

HULL FIBER FROM DDGS AND CORN GRAIN AS ALTERNATIVE FILLERS IN  
POLYMER COMPOSITES WITH HIGH DENSITY POLYETHYLENE

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**Title**

Hull Fiber from DDGS and Corn Grain as Alternative Fillers in Polymer  
Composites with High Density Polyethylene

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State University's regulations and meets the accepted standards for the degree of

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## ABSTRACT

The steady increase in corn based ethanol production has resulted in a dramatic rise in the supply of its co-product known as distillers' dried grain with solubles (DDGS). Currently, the main outlet for DDGS is the animal feed industry, but the presence of fibers makes them indigestible by non-ruminants such as swine and poultry. Separation of fiber from DDGS would increase the nutritional value of DDGS with higher protein and fat contents and reduced fiber content. The fiber from DDGS can be separated through a physical separation process known as elusieve. The DDGS fiber has the potential to be used as a fiber filler in thermoplastic composites. This research project evaluates DDGS fiber as a filler in thermoplastic composites. The fibers from corn hull and DDGS have been used as fillers at 30% and 50% fiber loading in high density polyethylene (HDPE) composites and compared against a standard oak fiber filler composites at a lab scale. DDGS and corn fiber composites showed comparable mechanical properties as the oak wood fiber HDPE composites. Further evaluation was completed on the performance of composite samples at commercial scale with six combinations of oak fiber, corn hull fiber and DDGS fiber with fiber loading maintained at 50%, and then samples were exposed to UV accelerated weathering for 2000 h. The UV weathering decreased the mechanical properties of all the exposed samples compared to the unexposed samples. Also, UV weathering resulted in a severe chain scission of the HDPE polymer, increasing their crystallinity. The performance of mercerized or sodium hydroxide (NaOH) treated DDGS fiber as filler was investigated by characterizing the effects of treated and untreated DDGS fibers on physical, mechanical, and thermal properties of HDPE composites. The NaOH treated DDGS fiber at 25% loading showed consistent improvement in flexural and tensile modulus of elasticities of the composites compared to the neat HDPE.

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## **DEDICATION**

To my Parents:

Ghanshyam Pandey and Pramila Pandey

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## LIST OF ABBREVIATIONS

ASTM .....	American Society for Testing and Materials
CDS.....	Condensed distiller's syrup
CLTE.....	Coefficient of Linear Thermal Expansion
DDGS.....	Distillers' dried grain with solubles
DOE .....	Department of Energy
GHG.....	Greenhouse gas
HDPE .....	High density polyethylene
MA .....	Maleic anhydride
MDI.....	Methylene diphenyl isocyanate
MFI .....	Melt Flow Index
NDF.....	Neutral Detergent Fiber
NMR .....	Nuclear Magnetic Resonance
PBAT .....	Poly (butylene adipate-co-terephthalate)
PE.....	Polyethylene
PHA.....	Polyhydroxyalkanoate
PLA.....	Poly lactic acid
PP .....	Polypropylene
PVC.....	Poly vinyl chloride
SEM .....	Scanning Electron Microscopy
TGA .....	Thermogravimetric Analyzer
USDA.....	United States Department of Agriculture
UV.....	Ultraviolet



## LIST OF SYMBOLS

1/2 .....	Half
°C .....	Degree celcius
% .....	Percent
cm.....	Centimeter
g.....	Gram
GPa.....	Gigapascal
h.....	Hour
J.....	Joule
kg.....	Kilogram
kN.....	Kilo newton
KV.....	Kilovolt
m .....	Meter
mg .....	Milligram
MHz .....	Megahertz
min .....	Minute
mL.....	Milliliter
mm .....	Millimeter
MPa.....	Megapascal
ppm .....	Parts per million
rpm .....	Revolutions per minute
W.....	Watt
wt.....	Weight

## **DISSERTATION ORGANIZATION**

This dissertation is comprised of the following sections: general introduction, four numbered chapters, general conclusions, and recommendations for future work. Chapter 1 is a general literature review that covers topics on the development of different natural fiber composites and problems associated with the development of natural fiber composites. Chapter 2, entitled “Fiber from DDGS and Corn Grain as Alternative Fillers in High Density Polyethylene Polymer Composites”, summarizes the effect of adding hull fiber from corn grain and distiller’s dried grain with solubles (DDGS) on material properties at two filler loadings of 30 and 50% weight in high density polyethylene composites. Chapter 3, entitled “Performance of UV weathered HDPE composites containing hull fiber from DDGS and corn grain”, presents the effects of UV exposure on DDGS and corn grain fiber composites. Chapter 4, entitled “Mercerization of DDGS fiber for improvement in material properties in high density polyethylene composites”, describes the effect of mercerized DDGS fiber as filler in HDPE composites. Chapter 4 is followed by the general conclusions from the overall project and some recommendations for future work.

## GENERAL INTRODUCTION

Composites are the materials that are made of two or more components combined to obtain a new material with properties better than those of the individual components. The advancements in fiber reinforced polymer and cement materials have led to them being used as the preferred building materials over the traditional concrete and steel materials [1]. The natural fiber polymer composites offer numerous advantages such as availability in abundance, light weight, non-abrasiveness, renewability, biodegradability, and high specific stiffness [2]. Many natural fibers such as coir [3], flax [4], hemp [5], bamboo [6], kenaf [7], abaca [8], and jute [9] have been used as reinforcing agents or fillers in the composite materials. Agricultural byproducts such as bagasse and fiber residues from wheat, corn, soybean, rice, and cotton can also be used as fillers in polymer composites [10-14].

The corn based ethanol industry has been growing steadily with proportionate increase in the generation of its major co-product known as distiller's dried grain with solubles (DDGS), mainly sold as animal feed due to its high protein content [15]. The presence of hull fiber in DDGS makes it difficult for the non-ruminants to digest it [16]. A physical separation process known as elusieve can separate DDGS into two fractions- a DDGS fraction with enhanced fat and protein content, and a fiber fraction [15]. The fiber fraction has the potential to be used as a filler in polymer composites [17, 18].

The outdoor applications of wood composites currently dominate the commercial market for natural fiber filled polymer composites. These composites in an outdoor application undergo various environmental stresses such as heat, moisture, and microbial attack. The ultraviolet (UV) rays cause the scission of polymer chains and attack the integrity of the fiber structure [17]. Natural fibers being hydrophilic in nature have poor interfacial bonding with the hydrophobic polymer matrices. This incompatibility leads to high moisture absorption causing dimensional

instability of composites, poor stress transfer, and loss of mechanical properties. This mismatch between the fiber and the matrix can be improved by chemical treatments such as mercerization, physical treatments, and coupling agents. The chemical treatment such as mercerization of fibers improves interfacial bonding. The characteristic features of mercerization are swelling of fiber, solubilization of hemicelluloses and lignin, reduction in degree of polymerization of cellulose, and higher mechanical interlocking sites on the mercerized fiber [19].

### **Research Objectives and Their Hypotheses**

The overall objective of this research project was to evaluate the performance of corn hull fiber and DDGS fiber, two agricultural byproducts, as fillers in thermoplastic composites. The specific objectives of this research were to:

I. Evaluate the performance of corn hull and DDGS fibers as fillers in high density polyethylene (HDPE) from petroleum based and bio based sources.

II. Evaluate the durability of corn and DDGS fiber filled high density polyethylene composites produced at a commercial scale under UV and moisture weathering.

III. Evaluate the effect of mercerization of DDGS fibers in improving interfacial bonding with HDPE in composites.

The underlying research hypotheses for the three objectives are:

(1) The corn hull and DDGS fibers have the molecular structure suitable for binding; therefore, these fibers can be used as alternative fillers in thermoplastics composites.

(2) The presence of very small amount of lignin, a main precursor to the initiation of UV degradation in wood composites, in corn hull and DDGS fibers may help in resisting the degradation effects of UV weathering in their composites.

(3) The mercerization of DDGS fiber will increase the surface roughness thus increasing the interacting sites on the fiber surface for better mechanical interlocking with the HDPE matrix.

## CHAPTER 1. LITERATURE REVIEW

### Fiber Reinforced Composites

Fiber reinforced composites comprises of synthetic fibers such as carbon, glass, and aramid incorporated in a polymer matrix to meet high strength/high modulus requirements for different material applications [20]. But in the last few decades, numerous concerns over environmental protection, proper degradation of synthetic composites at the end of their life cycle, and greenhouse gas emissions (GHG) have prompted the research community all over the world to explore other alternatives to the synthetic fiber composites. There has been a great surge from both academic institutions as well as by the composite industries to include natural fibers in place of synthetic fibers in polymer composites. The United States Department of Agriculture (USDA) and the Department of Energy (DOE) have set targets of having at least 10% of all basic chemical building blocks to be created from renewable and plant based sources in 2020 and increasing this contribution to 50% by 2050 [21].

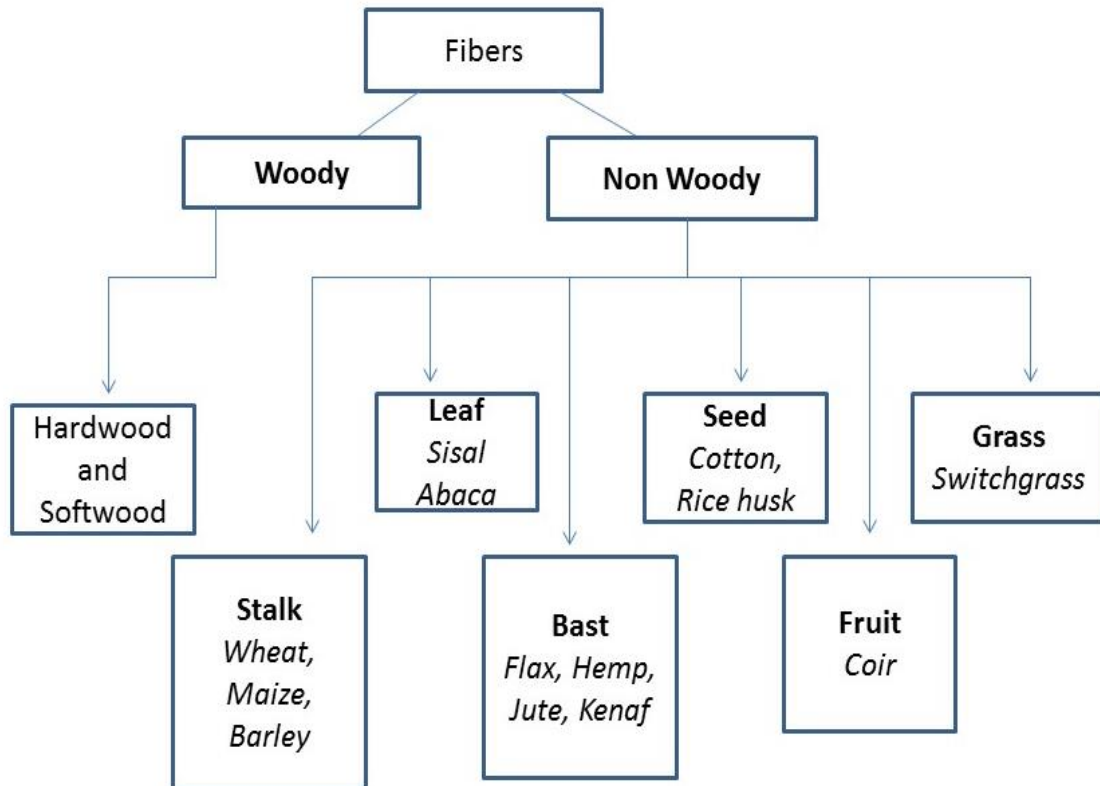
The numerous advantageous characteristics that natural fibers possess over glass fibers have led to their much-gained popularity in the composite industries. The ease of processing, renewability, sustainability, biodegradability, non-abrasiveness, low cost, and high specific strength make them desirable as reinforcement or filler in polymer composites [20].

Polymers can be mainly classified into two classes, thermoplastic and thermosetting. Commonly used matrices in thermoplastic composites are polypropylene (PP), polyethylene (PE), and poly vinyl chloride (PVC); while thermosetting matrices used are phenolic, epoxy and polyester [22].

#### Natural Fibers

There are two types of plants known as primary and secondary plants based on their utilization. Primary plants are plants that are grown for their fiber which include jute, hemp,

kenaf and sisal. Secondary plants are plants from which the fibers are produced as a byproduct. Examples of secondary plants are pineapple, oil palm, and coir. Fibers could be obtained from woody or non-woody plants. The plant fibers from non-woody plants can be categorized into six types (Fig.1.1) which are bast fibers, leaf fibers, seed fibers, core fibers, and grass and reed fibers.



**Fig.1.1.** Different types of plant based natural fibers

All types of cellulosic fibers can be used as reinforcement or filler in plastics including flax, hemp, jute, straw, wood fiber, rice husks, wheat barley, oats, rye, grass, kenaf, sisal, hyacinth, banana fiber, and pineapple leaf fiber. The main advantages of using lignocellulosic fibers are that they are neutral sources causing less net emission of carbon dioxide back to the environment at disposal, readily available at a much lower cost than synthetic fiber, and can be recycled easily. Though synthetic fibers have found extensive usage in composite materials for a

long time, their severe impact on environment cannot be ignored. The lignocellulosic fibers are renewable, widespread and easily available in comparison to glass or carbon fibers [23].

Natural fibers can have drastically different properties than synthetic fibers such as glass. For example, density of glass fibers is around 2500 kg/m<sup>3</sup> whereas density of plant fibers is in the range of 1300-1600 kg/m<sup>3</sup> (Table 1.1). Some of these fibers have specific strength quite comparable to glass fibers.

**Table 1.1.** Properties of different natural fibers and E-glass [24]

Fibers	Density (g/cm <sup>3</sup> )	Diameter (mm)	Tensile strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Price (USD/kg)
Flax	1.5	40-600	345-1500	27-39	2.7-3.2	3.11
Hemp	1.47	25-250	550-900	38-70	1.6-4	1.55
Jute	1.3-1.49	25-250	393-800	13-26.5	1.16-1.5	.925
Kenaf	1.5-1.6	2.6-4	350-930	40-53	1.6	.378
Ramie	1.5-1.6	.049	400-938	61.4-128	1.2-3.8	2
Sisal	1.45	50-200	468-700	9.4-22	3-7	.65
Curaua	1.4	7-10	500-1100	11.8-30	3.7-4.3	.45
Abaca	1.5	10-30	430-813	33.1-33.6	2.9	.345
E-glass	2.55	15-25	2000-3500	70-73	2.5-3.7	2

### Agricultural Residues

The utilization of agricultural residues has several advantages such as their availability, abundance and worldwide production. The agricultural residues are about one tenth to one eighth the price of agricultural fibers that can provide inexpensive sustainable composite properties [25]. Sunflower stalk, corn stalk and bagasse fibers have improved tensile, flexural and impact properties when combined with a coupling agent in thermoplastic composites [26]. The green renewable composites with wheat straw, corn stover, soy stalks and their hybrids with



polylactide showed that the combination of agricultural residues can lower the cost concerns related with supply chain of the natural fibers [26]. The advantages of natural fiber fillers include biodegradability and superior material performance evidenced with rice husk and bagasse fibers [26]. The addition of rice husk and bagasse fibers at high loading increased the tensile and flexural properties and biodegradability of the composites. The use of DDGS as a fiber filler with polyhydroxyalkanoate [27], PLA [28], polypropylene [29] and Polyethylene [30] resulted in desirable material properties.

## **DDGS**

DDGS is used as feed ingredients for livestock at a very low price. The value of DDGS as feed is measured in terms of its digestibility, total digestible nutrients, net energy, amino acid and mineral profiles [31]. The composition of DDGS is shown in Table 1.2.

The presence of cellulose and hemicelluloses in fiber portion of DDGS has been the focus of several studies. Firstly, these polysaccharides are not easily digestible by non-ruminants (swine and poultry). So, the fiber portion was of little value as feed ingredient to non-ruminants. Secondly, cellulose to ethanol based processes can make use of these extra polysaccharide sources to increase the feedstock for cellulosic bioethanol.

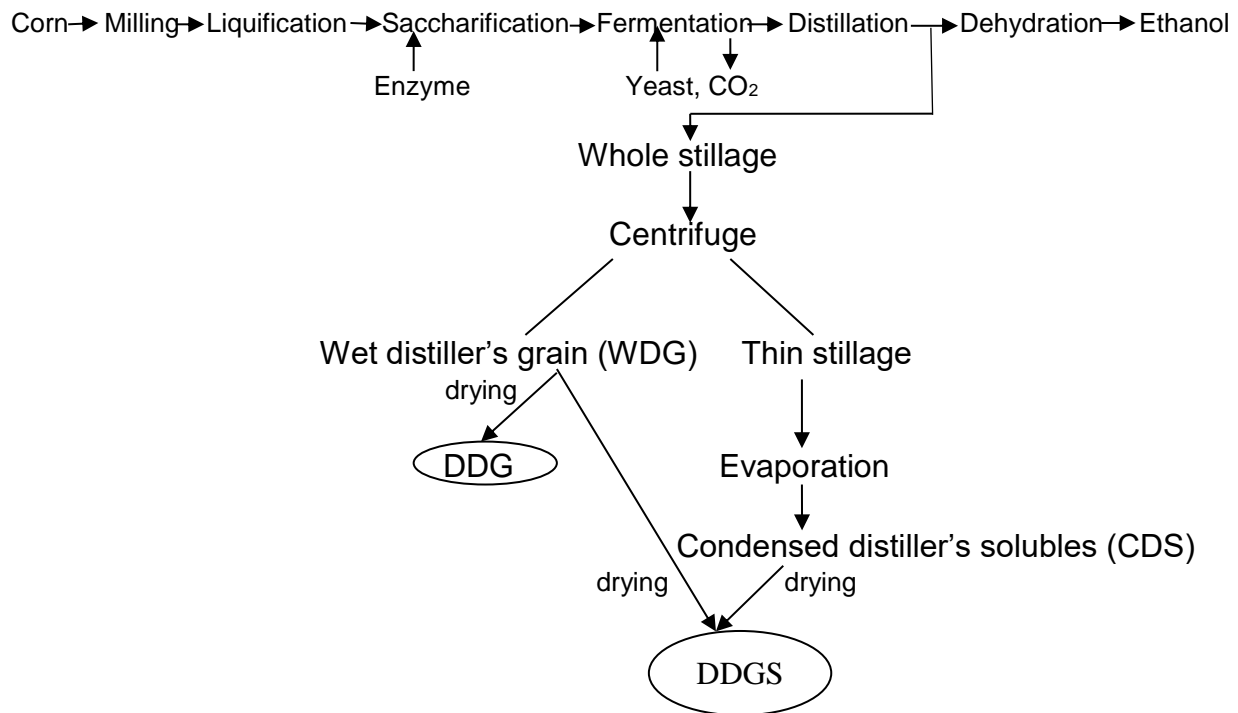
**Table 1.2.** Composition of DDGS on a dry basis [32]

Components	Mean (%)
Crude protein	31.3
Crude fat	11.9
Crude fiber	10.2
Starch	5.1
ADF	17.2
Ash	4.6

### **DDGS Production**

The corn ethanol production has seen a steady increase in the last few decades to 55 billion liters in 2015 [33]. Currently, more than 90% of the corn ethanol industries employ some variation of the dry grind process for ethanol production. The dry grind ethanol process differs from the corn wet milling process, as it lacks the steeping step at the front end (Fig. 1.2). Also, it uses little or no fractionation of the corn kernel components prior to saccharification of the starch and fermentation [34]. In this process, the whole grain is ground by a hammer mill into a course powder with a mean diameter of 1mm. In the next step, the mill corn is liquefied with the addition of enzyme, followed by a saccharification step, where starch in corn is converted into simple sugars. These sugars are next fermented by yeast cells. After fermentation, the slurry of yeast cells and unfermented residuals from corn grain flour pass through a stripper where ethanol is recovered. The portion left after separating ethanol is called whole stillage. The whole stillage consists of fiber, oil, protein, other unfermented grains and yeast cells. The whole stillage is centrifuged to produce a liquid fraction called thin stillage and a solid fraction known as wet distiller's grain (WDG). A part of thin stillage is recycled to slurry the ground grain. The remaining thin stillage is concentrated through multiple effect evaporators to produce a syrup called condensed distiller's solubles (CDS). The WDG is dried to obtain distiller's dried grain (DDG). When CDS is mixed with WDG and dried, it is called distiller's dried grain with

solubles (DDGS) [31]. The dry solid residue remaining after ethanol production is known as the DDGS.

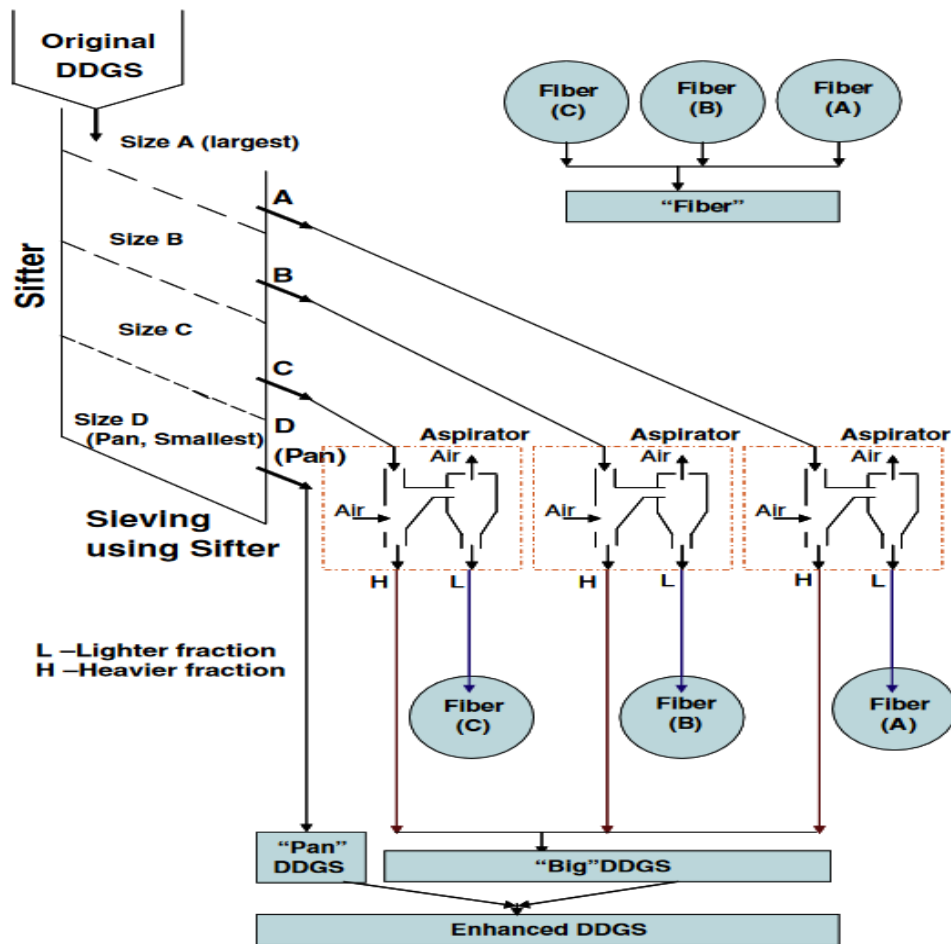


**Fig.1.2.** Different steps involved in the dry grind corn ethanol process

### Separation of DDGS Fibers

Elutriation or aspiration process was used to separate fiber fraction from DDGS [16]. In this process, DDGS particles under upward air flow are separated with combined effects of density, shape and size characteristics. When a particle falls, it experiences a downward gravitational force which is balanced by the upward drag and buoyancy force known as its terminal velocity [32]. The air velocity must be greater than the terminal velocity of the DDGS fraction and lower than the terminal velocity of non-fiber fractions to separate the fiber fraction. The flat shape of DDGS fiber combined with low mass would experience higher drag force thus possessing lower terminal velocity than less flat non-fiber DDGS fraction [32]. The drawback of this process is that the less dense and bigger DDGS fiber particles can be easily mixed with more dense and smaller non-fiber particles under air flow. To overcome this problem, a sieving step

was added to the existing elutriation process. By sieving DDGS into different sieve fractions and air classifying these sieve fractions separately, the mixing of small sized non-fiber can be effectively eliminated. The DDGS particles are first sieved into four to five sieving fractions and each fraction is elutriated to collect DDGS fibers except for the smallest sieve fraction which has lower fiber and higher protein and oil contents. The combination of elutriation and sieving is known as elusieve (Fig. 1.3) [15]. The use of elusieve for DDGS fiber separation was performed to add value to the corn ethanol production process. The elusieve process used on DDGS/corn flour results into two products- DDGS fraction with enhanced oil and protein content or corn flour with starch content, and elusieve fiber. Elusieved DDGS with increased protein and oil content and lower fiber has several advantages to offer such as improved digestibility in non-ruminants and increased nutritional value. Elusieved DDGS fraction can be worth \$5-20 per ton more than DDGS with lower fat and protein content [32]. Economic analysis for employing elusieve process for fiber separation in already existing dry grind ethanol plant processing corn at 2030 metric tonnes/day was estimated to be 1.1 yr [15]. The capital investment in this process was low due to simple equipment, sifters and aspirators.



**Fig. 1.3.** Schematic of elusieve processing (Reprinted with permission from Elsevier) [44]

### DDGS as a Filler in Polymer Composites

The role of DDGS as a filler in polymer composites has been explored in last few years. The inclusion of DDGS in polyethylene and polypropylene at 20 or 30% fiber content showed comparable tensile and flexural modulus to glass composites and had decreased tensile strength. The results showed that DDGS can be used as filler in plastics [35]. DDGS as a filler in poly (lactic acid) at 20% loading showed DDGS is a cost effective biodegradable filler for PLA composites that can provide resulted in enhanced mechanical properties in the PLA composites [36]. The use of DDGS showed its effectiveness as a filler in polyhydroxyalkanoate (PHA) polymer in preserving the dynamic mechanical properties and glass transition temperature of the material [37]. The interaction of DDGS with a coupling agent named methylene diphenyl

diisocyanate (MDI) in PLA polymer resulted in 25% increase in young's modulus at 20% DDGS loading and 1% MDI [38]. In poly (butylene adipate-co-terephthalate) or PBAT polymer composite increase in DDGS loading from 20 to 30% enhanced the tensile but flexural strength of the material decreased [39]. The biodegradation of PBAT matrix was enhanced by the addition of DDGS.

### **Factors Influencing Properties of Natural Polymer Composites**

Properties of natural fiber polymer composites are influenced by type, size, shape, composition, loading, dispersion, and orientation of fibers, matrix type, interfacial bonding, and composite manufacturing process [40]. For example, certain plant fibers such as flax and cotton has very high aspect ratio and specific strength resulting in stronger composites. Similarly, high cellulose content and even dispersion in the polymer matrix can result in better composite properties.

### **Polymer-Fiber Interaction**

Natural fiber based composites suffer from poor interfacial adhesion between natural fibers and polymer matrix because natural fibers are polar and polymer matrices are non-polar. Cellulosic fibers are hydrophilic in nature and absorb moisture whereas polymer matrices are hydrophobic. The different polarities of natural fibers and polymer matrices results in weak interfacial bond between them. This weak fiber-resin chemical bonds break easily through hydrolytic reactions and swelling of the resin when exposed to moisture [40].

It is of utmost importance that the fiber and matrix have good bonding to handle the stress from the applied load. The interaction between fiber and matrix can be improved by some physical or chemical modification to the fiber. Physical treatments include solvent extraction, laser,  $\gamma$ -ray and UV bombardment. Chemical modifications include acetylation, sialylation, alkali treatment, bleaching, grafting and other treatments reducing moisture sensitivity. The best

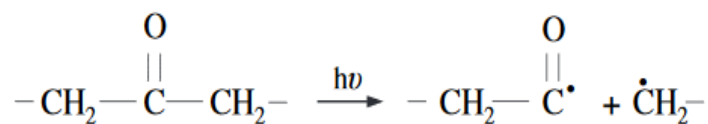
chemical treatment of the fiber is one that allows the fiber and matrix to bond through covalent forces [41]. In addition, chemical treatment of fibers sometimes coupling agents such as silanes and maleic anhydride (MA) are used [41].

### **UV Weathering**

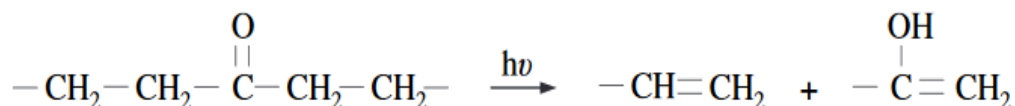
In outdoor applications such as decking, fencing, sliding, window framing, and roof tiles, the natural fiber polymer composites are affected by exposure to UV radiations. The poor resistance to UV rays can raise concern to their long-term performance. The UV degradation is initiated by sunlight which is enhanced by several environmental factors such as moisture, temperature, and air pollutants present in the outdoor environment. The degradation of natural fiber and polymer components in a composite material can occur through different degradation mechanisms.

The degradation of polyolefins originates from excited polymer-oxygen complexes introduced by catalyst residues, hydroperoxide groups, carbonyl groups and double bonds formed during polymer manufacturing. The degradation of the polyolefins can be initiated even by a small amount of these impurities [17].

The main precursor to photochemical degradation of polyolefins are carbonyl groups as they initiate the degradation process of polymers after absorbing the UV light [42]. The degradation of polymers can occur via Norrish type I and II reactions as presented in Fig. 1.4 [43]. The Norrish type I reaction involves the production of free radical intermediates because of cleaving of aldehydes and ketones that terminate via crosslinking or chain scission [43]. The termination step of chain scission and cross linking compete under photodegradation process. The chain scission results in lowering of molecular weight whereas the crosslinking increases the molecular weight by increasing the bonding between the polymer chains [43].



(a) Norrish I



(b) Norrish II

**Fig. 1.4.** Different mechanism of polymer degradation. a) Norrish I, b) Norrish II (Reprinted with permission from Elsevier) [43]

The type II reactions produce carbonyl and terminal vinyl groups and terminate through chain scission of the polymer chains [43]. The outcome of chain scission is an increase in chain mobility due to reduction in the density of chain entanglements in the amorphous phase, thereby allowing shorter molecules to crystallize faster.

The effect of weathering on lignocellulosic fiber initiates from lignin which is susceptible to UV radiation. This UV absorption by lignin leads to formation of lignin moieties with  $\alpha$ -carbonyl, biphenyl and ring conjugated double bond structures [44]. These free radicals may cause the degradation of lignin and induce photo oxidation of hemicellulose and depolymerization of cellulose [44]. Quinonoid compounds formed from lignin degradation are responsible for the color change in the lignocellulosic fibers under UV weathering.



The result of the photodegradation of the natural fiber polymer composites is the degradation of the surface of the materials. The weakening of fiber-matrix adhesion results into increased moisture absorption, matrix cracking, surface instability, swelling of fiber and loss in structural integrity and strength [17]. Several chemical modifications such as isocyanate, maleic anhydride, silane, and acrylic acid have been reported to neutralize the effect of photodegradation [45]. The mechanism of a coupling agent is to create a cross linking with the polyolefins and hydroxyl group in a fiber through specific functional groups present in the structure [45].

The accelerated weathering study of wood/polyolefins has been reported widely by various researchers [43]. The studies have shown the presence of wood causes discoloration of the composites because of an increase in carbonyl index [43]. The carbonyl index had similar impacts on the composites, but these effects were found to be restricted to the surface due to screening effect of the fiber particles [43].

### **Surface Modifications of Natural Fiber Fillers**

Natural fibers are hydrophilic in nature. The hydrophilicity of fibers means high degree of moisture absorption by them resulting in dimensional instability of the materials. Polymers are hydrophobic causing poor adhesion with hydrophilic fiber. The weak bonding at the fiber-polymer interface results in ineffective stress transfer, affecting mechanical properties of the fiber filled composite materials. The main goals of doing surface modification of fibers are to improve the interfacial bonding between matrix and fiber and to increase surface roughness and wettability of fibers leading to enhancement of mechanical properties of natural fiber reinforced composites. Surface modification of a fiber that can be performed through various physical and chemical treatments. Physical treatments include corona discharge, cold plasma, gamma-ray and UV bombardment [46]. Chemical treatments such as mercerization (alkali), grafting, acrylation,

permanganate, acetylation, silane and peroxide have already been used effectively on the natural fibers [46].

Physical treatments of fiber change the physical structure and surface properties of a fiber thus improving adhesion between the fiber and the matrix [46]. Corona discharge activates surface energy of cellulose thus affecting the melt viscosity of composites [46]. Cold plasma improves the functional properties of a fiber. Cold plasma causes chemical implantation, etching, polymerization, free radical formation, and crystallization. Physical treatments are energy intensive in comparisons to the chemical treatments, which are less energy consuming. Of all the chemical treatments used for improving fiber surface properties, only alkali and acetylation are the most used chemical methods. Alkali treatment is the preferred method for its effectiveness and low cost over other chemical methods.

### **Mercerization**

Mercerization or alkali treatment is the most commonly used chemical treatment of fiber fillers in thermoplastic or thermoset composites. The mechanism of alkali treatment is to cause swelling of the fiber thus changing their fine structure and morphology [47]. The hydroxyl groups present in the cellulose structure are broken down in the alkaline environment, forming water molecules and get removed from the fiber structure as shown in the equation 1.1 [47].



Alkali treatment directly influences the cellulosic fibril, the degree of polymerization and the solubilization of hemicellulose and lignin [47]. The outcomes of alkali treatment of a fiber to be used as filler or reinforcing agent in a polymer are: increased roughness for better mechanical interlocking and increase in possible reaction sites as the amount of cellulose exposed on the fiber surface increases [47]. Several concentrations (1, 2, 4, and 10%) of alkali were reported for

treating sisal fiber reinforced composites [48]. The results showed that the maximum tensile strength obtained from the 4% alkali treatment. Another study with sisal fiber reinforced polyester showed that higher concentrations up to 10% NaOH can weaken or damage the fiber due to excess delignification where 5% NaOH showed highest tensile strength [49].

### **Conclusions**

The dramatic increase in the production of DDGS, a byproduct of corn ethanol process, demands to develop value added product to increase sustainability of the corn ethanol industry. The DDGS fiber is indigestible by swine and poultry and can be used effectively separated from DDGS using elusieve process. The DDGS fiber could potentially be a suitable alternative as a filler in polymer composites. The UV exposure of the natural fiber composites leads to loss of structural integrity, surface degradation, scission of polymer chains, and color fading. DDGS and corn fiber, with its very low lignin content, could potentially reduce the UV degradation in polymer composites when used as a filler. To improve the interfacial bonding between DDGS/corn fiber and the polymer matrix, fibers can be subjected to physical and chemical treatments. Alkali treatment is the most cost-effective method to modify the fiber surface and to improve the fiber matrix adhesion.

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## **CHAPTER 2. FIBERS FROM DDGS AND CORN GRAIN AS ALTERNATIVE FILLERS IN POLYMER COMPOSITES WITH HIGH DENSITY POLYETHYLENE FROM BIO- BASED AND PETROLEUM RESOURCES<sup>1</sup>**

### **Abstract**

The steady increase in production of corn based ethanol fuel has dramatically increased the supply of its major co-product known as distiller's dried grain with solubles (DDGS). Large amount of DDGS and corn flour are used as an animal feed. The elusieve process can separate DDGS or corn flour into two fractions: DDGS fraction with enhanced protein and oil content or corn flour fraction with high starch content, and hull fiber. This study investigated the feasibility of using fiber from DDGS and corn grain as alternative fillers to wood fiber in high density polyethylene (HDPE) composites made with two different sources of polymers. Two fiber loading rates of 30% and 50% were evaluated for fiber from DDGS, corn, and oak wood (control) to assess changes in various physical and mechanical properties of the composite materials. Two HDPE polymers, a bio-based HDPE with a melt index of 0.34 g/10 min (Braskem), and a petroleum based HDPE with a melt index of 11.5 g/10 min (Marlex) were also compared as substrates. The low-melt index composite with 30% DDGS fiber loading showed the highest impact resistance (80 J/m) among all the samples. The flexural properties showed no significant difference between the two HDPE composites.

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<sup>1</sup> Chapter 2 consists of a revised version of a scientific manuscript that was approved for publication in October 2017 in the Journal of Polymers and the Environment. Authors: Pankaj Pandey, Sreekala Bajwa and Dilpreet Bajwa. Pankaj designed and conducted the experiments in this work, and is first and corresponding author of the manuscript. The co-authors provided advice throughout the work and assisted in the editing.

## Introduction

The importance of corn grain as major animal feed and renewable feedstock for ethanol production is well established. The production of corn in 2010 was  $316 \times 10^9$  kg of which 42.9% was used as animal feed and 41.8% was used for ethanol production [1]. The US Corn ethanol production has seen tremendous growth in the last two decades, from 5 billion liters in 1995 to 55 billion liters in 2015 [2]. Currently, more than 90% of ethanol facilities employ dry grind processing over wet milling due to savings on capital costs [3]. This process generates roughly 0.33 kg each of ethanol, DDGS and carbon dioxide for every 1 kg of corn grain processed [4]. The DDGS produced from corn ethanol process dramatically increased from  $2.7 \times 10^9$  kg in 2000 to  $40 \times 10^9$  kg by 2015 [2]. If the ethanol industry expands at a modest 10-15% per year, the supply of DDGS is projected to reach around  $70 \times 10^9$  kg by 2020 [4]. The DDGS is the non-fermentable remnants of the corn grain and yeast cells that contains approximately 26.8-33.7% protein, 39.2-61.9% carbohydrates (including fibers), 3.5-12.8% oils, and 2.0-9.8% ash all measured on dry weight basis [5]. DDGS has traditionally been used as livestock feed due to its high protein content and is used at low inclusion levels in swine and poultry diets because of high fiber content [6].

Corn grain is a major source of feed in livestock, swine and poultry industries due to its high starch content (~70%). The fiber in corn is not easily digested by non-ruminants such as poultry and swine. Also, during the corn ethanol production, only the starch fraction is utilized by the enzymes with fiber fraction remain unused. To enhance the feed value and to increase the productivity of corn ethanol production, the separation of fiber with elusieve process was developed [7,8]. The elusieve process is a combination of elutriation and sieving process which can separate DDGS or corn flour into two fractions: DDGS fraction with enhanced protein and oil content or corn flour with high starch content, and the hull fiber. Removal of the crude fiber



from DDGS and corn flour can improve the feed value in the poultry industry [9,10]. Therefore, alternate uses of fibers from DDGS and corn flour is to be explored to sustain the economic viability and reduce the environmental impact of corn ethanol production and corn agriculture. The hull fiber from DDGS or corn flour can potentially be used as a filler in natural fiber filled polymer composites.

In recent years, biocomposites that use agricultural fibers as fillers or reinforcement have gained attention as it adds value to agriculture and use a renewable source of fiber [11-13]. These composites are light in weight, easy to process, have comparable specific properties with synthetic composites, and cost effective. Despite having these advantages, the mismatch in chemical nature of fiber and polymer leads to an ineffective interfacial interaction between them. The fibers are hydrophilic in nature whereas the polymers are hydrophobic. This incompatibility between the fiber and the matrix results in an ineffective stress transfer and make them susceptible against the moisture absorption causing subsequent dimensional instability [13]. The interaction between the natural fiber and the polymer matrix can be improved by several methods such as chemical treatment (silane treatment [14], graft polymerization [15] and alkali [16]), and physical modifications [17].

Currently, there are no reported studies that investigated how bio-based HDPE will perform in comparison to a petroleum-based HDPE when used with corn or DDGS fiber as the filler. Bio-based HDPE is derived from ethylene gas which is likely similar in purity to that used in petroleum-based HDPE, and thus differences between the two types of HDPE will be due to differences in the polymerization process. A few studies have shown that DDGS can potentially be used as a raw material in different types of composites [4, 18, 19]. Our own preliminary research indicated that fiber from DDGS and corn substantially increased the water absorption but showed comparable mechanical properties to composites made with wood fiber. The aim of

this study was to investigate the feasibility of using fiber from DDGS and corn grain as potential fillers against oak fillers in thermoplastic composites with HDPE as the substrate and to evaluate a commercially available bio-based HDPE with low melt index against a petroleum based HDPE with high melt index.

## **Materials and Methods**

### **Design of Experiment**

A lab experiment was designed to evaluate the hypothesis the properties of HDPE composites made with the fibers from corn and DDGS will be comparable as with wood fiber. The experiment included 3 fiber types, two fiber loading rates and two different types of high density polyethylene. The three fiber types were DDGS fiber, corn grain fiber and oak wood fiber. The two loading rates used were 30% and 50% by weight. The loading rates of 30% and 50% were chosen because of the limitations with the lab-scale twin screw extruder that was not able to handle more than 50% fiber loading. A total of 12 formulations (3 fiber  $\times$  2 loadings  $\times$  2 HDPE) were designed for the extrusion run (Table 2.1). The composites contained 4% talc to uniformly distribute the heat and smooth the extrusion process. These twelve formulations were replicated five times to generate enough samples for testing all the physico-mechanical properties.

**Table 2.1.** Different composite sample formulations designed for the study

Formulation	Fiber Loading (wt %)	HDPE		Talc (wt %)
		Marlex (wt %)	Braskem (wt %)	
Corn 30, Marlex	30	66	-	4
DDGS 30, Marlex	30	66	-	4
Oak 30, Marlex	30	66	-	4
Corn 50, Marlex	50	46	-	4
DDGS 50, Marlex	50	46	-	4
Oak 50, Marlex	50	46	-	4
Corn 30, Braskem	30	-	66	4
DDGS 30, Braskem	30	-	66	4
Oak 30, Braskem	30	-	66	4
Corn 50, Braskem	50	-	46	4
DDGS 50, Braskem	50	-	46	4
Oak 50, Braskem	50	-	46	4

## Materials

Three different types of natural fibers from DDGS, corn grain, and oak wood were used as fillers in the study. The DDGS was supplied by Blue Flint Ethanol, USA, and elusieved at Mississippi State University. Mississippi State University also provided the elusieved corn grain fiber. Oak wood fiber was obtained from Southern Wood Services LLC (Macon, GA, USA). All three fibers were first passed through a 1 mm screen in a Wiley mill (Model 4, Thomas Scientific, NJ, USA). The screened fibers were particle sized in the range of 20-30 mesh (0.595-0.841 mm) in a Ro tap shaker (W.S. Tyler® Ro-Tap® 8in Sieve Shaker, USA). The oak wood flour mainly composed of cellulose (45.7%), hemicellulose (24.8%), and lignin (27.6%) [20]. The composition of DDGS and corn fiber in terms of neutral detergent fiber (NDF), protein, starch, fat, and ash are shown in Table 2.2. The bulk densities of the fibers were measured by

taking 100 g each of the dried fiber in a 250 ml graduated cylinder and leveling them inside by gently tapping the cylinder from outside. The bulk densities measured for DDGS, corn, and oak fiber were 446.9 kg/m<sup>3</sup>, 437.3 kg/m<sup>3</sup>, and 331.1 kg/m<sup>3</sup>, respectively.

**Table 2.2.** Composition of hull fiber from corn grain and DDGS and oak fiber on a dry basis

Components	Corn fiber (%)	DDGS fiber (%)	Oak fiber (%)
NDF	49.2	46.93	98.1
Protein	7.88	21.07	-
Starch	31.85	3.34	-
Fat	3.08	8.14	-
Ash	1.37	4.46	0.41

Two different types of high density polyethylene (HDPE) polymers used in this study were Marlex 9012 (Chevron Philips, The Woodlands, TX, USA), and Braskem SGF 4950 (Braskem, Sau Paulo, Brazil). The Marlex 9012 was produced from steam cracking of petroleum based resources whereas Braskem SGF4950 was produced from ethylene obtained from catalytic dehydration of sugarcane ethanol. Braskem claims their HDPE to have the same technical properties, appearance and versatility of applications as HDPE from fossil source. Both the HDPEs were obtained in the pellet form. The major difference between the two HDPEs was their melt flow index (MFI) (Table 2.3), which resulted from different polymerization processes, not from the ethylene source.

**Table 2.3.** Properties of the two HDPEs, Marlex and Braskem used in the study, as reported by the manufacturers

Polymer Properties	Marlex 9012 (Petroleum based)	Braskem SGF 4950 (Bio-based)	Test Method
Density, g/cm <sup>3</sup>	0.952	0.956	ASTM D1505
Melt flow index (190 °C/ 2.16 kg), g/10 min	11.5	0.34	ASTM D1238
Tensile yield strength, MPa	27	30	ASTM D638
Flexural modulus, MPa	1270	1350	ASTM D790

### Composite Manufacturing

All the fibers were first oven dried at 105 °C for 24 h to bring down the moisture content to less than 1%. In the next step, the dried fibers were hand mixed with HDPE and talc for all the formulations presented in Table 2.1. The homogeneous mixture was then compounded in a twin-screw co-rotating extruder (Leistritz Micro 18 GL 40 D, NJ, USA). The extruder had seven different temperature zones set at the following temperatures of 160 °C, 193 °C, 199 °C, 204 °C, 207 °C, 210 °C, and 213 °C sequentially from feed section to melting section. The die temperature at the exit was maintained at 213 °C. The screw rotation of the extruder was set at 150 rpm. The material was extruded into 3 mm diameter strands that were cooled by passing through a water bath and pelletized with a BT25 pelletizer (Scheer Bay Co., Bay City, MI, USA). The pelletized composite material was oven dried overnight at 80 °C. The test specimens were manufactured with a mini injection molder (Model SIM- 5080, Technoplas Inc., MA, USA) set at 200 °C into dog bone samples of 12.5 mm by 3.5 mm cross sectional size at the center, and 65 mm length.

## **Characterization of Physical, Mechanical and Thermal Properties**

### *Melt Flow Index (MFI)*

The MFI of the composite materials was determined in accordance with ASTM D1238 standard, using an extrusion plastometer (Tinius Olsen, Model MP 600, USA). The composite pellets were tested in five replicates at 2.16 kg load and 190 °C. The MFI was recorded as the amount of material that would pass through the nozzle of the plastometer in 10 min. The two HDPEs were subjected to Nuclear Magnetic Resonance (NMR) spectroscopy to understand the differences in their molecular structure. NMR was performed by dissolving 50 mg/ml of each HDPE in deuterated chloroform, and then scanning the solution with a 400 MHz NMR spectrometer (Bruker LC-MS, USA). A plot of chemical shift in ppm on x-axis versus intensity on y-axis was obtained.

### *Water Absorption*

The long term water absorption of composites samples was quantified as specified by ASTM D570 standard. Five samples from each formulation was tested for percentage moisture gain at 24h increments until the samples were saturated. The samples were immersed in water at 24 °C in a water bath for testing their water absorption properties. The composite samples used for the test were 30 mm long, 12.5 mm wide, and 3.5 mm thick.

### *Specific Gravity*

The samples were tested for their specific gravity using a specific gravity balance based on ASTM D792 standard. A non-corrosive wire cage was used to suspend the samples in water so that the weight of samples in water set at 24 °C can be measured. The sample dimensions used for the test were 30 mm long, 12.5 mm wide, and 3.5 mm thick.

### *Flexural Properties*

The flexural properties of the samples were measured according to the ASTM D790 standard that specifies three-point bending test method for unreinforced and reinforced plastics. The samples used for the test were 63 mm long, 12.5 mm wide and 3.5 mm thick. A crosshead speed of 1.3-1.4 mm/min was selected based on the span length of the samples. The universal testing machine from Instron (Model 5567, USA) with a 2 kN load cell was used for the test.

### *Impact Strength*

The impact strength of the samples was tested in accordance with ASTM D256 standard. The notched samples were tested for their impact resistance properties with an Izod impact tester (Tinius Olsen, Model Impact 104, USA). The sample dimensions used were 63 mm x 12.5 mm x 3.5 mm with a notch of 2 mm. The fractured surfaces of samples were examined with a JEOL JSM-6490LV scanning electron microscope (JEOL USA, Inc., Peabody MA, USA) at an accelerating voltage of 15 KV. The samples were first attached to cylindrical aluminum mounts with silver paint (SPI Products, West Chester, PA, USA) and then sputter coated with a conductive layer of gold-palladium (Cressington 108 Auto, Ted Pella Inc., Redding, CA, USA).

### *Coefficient of Linear Thermal Expansion (CLTE)*

The change in length of the samples under constant heat exposure was measured using the dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). The sample dimensions used for the test were 63 mm x 12.5 mm x 3.5 mm. A temperature ramp of 3 °C/min and temperature range of 30 °C to 50 °C were used for carrying out the test.

### *Differential Scanning Calorimetry (DSC)*

The thermal properties of the polymers and composites were determined using a differential scanning calorimeter (DSC Q20, TA Instruments USA). A reference pan (empty from inside) and a sample pan with sample weight of around 5-7 mg were placed on raised

platforms on the sensors and both were subjected to heating-cooling-heating cycles. Nitrogen gas was purged at 50 mL/min to provide controlled sample/atmosphere interactions without any thermal degradation. The pans were first heated from 25 °C to 200 °C at the rate of 10 °C/min and then kept at 200 °C isothermally for one minute to erase the thermal history before cooling again back to 25 °C. The cooling rate could not be controlled. During the cooling step, the heater simply shut off until the DSC cell cooled to 25 °C before heating the samples again to 200 °C at the rate of 10 °C/min in the second heating cycle. The room temperature remained the same (23 °C) during the DSC runs, so the cooling step that may have some variation among different samples was assumed to be similar. The crystallization temperature ( $T_c$ ) and crystallization enthalpy ( $\Delta H_c$ ) were calculated from the cooling run. The values of melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ) and the percentage crystallinity ( $X_c$ ) were calculated from the second heating run. The crystallinity of HDPE was measured as

$$X_c = \frac{\frac{\Delta H_m}{W_p}}{\Delta H_{m100}} \times 100\% \quad (\text{Equation 2.1})$$

where  $\Delta H_m$  is the experimental melting enthalpy of the composites,  $\Delta H_{m100}$  is the theoretical melting enthalpy of the fusion for 100% crystalline HDPE polymer (293 J/g) [21]. The  $W_p$  is the weight fraction of the HDPE in the composites corrected on the weight basis.

### **Statistical Analysis**

To determine the statistical significance at  $\alpha = 0.05$ , Fishers Least Square Difference (LSD) tests were performed on all 12 sets of samples using Minitab 17 (Minitab Inc., Penn State University, PA, USA). The error bars in the bar graphs represents the standard deviation of the sample.



## Results and Discussion

The extrusion operation with 30% loading was much smoother than with 50% loading. The extruded strands broke and required more pressure to extrude when the fiber loading was 50% for Braskem composites due to its low MFI and high fiber content. Also, the injection molded samples showed more exposed fiber (poor encapsulation) with 50% fiber loading while the samples with 30% loading had very smooth surface with completely encapsulated fibers (Table 2.4).

**Table 2.4.** Melt Flow Index (MFI) of Marlex and Braskem composite samples with their standard deviations. The letters in the bracket show the statistical significant difference between the composite formulations at  $\alpha=0.05$

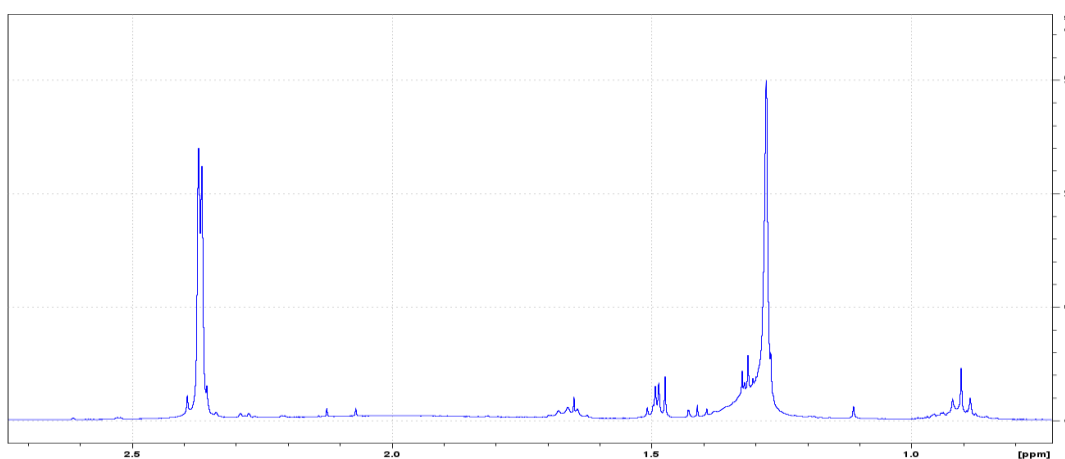
Fiber type with loading	Marlex HDPE (g/10 min)	Braskem HDPE (g/10 min)
Neat HDPE	11.5*	0.34*
Corn 30	3.57 $\pm$ 0.03 (c)	0.42 $\pm$ 0.07 (f)
DDGS 30	6.02 $\pm$ 0.48 (a)	0.30 $\pm$ 0.01 (f, g)
Oak 30	4.44 $\pm$ 0.15 (b)	0.16 $\pm$ 0.01 (f, g)
Corn 50	0.39 $\pm$ 0.09 (f)	0.11 $\pm$ 0.01 (g)
DDGS 50	1.97 $\pm$ 0.15 (d)	0.11 $\pm$ 0.01 (g)
Oak 50	1.22 $\pm$ 0.07 (e)	0.11 $\pm$ 0.01 (g)

\*As reported by the manufacturers

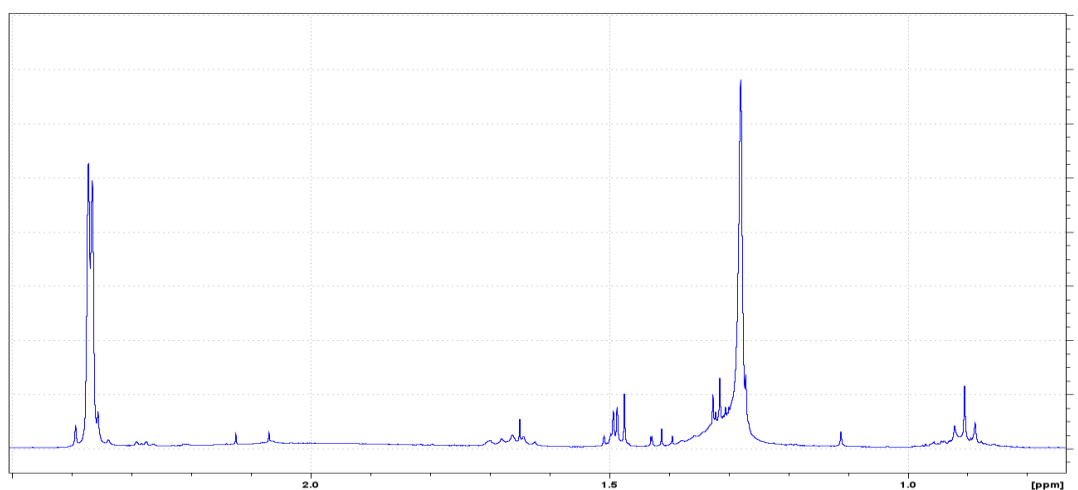
### Melt Flow Index (MFI) of Composite Samples

The fiber fillers decreased the MFI, compared to neat polymers (Table 2.1 & 2.4). This decrease in MFI was expected as both the type of fiber and fiber surface characteristics impacts the entanglement and mobility of the polymers [22]. Increase in fiber loading from 30 to 50% further decreased the MFI by one-third to one-ninth (Table 2.4), and thereby limiting the ability to flow smoothly. Of all the formulations with Marlex substrate, 50% corn composites showed the lowest MFI followed by 50% wood composites. The 30% DDGS composites showed the highest MFI of 6.02 g/10 min followed by 30% wood and 30% corn composite samples. Of all the Braskem composite samples, 30% corn and 30% DDGS fiber composites exhibited MFI

comparable to that of neat Braskem polymer. Other composite formulations had more than 50% decrease in MFI to the neat Braskem polymer. A high MFI is preferred as it saves energy and time during extrusion and injection molding. The NMR peak in 1.0-1.5 ppm range shows that Braskem polymer has more CH<sub>3</sub> groups than Marlex polymer (Fig 2.1 & 2.2). Also the proportion of CH<sub>2</sub> (2.0-2.5 ppm) and CH<sub>3</sub> (1.0-1.5 ppm) groups in Braskem corresponds to more alkyl groups respectively than in Marlex polymer. This explains the major difference in the MFI as polymers with branched chains flow more slowly than linear chains.



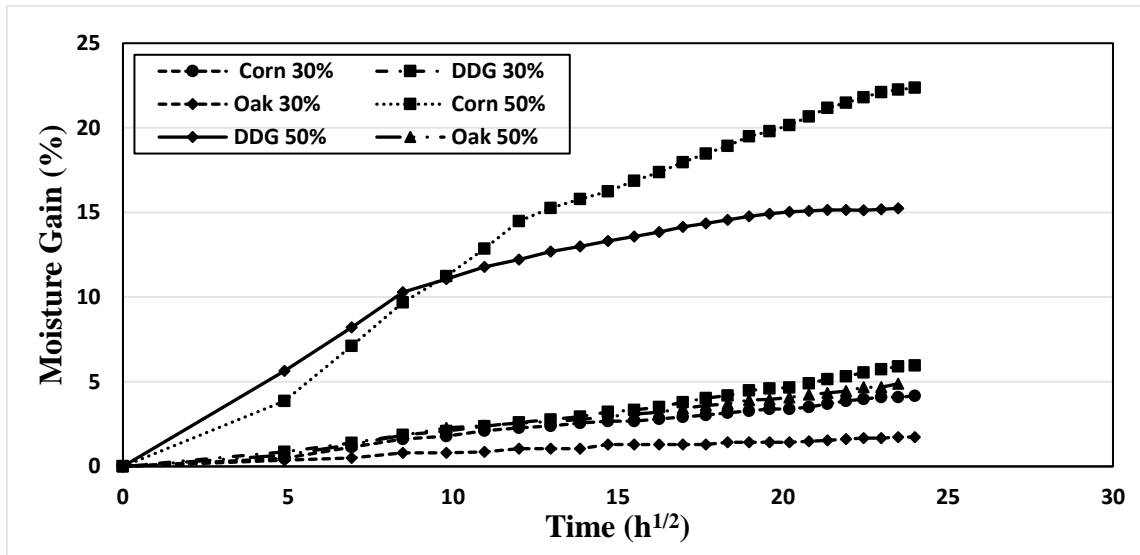
**Fig. 2.1.** NMR spectra for Braskem, the bio-based HDPE made from sugarcane ethanol (chemical shift on x-axis vs intensity on y-axis)



**Fig. 2.2.** NMR spectral of Marlex, the petroleum based HDPE (chemical shift on x-axis vs intensity on y-axis)

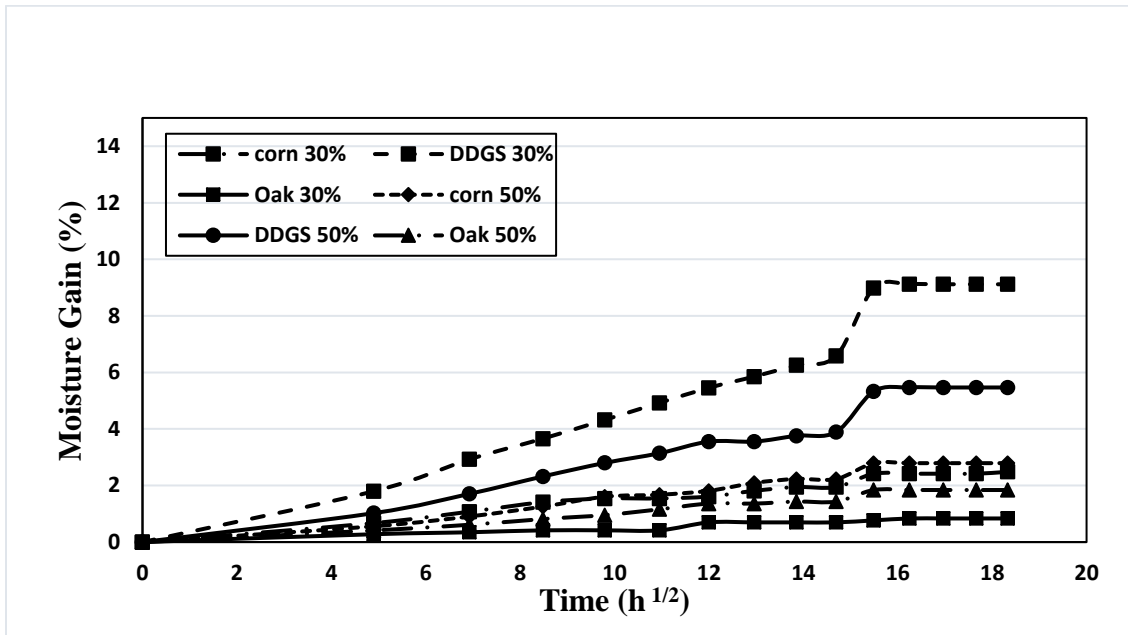
## **Water Absorption Properties**

The moisture absorption in natural fiber polymer composites is inherent as natural fibers being hydrophilic in nature have poor interfacial bonding with the hydrophobic polymer matrices. The absorption of moisture results in swelling of natural fibers and weakening of adhesion at the interface between the polymer and the fiber. The swelling and shrinking under exposure to water followed by drying change the internal packing of fibers and cause dimensional instability, causing degradation of physical and mechanical properties of the composites [23]. The long term water absorption behavior of Marlex composites over 600 h show that corn and DDGS fibers at 50% loading showed the highest saturation moisture absorption of approximately 23 and 15% respectively (Fig. 2.3). This high absorption can be a result of high amount of hemicelluloses in the fibers [24] and to the presence of relatively high amount of un-encapsulated fibers in the composites. The wood-HDPE composites showed a low moisture absorption of less than 5% at both 30 and 50% fiber loadings. Despite of having lower bulk density, the oak fiber composites showed better resistance to moisture absorption than DDGS and corn fiber composites. This is most likely due to the long spindle shape of oak fiber that interacts better with the HDPE matrix than granular and irregular shaped fibers such as DDGS and corn fiber [20]. The 30% DDGS loading followed the same trend as was also observed for 50% DDGS in HDPE matrix [25]. Also, 30% corn and 30% DDGS composite samples showed moisture gain comparable to 50% oak composites. Composites with 30% oak showed the lowest water absorption.



**Fig. 2.3.** Effect of fiber filler type and fiber loadings on water absorption of polymer composite samples containing Marlex HDPE as the substrate

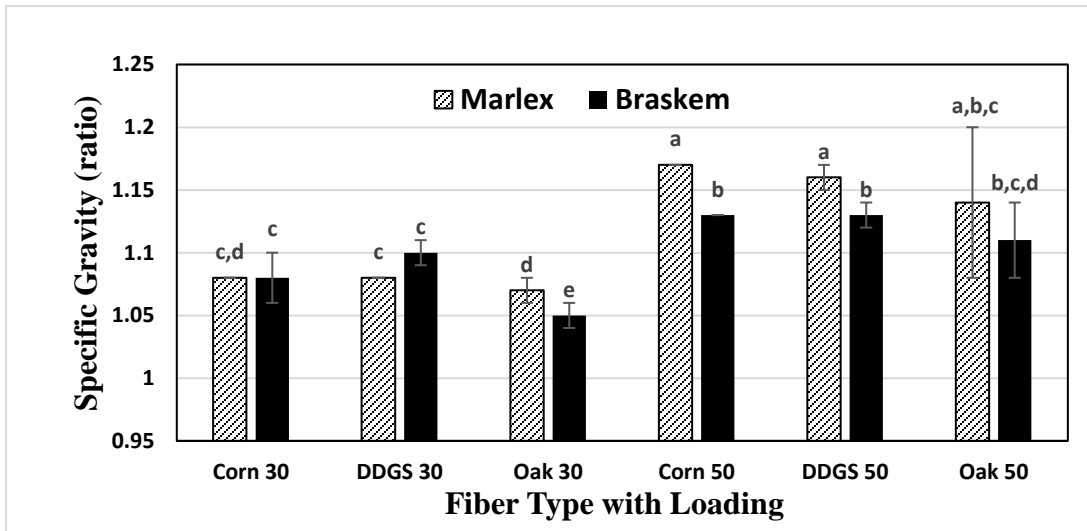
In Braskem composites, the samples with 30% DDGS and 50% DDGS fiber loading showed the largest moisture absorption of 9% and 5.5% respectively over a period of 336 h (Fig. 2.4). All other composite samples with Braskem showed moisture absorption of less than 3%. The Braskem composites showed significantly lower moisture absorption than the Marlex composites. The higher branched chain structure of Braskem polymer most likely had higher interlocking sites for fiber than Marlex polymer resulting in higher moisture resistance than the Marlex composites.



**Fig. 2.4.** Effect of fiber type and fiber loadings on water absorption of polymer composite samples containing Braskem as the substrate

### Specific Gravity Test

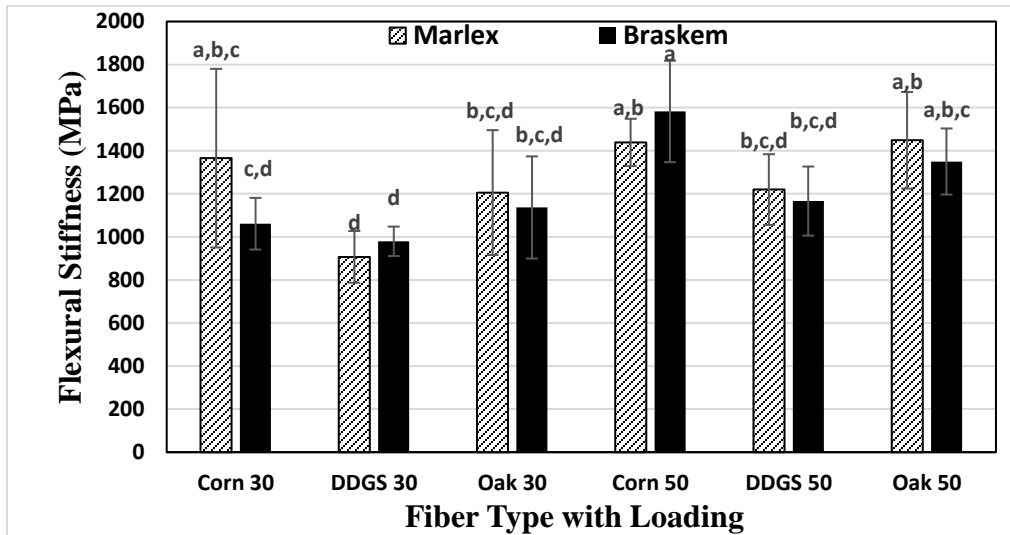
In many composite applications, a low specific gravity is preferred as it indicates low density and weight. Similar to many commercially available wood plastic composites, the lab samples exhibited specific gravities slightly above one, but well below 1.2 (Fig. 2.5). In the Marlex composites, all three fillers exhibited lower specific gravities at 30% loading than at 50% loading. The Braskem samples showed a similar trend with corn and DDGS samples at higher loading. An increase in fiber loading from 30 to 50% increased the specific gravity and therefore, density of the composite samples with both types of HDPEs.



**Fig. 2.5.** Specific gravity (ratio) of composite samples made with two different HDPEs and three fiber types at two fiber loading rates measured at 24 °C. Different letters in the label show statistically significant difference between the different formulations at  $\alpha = 0.05$

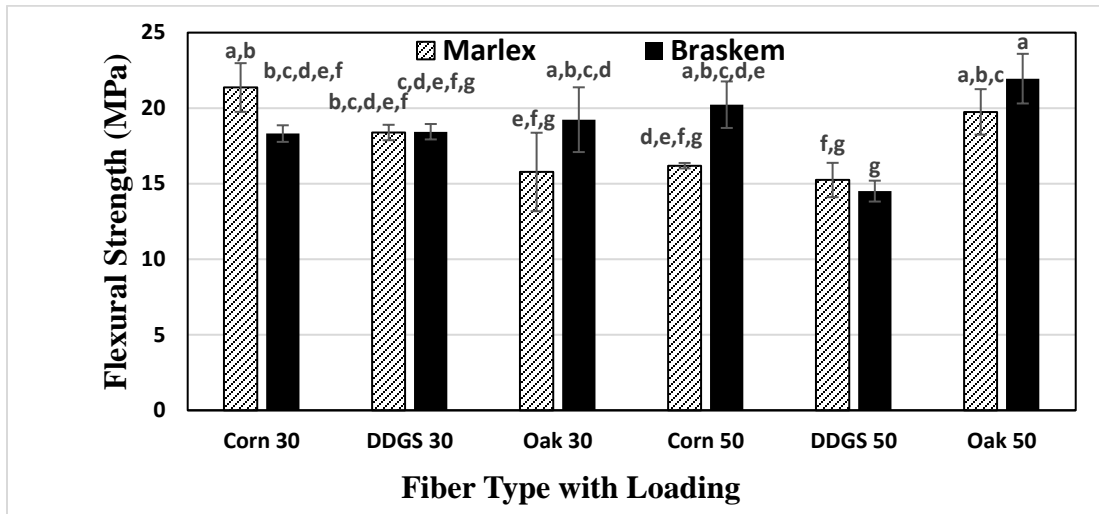
### Flexural Properties

When a sample is under flexural load, the material is subjected to the highest tensile and compressive stresses on the bottom and top surfaces, respectively. Therefore, the sample will fail under the weaker of the two properties. The Marlex composites showed no significant difference in their flexural stiffness or modulus between the fiber filler types (Fig. 2.6). An increase in filler loadings from 30 to 50% neither led to any improvement nor decline in the flexural stiffness properties of composite material with Marlex polymer. Both the corn and DDGS composite samples behaved as good as the control samples at both the loadings. This indicated that corn and DDGS fiber can replace oak as potential fillers at both 30 and 50% loadings to obtain the same flexural stiffness values. On the other hand, in the Braskem composite samples, only 50% corn showed a significant improvement in the stiffness of 49% when compared with its 30% corn sample (Fig. 2.6). No significant difference was observed between 30% corn, 30% DDGS, 30% oak and 50% DDGS and 50% oak samples.



**Fig. 2.6.** Flexural stiffness of thermoplastic composite samples made with two different HDPEs and three fiber types at two fiber loading rates. Different letters in the label show statistically significant difference between the different formulations at  $\alpha = 0.05$

Composites containing Marlex and Braskem HDPE showed similar flexural strengths. Marlex composite samples with 30% corn and 30% DDGS fibers were stronger than 30% oak samples, and similar to 50% oak samples under flexure (Fig. 2.7). This means that the corn and DDGS fiber fillers at 30% loading can replace 30% oak in HDPE composite samples for the better flexural strength. An increase in fiber loading from 30 to 50% did not affect flexural strength of Marlex composites except in the case of corn fiber filler. With corn fiber filler, an increasing fiber loading from 30 to 50% decreased flexural strength by 24%. In Braskem composites, no significant difference was observed in flexural strength between the fillers except for 50% DDGS fiber which exhibited lower flexural strength (Fig. 2.7). This decrease at higher fiber loading can be attributed to the poor adhesion between the fiber-matrix surface leading to micro cracks formation and non-uniform stress transfer due to agglomeration of fiber within the matrix [26].



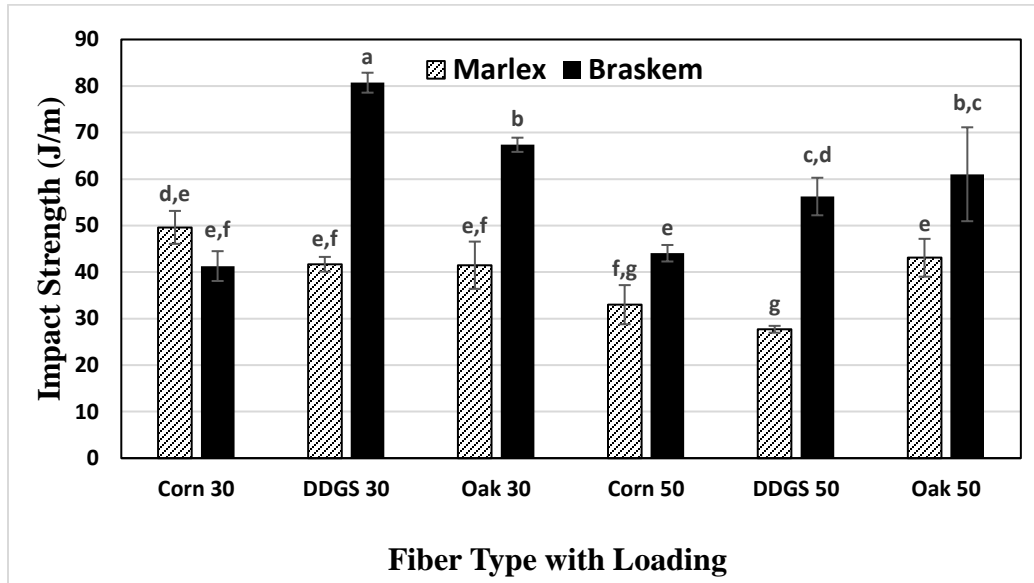
**Fig. 2.7.** Flexural strength of composite samples made with two different HDPEs and three fiber types at two fiber loading rates. Different letters in the label show statistically significant difference between the different formulations at  $\alpha = 0.05$

### Impact Strength

The impact strength of a composite is the energy required to completely break the specimen by the means of crack initiation and propagation. The notched impact strength basically measures the energy needed to propagate the existing crack from the notched tip which acts as a stress concentrating point. The neat Marlex and Braskem HDPEs showed impact strength of 100 and 150 J/m, respectively (not shown in Fig. 2.8). The higher molecular weight of the Braskem polymer than the Marlex polymer (high MFI corresponds to the low molecular weight) allows it to absorb higher energy during the fracture. Overall, Braskem composite samples showed better impact than Marlex. In the Marlex composite samples, all fiber fillers resulted in similar impact strengths at 30% loading (Fig. 2.8). Also, when the filler loading increased from 30 to 50%, both corn and DDGS samples exhibited a significant drop of 33 and 42% in impact strength, respectively. The higher loading means larger interface between the fiber and the polymer matrix. Poor interfacial bonding helps in crack propagation through the formation of micro-cracks in the micro-spaces between them. In Braskem composites, 30% DDGS sample exhibited the highest impact strength of 80 J/m and performed even better than

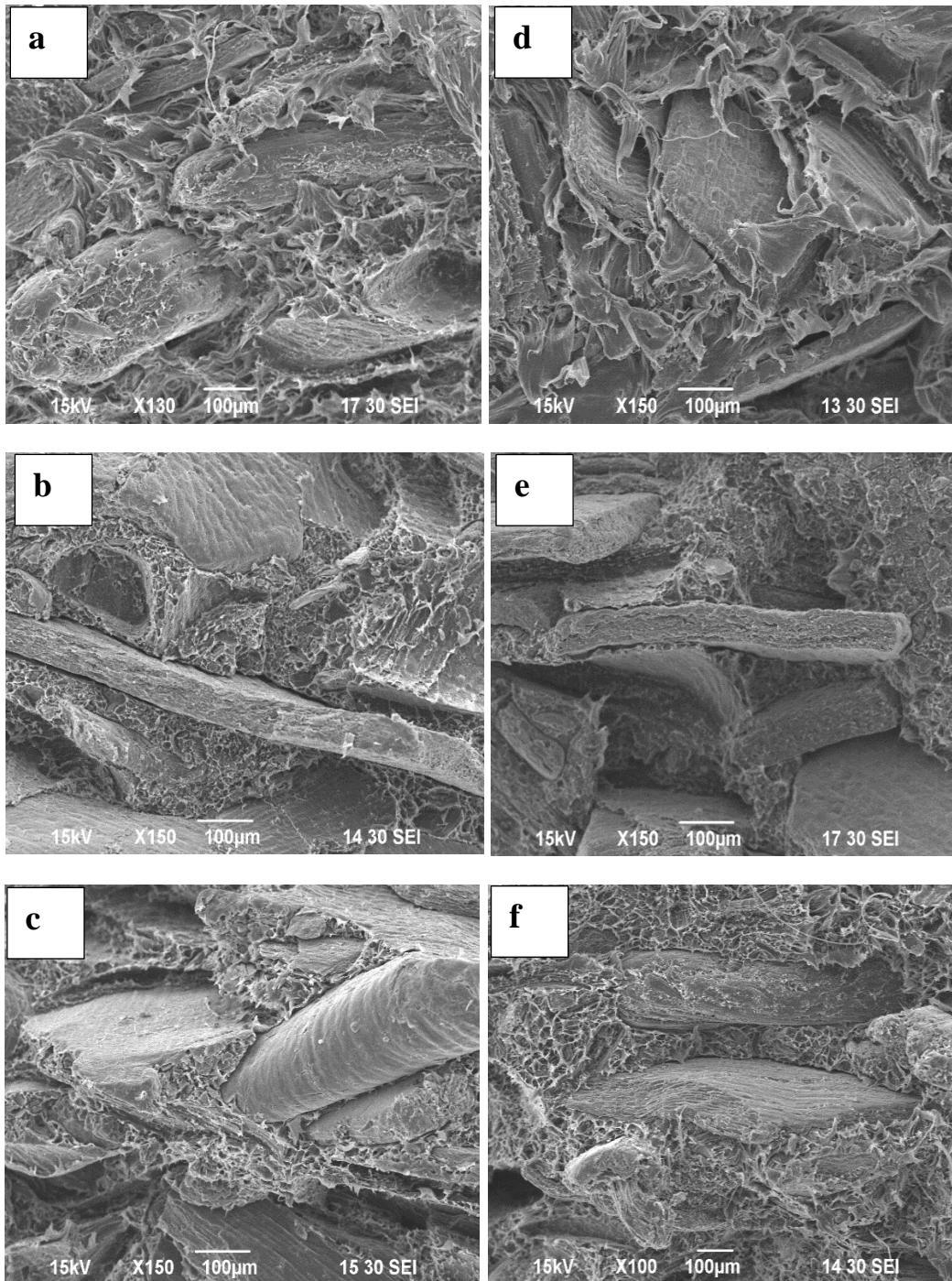


50% oak samples (Fig. 2.8). The corn samples at 30 and 50% loadings showed the lowest impact strength of 41 and 44 J/m respectively. The DDGS sample showed a decrease of 30% in impact strength when the loading increased from 30 to 50%. The Braskem samples exhibited significantly higher impact strength than the Marlex composites for 30% DDGS, 30% oak, and 50% DDGS samples.



**Fig. 2.8.** Impact strength of notched composite samples made with two different HDPEs and three fiber fillers at two fiber loading rates. Different letters in the label show statistically significant difference between the different formulations at  $\alpha = 0.05$

The SEM micrographs of impact fracture of composite samples show that corn samples had severe irregular surface fractures than DDGS and oak samples (Fig. 2.9). These fractures represent the interfacial area between the fiber and the matrix. The pulled out traces of fillers were seen in all the composite samples. The role of fibers in stress propagation is crucial as they act as stress transferring medium to the crack propagation in the materials. The appearance of fractured fiber in DDGS and oak wood indicate better interfacial bonding in their composites than the corn samples.

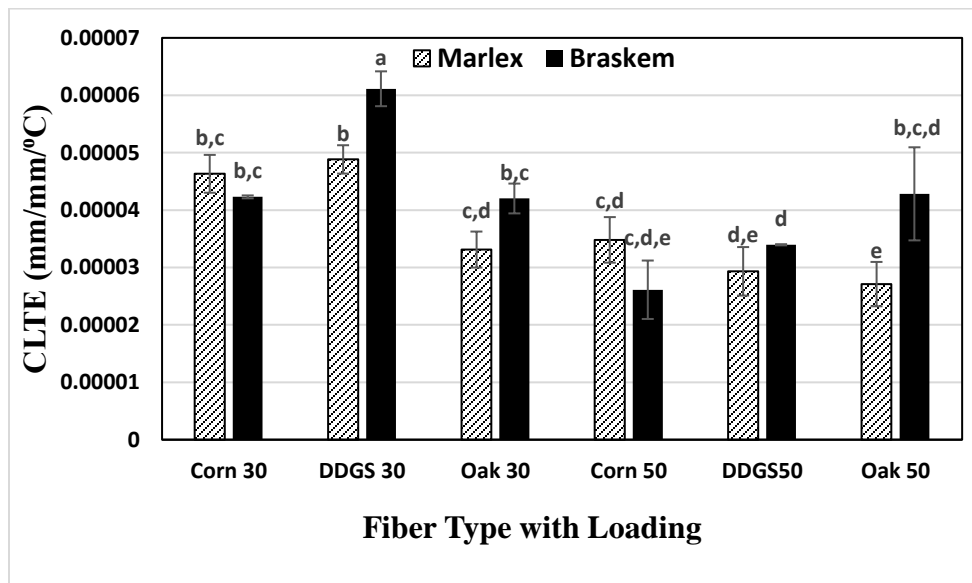


**Fig. 2.9.** Scanning electron microscopy images of the impact fractured samples at various filler loadings. a Corn 30, b DDGS 30, c Oak 30, d Corn 50, e DDGS 50, f Oak 50

### **Coefficient of Linear Thermal Expansion (CLTE)**

The CLTE is a measure of dimensional stability when a material is exposed to extreme temperatures. This is especially important in outdoor applications. A low CLTE value is

preferred as it indicates less thermal expansion with increasing temperatures. The 50% oak and 50% DDGS samples showed the lowest CLTE values among the Marlex composites whereas 30% DDGS exhibited the highest CLTE among the Marlex composites whereas 30% DDGS exhibited the highest CLTE (Fig. 2.10). In the Braskem composites, the 30% DDGS sample showed significantly higher CLTE value than all other formulations. The CLTE of a composite is an outcome of the mismatch between a fiber and a matrix. Plant fibers exhibit negative CLTE while polymers exhibit positive CLTE. Therefore, composites with good interfacial bonding tend to show very small positive CLTE. The fibers affect the CLTE of polymer composites by restricting the opening of polymer chain during heating [27].

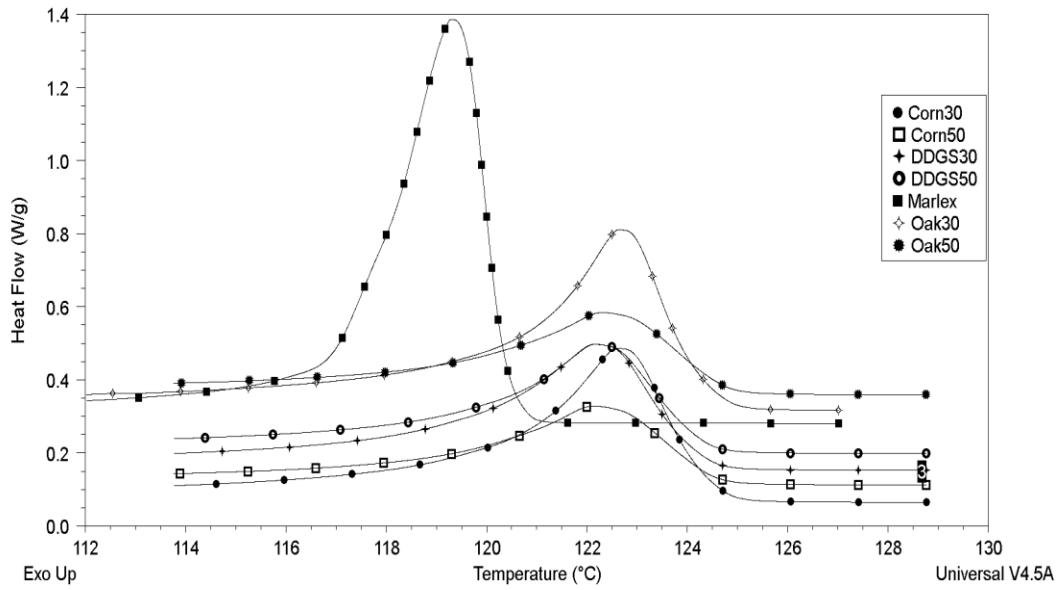


**Fig. 2.10.** Coefficient of Linear Thermal Expansion of composite samples made with two different HDPEs and three fiber types at two fiber loading rates. Different letters in the label show statistically significant difference between the different formulations at  $\alpha = 0.05$

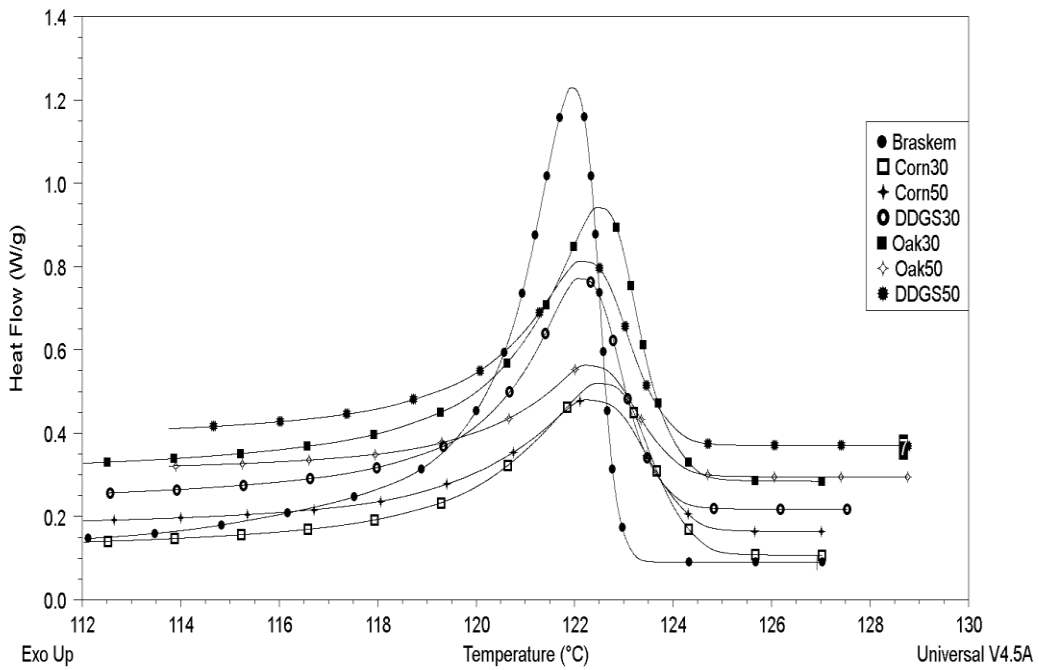
### Thermal Properties

The DSC scans illustrated the effect of fillers on the thermal behavior of the composites. The DSC plots of both the polymers and their filler composites are presented in Fig. 2.11 a & b and the values of their melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_m$ ), heat of crystallization ( $\Delta H_c$ ), and the percentage crystallinity ( $X_c$ ) are presented in Table 2.5. The neat Braskem polymer had higher crystallinity than the neat Marlex polymer. The

addition of fillers at both 30 and 50% loadings showed a slight increase in  $T_m$  for both the Marlex and Braskem composites. This increase in  $T_m$  can be attributed to the presence of fibers which hamper the melt flow ability of the polymers. The inclusion of fibers decreased the height of the thermograms and increased their crystallization peak widths compared to the neat polymers. This increase in the width of the exothermic peak signifies the slow nucleation rate and possibly uneven growth of crystallites. The decrease in crystallinity can be explained by the mechanical restraints provided by the fibers which affects the ability of HDPE chains to crystallize. The change in  $\Delta H_f$  was most likely from the structural imperfections introduced during the processing of materials and due to the presence of filler [28]. The slight increase in  $T_c$  shows nucleating effects of fillers in HDPE composites. The increase in  $T_m$  and  $T_c$  had no specific correlation with the type of filler and their loadings. Of all the composites, only 30% oak and 50% DDGS samples showed higher  $X_c$  (%) than the neat polymers in both the Marlex and Braskem composites. The chemical components of the fillers play a crucial role in their interactions with the polymer chains. The higher  $X_c$  and  $\Delta H_m$  and  $\Delta H_c$  for these two samples exhibit the effective nucleating capabilities of these fillers which eventually helps in the spherulite growth.



(a)



(b)

**Fig. 2.11.** The DSC plots from the cooling step for (a) Marlex composites and (b) Braskem composites

**Table 2.5.** Thermal properties of Marlex and Braskem composites obtained from the DSC runs: melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_m$ ), crystallization temperature ( $T_c$ ), heat of crystallization ( $\Delta H_c$ ) and degree of crystallinity ( $X_c$ )

Sample Name	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$X_c$ (%)
Neat Marlex	130.95	188.00	119.31	166	64.16
Corn 30, Marlex	132.08	177.27	122.6	147.59	60.50
DDGS 30, Marlex	132.02	161.36	122.17	142.00	55.07
Oak 30, Marlex	131.95	198.94	122.65	165.91	67.90
Corn 50, Marlex	133.97	149.41	122.16	130.22	50.99
DDGS 50, Marlex	131.87	198.76	122.17	171.59	67.84
Oak 50, Marlex	134.5	161.39	122.32	126.76	55.08
Neat Braskem	134.03	214.30	121.95	193.10	73.14
Corn 30, Braskem	135.96	175.00	122.46	155.76	59.73
DDGS 30, Braskem	135.80	191.21	122.08	170.61	65.26
Oak 30, Braskem	134.86	246.06	122.45	216.06	83.98
Corn 50, Braskem	137.67	198.46	122.24	175.17	67.73
DDGS 50, Braskem	135.92	245.65	122.17	205.80	83.84
Oak 50, Braskem	136.63	145.20	122.23	131.00	49.55

### Conclusions

The role of fibers from DDGS and corn grain as fillers in HDPE composite was investigated in the study, along with the impact of a biobased HDPE in comparison to a petroleum based HDPE. The bio-based Braskem composites exhibited a much lower MFI than that of petroleum-based Marlex composites. As noted in the introduction, bio-based HDPE is derived from ethylene gas which is likely similar in purity to that used in petroleum-based HDPE; thus, the low MFI of the Braskem HDPE was due to the polymerization process used to produce that HDPE. The inclusion of fiber fillers at both 30 and 50% decreased the MFI value greatly. The Braskem composite samples absorbed less moisture than Marlex based composite samples, low water absorption being a preferred quality in natural fiber HDPE composites. The flexural strength and modulus were similar for composites made with the bio-based Braskem and

petroleum-based Marlex as the HDPE source. Braskem composite samples also exhibited high impact strength compared to Marlex. The natural fiber fillers from DDGS and corn grain showed better flexural strength than oak fiber at 30% loading, which means oak fiber can be replaced by DDGS and corn fibers, without affecting its flexural strength. Braskem composites with 30% DDGS fiber filler showed the best impact strength properties. Higher fiber loading tended to provide more thermal stability to the composite samples by decreasing its thermal expansion. Incorporation of fillers increased the crystallization temperature of all the composite samples exhibiting their nucleating capabilities in the HDPE polymers.

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## **CHAPTER 3. PERFORMANCE OF UV WEATHERED HDPE COMPOSITES CONTAINING HULL FIBER FROM DDGS AND CORN GRAIN<sup>2</sup>**

### **Abstract**

The availability of distiller's dried grain with solubles (DDGS), the main co-product of corn ethanol production, exceeds its demand as feedstuff. A physical separation process named elusieve can separate the hull fiber from DDGS or corn flour to obtain DDGS with enhanced protein and oil content, or corn flour with higher starch content. This study was performed to investigate the potential of using the hull fiber separated with elusieve process on DDGS or corn flour as fillers in high density polyethylene (HDPE) composites at the commercial scale. Additionally, the degradation effects of UV accelerated weathering on this material were investigated. Commercial scale composite samples were made with six combinations of oak fiber, corn hull fiber and DDGS fiber, with the fiber loading maintained at 50%, and then the samples were subjected to UV accelerated weathering for 2000 h. The unexposed DDGS samples showed better resistance to moisture absorption (less than 5%) than the corn filler samples (18%). The specific gravity for all the filler composites was more than one for both unexposed and UV weathered composites. The DDGS fiber also showed higher flexural properties in oak25/DDGS25 than other filler composites. For all samples, the accelerated weathering resulted in a lightening during the first 1000 h of exposure, followed by a darkening at 2000 h of UV exposure. Overall, the UV weathering resulted in a chain scission of the HDPE polymer increasing the crystallinity of the polymer in the weathered filler composites.

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<sup>2</sup> Chapter 3 consists of a scientific manuscript that was approved for publication in July 2017 in the Journal of Industrial Crops and Products. Authors: Pankaj Pandey, Sreekala Bajwa, Dilpreet Bajwa and Karl Englund. Pankaj designed and conducted the experiments in this work and is the first and the corresponding author of the manuscript. The co-authors provided advice throughout the work and assisted in the editing.

## Introduction

Over the last few decades, natural fiber polymer composites have gained markets in building, landscaping and automobile applications because of their durability, low density, easy processing, high specific strength and stiffness, all at a low cost [1,2]. These composites are generally considered for non-structural components for indoor applications as well as outdoor products such as fencing, decking, and pavements [3,4]. In addition, agricultural residues and cellulosic byproduct streams have been investigated as alternate fiber fillers in polymer composites [5,6]. However, there is very limited research on the long-term performance of these polymer composites with agricultural byproduct as fillers under weathering agents such as UV light and moisture [7,8].

The external factors such as UV light, heat, moisture, and humidity together affect the integrity of the fiber-matrix structures in a composite causing photodegradation. The weathering of natural fibers results in the degradation of lignin into water soluble products such as carboxylic acids, quinone, and hydroperoxy radicals [9]. The polyolefins degrade due to the presence of chromophores such as catalyst residues, carbonyl groups, hydroperoxide group, and double bonds formed during the polymer manufacturing [10]. The degradation by carbonyl groups cause the most noticeable photodegradation through either of two reactions called as Norrish I or Norrish II reactions [11]. These two reactions have unique mechanisms: Norrish I reaction generates free radicals which ultimately results into either cross linking between chains or chain scission whereas Norrish II leads to the formation of carbonyl and terminal vinyl groups with chain scission [11].

Distiller's dried grains with solubles (DDGS) is the main co-product of corn ethanol from the dry grind process. It is the unfermented portion of the corn grain remaining in the concentrated form after the starch is utilized. The expansion of corn ethanol industries in the US

resulted in the dramatic increase in the production of DDGS from 9 million tons in 2005 to 40 million tons in 2015 [12]. Currently, DDGS is mainly used as a feed supplement for livestock and poultry, as only low levels of DDGS are acceptable as a feed supplement for non-ruminants because of its high fiber content [13]. A physical separation process named elusieve can separate hull fiber from both corn grain flour and DDGS to enhance the feed value by increasing the protein and oil content [14,15]. The DDGS with higher protein and oil content attracts \$5-20 more per ton because of the added nutritional value compared to the unprocessed DDGS containing hull fiber [16]. The benefits of DDGS without the hull fiber include increased weight gain in birds and a larger portion of the feed can be supplemented by elusieved DDGS [17,18]. The hull fibers extracted from DDGS and corn grain have shown good potential as a filler in polymer composites [19]. However, the long-term performance of composite containing DDGS fiber filler under UV moisture weathering has not been evaluated.

This study investigated the impact of accelerated UV weathering on the physico-mechanical, surface color, and surface degradation properties of the HDPE composites containing hull fiber from DDGS and corn grain.

## **Materials and Methods**

### **Materials**

An experiment was conducted at commercial scale to compare hull fibers from DDGS, corn grain and oak wood fiber as full or partial filler in HDPE composites. The DDGS was obtained from Midwest Ag Energy Group (ND, USA), and elusieved at Mississippi State University (MS, USA); the DDGS fiber had 46.9% neutral detergent fiber (NDF), 21.1% protein, 3.3% starch, and 8.1% fat by dry weight. The elusieved corn grain fiber was also obtained from Mississippi State University (MS, USA); the corn grain fiber had 49.2% NDF, 7.9% protein, 31.9% starch, and 3.1% fat by dry weight. The oak wood fiber was obtained from Southern

Wood Services LLC (GA, USA); the oak wood fiber consisted of cellulose (45.7%), hemicellulose (24.8%), and lignin (27.6%) by dry weight. The HDPE polymer (Petrothene LB 010000 (melt flow index: 0.50 g/10 min, density 0.953 g/cm<sup>3</sup>, tensile yield strength 27.3 MPa, and flexural modulus of elasticity 1275 MPa) was obtained from Equistar Chemicals (TX, USA). Zinc stearate (ZnSt) was used in some formulations to act as a lubricant during extrusion, and talc was used as an inorganic filler.

### Composite Manufacturing

The fibers from DDGS, corn, and oak were ground in a Wiley mill (Model 4, Thomas Scientific, NJ, USA) with a 1 mm sieve, and subsequently sieved through a 30-60 mesh (0.250 mm-0.595 mm) with a Ro-tap shaker (W.S. Tyler® Ro-Tap® 8in Sieve Shaker, 230V/50Hz, USA). The sized fibers were then oven dried at 105 °C until the moisture content was less than 1%. Prior to extrusion, all the components were mixed in the exact proportions specified for each formulation (Table 3.1). The mixture was then compounded and extruded with a counter rotating twin screw (L/D ratio of 28) Cincinnati extruder (Milacron, OH, USA) with five heating zone temperatures set between 160-180 °C. The sample material was extruded into bars with a rectangular profile of 35 mm wide and 10 mm thick.

**Table 3.1.** Formulation of the HDPE composite samples containing six different combinations of fiber fillers. All weight (wt) percentages are computed on dry basis

Sample Name	Fiber Loading, % wt	Polymer % wt	Lubricant % wt	Talc % wt
Oak50	50	42	4	4
Corn50	50	42	4	4
DDGS50	50	46	-	4
Oak25/Corn25	25/25 <sup>a*</sup>	42	4	4
Oak25/DDGS25	25/25 <sup>a*</sup>	46	-	4
Corn25/DDGS25	25/25 <sup>a*</sup>	46	-	4

\*25/25<sup>a</sup>- Denotes 25 percent by weight of each fiber in the mixed fiber composite

## **UV Weathering**

To simulate natural weathering conditions, the composite samples were placed in a QUV accelerated weathering tester (QUV/Spray, Q-Lab Co., USA) for a duration of 2000 h according to ASTM G154 [20]. The weathering cycle consisted of 8 h of UV exposure (UV-A lamps) at 60 °C, followed by a 4 h condensation cycle without UV lights at 50 °C. The UV irradiance used was 0.89 W/m<sup>2</sup> at 340 nm wavelength. The surface color of the samples was recorded three times: prior to UV weathering, at 1000 h of weathering and at 2000 h. The lightness (L) and chromaticity coordinates (a, b) were recorded with an X-rite color checker (X-Rite, Grand rapids, MI, USA). The weathered samples were conditioned at room condition for 30 days before performing the following physico-mechanical and characterization techniques on composite materials.

## **Composite Material Testing**

Composite samples before and after weathering were tested for water absorption, specific gravity, flexural, compression, and impact strength. Five samples were tested from each formulation before and after weathering to avoid potential biases due to homogeneity of material and testing conditions.

### *Water Absorption*

The water absorption of both unexposed and weathered composite samples was recorded according to the ASTM D570-98 [21]. Sample coupons in the size of 75 mm × 35 mm × 10 mm were cut, and dried at 50 °C for 24 h before immersing them in a water bath set at 23 °C. The weight gain by each sample was recorded every 24 h for 18 days for the unexposed samples and every 24 h for 15 days for the weathered samples. The reported results are the average of five samples.

### *Specific Gravity*

The specific gravity of the composite material was tested in accordance with Method A of ASTM D792 [22]. The test was performed to measure the specific gravity as the ratio of the mass of a given volume of a sample measured at 23 °C to the same volume of tap water at the same temperature with an analytical balance, a wire, a wooden block, and a small bucket as immersion vessel. The mass of the samples was first recorded in air before immersing it in the water with the wire cage to measure the weight loss of the sample in water. Five samples were used for the test.

### *Flexural Properties*

The flexural properties of both unexposed and weathered samples were tested according to the ASTM D7264 [23], a three-point bending test method for polymer composites. The weathered samples were first dried in an oven at 105 °C for 24 h to ensure the moisture content was same as those of the unexposed samples. The UV exposed surface of the weathered samples was used on the compression side for the test; the test samples had a span to depth ratio of 20:1. The crosshead motion rate was calculated based on the depth of the samples used in the test and a universal testing machine (Test Resources Inc, MN, USA) was used for testing the materials. Five samples were tested for each formulation.

### *Compression Properties*

The compression properties of the unexposed and UV weathered composite samples were measured in accordance with ASTM D6108 [24]. The crosshead rate was controlled in order to have a strain rate of 0.76 mm/mm/min. Sample coupons of 28 mm × 14 mm × 9.5 mm were placed between the compression platens in the universal testing machine (Test Resources Inc, MN, USA) to obtain compressive strength and modulus of elasticity (MOE). Five samples were tested for each formulation.

### *Impact Strength*

The impact strength for notched samples were measured in accordance with ASTM D256 [25]. The sample dimensions used for the test were 63 mm × 12.5 mm × 3.5 mm with a notch of 2 mm cut in the middle of the sample. An Izod impact tester (Tinius olsen, Model Impact 104, USA) was used for reporting the impact strength of the samples. Five samples were tested for each formulation.

### **Surface Analysis**

#### *Light Microscopy Images*

The surface morphology of UV weathered samples was compared with the unweathered samples by inspecting the specimens under a light microscope SZM 7045 (AmScope, Irvine, CA, USA) at a magnification of 30X.

#### *Color Change*

The change in surface color of the weathered composites was measured with an X-rite color checker (X-Rite, Grand rapids, MI, USA) using L\*, a\*, and b\* coordinates in the CIELAB color system, where L\*, a\* and b\* represent the lightness and the chromaticity coordinates, respectively. Each specimen was marked at the same three distinct locations to record the changes in L\*, a\*, and b\* values at 0 h (before UV weathering), 1000 h, and 2000 h of UV weathering. The color change ( $\Delta E$ ) was calculated according to the following Euclidean equation:

$$\Delta E = \sqrt{(\Delta L^* )^2 + (\Delta a^* )^2 + (\Delta b^* )^2} \quad (\text{Equation 3.1})$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are the total changes in L\*, a\*, and b\* values after a specific period of weathering. An increase in L\* value means the sample is lightening. A positive  $\Delta a^*$  indicates a color shift toward red, and a negative  $\Delta a^*$  signifies a color shift toward green. A positive  $\Delta b^*$  signifies a shift toward yellow, and a negative  $\Delta b^*$  signifies a shift toward blue.

## **Thermal Analysis**

### *Thermal Stability*

The thermal properties of the fillers and composites were determined with a ThermoGravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC). The thermal stability of oak, corn, and DDGS fibers were determined with a Q500 Thermal Gravimetric Analyzer (TA instruments, USA). Two types of DDGS were analyzed for TGA: untreated, and heat treated at 105 °C. About 30 mg of fibers were placed in a platinum pan and heated from 25 °C to 800 °C at a ramp rate of 20 °C/min under a 60 mL/min air flow. The results were analyzed with TA instruments Universal Analysis software.

### *Thermal Transition*

The DSC of the unexposed and UV weathered composites were measured by a differential scanning calorimeter (DSC Q20, TA Instruments, USA). The samples were prepared by scrapping the surface of the composites by knife up to a depth of 0.3 mm. Approximately 3-5 mg of samples were placed in a hermetically sealed aluminum pan. These samples were compared to an empty reference pan during three consecutive heating-cooling-heating cycles. They were first heated from 25 °C to 200 °C at a heating rate of 10 °C/min and kept isothermally at 200 °C for 3 min to erase their previous thermal history. In the next step, the samples were cooled off to 25 °C; the cooling rate was not controlled. The variation occurring during the cooling rate were assumed to be similar for all the composite samples. Finally, the samples were heated again to 200 °C at 10 °C/min and kept isothermally at 200 °C for another 3 min. Nitrogen gas was purged (50 mL/min) to prevent thermal degradation of samples during all DSC runs. The first cooling run determined the crystallization temperature ( $T_c$ ) and crystallization enthalpy ( $\Delta H_c$ ) of the samples whereas the percentage crystallinity ( $X_c\%$ ), heat of fusion ( $\Delta H_f$ ) and



melting temperature ( $T_m$ ) were measured from the second heating run. The crystallinity was measured as

$$Xc\% = \frac{\frac{\Delta H_m}{W_p}}{\Delta H_{m100}} \times 100\% \quad (\text{Equation 3.2})$$

where  $\Delta H_m$  is the experimental melting enthalpy of the composites,  $\Delta H_{m100}$  is the theoretical melting enthalpy of the fusion for 100% crystalline HDPE polymer (293 J/g) [26]. The  $W_p$  is the weight fraction of the HDPE in the composites corrected on the weight basis.

### **Statistical Analysis**

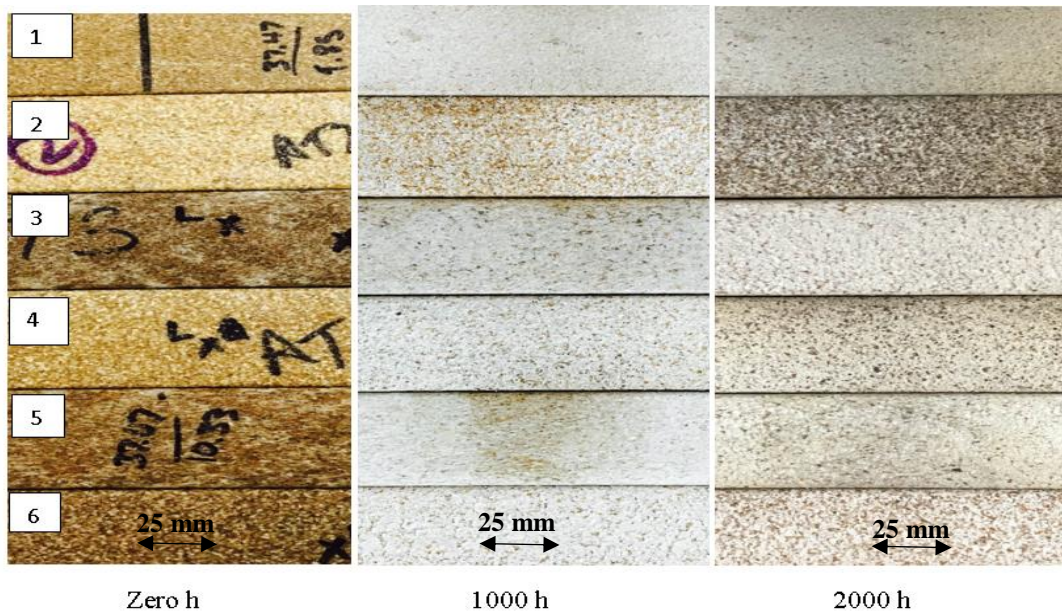
In order to determine the statistical significance at  $\alpha = 0.05$ , first the two sample t-test was performed to compare the means of unweathered sample with UV weathered samples. To identify the impact of different filler types in unexposed and unweathered samples, Fishers Least Square Differene (LSD) tests were performed on all 12 sets of samples at  $\alpha = 0.05$  using Minitab 17 (Minitab Inc., Penn State University, PA, USA). The error bars in the bar graphs represent the standard deviation of the sample.

### **Results and Discussion**

During the initial commercial trials, the composites containing DDGS fiber filler did not extrude smoothly. After heat treatment of the fiber at 105°C, the extrusion was smooth and easy. Therefore, heat treated DDGS fibers were used in all the samples used in this study. Also, no lubricant was used in samples containing DDGS fiber as our past trials at lab scale indicated that the fat in the DDGS fiber provided adequate lubrication. Composite samples containing oak and corn fiber fillers were aided with ZnSt as the lubricant during extrusion. The impact of UV weathering on the morphology and physico-mechanical properties of the six different composite formulations is described below.

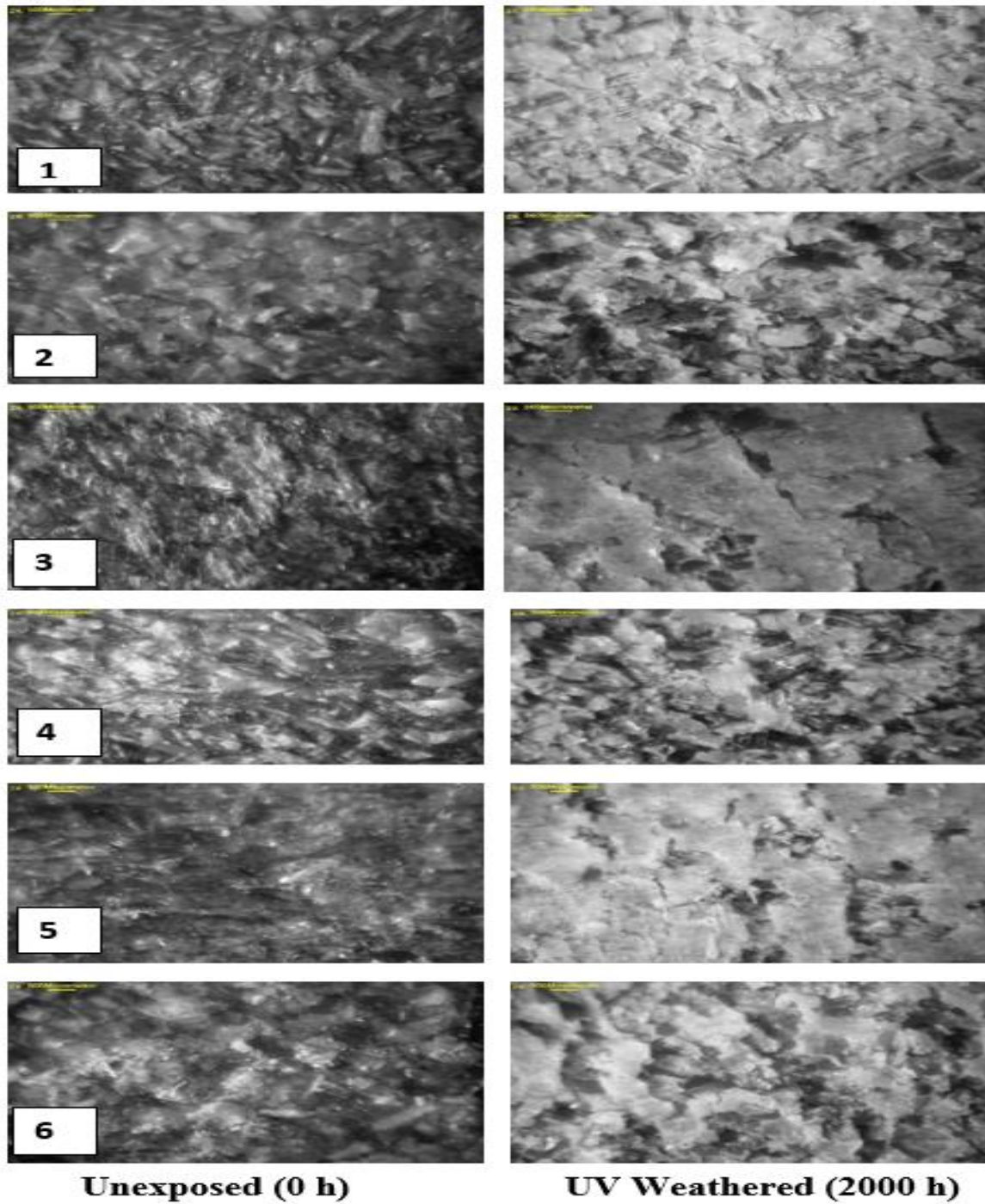
## **Visual Appearance and Surface Morphology**

The visual inspection of UV weathered samples performed at 1000 h showed discoloration of all the composite samples as a result of degradation of the composites' surface (Fig. 3.1). This discoloration is caused by bleaching of natural fiber and degradation of the HDPE under UV exposure, which are reported to occur mostly in the first 700 h [27]. The composite samples with corn fiber filler showed fiber protrusion together with visible micro cracks on the surface whereas the samples with oak and the DDGS fiber fillers showed only a whitening effect (Fig. 3.1). When the samples were exposed for another 1000 h, all the samples' surface turned darker due to an oxidation reaction on the surface as reported by [28]. Vigorous fiber protrusion of corn fiber-filled composite samples showed the detrimental effect of UV and condensation cycles on the integrity of their composites. The presence of starch and proteins in corn-filled composites may have played a crucial role in their degradation behavior. The oak filler was highly susceptible to discoloration due to the specific chromophore groups present in the lignin. The corn starch degradation by UV light may have resulted in the cleavage of glycosidic bonds, shortening of amylose chains, and a debranching of the amylopectin due to the formation of free radicals [29]. The proteins are susceptible to photo oxidation which denatures their primary structure and leads to the formation of protein carbonyls [30].



**Fig. 3.1.** The visual pictures taken for (1) Oak50, (2) Corn50, (3) DDGS50, (4) Oak25/Corn25, (5) Oak25/DDGS25, and (6) Corn25/DDGS25 composite samples at 0 h, 1000 h, and 2000 h

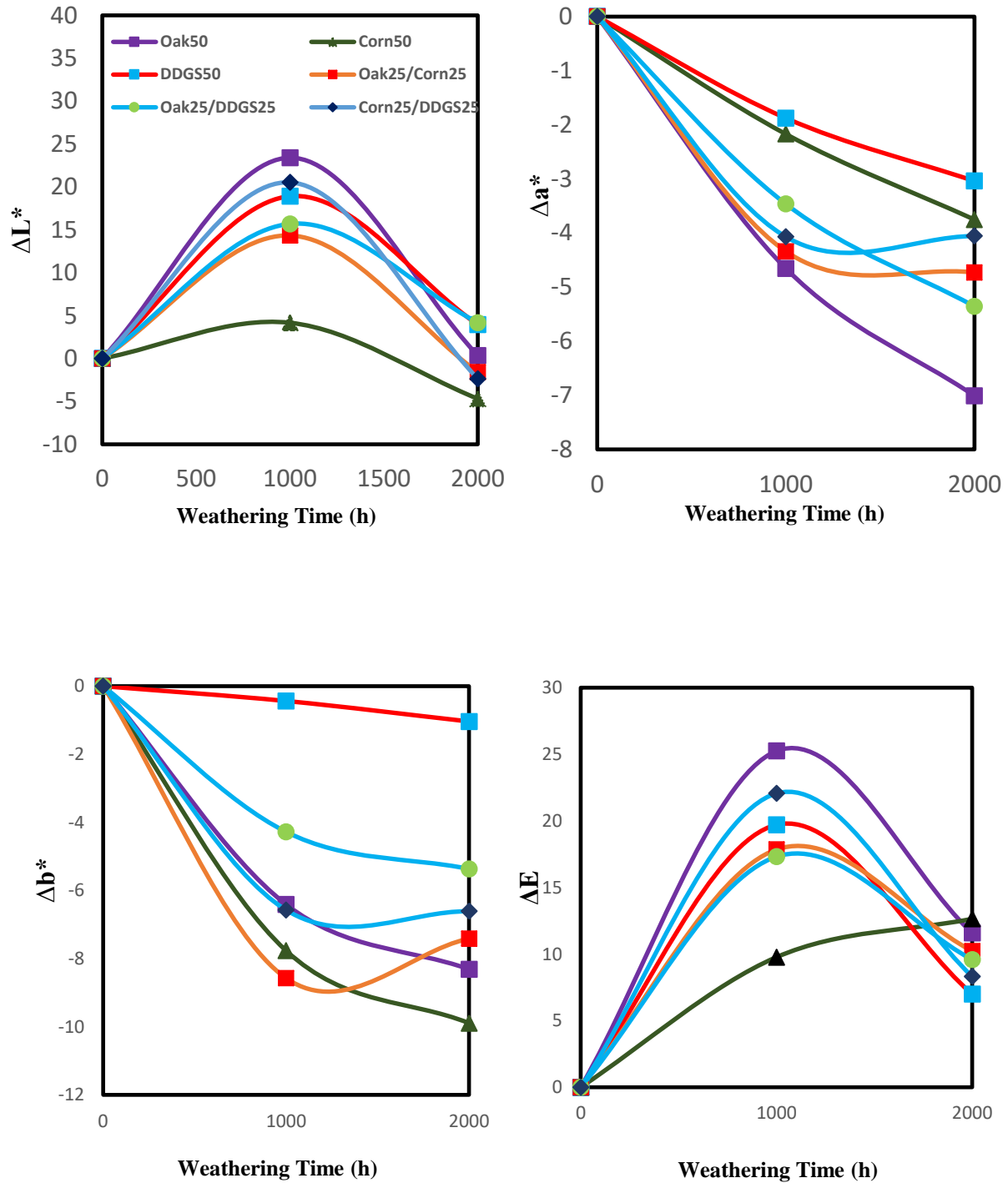
Before weathering, the surface of all the composites showed good encapsulation of the fibers by the HDPE matrix (Fig. 3.2). After 2000 h of UV exposure, all the samples showed cracks on the surface showing polymer breakage and degradation, and exposure of the previously encapsulated fiber fillers. The cracks in natural fiber polymer composite is a common phenomenon due to the polymer chain scission which allows polymer to crystallize quickly leading to surface cracking during UV accelerated weathering [31]. Sometimes, spontaneous cracking of HDPE also occurs from secondary crystallization also known as chemicrystallization [32].



**Fig. 3.2.** Light microscope images taken for unweathered and weathered samples for (1) Oak50, (2) Corn50, (3) DDGS50, (4) Oak25/Corn25, (5) Oak25/DDGS25, and (6) Corn25/DDGS25 at the magnification of 30X

## Color Change During UV Weathering

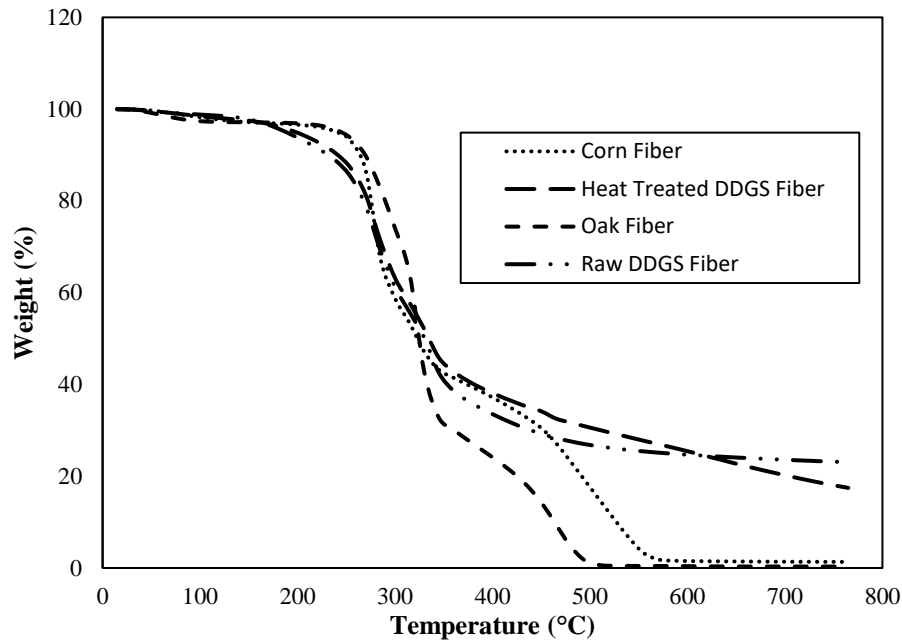
The composite treatment with 50% oak fiber filler showed the highest change in surface color, which was indicated by a lightness ( $\Delta L^*$ ) change of 23.4, due to UV weathering (Fig. 3.3). The corn50 treatment showed the lowest change in surface color of 4.2 after 1000 h of UV exposure. The lignin present in the oak fiber oxidizes due to the transformation of paraquinone to hydroquinone causing a photobleaching effect [33]. The lightness change was the highest at 1000 h exposure but decreased dramatically at 2000 h exposure, showing a darkening effect. The corn50 composites exhibited a negative  $\Delta L^*$ , between 1000 h and 2000 h exposure, indicating that the samples became darker due to severe effects of UV radiations along with condensation cycles. The lightening due to UV weathering is most likely from photo degradation of both fiber fillers and the HDPE. The natural fibers and HDPE react to UV light via different mechanism of degradation. The change in  $\Delta a^*$  and  $\Delta b^*$  for all the composites were small and negative at both 1000 h and 2000 h exposures signifying a color shift towards blue-green. The change in  $\Delta E$ , the total color change observed in the composites, followed almost the same pattern as of  $\Delta L^*$ . The change in  $\Delta E$  was higher than reported for HDPE fiber composites together with coupling agent [7].



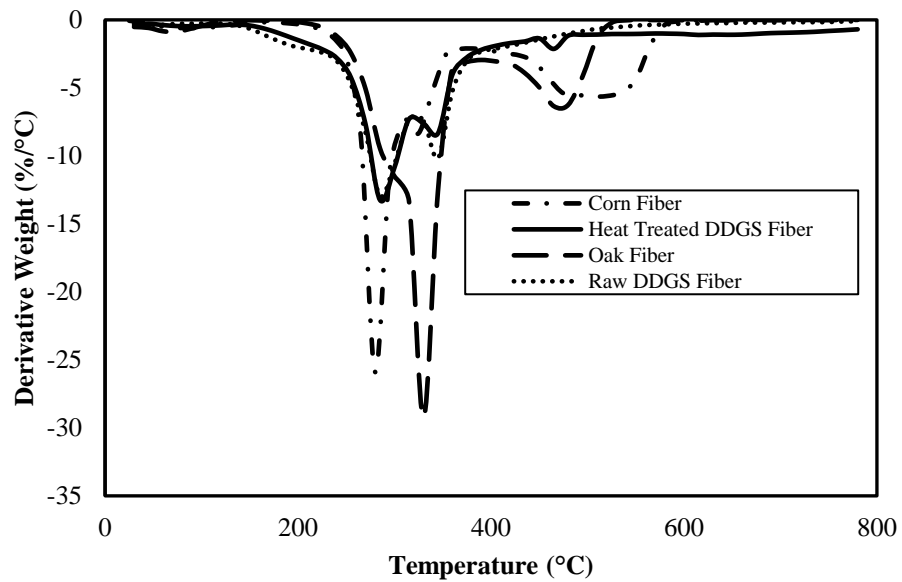
**Fig. 3.3.** Changes in lightness ( $\Delta L^*$ ), chromaticity coordinates ( $\Delta a^*$  and  $\Delta b^*$ ) and total color change ( $\Delta E$ ) as a function of weathering time in HDPE composites containing 6 different fiber filler combinations of Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 under unexposed and weathered conditions

## **Thermal Degradation of Fiber Fillers**

The thermal degradation of fibers recorded with a TGA showed that the three fibers had a slight difference in thermal degradation (Fig. 3.4). The degradation of oak and corn fibers occurred in two and three steps, respectively. The first degradation occurred in the temperature range of 250-300 °C in which 55% and 68% weight loss was observed for corn and oak fibers respectively (Fig. 3.4 & 3.5). The second step occurred at 300-350 °C and the third step at 400-600 °C leading to complete degradation of the fibers. The untreated and heat treated DDGS fibers showed similar decomposition behavior between 150-400 °C with approximately 65% and 60% weight loss, respectively. This temperature range was important as the DDGS fiber composites were manufactured in this temperature range. The degradation of both raw and heat treated DDGS occurred mainly in two steps: the first stage of 150- 250 °C corresponding to the thermal degradation of hemicelluloses, and the second step of 250- 375 °C corresponding to the thermal degradation of cellulose [34]. The untreated DDGS fiber did not show a third degradation peak whereas the heat treated DDGS fiber showed a small peak between 450 °C and 500 °C which is attributed to degradation of aromatic rings of lignin and of the residue formed during the first degradation step. The final weight loss percentage for untreated and heat treated DDGS at 800 °C was about 75% and 84% respectively.



**Fig. 3.4.** The thermogravimetric curves of corn, heat treated DDGS, oak, and raw DDGS fibers



**Fig. 3.5.** The differential thermogravimetric curves of corn, heat treated DDGS, oak, and raw DDGS fibers

### Thermal Properties of Composites

The melting and crystallization curves obtained with a differential scanning calorimeter helps to determine the changes in the melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_f$ ), heat of crystallization ( $\Delta H_c$ ) and percent crystallization ( $X_c\%$ ) before and



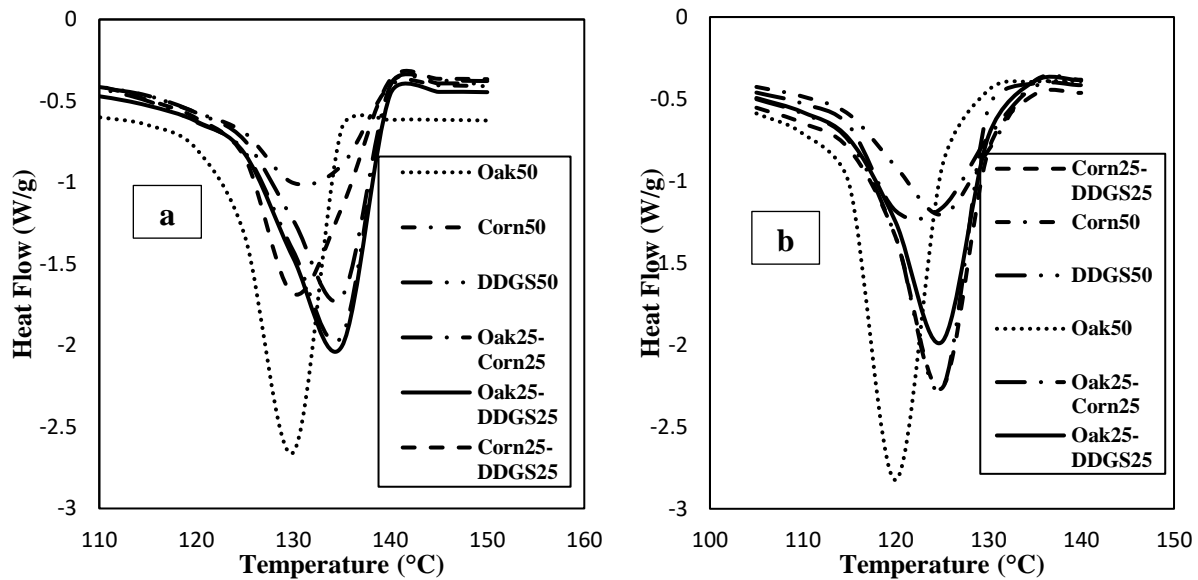
after weathering (Table 3.2, Fig. 3.6). The different fiber filler treatments did not show much difference in  $T_m$  and  $T_c$ . The similar  $T_c$  in unexposed and UV weathered samples shows that fillers had no effect on the nucleation. However, the heat of fusion, heat of crystallization and degree of crystallinity were significantly lower for the corn50 composite. The addition of the fiber fillers to HDPE changes the crystallinity of the polymer composites. (Table 3.2). The corn50 fiber filled composites hindered the growth of crystals resulting in a decrease in crystallinity to 38% compared to the calculated crystallinity of 59% for the neat HDPE polymer (not shown in the Table 3.2). The increase in  $X_c$  (%) of composites after UV weathering can be attributed to the chain scission of the polymer during the UV accelerated weathering. The chain scission reduces the density of entanglements in the amorphous region thus allowing small molecules to crystallize easily due to their high mobility [11].

**Table 3.2.** Thermal properties of unexposed and UV weathered composites under Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 fiber filler treatments, obtained with a differential scanning calorimeter. The properties listed include melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_f$ ), heat of crystallization ( $\Delta H_c$ ) and degree of crystallinity ( $X_c\%$ )

Properties	Oak50	Corn50	DDGS50	Oak25/Corn25	Oak25/DDGS25	Corn25/DDGS25
$T_m$ ( $^{\circ}\text{C}$ ) (unexposed)	130.5	133.1	134.4	134.2	134.1	132.4
$T_c$ ( $^{\circ}\text{C}$ ) (unexposed)	122.9	122.8	122.8	122.7	123.0	122.8
$\Delta H_f$ (J/g) (unexposed)	103.6	47.8	93.3	75.5	88.0	88.4
$\Delta H_c$ (J/g) (unexposed)	91.3	48.9	89.2	76.7	89.2	89.9
$X_c$ % (unexposed)	74.2	38.9	69.2	61.4	65.3	65.6
$T_m$ ( $^{\circ}\text{C}$ ) (UV weathered)	121.4	123.7	124.0	122.2	124.1	123.9
$T_c$ ( $^{\circ}\text{C}$ ) (UV weathered)	112.1	119.5	114.5	114.3	114.7	114.6
$\Delta H_f$ (J/g) (UV weathered)	121.7	66.5	98.2	71.4	100.2	105.5
$\Delta H_c$ (J/g) (UV weathered)	96.9	55.5	72.4	58.9	80.8	60.5
$X_c$ % (UV weathered)	98.9	54.1	72.9	58.0	74.3	78.3

All the UV weathered samples showed a decrease of 8-12 $^{\circ}\text{C}$  in  $T_m$  and 3-11 $^{\circ}\text{C}$  in  $T_c$ .

The decrease in  $T_m$  for UV weathered composites can be due to the smaller and less thermally stable crystal molecules formed after degradation and recrystallization, and due to the presence of defects like carbonyl and hydroperoxides [33]. The decrease in  $T_c$  is likely due to the characteristic delay in the crystallization at lower temperature as it requires greater super cooling for the germination to occur. In addition, the chain scission of polymer chains causes small molecules to crystallize easily. The UV weathered composites showed higher heat of fusion ( $\Delta H_f$ ) than their unexposed samples due to their increased crystallinity resulting from the chemicrystallization.



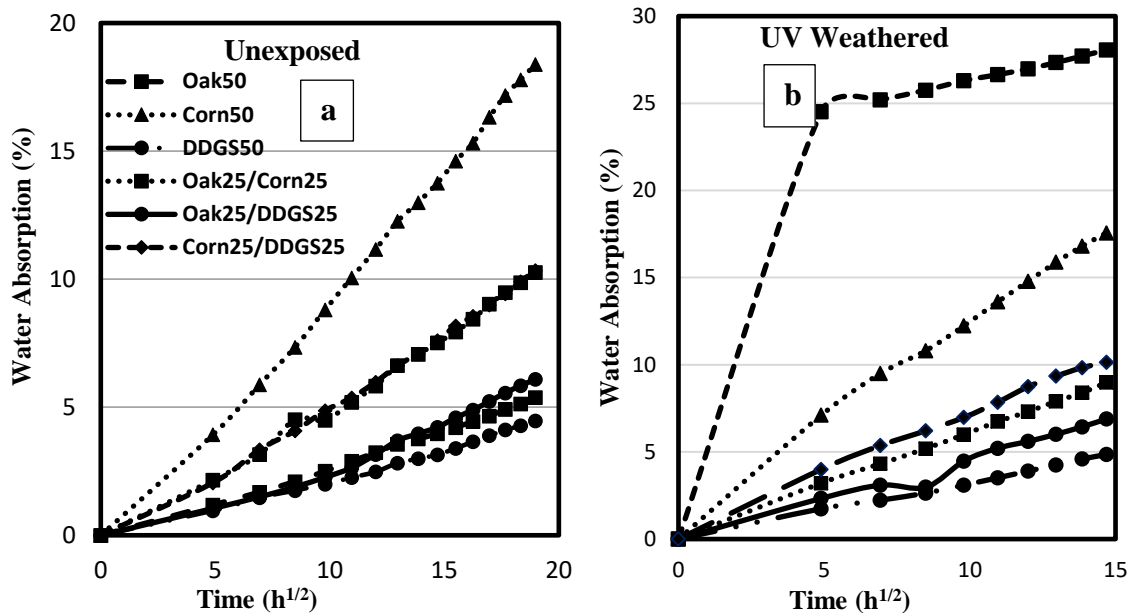
**Fig. 3.6.** The melting temperature curves for (a) Unexposed and (b) UV weathered composites for Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 composites

### Water Absorption

The composite samples before and after weathering exhibited a linear relationship between the percentage moisture gain against the square root of time (Fig. 3.7) with the exception of one formulation. The UV weathered composite containing 50% of oak fibers showed a distinctly different bilinear trend that was also reported for other HDPE composites containing natural fibers [35]. The linear trend between water absorption and the square root of time indicate that the composite materials followed the Fick's diffusion law during the uptake of water. The unexposed samples with 50% corn fiber filler (corn50) showed the highest moisture absorption of 18% after 15 days, whereas composites with 50% oak or 50% DDGS fiber filler showed much lower moisture absorption of 5% each. This affinity of corn50 composite for water can be attributed to the presence of hygroscopic starch in addition to the cellulose and hemicelluloses. The abundance of these carbohydrates in the corn fiber filler made it susceptible to moisture by serving as entry points for water. The appearance of micro-cracks on the composite surface also favored the moisture absorption in corn50 composites. The absorbed

water leads to swelling of the fiber causing the formation of micro cracks and dimensional instability of the composites. When the corn fiber filler was mixed with oak or DDGS fibers as in oak25/corn25 and corn25/DDGS25 composites respectively, the moisture absorption decreased to a moderate level of 5 to 11% after 18 days. The unweathered composites containing oak and DDGS fiber fillers absorbed the least moisture showing the role of hydrophobic lignin, fat and proteins in resisting the moisture. The 24 h water absorption of all composites materials before weathering varied from 1% to 3.9%, which is comparable to the values reported for commercially available wood plastic composites [36].

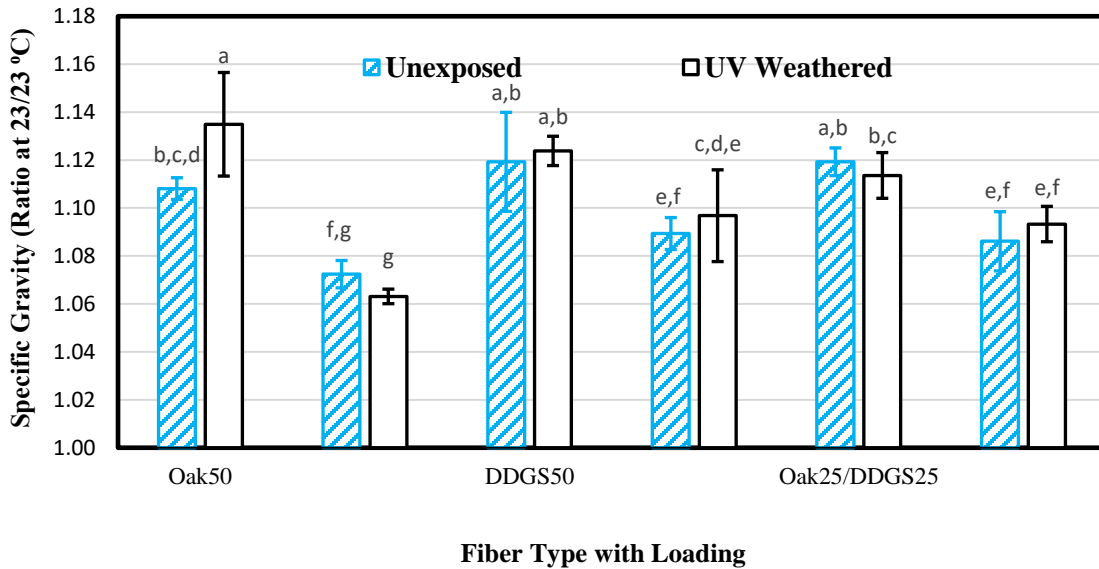
The moisture absorption of composites samples after 2000 h of weathering followed similar trends as those of the unexposed samples with the only exception observed for the samples with 50% oak fiber filler. The moisture absorption of Oak50 samples was four and half times higher than the unexposed oak50 sample. This jump in moisture gain was expected as the UV exposure oxidizes lignin on the surface leaving the composite surface rich in cellulose and hemicelluloses allowing high water absorption. The composite samples with corn and DDGS fiber fillers were degraded by the UV weathering and showed 50 to 100% increase in water absorption after 9 days of exposure to water. The UV weathering approximately doubled the 24-h water absorption for all samples except the Oak50 samples. This increase in water absorption was expected as UV weathering degraded both the polymer and the natural fiber in the composite, making the fibers more susceptible to water.



**Fig. 3.7.** The water absorption of (a) unexposed, and (b) UV weathered samples of HDPE composite materials containing different fiber fillers such as Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25

### Specific Gravity

The specific gravity of composite samples is important as they are often used as a replacement for wood in building and outdoor applications. For applications replacing wood, a specific gravity close to or less than one is preferred. The composite samples with various fiber filler combinations showed average specific gravities of 1.07 to 1.12 before weathering and 1.06 to 1.14 after weathering (Fig. 3.8). These values are well within the range of the 0.7 to 1.46 reported for commercially available wood plastic composites [36]. The lowest specific gravity of 1.06 was observed for the UV weathered corn50 sample. Weathering did not influence the specific gravity of the composite materials, except for composites with oak fiber filler. There was a significant difference between weathered and unexposed samples with 50% oak filler.



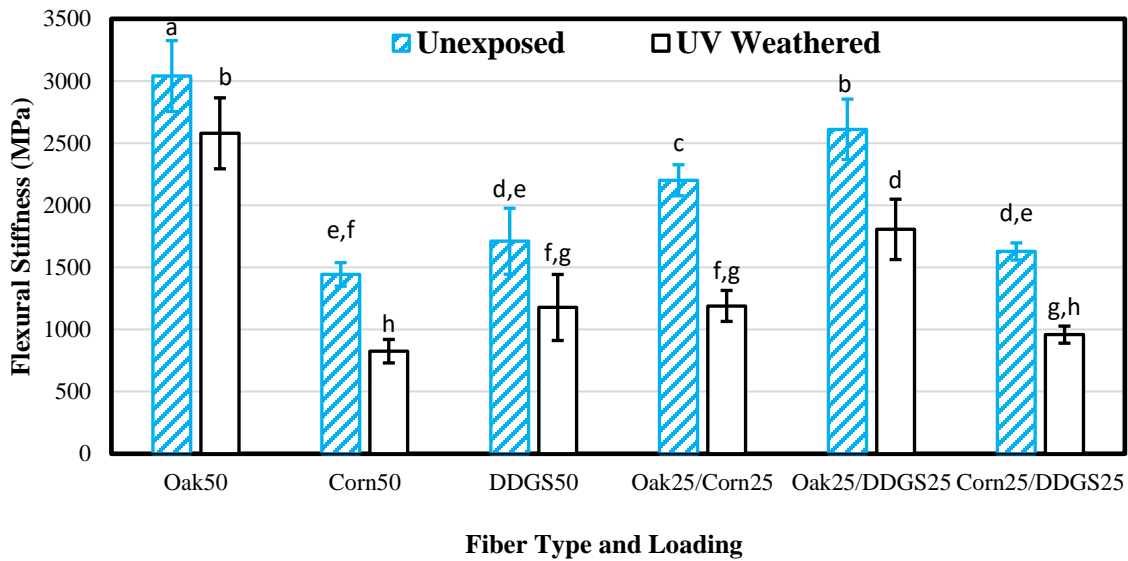
**Fig. 3.8.** Specific gravity of HDPE composites containing fiber fillers such as Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25 and Corn25/DDGS25 under unexposed and UV weathered conditions. Different letters in the label show that there is significant difference between those treatments at  $\alpha = 0.05$

### Flexural Properties of the Composites

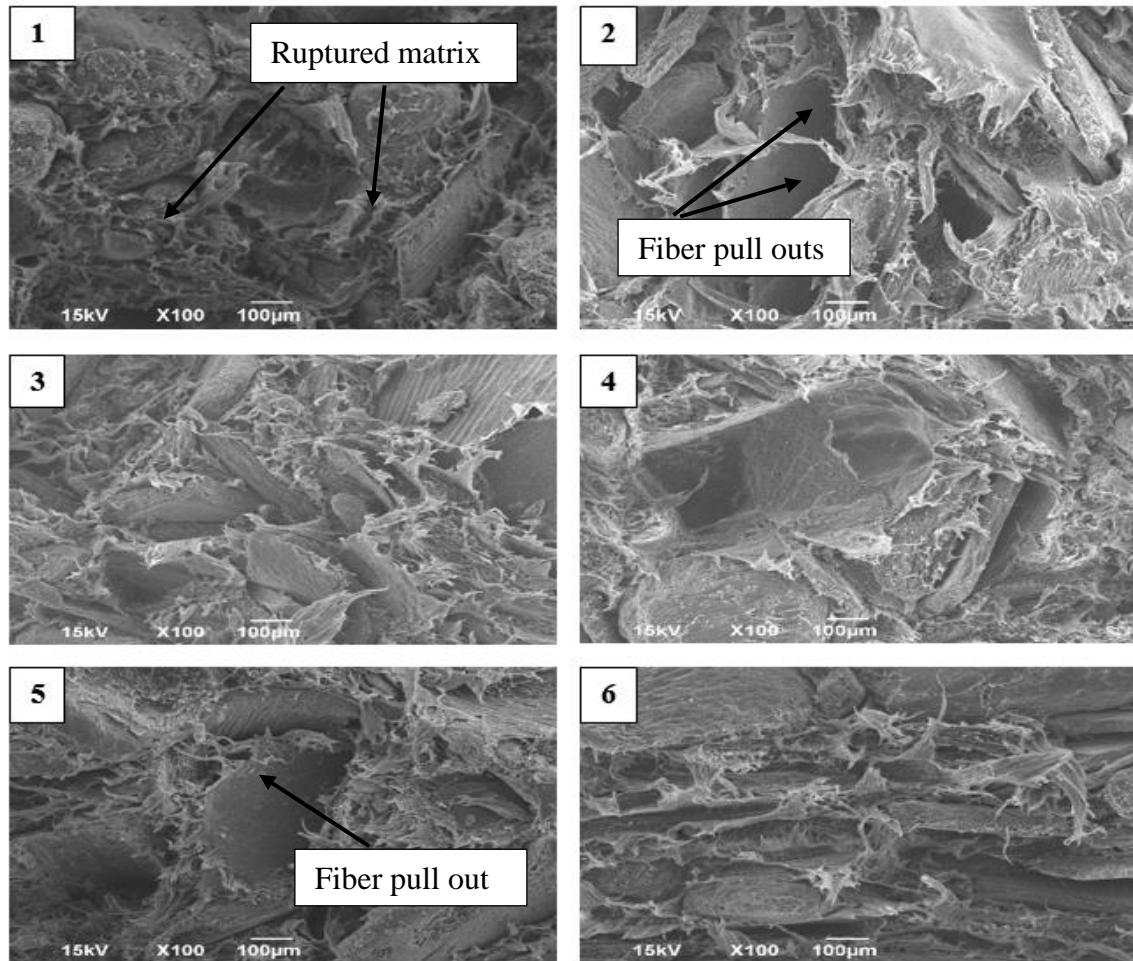
The flexural stiffness of the unexposed composites showed wide variations, where the 50% oak fiber filler treatment showed the highest values of 3039 MPa. The 50% corn and 50% DDGS fiber fillers showed lower stiffnesses or modulus of elasticities (MOEs) of 1444 MPa and 1710 MPa, respectively (Fig. 3.9). Mixing corn or DDGS fiber with oak fiber increased the composite stiffness by about 53% for both types of fibers. The combination of corn and DDGS in corn25/DDGS25 composite showed a lower MOE of 1628 MPa compared with the control. The high flexural performance with Oak50 can be attributed to its prismatic shape which allows higher aspect ratio than the lamellar shaped hull fibers (Fig. 3.10).

The UV weathering decreased the stiffness of all composite samples. The 50% corn filler sample showed the highest drop in flexural stiffness of approximately 50%. The corn filler composite with partial substitution of either oak or DDGS filler showed a decrease in MOE of at least 40% compared with the same unexposed composite. The DDGS50 sample also showed a

drop of around 30% due to UV weathering compared with the unexposed sample. The UV weathering and moisture absorption resulted in micro cracks in HDPE matrix due to swelling of fiber particles which reduces the efficiency of stress transfer between the fiber and the matrix.



**Fig. 3.9.** Flexural stiffness of unexposed and UV weathered materials containing fiber fillers such as Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25. Different letters show the significant difference between those treatments at  $\alpha = 0.05$



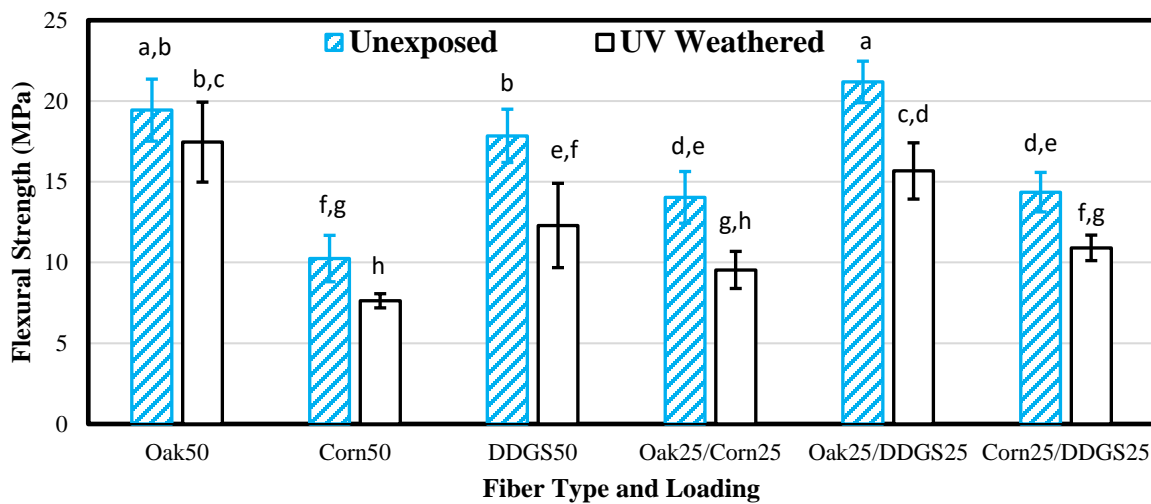
**Fig. 3.10.** Scanning electron microscope (SEM) images of the fractured surface showing the fiber-polymer interface for composite samples (1) Oak50, (2) Corn50, (3) DDGS50, (4) Oak25/Corn25, (5) Oak25/DDGS25, and (6) Corn25/DDGS25

The fractured surface of UV exposed composite samples was examined under scanning electron microscope (SEM) to understand the failure mechanism and fiber-matrix adhesion of the composite materials (Fig.3.10). All the samples showed a common mechanism of defibrillation of the matrix under flexure load, of which corn50 and DDGS50 samples showed higher fiber pull outs compared with other samples. The fiber pull outs show that corn and DDGS fiber had poor interfacial bonding with the matrix.

The composite samples containing oak25/DDGS25 fibers each exhibited the highest flexural strength, which was similar to the oak50 samples (Fig. 3.11). The DDGS50 samples



showed high flexural strength similar to that of Oak50 but slightly less than the oak25/DDGS25. The Corn50 samples showed the lowest flexural strength of 10 MPa. The UV exposure of composite samples significantly reduced the flexural strength of all composite materials except those with 50% oak fiber filler. The DDGS fiber filled sample showed higher loss in flexural strength than corn filled samples. The oak25/corn25 sample showed the highest loss in flexural strength of 32% due to weathering. The screening effect by oak fiber doesn't allow the UV light and moisture to penetrate deeper from the surface layer may explain the retention of strength in oak50 composite [37]. The extensive surface degradation of corn samples resulted into ineffective stress transfer causing loss of flexural strength.

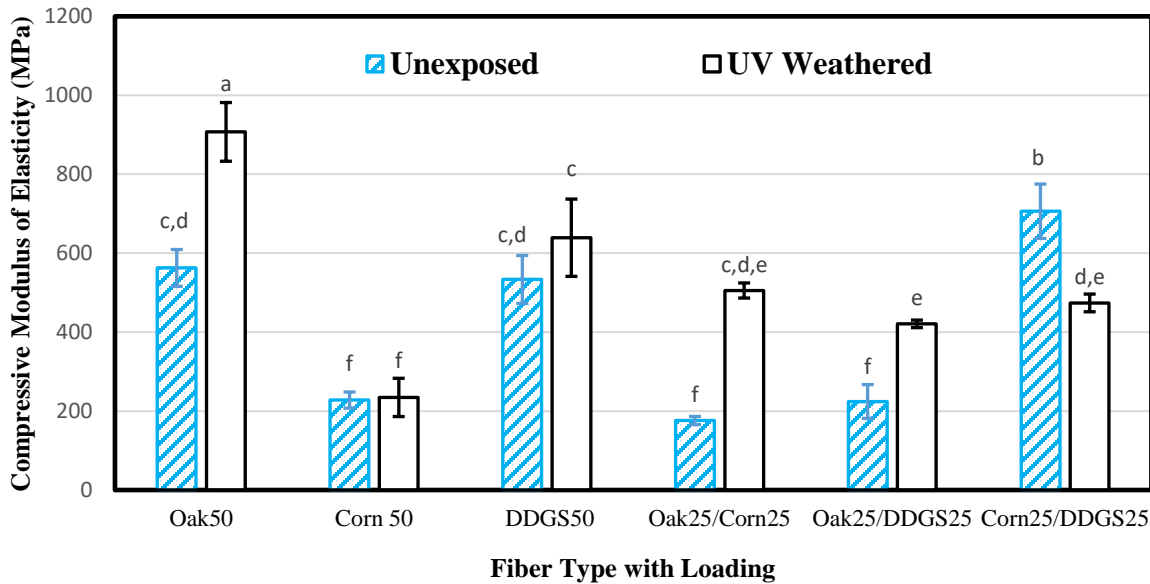


**Fig. 3.11.** Flexural strength of unexposed and UV weathered materials containing fiber fillers such as Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25. Different letters show the significant difference between those treatments at  $\alpha = 0.05$

### Compression Properties of the Composites

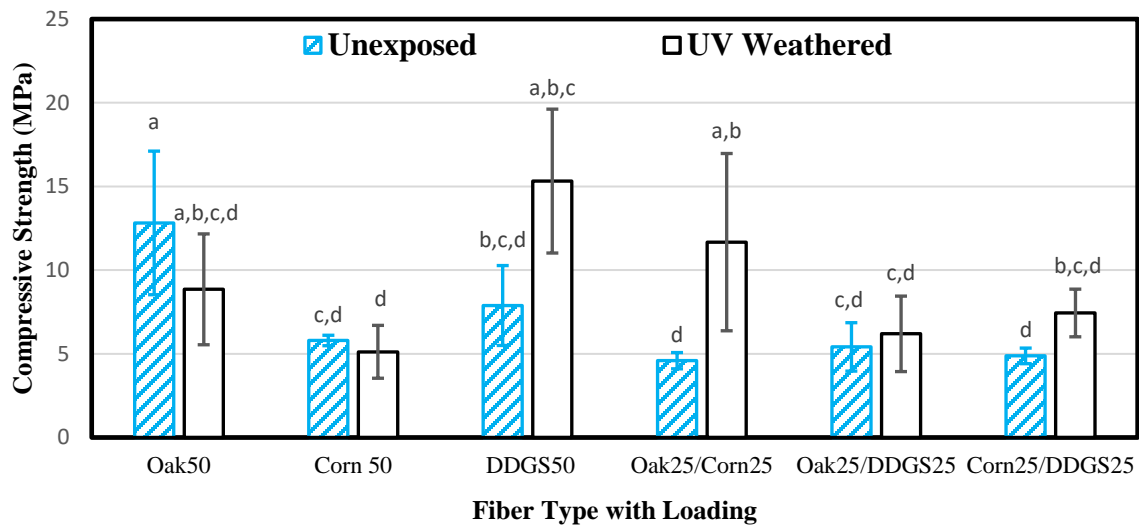
The effect of UV weathering on filler composites showed a significant change in the compressive MOE properties (Fig. 12). The corn50 and DDGS50 fiber filled composites showed no changes in the MOE after UV weathering. The composite samples containing oak fiber filler showed an increase in MOE after UV weathering. This increase in MOE shows that the

combination of oak with either of corn or DDGS at 25% fiber loading interacts well with each other.



**Fig. 3.12.** The compressive MOE of both unexposed and UV weathered samples from Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 composites. Different letters show the significant difference between different filler treatments in unexposed and UV weathered samples measured at  $\alpha = 0.05$

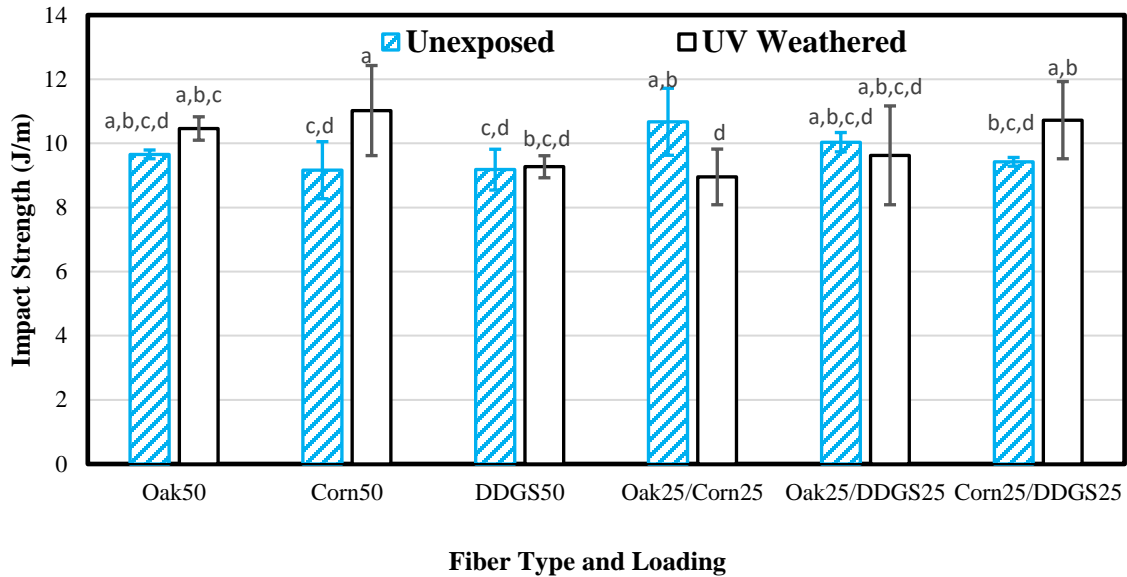
The compressive strength properties showed no significant difference between the unexposed and UV weathered samples except with oak25/Corn25 and corn25/DDGS25 treatments (Fig. 3.13). The DDGS50 sample showed higher strength than corn50 sample after weathering indicating that DDGS fiber is a good fiber filler for outdoor applications where the material will be subjected to UV weathering. When mixed with either corn or oak the DDGS composites showed a drop in strength in the UV weathered samples. The compressive strength did not follow the same behavior as of compressive stiffness.



**Fig. 3.13.** The compressive strength of both unexposed and weathered samples from Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 composites. Different letters show the significant difference between different filler treatments in unexposed and UV weathered samples measured at  $\alpha = 0.05$

### Impact Strength

All composite samples showed relatively similar impact strength in the range of 8.95-11 J/m (Fig. 3.14). The UV weathering of the composite materials caused a significant drop in impact strength in oak25/Corn25 treatment, and a significant increase in Corn50 treatment. This may be due to the same fiber loading in the HDPE matrix and to the limited penetration of UV degradation through the top surface layer. The embrittlement caused by UV weathering to exposed surface layer is not transferred to the inner surfaces.



**Fig. 3.14.** The impact strength of both unexposed and weathered samples from Oak50, Corn50, DDGS50, Oak25/Corn25, Oak25/DDGS25, and Corn25/DDGS25 composites. Different letters show the significant difference between different filler loadings in unexposed and UV weathered samples measured at  $\alpha = 0.05$

### Conclusions

The results indicate that hull fiber from corn grain and DDGS can be viable as full or partial alternatives for wood fiber in HDPE composites. They exhibited properties that may be favorable or unfavorable for specific applications for example, the DDGS fiber filled composites can be a material of choice for applications where low moisture absorption is required and UV exposure is expected. Additionally, replacing a part of oak in mixed fiber composite with DDGS can be a viable option for applications where good flexural properties are required. The corn fiber composites showed poor moisture resistance and stress transfer efficiency in both unexposed and weathered composites. From the aesthetics aspect, DDGS and corn samples showed much less discoloration compared with oak50 sample. Although the color change was not high after 2000 h exposure time, the photodegradation of the surface disrupted the integrity of the material and the formation of micro cracks was very common. The fiber type did not have any effect on melting and crystallization temperature for both unexposed and UV weathered

samples. The accelerated UV weathering did not change the impact resistance of the composites but resulted into the drop in melting and crystallization transition temperatures for all the composite samples. The chain scissions and reduction of chain entanglements are common effects of UV weathering in the composite materials.

### **Acknowledgements**

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## **CHAPTER 4. MERCERIZATION OF DDGS FIBER FOR IMPROVED PERFORMANCE AS A FILLER IN THERMOPLASTIC COMPOSITES**

### **Abstract**

The increase in the production of distiller's dried grain with soluble (DDGS), a major co-product of corn ethanol process, provides an excellent opportunity to develop value-added products. The fibers from DDGS, separated by elusieve process, were treated in a sodium hydroxide (NaOH) solution to investigate their performance as fillers in high density polyethylene (HDPE) composites. The composite material properties were characterized by water absorption, tensile, flexural, and impact tests. Composite samples were manufactured with NaOH treated DDGS fiber at 25% and 50% loading. Addition of both untreated and NaOH treated 25% DDGS fiber to HDPE resulted in moisture absorption of less than 5%. At 50% fiber loading, composites with untreated DDGS fiber exhibited 15% moisture absorption compared to 25% moisture absorption observed for alkali treated DDGS fiber, after 30 days of water exposure. The addition of treated and untreated DDGS fibers increased the tensile modulus but decreased the tensile strength of composites compared to neat HDPE. Under flexural load, the composite with 25% alkali treated DDGS fiber composite samples showed higher flexural modulus and flexural strength than untreated 25% DDGS composites. An increase in fiber loading from 25% to 50% decreased impact resistance of composites with both untreated and alkali treated DDGS fibers. The thermal stability of composites with alkali treated DDGS fibers increased in the temperature range of 150-230 °C, corresponding to hemicellulose degradation, in comparison to those with untreated DDGS fiber.



## Introduction

The depletion of petroleum resources and negative impacts of conventional synthetic fiber composites on environment have stimulated the interest of automobile, aircraft, building and packaging industries to replace petroleum based analogs with sustainable materials. Natural fibers are a suitable replacement for synthetic fibers in polymer composites. Natural fibers have several advantages such as abundance, low cost, biodegradability, high sound absorption, fracture resistance, low density, acceptable specific strength and easy processing [1, 2].

The natural fibers are polar in nature, whereas polymers are non-polar materials. This mismatch in properties results in poor compatibility between the fiber and the polymer matrix, resulting in poor interfacial bonding and high moisture absorption by fibers. Weak interfacial adhesion prevents the stress transfer from the matrix to the fiber under applied load. The interaction between the fibers and matrix can be improved by changing in the surface properties of the fiber. Natural fibers can be modified through physical or chemical treatments. Physical treatments change structural and surface properties of the natural fibers by changing the surface energy, thus increasing their compatibility with the polymer and improving their mechanical bonding to polymers. Different physical treatments such as corona discharge [3], cold plasma [4], gamma-ray [5] and UV bombardment [6] and chemical treatments such as mercerization (alkali) [7-9], grafting [10-12], acrylation [13], permanganate [14], acetylation [15-17], silane [18] and peroxide [19] have already been used effectively on the natural fibers.

Alkali treatment is a simple, inexpensive and effective method for surface modification of fibers. Alkali treated fibers have been reported to show increased surface area, which in turn leads to better interfacial bonding with polymer matrix [8,9].

Distillers' dried grain with solubles (DDGS) is the main co-product produced from corn ethanol fermentation. The production of DDGS has seen tremendous increase in the last few

years [20]. The fiber fraction of DDGS isolated by a physical separation process named elusieve [21]. This separated DDGS fibers have the potential to be used as filler in polyolefin composites [22].

Currently, there are no reported studies that investigated how mercerization or sodium hydroxide (NaOH) treatment of DDGS fiber affects their performance as fillers in HDPE composites. The aim of this study was to investigate the performance of NaOH treated DDGS fibers compared to untreated DDGS fibers as fillers in HDPE composites.

## **Materials and Methods**

### **Materials**

The DDGS was supplied by Midwest Ag Group (Underwood, ND), and the DDGS fibers were separated using an Elusieve process at Mississippi State University (Starkville, MS). The polymer used was Marlex 9006 high density polyethylene (HDPE), manufactured by Chevron Phillips (The Woodlands, TX). The neat HDPE had a density of 0.952 (g/cm<sup>3</sup>), melt Index of 5.2 g/10 min measured at 190 °C with 2.16 kg, tensile yield strength of 18 MPa and flexural modulus of 612 MPa. The sodium hydroxide (NaOH) pellets were obtained from Sigma Aldrich (Fargo, ND).

### **Mercerization**

The DDGS fiber was first sized and screened through a 1 mm sieve using a Wiley mill (Model 4, Thomas Scientific, Swedesboro, NJ). The material was again screened to obtain fiber in the range of 0.250 mm-0.595 mm (30-60 mesh) using a Ro-Tap shaker (W.S. Tyler® Ro-Tap® 8in Sieve Shaker, Mentor, OH). After screening, the DDGS fiber was dried in an oven for 24 h at 105 °C to bring the moisture content below 1%.

The DDGS fibers were mercerized by immersing the fibers in a 0.1M NaOH solution in a 500 ml Erlenmeyer flask, kept at room temperature (~24 °C) for 1 h. After the 1 h treatment, the

fibers were washed by the tap water until the pH observed was 7, indicating all the NaOH residue was removed. The treated fibers were next oven dried at 105 °C for 24 h. The composition analysis of untreated and NaOH treated DDGS fibers was performed by AOAC methods [23].

### **Manufacturing of Composites**

A laboratory experiment was conducted with two fiber treatments (NaOH treated and untreated), and two fiber loading (25% and 50% by weight) factors, resulting in four types of composites. Samples were also made from neat HDPE for comparison. To manufacture composite samples, the dried fibers were mixed with the HDPE at two different fiber loadings of 25 and 50 weight % and compounded in a twin-screw co-rotating extruder (L/D ratio of 18, Leistritz Micro 18 GL/-40 D, Allendale, NJ). The extruder barrel zones were set at temperatures between 160-195 °C and the die temperature was set at 195 °C. The extruder was operated at 150 rpm. The material was extruded into 3 mm diameter strands that were cooled through a water bath, before pelletizing with a BT25 pelletizer (Scheer Bay Co., Bay City, MI). The pelletized composite material was oven dried overnight at 80 °C before injection molding into test specimens. The test specimens were manufactured with an injection molder (Model SIM- 5080, Technoplas Inc., Norwood, MA) set at 190 °C into dog bone samples of 12.5 mm by 3.5 mm cross sectional size at the center, and 65 mm length. The composite samples were stored in a sealed plastic bags before performing various tests.

### **Fiber Characterization**

The morphologies of untreated and alkali treated DDGS fibers were examined under a Leitz Laborlux microscope (Laborlux S, Leitz, Wetzlar, Germany) for fiber surface characteristics. The images were captured using a 40X magnification.

The thermal properties of the NaOH treated and untreated DDGS fibers were determined using a Q500 Thermal Gravimetric Analyzer (TA instruments, New Castle DE, USA). About 30 mg of fibers were placed in a platinum pan and heated from 25 °C to 800 °C at a ramp rate of 20 °C/min under a 60 mL/min air flow. The results were analyzed with TA instruments Universal Analysis software.

## **Characterization of Physical and Mechanical Properties of Composites**

### *Melt Flow Index (MFI)*

The MFI of the neat HDPE and the composite materials was determined in accordance with ASTM D1238 [24] standard using an extrusion plastometer (Tinius Olsen, Model MP 600, USA). The HDPE and composite pellets were tested in five replicates at 2.16 kg load and 190 °C. The MFI was recorded as the amount of material that would pass through the nozzle of the plastometer in 10 min.

### *Water Absorption*

The long term water absorption of composites was quantified as specified by ASTM D570 [25] standard. The samples were immersed in water at 24 °C in a water bath. Five samples from each formulation were tested for percentage moisture gain at 24 h increments, and the test continued until the sample weight change stabilized. The composites used for the test were 30 mm long, 12.5 mm wide, and 3.5 mm thick.

### *Tensile Properties*

The tensile properties such as stiffness and strength of the samples were measured according to ASTM D638 [26]. The samples used for the test were 63 mm long, 10 mm wide in the center and 3.5 mm thick. The crosshead speed was set at 5 mm/min. The universal testing machine Instron (Model 5567, Norwood, MA, USA) installed with a 2 kN load cell was used for the test.

### *Flexural Properties*

The flexural properties such as stiffness and strength of the samples were measured according to the ASTM D790 [27] standard that specifies three-point bending test method for unreinforced and reinforced plastics. The samples used for the test were 63 mm long, 12.5 mm wide and 3.5 mm thick. A crosshead speed of 1.3 mm/min was selected based on the span length of the samples. The flexural properties were evaluated using universal testing machine as described earlier.

### *Impact Strength*

The impact strength of the samples was tested in accordance with ASTM D256 [28] standard. The notched samples were tested for their impact resistance properties using an Izod impact tester (Tinius Olsen, Model Impact 104, Horsham, PA, USA). The sample dimensions were 63 mm x 12.5 mm x 3.5 mm (LxWxH) with a notch of 2 mm. The microscopy images of the impact fractured sample were examined under a Leitz Laborlux S digital microscope at 40X magnification.

### **Statistical Analysis**

To compare the properties of composites from different groups, Fishers Least Square Difference (LSD) tests were performed on all the 10 treatments using Minitab 17 (Minitab Inc., Penn State University, PA, USA). The error bars in the bar graphs represent the standard deviation of the group.

## **Results and Discussion**

### **Composition Analysis of Untreated and NaOH Treated DDGS Fibers**

The composition analysis of DDGS fibers showed that NaOH treated DDGS fibers had higher NDF concentration due to solubilization and loss of hemicelluloses and lignin during alkali treatment (Table 4.1). The alkali treatment of 0.1 M for a residence time of 1h proved to be

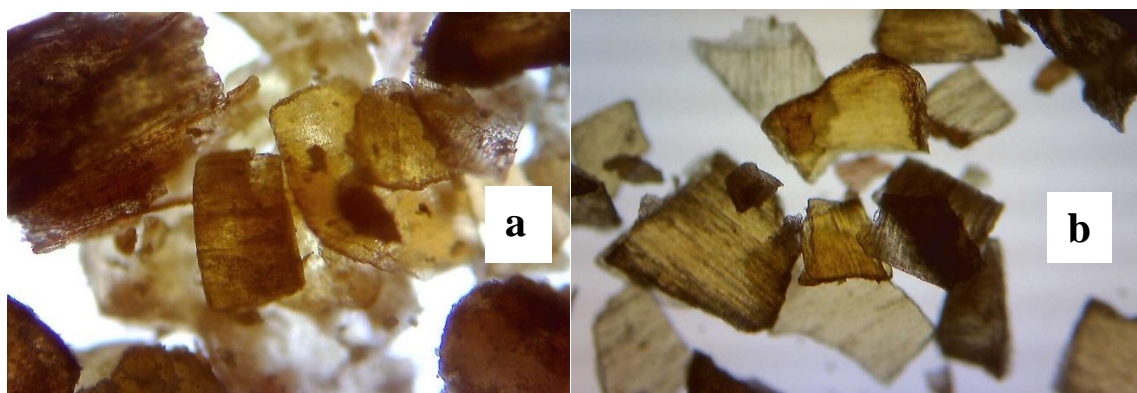
strong enough for solubilization of protein, starch, and fat contents that was present in the untreated DDGS fibers.

**Table 4.1.** Composition of untreated and NaOH treated DDGS fibers computed on a dry basis, performed by Animal Sciences lab (NDSU)

Components	Untreated DDGS fiber (%)	NaOH treated DDGS fiber (%)
NDF	53.20	76.8
Protein	34.21	15.62
Starch	4.04	1.54
Fat	4.04	0.81
Ash	4.45	3.02

### Morphology of Untreated and Alkali Treated DDGS Fibers

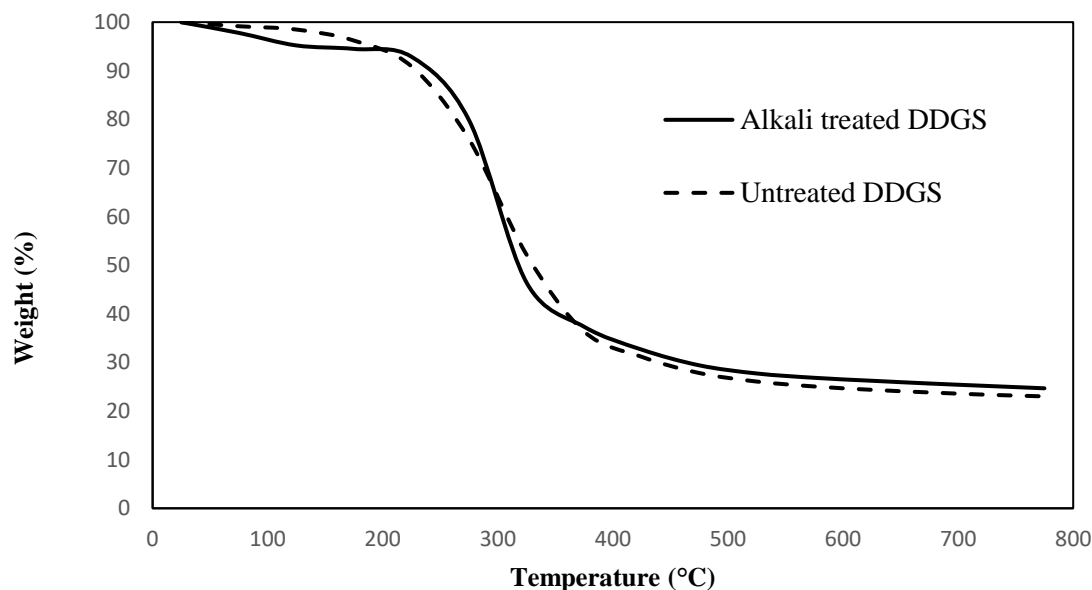
The NaOH treated fibers exhibited cleaner untreated DDGS fibers (Fig. 4.1a &b). The effects of alkali treatment include solubilization of hemicelluloses, lignin, wax, and oil covering the surface of the fiber [29]. The yellowish appearance of untreated DDGS fiber was mainly from the oil present on the surface which was not visible for the alkali treated DDGS fiber. The alkali treated DDGS fibers showed rough surface and more cellulose exposure which helps in improving the fiber-matrix adhesion.



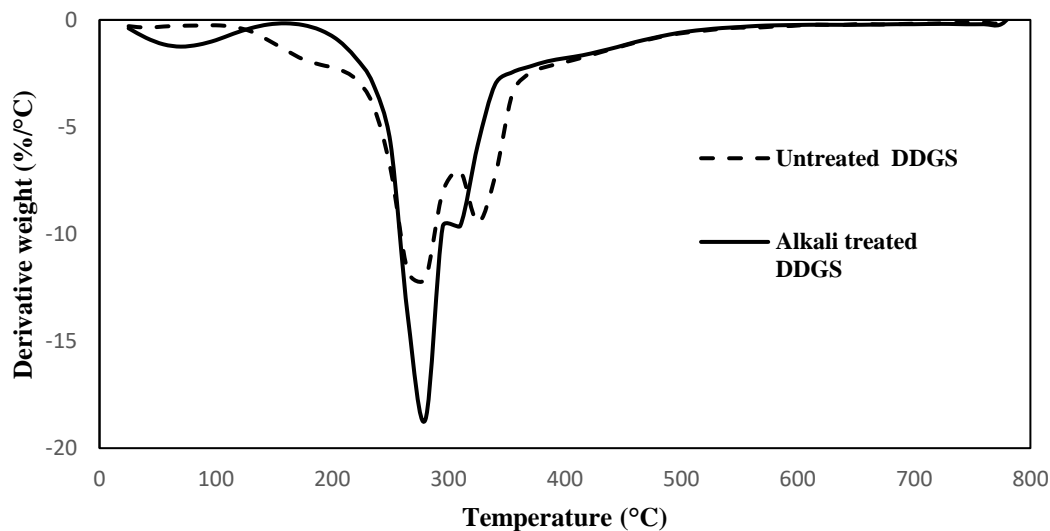
**Fig. 4.1.** The microscopy images of a. untreated DDGS fiber and b. alkali treated DDGS fiber at 40X magnification

## Thermogravimetric Analysis of DDGS Fibers

The thermogravimetric curves showed difference in the degradation rate of alkali treated DDGS as compared to the untreated DDGS fiber (Fig. 4.2 & 4.3). Alkali treated DDGS fiber lost 10% weight around 100 °C, representing moisture loss from the fiber. The thermal degradation of alkali treated DDGS fiber remained constant between 150 and 230 °C temperature range, corresponding to hemicellulose degradation. The higher degradation in alkali treated DDGS fiber in the hemicellulose range is an indication that mercerization partially solubilized the hemicellulose in treated DDGS fiber. Between 230 and 360 °C temperature range, corresponding to cellulose degradation, the alkali treated and untreated DDGS fiber showed weight loss of approximately 64 and 68% respectively. At the end of the test, DDGS fibers showed a final weight loss percentage of around 75%.



**Fig. 4.2.** Thermogravimetric curves for untreated and alkali treated DDGS fibers



**Fig. 4.3.** Differential thermogravimetric curves for untreated and alkali treated DDGS fibers showing their thermal degradation

#### Melt Flow Index (MFI) of DDGS composites

The addition of DDGS fiber in HDPE polymer decreased its MFI as expected (Table 4.2). The addition of 25% untreated or NaOH treated DDGS reduced the MFI from 5.2 to 3.93 and 3.5 g/10 min, respectively. The MFI decreased further to 1.7 and 0.98 g/10 min for untreated and NaOH treated fibers respectively when the loading of fibers was increased to 50%. The presence of fibers hampers the ability of HDPE chains to flow smoothly, thus reducing the MFI.

**Table 4.2.** Melt flow index of neat HDPE and untreated and NaOH treated DDGS composites

Sample Formulations	MFI- Untreated (g/10 min)	MFI- Alkali treated (g/10 min)
Neat HDPE	5.2 ± 0.40 (a)*	
DDGS25 (25% DDGS fiber)	3.93 ± 0.20 (b)**	3.51 ± 0.18 (c)
DDGS50 (50% DDGS fiber)	1.7 ± 0.16 (d)	0.98 ± 0.31 (e)

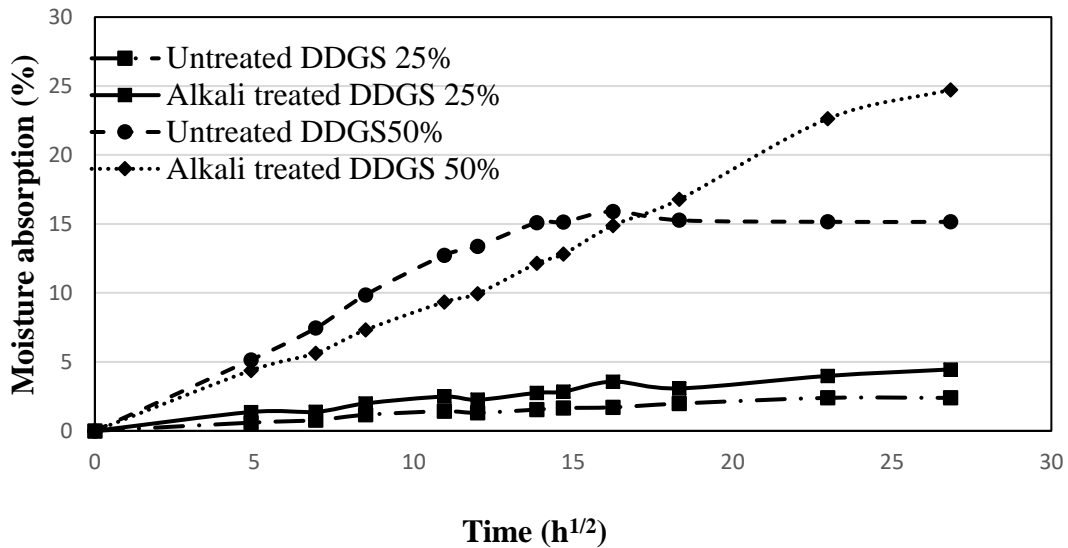
\* ± indicates the standard deviation of the treatment

\*\* letters in parentheses indicate significant difference between the treatments at  $\alpha = 0.05$



## **Water Absorption of Composites**

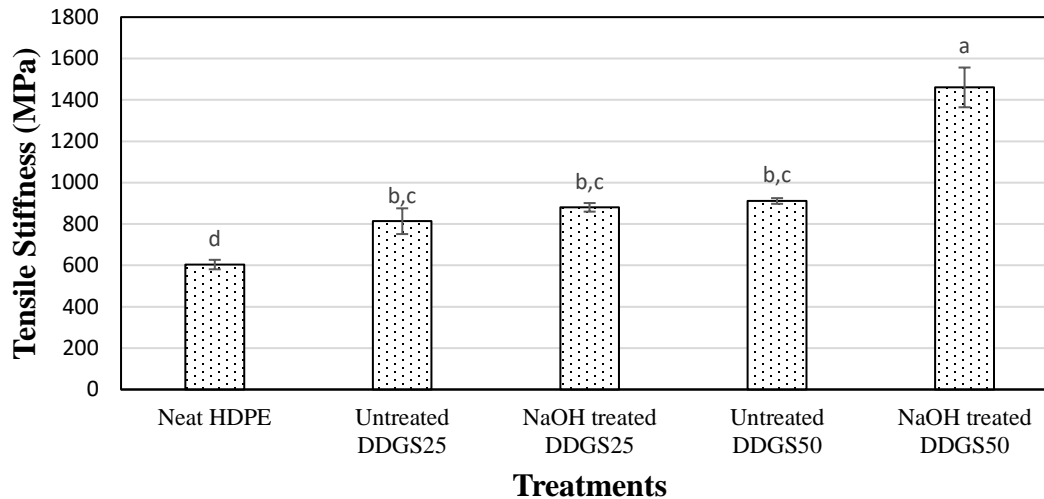
The composite samples with 25% untreated or alkali treated DDGS fiber absorbed less than 5% moisture after an exposure time of 30 days (Fig. 4.4). The low moisture absorption by the DDGS25 samples indicates that the HDPE polymer sufficiently encapsulated DDGS fibers, thus inhibited the entry of moisture in the composites. When the DDGS fiber loading was increased to 50%, the composite samples exhibited high moisture absorption after the initial 24 h. The untreated DDGS50 samples showed consistently higher moisture absorption than the alkali treated DDGS50 up to 264 h after which the alkali treated DDGS50 samples started to absorb moisture more rapidly than the untreated samples. The final moisture absorption of alkali treated DDGS50 samples was around 25% compared to 15% observed for the untreated DDGS50 sample after 30 days. The alkali treatment removes lignin, pectin, waxy substance and natural oil covering the surface of cell wall, thus exposing cellulose fibrils [30]. Change in morphology may create more void to water penetrate inside the alkali treated samples. It is also possible that the fiber encapsulation was relatively poor for composite with 50% fiber loading h contributing to higher water absorption.



**Fig. 4.4.** The moisture absorption of untreated and alkali treated DDGS composite samples at 25% and 50% fiber loadings plotted against square root of time

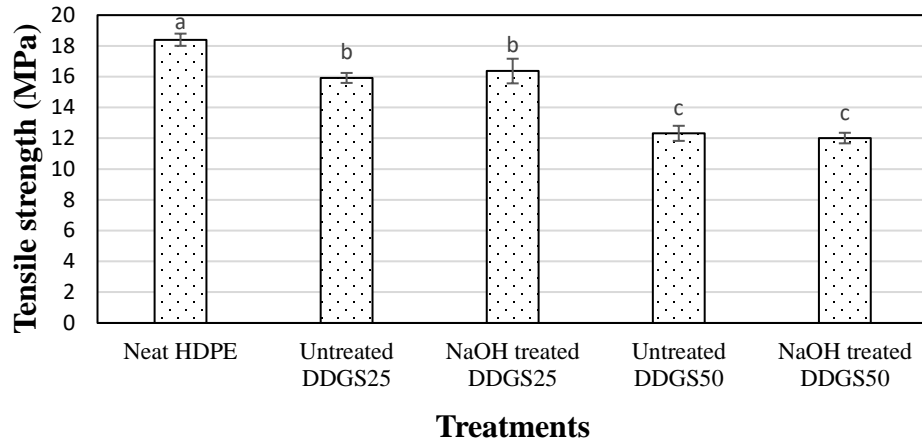
#### Tensile Properties of DDGS Composites

The inclusion of DDGS fiber in HDPE matrix resulted in significant increase in the tensile modulus (Fig. 4.5). The DDGS25 composite samples exhibited increased stiffnesses that were 35% and 46% higher for the untreated and alkali treated samples respectively than the neat HDPE sample. This increase was most likely due to higher tensile stiffness of DDGS fiber and fiber encapsulation by matrix at 25% fiber loadings. When the fiber loading increased to 50%, the tensile stiffness of the untreated and NaOH treated DDGS50 samples showed an increase of 51% and 142%, respectively, compared to the neat HDPE. The alkali treated DDGS50 composite had the highest tensile stiffness of 1428 MPa. In addition, alkali treated DDGS25 sample showed tensile stiffness comparable to the untreated DDGS50 sample.



**Fig. 4.5.** Tensile modulus of neat HDPE, untreated and alkali treated DDGS fiber composites. Different letters in the label show statistically significant difference between the different formulations at  $\alpha=0.05$

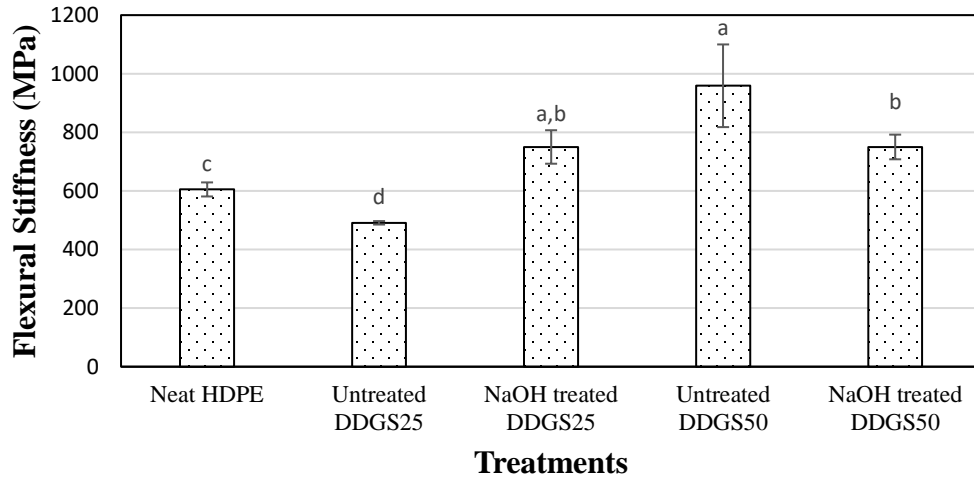
The DDGS fiber filled composites showed reduced tensile strength than the neat HDPE (Fig. 4.6). The tensile strength of a material is determined by the weakest part of a sample which is the interfacial region of a composite sample due to the incompatibility between the hydrophilic fiber and hydrophobic matrix. When the fiber loading increased from 25 to 50%, the tensile strength decreased as the interfacial adhesion between the fiber and the matrix further weakened. This may be due to the inadequate wetting of the fiber by the matrix, leading to crack formation in the interfacial area. Also, the higher fiber loading leads to voids in the interfacial areas in the composites [31]. The alkali treatment of fibers had no effect on the tensile strength of composites. The tensile strength decreased by about 25% when neat HDPE was filled with 50% DDGS fiber.



**Fig. 4.6.** Tensile strength of neat HDPE, untreated and alkali treated DDGS fiber composites. Different letters in the label show statistically significant difference between the different formulations at  $\alpha=0.05$

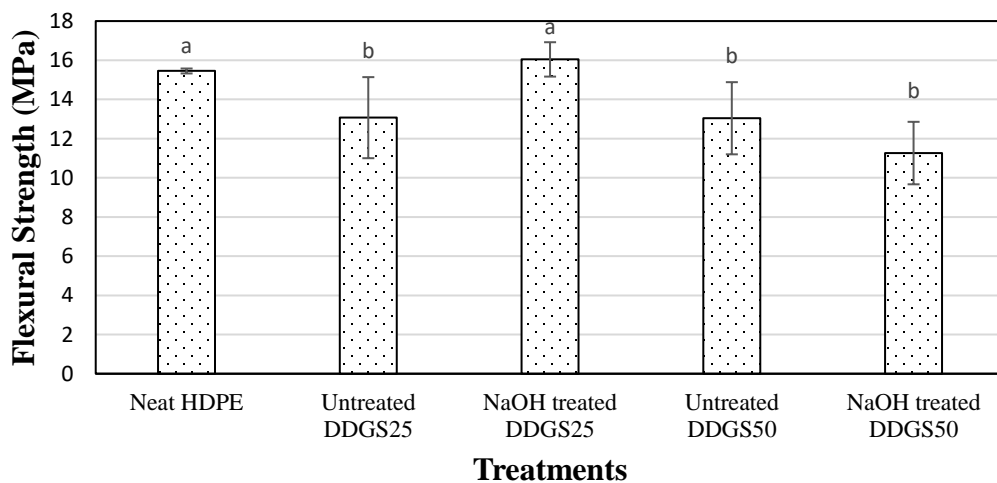
### Flexural Properties of Composites

The inclusion of untreated DDGS fiber at 25% loading into HDPE resulted in a 23% decrease in flexural stiffness whereas all other composite treatments showed an increase in flexural stiffness (Fig. 4.7). For example, addition of treated DDGS fiber increased flexural stiffness by 24%. This increase in flexural stiffness of alkali treated DDGS25 sample was due to improved interaction between the fiber and the matrix. The modulus of a composite is determined by the modulus of fiber and matrix, fiber content and orientation. When the fiber loading was increased to 50%, the untreated DDGS50 samples showed an increase in stiffness of 59% whereas alkali treated DDGS50 exhibited similar stiffness as of the alkali treated DDGS25 when compared to the neat HDPE.



**Fig. 4.7.** Flexural stiffness of neat HDPE, untreated and alkali treated DDGS fiber composites. Different letters in the label show statistically significant difference between the different formulations at  $\alpha=0.05$

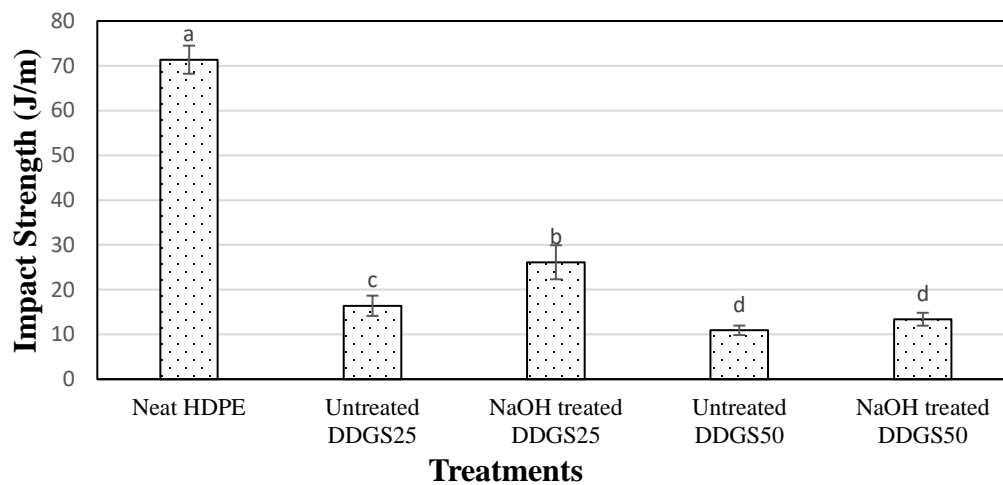
The tensile strength of DDGS composites at 25% loading showed that alkali treatment improved the tensile strength, indicating improved interfacial bonding between the fiber and the HDPE matrix (Fig. 4.8). At 50% fiber loading, the flexural strength of composites with treated and untreated DDGS fiber fillers were similar, and comparable to those of composites with 25% untreated fiber. The alkali treated DDGS25 sample had higher flexural strength than both the untreated and alkali treated DDGS50 samples by 23 and 42%, respectively.



**Fig. 4.8.** Flexural strength of neat HDPE, and untreated and alkali treated DDGS fiber composites. Different letters in the label show statistically significant difference between the different formulations at  $\alpha=0.05$

## Impact Strength of Composites

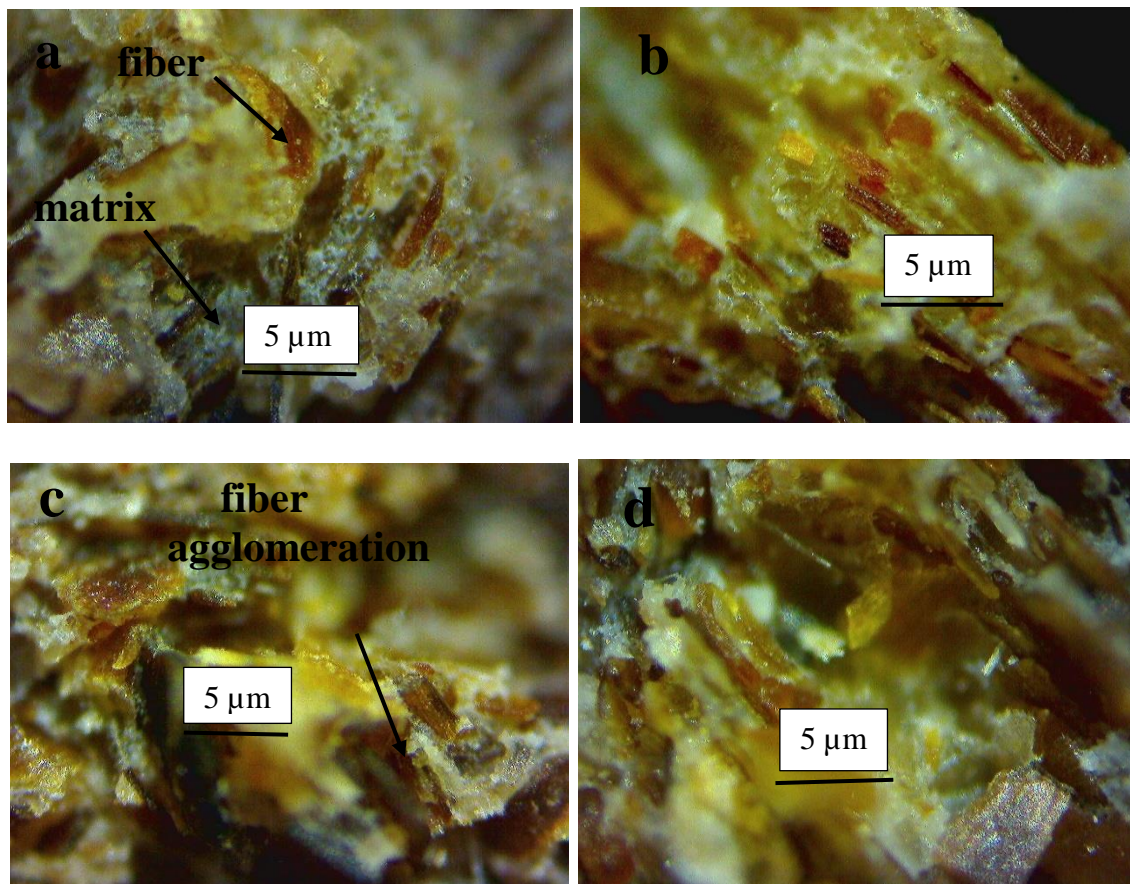
The notched impact strengths of composite samples decreased with increase in filler loadings from 25 to 50% (Fig. 4.9). The impact strength of composites is dependent on the fiber concentration, shape, orientation, and interfacial area between the fiber and the matrix [32]. The neat HDPE sample showed the highest impact strength of 71 J/m. Addition of the fiber filler reduced the impact strength to up to one seventh. The composite samples with 25% alkali treated DDGS had higher impact strength than untreated DDGS25 indicating improvement in interfacial bonding between the treated fiber and the matrix.



**Fig. 4.9.** Impact strength of neat HDPE, and untreated and alkali treated DDGS fiber composites. Different letters in the label show statistically significant difference between the different formulations at  $\alpha=0.05$

The microscopy images of impact fractured DDGS samples showed DDGS fiber loading of 25% had better fiber encapsulation by the HDPE matrix than for the 50% DDGS samples (Fig. 4.10). The NaOH treated DDGS fiber had much cleaner surface than than the untreated fiber showing the effectiveness of alkali treatment in increasing the surface roughness. The fiber loading of 50% showed agglomeration of fibers with irregular deposits of HDPE matrix illustrating the weak fiber matrix interactions. In addition, some fibers at the fractured surface showed no traces of the matrix exhibiting poor encapsulation by the HDPE polymer at 50% loading. The poor

dispersion of fibers and ineffective encapsulation of fibers by the HDPE matrix at 50% loadings are consistent with the impact resistance results.



**Fig. 4.10.** Microscopy images of impact fractured DDGS composite surface examined at magnification of 40X. Figure show composites with a. 25% Untreated DDGS fiber, b. 25% NaOH treated DDGS fiber, c. 50% untreated DDGS fiber and d. 50% NaOH treated DDGS fiber

### Conclusions

The alkali treatment of DDGS fiber resulted in the solubilization of non-cellulosic components and increased surface roughness. Alkali treatment of DDGS fibers decreased the water absorption of composite materials during the first 10 days of water exposure, after which the composite with 50% alkali treated DDGS showed sharp increase in water absorption. The addition of DDGS fibers in HDPE increased the modulus properties of the composite samples but decreased the strength properties limiting their applications to non-structural materials. The poor encapsulation of the DDGS fibers and weak interfacial bonding resulted in decreased

strength properties. The composite samples with NaOH treated DDGS fiber at 25% loading showed increased flexural properties. This may be attributed to better interfacial interaction due to the mechanical interlocking pockets in the NaOH treated fiber for HDPE matrix. The high fiber loading of 50% led to ineffective encapsulation of the fibers by the matrix.

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## CHAPTER 5. GENERAL CONCLUSIONS

In recent years, the production of distiller's dried grain with solubles (DDGS) has increased proportionately with increase in the production of corn based ethanol. The fiber component in DDGS is not easily digestible by poultry and swine. The separation of fiber makes the DDGS amenable to the non-ruminants and increases its nutritional characteristics due to higher protein and oil contents. This dissertation focuses on exploring the feasibility of using DDGS fibers as fillers in thermoplastic composites.

The DDGS 30% composites showed better flexural strength than oak 30% composites, so they can replace the oak fiber for applications requiring similar flexural properties. The DDGS 30% composites exhibited the highest impact strength and melt flow index. The major drawback of using DDGS fibers as fillers were their high affinity for water absorption at both 30 and 50% loadings.

For further evaluation of the DDGS composite performance under accelerated weathering, a commercial scale study was conducted. The hypothesis for the study was that DDGS has very low lignin which degrades material when exposed to outdoor weather. The less decolorization and constant water absorption of DDGS composites after UV weathering justifies the hypothesis. There was a loss of flexural properties for all the composite samples but the combination of DDGS and oak fiber, each at 25% loading, showed similar properties to the oak fiber composites. The photodegradation of the high density polyethylene (HDPE) was the common effect leading to severe chain scissions and decreased material properties.

In another hypothesis, mercerization or sodium hydroxide (NaOH) treatment of DDGS fibers was considered to improve their performance as fillers in HDPE composites. The mercerized DDGS fiber at 25% loading showed better stiffness properties than the untreated

DDGS fibers at the same loadings. The high fiber loading of 50% did not show increase in material properties.

The role of DDGS fiber as filler is very effective in terms of cost savings. The DDGS is available at a very low cost and replacing a part of expensive plastics by DDGS fiber can present a great opportunity in material engineering.

## CHAPTER 6. RECOMMENDATIONS FOR FUTURE WORK

The inclusion of DDGS and corn hull fiber in HDPE composite has shown potential to be used as an alternative filler. Our investigations showed that DDGS and corn hull fibers can act as alternative to oak wood fiber to obtain comparable mechanical properties.

The accelerated weathering of composites from hull fibers from corn grain and DDGS showed better resistance to color fading and higher resistance to moisture after 2000 h of UV weathering compared to oak composites. However, DDGS fiber composites mostly resulted in lower mechanical properties than oak-based composites. The performance of DDGS fiber filled composite materials can be enhanced by adding coupling agents. Therefore, future research should focus on the impact of coupling agent for improved material properties.

Alkali treatment of DDGS fiber has shown increase in tensile and flexural stiffness at 25% loadings. The mercerization of DDGS fiber can be optimized by considering variables such as sodium hydroxide concentration, residence time and the effect of heating at different temperatures. Because the DDGS fiber has high amount of carbohydrates and proteins, unlike any other natural fiber, a chemical method that can selectively solubilize protein and oil without interfering with cellulose and hemicellulose, should be investigated in the future.