wt %)	Composites
No. 22	BNHF : 05	HDPE : 95	05:95 (wt %) BNHF: HDPE
No. 23	BNHF : 10	HDPE : 90	10:90 (wt %) BNHF: HDPE
No. 24	BNHF : 15	HDPE : 85	15:90 (wt %) BNHF: HDPE
No. 25	BNHF : 20	HDPE : 80	20:85 (wt %) BNHF: HDPE
No. 26	BNHF : 25	HDPE : 75	25:75 (wt %) BNHF: HDPE
No. 27	BNHF :30	HDPE : 70	30:70 (wt %) BNHF: HDPE
No. 14	BNHF : 00	HDPE : 100	100 (wt %) HDPE
No. 15	Treated BNHF : 05	HDPE : 95	05:95 (wt %) treated BNHF: HDPE
No. 16	Treated BNHF : 10	HDPE : 90	10:90 (wt %) treated BNHF: HDPE
No. 17	Treated BNHF : 15	HDPE : 85	15:90 (wt %) treated BNHF: HDPE
No. 18	Treated BNHF : 20	HDPE : 80	20:85 (wt %) treated BNHF: HDPE
No. 19	Treated BNHF : 25	HDPE : 75	25:75 (wt %) treated BNHF: HDPE
No. 20	Treated BNHF :30	HDPE : 70	30:70 (wt %) treated BNHF: HDPE

3.3.3 Characterization of BNHF reinforced HDPE composites

The untreated and treated Betel nut husk fiber and their reinforced HDPE composite materials were characterized by FT-IR Spectroscopy and scanning Electron Microscopy as stated below.

3.3.3.1 FTIR spectroscopy

FTIR spectrums were taken for untreated and $NaIO_4$ 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 100 mg of dried powdered potassium bromide in a small agate mortar pestle. The mixture was taken to make pellets by applying vacuum pressure. The samples were then loaded into FTIR spectrometer (Forntier, PerkinElmer, USA) in 4000-700 cm^{-1} wave length range. IR spectra were obtained in the printed form.

3.3.3.2 Scanning electron microscopy (SEM)

The surface of BNHF, treated BNHF and fracture surface of tensile test of 10 wt % treated and treated fiber loaded BNHF-HDPE composite 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 untreated BNHF, treated BNHF and the fracture surface of the untreated and treated BNHF-HDPE composites. The photographs are presented in the result and discussion section.

3.3.4 Mechanical properties of composites

Tensile test and Impact test of all prepared BNHF-HDPE composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods. Specification and picture of the used machines, operating condition and dimension of test specimens are given below.

3.3.4.1 Tensile properties of the composites

The tensile test of all treated and untreated betel nut husk fiber reinforced polymer composites were measured 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 and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves and the maximum load values were recorded by the instrument and noted after the completion of the test.

3.3.4.2 Impact test

Izod impact tester machine, Qualitest, North America was used for impact test of prepared sample. Izod impact test methods ASTM D256-02 were used to perform Izod impact test for all samples. The length, width and thickness of the specimen are 64 mm, 12.7 mm and 3.2 mm respectively. V-shaped notched specimens were used. A total of ten samples were tested and the mean value of the absorbed energy taken. The impact strength (J/m^2) was calculated by dividing the recorded absorbed impact energy with the cross-sectional area of the specimens.

3.3.5 Thermal properties of composites

3.3.5.1 Thermo gravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC)

The thermo gravimetric analysis and differential scanning calorimetric analyses of the 10 wt % of treated, untreated and100% HDPE 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 min^{-1} in a nitrogen atmosphere. Ten mg of the sample was heated in the sample pan.

3.3.6 Water absorption test of composite

The water absorption behavior of the developed composites of sodium *metap*eriodate treated and untreated betel nut husk fiber-HDPE composites were carried out following ASTM D570-99 standard method. 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 80 °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 was calculated by following the Eq. (1). Three specimens were taken to calculate average results and presented in the results and discussion section.

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

Where, W_0 is the dry initial weight, W_1 is the weight after immersion in water.

3.3.7 Biodegradability of Composites

Biodegradability (BD) of composite was determined by measuring the weight loss of the specimens which are buried in soil. The selected each specimen was buried in the gardening soil. At two days intervals, water was poured in the soil to keep the humid condition. After burial of 90 days the specimens were exposed from the soil. The specimens were then washed with water and dried at 80 °C in an oven up to a constant weight. Due to biodegradation the weight loss (%) is calculated according to the following formula.

$$\mathrm{BD}(\%) = \frac{(\mathrm{w_{bb}} - \mathrm{w_{ab}})}{\mathrm{w_{ab}}} \times 100$$

Where $\mathrm{w_{bb}}$ and w_{ab} are the dry weights of composites before and after the burial, respectively.

3.4 Results and Discussion

3.4.1 FTIR analysis of Sodium *meta* periodate treated BNHF

Fig.3.1 shows the infrared spectra of treated and untreated betel nut fiber. Both treated and untreated fibers were characterized by FTIR spectroscopy to confirm the chemical reaction of sodium *meta* periodate with lignocelluloses element of fibers. The IR spectra of treated fibers clearly showed the characteristic bands of aldehyde group at the region of 2920 cm $^{-1}$ due to C-H stretching. The peak 1738 cm^{-1} was seen in untreated fiber which disappeared upon chemical treatments. This is due to the removal of carboxylic group by chemical treatment. The peak assignments to the absorption bands corresponding to various groups are summarized in Table3.2 and 3.3. Figure 3.2 shows the ATR-FTIR spectra of treated and untreated BNHF-LDPE composites. The characteristic absorption band of lignin and hemi-cellulose at 1738 cm^{-1}was disappeared in treated BNHF-LDPE composite.

Table 3.2: FTIR spectral data of untreated raw betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3422.40	-OH stretching from the cellulose, hemicellulose and lignin
~ 2919.57	C-H vibration in aromatic ring and alkanes
~1738.37	C=O stretching from the lignin and hemicellulose
~ 1610.31	C=C stretching from aromatic in-plane
~ 1513.87	C=C stretching in aromatic skeletal ring due to lignin
~ 1428.43	C-C stretching from aromatic ring

Table 3.3: FTIR spectral data of sodium meta-periodate treated betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3423.26	-OH stretching from the cellulose, hemicellulose and lignin
~ 2920.18	C-H vibration in aromatic ring and alkanes
~ 1608	C=C stretching from aromatic in-plane
~ 1508.2	C=C stretching in aromatic skeletal ring due to lignin
~ 1420	C-C stretching from aromatic ring

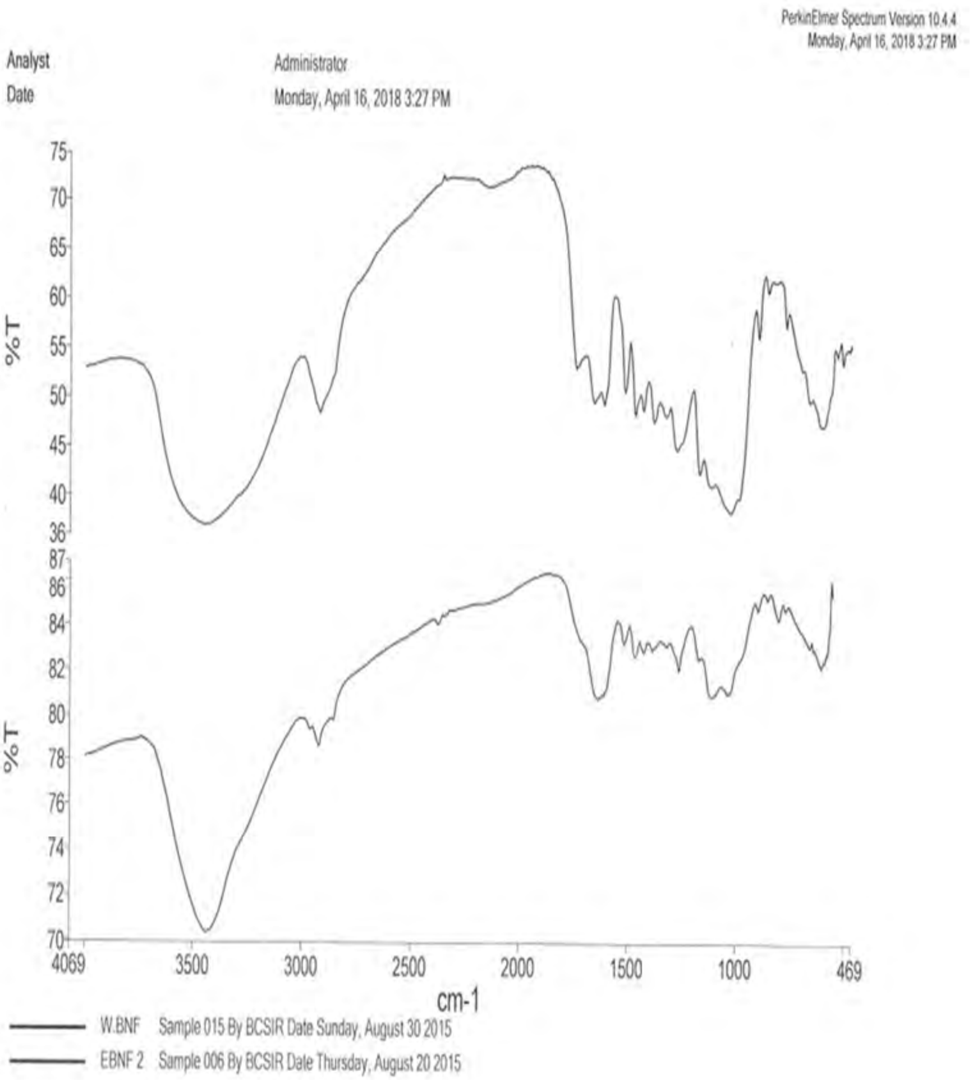


Figure 3.1 : FTIR of betel nut fiber (upper) and treated betel nut fiber (lower).

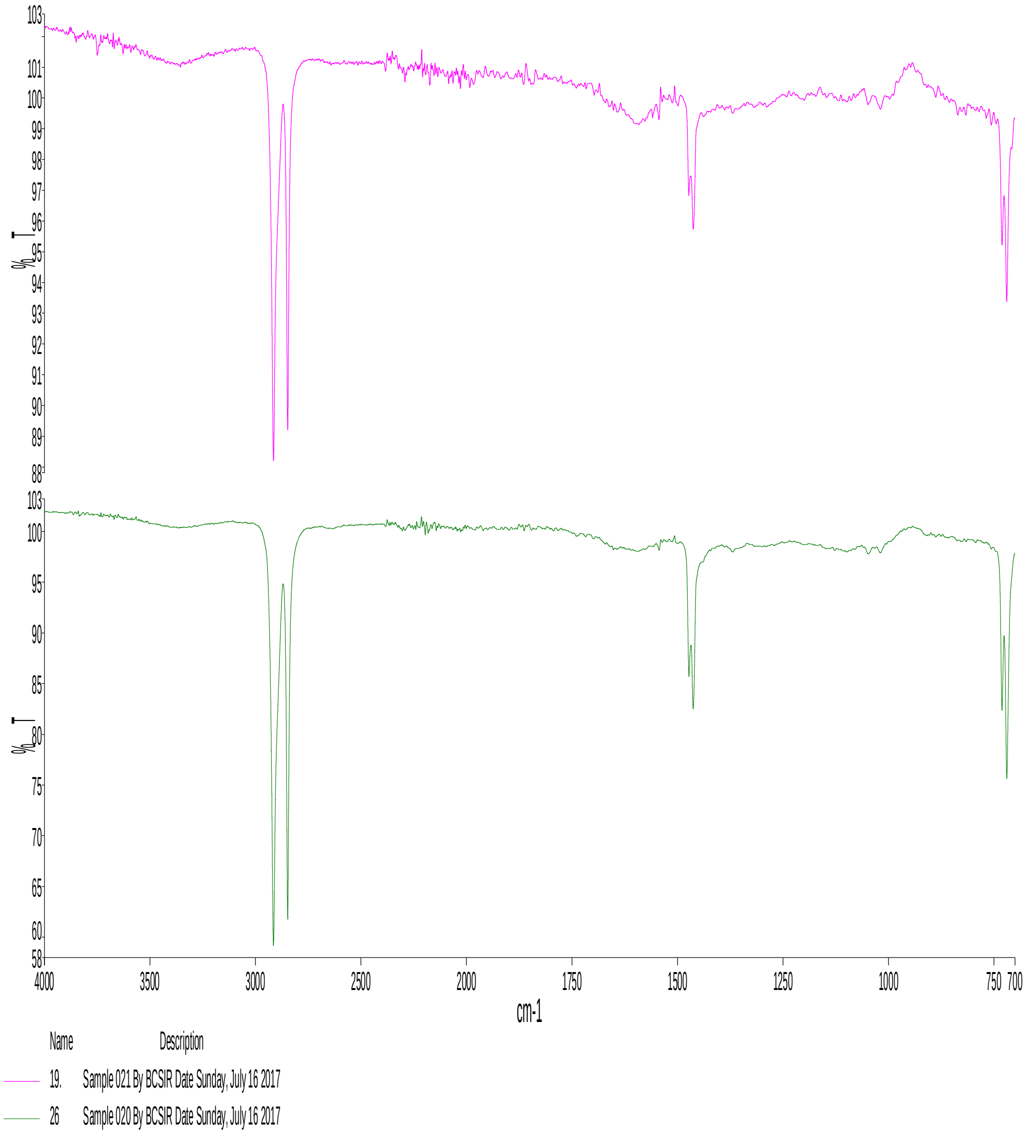
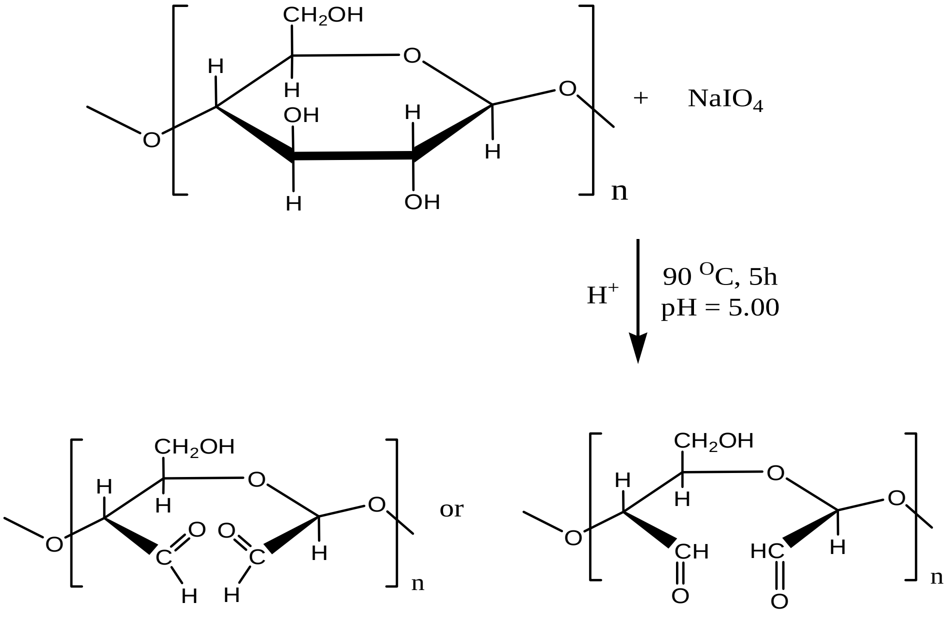


Figure 3.2 : ATR spectra of BNHF- HDPE composite



Dialdehyde Cellulose in Betelnut Husk Fiber

Scheme 3.1 Oxidation reaction of cellulose in BNHF with sodium *meta*-periodate

3.4.2 Morphological Characterization of Untreated and Sodium *meta*-periodate Treated Betel Nut Fiber reinforced HDPE composite

The surface morphology of the untreated fiber, treated fiber and their reinforced composites were studies by scanning electron microscope (SEM) and the pictures are given in figure 3.3, 3.4, 3.5 and 3.6 respectively. From the analysis of SEM image of untreated and treated betel nut husk fiber (BNHF) it was found that treated BNHF was more fibrous then untreated BNHF. The SEM image of treated BNHF-HDPE composite indicated the better interfacial adhesion between treated BNHF-HDPE composite as compared to untreated BNHF-HDPE composite.

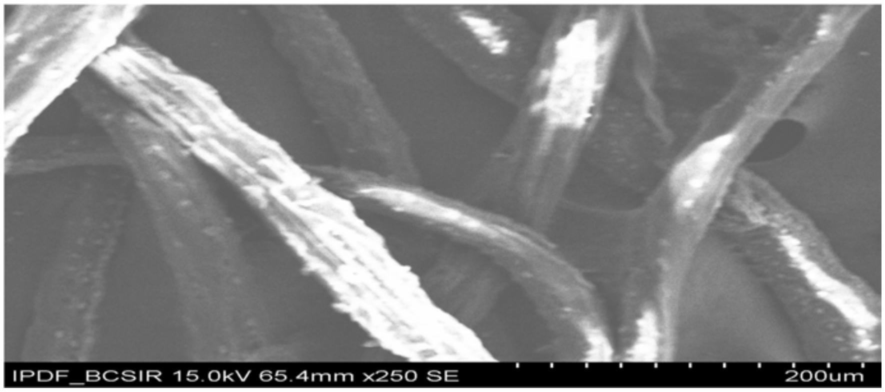


Figure 3.3 SEM of untreated BNHF

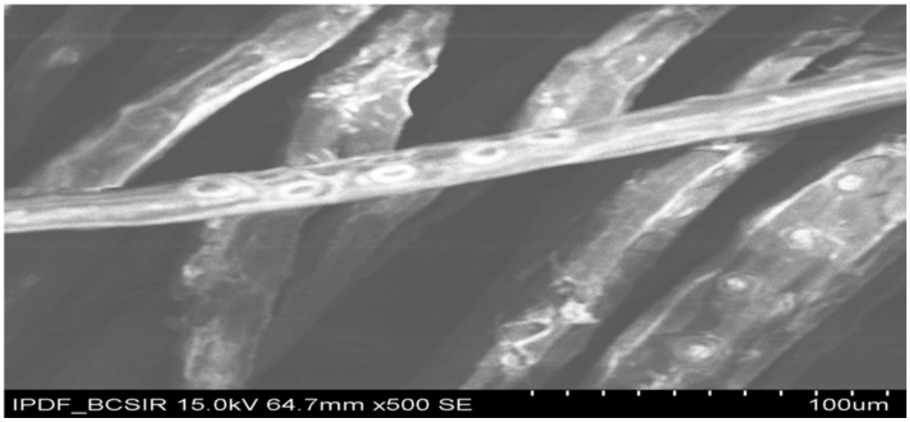


Figure 3.4 SEM of treated BNHF

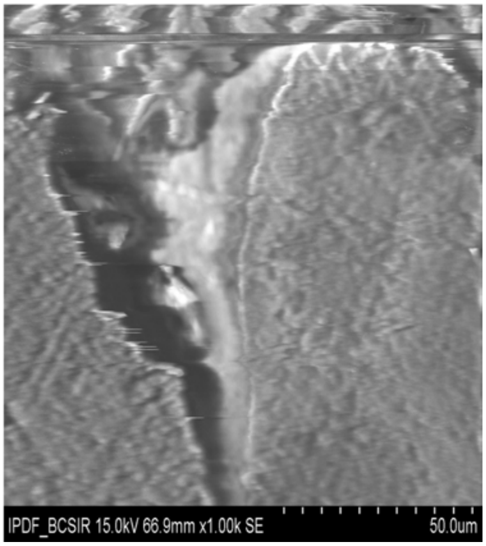


Figure 3.5 SEM image of treated BNHF-HDPE composite

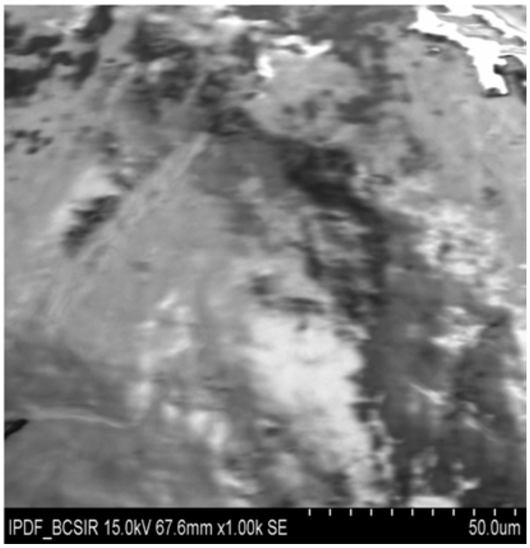


Figure 3.6 SEM of untreated BNHF-HDPE composite

3.4.3 Tensile strength and elongation at break of untreated and treated BNHF reinforced HDPE composites

The tensile strengths of the untreated and treated BNHF-HDPE composites are shown in figure 3.7. It is observed from the figure that the tensile strengths of the composites increased up to 10 wt% fibers loading composites then decreased with increasing the fiber loading (wt%). The elongations at break of untreated and treated BNHF-HDPE composites are shown in figure 3.8. Elongation at break of all composites decreases with increasing fiber loading (wt %) of composites. Tensile properties of all treated BNHF-HDPE composites are higher than that of untreated BNHF-HDPE composites. The tensile strength and ductility were better in the case of treated BNHF-HDPE composites than that of untreated BNHF-HDPE composites. This may due to the improvement of the fiber-matrix interfacial adhesion in composites made by sodium periodate treatment.

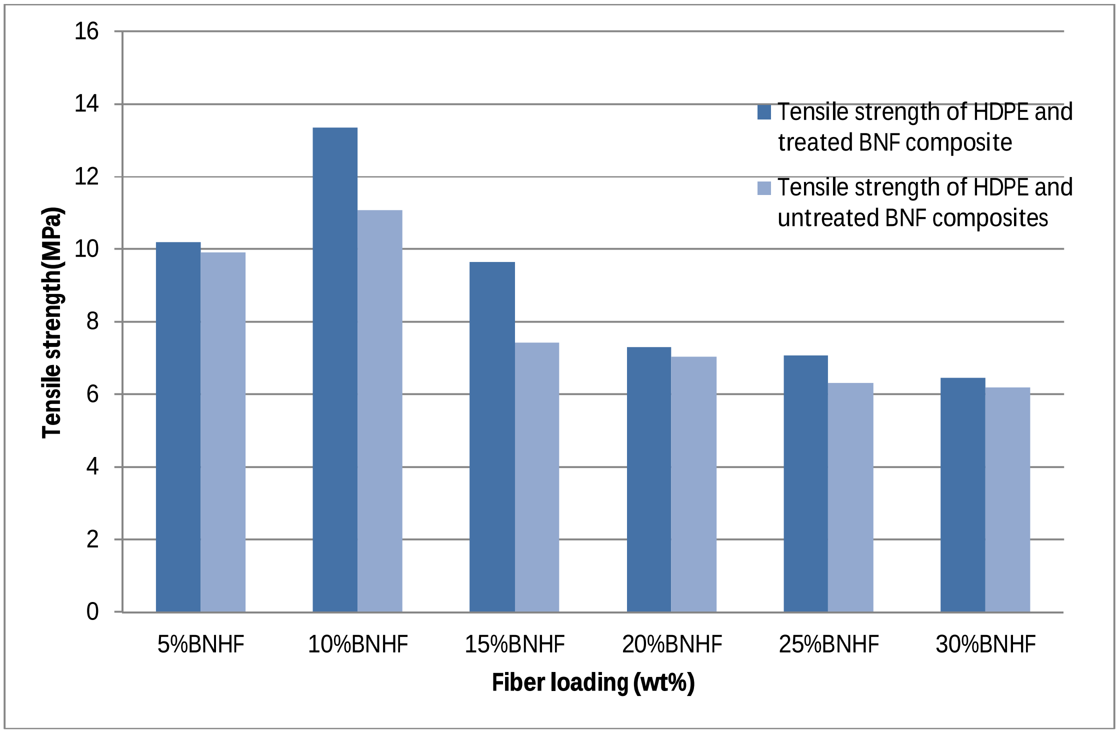


Figure 3.7: Tensile strength of $NaIO_4$ treated and untreated BNHF- HDPE composite.

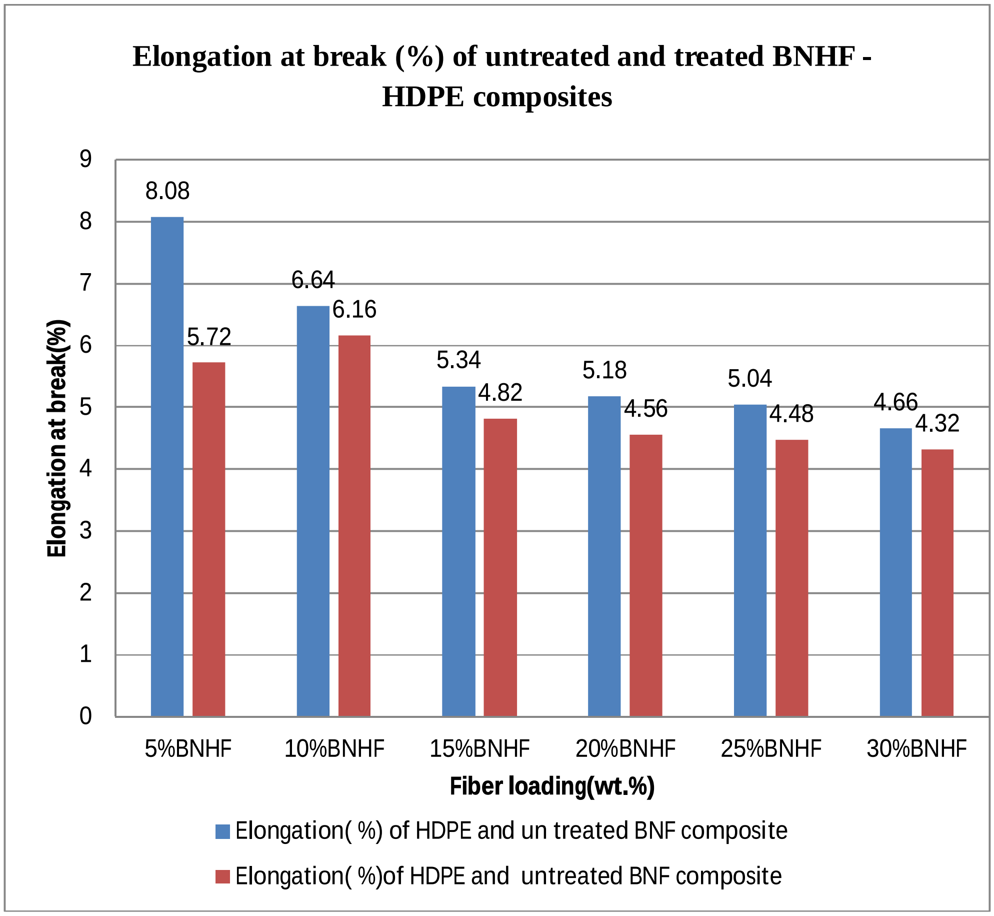


Figure 3.8: Elongation at break (%) untreated and $NaIO_4$ treated BNH-HDPE composites

3.4.4 Izod Impact Strength

The Izod impact test of prepared BNHF- HDPE composite samples were performed according to Izod impact test method ASTM D256-02. A total of ten samples were tested and the mean value of the absorbed energy taken. The impact strength (J/m^2) was calculated by dividing the recorded absorbed impact energy with the cross-sectional area of the specimens. The results of impact energy per area for untreated and treated BNHF-HDPE composites are given in figure 3.9. The treated fiber loaded composites have higher impact strength than untreated fiber loaded BNHF-HDPE composites. The impact strength decreases with increasing fiber loading (wt %) of both treated and untreated BNHF-LDPE composites.

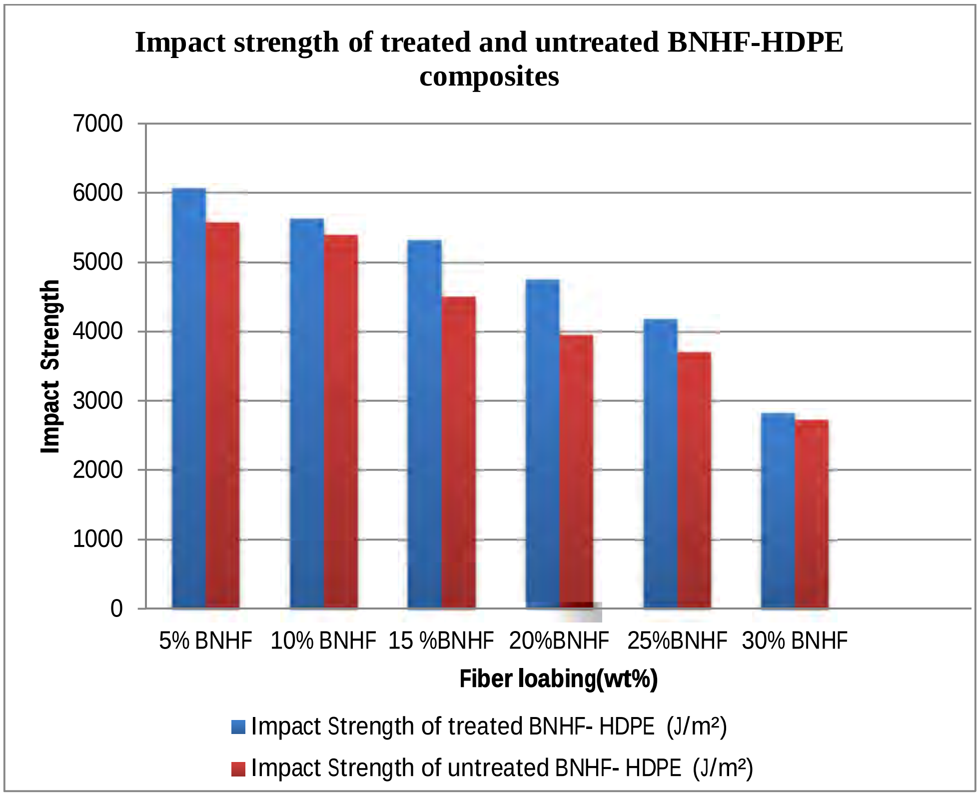


Figure 3.9: Impact strength of treated and untreated BNHF-HDPE composites

3.4.5 Thermal properties of Untreated and treated Betel Nut Fiber Reinforced HDPE Composites

Thermal properties of neat HDPE, 10 wt% untreated and treated BNHF-HDPE composites were evaluated by Differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). The thermo grams of HDPE granules and there optimized (%) BNHF reinforced composites presented in the figure 3.10, 3.11 and 3.12 respectively. It is observed from the figures that almost same thermal properties were found for treated and untreated BNHF-HDPE composites. But neat HDPE showed slightly higher thermal stability than the BNHF-HDPE composites. The melting temperature of neat HDPE and untreated BNHF-HDPE and treated BNHF-HDPE composites were found at 133.5 ºC , 132.9 ºC and 132.8 ºC respectively. It was observed in the thermo grams that degradation start at 505ºC and 93.74 % mass change was completed at 575 °C for HDPE granules where as the mass change started at 388.7ºC and 13.9% mass change was completed at 459.8°C and 84.51% degradation is done at 560 °C for BNHF reinforced HDPE composite and the 2.76% residual mass was got at 947.8 ºC. In case of treated BNHF reinforced HDPE composite the mass change started at 361.4°C and 4.03% mass change was completed at 482.8 °C and 93.18% degradation is done at this temparature.12.85% residual mass was got at 947.8 ℃. So addition of treated and untreated BNHF with HDPE didn’t affect the melting temperature of neat HDPE.

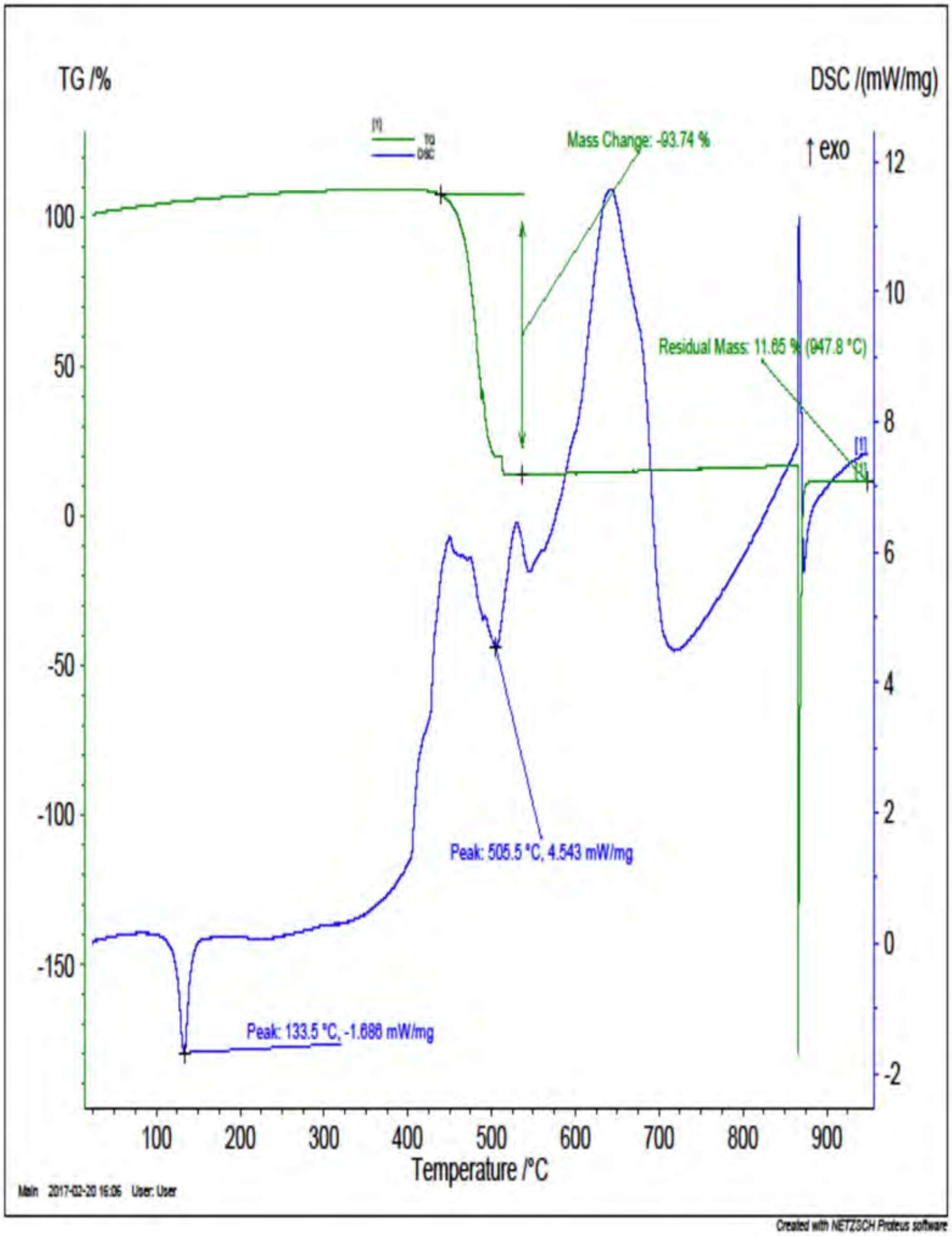


Figure 3.10: TGA and DSC curve of HDPE

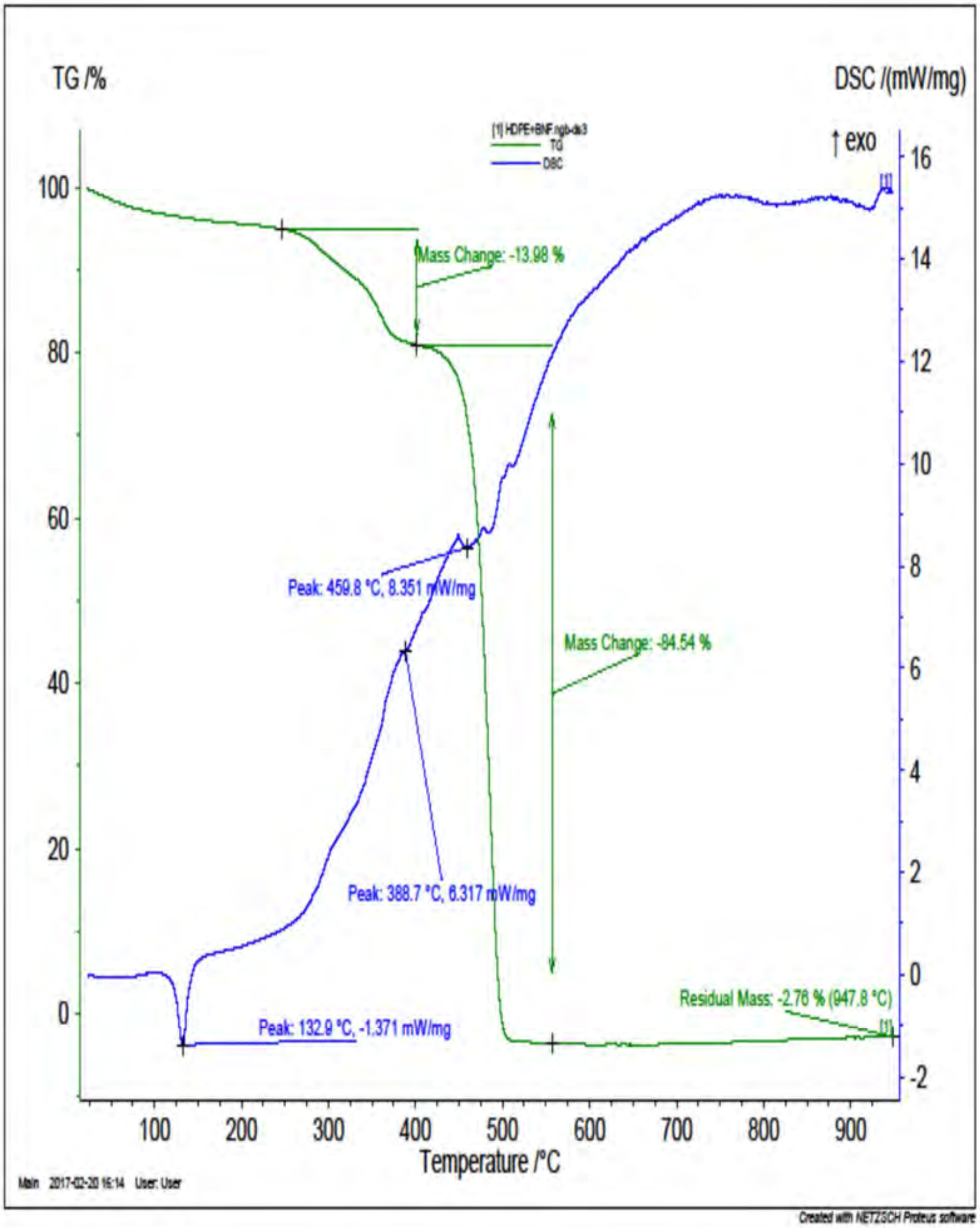


Figure 3.11: TGA &DSC curve of untreated BNHF and HDPE composite.

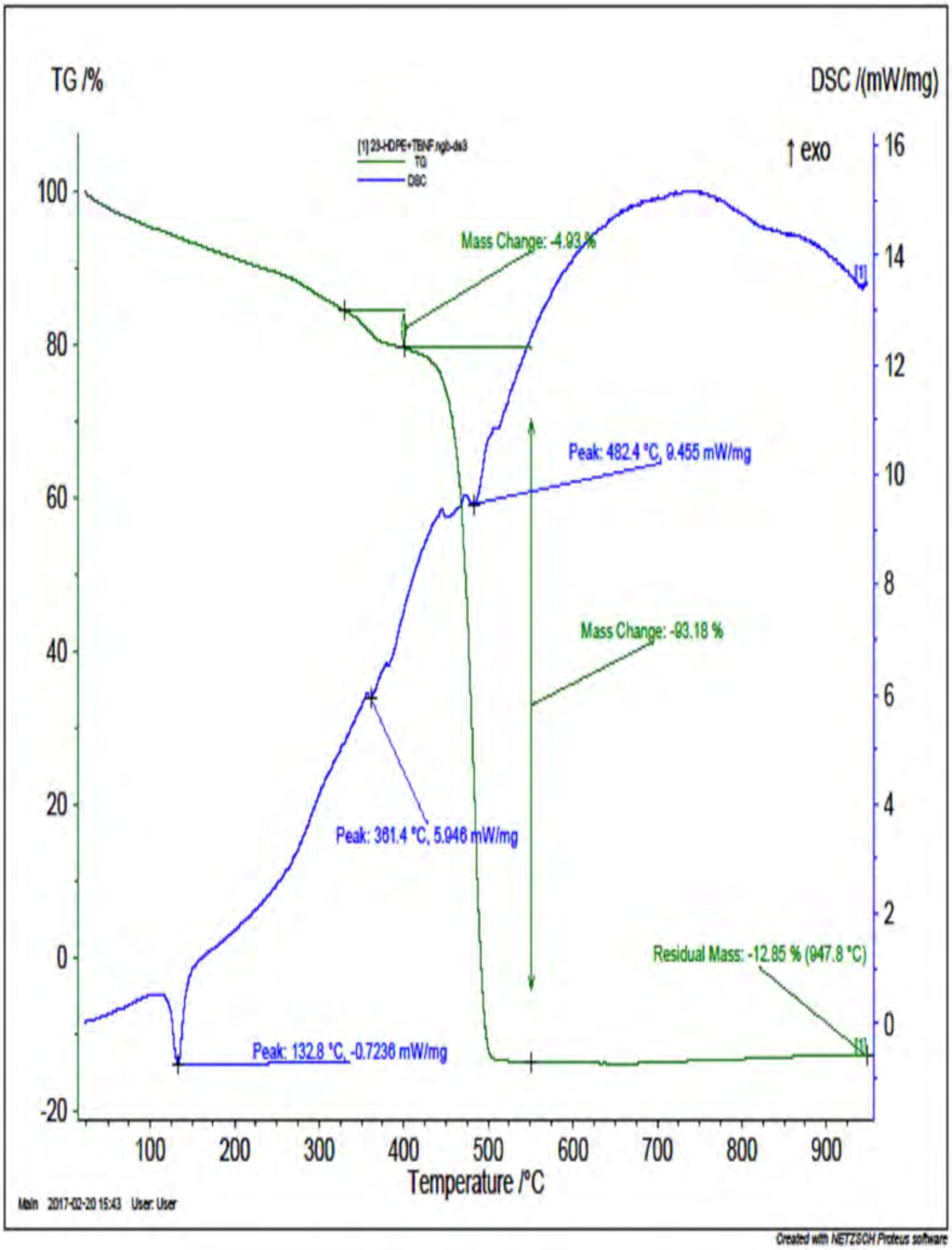


Figure 3.12: TGA &DSC curve of treated BNHF and HDPE composite.

3.4.6 Water absorption of Treated and untreated BNHF- HDPE composite

Water absorption test results of all treated and untreated betel nut husk fiber-HDPE composites are shown in Figure 3.13. 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-HDPE composites is higher than that of treated betel nut husk fiber-HDPE 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-HDPE composites than untreated betel nut husk fiber-HDPE composites.

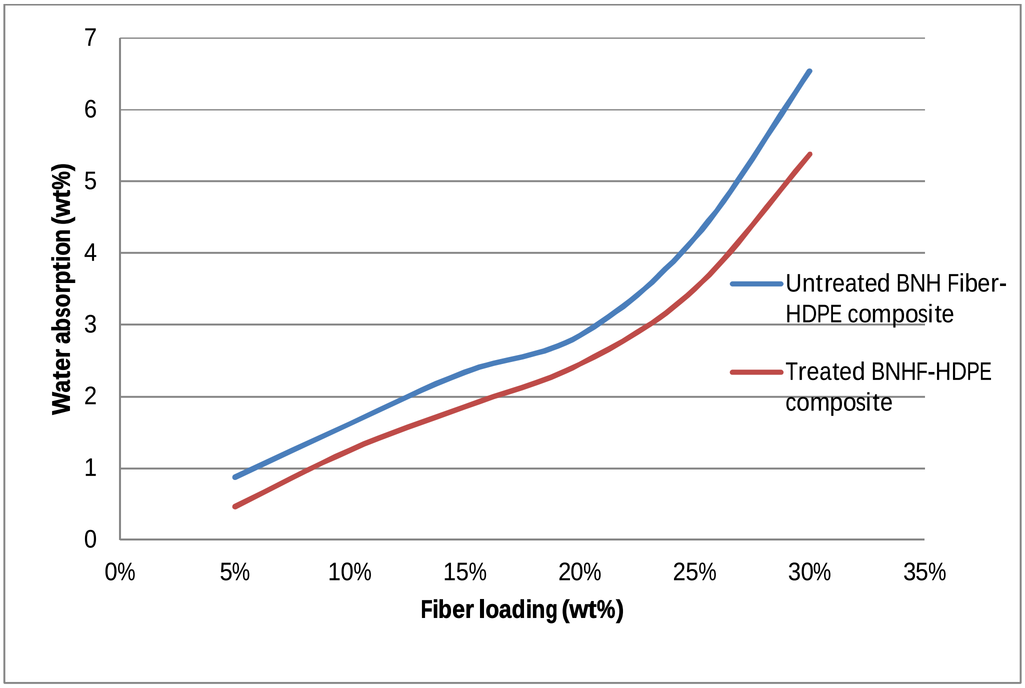


Figure 3.13: Water absorption of untreated and treated BNHF-HDPE composites

3.4.7 Biodegradability of Composites

The soil biodegradation tests of all prepared composites were carried out and the results are given in figure 3.14. The soil degradation of treated and untreated betel nut husk fiber reinforced composites was very low. Biodegradability increased with increasing fiber loading. The treated fiber was poorly degradable then untreated fiber.

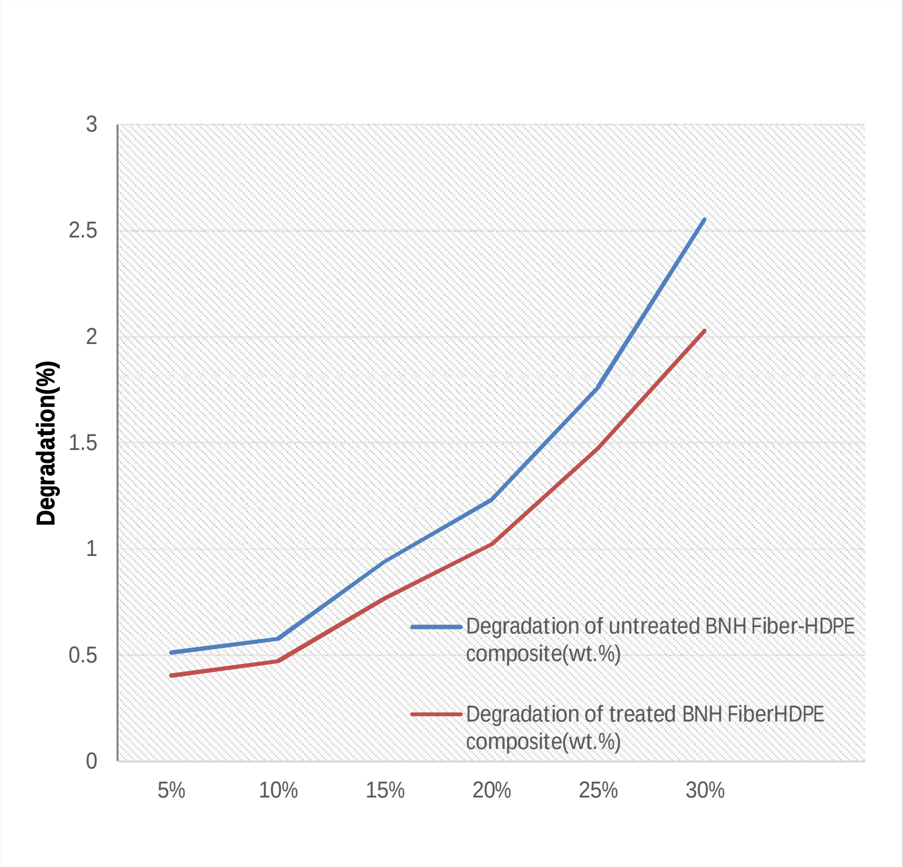


Figure 3.14 Biodegradation of untreated and treated BNHF-HDPE composites

3.5 Conclusion

The extraction and characterization of betel nut husk fibers were done and used as a reinforcing material with HDPE matrix at different wt. percentages. Chemical treatment of extracted fibers with sodium *meta* periodate showed improved mechanical properties for the treated BNHF-HDPE composites comparing with the untreated BNHF-HDPE composites. FTIR spectra and SEM analyses of fibers also evidenced the occurrence of chemical modification in treated BNHF. The mechanical properties of the composites showed that the treated BNHF-HDPE composites had significant improvement at 10 wt% treated BNHF loading. SEM micrographs also revealed the evidence of improved mechanical properties for treated BNHF-HDPE composites than untreated BNHF-HDPE composites. No significant changes have been found from thermal properties of treated and untreated BNHF-HDPE composites. Thermal stability of pure HDPE was slightly higher than that of treated and untreated BNHF-HDPE composites.

CHAPTER- 4

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED POLYPROPYLENE COMPOSITE

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED POLYPROPYLENE COMPOSITE

4.1 Introduction

Natural fibers from renewable resources are gaining interest to be used as reinforcement in polymer composites to provide benefits to the environment with respect to the degradability and utilization of renewable materials [99]. Natural fiber such as flax, hemp, jute coir etc. based polymer composites form a new class of materials which have good potential to be used in polymer composites in many applications. The attractive features of these fibers are light weight, high specific modulus, non-toxicity, friendly processing and absorbed CO_2 during their growth [100,101]. These benchmark properties open the wide area for natural fibers to be used in composite sector with consequences for the partial replacement of traditional synthetic fibers. However, these green sources of fibers are not problems free. Their structural compositions (such as cellulose, hemicelluloses, lignin, pectin and waxy substances) allow moisture absorption from the environment which leads to poor bonding with the matrix materials [102]. Certain chemical treatment on natural fibers is needed to enhance the performance as reinforcement in polymer composite materials. The chemical modification directly influences the fibers structures and changes their compositions. As a result, moisture absorption tendency by the fiber is reduced facilitating better bonding with the matrix materials. This provides better mechanical and thermal properties of fiber and composites [100]. Environmental 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 [101-104]. 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 [105]. 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, pineapple, banana and oil palm empty fruit bunch fibers have been shown that ligno-cellulosic fibers have the potential to be an effective reinforcement in thermoplastics and thermosetting materials [106]. 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 [107]. 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 [108-110]. 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 [111]. 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, hemi cellulose 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 [112].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 [113].

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.

4.2 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 Poly propylene from advance chemicals, Saudi Arabia was used as polymer matrix.

Experimental

4.3.1 Treatment of betel nut fiber with hydrogen peroxide

The oven dried raw betel nut fibers were cut into 1mm 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^{o}C temperature and pH 9.00. These reaction parameters were optimized by following FTIR analyses. The reaction mixture was stirred by glass rod occasionally. After competition 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^{o}C for constant weight. These oxidized fibers were used for composite fabrication.

4.3.2 Fabrication of BNHF reinforced polypropylene polymer composites

Before fabrication of composites treated and untreated betel nut husk fibers were dried in an oven at 80^{o}C for 24 hours. Polypropylene was granulated in a grinder and dried at 80^{o}C for 3 hours. The PP and BNHF were dry-blended in a blender for one minute. These mixtures were then moulded in a compression moulding machine (Paul-Otto Weber Press Machine) at a molding temperature of 180^{o}C. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table 4.1. 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, impact and water absorption properties.

Table 4.1: Different weight fraction of betel nut fiber reinforced polypropylene composites

Sample Number	Reinforcing material (wt%)	Polymer matrix (wt%)	Composites
No. 22	BNHF : 05	Polypropylene : 95	05:95 (wt %) BNHF: PP
No. 23	BNHF : 10	Polypropylene : 90	10:90 (wt %) BNHF: PP
No. 24	BNHF : 15	Polypropylene: 85	15:90 (wt %) BNHF: PP
No. 25	BNHF : 20	Polypropylene : 80	20:85 (wt %) BNHF: PP
No. 26	BNHF : 25	Polypropylene: 75	25:75 (wt %) BNHF: PP
No. 27	BNHF :30	Polypropylene : 70	30:70 (wt %) BNHF: PP
No. 14	BNHF : 00	Polypropylene:100	100 (wt %) Polypropylene(PP)
No. 15	Treated BNHF : 05	Polypropylene : 95	05:95 (wt %) treated BNHF: PP
No. 16	Treated BNHF : 10	Polypropylene : 90	10:90 (wt %) treated BNHF: PP
No. 17	Treated BNHF : 15	Polypropylene : 85	15:90 (wt %) treated BNHF: PP
No. 18	Treated BNHF : 20	Polypropylene : 80	20:85 (wt %) treated BNHF: PP
No. 19	Treated BNHF : 25	Polypropylene : 75	25:75 (wt %) treated BNHF: PP
No. 20	Treated BNHF: 30	Polypropylene: 70	30:70 (wt %) treated BNHF: PP

4.3.3 Characterization of BNHF reinforced polypropylene composites

The untreated and treated Betel nut husk fiber and their reinforced polypropylene composite materials were characterized by FT-IR Spectroscopy and scanning Electron Microscopy as stated below.

4.3.3.1 FTIR spectroscopy

FTIR spectrums were taken for untreated and H_2O_2 treated polypropylene 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 100 mg 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, Perkin Elmer, USA) in 4000-700 cm^{-1} wavelength range. IR spectra were obtained in the printed form.

4.3.3.2 Scanning electron microscopy (SEM)

The surface of BNHF, treated BNHF and fracture surface of tensile test of treated and treated BNHF-PP composite 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 untreated BNHF, treated BNHF and the fracture surface of the BNHF-PP composites. The photographs are presented in the result and discussion section.

4.3.4 Mechanical properties of composites

Tensile test and impact test of all prepared BNHF-PP composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods. Specification and picture of the used machines, operating condition and dimension of test specimens are given below.

4.3.4.1 Tensile properties of the composites

The tensile test of all treated and untreated betel nut husk fiber reinforced PP polymer composites were measured 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 and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves was recorder by the instrument. The maximum load values were also recorded by the instrument which can be recalled after the completion of the test. The highest load in the tensile test gave the ultimate strength.

4.3.4.2 Impact test

The Izod impact test of all prepared BNHF-PP composite samples were performed according to Izod impact test methods include ASTM D256-02. QPI-IC-21J universal Charpy/ Izod Analog Impact tester machine from Qualitest, North America were used to perform Izod impact test for all samples. The width, thickness and length of the specimen are 64 mm, 12.7mm and 3.2 mm respectively. V-shaped notched specimens were used.

4.3.5 Thermal properties of composites

4.3.5.1 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis

The thermo gravimetric analysis and differential scanning calorimetric analysis of the 10 wt% of treated BNHF-LDPE composite , untreated BNHF-LDPE composite and 100% PP 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 min^{-1} in a nitrogen atmosphere. Ten mg of the sample was heated in the sample pan.

4.3.6 Water absorption test of composites

The water absorption behavior of the developed composites of hydrogen peroxide treated and untreated betel nut husk fiber-PP composites were carried out following ASTM D570-99 standard method. The dimension of each test specimens was 39 mm × 10mm × 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. (4.1). Three specimens were taken to calculate average results and presented in the results and discussion section.

$$W = \left(\frac{W_1 - W_0}{W_0}\right) \times 100 \tag{4.1}$$

Where, W_0 is the dry initial weight, W_1 is the weight after immersion in water.

4.3.7 Biodegradability of Composites

Biodegradability (BD) of composite was determined by measuring the weight loss of the specimens which are buried in soil. The test was done by using the gardening soil collected from local market. The selected each specimen was buried in the aforesaid soil and incubated at room temperature (25–30 °C). At two days intervals, water was poured so that the soil was kept in humid condition. After burial of particular time the specimens were exposed from the soil, where the burial duration was 90 days. Thereafter, the specimens were washed with water and dried at 40 °C in a vacuum oven up to a constant weight. Due to biodegradation the weight loss (%) was calculated according to the following formula (Eq.4. 2):

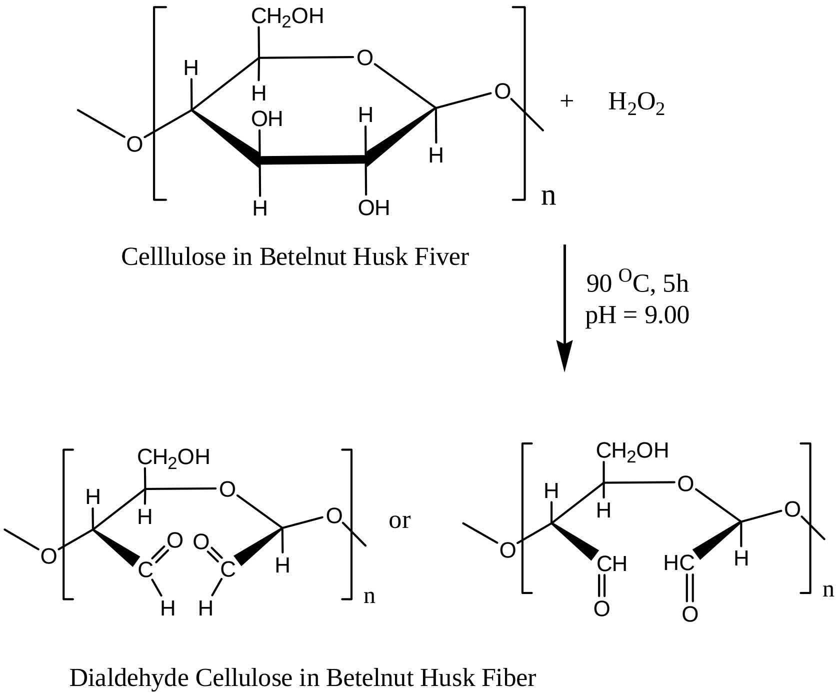
$$BD(\%) = \frac{(w_{bb} - w_{ab})}{w_{ab}} \times 100 \tag{4.2}$$

Where w_{bb} and w_{ab} are the dry weights of composites before and after the burial, respectively.

4.4 Results and discussion

4.4.1 Surface modification of BNHF

Chemical treatment of BNHF with hydrogen peroxide was carried out and optimized the reaction parameters. The reaction of hydrogen peroxide with cellulose in BNHF at 90°C yielded the oxidized product 2,3-diaidehyde cellulose(BNHF).this reaction was conducted at pH 9. The oxidizing product is dependent on the pH of the reaction medium. In cellulose anhydro-glucose three hydroxyl group are present, one is primary hydroxyl group (at C_6) and other two are secondary hydroxyl group(at C_2 and C_3 group)Though primary alcohols are more reactive then secondary alcohol but hydrogen peroxide break the anhydro-glucose ring between carbon atom C2 and C3 and convert the two secondary hydroxyl groups to aldehyde groups. It was presented in the scheme 4.1.



Scheme-4.1: Oxidation reaction of cellulose in BNHF with hydrogen peroxide

4.4.2 FTIR analysis of hydrogen peroxide treated BNHF

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 4.1 and figure 4.2 respectively. The FT-IR spectrum of BNHF-PP composites are shown in figure 4.3. The reaction of hydrogen peroxide with cellulose in BNHF at 90^0C yielded the oxidized product dialdehyde-cellulose in BNHF. In both figure 4.1 and 4.2, the broad peak at 3393 cm^{-1} which appears in both spectra is attributed to O-H frequency. The FTIR spectra of treated fiber (fig-4.2) clearly shows the characteristic bands of aldehyde group at the region of 2919cm^{-1} and 2849 cm^{-1}due to C-H stretching. Another sharp peak at 1645.61cm^{-1}due to C=O stretching of aldehyde group in treated BNHF. In figure 4.1, a sharp peak at 1738.37cm^{-1} is due to C=O stretching vibration of carboxylic acid and ester component of hemicelluloses in untreated BNHF. In treated BNHF the peak 1738.37cm^{-1} is corresponding to C=O stretching vibration of hemicelluloses disappeared due to the removal of lignin and hemicelluloses [114]. In figure 4.3 doublet absorptions at 2900-2880 cm^{-1} due to C-H vibration of - (CH_3) group of PP, absorption at 997, 890, 842, and 807 cm^{-1} are due to the crystalline phase of PP. Absorption at 978 cm^{-1} due to the amorphous phase of PP. In ATR-FTIR spectra of treated and untreated BNHF-PP composite absorption peak of fibers were dominated by PP matrix.

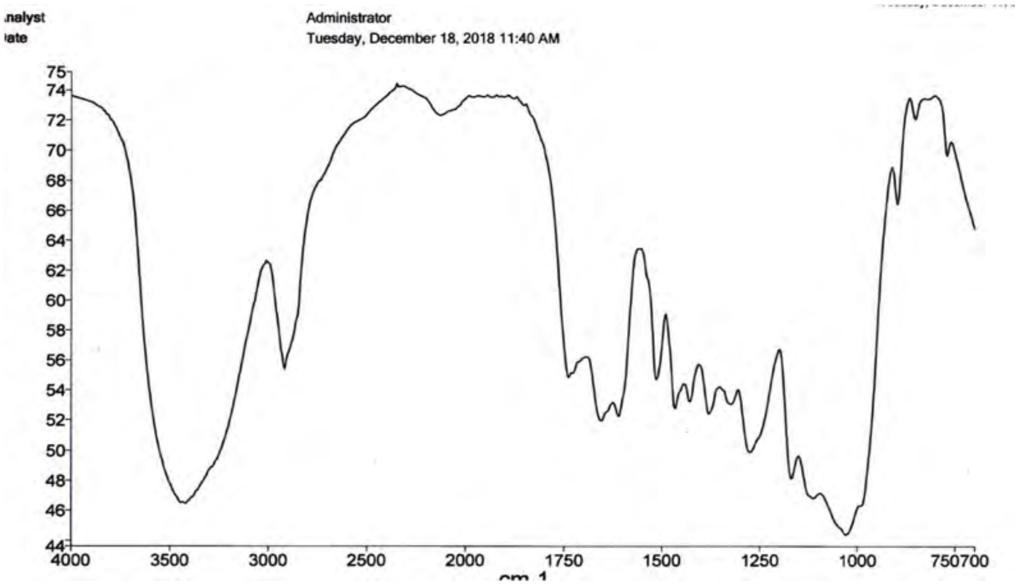


Figure 4.1: FTIR spectra of untreated BNHF

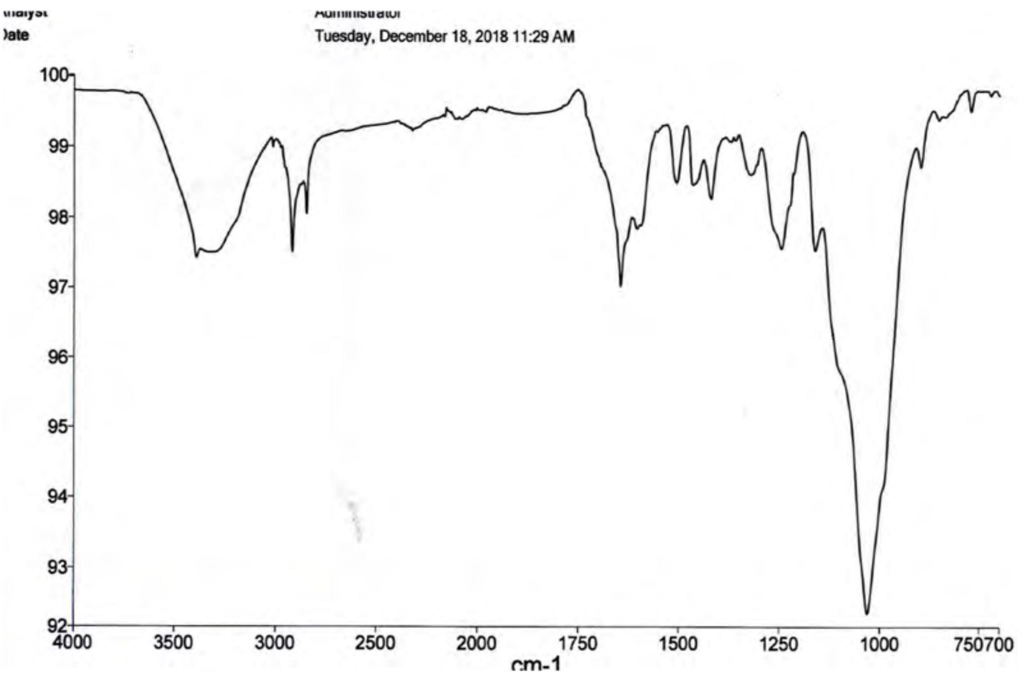


Figure 4.2 FTIR spectra of hydrogen peroxide treated BNHF

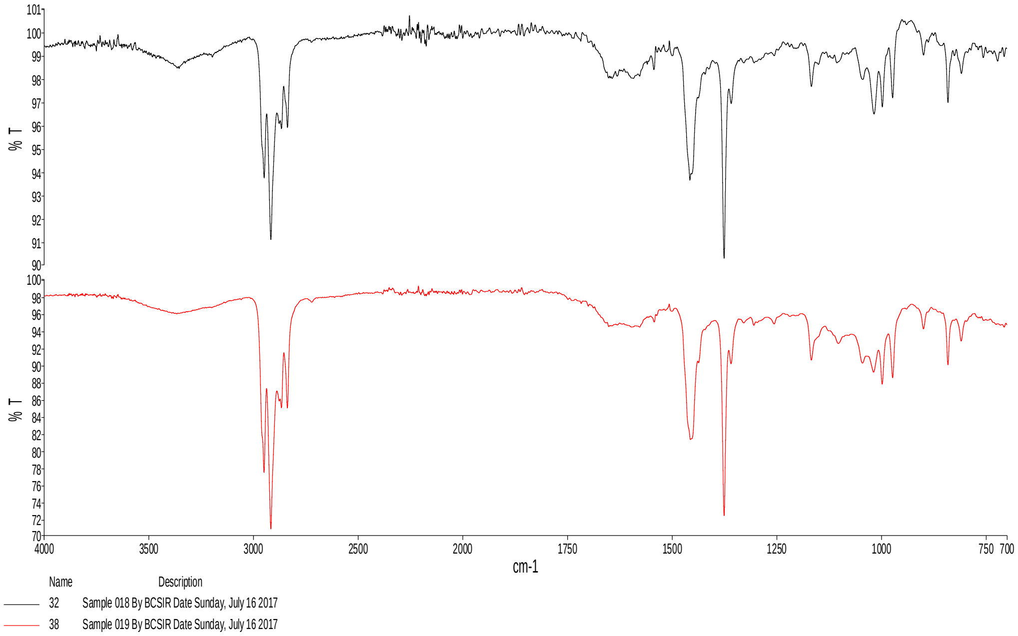


Figure 4.3: ATR-FTIR spectra of untreated BNHF- PP composite (upper) and treated BNHF- PP composite (lower)

4.4.3 Scanning electron microscopic (SEM) investigation of BNHF-PP composites

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 composites and treated BNHF-PP composites are examined using a field emission scanning electron microscope. From the analysis of SEM image of untreated and treated BNHF-PP composites (Figure-4.4, 4.5) it is found that treated BNHF is more fibrous then untreated BNHF. SEM image of treated BNHF-PP composite indicate 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.

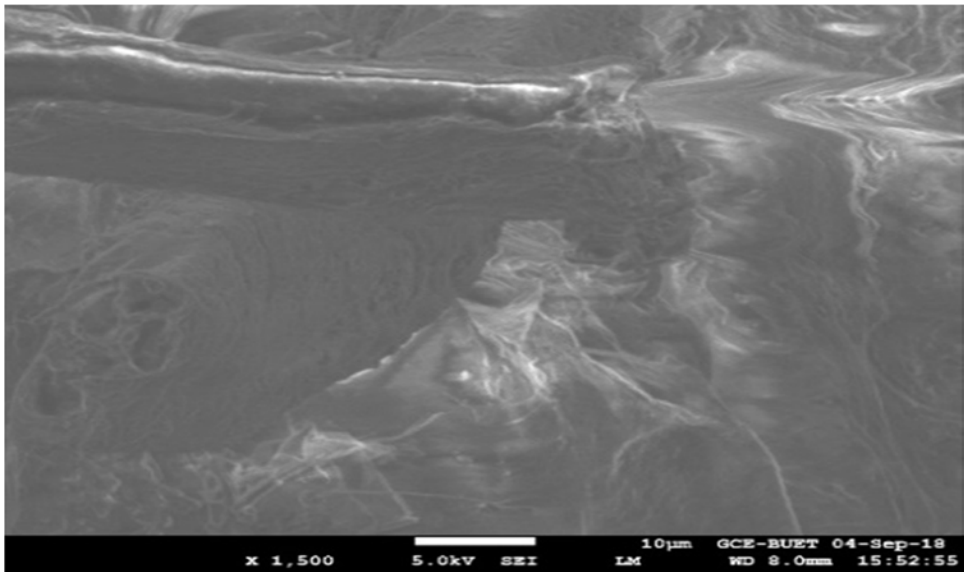


Figure-4.4 SEM image of untreated BNHF -PP composite

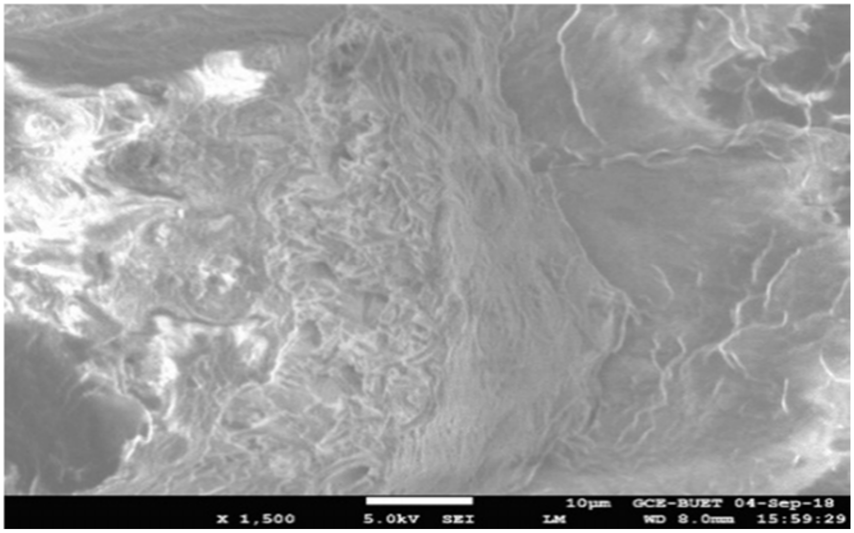


Figure-4.5 SEM image of treated BNHF-PP composite

4.4.4 Tensile strength and elongation at break of untreated and treated BNHF reinforced PP composites

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-4.6 and figure-4.7 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 [115]. The noticeable decrease of tensile strength of the composite was 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.

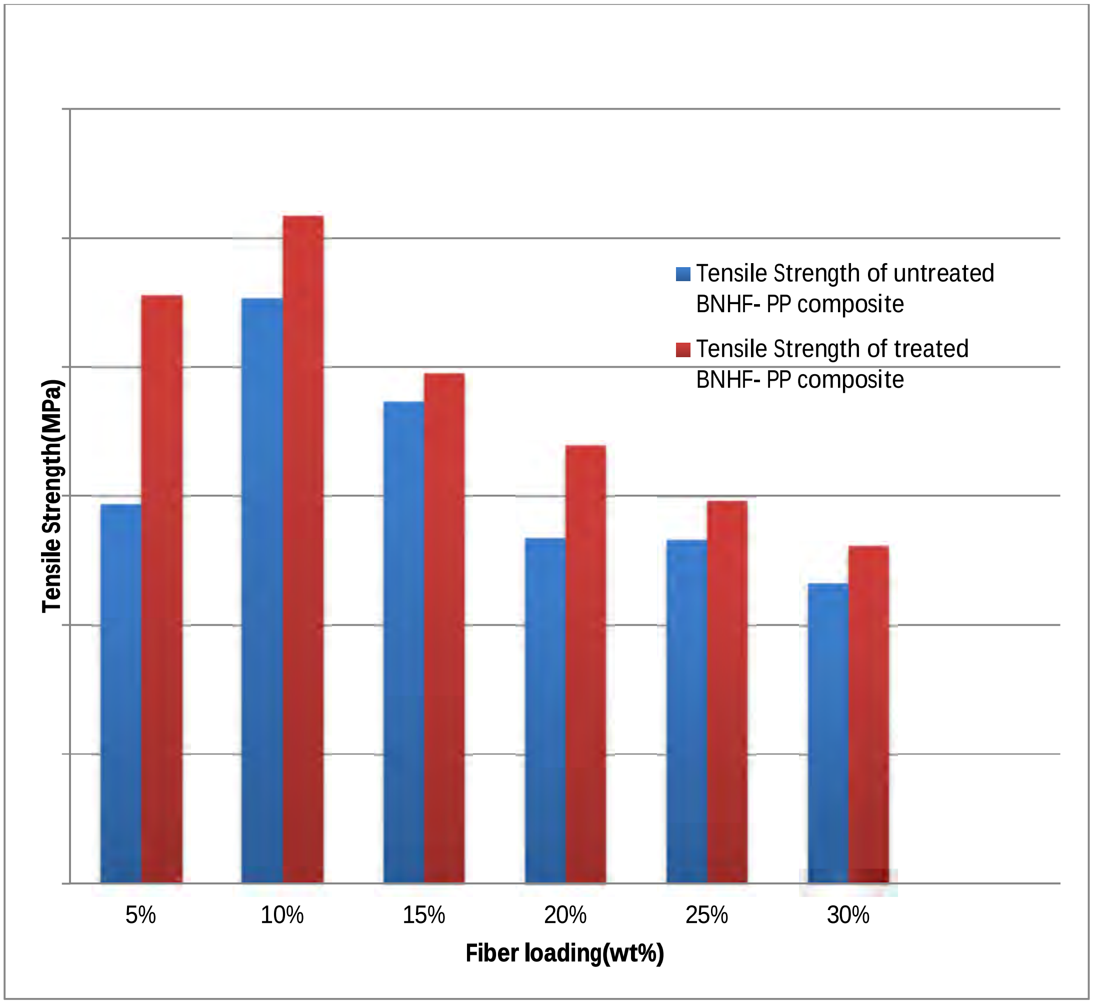


Figure 4.6: Tensile strength of different wt% of untreated and treated BNHF-PP composites.

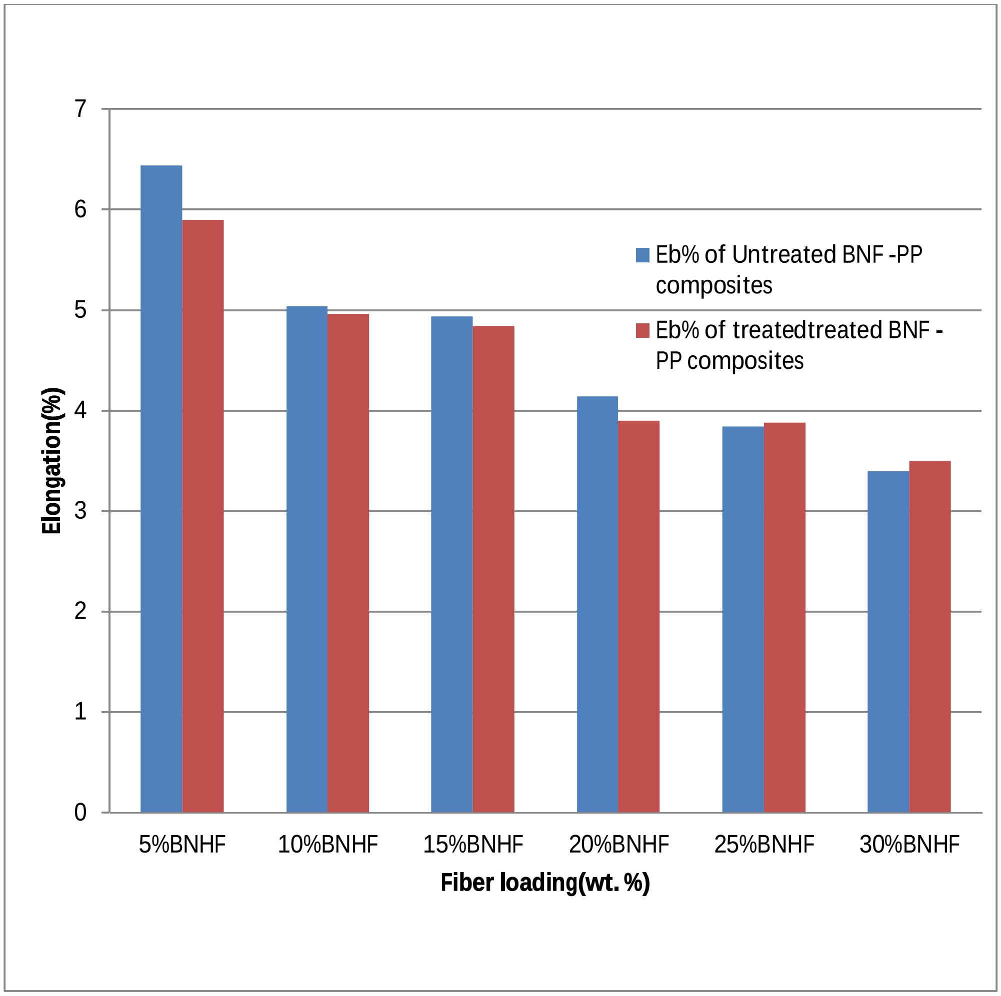


Figure 4.7: Elongation at break (%) vs. fiber loading (%) curve of untreated and treated BNHF- PP composites.

4.4.5 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analyses of BNHF- PP composite

Thermo-gravimetric analyses and differential scanning calorimetric analyses of the compression moulded PP, 10 wt% untreated BNHF-PP composites and treated BNHF-PP composites were recorded and presented in Figure-4.8, figure- 4.9 and figure-4.10 respectively. For compression moulded PP, degradation start at 456.7ºC and 99.98 % mass change was completed at 500ºC whereas the mass change started at 400ºC and 5.51% mass change was completed 434.6ºC and another degradation start at 457.7 ºC and 89.57% mass loss was done at 520ºC for treated BNHF-PP composite. The thermograph of untreated BNHF-PP composite showed that degradation of composite start at 358.3ºC and 4.27% mass change was done at 400ºC temperature, another degradation start at 461.8 ºC and 95.43% mass loss was completed at 500 ºC. DSC is used to identify melting temperature and amount of energy absorbed or release by materials. The melting temperature for PP composite found at 165.4 ºC, untreated BNHF-PP composite at 167 ºC and treated BNHF-PP composite at 168.1 ºC. 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.

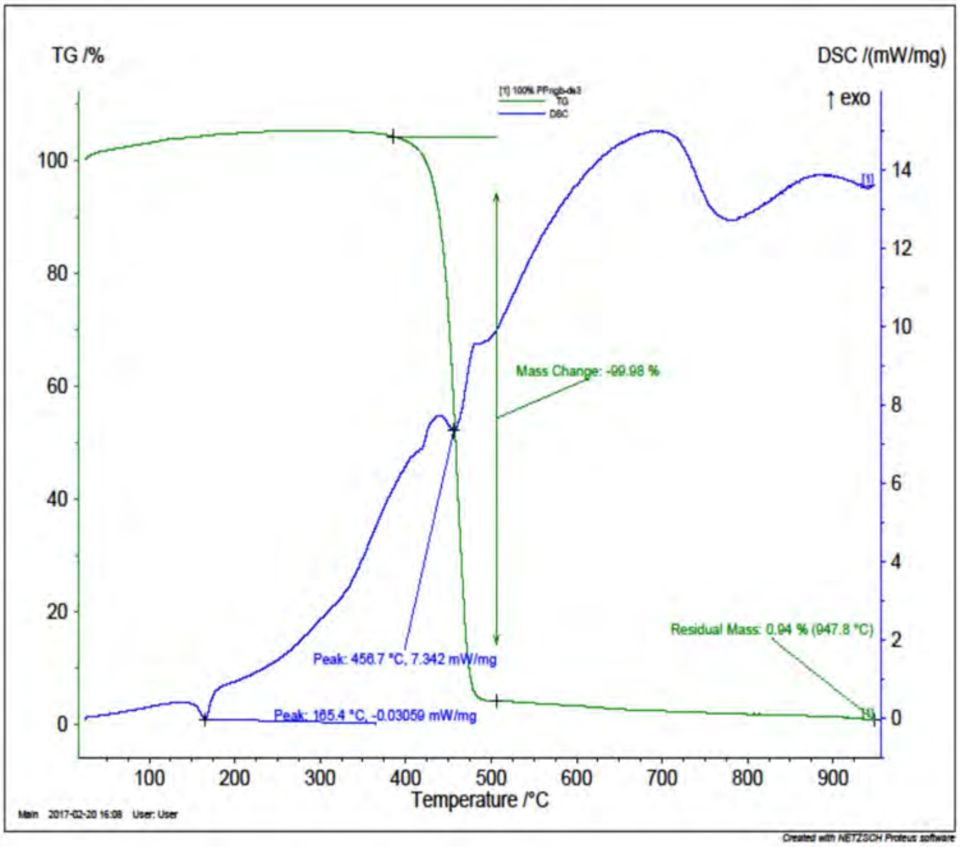


Figure 4.8: TGA and DSC curve of 100% PP

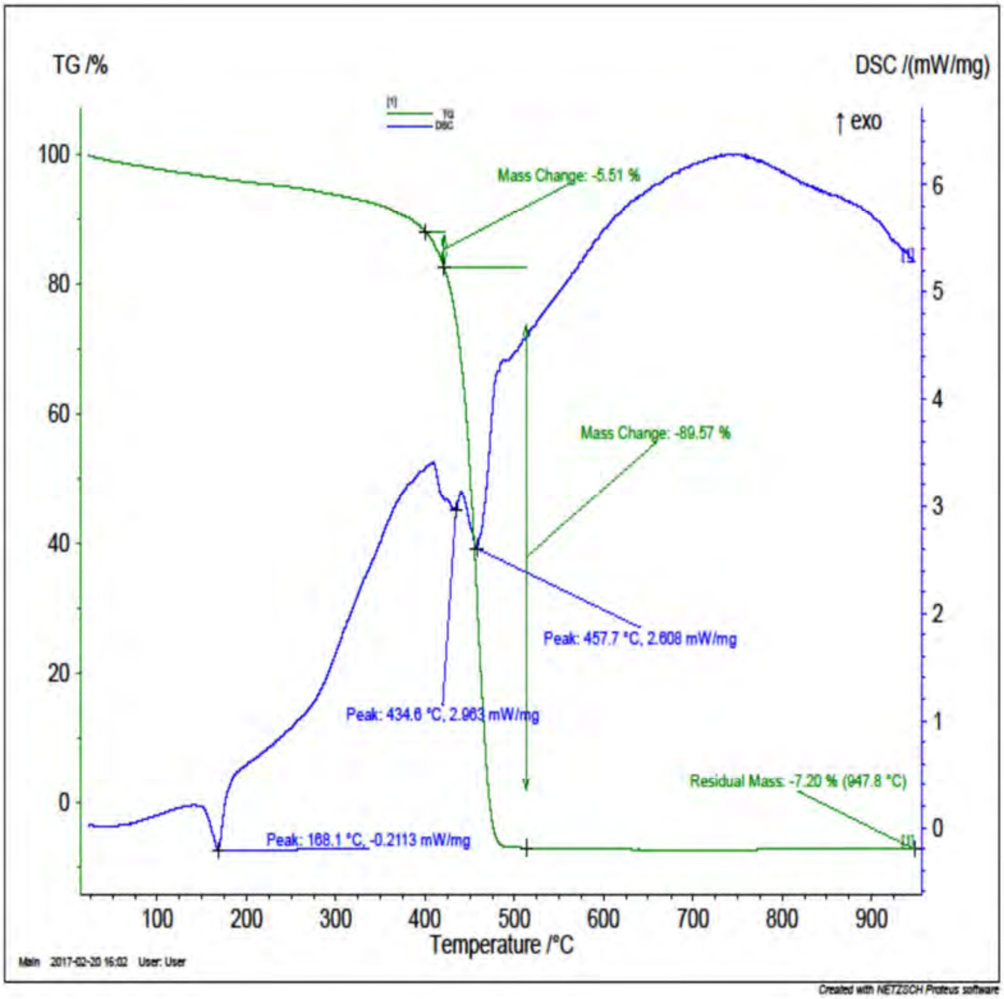


Figure4.9: TGA and DSC curve of treated BNHF- PP composite

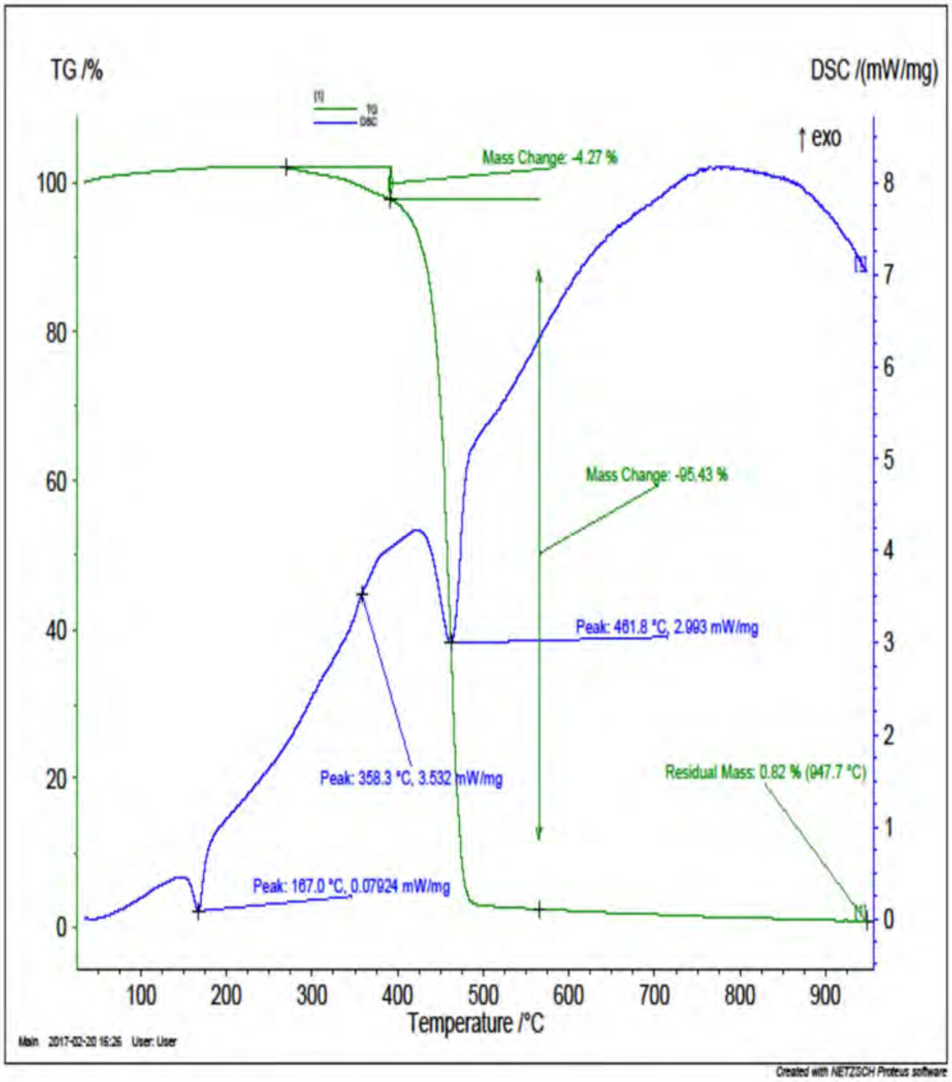


Figure 4.10: TGA and DSC curve of untreated BNHF-PP composite

4.4.6 Izod Impact Strength

The results of Impact strength of treated and untreated BNHF-PP were recorded and presented in figure 4.11. It is clearly depicts the decrease in the impact strength as we increase in the fiber loading (wt %) in BNHF-PP composites. All treated BNHF-PP composites showed higher impact strength than the untreated BNHF- PP composite. Fiber modifications increase the impact strength of BNHF-PP composites.

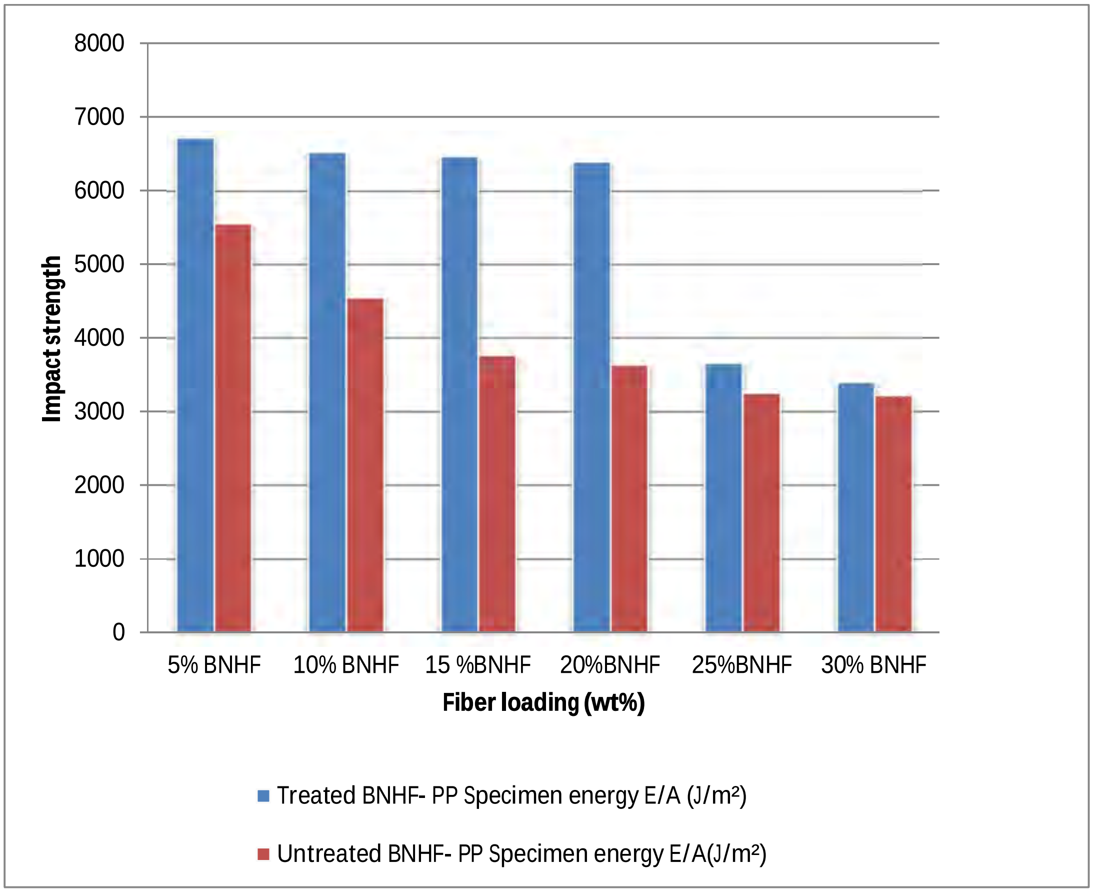


Figure 4.11: Impact strength Vs fiber loading (wt %) of Treated BNHF-PP and Untreated BNHF-PP composite

4.4.7 Water absorption of Treated and untreated BNHF- PP composite

Water absorption test results of all treated and untreated betel nut husk fiber-PP composites are shown in Figure 4.12. 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.

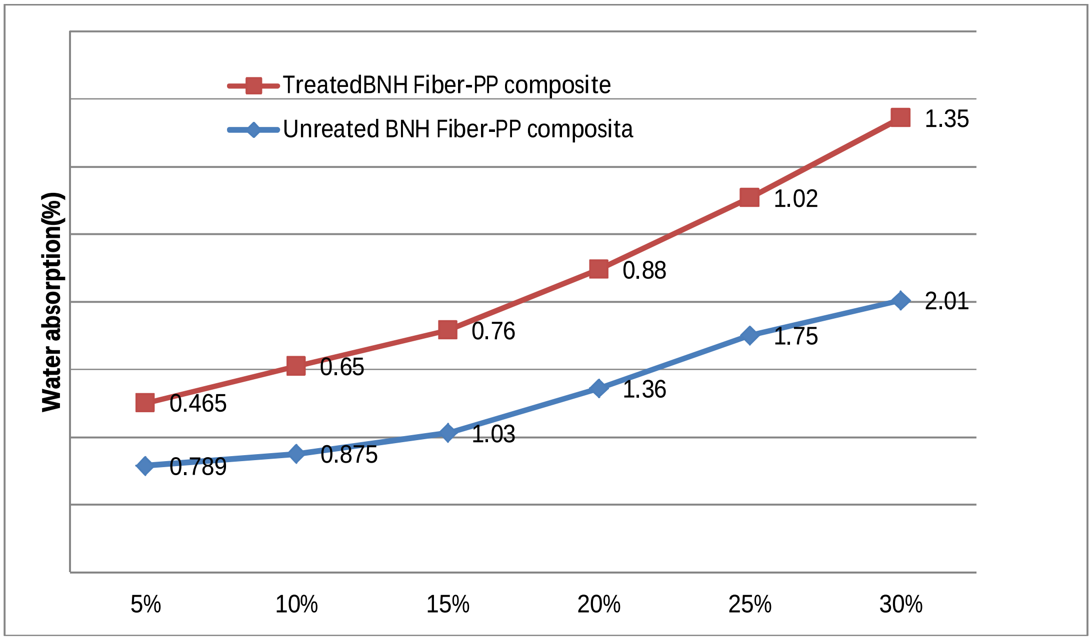


Figure 4.12: Water absorption (%) Vs fiber loading (wt %) curve of Treated and Untreated BNHF-PP Composites

4.4.8 Biodegradation of Treated and untreated BNHF- PP composite

The biodegradation properties of treated and untreated BNHF-PP composites were studied in garden soil at an average spring temperature of (25–30 °C). Figure 4.13 showed the soil degradation behavior of the treated and untreated BNHF-PP composite. The degradation of pure pp is almost zero and treated BNHF-PP composites are less degradable then untreated BNHF-PP composites.

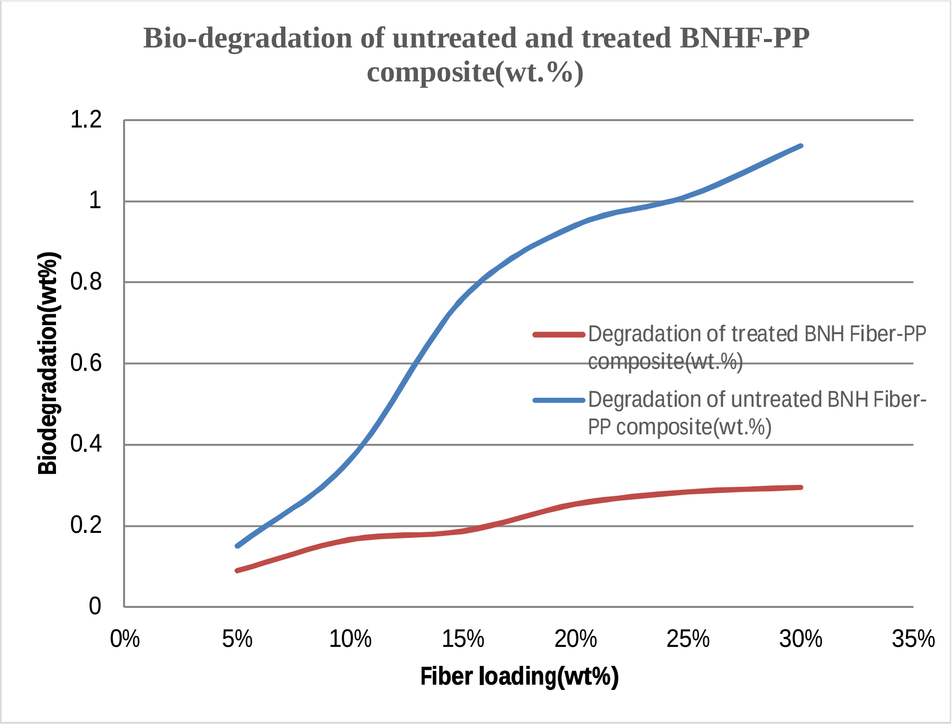


Figure 4.13: Biodegradation (%) Vs fiber loading (wt %) of treated and untreated BNHF-PP composites

4.5 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. Water absorption test also exhibited less water absorption of treated BNHF-PP composites then untreated 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. Biodegradability test result showed that the treated BNHF-PP composites are less biodegradable then untreated BNHF-PP composites. 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.

CHAPTER 5

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED POLYSTYRENE COMPOSITE

PREPARATION OF BETEL NUT HUSK FIBER REINFORCED POLYSTYRENE COMPOSITE

5.1 Introduction

Basically, a composite is a unification of numerous components, as a whole which acts as a new material with the expected superior properties. Typically, composites are made up of two phases; these are a continuous phase or matrix and a discontinuous phase or reinforcement. The necessary condition to be a composite material is the bonding between the matrix and reinforcement, rather than it will be a structure. The site of this necessary bonding of composite material is the fiber-matrix interface, and often this site also considered as a distinct phase called the inter phase. The mechanical performances of a composite material are linked with the bonding strength of fiber-matrix interface, geometry and dissemination of the reinforcement, along with the properties of the discrete phases also. The improvement of mechanical performances of composites is done by the possible two ways; firstly, rising the act of material system capability and secondly, improving the properties of discrete phases. It is thought that the properties of fiber reinforced composites can be further improved if the matrix is modified by the addition of NPs [116].The reinforcing effect of betel nut husk fiber (BNHF) in polystyrene (PS) matrix was studied in this research work. Polystyrene is made from the aromatic monomer styrene and so polystyrene is an aromatic polymer. Both polypropylene and polystyrene are similar in applications except some specific applications of them. With this aim betel nut husk fibers were chemically modified with sodium hypochlorite. Treated and untreated BNHF were used for composite fabrication as reinforcing material with polystyrene in different weight fraction of fiber loading. The composites were characterized by FT-IR and SEM analysis and their physico-mechanical and thermal properties were analyzed by tensile test, TGA and DSC analysis.

5.2.1 Matrix polymer:

General purpose polystyrene (PS) from Supreme (SPL) was used as polymer matrix.

5.2.2 Reinforcing material

Matured betel nut fruit were collected from local betel nut plantation field, Barisal, Bangladesh. From the fibrous part of the fruit betel nut husk fibers were extracted. These extracted fibers are used as reinforcing material.

5.3 Experimental

5.3.1 Chemical Treatment of betel nut fiber with Sodium hypochlorite

The washed oven dried raw betel nut fibers were cut in 1mm to 3 mm length. Sodium hypochlorite solution (0.1 N) was prepared in distilled water. The pH of the solution was adjusted to 5 by adding dilute sulfuric acid drop wise. The dried fibers were then immerged in this solution. The fiber to liquor ratio was 1:30 (w/v). The reaction was carried out for 5 hours at 70°C temperature and pH 5.00. The reaction mixture was stirred by glass rod occasionally. After complete the reaction, the mixture was cooled, then filtered to isolate the 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. This oxidize fibers were used for composite fabrication with polystyrene.

5.3.2 Fabrication of BNHF reinforced Polystyrene (PS) polymer Composites

Treated and untreated betel nut husk fibers were dried in an oven at 105^{o}C for 24 hours. Polystyrene was granulated in a grinder and dried at 80^{o}C for 3 hours. The PS and BNHF were dry-blended in a blender for one minute. These mixers were then moulded in a compression moulding machine at a molding temperature of 190^{0}C. 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. The composition ratio of composites is shown in the table 5.1. Finally, the compression moulded composites were cut to make specimens of suitable dimension to measure tensile and water absorption properties.

Table 5.1: Different weight fraction of betel nut fiber reinforced Polystyrene (PS) composites.

Sample Number	Reinforcing material (wt%)	Polymer matrix (wt%)	Composites
No. 22	BNHF : 05	Polystyrene : 95	05:95 (wt %) BNHF: PS
No. 23	BNHF : 10	Polystyrene : 90	10:90 (wt %) BNHF: PS
No. 24	BNHF : 15	Polystyrene : 85	15:90 (wt %) BNHF: PS
No. 25	BNHF : 20	Polystyrene: 80	20:85 (wt %) BNHF: PS
No. 26	BNHF : 25	Polystyrene: 75	25:75 (wt %) BNHF: PS
No. 27	BNHF :30	Polystyrene : 70	30:70 (wt %) BNHF: PS
No. 14	BNHF : 00	Polystyrene 100	100 (wt %) Polystyrene (PS)
No. 15	Treated BNHF : 05	Polystyrene : 95	05:95 (wt %) treated BNHF: PS
No. 16	Treated BNHF : 10	Polystyrene : 90	10:90 (wt %) treated BNHF: PS
No. 17	Treated BNHF : 15	Polystyrene : 85	15:90 (wt %) treated BNHF: PS
No. 18	Treated BNHF : 20	P Polystyrene : 80	20:85 (wt %) treated BNHF: PS
No. 19	Treated BNHF : 25	Polystyrene	25:75 (wt %) treated BNHF: PS
No. 20	Treated BNHF :30	Polystyrene: 70	30:70 (wt %) treated BNHF: PS

Figure 5.1: Image of BNHF-PS composite

5.3.3 Characterization of BNHF reinforced polystyrene composites

The untreated and treated betel nut husk fiber and their reinforced PS composite materials were characterized by FT-IR Spectroscopy and Scanning Electron Microscopy (SEM) as stated below.

5.3.3.1 FTIR spectroscopy

FTIR spectrums were taken for untreated and sodium hypochlorite treated BNHF samples. The treated and untreated betel nut husk fibers were used to make pellet with potassium bromide to take FT-IR. Approximately 0.5 mg 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 (Frontier, PerkinElmer, USA) in 4000-700 cm^{-1} wavelength range. IR spectra were obtained in the printed form.

5.3.3.2 Scanning electron microscopy (SEM)

The surface of BNHF, sodium hypochlorite treated BNHF and fracture surface of tensile test sample of 10 wt% of treated and untreated BNHF-PS composite 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 untreated BNHF, treated BNHF and the fracture surface of the BNHF-PS composites. The photographs are presented in the result and discussion section.

5.3.4 Mechanical properties of composites

Tensile test and Impact test of all prepared BNHF-PS composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods. Specification and picture of the used machines, operating condition and dimension of test specimens are given below.

5.3.4.1 Tensile properties of the composites

The tensile test of all treated and untreated betel nut husk fiber reinforced PS polymer composites were measured 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 cross head speed of the test was 10 mm /min and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves were obtained by the instrument in printed form. The maximum load values were also recorded by the instrument which could be recalled after the completion of the test. The highest load in the tensile test gave the ultimate strength.

5.3.5 Thermal properties of composites

5.3.5.1 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis

The thermo gravimetric analysis and differential scanning calorimetric analysis of the 10 wt.% of treated, untreated BNHF-PS composites and100% PS 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 min^{-1} in a nitrogen atmosphere. Ten mg of the sample has heated in the sample pan.

5.3.6 Water absorption test of composite

The water absorption behavior of sodium hypochlorite treated and untreated betel nut husk fiber-PS composites were carried out following ASTM D570-99 standard method. The dimension of each test specimens was 39 mm×10 mm×4 mm. 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 80°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. (5.1). Three specimens were taken to calculate average results and presented in the results and discussion section.

$$W = \left(\frac{W_1 - W_0}{W_0}\right) \times 100 \tag{5.1}$$

Where, W_0 is the dry initial weight, W_1 is the weight after immersion in water.

5.3.7 Biodegradability of Composites

Biodegradability (BD) of composite was determined by measuring the weight loss of the specimens which are buried in soil. The test was done by using the gardening soil collected from local market. The selected each specimen was buried in the aforesaid soil at an average spring temperature of (25–30 °C). At two days intervals, water was poured so that the soil was kept in humid condition. After burial of particular time the specimens were exposed from the soil, where the burial duration was 90 days. Thereafter, the specimens were washed with water and dried at 40 °C in a vacuum oven up to a constant weight. Due to biodegradation the weight loss (%) is calculated according to the following formula (Eq. 5.2):

$$BD(\%) = \frac{(W_{bb} - W_{ab})}{W_{ab}} \times 100 \tag{5.2}$$

Where W and W_{ab} are the dry weights of composites before and after the burial, respectively.

5.4 Results and discussions

5.4.1 Reaction of cellulose in BNHF with sodium hypochlorite

The presence of hydrophilic hydroxyl groups on the fiber surface occur several problem for reinforcement. This hydrophilic nature hinders effective reaction with the matrix. In addition to this, pectin and waxy substance covers the reactive functional groups of the fiber and act as a barrier to interlocking with the matrix. The fiber surface needs to be modified with different chemical treatment, reactive additives and coupling agents to optimize effective interfacial bonding between fiber and matrix. Better mechanical and thermal properties of the composites can be achieved by chemical treatment. Chemical treatment of betel nut fiber was carried out with sodium hypochlorite at optimized parameters. The reaction of cellulose in betel nut fiber with the solution of sodium hypochlorite yielded the oxidized dialdehyde cellulose in BNHF. The primary hydroxyl group of cellulose oxidized to carboxyl group by the action of sodium hypo chloride**.** These oxidized BNHF increase the mechanical properties of composites as compared to untreated BNHF-PS composites.

5.4.2 FTIR analysis

FTIR spectroscopic analysis of sodium hypochlorite treated and untreated BNHF was done to characterize the fiber. The FT-IR spectra of untreated and sodium hypochlorite treated betel nut fiber has been shown in figure 5.2 .The peak assignments of the absorption band corresponding to various groups are summarized in table 5.2 and table 5.3. It is clear from the figures that the absorption band at 1738.09 cm^{-1}of untreated BNHF have disappeared completely in the treated BNHF. This indicates that the treatment of betel nut husk fibers had removed the impurities, hemicelluloses and part of lignin.

Table 5.2 FT-IR spectroscopic data of untreated BNHF fiber.

Position of bands (cm^{-1})	Peak assignments
~ 3335.09	-OH stretching from the cellulose, hemicellulose and lignin
~ 2938.64	C-H vibration in aromatic ring and alkanes
~1738.09	C=O stretching from the lignin and hemicelluloses
~ 1603.91	C=C stretching from aromatic in-plane
~ 1507.81	C=C stretching in aromatic skeletal ring due to lignin
~ 1425.48	C-C stretching from aromatic ring

Table 5.3 FT-IR spectroscopic data of sodium hypochlorite treated BNHF fiber.

Position of bands (cm^{-1})	Peak assignments
~ 3335.09	-OH stretching from the cellulose, hemicellulose and lignin
~ 2897.58	C-H vibration in aromatic ring and alkanes
~ 1604.24	C=C stretching from aromatic in-plane
~ 1508.72	C=C stretching in aromatic skeletal ring due to lignin
~ 1424.58	C-C stretching from aromatic ring

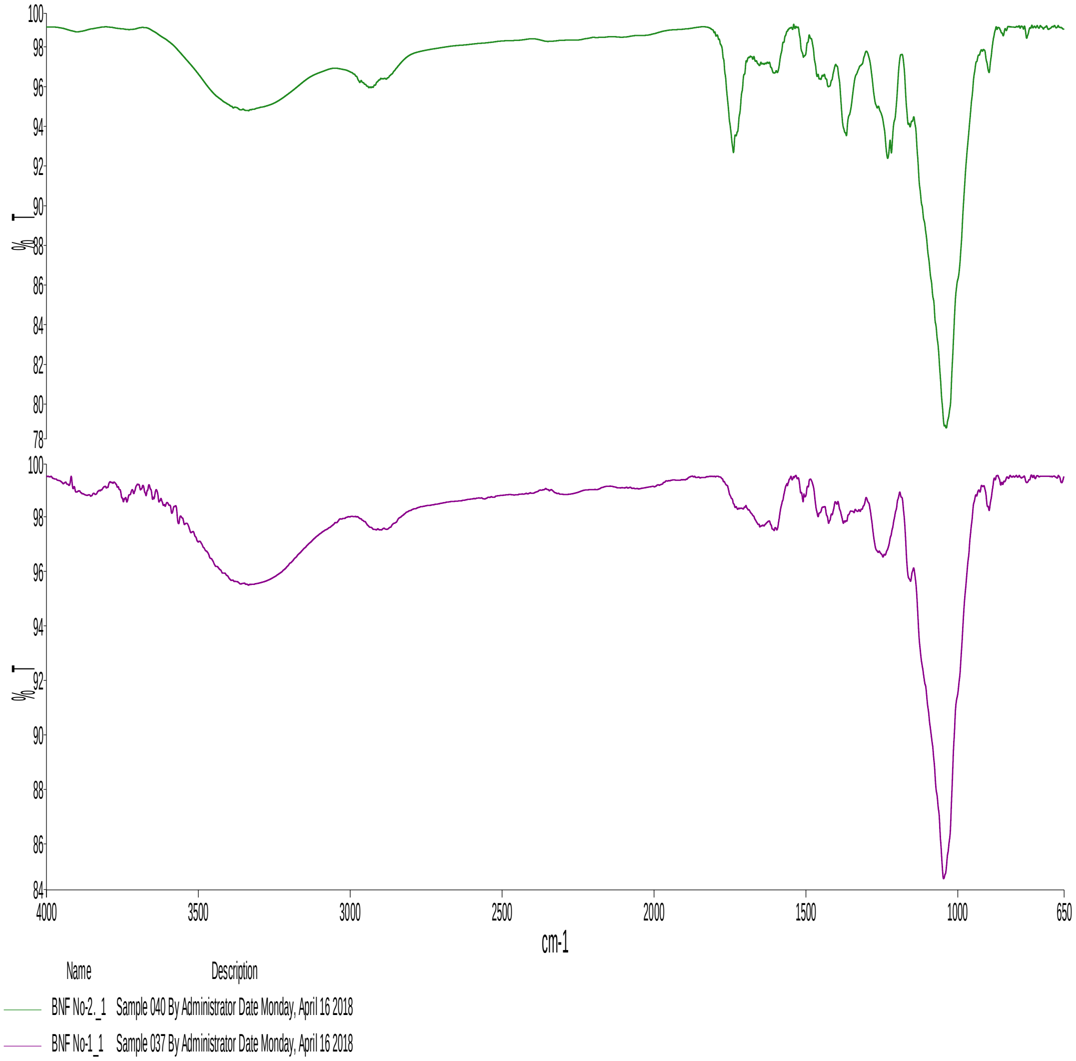


Figure 5.2 FT-IR spectrum of untreated (upper) and sodium hypochlorite treated betel nut husk fiber (lower).

5.4.3 Morphological characterization of treated and untreated BNHF reinforced PS composite:

To examine the surface morphology of prepared composite scanning electron microscopy (SEM) is an excellent technique. The SEM image of tensile specimen fracture surfaces are shown in Figure 5.3 and 5.4. The composite of sodium hypochlorite treated betel nut husk fiber reinforced polystyrene showed uniform dispersion of fiber into the polymer matrix and have good bonding characteristics (figure- 5.3) The fracture surface of the composite of untreated 10% BNHF fiber loaded PS composite shows numerous voids with fiber agglomeration (figure 5.4), these indicates the poor interfacial bonding between fiber and the polymer matrix. Figure 5.4 shows fiber pull out, deboning and fiber agglomeration which reduce the tensile strength of untreated BNHF-PS composite.

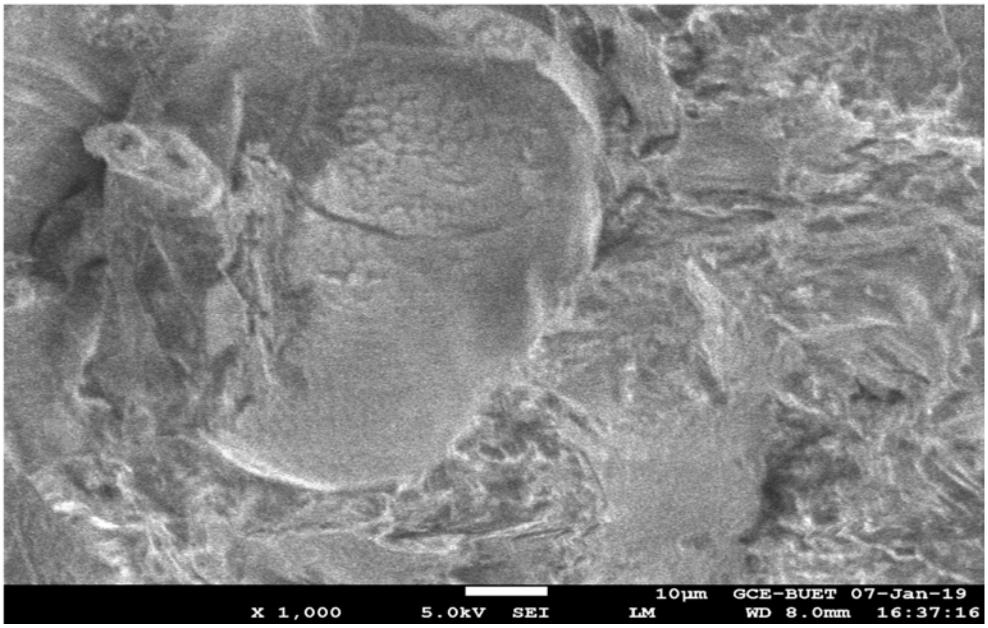


Figure 5.3: SEM Image of Treated BNHF-PS composite

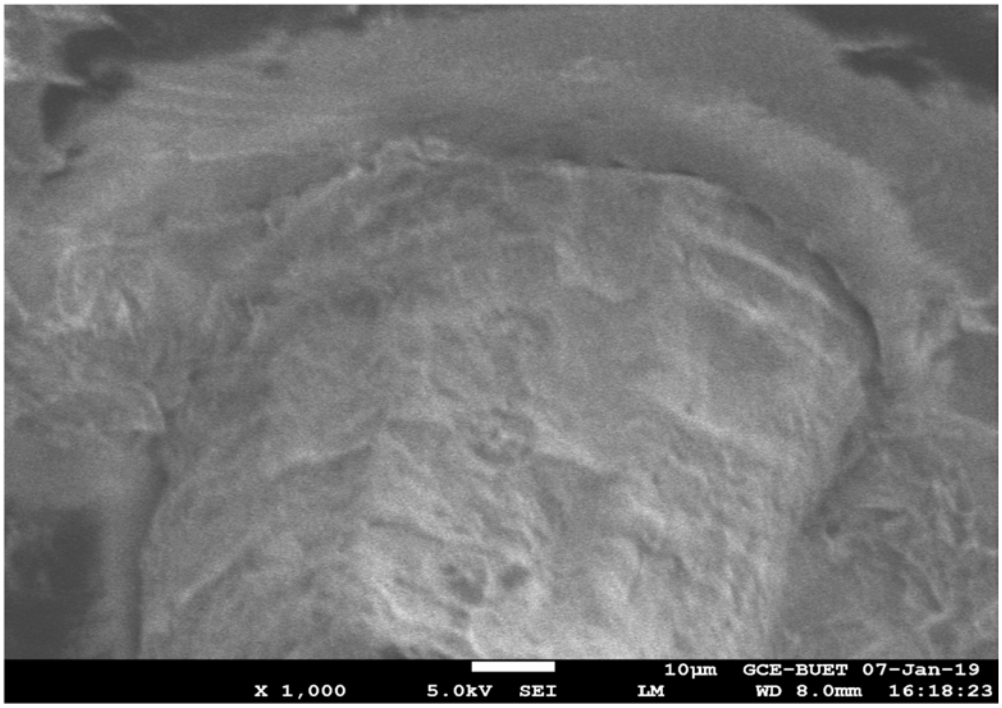


Figure 5.4: SEM Image of Untreated BNHF-PS composite

5.4.4 Tensile strength and elongation at break of untreated and treated BNHF reinforced PS composites

Figure-5.5 and figure-5.6 respectively shows 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. The tensile strength of untreated and treated BNHF reinforced PS 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. The noticeable decreases of tensile strength of the composite were observed as fiber loading increased from 15% to 30%. Tensile properties of all treated BNHF-PS composites were higher than that of untreated BNHF-PS composites. This may be due to the improvement of the fiber-matrix interfacial adhesion in composite made by chemical treatment. The decrease in the values of elongation at break with increasing the fiber loading wt. % was observed due to more brittle character of reinforced composites, especially for untreated BNHF-PS composites.

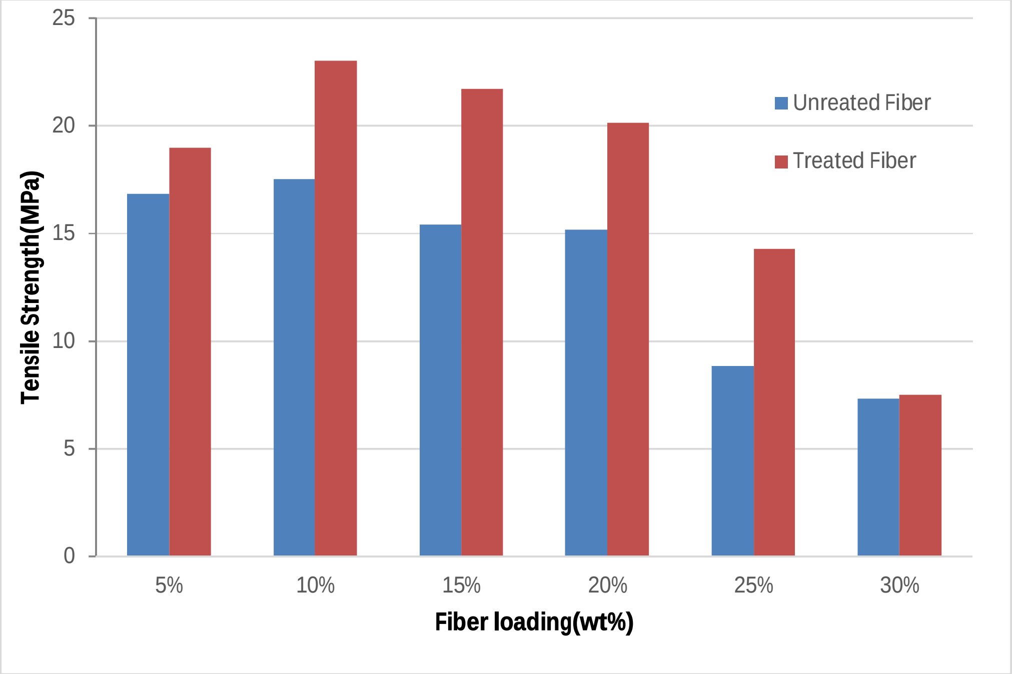


Figure 5.5: Tensile strength of untreated BNHF-PS and NaOCl treated BNHF-PS composites

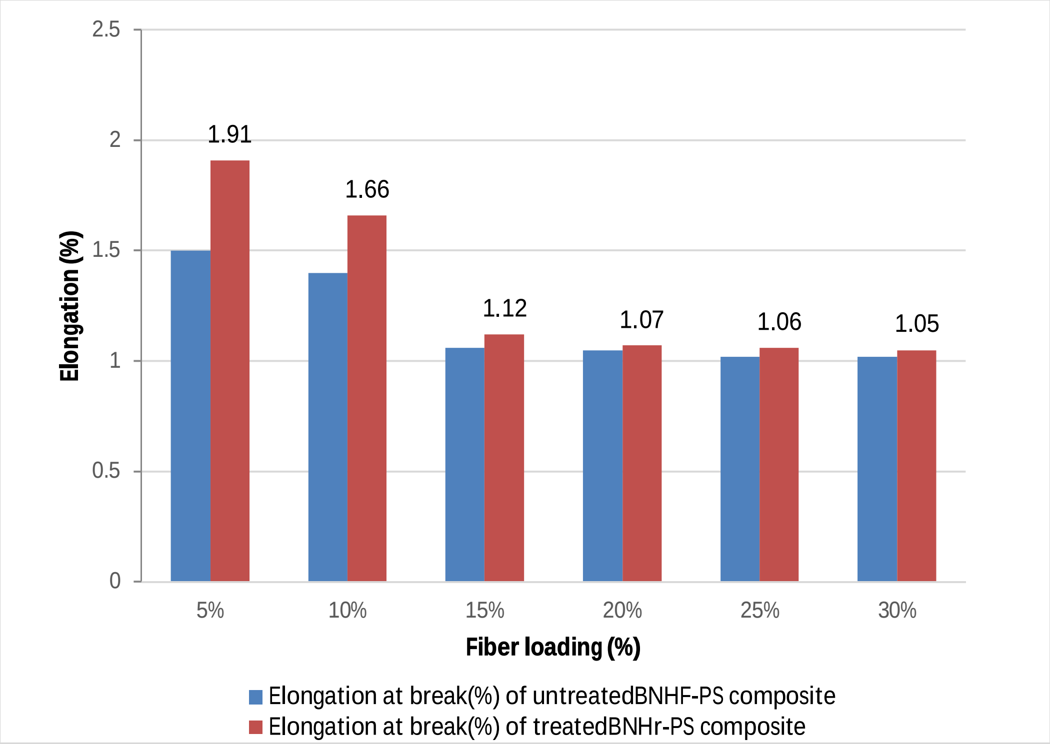
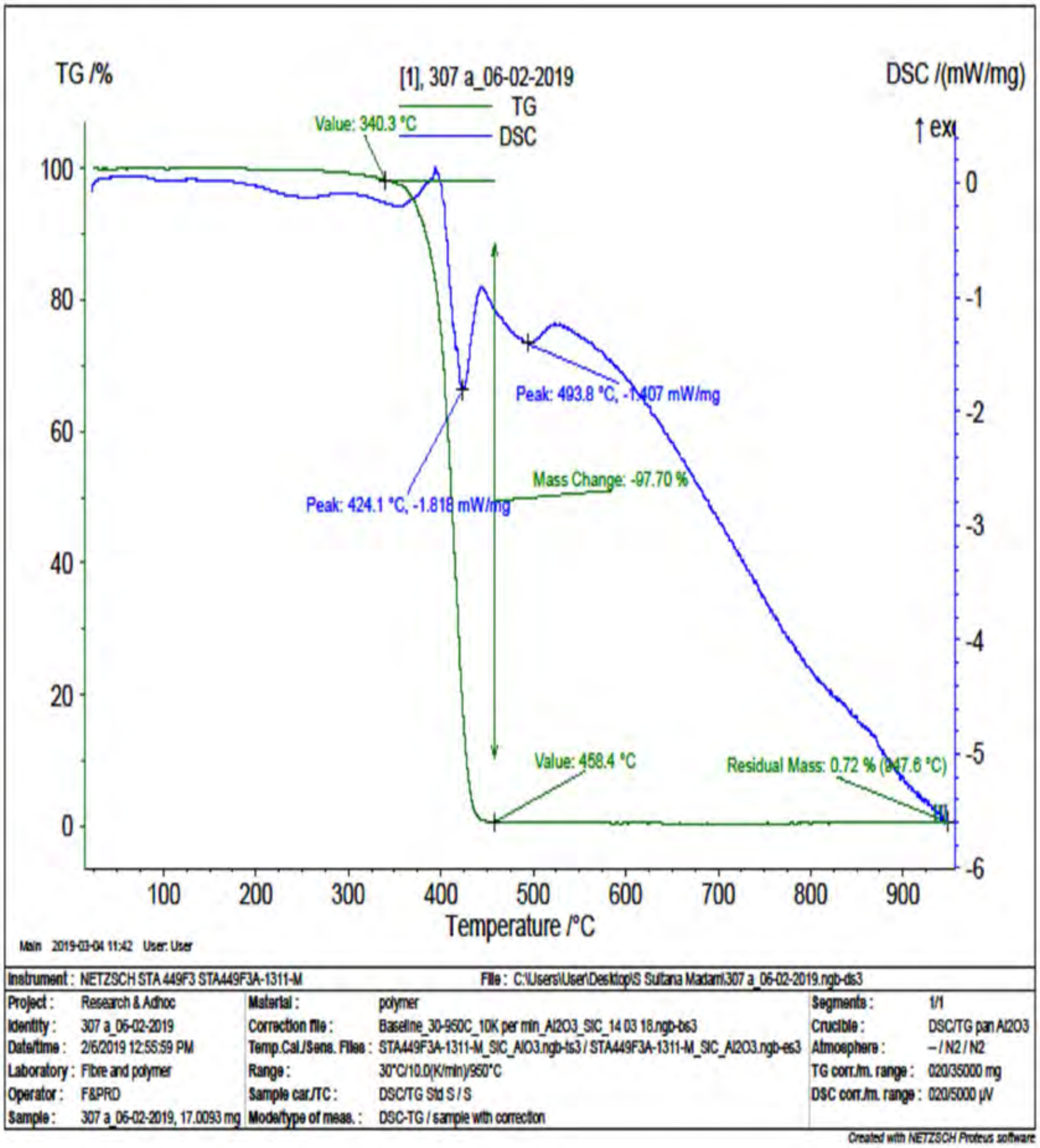


Figure 5.6: Elongation of untreated BNHF-PS and NaOCl treated BNHF-PS composite

5.4.5 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis of BNHF- PS composite

Thermo-gravimetric analysis and differential scanning calorimetric analysis of the compression moulded PS, 10 wt. % treated and untreated BNHF-PS composites were done to examine the degradation attributes of fiber at different stages of treatment. The recorded TGA and DSC thermographs are presented in figure-5.7, figure-5.8 and figure-6.9 respectively. Degradation start at 340.3 ºC and 97.70 % mass change was completed at 454.4ºC for PS polymer whereas the mass change started at 272.6ºC and 92.86% mass change was completed at 474.9ºC for the treated BNHF-PS composite. The degradation start at 267 ºC and 95.46% mass change was observed at 475.5ºC for BNHF-PS composite. DSC is used to identify melting temperature and amount of energy absorbed or release by materials. Tm of polystyrene, BNHF-PS composite and treated BNHF-PS are 424.1ºC, 436.9ºC and 426.2ºC respectively. Almost same thermal properties were found for treated and untreated BNHF-PS composites. Treated BNHF enhanced the thermal properties of BNHF-PS composites materials.



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Instrument : NETZSCH STA 449F3 STA449F3A-1311-M
File : C:\Users\User\Desktop\S Sultana Madam\307 a_06-02-2019.ngb-ds3

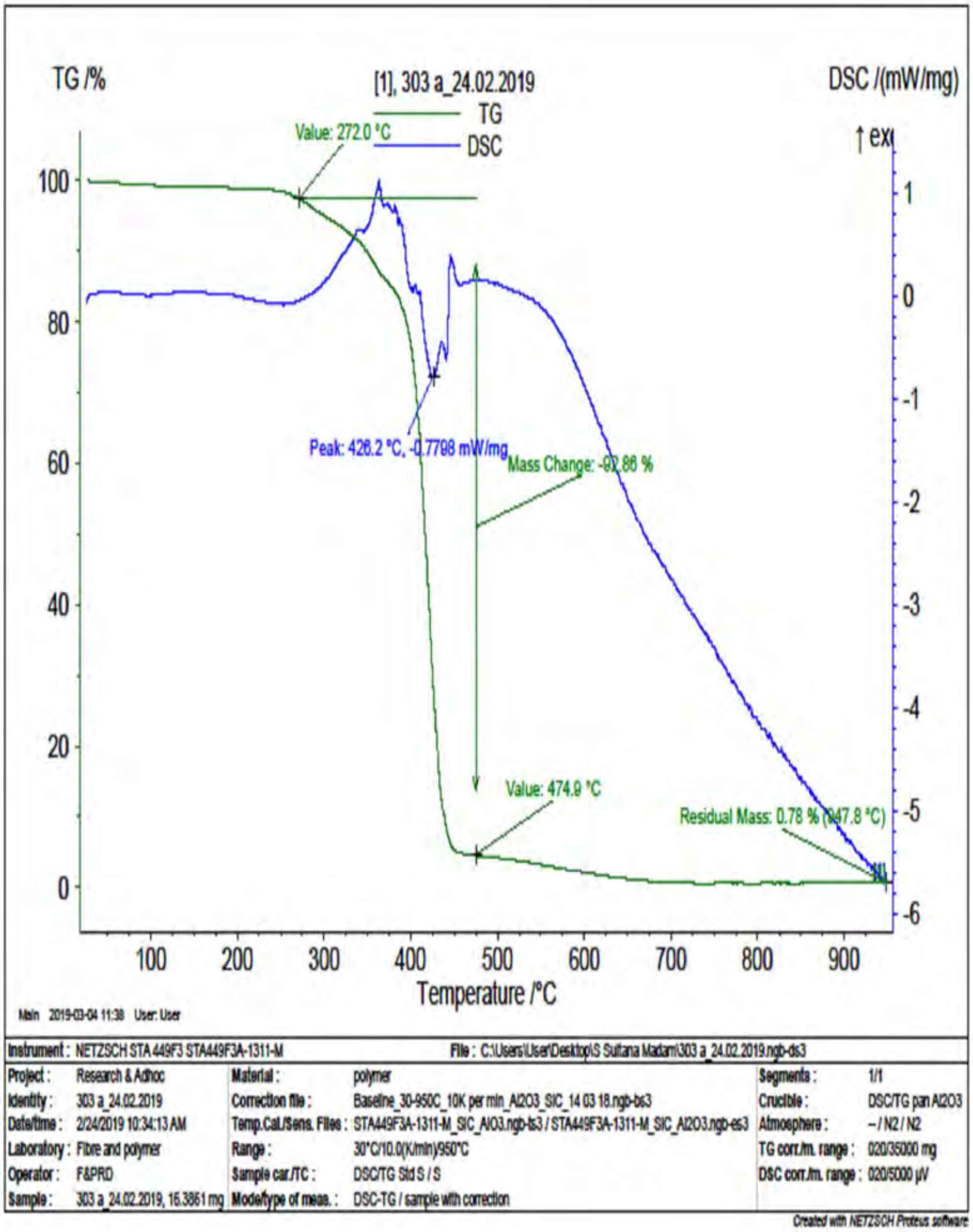
Project : Research & Adhoc
Identity : 307 a_06-02-2019
Date/time : 2/6/2019 12:55:59 PM
Laboratory : Fibre and polymer
Operator : F&PRD
Sample : 307 a_06-02-2019, 17.0093 mg

Material : polymer
Correction file : Baseline_30-950C_10K per min_Al2O3_SIC_14 03 18.ngb-bs3
Temp.Cal./Sens. Files : STA449F3A-1311-M_SIC_AlO3.ngb-ts3 / STA449F3A-1311-M_SIC_Al2O3.ngb-es3
Range : 30°C/10.0(K/min)/950°C
Sample car./TC : DSC/TG Std S / S
Mode/type of meas. : DSC-TG / sample with correction

Segments : 1/1
Crucible : DSC/TG pan Al2O3
Atmosphere : -- / N2 / N2
TG corr./m. range : 020/35000 mg
DSC corr./m. range : 020/5000 µV

Created with NETZSCH Proteus software

Figure 5.7: TGA and DSC of PS



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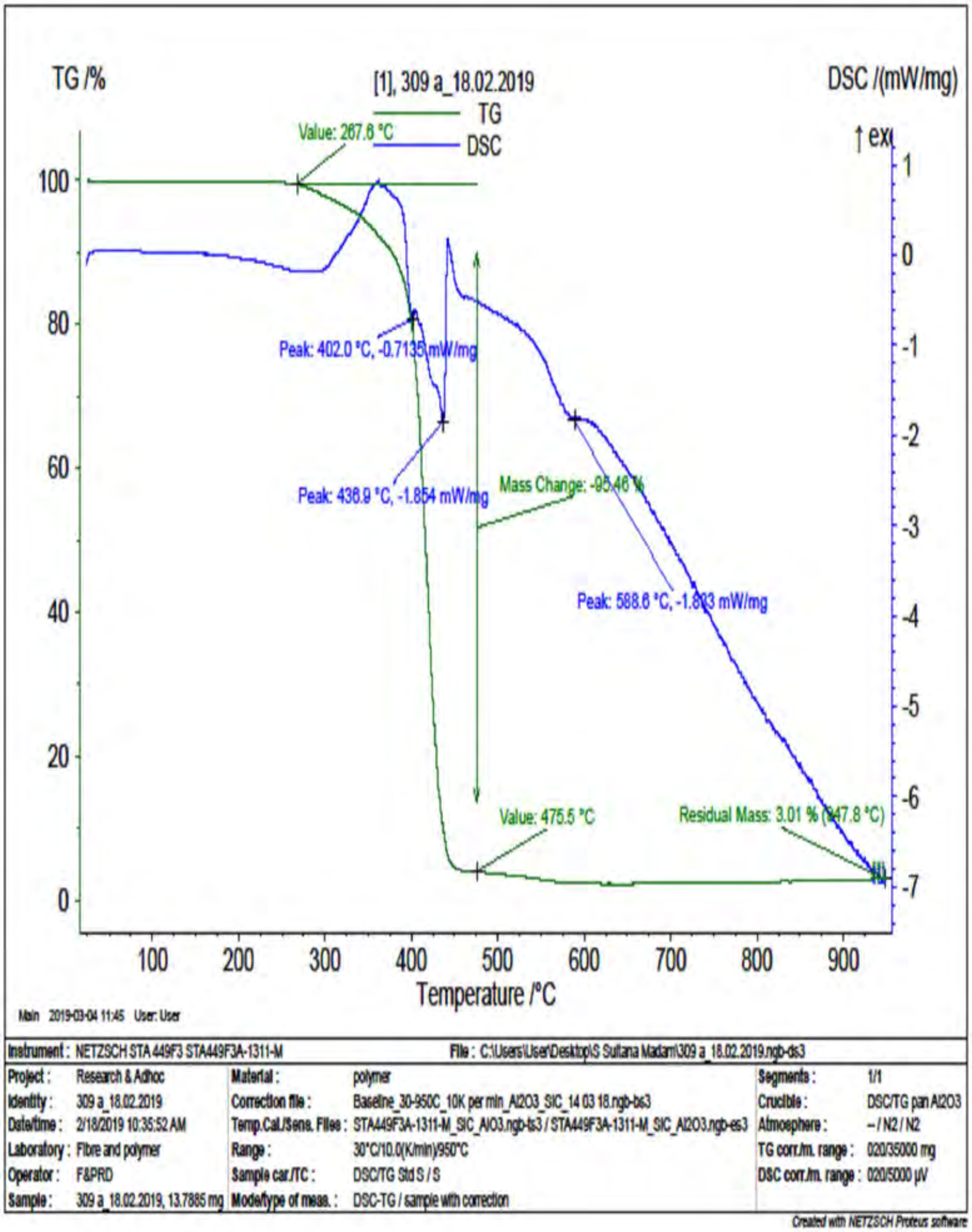
Laboratory :	Fibre and polymer	**Range :**	30°C/10.0(K/min)/950°C	**TG corr./m. range :**	020/35000 mg
Operator :	F&PRD	**Sample car./TC :**	DSC/TG Std S / S	**DSC corr./m. range :**	020/5000 µV
Sample :	303 a_24.02.2019, 15.3861 mg	**Mode/type of meas. :**	DSC-TG / sample with correction		

Figure 5.8: TGA &DSC curve of treated BNHF-PS composite



Instrument : NETZSCH STA 449F3 STA449F3A-1311-M
File : C:\Users\User\Desktop\S Sultana Madam\309 a_18.02.2019.ngb-ds3

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Laboratory :	Fibre and polymer	Range :	30°C/10.0(K/min)/950°C	TG corr./m. range :	020/35000 mg
Operator :	F&PRD	Sample car./TC :	DSC/TG Std S / S	DSC corr./m. range :	020/5000 µV
Sample :	309 a_18.02.2019, 13.7885 mg	Mode/type of meas. :	DSC-TG / sample with correction		

Figure 5.9: TGA &DSC curve of untreated BNHF-PS composite

5.4.6 Water absorption of Treated and untreated BNHF- PS composite

Water absorption test results of all treated and untreated betel nut husk fiber-PS composites are shown in Figure 5.10. From this figure it is shown that, water absorption increases with increasing fiber loading for all composites but water absorption of untreated betel nut husk fiber-PS composites is higher than that of treated betel nut husk fiber-PS composites. This may be due to the hydrogen bonding formation of water molecules with the hydroxyl groups in the constituents of lignin, hemi-cellulose and cellulose of untreated betel nut husk fibers. The fiber treatment lead to the reduction of water absorption due to effective interfacial adhesion between fiber and matrix in composites as well as improved hydrophobicity of fibers involved with. So, dimension stability will be higher for treated betel nut husk fiber-PS composites than untreated betel nut husk fiber-PS composites.

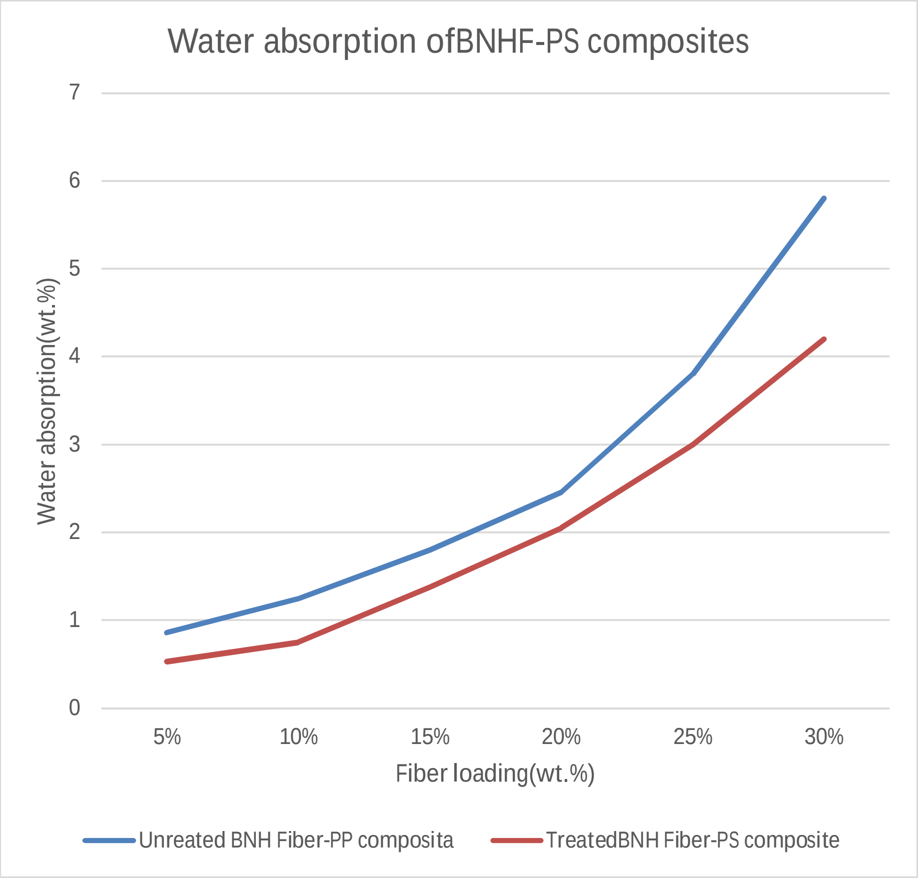


Figure 5.10: Water absorption (%) Vs fiber loading (%) of untreated BNHF-PS and treated BNHF-PS composites.

5.5 Conclusion

The surface modification of BNHF with sodium hypochlorite (0.1 N) removes the impurities and hemicelluloses and reduces the lignin content of fibers. Hemi-cellulose, lignin, and -OH group in untreated betel nut fiber hamper the good interfacial bonding between fiber and matrix. FT-IR spectra of untreated and treated BNHF supported the evidence of removal of hemicelluloses, lignin from treated BNHF. Sodium hypochlorite treatment of BNHF reduces the moisture absorption property and improves the interfacial adhesion between fibers and matrices in composites. For treated BNHF-PS composite interfacial fiber-polystyrene interaction is good. Uniform dispersion of fiber was observed, which confirmed by SEM results. The enhancement of thermal and mechanical properties of the treated BNHF-PS was found. Chemical treatment results the better compatibility between the fibers and matrices of the treated BNHF-PS composites.

CHAPTER 6

STUDIES ON THE PROPERTIES OF CELLULOSE AND NANO- CELLULOSE OBTAINED FROM BETEL NUT HUSK FIBER AND THEIR REINFORCED BIODEGRADABLE POLYMER COMPOSITES

STUDIES ON THE PROPERTIES OF CELLULOSE AND NANO-CELLULOSE OBTAINED FROM BETEL NUT HUSK FIBER AND THEIR REINFORCED BIODEGRADABLE POLYMER COMPOSITES

6.1 Introduction

Cellulose has attracted much attention from many researchers, due its availability and excellent properties, especially in the form of nano-fibers. Cellulose existing in natural fiber is the most abundant biopolymer on the earth. It has been used as a manufacturing material for several commodities in the food and pharmaceutical industries, as well as in paint, textiles, etc however, cellulose application in high value-added applications is still limited due to its hygroscopic nature and lack of melting properties. In recent years a wider application of cellulose has been proposed at the nanostructure level for developing various biocompatible products as well as a variety of commercial cellulose derivatives [121-123]. Although it is extracted from native cellulose it possesses remarkably high physical properties with special surface chemistry. Nano-cellulose has gained increasing interest for a wide range of applications relevant to the fields of materials science and biomedical engineering due to its renewable nature, anisotropic shape, excellent mechanical properties, good biocompatibility, tailor able surface chemistry, and interesting optical properties. A new scope of nano-cellulose application is still under investigation in fields such as photonics, films and foams, surface modifications, nano-composites, flexible optoelectronics, and medical devices like scaffolds for tissue regeneration. The most beneficial property of nanocellulose research is the green nature of the particles, their fascinating physical and chemical properties, and the diversity of applications that can be derived from this material [124].

Betel nut husk fiber (BNHF) is an important agricultural waste material which has high cellulose content. Cellulose can be extracted from betel nut fiber. Numerous efforts have been focused on using from these renewable materials resources for composite reinforcement. The addition of cellulose nanofibers in polymer matrix is a great interest to replace the nanofiller from non-renewable materials. Thus in order to use nanocellulose for universal application, it is necessary to develop a sustainable and environmentally friendly processing technique. In this piece work an improved new extraction procedure of cellulose from BNHF has been developed and the nano-cellulose was successfully isolated by chemical and mechanical treatment.

Polyvinyl alcohol (PVA) is a water soluble polymer which has widespread use in many areas of industrial applications such as textiles, paints, and adhesive industries and it is also a very promising candidate for the preparation of biodegradable plastics. This is because of its biodegradability, biocompatibility, chemical resistance and excellent physical properties. Hydrogen bonding between cellulose chains in cellulose nanofibers causes agglomeration or entanglement of nanofibers in the polymer matrix. Therefore, to reduce the interaction between hydroxyl groups, the cellulose nanofibers are maintained in the form of suspension in water. Thus the use of cellulose nanofibers without modification for the composites is limited to water soluble polymer [116].

In this study, nano-cellulose was extracted from betel nut husk fiber. The effect of sonication on particle size of the nano-cellulose was studied. These cellulose and nanocellulose reinforced polyvinyl alcohol (PVA) composites have been successfully prepared analyzed and reported in this chapter.

6.2 Materials

Betel nut husk fibers were used as reinforcing material in this research work. Betel nut fruit husk were extracted from collected betel nut fruits from local plantation field.

6.3 Chemicals

The analytical grade sodium hydroxide, sulfuric acid, polyvinyl alcohol, and other chemicals were used in this study. The chemicals used in this study have been listed in chapter two.

6.4 Experimental

6.4 .1 Analysis of the constituent of betel nut husk fiber

The extracted betel nut husk fibers were taken and rejected the hard portion manually. The fibers were washed with soap flake first and then with distilled water. Finally the washed fibers were dried at 105^0C in an oven and stored.

6.4.1.1 Estimation of aqueous extract

Dried fibers were heated with distilled water at 60 °C for 2 hours and then the fibers were separated by filtration. Collected fibers were dried at 105 °C for constant weight. The calculated loss in weight gave the amount of aqueous extract in fiber.

6.4.1.2 Estimation of Fatty and Waxy Matters

Dried fibers were immersed in benzene –alcohol mixture (2:1 by volume) contained in a beaker in the ratio of 1 gm dried fiber per 100 ml of the mixture and then allowed to stand for 10 hours then the fibers were washed several times with fresh benzene –alcohol mixture and finally with alcohol. Then the fibers were dried at 105 °C for constant weight. The loss in weight on extraction with solvent mixture gives the amount of fatty and waxy matters present in betel nut fiber.

6.4.1.3 Estimation of Pectic Matters

The dried de-waxed fibers were taken in a beaker and heated with 0.5% ammonium oxalate solution in the ratio of 1 gm fiber per 100 ml of the solution at 70-80 °C for three days in a heating mantle. As evaporation went on the loss of water was compensated by adding hot distilled water to keep the level of the solution constant throughout the process. The fibers were then filtered, washed thoroughly with hot distilled water and then dried at 105 °C for constant weight. The loss in weight gave the amount of pectic matters in fiber.

6.4.1.4 Estimation of lignin

De-waxed and de-pectinised fibers were dried at 105 °C and then treated with 72% H_2SO_4 (15 ml for 1 gm of fiber) with frequently stirring at ordinary temperature. The mixture is allowed to keep for 2 hours and then diluted to 3% acid concentration. The mixture was refluxed for 4 hours and then it was allowed to stand for over-night and filtered through a sintered funnel than dried at 105 °C for constant weight. The weight of the residue gave the amount of lignin content in betel nut fiber.

6.4.1.5 Estimation of α-cellulose and hemi cellulose

A suitable amount of de-waxed and de-pectinised fibers were taken to dry at 105^0C. Dried fibers were then treated with sodium chlorite (0.7%) solution buffered at pH 4 in the ratio of 1 gm fiber 80 ml liquor at 90-95°C for 90 minutes; 1ml buffer solution of sodium acetate and acetic acid of pH 4 is added for every 10 ml of chlorite solution to stabilize the constant pH. The fiber is then filtered, washed throughly with distilled water, then treated with 2% sodium *meta* -bisulphite solution for 15 minutes again filtered and washed thoroughly. In this step all non-cellulosic maters of fibers were removed by treatment of bleaching agent, sodium chlorite where chlorite hollo–cellulose a combination of α-cellulose and hemi cellulose is obtained. The cellulosic materials chlorite holo-cellulose was obtained in the sintered funnel. Chlorite holo-cellulose was dried at 105°C until constant weight was obtained. Chlorite hollo-cellulose was treated with 24% KOH solution for 4 hours with occasional stirring (1 gm fiber in 100 ml of the alkali solution). By this treatment hemi cellulose went into solution and α-cellulose remains un-dissolved. The α-cellulose was separated by filtration, washed thoroughly with 2% acetic acid solution, finally, with distilled water and dried at 105 °C for constant weight. The obtained weight of α- cellulose was deducted from the weight of holo- cellulose to calculate the amount of hemi cellulose present in fiber.

6.4 .2 Extraction of cellulose from Betel nut husk fibers

To extract cellulose from betel nut fiber, the fibers were immersed in de-ionized water and boiled at 100 °C for three hours and then washed with de-ionized water. The fiber was then dried in an oven. 5 g of oven dried fiber was placed into a 500 mL Erlenmyner flask, to which 200 ml of de-ionized water (having a temperature of 90°C) was then added followed by 10 mL of acetic acid and 7.5 g of 80% (w/w) $NaClO_{2.}$ An optional 25 mL Erlenmeyer flask was inverted in the neck of the reaction flask. The flask was then kept in a water bath at 90°C for 60 minutes at that time 10 ml of acetic acid and 7.5 g of 80% (w/w) $NaClO_2$ were added with shaking. The 60 minutes cycle was repeated for up to 5 cycles. The reaction was stopped by adding cold water. The reaction mixture was then filtered, washed with cold water and acetone and dried at 105°C in oven until the crucible weight was constant. The holo-cellulose content was calculated. The collected holo-cellulose was treated with 17.5% NaOH solution at room temperature for three hours with occasional stirring to obtain cellulose. The solution mixture was then filtered and washed several times with distilled water. Cellulose was then dried in open air and in oven at 80°C for five hours.

6.4.3 Preparation of nano-Cellulose

Cellulose extracted from Betel nut fruit husk fibers was converted to cellulose nano fiber by a chemical technique to examine their potential use as reinforcement in bio-composite applications. The cellulose isolated from betel nut fibers were subjected to acid hydrolysis using 62% (w/w) sulfuric acid. The ratio of fiber to acid was 1:8 (w/v) and hydrolysis proceeded under stirring (500 rpm) at 50^{o}C for 1 hour. The reaction mixture was diluted ten times volume with de-ionized water to quench the reaction. The suspension was centrifuged at 8500 rpm for 21 min to remove excess acid and water. The precipitated was repeatedly rinsed and centrifuged with deionized water until the suspension remained at neutral pH. The suspension was then sonicated for three hours (optimized) to created cellulose crystals of colloidal dimensions. Cellulose nano fibers were characterized by FTIR, Nano zeta seizer and its structural morphology was studied by Scanning electron microscope.

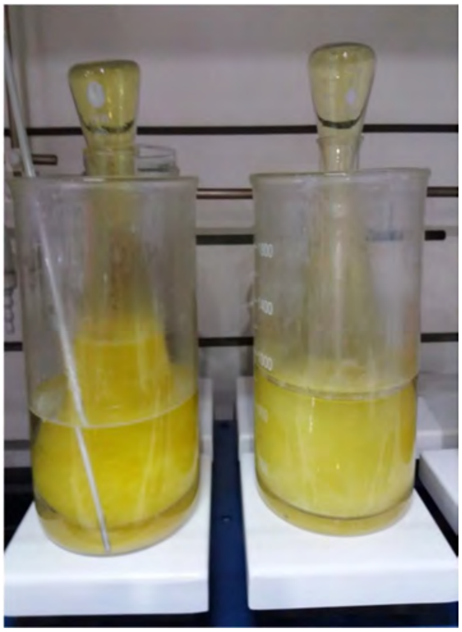


Figure 6.1: BNHF holocellulose preparation

Figure 6.2: BNHF - Cellulose preparation

Figure 6.3: Image of holocellulose

Figure 6.4: Image of Cellulose

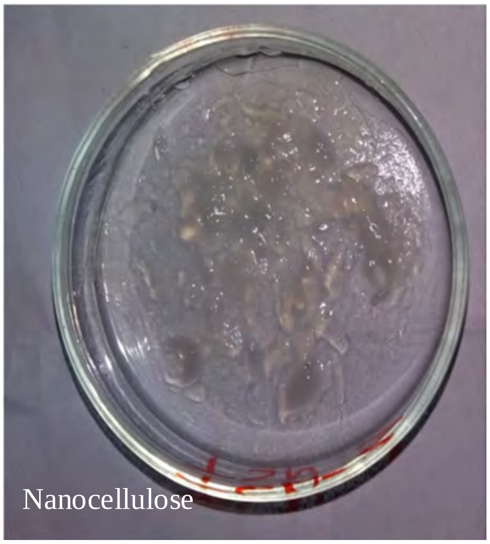


Figure6.5: Picture of prepared nano-cellulose

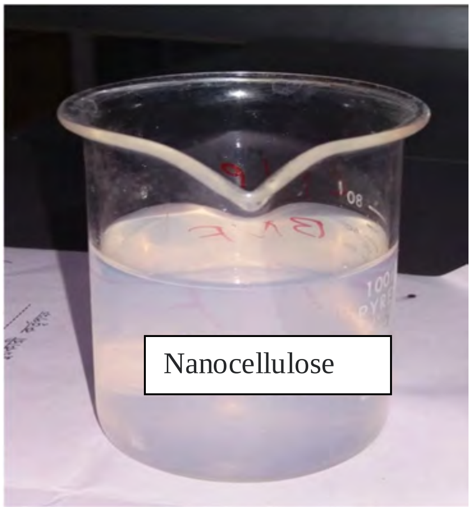


Figure 6.6 Picture of NC suspension

Figure 6.7: Picture of NC-PVA suspension

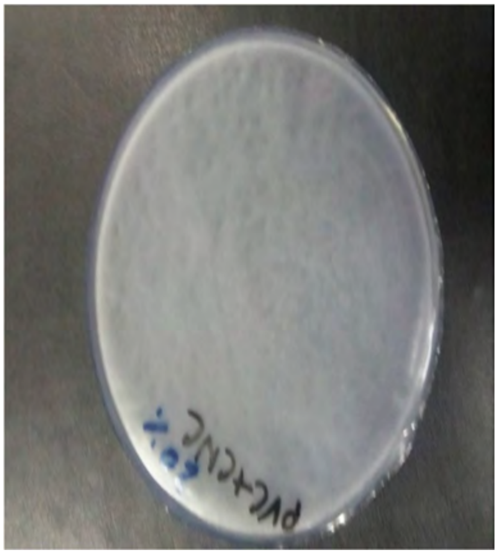


Figure 6.8: Picture of PVA-NC composite

6.4.4 Preparation of Betel Nut Husk Nano Cellulose by Mechanical Milling

Cellulose extracted from betel nut fiber converted nano cellulosic fiber by milling process. The milling process was done in two steps, the primary process was rotary milling and second process is high energy planetary ball milling, The Cellulose extracted from betel nut fiber were passed through a rotary mill fitted with a 0.08 mm sieve which operates at a speed of 3000 rpm. The collected cellulose were milled at a speed of 4500 rpm for 80 hours using high energy planetary ball milling by SFM-1 Desk-Top planetary Ball Miller (MTI Corporation) to prepare nano cellulose fiber.

6.4.5 Preparation of cellulose and nanocellulose reinforced polyvinyle alchohol composites

Cellulose and nano cellulose of betel nut husk fiber were used to prepare PVA - cellulose and PVA-nanocellulose composites. 10 wt% of PVA solution was prepared in hot water at 80°C and the different weight fraction of cellulose and high dispersed nanocellulose suspension were mixed with this solution and stirred at 700 rpm for 30 minutes, then dispersed by using a homogenizer for 30 minutes. The mixtures were degassed by allowing them with caps at room temperature overnight. Subsequently, the mixtures were cast in petri dishes and dried at room temperature for several days. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table 6.1. The resulting films were characterized by FT-IR and SEM analysis. The mechanical property of prepared sample was studied by tensile test and thermal properties were analyzed by TGA and DSC.

Table 6.1: Different weight fraction of Cellulose, nano cellulose reinforced Polyvinyl alcohol composites.

Cellulose - PVA Composites (wt. %)	**Nanocellulose-PVA composites (wt. %)**
05:95 (wt %) Cellulose: PVA	05: 95 (wt %) Nanocellulose: PVA
04:96 (wt %) Cellulose: PVA	03:96 (wt %) Nanocellulose: PVA
03:97 (wt %) Cellulose: PVA	02:97 (wt %) Nanocellulose: PVA
02:98 (wt %) Cellulose: PVA	01:98 (wt %) Nanocellulose: PVA
01:99 (wt %) Cellulose: PVA	01:99 (wt %) Nanocellulose: PVA
100 (wt %) PVA	100 (wt %) PVA

6.4.6 Characterization of betel nut cellulose, nanocellulose and composites

6.4.6.1 Particle size and zeta potential measurement

The particle size of prepared nano-cellulose was analyzed using Malvern Zeta sizer Nano ZS (Malvern Instruments, UK). This equipment uses dynamic light scattering to measure the diffusion of particles moving under Brownian motion and convert this to size and size distribution. It also uses laser Doppler micro electrophoresis to apply an electric filed to the dispersion of particles which then move with a velocity related to their zeta potential.

6.4.6.2 FTIR spectroscopy

The FTIR spectrum of cellulose, nano-cellulose and their reinforced composites were taken by FTIR spectrometer. Cellulose, nano-cellulose and betel nut husk micro fibers were used to make pellet with potassium bromide to take FT-IR. On the other hand, FTIR spectra of cellulose, nano-cellulose and their reinforced PVA composites were recorded over the frequency range 4000–700 cm^{-1} using FTIR spectrometer (PerkinElmer, USA, Model Forntier, serial no. 101393). FT-IR spectra were obtained in the printed form.

6.4.6.3 Scanning electron microscopy (SEM)

The surface of Cellulose, nano-cellulose and fracture surface of tensile test sample of cellulose and nano-cellulose reinforced PVA composites samples were 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 Cellulose, nano-cellulose and fracture surface of tensile test sample of cellulose and nano-cellulose reinforced PVA composites. The photographs are presented in the result and discussion section.

6.4.7 Mechanical properties of composites

Tensile test of all prepared cellulose and nano-cellulose reinforced PVA composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods. Specification and picture of the used machines, operating condition and dimension of test specimens are given below.

6.4.7.1 Tensile properties of the composites

The tensile test of all prepared cellulose and nano-cellulose reinforced PVA composites were measured 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 cross head speed of the test was 10 mm/min and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves were obtained by the instrument. The maximum load values were also recorded by the instrument which can be recalled after the completion of the test. The highest load in the tensile test gave the ultimate strength.

6.4.8 Thermal properties of composites

The thermal properties of optimized tensile tested sample were analyzed by Simultaneous Thermal Analyzer (STA), Model No F_3 Jupiter serial no STA 449 F - 3A – 1311- M NETZSCH.

6.4.8.1 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis

The thermo gravimetric analysis and differential scanning calorimetric analysis of the cellulose, nano-cellulose and betel nut husk micro fiber reinforced PVA composites were recorded on a STA 449F3 NETZSCH thermal analysis instrument in the temperature range of 30-950 °C and the heating rate was set as 30°C/10(K/min)/ 950°C in a nitrogen atmosphere. Ten mg of the sample was heated in the sample pan.

6.5 Results and Discussion

6.5.1 Chemical constituent of betel nut husk fiber

Betel nut husk fibers (BNHF) contain cellulose, hemi-cellulose, lignin and other constituent in small amount. BNHF was extracted and analyzed. The ingredients found in BNHF are presented in table-6.2

Table 6.2: Main chemical constituent of betel nut fiber

1. Aqueous Extract	= 0.5647%
2. Fatty and waxy maters	= 1.3796%
3. Pectic maters	= 0.9173%
4. Lignin	= 14.865%
5. α-cellulose	= 51.0776%
6. Hemi cellulose	= 14.8653%
7. Ash	= 7.6877%

6.5.2 Characterization of cellulose and nano-cellulose:

6.5.2.1 FTIR analysis:

Fourier transform infrared (FTIR) analysis is an advanced technique to obtain the structure of a sample. Figure-9 shows the comparative spectra of betel nut husk fiber, cellulose and nano-cellulose. As depicted in Figure 7.9, the broad peak at 3330 cm^{-1} which appears in al spectra is attributed to the O–H frequency, whereas the peaks at 2893.12 cm^{-1} , 2892 cm^{-1} and 2919.99 cm^{-1} predominantly arise from C–H stretching [117]. After chemical and ultrasonic treatment, the prominent peak of betel nut husk fiber at 1731 cm^{-1} corresponds to ester carbonyl vibrations from the acetyl, ferulic and pcoumeric acids of lignin or hemi-cellulose. It indicates that most of the lignin has been removed from BNHF during the chemical treatment. A stretching peak detected at 1609 cm^{-1} for unbleached fiber is attributed to the carbonyl group of the acetyl ester in hemi-cellulose and the carbonyl aldehyde in lignin. The absence of this peak in cellulose and nano-cellulose be due to the removal of lignin and hemi-cellulose. The 15013.85 cm^{-1} and 1428.3 cm^{-1} peaks in the BNHF represent aromatic ring vibration and C-H deformation of lignin, respectively. The disappearance of this peak in cellulose indicates the removal of lignin. Peak at 1027.98 cm^{-1}, 895.17 cm^{-1} in cellulose and 1024.09 cm^{-1}, 894.04 cm^{-1} in nano-cellulose are associated with the C–O stretching and C_1–H deformation vibration of cellulose [119].

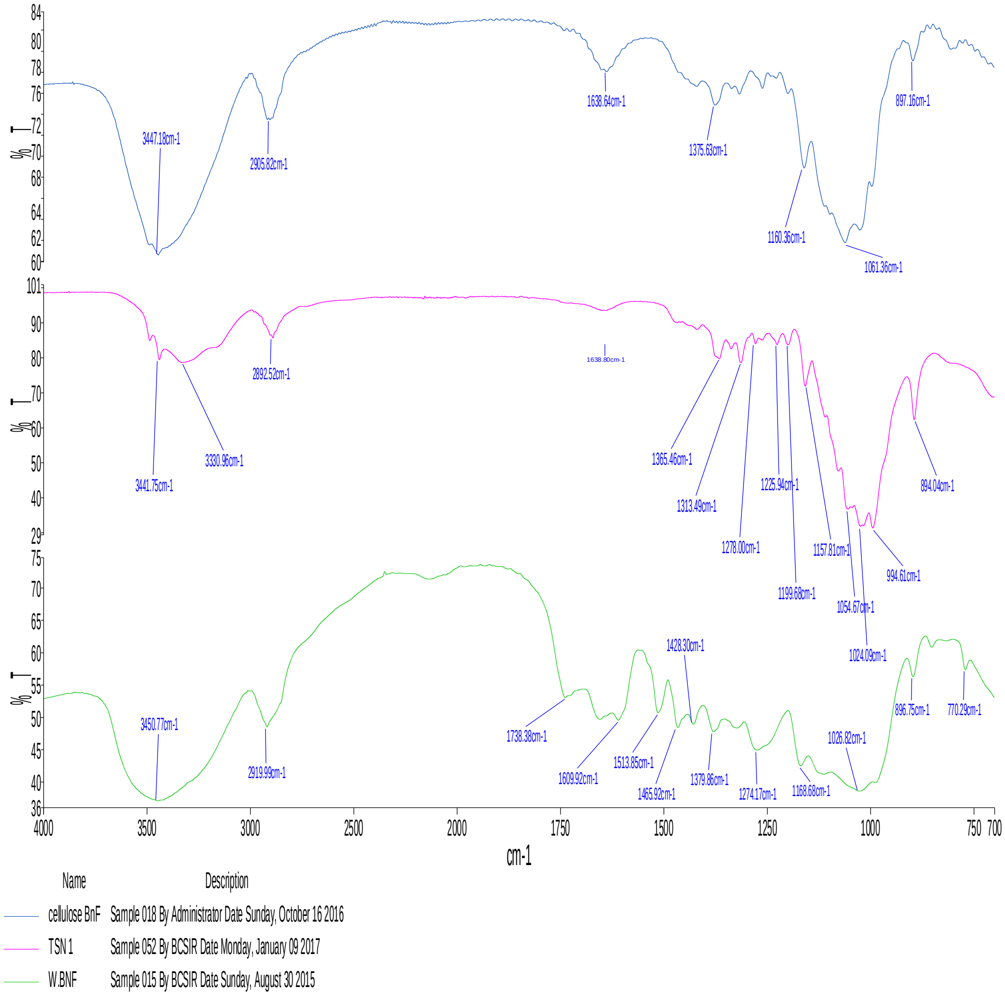


Figure 6.9: FTIR spectra of cellulose (upper), nano-cellulose (middle) and betel nut husk fiber (lower)

6.5.2.2 Scanning electron microscopy analysis (SEM)

The surface of Cellulose, nano-cellulose and fracture surface of tensile test sample of cellulose and nano-cellulose reinforced PVA composites samples were observed under the field emission scanning electron microscope (JEOL JSM-7600F). The SEM images of Cellulose, nano-cellulose shown in figure-7.10 and fracture surface of tensile test sample of cellulose and nano-cellulose reinforced PVA composites are shown in figure-7.11. Uniform dispersion of fiber and good interfacial bonding of fiber and matrix was observed in the nano cellulose- PVA composite.

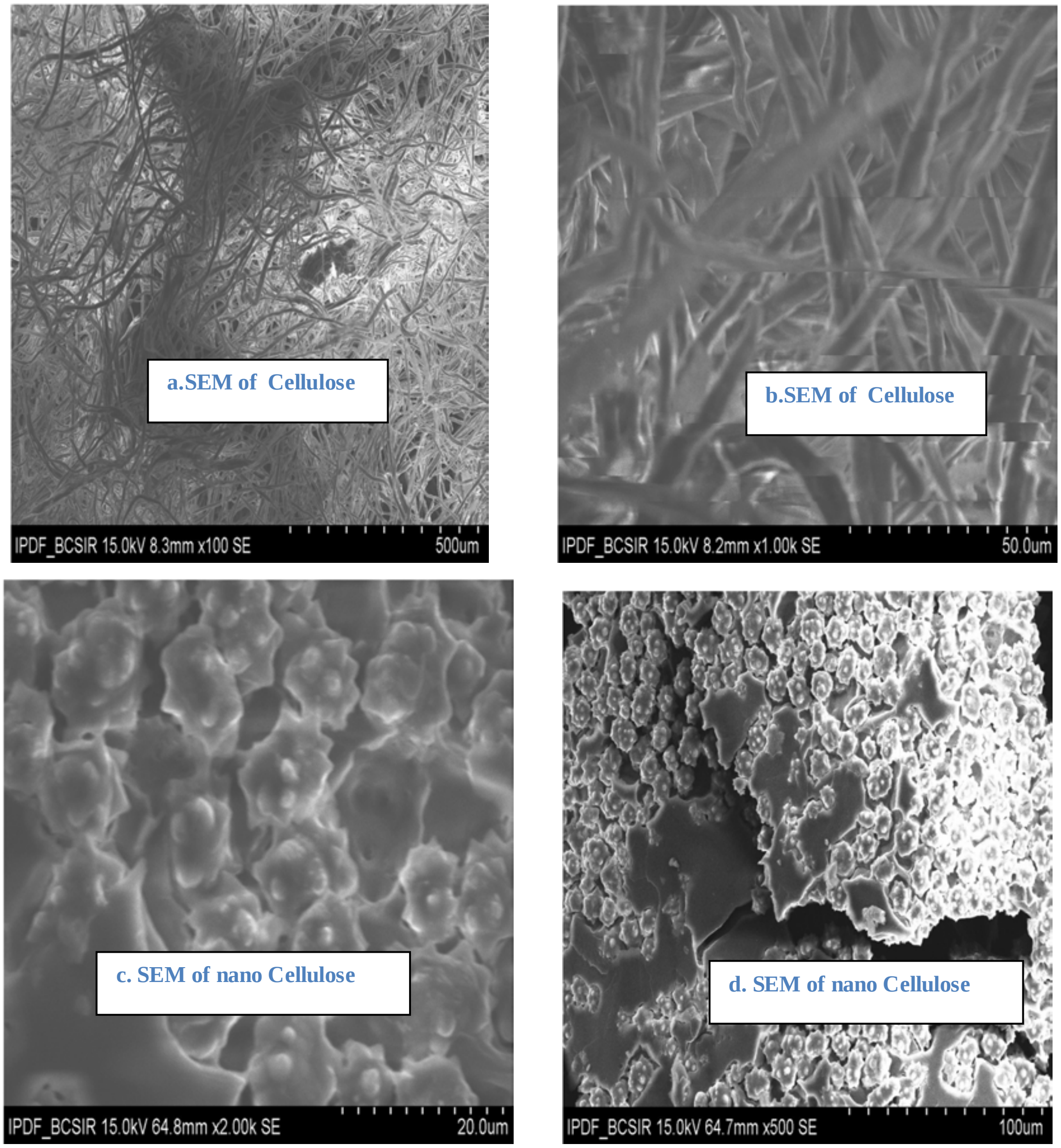


Figure 6.10: SEM of cellulose (a, b) nano-cellulose (c, d)

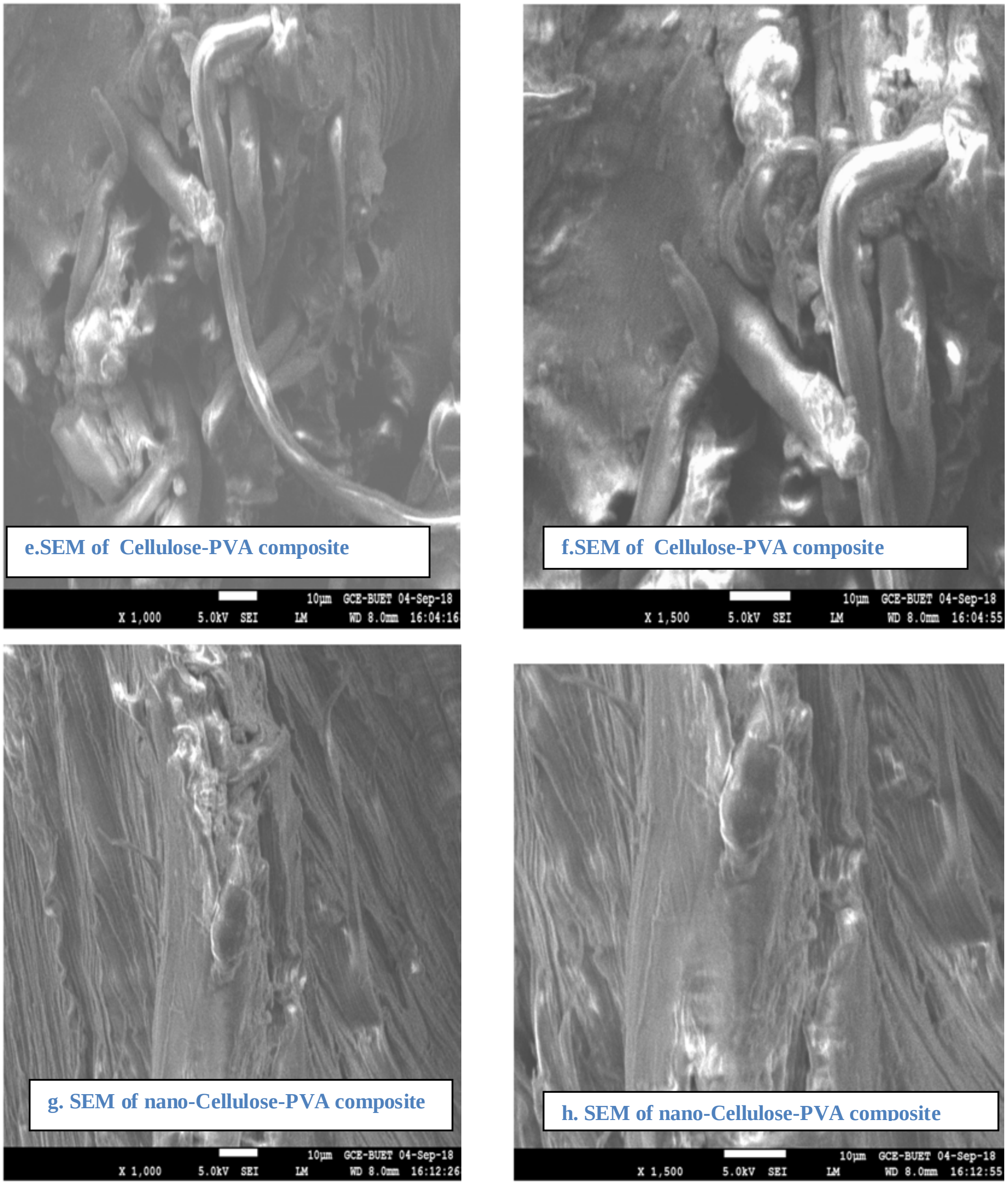


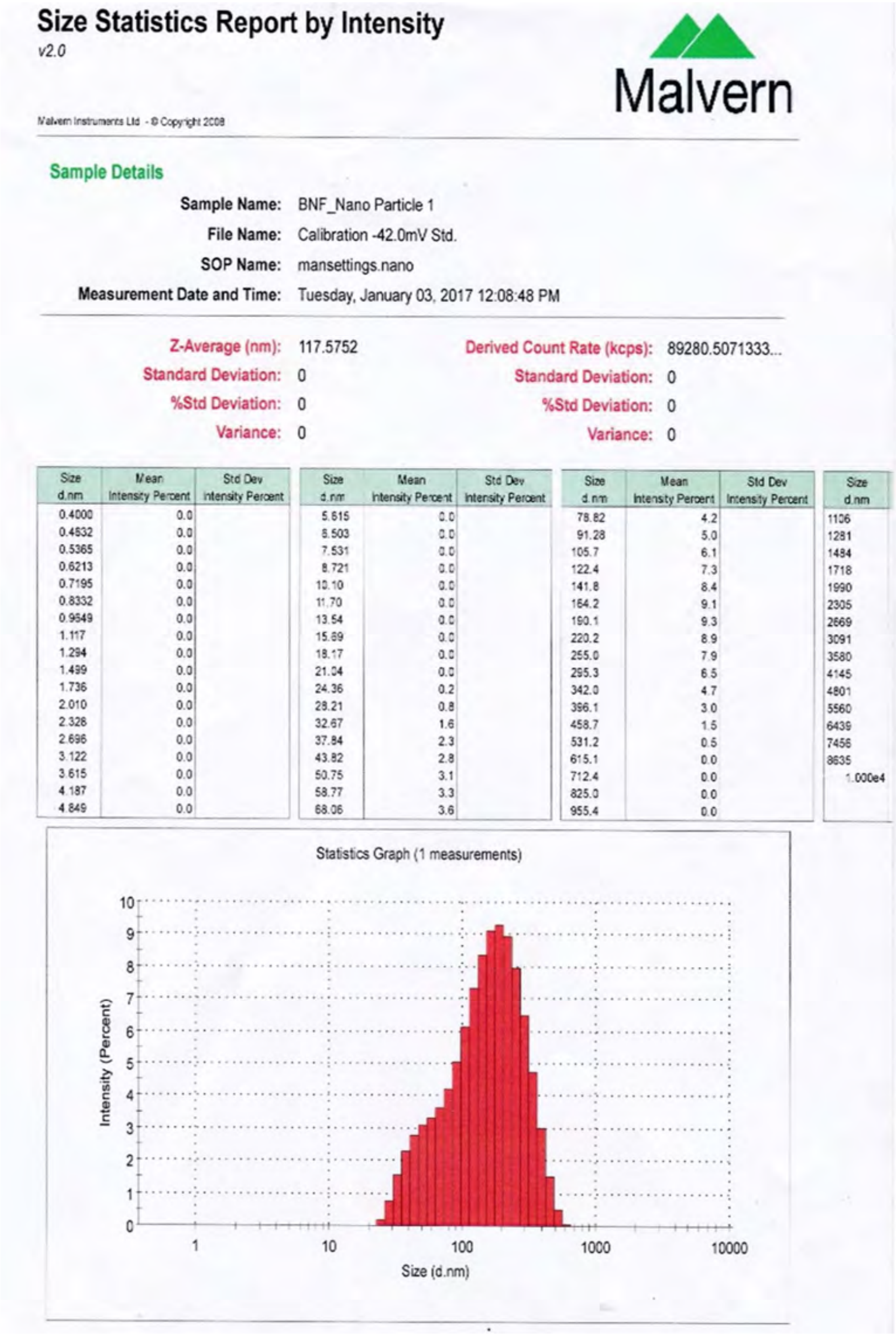
Figure 6.11 SEM of cellulose-PVA composite (e, f) and nano-cellulose-PVA composite (g, h)

6.5.2.2 Measurement of particle size and zeta potential of nano cellulose:

The particle size of prepared nano-cellulose and BNHF nano-fiber were analyzed using Malvern Zeta sizer Nano ZS (Malvern Instruments, UK). The particle size and zeta potential of prepared nano cellulose were measured by the instrument and the results were taken in printed form (Figure 6.12, 6.13, 6.14, 7.15, 6.16 and 6.17). The time of acid hydrolysis and effect of sonication on particle size was studied. In optimized acid concentration was 62% (w/w), reaction time one hour at 50°C temperature. The reaction temperature, acid concentration and reaction time were optimizing by conducting series of reaction. If reaction temperature is low (25°C) than the reaction process recurred long time, The particle size distribution report showed that without sonication the average particle size after hydrolysis was 117.6 nm. After three hours sonication the average size was found 68.27 nm. The zeta potential of prepared nano cellulose was -39.1 mV and the colloidal nano suspension was very stable. The sonication time decrease zeta potential and it was -19.7. Analytical reports of prepared nano cellulose are presented in figure 6.12 to 6.17. In mechanical milling process of nano cellulose preparation the milling time was important factor for particle size. The particle size resulted in three main groups for every 20h, 45h and 60 h. The size distribution results of prepared nano cellulose via milling process are presented in Table 6.3.

Table 6.3: Particle size of nano-cellulose (by ball milling)

Milling time (hours)	Peak 1		Peak 2		Peak 3	
	Size(nm)	Intensity	Size(nm)	Intensity	Size(nm)	Intensity
20	50.17	100	-	-	-	-
45	43.82	100	-	-	-	-
60	15.99	100	-	-	-	-



Size Statistics Report by Intensity
v2.0

Malvern

Malvern Instruments Ltd - © Copyright 2008

Sample Details

Sample Name: BNF_Nano Particle 1
File Name: Calibration -42.0mV Std.
SOP Name: mansettings.nano
Measurement Date and Time: Tuesday, January 03, 2017 12:08:48 PM

Z-Average (nm): 117.5752
Standard Deviation: 0
%Std Deviation: 0
Variance: 0

Derived Count Rate (kcps): 89280.5071333...
Standard Deviation: 0
%Std Deviation: 0
Variance: 0

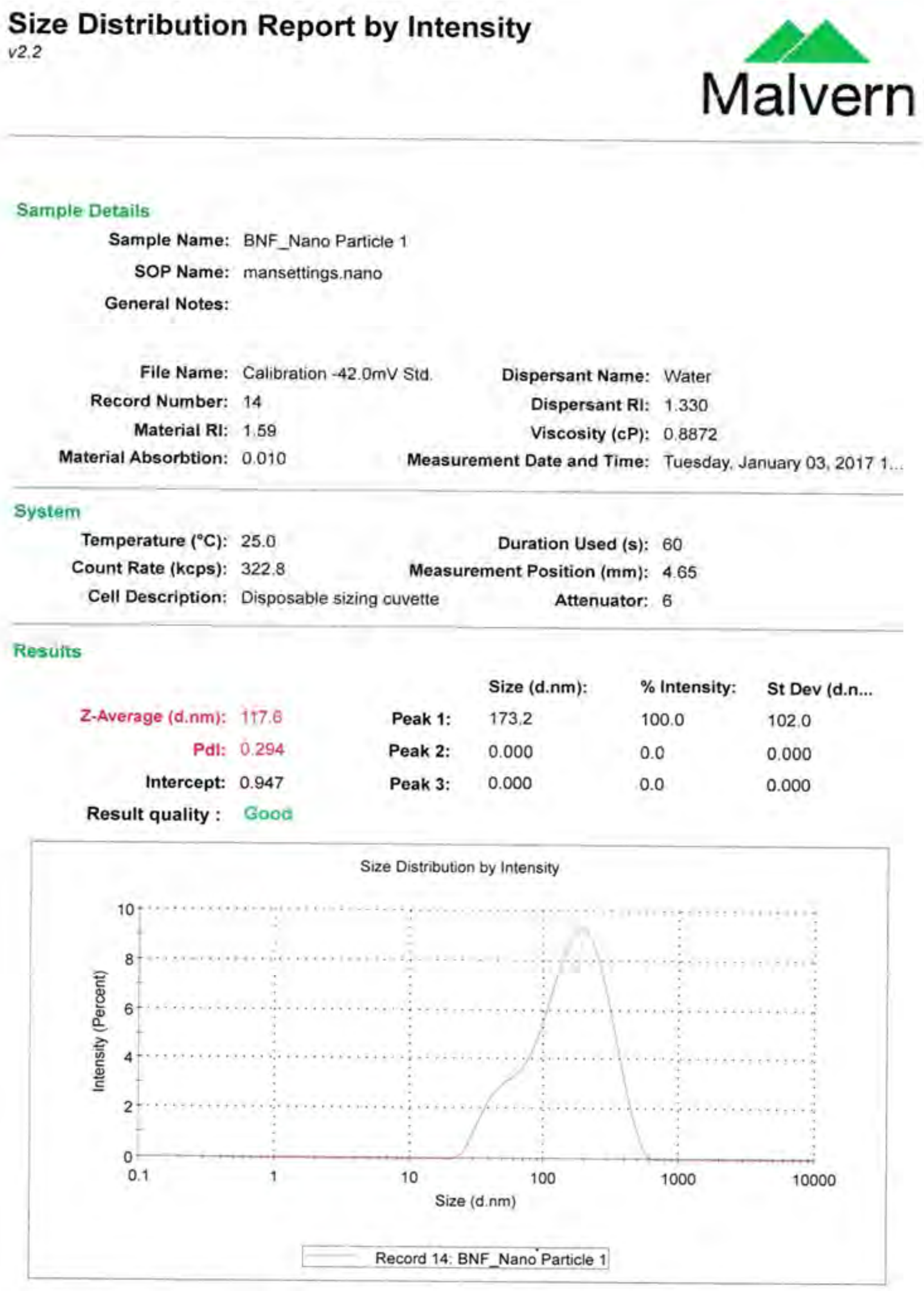
Size d.nm	Mean Intensity Percent	Std Dev Intensity Percent
0.4000	0.0	
0.4632	0.0	
0.5365	0.0	
0.6213	0.0	
0.7195	0.0	
0.8332	0.0	
0.9649	0.0	
1.117	0.0	
1.294	0.0	
1.499	0.0	
1.736	0.0	
2.010	0.0	
2.328	0.0	
2.696	0.0	
3.122	0.0	
3.615	0.0	
4.187	0.0	
4.849	0.0	

Size d.nm	Mean Intensity Percent	Std Dev Intensity Percent
5.615	0.0	
6.503	0.0	
7.531	0.0	
8.721	0.0	
10.10	0.0	
11.70	0.0	
13.54	0.0	
15.69	0.0	
18.17	0.0	
21.04	0.0	
24.36	0.2	
28.21	0.8	
32.67	1.6	
37.84	2.3	
43.82	2.8	
50.75	3.1	
58.77	3.3	
68.06	3.6	

Size d.nm	Mean Intensity Percent	Std Dev Intensity Percent
78.82	4.2	
91.28	5.0	
105.7	6.1	
122.4	7.3	
141.8	8.4	
164.2	9.1	
190.1	9.3	
220.2	8.9	
255.0	7.9	
295.3	6.5	
342.0	4.7	
396.1	3.0	
458.7	1.5	
531.2	0.5	
615.1	0.0	
712.4	0.0	
825.0	0.0	
955.4	0.0	

Size d.nm
1106
1281
1484
1718
1990
2305
2669
3091
3580
4145
4801
5560
6439
7456
8635
1.000e4

Figure 6.12 Size Statics Report of nano cellulose by Intensity



Size Distribution Report by Intensity
v2.2

Malvern

Sample Details

Sample Name: BNF_Nano Particle 1
SOP Name: mansettings.nano
General Notes:

File Name: Calibration -42.0mV Std.
Record Number: 14
Material RI: 1.59
Material Absorbtion: 0.010
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Measurement Date and Time: Tuesday, January 03, 2017 1...

System

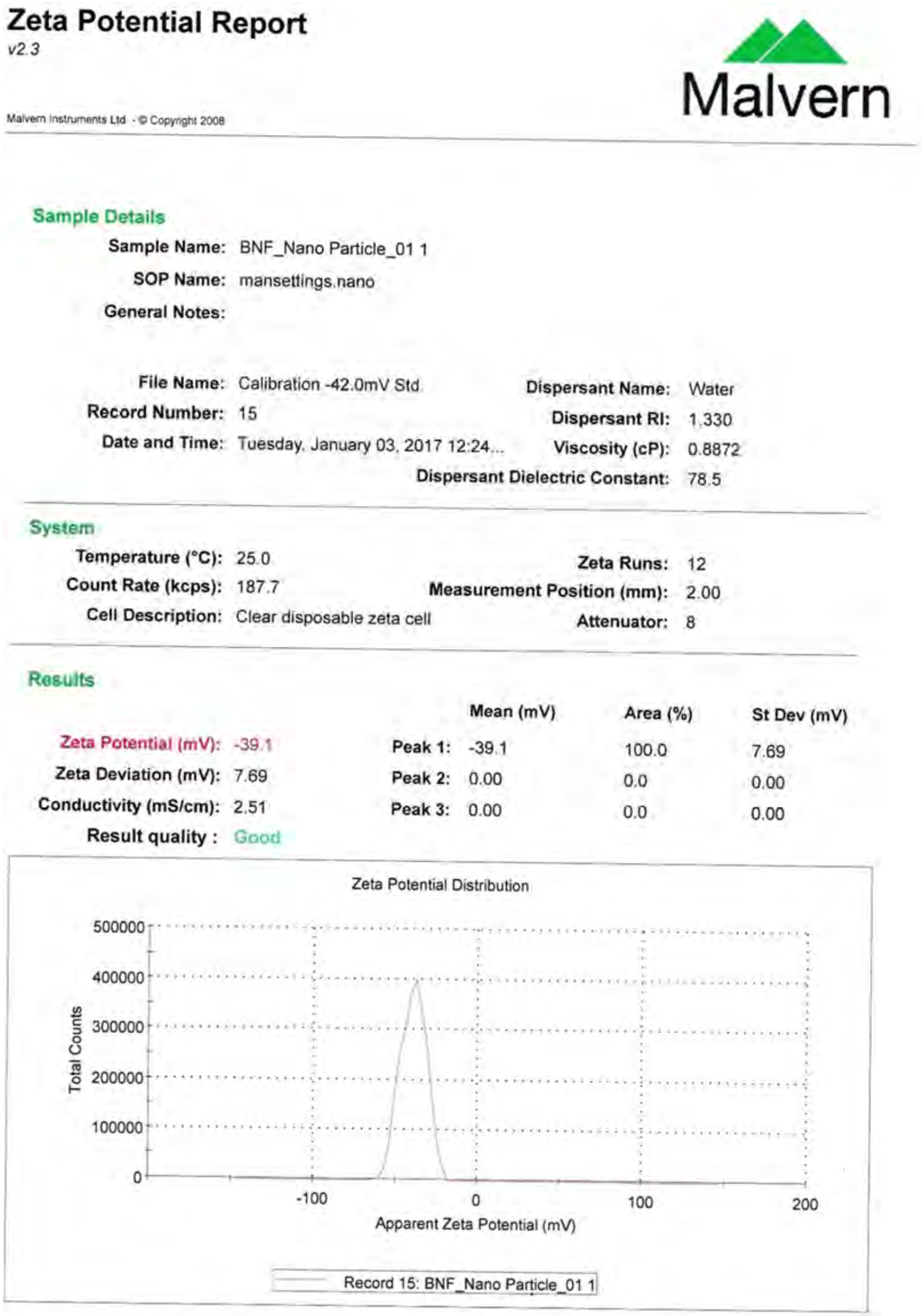
Temperature (°C): 25.0
Count Rate (kcps): 322.8
Cell Description: Disposable sizing cuvette
Duration Used (s): 60
Measurement Position (mm): 4.65
Attenuator: 6

Results

Z-Average (d.nm): 117.6
PdI: 0.294
Intercept: 0.947
Result quality : Good

	Size (d.nm):	% Intensity:	St Dev (d.n...
Peak 1:	173.2	100.0	102.0
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

Figure 6.13: Size Distribution Report nano cellulose by Intensity



Zeta Potential Report

v2.3

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Malvern

Sample Details

Sample Name: BNF_Nano Particle_01 1

SOP Name: mansettings.nano

General Notes:

File Name: Calibration -42.0mV Std

Record Number: 15

Date and Time: Tuesday, January 03, 2017 12:24...

Dispersant Name: Water

Dispersant RI: 1.330

Viscosity (cP): 0.8872

Dispersant Dielectric Constant: 78.5

System

Temperature (°C): 25.0

Count Rate (kcps): 187.7

Cell Description: Clear disposable zeta cell

Zeta Runs: 12

Measurement Position (mm): 2.00

Attenuator: 8

Results

Zeta Potential (mV): -39.1

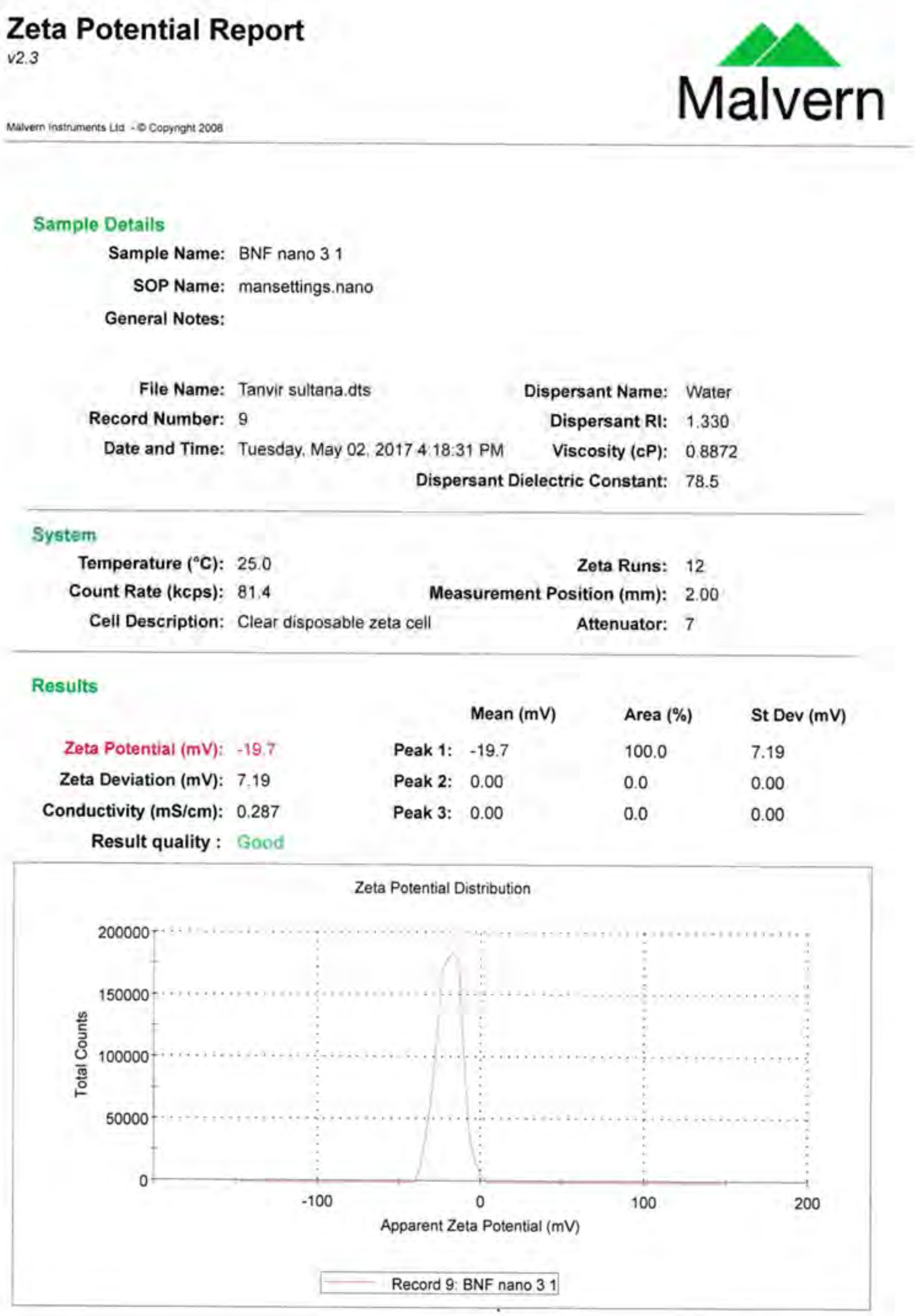
Zeta Deviation (mV): 7.69

Conductivity (mS/cm): 2.51

Result quality : Good

	Mean (mV)	Area (%)	St Dev (mV)
Peak 1:	-39.1	100.0	7.69
Peak 2:	0.00	0.0	0.00
Peak 3:	0.00	0.0	0.00

Figure 6.14: Zeta Potential Report of Nanocellulose



Zeta Potential Report

v2.3

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Malvern

Sample Details

Sample Name: BNF nano 3 1
SOP Name: mansettings.nano
General Notes:

File Name: Tanvir sultana.dts
Record Number: 9
Date and Time: Tuesday, May 02, 2017 4:18:31 PM

Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Dispersant Dielectric Constant: 78.5

System

Temperature (°C): 25.0
Count Rate (kcps): 81.4
Cell Description: Clear disposable zeta cell

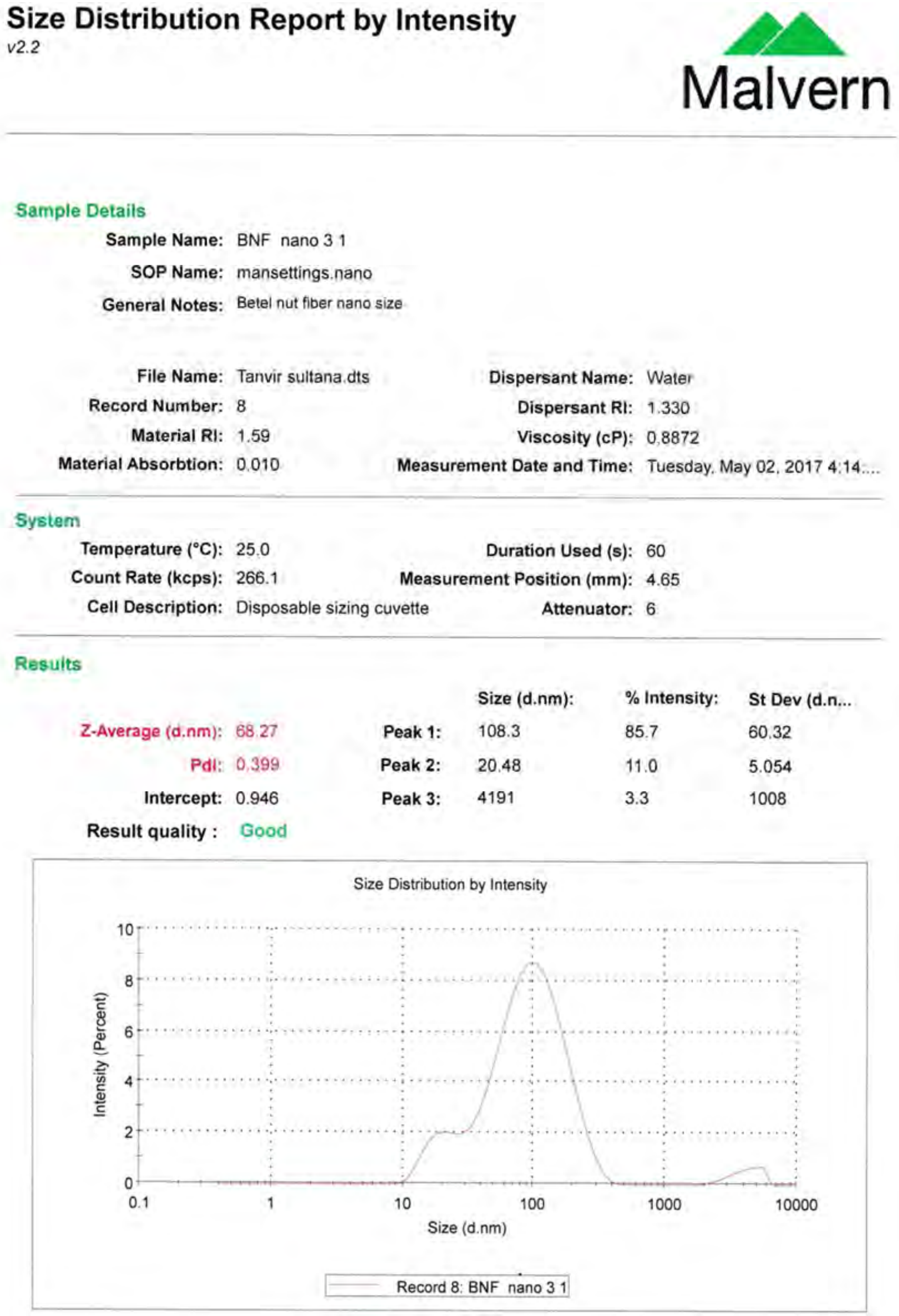
Zeta Runs: 12
Measurement Position (mm): 2.00
Attenuator: 7

Results

Zeta Potential (mV): -19.7
Zeta Deviation (mV): 7.19
Conductivity (mS/cm): 0.287
Result quality : Good

	Mean (mV)	Area (%)	St Dev (mV)
Peak 1:	-19.7	100.0	7.19
Peak 2:	0.00	0.0	0.00
Peak 3:	0.00	0.0	0.00

Figure 6.15 Zeta Potential Reports (sonicated nano cellulose)



Size Distribution Report by Intensity

v2.2

Malvern

Sample Details

Sample Name: BNF nano 3 1

SOP Name: mansettings.nano

General Notes: Betel nut fiber nano size

File Name: Tanvir sultana.dts

Record Number: 8

Material RI: 1.59

Material Absorbtion: 0.010

Dispersant Name: Water

Dispersant RI: 1.330

Viscosity (cP): 0.8872

Measurement Date and Time: Tuesday, May 02, 2017 4:14:...

System

Temperature (°C): 25.0

Count Rate (kcps): 266.1

Cell Description: Disposable sizing cuvette

Duration Used (s): 60

Measurement Position (mm): 4.65

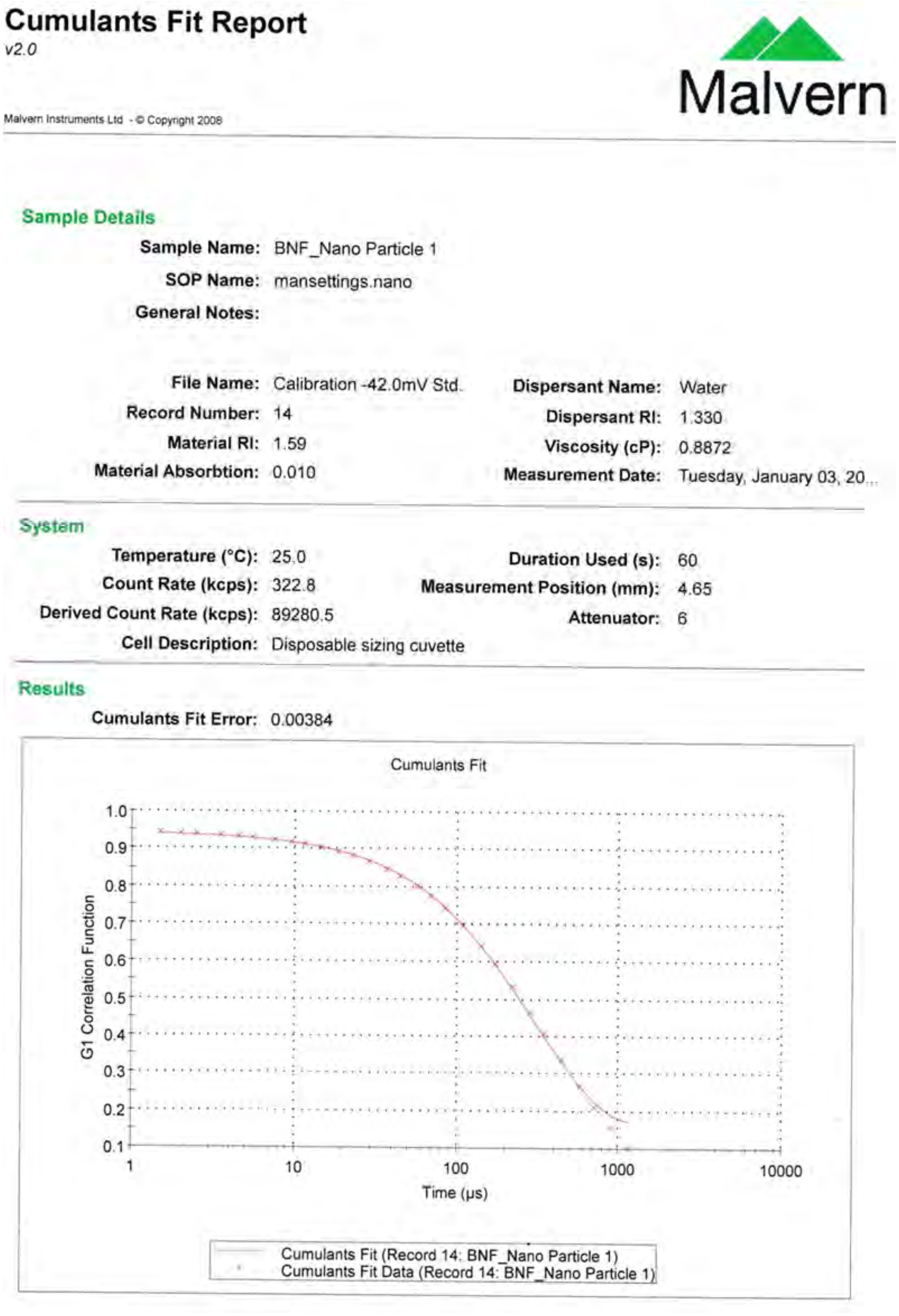
Attenuator: 6

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	68.27	**Peak 1:**	108.3	85.7	60.32
PdI:	0.399	**Peak 2:**	20.48	11.0	5.054
Intercept:	0.946	**Peak 3:**	4191	3.3	1008

Result quality : Good

Figure 6.16 Size distribution report (after sonication)



Cumulants Fit Report
v2.0

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Sample Details

Sample Name: BNF_Nano Particle 1
SOP Name: mansettings.nano
General Notes:

File Name:	Calibration -42.0mV Std.	**Dispersant Name:**	Water
Record Number:	14	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date:**	Tuesday, January 03, 20...

System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	322.8	**Measurement Position (mm):**	4.65
Derived Count Rate (kcps):	89280.5	**Attenuator:**	6
Cell Description:	Disposable sizing cuvette		

Results

Cumulants Fit Error: 0.00384

Cumulants Fit

Cumulants Fit (Record 14: BNF_Nano Particle 1)
Cumulants Fit Data (Record 14: BNF_Nano Particle 1)

Figure 6.17 Cumulants Fit Report

6.5.3 Tensile properties of composites:

The effect of fiber loading (wt%) on tensile strength and elongation properties of cellulose and nanocellulose reinforced polyvinyle alcohol composites are given in figure 6.18 and 6.19. From thise figure the increases of tensile strength with increasing the fiber loading (wt%) up to 2% fiber for both cellulose and nano cellulose reinforced PVA composite then dicreases. Nano cellulose reinforced PVA composite showed higher tensile strength than cellulose -PVA composite which indicate the good dispersion of nano fiber in PVA matrix and good interfacial adhesion between PVA and nano cellulose. Nano cellulose reinforcement in PVA composite cnhanced the tensile strength of composites. 2%cellulose and nano cellulose reinforced -PVA composite give the highest tensile strength. Elongation% dicreases with increeasing the fiber loading of composites but nano cellulose reinforced PVA composites showed higher elongation percentages .

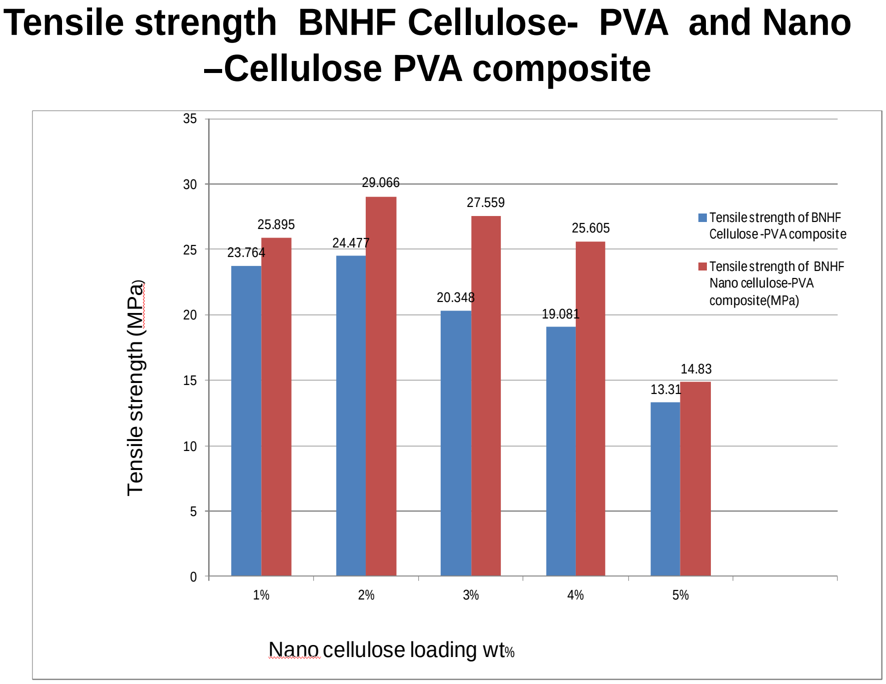


Figure- 7.18 Tensile strength of cellulose and nano cellulose reinforced PVA composite

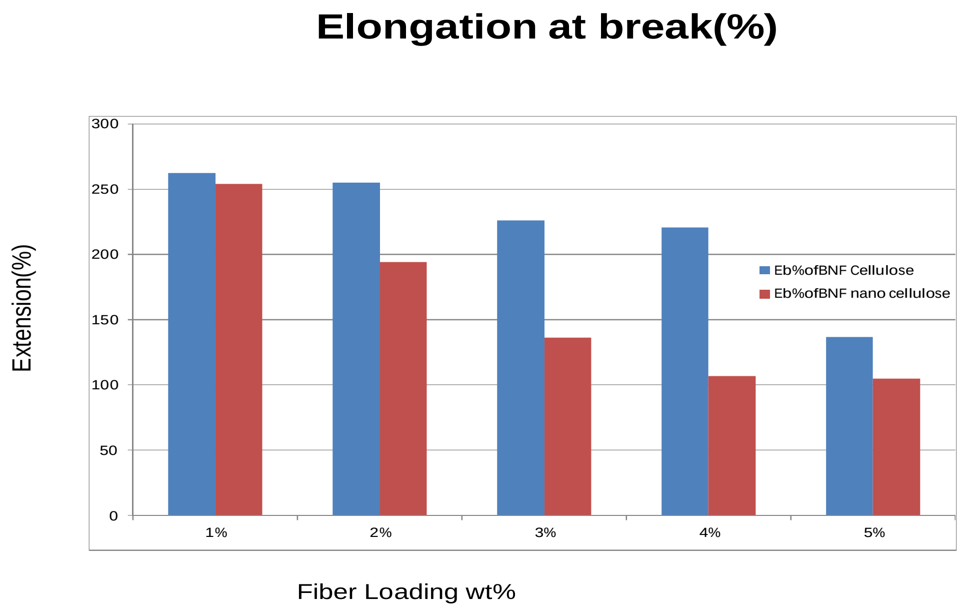


Figure-6.19 Elongation at break of cellulose and nano cellulose reinforced PVA composites

6.5.3 Thermal properties of composites:

In order to understand the thermal stability of cellulose, nano cellulose, PVA and its cellulose and nano-composites TGA measurements were carried out. Both TGA thermographs of all PVA and their nano-composites show similar patterns, i.e. three main weight loss regions. The first region (75-160°C) is due to the evaporation of water, and the weight loss of the film in these ranges is about 5-10 wt%. The second transition region (260-390°C) is due to the structural degradation of PVA nano-composite films and the total of weight loss in this range was approximately 74 wt%. The third region occurred above 390°C, due to the cleavage backbone of PVA nano-composite films or the decomposition of carbonaceous matter. The total weight loss in this range was more than 95 wt% at 500°C. Figure 6.20, 6.21, 6.22 and 6.23 shows that all PVA-cellulose and nano-cellulose composites start to degrade at higher temperatures than those of PVA. This indicates that the addition of cellulose and nano-cellulose fiber can improve thermal stability of PVA, thus confirming the enhanced thermal stability due to a strong hydrogen bonding between the hydroxyl groups of nano-cellulose and the PVA matrix.

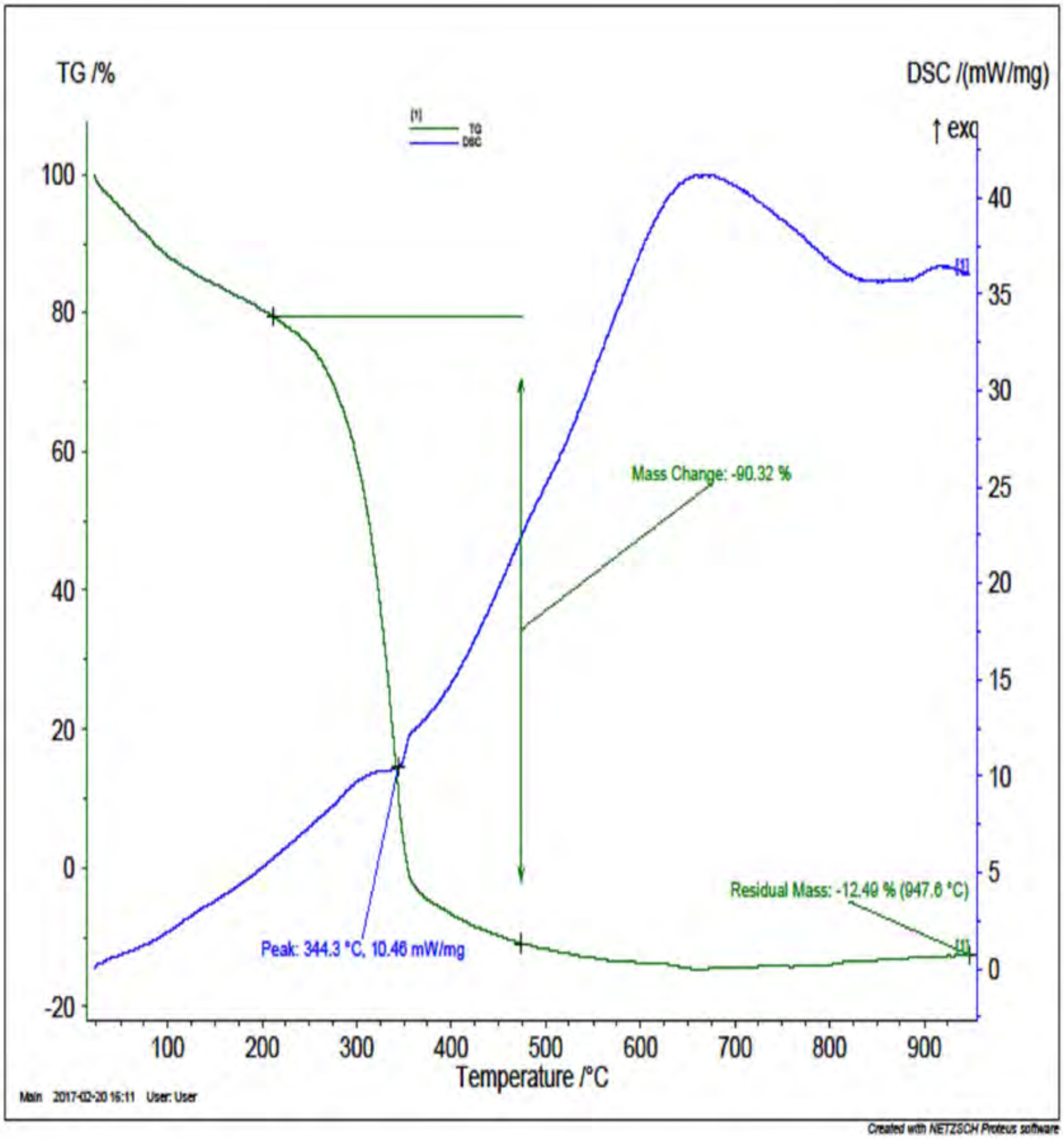


Figure6.20 TGA and DSC curve of cellulose

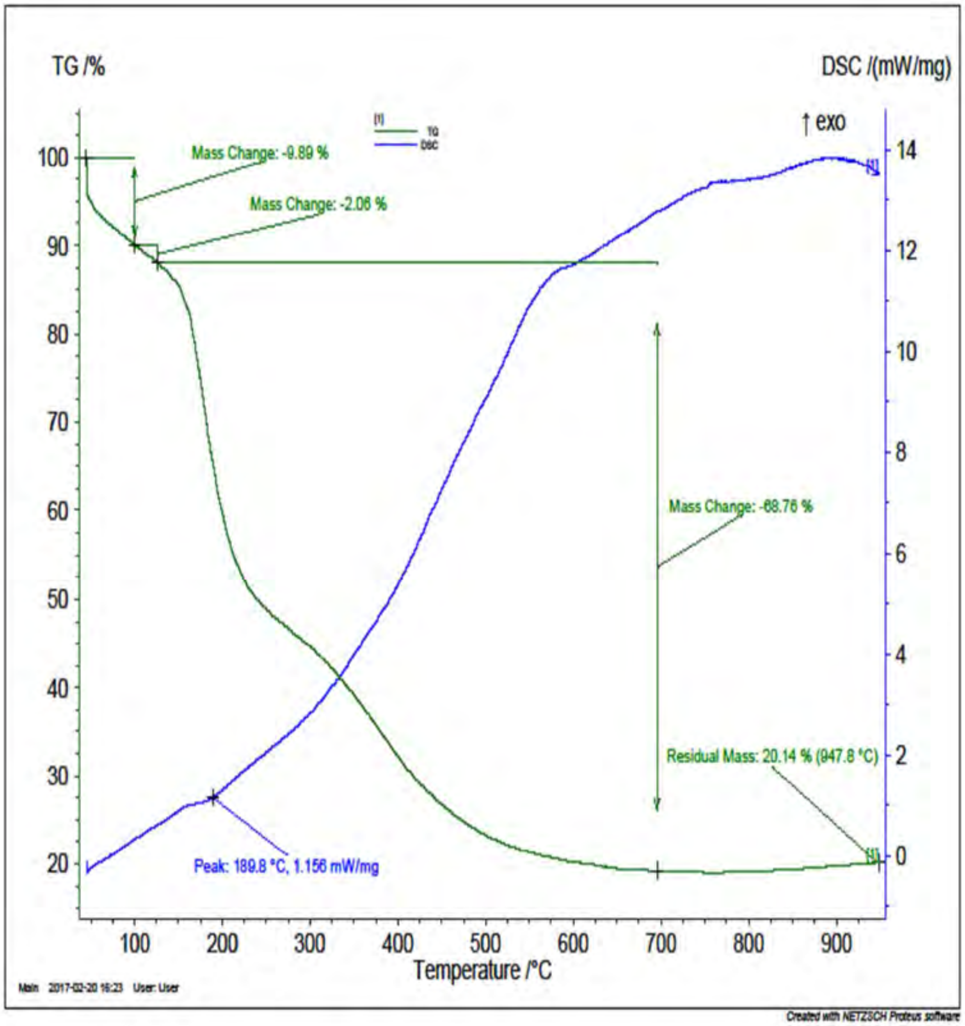


Figure: 6.11 TGA and DSC of nano-cellulose

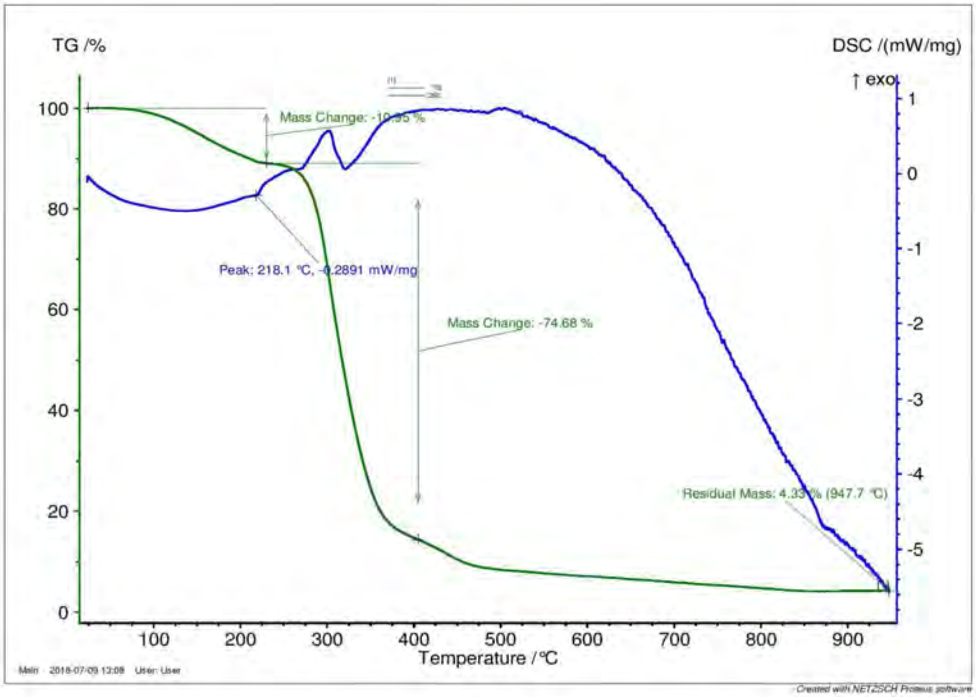


Figure 6.22 TGA and DSC curve of cellulose-PVA composite

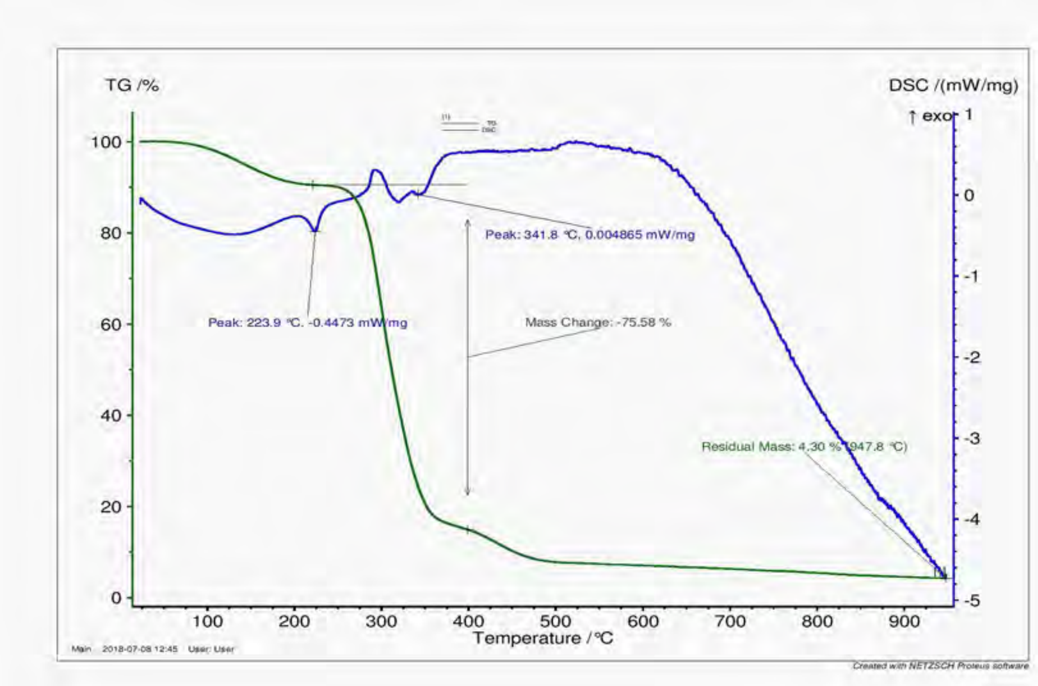


Figure 6.23 TGA and DSC curve of nano- cellulose PVA composites

6.6 Conclusion

Extraction Procedure of cellulose from BNHF was optimized and nano cellulose was successfully prepared from cellulose of BNHF. The reaction parameter of nano cellulose synthesis by acid hydrolysis was optimized. Sonication decreased the particle size of nano cellulose from 117 nm to 68 nm. Cellulose and nano cellulose has reinforcing effect in PVA matrix to prepare composites. The properties of the composites and were analyzed. Prepared nano cellulose suspension was very stable and the particle size of nano cellulose after sonication was 68.27nm. The mechanical and thermal property of prepared nano cellulose-PVA composites have higher values than cellulose -PVA composites. These materials can be used for biomedical applications and provides an opportunity for efficient utilization of waste betel nut husk fiber.

CHAPTER 7

STUDIES ON BETEL NUT HUSK MICRO FIBER REINFORCED BIODEGRADABLE POLYMER COMPOSITES

STUDIES ON BETEL NUT HUSK MICRO FIBER REINFORCED BIODEGRADABLE POLYMER COMPOSITES

7.1 Introduction

The abundant availability of natural fibrous materials presents a widespread potential that can be smartly exploited in various sectors of industry. The utilization of plastics has become a vital feature in various commodities and industries [125]. However, this vast consumption causes environmental pollution and accumulation in disposal systems as most conventional plastics are resistant to degradation. Nowadays, the development of biodegradable polymers to overcome this problem has become one of the main areas of interest of researchers. Over the past decades, the awareness of environmental impact, depletion of oils and gases resources and increasing concern of green house effect has become one of a critical factor in developing and manufacturing a new product. Beside the product cost, functionality and reliability, the element of "sustainability", "eco-friendly" and "green material" had become a major requirement in new products designing [126]. When developing a new product, it is illustrative to move between the three corners: Ecology, Equity and Economy in order to obtain a suitable balance so that each category can be fulfilled in the best way [127]. Betel nut husk fiber most abundant agricultural waste. One important biodegradable polymer is poly-acrylic acid (PAA).The unique properties of poly acrylic acid is that it exists as liquid at pH 5 and a gel at pH 7. Fiber surface treatment can enhance the mechanical performance of polymeric composites. In this study BNHF micro fiber was prepared using high energy planetary ball miller and BNHF reinforced polyacrylic acid composite was prepared successfully, analyzed and reported in this chapter.

7.2 Experimental

7.2.1 Preparation of BNHF microfiber

Betel nut fiber and $NaIO_4$ treated betel nut husk fiber were converted micro-fiber by milling process. The milling process is taken in two steps, the primary process is rotary milling and second process is high energy planetary ball milling. The Betel nut husk fibers were passed through a rotary mill fitted with a 0.08mm sieve. The collected Betel nut husk powder were milled at a speed of 4500 rpm for 20 hours using high energy planetary ball milling by SFM-1 Desk-Top planetary Ball Miller, MTI Corporation to synthesized BNHF micro fiber.

Figure 7.1: Extracted betel nut husk fiber

Figure 7.2: Betel nut husk micro fiber

Figure 7.3: Analytical Shiver

Figure 7.4: Ball miller

7.2.2 Preparation of betel nut-micro fiber and cellulose reinforced polyacrylic acid composites

Cellulose and betel nut micro fiber reinforced Poly-acrylic acid composites with different wt% were prepared by solvent casting methods. Poly-acrylic acid water solution (10 wt%, pH 5) and the high dispersed betel nut micro fiber suspension were mixed and stirred at 700 rpm for 30 min at 90°C, then dispersed by using a homogenizer for 20 min . The mixtures were degassed by allowing them with caps at room temperature overnight. Subsequently, the mixtures were cast in Petri dishes and dried at room temperature for several days. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table 7.1

Table 7.1: Different weight fraction of Cellulose, nano cellulose and betel nut micro fiber reinforced Poly-acrylic acid composites.

BNHF cellulose-PAA Composites	MicroBNHF-Poly-acrylic acid Composites	MicroTBNHF-Poly-acrylic acid Composites
05:95 (wt %) BNHF: PAA	05:95 (wt %) BNHF: PAA	05:95 (wt %)TBNHF: PAA
10:90 (wt %) BNHF: PAA	10:90 (wt %) BNHF: PAA	10:90 (wt %) TBNHF: PAA
15:90 (wt %) BNHF: PAA	15:90 (wt %) BNHF: PAA	15:90 (wt %) TBNHF: PAA
20:85 (wt %) BNHF: PAA	20:85 (wt %) BNHF: PAA	20:85 (wt %) TBNHF: PAA
25:75 (wt %) BNHF: PAA	25:75 (wt %) BNHF: PAA	25:75 (wt %) TBNHF: PAA
100 (wt %) PAA	100 (wt %) PAA	100 (wt %) PAA

7.2.4 Scanning electron microscopy (SEM) analyses

The fracture surface of tensile test sample of cellulose and nano-cellulose and betel nut micro fiber and its reinforced Poly-acrylic acid composites samples were 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 treated and untreated micro BNHF and fracture surface of tensile test sample of cellulose and betel nut micro fiber reinforced Poly-acrylic acid composites. The photographs are presented in the result and discussion section.

7.2.5 Mechanical properties of composites

Tensile test of all prepared cellulose -PAA, treated and untreated betel nut micro fiber reinforced Poly-acrylic acid composites were carried out to investigate the mechanical properties of composites according to the appropriate ASTM methods.

7.2.6. Tensile properties of the composites

The tensile test of all prepared sample of cellulose, treated and untreated betel nut micro fiber reinforced poly-acrylic acid composites were measured using a universal tensile testing machine, model: 1410 Titans, capacity: 5 kN, 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 and gauge length was 50.00 mm. Each test of the specimen was performed until tensile failure occurred. Six to ten specimens of each composition were tested and the average values were reported by calculating maximum five values. The load versus elongation curves were obtained by the instrument. The maximum load values were also recorded by the instrument which can be recalled after the completion of the test. The highest load in the tensile test gave the ultimate strength.

Figure -7.5: Tensile testing machine

7.2.7 Thermal properties of composites

The thermal properties of optimized tensile tested sample were analyzed by Simultaneous Thermal Analyzer (STA), Model No F_3 Jupiter serial no STA 449 F - 3A – 1311- M NETZSCH.

7.2.8 Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis

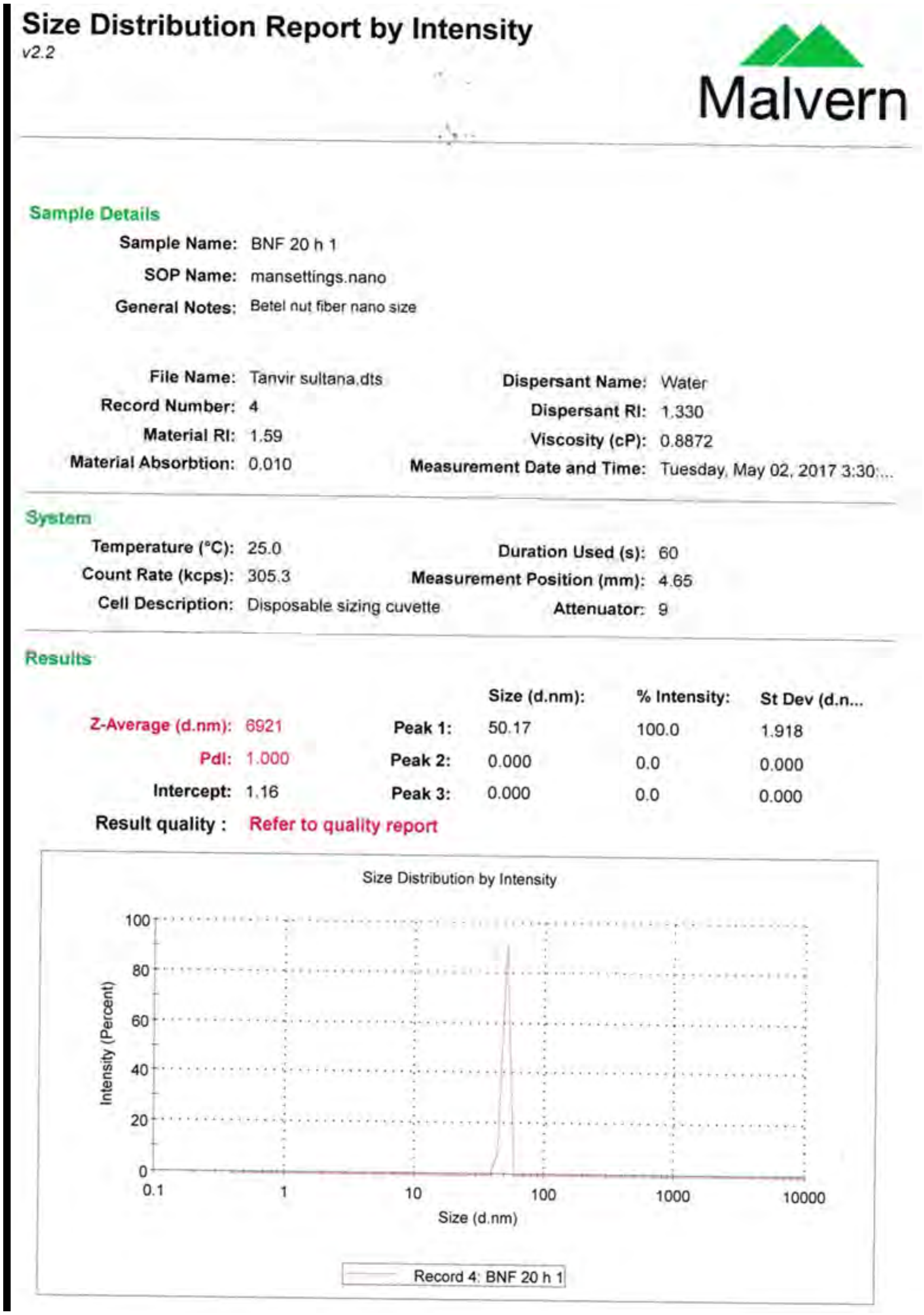
The thermo gravimetric analysis and differential scanning calorimetric analysis of cellulose, nano-cellulose and betel nut micro fiber reinforced poly-acrylic acid composites were recorded on a STA 449F3 NETZSCH thermal analysis instrument in the temperature range of 30-900 °C and the heating rate was set as 30°C min^{-1} in a nitrogen atmosphere. 10 mg of the sample has heated in the sample pan.

7.3. Result and discussion

This research work was done to study method of preparation of micro BNHF and investigate the reinforcing effect of treated and untreated betel nut micro fiber, BNHF cellulose in PAA matrix. BNHE micro fiber was prepared by mechanical milling. The mechanical and thermal properties of prepared composites were analyzed.

7.3.1 Particle size of treated and untreated micro BNHF

Particle size of ball milled BNHF were measured using Nano ZS (Malvern Instrument, UK),this instrument uses dynamic light scattering to measure the diffusion of particles moving under Brownian motion and convert this to size and size distribution. It also uses laser Doppler micro electrophoresis to apply an electric filed to the dispersion of particles which then move with a velocity related to their zeta potential. With increasing the milling time, particle size of fiber was decreased. 20 hours milling product of treated and untreated BNHF were used for composite fabrication. Average size of 20 hours ball milled BNHF was found 6921 nm.



Size Distribution Report by Intensity

v2.2

Malvern

Sample Details

Sample Name: BNF 20 h 1
SOP Name: mansettings.nano
General Notes: Betel nut fiber nano size

File Name:	Tanvir sultana.dts	**Dispersant Name:**	Water
Record Number:	4	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	Tuesday, May 02, 2017 3:30:...

System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	305.3	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	9

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	6921	**Peak 1:**	50.17	100.0	1.918
PdI:	1.000	**Peak 2:**	0.000	0.0	0.000
Intercept:	1.16	**Peak 3:**	0.000	0.0	0.000

Result quality : Refer to quality report

Figure 7.6: Particle size of BNHF

7.3.1 Scanning electron microscopic (SEM) analyses

Scanning electron microscopy (SEM) is an important tool to study the surface morphology study of materials. The surface of micro BNHF, cellulose and fracture surface of tensile specimen cellulose-PAA, treated micro BNHF-PAA and untreated micro-BNHF-PAA are examined using a field emission scanning electron microscope. From the analysis of SEM image of untreated and treated BNHF-PAA composites (Figure-7.9, 7.10) it is found that treated BNHF is more fibrous then untreated BNHF. SEM image of treated BNHF-PAA composite indicate the better interfacial adhesion between treated BNHF-PP composite as compared to untreated BNHF-PAA composite. The improved fiber–matrix interaction is found in cellulose- PAA composite. It exhibits better porous, surface morphology with very good uniformity.

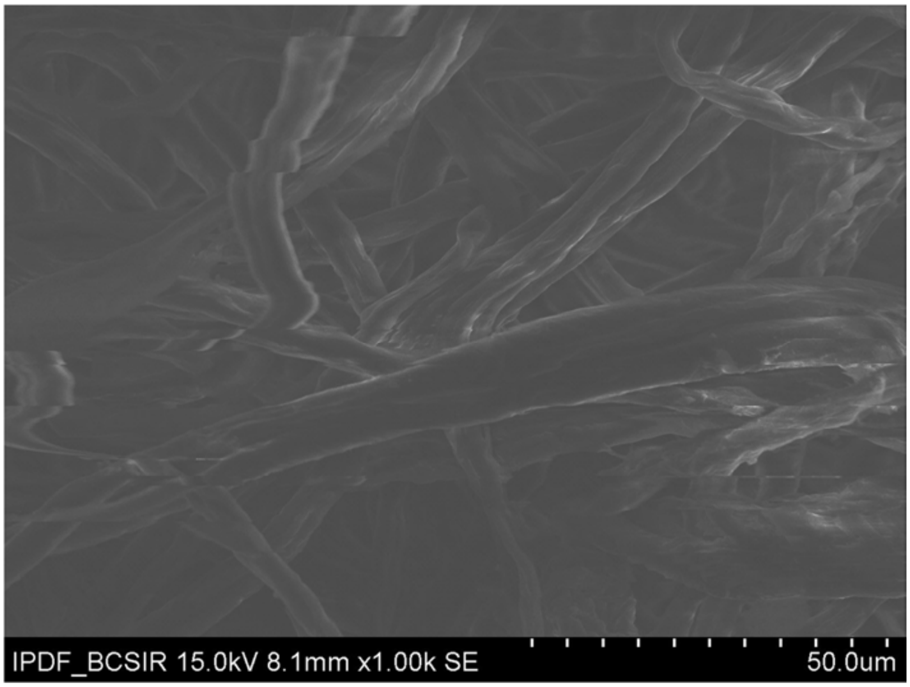


Figure: 7.7 SEM image of cellulose

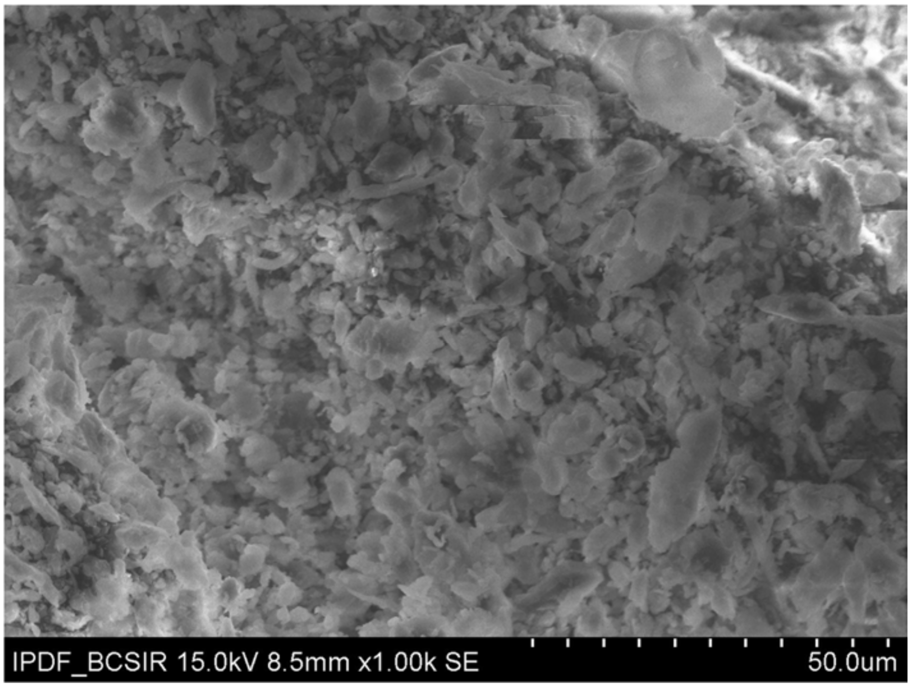


Figure: 7.8 SEM image of treated micro BNHF

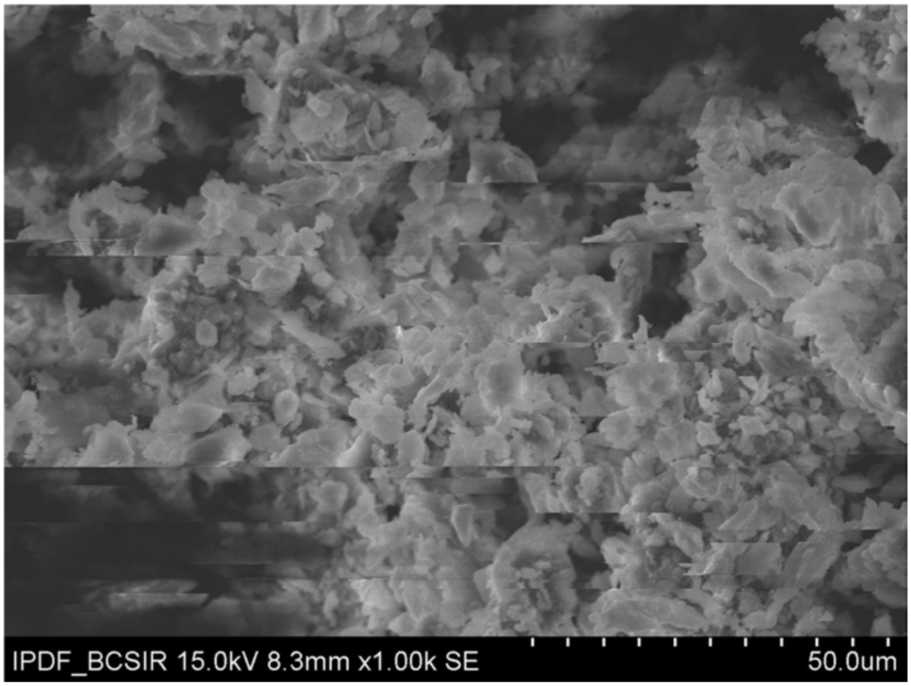


Figure: 7.9 SEM image of untreated micro BNHF

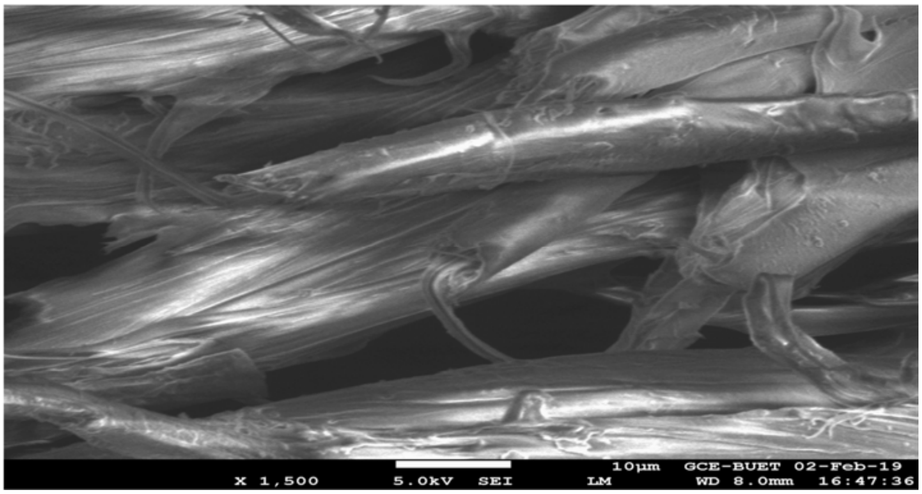


Figure7.10 SEM image of Cellulose-PAA composite

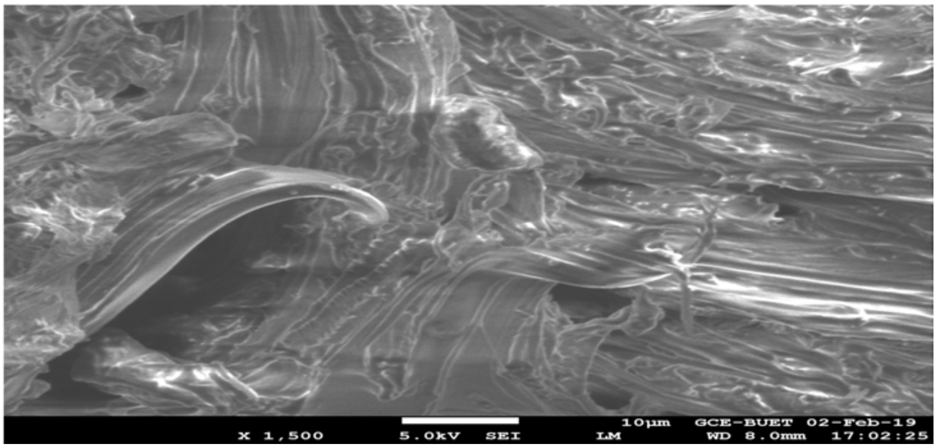


Fig.7.11 SEM image of micro TBNHF-PAA composite

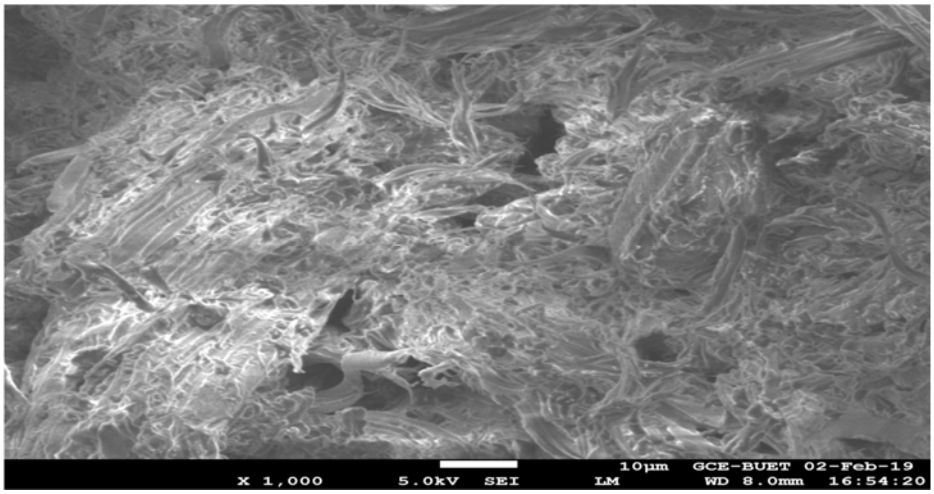


Fig.7.12 SEM image of untreated micro BNHF-PAA composite

7.3.2 Tensile Properties of PAA composites

Cellulose -BNHF, treated and untreated micro BNHF reinforced polyacrylic acid composites were prepared and their tensile strength and elongation properties were performed with standered test methodes. Results are given in figure 7.13 and 7.14 .The tensile strength increases with increaseing the fiber loading up to15% of fiber loading in composites. 15% fiber reinforced composites showed better results. Chemical treatment also have positive effect on tensile property. Enhanced tensile strength of treated micro BNHF-PAA composite indicate that good dispersion of fiber in PAA matrix and good interfacial adhesion between PAA and fiber was achived. Cellulose reinforcement in PAA composite enhanced the tensile strength. Cellulose-PAA composite showed the highest tensile strength and elongation.

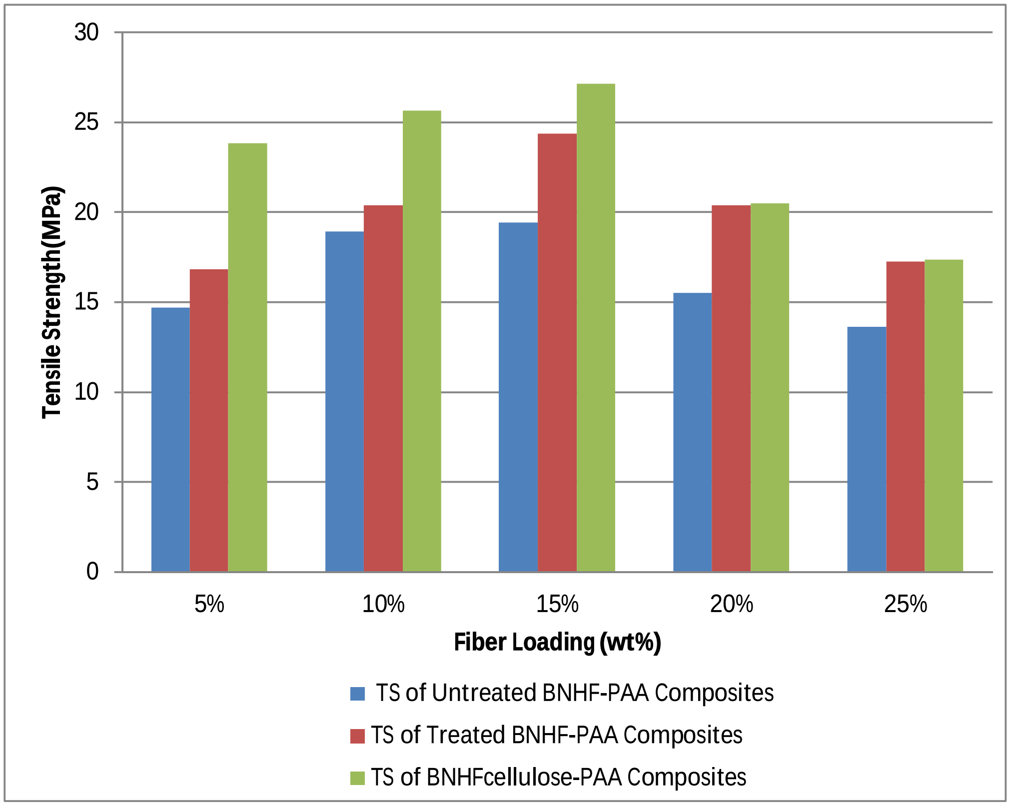


Figure 7.13 Tensile Strength Vs fiber loading (wt %) of cellulose-PAA, treated and untreated micro BNHF- PAA composite

Table 7.2 :Tensile strength of PAA composites

Fiber weight fraction (%)	TS of Untreated BNF-PAA composites	TS of Treated BNHF-PAA Composites	TS of BNHF cellulose-PAA Composites
5%	14.685	16.823	23.824
10%	18.942	20.369	25.675
15%	19.452	24.378	27.127
20%	15.543	20.391	20.532
25%	13.624	17.261	17.356

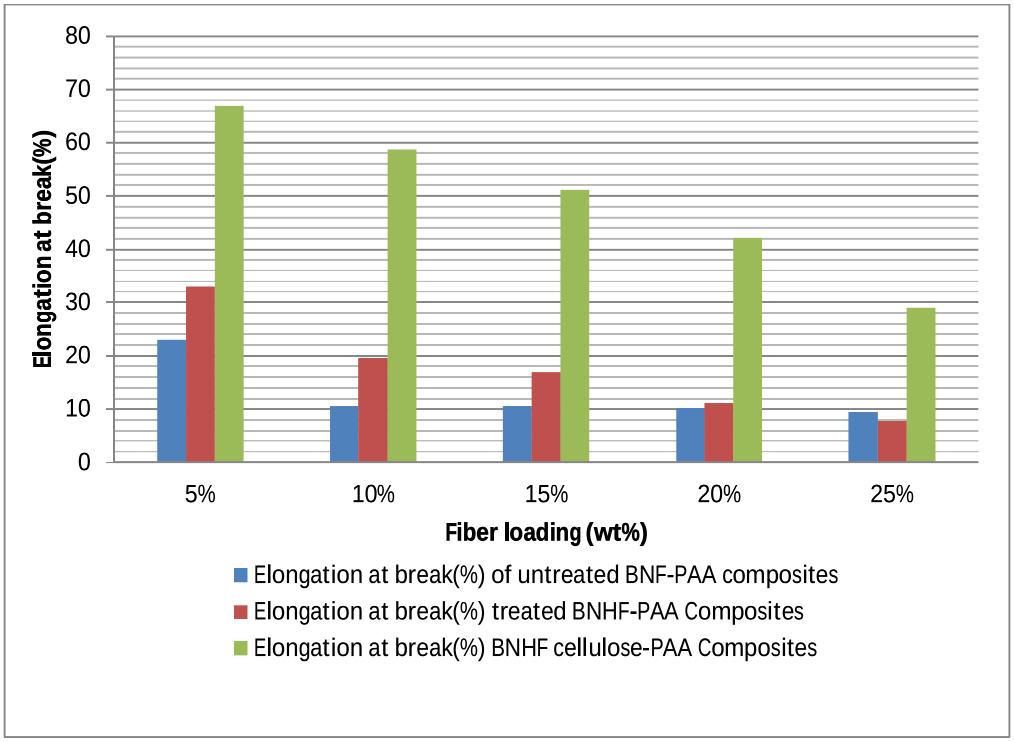


Figure 7.14 Elongation properties Vs fiber loading (wt %) of BNHF- PAA composites

7.3.3 Thermal properties of composites:

The thermal stability of cellulose, micro BNHF, PAA and its composites were measured by TGA and DSC analysis. PAA and its composites showed similar thermal degradation patterns, i.e. three main weight loss regions. The first region (55-180°C) is due to the evaporation of water, and the weight loss of the weight in these ranges is about 5-10 wt%. The second transition region (200-350°C) is due to the structural degradation of PAA nanocomposite films and the total of weight loss in this range was approximately 83 wt%. The third region occurred above 390°C, probably due to the cleavage backbone of PAA composite films. The total weight loss in this range was more than 90 wt% at 900°C. Figure 7.15, 7.16, 7.17 and 7.18 shows thermal properties of cellulose, untreated micro BNHF-PAA composite, treated micro BNHF-PAA composite, and cellulose PAA composites respectively.

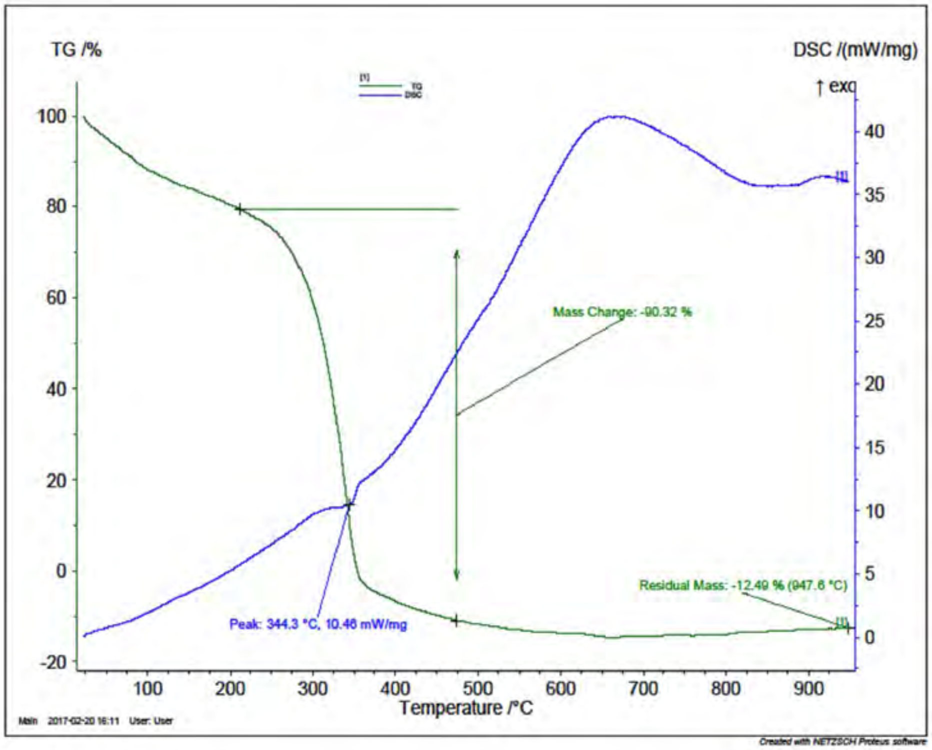
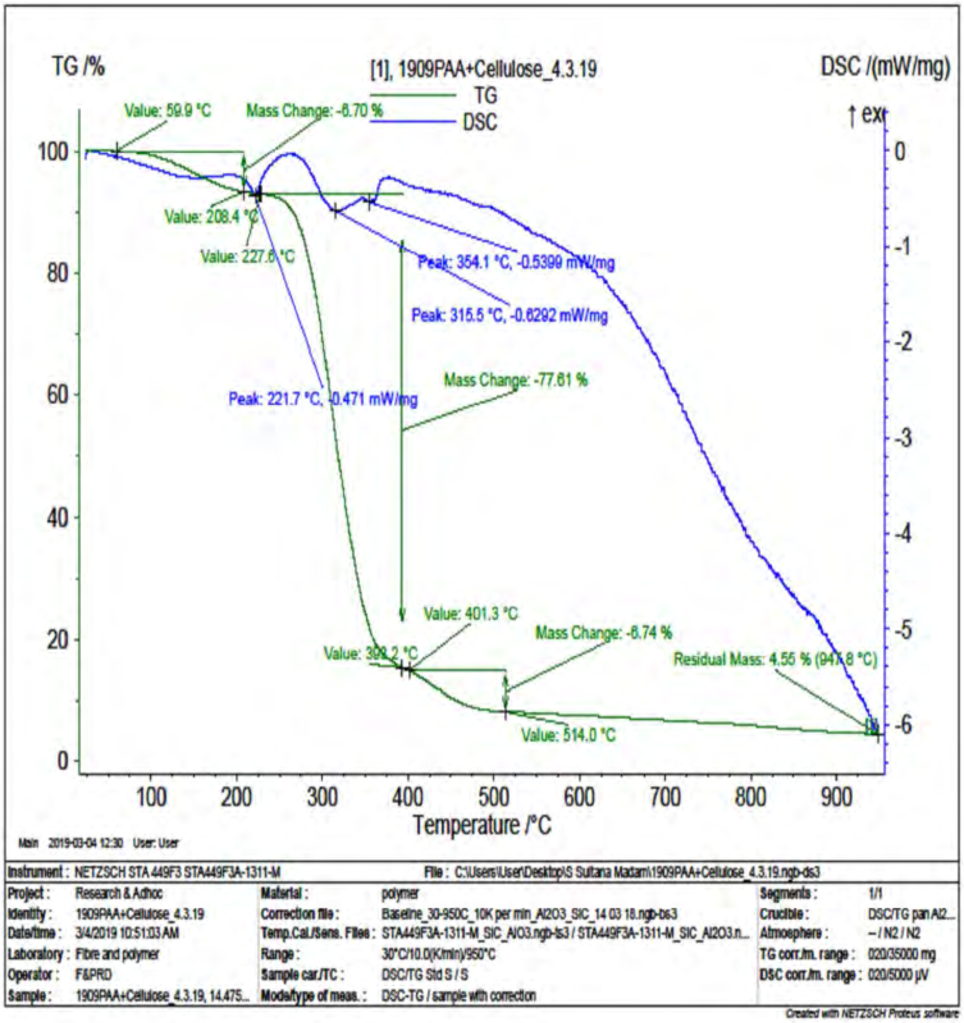


Figure7.15 TGA and DSC curve of cellulose



Instrument : NETZSCH STA 449F3 STA449F3A-1311-M
File : C:\Users\User\Desktop\S Sultana Madam\1909PAA+Cellulose_4.3.19.ngb-ds3

Project : Research & Adhoc
Identity : 1909PAA+Cellulose_4.3.19
Date/time : 3/4/2019 10:51:03 AM
Laboratory : Fibre and polymer
Operator : F&PRD
Sample : 1909PAA+Cellulose_4.3.19, 14.475...

Material : polymer
Correction file : Baseline_30-950C_10K per min_Al2O3_SIC_14 03 18.ngb-bs3
Temp.Cal./Sens. Files : STA449F3A-1311-M_SIC_AlO3.ngb-ts3 / STA449F3A-1311-M_SIC_Al2O3.n...
Range : 30°C/10.0(K/min)/950°C
Sample car./TC : DSC/TG Std S / S
Mode/type of meas. : DSC-TG / sample with correction

Segments : 1/1
Crucible : DSC/TG pan Al2...
Atmosphere : -- / N2 / N2
TG corr./m. range : 020/35000 mg
DSC corr./m. range : 020/5000 µV

Figure7.16 TGA and DSC of cellulose- PAA composite

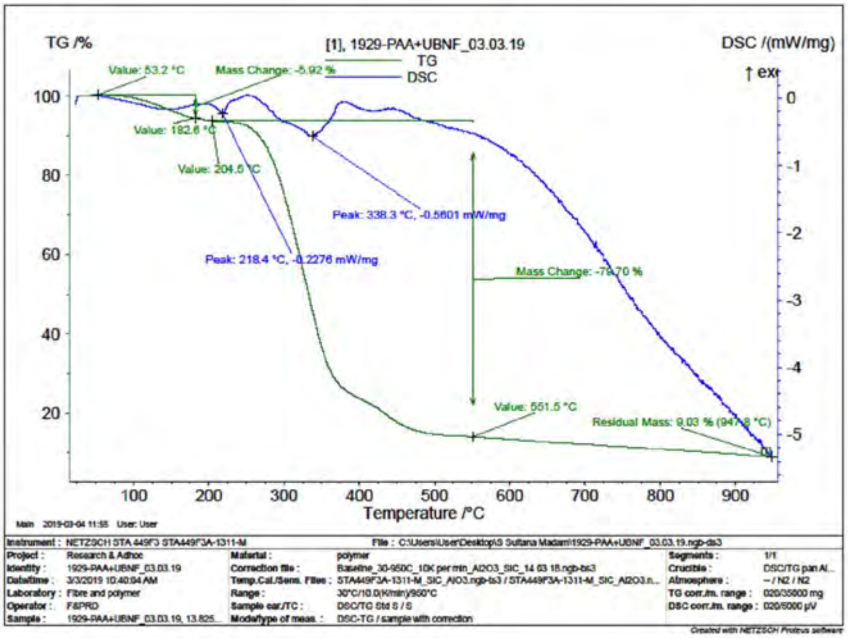


Figure7.17 TGA and DSC of PAA-untreated micro BNHF composite

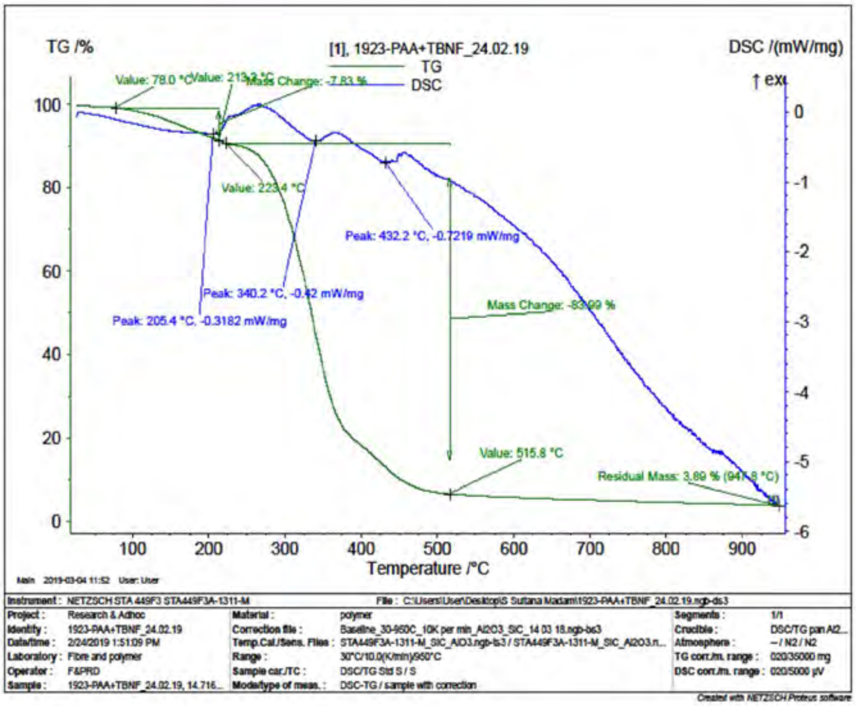


Figure7.18 TGA and DSC curve of PAA-treated micro BNHF composite

7.4 Conclusion

Micro betel nut husk fibers were successfully prepared by mechanical milling process. Polyacrylic acid based composites were prepared by reinforcing with cellulose of BNHF, untreated micro BNHF and treated micro BNHF respectively. Mechanical, thermal and morphological properties of all fiber and prepared composites were studied. Highest tensile strength were found for 15 wt% cellulose-PAA, treated micro BNHF-PAA, and untreated micro BNHF-PAA composite respectively. Thermo gravimetric analysis of are almost same for cellulose BNHF-PAA, treated micro BNHF-PAA, and untreated micro BNHF-PAA composites. SEM image of treated BNHF micro fiber reinforced PAA composites showed good dispersion of fiber and matrix in composites. This study of betel nut husk fiber provides an opportunity for efficient utilization of such a material which otherwise has become a threat of environment due to its burning.

SUMMARY & REFFERENCES

SUMMARY

The experimental determination and theoretical interpretation of these studies is summarized below:

In this research work different types of betel nut *(Areca catechu)* husk fiber reinforced thermoplastics were prepared by compression moulding technique. Waste betel nut husk fibers were extracted from betel nut fruit and the chemical composition of fibers were analyzed. To improve the properties of BNHF reinforced thermoplastics, different types of chemical treatment were carried out. The effects of this treatment on physico-mechanical and thermal properties of the composites were studied. Different types of non-biodegradable polymer such as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) were used as matrix material.

BNHF were extracted and used to prepare sodium hydroxide treated and untreated BNHF reinforced low density polyethylene (LDPE) composites. Extracted and washed BNHF were treated with sodium hydroxide to improve their adhesion to LDPE matrices. Chemical treatment of BNHF with sodium hydroxide was carried out and the change in the functional group of treated BNHF was studied by FT-IR spectroscopic analyses. Sodium hydroxide treated and untreated BNHF were used in this case of research as reinforcing materials to find out their effects on LDPE composites. Different types of compression molded BNHF-LDPE composites were prepared using different weight percent of treated and untreated BNHF with compositions 5, 15, 20, 25 and 30 wt% in LDPE. The tensile, water absorption and morphological properties were studied for all composites. Enhancement in the tensile, water absorption and morphological properties were shown in the treated BNHF -LDPE composites. Alkaline treatment reduced the water absorption and increased the tensile properties of treated betel nut husk fiber-LDPE composites. Morphological analyses showed the evidence of stronger interfacial adhesion between the fibers and matrices in the alkali treated BNHF-LDPE composites than the untreated BNHF-LDPE composites.

BNHFs were used as reinforcing materials to prepare high density polyethylene (HDPE) matrix based composites. Extracted fibers were also chemically treated with sodium *meta*-periodate to enhance its compatibility with the HDPE matrix. Treated BNHF characterized by Fourier transform infrared (FTIR) spectroscopic analyses. Different wt.

percentages (5, 10, 15, 20, 25 and 30%) of both treated and untreated betel nut husk fibers were used to prepare compression moulded HDPE composites to achieve better interfacial bonding and mechanical properties. Tensile strength, elongation at break, TGA-DSC, Scanning Electron Microscopy (SEM) etc properties were analyzed for all treated and untreated betel nut husk fibers reinforced HDPE composites. It was found that 10% (w/w) treated fiber reinforced HDPE composites showed better results than all other composites.

Extracted BNHFs 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. 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 and morphological properties of the treated BNHF-PP composites than untreated BNHF-PP composites. Almost similar thermal properties were found for both treated and untreated BNHF-PP composites.

The reinforcing effect of betel nut husk fiber (BNHF) in polystyrene (PS) matrix was also studied in this research work. Polystyrene is an aromatic polymer and both polypropylene and polystyrene are similar in applications except some specific applications of them. Betel nut husk fibers were chemically modified with sodium hypochlorite and both treated and untreated BNHFs were used for composite fabrication as reinforcing material with polystyrene in different weight fraction. Sodium hypochlorite treatment of BNHF reduces the moisture absorption property and improves the interfacial adhesion between fibers and matrices in composites. So, treated BNHF-PS composites showed better compatibility between the fibers and matrices than untreated BNHF-PS composites by the analytical results of tensile, thermal and morphological characterization. Extraction process of cellulose from BNHF has been improved and optimized. Preparation of nano cellulose from cellulose of BNHF has also been developed and optimized. The size of synthesized nano cellulose was 68 nm. It was characterized by SEM, FTIR analyses and nano zetasizer. Nano cellulose has many potential applications including biodegradable composites. PVA based biodegradable composites were prepared by reinforcing with cellulose and nano cellulose of BNHF. Higher tensile and thermal properties were found for nanocellulose - PVA composites than cellulose PVA composite. SEM observation also proved the strong bonding between nano fiber and PVA in nano composites than cellulose -PVA composites. A comparative investigation has been done on the prepared cellulose-PAA, treated and untreated micro BNHF-PAA composites. From these biodegradable composites, cellulose of BNHF reinforced PAA composites showed better tensile, thermal and morphological properties.

BNHF is an agricultural waste material and the production techniques of all treated betel nut husk fibers, nanofibers reinforced matrix polymer composites and nano-composites are comparatively simple. So, these composites and nano-composites will be competitive and cost-effective products for industrial purposes.

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APPENDIX

LIST OF PUBLICATIONS

Journal Papers:

1. Tanvir, S., Shahin. S., Husna, P, N., Wahab, K, Md., Effect on the Properties of Low -density Polyethylene Composites Reinforced with Treated and Untreated Betel Nut Husk Fibers, *International Journal of Advanced Research*, vol 6(2), pp 202-209, 2017
2. Tanvir, S., Shahin. S., Husna, P, N., Wahab, K, Md., Characterization of Sodium meta-Periodate Modified Betel Nut Husk Fibers Reinforced HDPE Composites**,** *European Journal of Advances in Engineering and Technology*, vol.5(8) pp 677-68, 2018.
3. Tanvir, S., Shahin. S., Husna, P, N., Wahab, K, Md., Impact on Morphological, Physicomechanical and Thermal Properties of Polypropylene Composite Reinforced with Chemically Modified Betel Nut Husk Fiber, *European Journal of Advances in Engineering and Technology*, *Int. J. Adv. Res***.** vol**.**7(2), pp 1111-1119. 2019.

Conference Papers:

1. Physico-mechanical Thermal Properties of Betel Nut Fiber Reinforced Polymer Composites, 24th Global Organic and Inorganic Chemistry Conference 2018, July 18-19, Atlanta, USA.
2. Effect on the Properties of Low -density Polyethylene Composites Reinforced with Treated and Untreated Betel Nut Husk Fibers, International Chemical Congress 2008, March 08-10, Nepal.
3. Mechanical Thermal and Morphological Study of Betel Nut Husk Nano-cellulose Reinforced PVA Composites, Bangladesh Chemical Congress 2018, October 17-19, 2018, Dhaka Bangladesh.

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RESEARCH ARTICLE

EFFECTS ON THE PROPERTIES OF LOW DENSITY POLYETHYLENE COMPOSITES REINFORCED WITH TREATED AND UNTREATED BETEL NUT HUSK FIBERS.

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Abstract

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Betel nut *(Areca catechu)* husk fibers (BNHF) were extracted and used to prepare sodium hydroxide treated and untreated BNHF reinforced low density polyethylene (LDPE) composites. Extracted and washed BNHF were treated with sodium hydroxide to improve their adhesion to LDPE matrices. Chemical treatment of betel nut husk fibers with sodium hydroxide was carried out and the change in the functional group of treated BNHF was studied by FT-IR spectroscopic analyses. Sodium hydroxide treated and untreated BNHF were used in this case of research as reinforcing materials to find out their effects on LDPE composites. Different types of compression molded BNHF-LDPE composite were prepared using different weight percent of treated and untreated BNHF with compositions 5, 15, 20, 25 and 30 wt% in LDPE. The tensile, water absorption and morphological properties were studied for all composites. Enhancement in the tensile, water absorption and morphological properties were shown in the treated BNHF -LDPE composites. Alkaline treatment reduced the water absorption and increased the tensile properties of treated betel nut husk fiber-LDPE composites. Morphological analyses showed the evidence of stronger interfacial adhesion between the fibers and matrices in the alkali treated BNHF-LDPE composites than the untreated BNHF-LDPE composites.

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Introduction:-

Over the last few years, as a result of the growing environmental awareness about greenhouse gas emissions and environmental pollution, manufacturers and scientists are keen to study novel environmental friendly materials. Intensive research and developments have been carried out by many researchers, engineers and scientists to develop biodegradable and sustainable composites using natural fibers (1). Synthetic fibers like carbon and glass though exhibits excellent mechanical, thermal properties and durability but difficulties in disposal processing which produce lot of black smoke and bad odors. In order to overcome this problem, necessity of natural fibers based composites is demanding to make the world ‘green’. The composites referred to as bio-composites which are combine natural fibers such as kenaf, jute, hemp and sisal with biodegradable or non-biodegradable polymers (2). Natural fibers are cheaper and substitute for synthetic fibers. Compared with synthetic fibers, natural fibers have many advantages like low density, cheaper, high strength, high stiffness, no harm to environment, renewable sources and biodegradable properties (3).

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In this research work, betel nut husk fibers were used as reinforcing materials with thermoplastics to make composites. Betel/ Areca nut is the seed of Areca palm and *Areca catechu* is a species of palm which grows mainly in the Southeast Asia and South Asia region. It is abundantly available in Bangladesh as waste fibers of betel nut fruits. Composites made with natural fibers offers use in various applications such as aerospace, leisure, construction, households, sport, packaging, automotive industries by replacing metallic components due to their inherent light weight and immune to corrosion(2, 4). However due to hydrophilic nature of natural fibers give rise to incompatibility between fiber and polymer in composites. This leads to undesirable properties of the composites. Hence fiber surface is modified with coupling agent in order to have interfacial adhesion between fiber and matrix(2). Natural fibers are composed of cellulose, hemicelluloses, lignin, pectin, wax, and ash. Chemical treatment of the natural fibers can overcome the limitations due to hydrophilic nature by cleaning the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness(5). Swain *et al.* worked on abrasive wear behavior of surface modified jute fiber reinforced epoxy composite (6). They reported that benzoyl chloride treated based composite notably gave better abrasive wear resistance than the untreated and alkali treated based composite. This was due to the high-interfacial adhesion and low-composite porosity. Siregar *et al.* investigated and reported on effect of the alkali (NaOH) treatment on the mechanical properties of pineapple leaf fiber (PALF) reinforced high impact polystyrene (HIPS) composites(7). They obtained highest mechanical properties value for the short PALF treatment with NaOH concentration of 4%. Prasad *et al.* investigated on effect of the alkali (NaOH) treatment followed by bleaching with H_2O_2 on tensile properties of short jute fiber reinforced polypropylene and reported about small increase in the strength of composite with treated fibers compared to composite with untreated fibers(8). In a review by Ram *et al.*, it is shown that some works were done in the field of replacing existing industrial safety helmet material acrylonitrile butadiene styrene (ABS), with variety of polymer composites(9). The study shows that hybrid polymer composites have good potential to replace ABS in safety helmets. Desai *et al.* also reported in a review on effectiveness of Areca (betel) fiber as a reinforcing material in eco-friendly composites(10). The review report states that in the recent past, it has been noticed that not much appreciable research been carried out on the optimized surface treatment, manufacturing techniques, and product application using the areca fibers. Hence, there are more opportunities to develop economical and ecologically superior engineered material by utilizing these areca fibers and its composites.

In this piece of research work, betel nut husk fibers were treated with sodium hydroxide to improve its adhesion with LDPE. The aim of this research is to find out the effects of treated and untreated BNHF loading on the physico-mechanical properties of betel nut husk fiber-LDPE composites.

Experimental Part:-

Materials:-

Low density polyethylene (LDPE) was purchased from Polyolefin Company Pvt. Ltd., Singapore. Melting point of this LDPE was found to be 115°C. Betel nuts were collected from Barisal, Bangladesh and the BNHF were extracted from these betel nuts. Sodium hydroxide was collected from Merck, Germany.

Processing of betel nut husk fibers:-

Betel nut husk fibers were extracted from collected betel nuts. The fibers were cutted into 1 to 3 mm pieces. Fibers were sieved and dried after washing.

Surface modification of betel nut husk fibers(BNHF) by sodium hydroxide:-

Aqueous solution of sodium hydroxide (6%) was prepared to conduct reaction with BNHF. Dried betel nut husk fibers were immersed in that solution for one hour at room temperature approximately 25°C and the fibers were stirred occasionally with a glass rod. Fiber to liquor ratio was 1:20 (w/v). The alkali treated BNHF were thoroughly washed in tap water and then immersed in distilled water for 24 hrs. Finally, fibers were washed with distilled water to remove the alkali completely and the pH was measured until it was found neutral. The alkali treated BNHF were dried in air first then further dried in an oven to get a constant weight.

FT-IR spectroscopic characterization of untreated and treated betel nut husk fibers:-

The infrared spectra of untreated and treated BNHF were recorded on a FT-IR/NIR Spectrometer (Forntier, Perkin Elmer, USA). To take FT-IR, the treated and untreated betel nut husk fibers were used to make pellet with potassium bromide. Approximately 0.5 mg of dried and powdered BNHF was mixed with approximately 100 mg 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. IR spectra were obtained in the printed form.

Fabrication of composites by compression moulding technique:-

Before fabrication of composites treated and untreated betel nut husk fibers were dried in an oven at 80 °C for 24 hours. LDPE was granulated in a grinder and dried at 80 °C for 3 hours.

The LDPE 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 150 °C. These procedures were followed for all the composites fabricated in the ratio of composition shown in the Table I:

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

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

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.

Water absorption test of composites:-

Sodium hydroxide treated and untreated betel nut husk fiber-LDPE composites were used to conduct water absorption tests. The dimension of each test specimens were 39 mm x 10 mm x 4 mm and the testing was carried out following ASTM D 570-99 standard method. The composite specimens were immersed in boiling distilled water bath according to ASTM D 570-99 standard method. Three specimens were taken to calculate average results and presented in the results and discussion section.

Tensile properties of the composites:-

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

Results and Discussion:-

FTIR spectroscopic characterization of untreated and alkali treated betel nut husk fibers:-

The FTIR spectra of untreated and alkali treated BNHF are shown in figure 1. Sodium hydroxide treatment was done to improve the adhesion between fiber and matrix in the composites. The characteristic bands of untreated and alkali treated BNHF are summarized in table II and table III respectively. It is clear from the figures that the absorption band at 1738.37 cm^{-1} of untreated BNHF have disappeared completely in the treated BNHF. This indicates that the alkali treatment of betel nut husk fibers had removed the impurities, hemicelluloses and part of lignin. The similar FT-IR results were also reported[11] by Oushabi *et al* in the case of alkali treated date palm fibers.

Table II:-FTIR spectral data of untreated raw betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3422.40	-OH stretching from the cellulose, hemicellulose and lignin
~ 2919.57	C-H vibration in aromatic ring and alkanes
~1738.37	C=O stretching from the lignin and hemicellulose
~ 1610.31	C=C stretching from aromatic in-plane
~ 1513.87	C=C stretching in aromatic skeletal ring due to lignin
~ 1428.43	C-C stretching from aromatic ring

Table III:-FTIR spectral data of sodium hydroxide treated raw betel nut husk fiber

Position of bands (cm^{-1})	Peak assignments
~ 3423.26	-OH stretching from the cellulose, hemicellulose and lignin
~ 2922.18	C-H vibration in aromatic ring and alkanes
~ 1609.86	C=C stretching from aromatic in-plane
~ 1509.06	C=C stretching in aromatic skeletal ring due to lignin
~ 1425.39	C-C stretching from aromatic ring

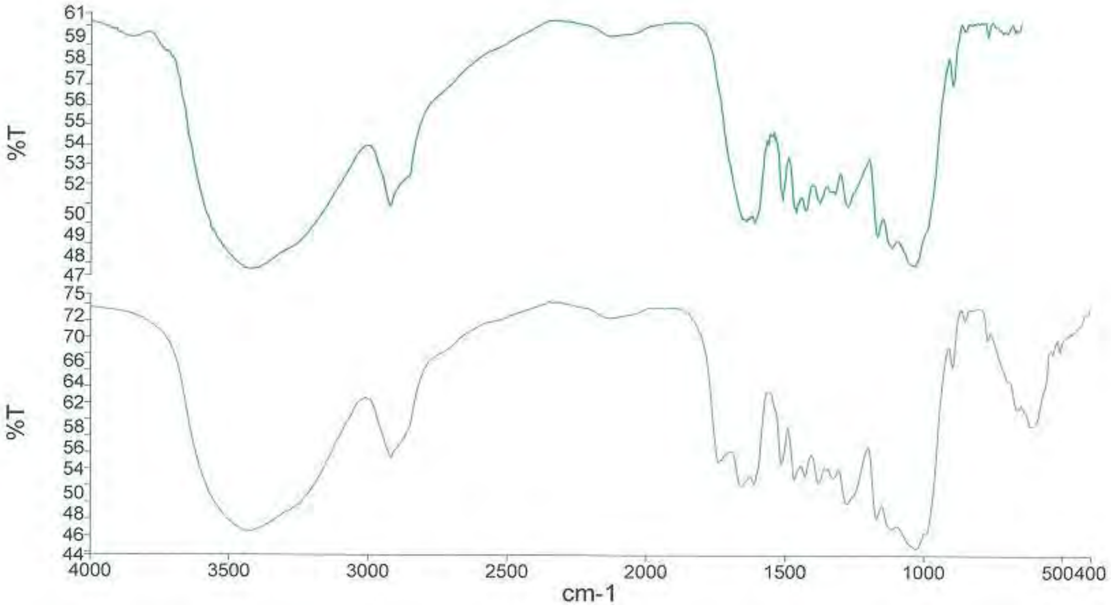

Fig 1:- FTIR spectra of untreated betel nut husk fiber (lower) and sodium hydroxide treated betel nut husk fiber (upper)

Tensile properties of untreated and treated betel nut husk fiber reinforced low density polyethylene (LDPE) composites:-

Tensile strength and elongation at break:-

The tensile strengths of the untreated and treated BNHF-LDPE composites are shown in figure 2. It is observed from the figure that the tensile strengths of the composites increased up to 10 wt% fibers loading & then decreased. The elongations at break of untreated and treated BNHF-LDPE composites are shown in figure 3. Elongation at break of all composites decreases with increasing fiber loading (Fig.3). Tensile properties of all treated BNHF-LDPE composites are higher than that of untreated BNHF-LDPE composites. The tensile strength and ductility were better in the case of BNHF-LDPE composites than that of untreated BNHF-LDPE composites. This may be the reason for the improvement of the fiber-matrix interfacial adhesion in composites made by alkali treatment.

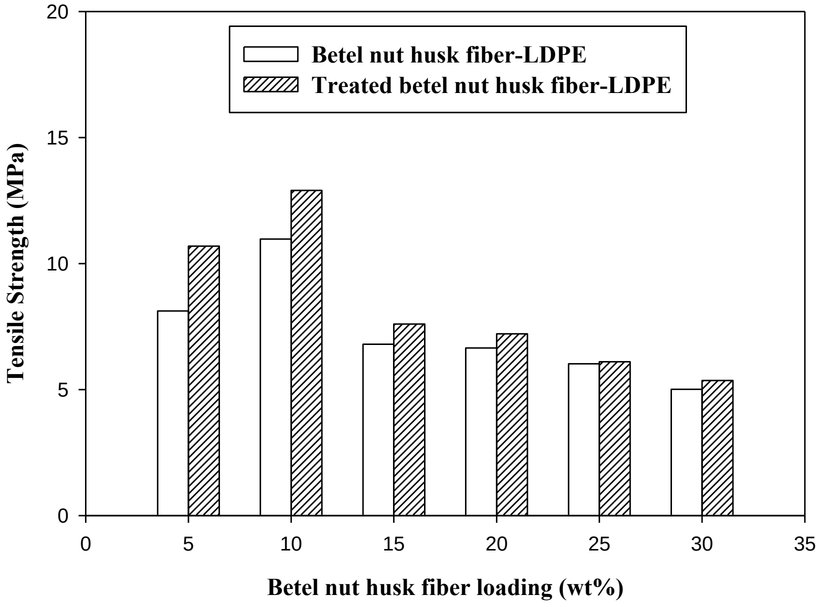

Fig 2:- Tensile strength (MPa) vs betel nut husk fiber (wt%) curves for raw & treated betel nut husk fiber-LDPE composites

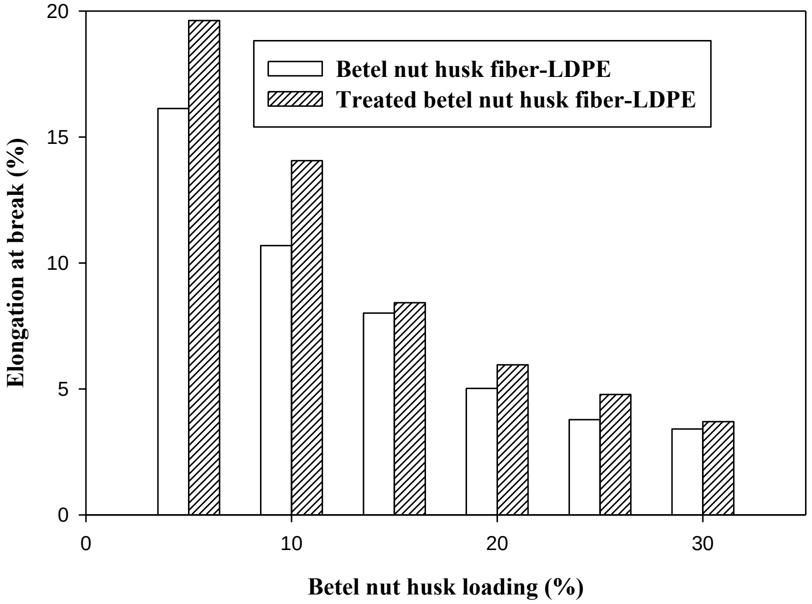

Fig 3:- Elongation at break(%) vs betel nut husk loading (%) curves for raw & treated betel nut husk-LDPE composites

Water absorption:-

Water absorption test results of all treated and untreated BNHF-LDPE composites are shown in Fig.4. It is clear from the figure that water absorption increases with increasing fiber loading for all composites but water absorption of untreated BNHF-LDPE composites is higher than that of treated betel nut husk fiber-LDPE composites. This may be due to the hydrogen bonding formation of water molecules with the hydroxyl groups in the constituents of lignin, hemicelluloses and cellulose of untreated BNHF. Alkali treatment of BNHF removes their hemicelluloses completely and reduces the lignin part. So treated betel nut husk fiber-LDPE composites show less water absorption than untreated BNHF-LDPE composites. So dimension stability will be higher for treated betel nut husk fiber-LDPE composites than untreated BNHF-LDPE composites.

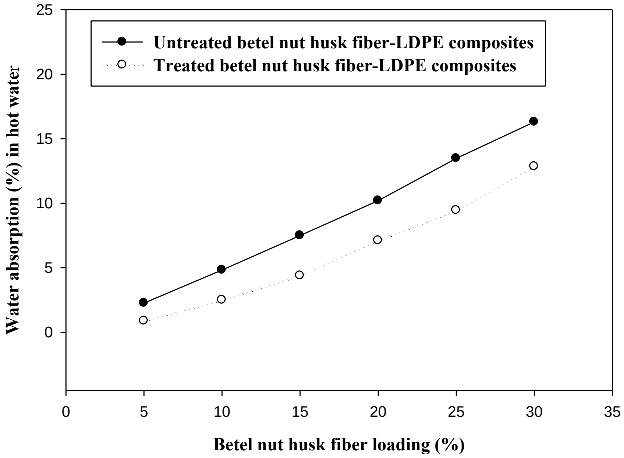

Fig 4:- Hot water absorption (%) vs fiber loading (%) curves for untreated and treated betel nut husk fiber-LDPE composites

Morphological analyses:-

The Scanning electron microscopy (SEM) images of treated and untreated betel nut husk fiber-LDPE composites are shown in figure 5 and 6 respectively. The SEM Micrograph of fracture surfaces of 25 wt-% alkali treated BNHF-LDPE composite shows uniform dispersion and better interfacial adhesion between the fiber and matrix in figure 6. The weak interfacial adhesion between the fiber and matrix is observed in figure 5 which represents the fracture surface of 25 wt-% untreated BNHF-LDPE composites. So it may be concluded that alkali treated fibers are able to improve the compatibility between the fiber and matrix in the composites.

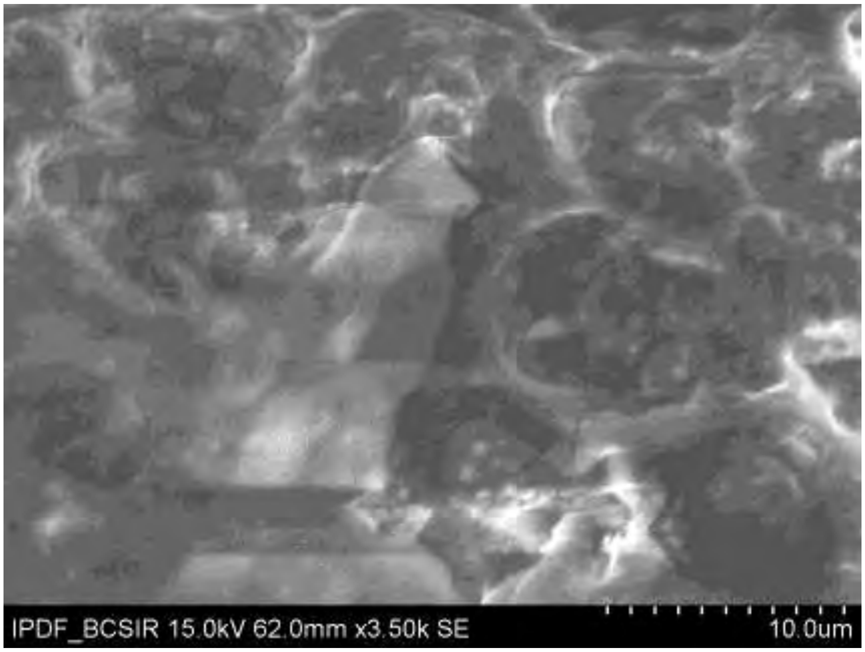

Fig 5:- SEM image of untreated 25 wt-% betel nut husk fiber-LDPE composite

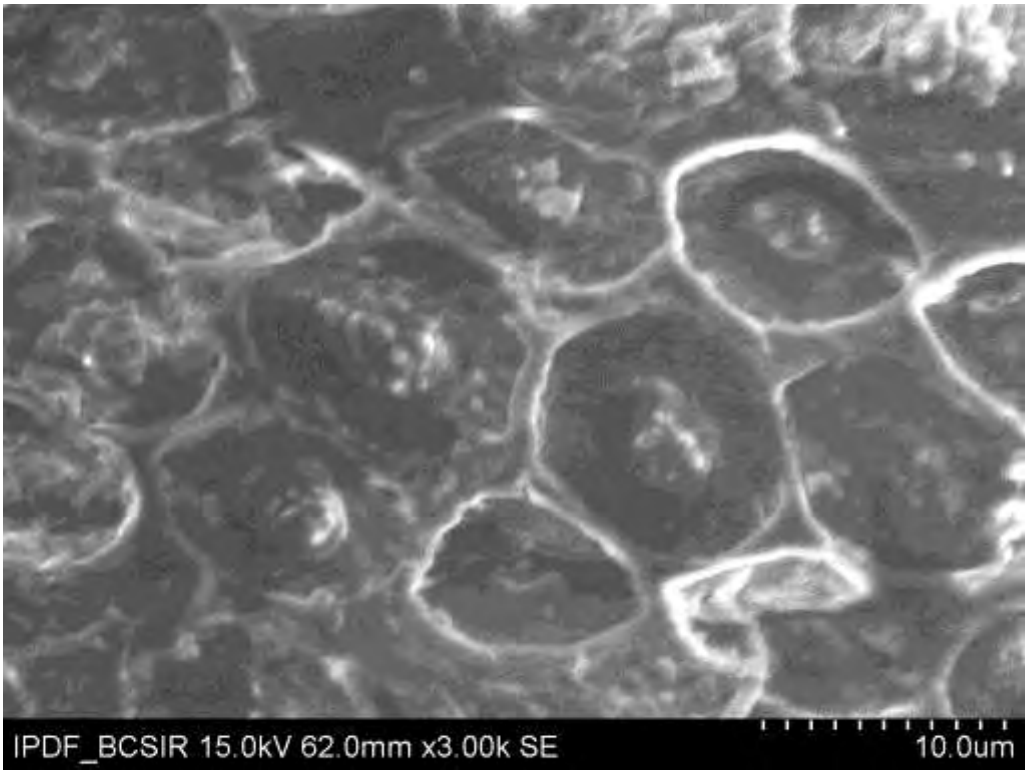

Fig 6:- SEM image of alkali treated 25 wt-% betel nut husk fiber-LDPE composite

Conclusion:-

The treatment of betel nut husk fibers with NaOH (6%) removes the impurities and hemicelluloses and reduces the lignin content of fibers. FT-IR spectroscopic analyses also supported the evidence of removal of hemicelluloses. Alkali treatment of BNHF reduces the moisture absorption property and improves the interfacial adhesion between fibers and matrices in composites. The enhancement of the hydrophobicity in BNHF due to alkali treatment results the better compatibility between the fibers and matrices of the LDPE composites. The tensile properties of treated BNHF -LDPE composites are higher than that of untreated betel nut husk fiber-LDPE composites. The reduction of water absorption in the alkali treated betel nut husk fiber-LDPE composites will increase their dimensional stability. The morphological observation also proves the strong interfacial bonding between fibers and matrices in the alkali treated BNHF-LDPE composites. So this research may provide valuable contributions to developing betel nut husk fibers as sustainable reinforcements in thermoplastic based composites.

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Characterization of Sodium *meta*-Periodate Modified Betel Nut Husk Fibers Reinforced HDPE Composites

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ABSTRACT

Short betel nut husk fibers (BNHF) were used as reinforcing materials to prepare high density polyethylene (HDPE) matrix based composites. Waste betel nut husk fibers were extracted from betel nut fruit and the chemical composition of fibers were analyzed. Extracted fibers were also chemically treated with sodium meta-periodate to enhance its compatibility with the HDPE matrix. Treated BNHF characterized by Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopic analyses. Different wt. percentages (5, 10, 15, 20, 25 and 30%) of both treated and untreated betel nut husk fibers were used to prepare compression moulded HDPE composites to achieve better interfacial bonding and mechanical properties. Tensile strength, elongation at break, TGA-DSC, Scanning Electron Microscopy (SEM) etc properties were analyzed for all treated and untreated betel nut husk fibers reinforced HDPE composites. It was found that 10% (w/w) treated fiber reinforced HDPE composites showed better results than all other composites.

Key words: High Density Polyethylene, Betel nut husk fiber, Composites, Tensile strength, Scanning Electron Microscopy

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INTRODUCTION

Composites are materials consisting of two or more chemically distinct constituents, on a macro-scale, having a distinct interface separating them. One or more discontinuous phase therefore, is embedded in a continuous phase to form a composite. The discontinuous phase is usually harder and stronger than the continuous phase and is called the reinforcement, whereas, the continuous phase is termed the matrix [1]. Environmental friendly greener materials like natural fibers are promising alternative materials to traditional glass fibers due to their good specific strength, low cost, renewability, market appeal, fully biodegradable nature and non-abrasive character [2]. Natural fiber used as reinforcement can be classified into many categories i.e. inner bark, seed, straw fiber, leaf, and grass fiber. Hardwood saw dusts, jute fibers, palm fibers, coconut fibers, rice straw fibers are used as reinforcements in polymer composites due to low cost, low density and biodegradability [3-7]. In the past agro based waste products have been used as natural sources to collect natural fibers suitable for agro-tech protective clothing [8]. Instead of glass or carbon fiber and inorganic fillers, natural fibers from natural sources are more potential as biodegradable reinforcing materials. From different research work and application in various fields it has been proved that natural fiber reinforced and thermoplastic polymer matrix based composites are much more applicable. To prepare thermoplastic composites various matrix materials like HDPE, polypropylene(PP) [9-11], polyvinylchloride (PVC) [12-13], polyethylene (PE) [14-17], polystyrene (PS) [18] and poly(lactic acid) (PLA) [19] used with reinforcing agent such as betel nut fiber, kenaf, wood, flax, cotton, hemp, Kraft pulp, pineapple leaf, coconut husk, areca fruit, oil palm, abaca, sisal, henequen leaf, jute, banana, ovine leather, and straw etc.

A wide range of agro-based fibers is being utilized as the main structural components or as reinforcing agents in the fiber-matrix based composite materials which are used from decorative, interior design and automotive interior components. Uses of different natural fibers which works as reinforcing agent are also described elsewhere [5-7]. In addition, natural fibers are now being widely used as fillers in the different industries like plastic industry to acquire expected results as well as to reduce the price of the finished product [8].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, hemi-cellulose and lignin are the main component of natural fiber and hence natural fibers are commonly termed as ligno-cellulosic materials. These constituents make natural fibers hygroscopic and hydrophilic which they have poor compatibility with hydrophobic polymer matrix in natural fiber reinforced polymer composites. Better fiber matrix interfacial bonding can be achieved by the surface treatment of natural fiber. Many Researchers have analyzed that the chemical modification of the natural fibers optimizes the interfacial locking between the fiber and the matrix and improving the other properties. During this process hydroxyl groups which are on natural fibers were activated or some new functional groups will be introduce, which will create effective interlock bonding with the matrix. Chemical treatments used as surface modifications have been studied by many researchers by using base, permanganate, acetic anhydride, silane and maleic anhydride [17].

In Bangladesh, *Areca catechu* tree is found everywhere as well as widely found in the coastal area. Betel nut husk fiber which is generally unusable is extracted from the betel nut fruit. This biodegradable fiber is cheap and easily used to prepare composite materials. The aim of this research work is to characterize the extracted betel nut husk fibers and to use it as a reinforcing material with HDPE matrix at different wt. percentages. Another aim of this research work is to treat the extracted fibers chemically, which could improve the properties of the composites. Sodium *meta*-periodate was used for treatment with betel nut husk fibers. The novelty of this work is the chemical modification of betel nut husk fibers with sodium *meta*-periodate. Different types of properties such as tensile strength, elongation at break, water uptake, TGA-DSC analysis, soil degradation test as well as scanning electron [17]microscopy (SEM) etc were analyzed for all treated and untreated BNHF reinforced HDPE composites and reported in this paper. These composites can be used in automobile sector, interior design, aircraft sector and making furniture etc.

EXPERIMENTAL METHODS

Materials

Betel nut empty fruits were collected from a local plantation field in Bangladesh. A commercial grade high density polyethylene (HDPE) from PTT Global Chemical Public Company, Thailand was used as polymer matrix. Analytical grade sodium *meta*-periodate and other reagents were used from Merck, Germany.

Fiber Extraction

Betel nut husk fibers were soaked in water at room temperature for 15 days for retting. The retted fibers were separated by hand stripping. The retted fibers were brushed and cleansed with agitated water, and washed thoroughly with distilled water. Fibers were then dried in sunlight for about three days. The extracted fibers were dried at 105°C in an oven for constant weight.

Chemical treatment of betel nut husk fibers with sodium *meta*-periodate

The dried betel nut husk fibers were clean manually and cut into 1 cm in length, fibers were then washed with distilled water and dried in open air. The air dried fibers were oven dried at 105 °C for 5 hours. Sodium *meta*-periodate solution (0.6 M) was prepared in distilled water. Dried fibers were immersed in sodium *meta*-periodate solution. Fiber to liquor ratio was 1:16 (w/v). The pH of the solution adjusted to 5 by adding sulfuric acid. The reaction was carried out for 4 hours at 90 °C. The reaction mixture was stirred occasionally. The mixture was cooled and filtered to isolate oxidized fibers. The fibers were thoroughly washed in tap water and finally washed with distilled water. The washed oxidized fibers were air dried. The air dried fiber was dried in an oven at 105 °C for constant weight. These oxidized fibers were used for composite fabrication.

Preparation of BNHF reinforced HDPE polymer Composites

The fabrication of untreated and sodium *meta* periodate treated BNHF reinforced HDPE composites were carried out by compression molding technique. The mould (12×15 cm^2) was cleaned and filled with dry blended mixture of fibers and HDPE powders to prepare composites. The weight fraction 5%, 10%, 15%, 20%, 25%, 30% of untreated and treated BNHF was carefully controlled during the mixing of two ingredients. The composites were hot pressed under 160°C temperature and 200 N pressures.

Table -1 Different weight fraction of BNHF reinforced HDPE composites

Formulation	Fiber content (wt %)	HDPE powder (wt %)
No. 1	5	95
No. 2	10	90
No. 3	15	85
No. 4	20	80
No. 5	25	75
No. 6	30	70
No. 7	00	100

Table -2 Different weight fraction of $NaIO_4$ treated BNHF reinforced HDPE composites

Formulation	Fiber content (wt %)	HDPE powder (wt %)
No. 8	5	95
No. 9	10	90
No. 10	15	85
No. 11	20	80
No. 12	25	75
No. 13	30	70

Characterization of Fibers and Composites

ATR-FTIR spectroscopic characterization of untreated and treated betel nut husk fibers

The ATR-FTIR spectra of untreated and treated BNHF were recorded on a FT-IR/NIR Spectrometer (Frontier, PerkinElmer, USA).

Mechanical Properties of the Composites

Tensile strength and elongation at break test

The tensile properties of all untreated and chemically treated BNHF reinforced HDPE composites prepared were carried out using a universal testing machine, model -1410 Titans, James Heal, UK. The load capacity was 5000 N, efficiency was within ± 1%. The crosshead speed was 50.00 mm / min and gauge length was 50.00 mm. The tensile strength measurements were carried out according to ASTM D-3039 method at a standard laboratory atmosphere of 30 °C and relative humidity.

Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis

The thermo gravimetric analysis and differential scanning calorimetric analysis of the prepared 30 wt% treated and untreated BNHF-HDPE composites were recorded on a STA 449F3 NETZSCH thermal analysis instrument in the temperature range of 0-900 °C.

Scanning electron microscopic (SEM) investigation

Scanning electron microscopy (SEM) is an important tool to the surface morphology study of materials. The raw untreated betel nut husk fiber, treated betel nut husk fiber and the fracture surface of tensile specimens of prepared 30 wt% treated and untreated BNHF-HDPE composites were examined using a Hitachi S-4000 field emission scanning electron microscope, operated at 5 kv.

RESULTS AND DISCUSSION

Characterization of BNHF

BNHF was extracted and analyzed. The analyzed ingredients are found in BNHF are presented below:

1. Aqueous Extract = 0.5647%
2. Fatty and waxy maters = 1.3796%
3. Pectic maters = 0.9173%
4. Lignin = 14.865%
5. α-cellulose = 51.0776%
6. Hemi cellulose = 14.8653%
7. Ash = 2.6877%

Surface modification of raw betel nut husk fiber with sodium *meta*-periodate

Fig. 1 shows the ATR-FTIR spectra of treated and untreated betel nut husk fibers. Both treated and untreated fibers were characterized by ATR-FTIR spectroscopy to confirm the chemical reaction of sodium *meta*-periodate with lignocelluloses element of fibers. The IR spectrum of treated fibers clearly showed the characteristic bands of aldehyde group at the region of 2920 cm^{-1} due to C-H stretching. The peak at 1738 cm^{-1} seen in untreated fiber which was disappeared upon chemical treatment. This was due to the removal of carboxylic group by chemical treatment.

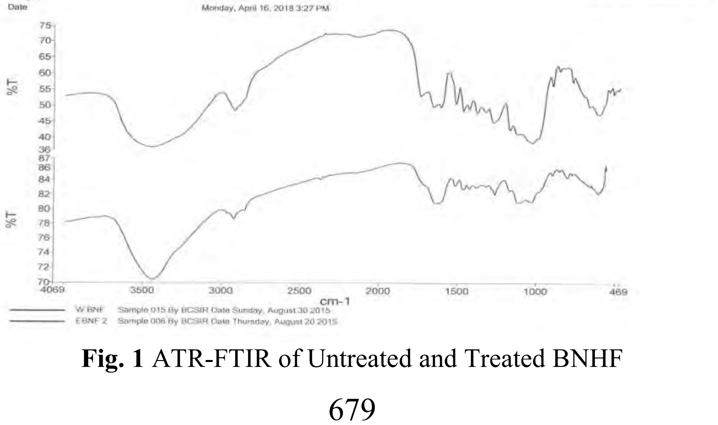


Fig. 1 ATR-FTIR of Untreated and Treated BNHF

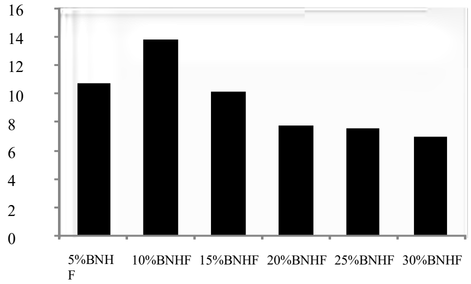


Fig. 2 Tensile strength *vs* wt % of untreated BNHF of untreated BNHF-HDPE composites

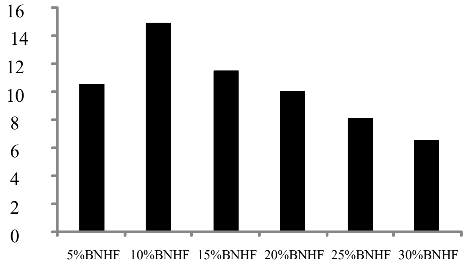
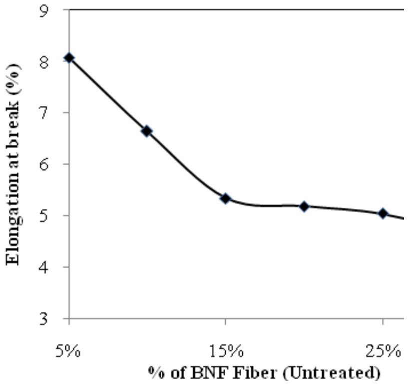


Fig. 3 Tensile strength *vs* wt % of $NaIO_4$ treated BNHF of BNHF-HDPE composites



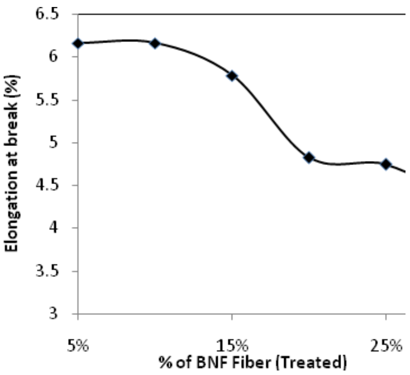


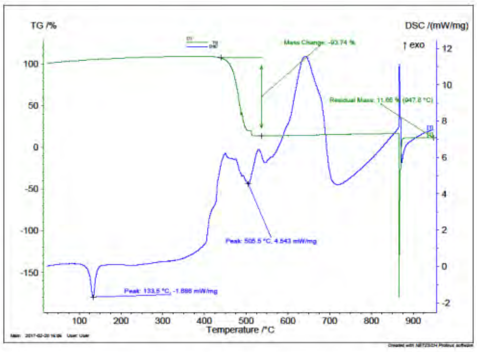
Fig. 4 Elongation at break (%) *vs* wt % of untreated BNHF of untreated BNHF-HDPE composites

Fig. 5 Elongation at break (%) *vs* wt % of BNHF of treated BNHF-HDPE composites

Mechanical Properties of Untreated and Treated Betel nut Fiber Reinforced HDPE composites

Tensile strength, elongation at break and of untreated and chemically treated BNHF reinforced HDPE composites were studies and there results are presented below:

The tensile strengths of the untreated and treated BNHF-HDPE composites are shown in figure 2 and figure 3. It is observed from the figure that the tensile strengths of the composites increased up to 10 wt% fibers loading & then decreased. The elongations at break of untreated and treated BNHF-HDPE composites are shown in figure 4 and figure 5. Elongation at break of all composites decreased with increasing fiber loading. Tensile properties of all treated BNHF-HDPE composites were higher than that of untreated BNHF-HDPE composites. The tensile strength and ductility were better in the case of treated BNHF-HDPE composites than that of untreated BNHF-HDPE composites. This may be the reason for the improvements of the fiber-matrix interfacial adhesion in composites made by sodium periodate treatment.



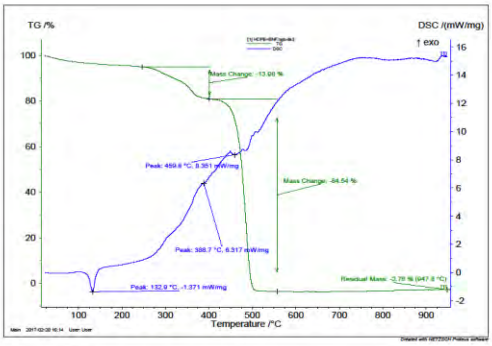


Fig. 6 TGA &DSC curve of HDPE

Fig. 7 TGA &DSC curve of 10 wt% untreated BNHF-HDPE composite

Thermal properties of Untreated and Treated Betel Nut Fiber Reinforced HDPE Composites

Thermal properties of neat HDPE, 10 wt% untreated and treated BNHF-HDPE composites were evaluated by Differential scanning calorimetery (DSC) and thermo gravimetric analysis(TGA) and the pictures of DSC and TGA curves were presented in the figures 6, 7 and 8 respectively. It is observed from the figures that almost same thermal properties were found for treated and untreated BNHF-HDPE composites. But neat HDPE showed slightly higher thermal stability than the BNHF-HDPE composites. The melting temperature of neat HDPE and untreated and treated BNHF-HDPE composites were found at 133.5^{0}C, 132.9^{0}C and 132.8^{0}C respectively. So addition of treated and untreated BNHF with HDPE didn't affect the melting temperature of neat HDPE.

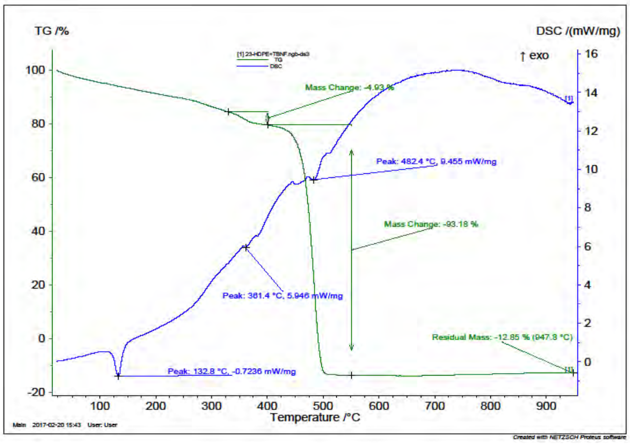


Fig. 8 TGA &DSC curve of 10 wt% treated BNHF-HDPE composite

Morphological Characterization of Untreated and Sodium meta periodate Treated Betel Nut Fiber reinforced HDPE composites

The surface morphology of the untreated fiber, treated fiber and their composites of 30 wt% untreated and treated BNHF with HDPE were studies by scanning electron micrograph (SEM) images and presented in the figures 9 to 12 respectively. From the analyses of SEM images of untreated and treated BNHF, it was found that treated BNHF was smoother surface than the untreated BNHF. The SEM images of treated BNHF-HDPE composite indicated the better interfacial adhesion between treated BNHF and HDPE matrix as compared to untreated BNHF-HDPE composite.

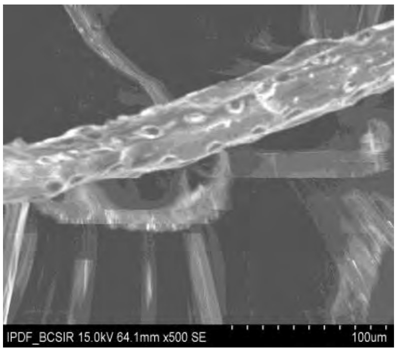


Fig. 9 SEM image of untreated BNHF

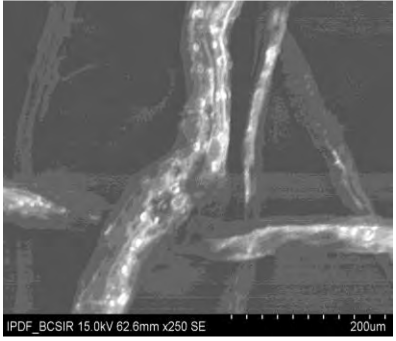


Fig. 10 SEM image of treated BNHF

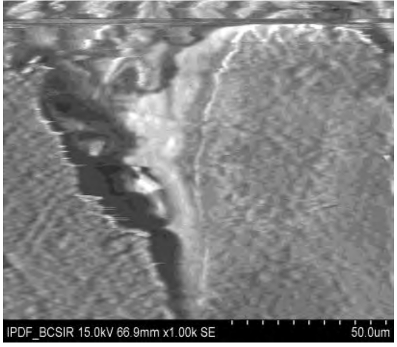


Fig. 11 SEM image of untreated BNHF-HDPE composite

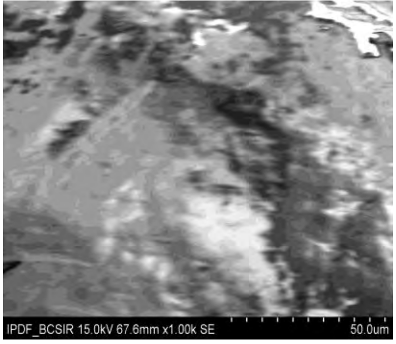


Fig. 12 SEM image of treated BNHF-HDPE composite

CONCLUSIONS

The extraction and characterization of betel nut husk fibers were done and used as a reinforcing material with HDPE matrix at different wt. percentages. Chemical treatment of extracted fibers with sodium meta periodate showed improved mechanical properties for the treated BNHF-HDPE composites comparing with the untreated BNHF-HDPE composites. ATR-FTIR spectra and SEM analyses of fibers also evidenced the occurrence of chemical modification in treated BNHF. The mechanical properties of the composites showed that the treated BNHF-HDPE composites had significant improvement at 10 wt% treated BNHF loading. SEM micrographs also revealed the evidence of improved mechanical properties for treated BNHF-HDPE composites than untreated BNHF-HDPE composites. No significant changes have been found from thermal properties of treated and untreated BNHF-HDPE composites. Thermal stability of pure HDPE was slightly higher than that of treated and untreated BNHF-HDPE composites. Therefore, BNHF-HDPE composites would be biodegradable materials.

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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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Betel nut husk fiber, Polypropylene, Chemical treatment, Tensile Strength, SEM, TGA and DSC.

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 betterfiber 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 Poly propylene 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 90^0C temperature. These reaction parameters were optimized by following ATR-FTIR analyses. The reaction mixture was stirred by glass rod occasionally. After competition 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 105^0C 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^oC for 24 hours. Polypropylene was granulated in a grinder and dried at 80^oC 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 180^0C. 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 bromideto 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 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 × 10mm × 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 percentageis 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.

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

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 and100% 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 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.

$$\text{Cellulose in BNHF + Hydrogen peroxide} \xrightarrow{\text{3hrs, }90^{\circ}\text{C and pH=9}} \text{Dialdehyde-cellulose in BNHF}$$

(10 wt.% solution in distilled water)

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°C yielded the oxidized product dialdehyde-cellulose in BNHF. In both figure 1 and 2, the broad peak at 3393 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 2919cm^{-1} and 2849cm^{-1}due to C-H stretching, another sharp peak at 1645.61cm^{-1}due to C=O stretching of aldehyde group in treated BNHF. In figure 1, a sharp peak at 1738.37cm^{-1} is due to C=O Stretching vibration of carboxylic acid and ester component of hemicelluloses in untreated BNHF. In treated BNHF the peak 1738.37cm^{-1} is corresponding to C=O Stretching vibration of hemicelluloses disappeared due to the removal of lignin and hemicelluloses (14).

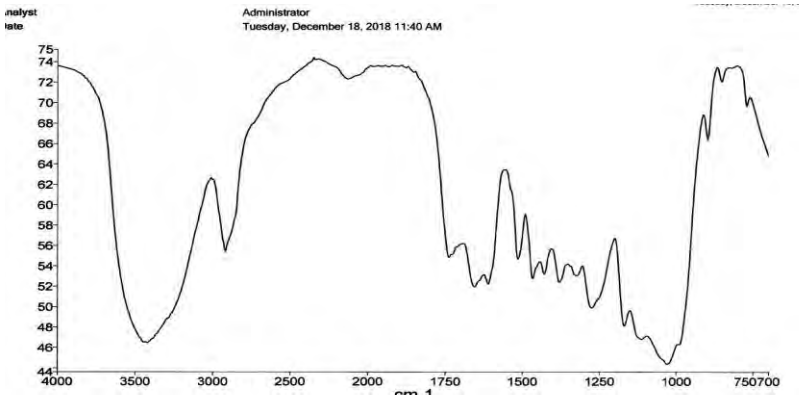

Figure 1:-FTIR of untreated BNHF

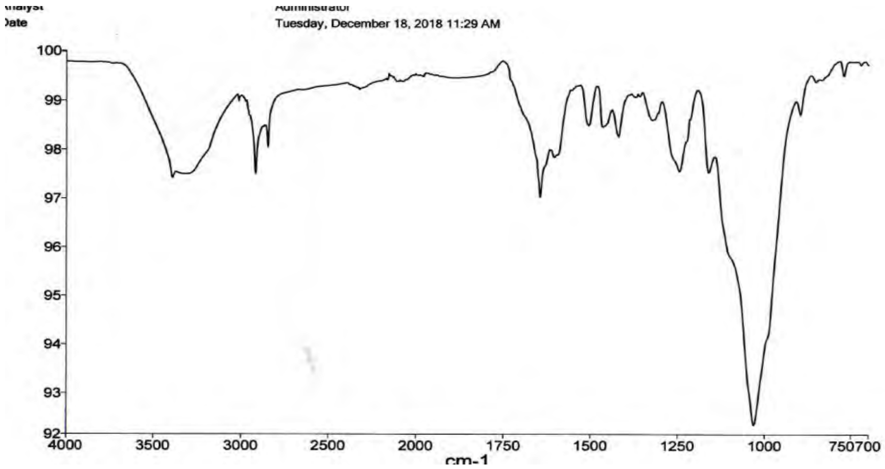

Figure 2:-FTIR of hydrogen peroxide treated BNHF

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.

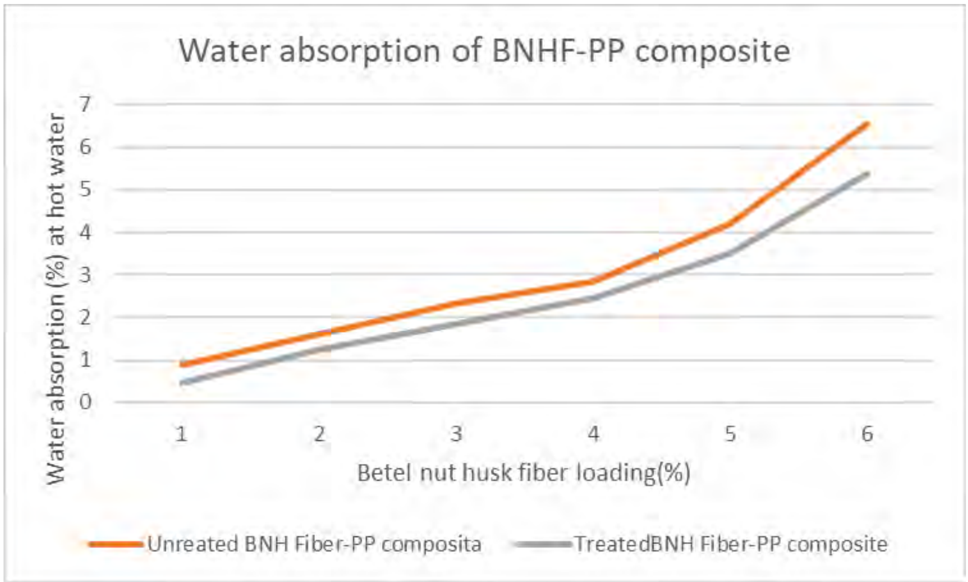

Figure 3:-Water absorption of Treated and Untreated BNHF-PP Composites

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.

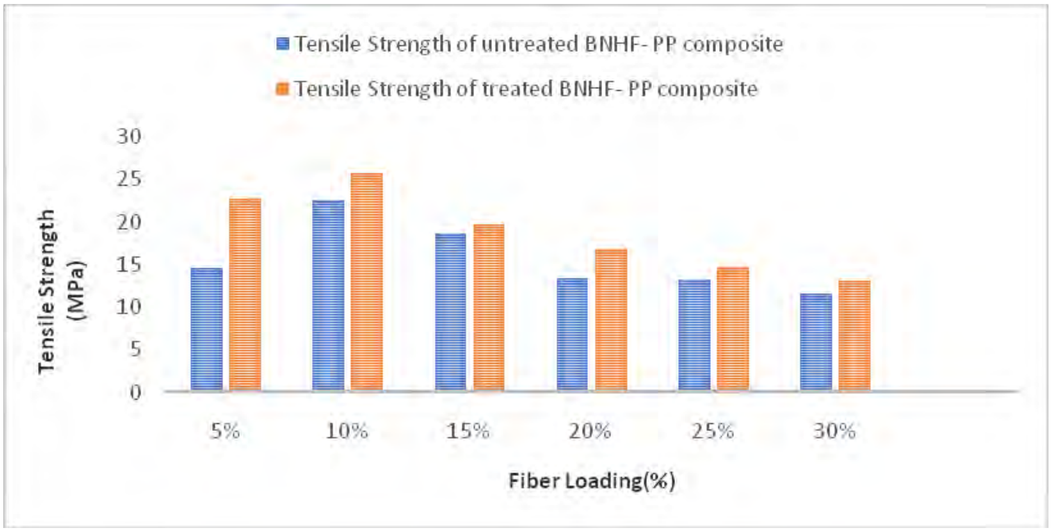

Figure 4:-Tensile strength vs fiber loading (wt. %) of untreated and treated BNHF-PP composites.

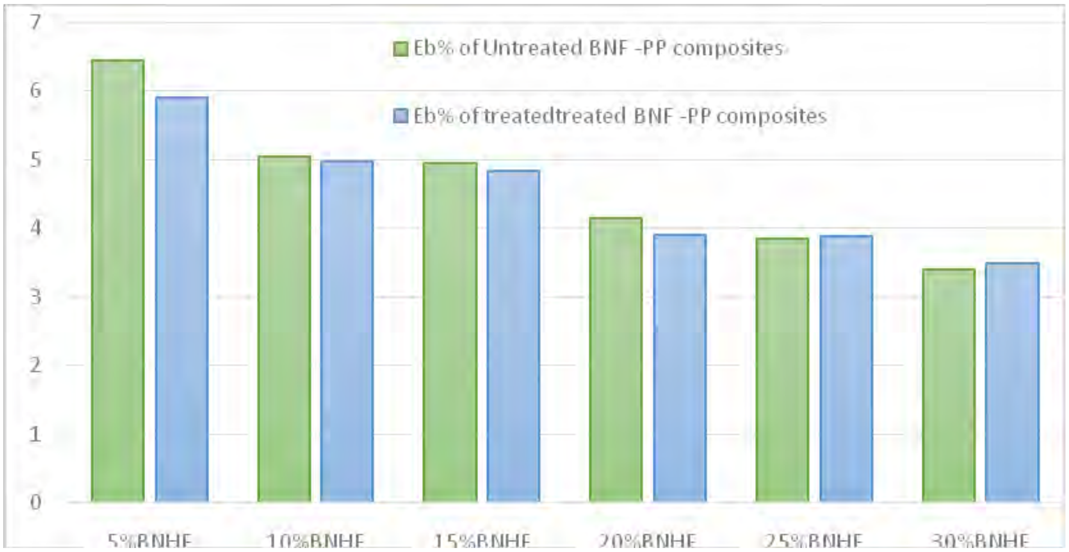

Figure 5:-Elongation at break (%) vs fiber loading (wt. %) of untreated and treated BNHF - PP composites.

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 456.7ºC and 99.98 % mass change is completed at 500ºC for PP polymer whereas the mass change started at 434.6ºC and 5.51% mass change is completed at 434.6ºC and 89.57% degradation is done at 520ºC for untreated for BNHF reinforced PP composites. In case of treated BNHF-PP composite, degradation started at 450ºC and 95.43 % mass change is completed at 550ºC. 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.

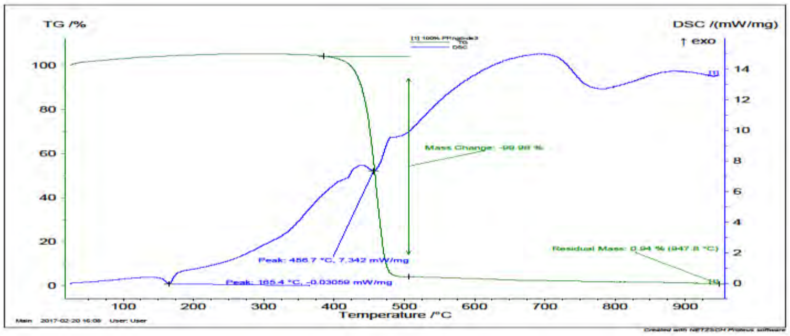

Figure 6:-TGA and DSC of 100% PP

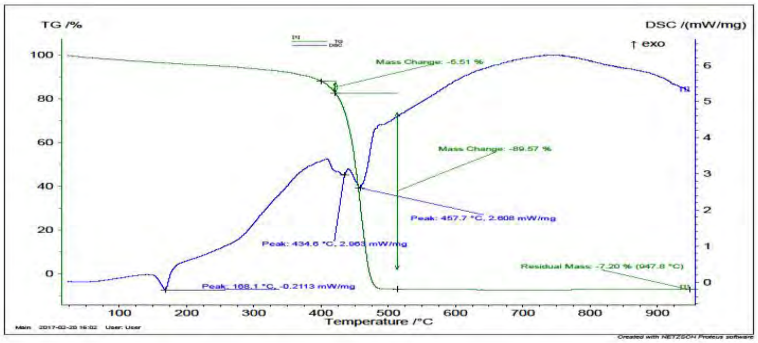

Figure 7:-TGA and DSC of untreated BNHF-PP composite

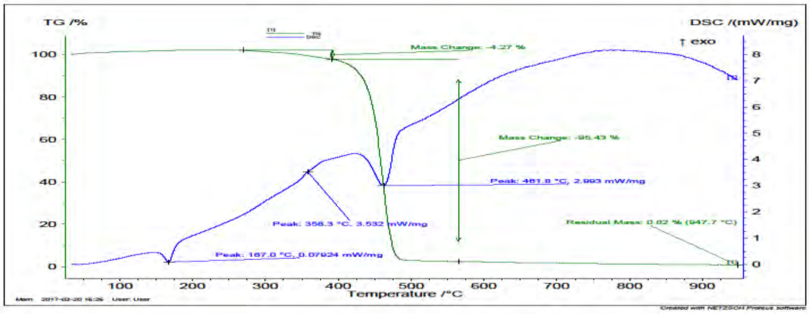

Figure 8:-TGA and DSC of treated BNHF- PP composite

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 then untreated BNHF. SEM image of treated BNHF-PP composite indicate 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.

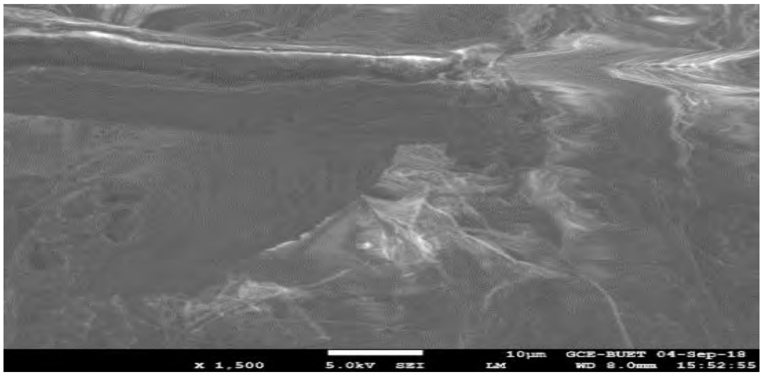

Figure-9:-SEM of untreated BNHF -PP composite

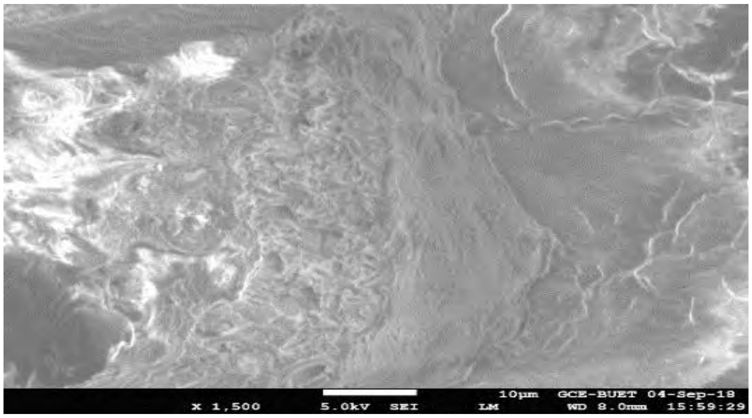

Figure-10:-SEM of treated BNHF-PP composite

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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OL11 Effects on The Properties of Low Density Polyethylene Composites Reinforced With Treated and Untreated Betel Nut Husk Fibers

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Betel nut *(Areca catechu)* husk fibers (BNHF) were extracted and used to prepare sodium hydroxide treated and untreated BNHF reinforced low density polyethylene (LDPE) composites. Extracted and washed BNHF were treated with sodium hydroxide to improve their adhesion to LDPE matrices. Chemical treatment BNHF of betel nut husk fibers with sodium hydroxide was carried out and the change in the functional group of treated BNHF was studied by FT-IR spectroscopic analyses. Sodium hydroxide treated and untreated BNHF were used in this case of research as reinforcing materials to find out their effects on LDPE composites. Different types of compression molded BNHF-LDPE composite were prepared using different weight percent of treated and untreated BNHF with compositions 5, 15, 20, 25 and 30 wt% in LDPE. The tensile, water absorption and morphological properties were studied for all composites. Enhancement in the tensile, water absorption and morphological properties were shown in the treated BNHF-LDPE composites. Alkaline treatment reduced the water absorption and increased the tensile properties of treated betel nut husk fiber-LDPE composites. Morphological analyses showed the evidence of stronger interfacial adhesion between the fibers and matrices in the alkali treated BNHF-LDPE composites than the untreated BNHF-LDPE composites.

Keywords:- Betel nut husk fiber, LDPE, composite, tensile strength, water absorption etc.

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Physicomechanical and thermal properties of betel nut husk nanofiber reinforced polymer composites

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Cellulose extracted from Betel Nut husk fiber was converted to cellulose nanofiber by chemical and mechanical technique to examine their potential for use as reinforcement fiber in biocomposite applications. The cellulose isolated from betel nut husk fiber was subjected to acid hydrolysis using 62% sulfuric acid under ultrasonic treatment. The product was allowed to stand at room temperature to cool and the acid was removed by washing, centrifuged and dialysis with distilled water at room temperature. Betel nut husk fiber was also converted to nanofiber by the milling process. The present work was to investigate the possibility of breaking down the structure to submicron and nanoparticles by high energy planetary ball milling by SFM-1 Desk-Top planetary Ball-Miller, MTI Corporation. Cellulose nanofiber reinforced polymer composites were prepared with different weight percentages (1 wt% to 5 wt%) via casting methods. The tensile, thermal and morphological properties were studied for all composites. Enhancement in the tensile, thermal and morphological properties was shown in the nano-cellulose reinforced composites. Cellulose nanofiber and its reinforced polymer composites were characterized by FTIR, TGA, DSC, Nano Zetasizer, and X-ray diffraction. Its structural morphology was also studied by scanning electron microscope.

Biography

Tanvir Sultana is a PhD student of Bangladesh University of Engineering and Technolog, BUET, Dhaka under the supervision of Professor Md Wahab Khan. She has published 3 papers in the reputed journal. She is a PhD fellow of Bangladesh University Grant Commission (UGC). She is an Assistant Professor of Chemistry of the government college of Bangladesh under Ministry of Education.

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Notes:

OPB25

MECHANICAL,THERMAL AND MORPHOLOGICAL STUDY OF BETEL NUT HUSK NANO CELLULOSE REINFORCED PVA COMPOSITIES

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Cellulose extracted from Betel Nut husk fiber were converted to cellulose nano fiber by chemical and mechanical technique to examine their potential for use as reinforcement fiber in bio composite applications. The cellulose isolated from betel nut husk fiber were subjected to acid hydrolysis using 62% sulfuric acid under altrasonic treatment. Betel nut husk cellulose were also converted to nano cellulose by milling process. The present work was to investigate the possibility of breaking down the structure to sub micron and nano particles by high energy planetary ball milling by SFM-1 Desk-Top planetary Ball Miller, MTI Corporation. Cellulose nano fiber reinforced PVA polymer composites were prepared with different weight percentages (1 wt% to 5 wt%) of cellulose and nano cellulose via custing methods. Cellulose nano fiber and its reinforced polymer composites were characterized by FTIR, TG, DSC, Nano Zetasizer and X-ray diffraction. Its structural morphology was also studied by Scanning electron microscope. Enhancement in the tensile thermal and morphological properties was shown in the nano cellulose reinforced composites.