

EVALUATION OF THE THERMAL, MECHANICAL AND RHEOLOGICAL  
PROPERTIES OF RECYCLED POLYOLEFINS RICE HULL COMPOSITES

A Thesis

Presented in Partial Fulfillment of the Requirements for the

Degree of Master of Science

with a

Major in Chemical Engineering

in the

College of Graduate Studies

University of Idaho

by

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August 2020

### Authorization to Submit Thesis

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## Abstract

The elevated amount of polyolefin production, low recycling rate and increased landfill has created an environmental concern, and more innovative studies are still ongoing to reuse and reduce this waste efficiently. One out of many remedies, is the manufacture of composites with a polyolefin matrix and a reinforcing filler. The use of natural fibers as fillers for polyolefins has evidently proven to improve physical, mechanical, thermal and flow properties. Different factors affect the final product properties of a composite from fiber particle size, interfacial bonding between matrix, processing temperature amongst many. Hence, this research was done to investigate the influence of rice hulls of different sizes (<0.5 mm and <1 mm) used as reinforcement for common polyolefins of recycled high-density polyethylene (rHDPE) and polypropylene (rPP) rice hulls composites. Mechanical characterization of the composites was done using dynamic mechanical analysis (DMA) and tensile testing. Thermal characterization was achieved via differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and thermomechanical analysis (TMA). Flow properties were determined using melt flow rate (MFR), dynamic and capillary rheological methods. Surface chemistry analysis was performed using Fourier Transform Infrared (FTIR) Spectroscopy. Results showed an increase in tensile and viscoelastic properties for the <0.5 mm rice hull composites for both polyolefins. These results were compared to those of virgin polyolefin rice hull composites and wood plastic composites (WPC). It was evident that recycled polyolefin rice hulls composites can be used as replacements for wood and virgin polyolefin composites since they exhibited similar properties.

## Acknowledgment

My utmost gratitude goes to the Almighty God for keeping me sane through the years and giving me the strength to persistently push through. I also will like to appreciate my academic advisor Dr. Armando G. McDonald for giving me the privileged opportunity to work with him, his stern supervision, guidance, and sincere realistic advice through the semesters. To my committee members, Dr. Eric Aston, and Dr. Michael Maughan, I would like to say thank you for being available, your contributions and for making my years less frustrating.

My gratitude also goes to the Chemical Engineering faculty members, Dr. Wudneh Admassu (Woody), Dr. Soumya Srivastava, Dr. Vivek Utgikar and Dr. Mark Roll for their patient teachings, advice, and expertise.

I would like to sincerely appreciate the financial efforts, words of encouragement and prayers of my parents Engr and Mrs. Peter Orji, I pray that God keeps you both alive to reap the good fruits of your labor. To the families of Dr. Ebenezer Jones-Mensah, Mr., and Mrs. Nwamba, Mr., and Mrs Popoola, Joel and Yvonne Oduro-Afriyie, thank you so much for your constant advice and prayers. I am also grateful for the moral support of my colleagues, classmates, and friends; Jackie Martinez, Ernestina Boateng, Paul Dania, Crystal Gallegos, Courtney Molvig, Kimberly Bowlby, Maryam Abbasi, Dikshya Pokhrel, and especially, Farid Sotoudehniakarani for his patient assistance when needed.

I wish to express my gratitude to the Idaho State Board of Higher Education, Idaho Global Entrepreneurial Mission (IGEM) grant for funding this project.

### **Dedication**

This thesis is dedicated to God Almighty, Engr. And Mrs. Peter Orji and my siblings.

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## List of Abbreviations and Symbols

### Abbreviations

aPP	Atactic Polypropylene
DMA	Dynamic Mechanical Analysis
DTG	Differential Thermogravimetric
FTIR	Fourier-Transform Infrared
HDPE	High Density Polyethylene
<i>i</i> PP	Isotactic Polypropylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low-density Polyethylene
MAPE	Maleated Anhydride Polyethylene
MAPP	Maleated Anhydride Polypropylene
MFR	Melt Flow Rate
PP	Polypropylene
rHDPE	Recycled High Density Polyethylene
RH/RHA	Rice Hulls/Rice Hulls Ash
RHPC	Rice Hulls Polyolefin Composites
rPP	Recycled Polypropylene
sPP	Syndiotactic Polypropylene
TGA	Thermogravimetric Analysis
TMA	Thermo-Mechanical Analysis
WA	Water Absorption
WPC	Wood Plastic Composites

### Symbols

$\Delta H_m$	Melting Enthalpy of Peak
$\Delta H_0$	Theoretical Enthalpy of Fusion
G' or E'	Storage Modulus
G'' or E''	Loss Modulus
$\delta$	delta
$W_f$	Weight Fraction

$M_f$	Maximum Moisture Content
$h$	Sample Thickness or Height
$l$	Length
$w$	Width
$\eta^*$	Complex Viscosity
$D_f$	Diffusivity
$\gamma_a/\gamma$	Apparent Shear Rate/True Shear Rate
$Q$	Volumetric Flow Rate
$X_c$	Percent Crystallinity
$\tau$	Shear Stress

## Chapter 1: Overview and Research Objectives

### 1.1 Overview

The increased rate of non-biodegradable plastics production and usage has led to the continuous search for more innovative recycling and reuse of waste plastics in composite production with the intent of improving and promoting sustainability [1, 2]. Amongst these disposed plastics, are polyolefins mostly applied industrially for packaging due to their low cost, non-toxicity, availability, easy synthesis, and light weight [3]. This recognition has yielded the annual production of polyolefins which are about half of the 359 million metric tons of plastics globally produced as recorded in 2018 [3-5].

Polyolefins which are high molar mass hydrocarbons, collectively include thermoplastic polymers of mainly polyethylene (PE) and isotactic polypropylene (*i*-PP) polymerized from their olefin monomers [2]. Recycling polyolefins in the past years has proven to help improve plastic waste management with the additional goal of substituting virgin polyolefins. It is important to note that the dependency of this substitution for future applications, lies in the purity of the retrieved plastic [6]. But the major problems hindering this objective during recycling include the presence of contaminants (food residue, labels, caps, chemicals etc.) and sorting which creates a heterogeneous and unwanted blend of components [7]. Due to the high shear force and temperatures polyolefins undergo during reprocessing, thermal and structural degradation occurs. This could be due to photooxidative or oxidative reactions that take place leading to either chain scission, branching or crosslinking thus creating the quest for better ways of improving their performance [8,9]. Several research processes involving the reinforcement of polyolefins with additives and most importantly, natural fiber fillers in “composites” has shown to improve polyolefin properties while promoting sustainability [10-12].

Natural fiber-polyolefin composites which are a mixture of biodegradable fibers and plastics creates a stiffer polymer matrix with better strength properties [13]. The properties of the composites are solely dependent on the type of fiber, size, geometry, and polymer matrix used. There are a wide range of natural fibers with good aspect (length/diameter) ratios that have been used in composite preparation to provide significant reinforcement and they include wood, hemp, bamboo, jute, corncob, etc. [14-17]. These fibers act as reinforcements

in polyolefin composites. The chemical and structural composition of these natural fibers greatly affect their physical and mechanical properties which in turn play a major role in the composite matrix. A high cellulose content increases the properties of tensile strength and modulus [18]. One of the natural fibers which has received a large recognition due to its low cost, biodegradability, weathering resistance and stability is rice hulls; obtained from the outer layer of rice seed, a staple global food and major crop in the world. Significant rice growing regions include Asia, Pacific and North America with China been the highest producing country [19].

Rice hulls (RH) are a by-product of rice milling that is considered an agricultural-based waste and a fuel in most rice producing countries constituting to the tens of millions of tons produced globally per annum [20]. According to Mofijur *et al.* (2019), an estimated total of 154 million tons of RH were produced by the top 20 rice producing countries in 2017 [21]. Industrially, RH are used mostly for energy production by combustion, ethanol biofuel production, filter aids in lautering during brewing, and a source of fertilizer amongst others [22-24]. Its low-density, moisture content range from 8.66% to 10.44%, light weight, availability and renewable potential also make it highly considerable in the production of rice hull polyolefin composites (RHPC) [25].

Polyolefin composites are commonly fabricated from either, extrusion, compression molding or injection molding with a high exposure to shear stress under applied force. From previous research, RH has been compounded with most polyolefins of high density polyethylene (HDPE) [26], polypropylene (PP) [27], low density polyethylene (LDPE) [28], polystyrene (PS) [29] and has shown to exhibit better physical, mechanical, thermal properties. Applications of these composites can be seen in building panels due to their high resistance to biological attack and stability in the presence of moisture, automotive parts, frames, and interior panels (doors and windows).

As a result of the high hydrophilicity of the natural fibers, problems of interfacial bonding with the hydrophobic surface of the polyolefins makes it difficult for proper wetting of the fiber in the matrix [30]. The hydrophilicity of the fiber shows the important of drying most natural fibers before processing since they absorb moisture. Another contribution to the problem of non-homogenous composites is the presence of impurities and a silicon-cellulose membrane of the RH. This further leads to the building of unwanted agglomerates during

processing [31]. Researchers have resolved to using several processes like natural fiber modification, silane treatments, acetylation, maleated graft polymer binders to improve composite matrices [32-34].

### 1.1.1 Physical Properties of Rice Hulls

Due to the numerous species of RH fibers, aspect ratios vary widely but they are mostly of uniform size within a specie with a length range of 5 mm – 10 mm and width of 2.5 mm – 5 mm (Figure 1.1). With most RH in their physical state been straw colored as seen in Figure 1.1, a true low-density range of  $86 \text{ kg/m}^3$  to  $114 \text{ kg/m}^3$  has been recorded with bulk density increasing to about four times when grinded. The presence of the silica in the outer layer gives its hardness [25, 35].



Figure 1.1: Whole Rice Hulls

### 1.1.2 Chemistry of Rice Hulls

Rice hull (RH), a low-cost plant residue (20% by weight) is lignocellulosic containing about 35% cellulose, 25% hemicellulose, 25% - 30% lignin 15% - 20% silica. The silica is located on the outer layer to protect the seed from insects, microorganisms and improve flame retardancy [36,37]. RH has a smoother inner surface with wax and fats to protect the grain. The outer surface which provides it with its abrasiveness, consists of wavy cell walls and cells that are rectangular or elliptical randomly arranged in axial rows [38]. The four structural layers of RH includes an outer epidermis with surface hairs, hypoderm fibers of sclerenchyma, spongy parenchyma cells and inner epidermis [39].

With the existing problems encountered with composite preparations, structural, physical, and chemical properties of the fibers will affect the effective nature of the composite blend and needs to be understood for necessary modifications.

## Cellulose

Cellulose, a major structural component in plants, is a polysaccharide consisting of repeating units of  $\beta$ -D-glucose linked by  $\alpha$ -1,4 glycosidic linkage with alternating  $-\text{CH}_2\text{OH}$  groups forming long linear polymer chains (Figure 1.2). These units are closely packed together forming a rigid structure in the absence of side chains. Cellulose microfibrils are responsible for the mechanical strength in plants with both crystalline and amorphous regions. These microfibrils are formed by the intermolecular interaction of hydroxyl groups from bundles of cellulose chains via hydrogen bonds [25, 39].

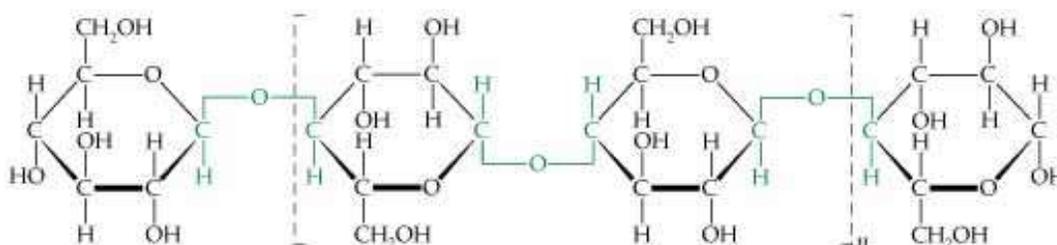


Figure 1.2: Molecular structure of cellulose [40]

Cellulose in rice hulls are considered to have high crystalline segments contributing to its insolubility in water and increased tensile strength and modulus (Figure 1.3). Amorphous regions of cellulose are responsible for the hydrophilicity of natural fibers due to their exposed hydroxyl groups that bond faster with molecules of water. The hydrogen bonds at these intermolecular regions has lower frequencies. A few hydroxyl groups are also present in the crystalline regions of cellulose [41].

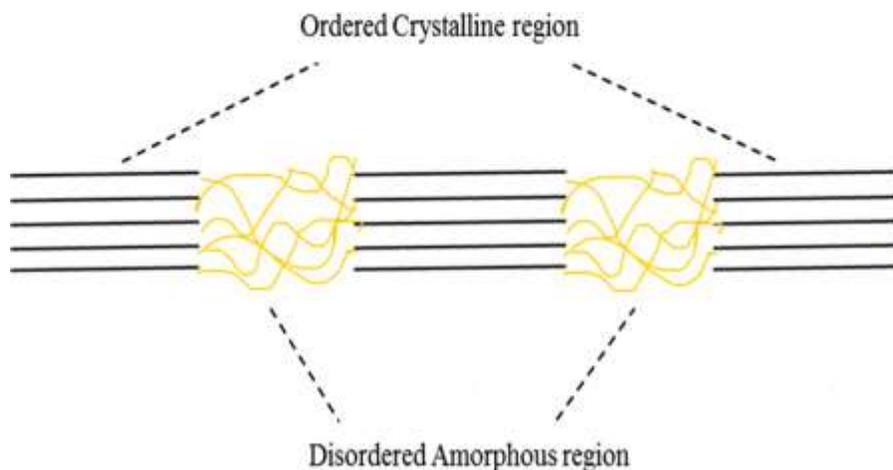


Figure 1.3: Diagram showing amorphous and crystalline regions of cellulose [42]

## Hemicellulose

The composition of hemicelluloses differs among plants and are made up of 5 to 6 carbon ring polysaccharide sugars with a degree of branching. Hemicelluloses contain long chains of hexose, pentoses and can be found in fruits, plants, and other grain hulls. Pentosans, the main hemicelluloses found in RH is a glucuronoxylan and can be hydrolyzed to xylose. The degree of polymerization for hemicelluloses is also lower than that of cellulose. The acid residues attached to hemicelluloses make them more susceptible to water intake and prone to biodegradation and attack. Degradation of hemicelluloses has been observed to occur at lower temperatures than cellulose which leads to the disintegration of the fibers into cellulose microfibrils and further low fiber bundle strength [25, 35].

## Lignin

Most of the lignin in rice hulls is combined chemically with the hemicellulose [39]. Lignin is complex 3-dimensional polymer, insoluble in most solvents and is dependent of plant species and class. Lignin as seen in figure 1.4, is a hydrocarbon polymer which consists of aliphatic and aromatic components in its hydrophobic nature. It is amorphous and responsible for the rigidity of plants fixating the cellulose fibers into a stiff piece.

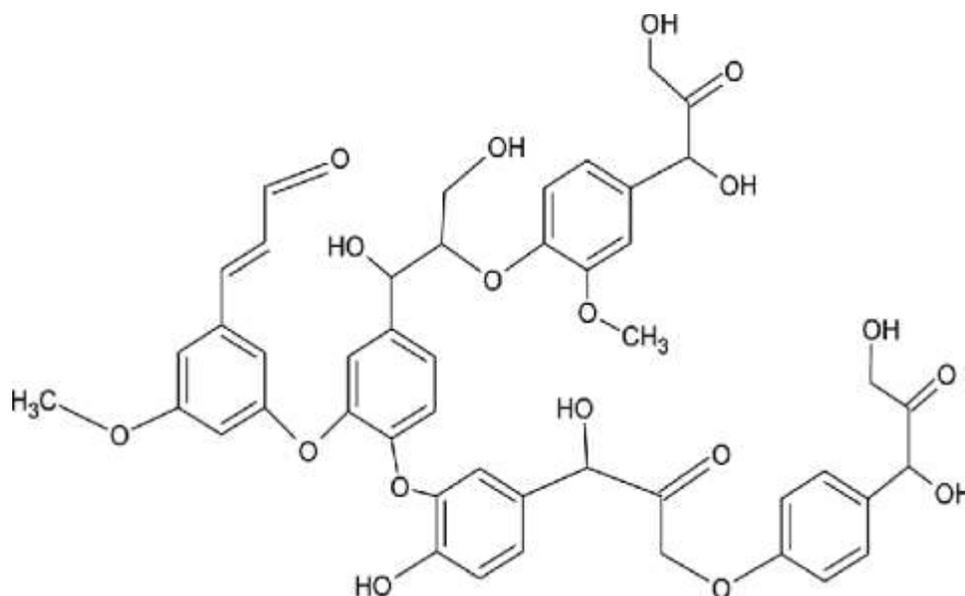


Figure 1.4: Chemical structure of Lignin [43]

Lignin's crosslinked nature (Figure 1.4) is because of the free radical polymerization of 3 monolignols: coniferyl alcohol, synapyl alcohol, and *p*-coumaryl alcohol. The crosslinked and condensed structure arises from free radical coupling of the lignin monomers which makes it like a thermoset matrix. Due to this property, possible stress transfer in the microfibrils leads to photochemical degradation when exposed to ultraviolet light [25, 35, 43].

### **Pectin**

Pectin is a complex polysaccharide also found in rice hull fibers with a very hydrophilic nature due to the carboxylic acid groups. It is also a heterogalacturonan with linear chains of  $\alpha$ -1,4 linked D-galacturonic acid and some branched  $\alpha$ -(1-2)-L-rhamnosyl- $\alpha$ -(1-4)-D-galacturonosyl segments. Pectin which can be hydrolyzed, as well as lignin and hemicelluloses, at higher temperatures, has different structural forms depending on the plant [41].

### **Lipids, Proteins, Vitamins and Organic acids**

The lipids in rice hulls is known to contain free fatty acids and fall within the range of 0.39% – 1%, protein range of 1.9% - 3% with oxalic and citric acid been the most organic acids found in rice hulls amongst others [39]. Different levels of thiamin, riboflavin and niacin vitamins have also been observed in rice hulls.

### **Inorganic Component**

Rice hull ash (RHA) varying from 13.2% to 29% of the weight of RH constitute most of the inorganic part with the silica content of the ash been about 94% to 96%. Due to the combustion or gasification of RH for energy production, this inorganic substrate is formed with its properties depending on the specie of rice hulls and the process used during combustion [44]. The application of RHA has also been recognized industrially in cement blend production, steel industries, as a silica source for other uses and as fillers in polymer studies [45].

### 1.1.3 Polyolefins

Polyolefins are a general term for common thermoplastics of mainly polyethylene and isotactic polypropylene made from repeating units of their monomers or olefins that comprise of only hydrogen and carbon atoms [3, 46]. Their degree of crystallinity ranges from liquidlike to rigid solids with properties depending on these forms. Polyolefins are mostly synthetic and polymerized using catalysts. The four major catalysts used are namely, Ziegler-Natta, Phillips, metallocene and late transition metal catalysts developed from the 1950s to 1990s. Polymerization reactions for polyolefin synthesis can also be divided into two categories: addition (free radical) and step growth (coordination) polymerization with the addition reaction involving chain initiation, chain propagation and chain termination. This results in the covalent bonding of monomers to form repeating chains which occurs due to free radicals' activation of the double or triple bonds in the monomers. For the step growth reaction, a by-product is condensed without the dependency on chemical bonds. Catalysis and synthesis of polyolefins are mostly done in reactors of varying types with their different configurations, advantages, and disadvantages [46].

Due to the increasing pollution and long-term biodegradation problems of polyolefins, methods of recycling and reuse are still been researched and applied to improve sustainability for a friendlier environment. With reuse been the primary option, recycling polyolefins involves methods ranging from mechanical (secondary), chemical (tertiary) to energy recovery (quaternary). Mechanical recycling involves the collection, sorting, washing, drying and milling of the polyolefins into flakes or pellets for further molten state reprocessing to final products via different molding techniques. Chemical recycling is the chemical structural change and conversion of the matrix into new materials or monomers whilst energy recovery uses controlled combustion [1, 47-49].

Although the most widely used, challenges with the mechanical recycling method includes heterogeneity in the presence of contaminants and the continuous thermal degradation of the polyolefins with increased exposure to heat, stress, and force. This yields a decline in the properties of polymer matrix [3, 50]. A better understanding of the structural conformation and properties of these polyolefins will enable proper optimization in reprocessing techniques and composites production.

### 1.1.3.1 Polyethylene

Polyethylene (PE) is a semi-crystalline polyolefin with multiple repeating units (Figure 1.5) of the simplest alkene monomer, ethylene ( $\text{CH}_2=\text{CH}_2$ ). It is used to make a variety of packaging films, bottles, automobile fuel tanks, and so forth. PE is classified into different grades based on branching and density which influences its mechanical and thermal properties. These grades are, LDPE, HDPE and linear low-density polyethylene (LLDPE) as shown in Figure 1.6. The mechanical properties are also influenced by molecular weight distribution, processing condition, stereoregularity etc. The melting temperature of PE which plays a major factor during processing falls within the range of  $98\text{ }^\circ\text{C}$  to  $140\text{ }^\circ\text{C}$  depending on the grade. Although HDPE, LLDPE and LDPE belong to the same group, their degradation occurs differently [51].

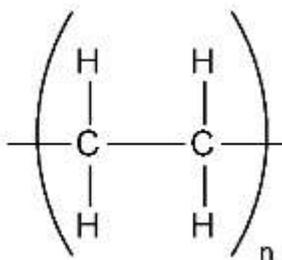


Figure 1.5 :Simplest chemical structure of polyethylene [52]

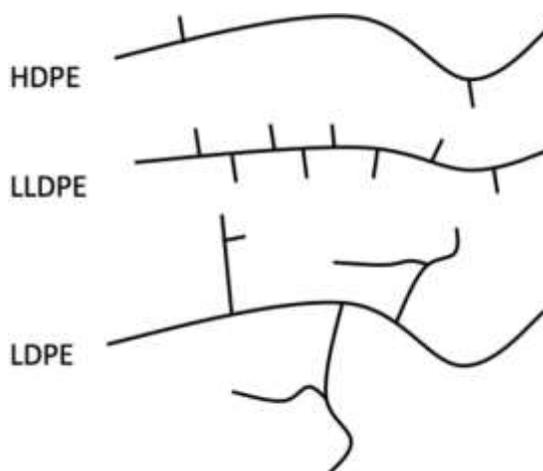


Figure 1.6: Structural forms of different PE grades [53]

HDPE is also considered a linear PE with high crystallinity to amorphous regions and a density range of 950 kg/m<sup>3</sup> to 956 kg/m<sup>3</sup>. It is the oldest used grade of PE with applications in plumbing pipes, milk jugs and automotive fittings due to its electrical insulation properties, stiffness and high resistance to concentrated acids, alcohols, and corrosion. These enhanced mechanical properties can be attributed to the metallocene or Ziegler-Natta catalysis reactions used during its ionic polymerization which gives it a better molecular weight distribution [46, 54].

LDPE which has short and long chains is a branched form of PE prepared by radical polymerization. These long chains have a high degree of branching and are responsible for its viscoelastic properties whilst the shorter chains contribute to its solid-state properties. LDPE has a density range of 910 kg/m<sup>3</sup> to 940 kg/m<sup>3</sup> with more amorphous to crystalline regions which makes it more flexible than HDPE. LDPE due to its low crystallinity has a transparent glossy surface and is mostly used in plastic packaging films [46, 55].

LLDPE is a copolymer of ethylene with a conformation between HDPE and LDPE. It is copolymerized with either 1-butene, 1-hexene or 1-octene with density varying from 915 kg/m<sup>3</sup> to 925 kg/m<sup>3</sup> and a higher tensile strength when compared to LDPE [55]. LLDPE is mostly used in film application because of its toughness, transparency, and flexibility.

### 1.1.3.2 Polypropylene

Polypropylene (PP) is a non-polar, linear, polymorphic, semi-crystalline polymer (Figure 1.7) synthesized from the monomer propylene (CH<sub>2</sub>=CHCH<sub>3</sub>), which is a by-product of petroleum refining. PP can be synthesized either with metallocene or Ziegler-Natta catalysts. PP made from metallocene tend to have higher rigidity, toughness and temperature tolerance but have a lower melting point [56]. As a result of the steric interlinkage of the methyl groups, a more rigid polymer than PE with better tensile, flexural, and compressive strength is obtained [51, 56].

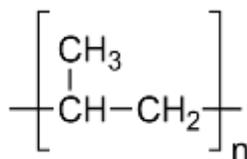


Figure 1.7: Repeating unit of PP

PP is also affected by stereoregularity with the most common forms: isotactic, syndiotactic and atactic, having different configurations (Figure 1.8). It can also be in the form a homopolymer, containing only propylene units, or a random copolymer with ethylene as a comonomer at levels of 1% to 8%. An impact grade polymer also exists when there is a mixture of homopolymers and random copolymers with higher ethylene contents of 6% to 18%. PP has a low density and good resistance to impact [56]. Its applications are seen in automotive industries, laboratory equipment, consumer goods (yoghurt containers, margarine tubs), and furniture market due to its good resistance to environmental stress cracking, sensitivity to microbial attacks and the ability to maintain its mechanical and electrical properties at high temperatures. It also has a density range of  $904 \text{ kg/m}^3$  to  $908 \text{ kg/m}^3$  based on either a homopolymer or a random copolymer [57].

Isotactic polypropylene (iPP), is the highest crystalline form of PP prepared using Ziegler-Natta coordination catalysts. It remains the most widely used PP industrially with its methyl groups arranged on the same side of the backbone.

Syndiotactic polypropylene (sPP) has its methyl groups on alternating sides of the polymer backbone and is synthesized using metallocene catalysts or soluble coordination catalysts having a lower stereoregularity than iPP.

Atactic polypropylene (aPP) has a random distribution of the methyl groups on either side of the backbone. It is obtained from low stereoregular iPP by extraction which involves boiling n-heptane yielding a sticky polymer used in adhesives and roof tar [56, 57].

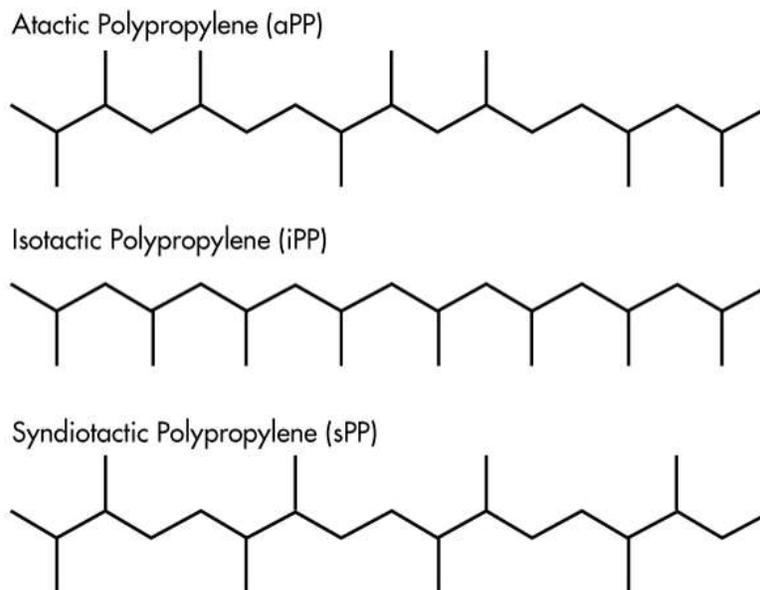


Figure 1.8 : Structural configuration of PP types [58]

#### 1.1.4 Effect of Reprocessing on Polyolefins

Reprocessing, which is a way of recycling polyolefins, involves operations that utilizes non-contaminated, homogenous, waste plastics with the intent to fabricate products having properties like virgin plastics. This goal is still a challenge due to the degradation of polymers that is inevitable during these processes. During the life span of polyolefins, different natural factors could affect their degradation from chemical, mechanical to light radiation factors [59]. But this becomes more intense during reprocessing due to thermomechanical factors of high temperature and shear stress. Degradation involves the change in the molecular structure and properties of the polyolefins. This degradation mostly involves thermo-oxidation from peak temperatures, which leads to either molecular weight reduction from chain scission, crosslinking leading to an increase in molecular weight or side chain reactions causing cyclization [60, 61]. The three main steps of degradation are chain initiation, chain propagation and chain termination occur during degradation.

Chain initiation involves the formation of free radicals thermally with the cleavage of carbon-hydrogen bonds. These free radicals react with oxygen in the propagation stage to form hydroperoxides and studies show that more stable radicals are formed by polymers with

low carbon-hydrogen bond strength which makes them more oxidizable. Chain branching reactions has also been observed to occur after propagation due to the decomposition of the hydroperoxides to form more radicals leading to an increased oxidation rate. Chain termination occurs due to the covalent bond reactions between two peroxy radicals in the presence of air with further formation of oxygenated products of either alcohol, ketones, aldehydes, esters, or acids [59-63].

Degradation of PE varies with respect to grade and initial synthesis and its thermo-oxidation involves continuous crosslinking with repeating cycles which causes an increase in viscosity and molecular weight leading to a stiff polymer [64]. Several studies have observed the structural change of PE during reprocessing and have shown the presence of chain branching and scission [65-67]. The degree of chain branching is responsible for the oxidation in the PE crystalline regions. Oblak *et al* [68], observed the chain branching of HDPE within the first 30 reprocessing cycles via extrusion, with chain scission and crosslinking occurring afterwards. They also claimed that the 10 times recycled HDPE, still had same properties as the virgin polyolefin and has 80% of its original properties after 100 cycles of reprocessing. Studied degradation behavior of LDPE also showed an initial chain scission in the first reprocessing cycle with crosslinking been dominant in consequent cycles [69]. LDPE tends to form more free radicals compared to LLDPE and HDPE due to more branching points it has and loose hydrogen which free radicals get attracted to. LLDPE which is more linear compared to LDPE undergoes more chain scission over a range of temperatures [70].

Since polypropylene has a tertiary hydrogen atom on the methyl group, it is prone to oxidation leading to a faster chain scission than PE. This free radical chain reaction causes a cleavage in the carbon-hydrogen covalent bond producing free radicals with unpaired electrons which leads to a loss in molecular weight. This progresses to further reactions and formation of more free radicals in chain branching [62]. This decrease in PP molecular weight leads to loss of ductility and a brittle polymer. Studies show a high rate of chain scission occurring after 19 cycles of reprocessing with PP acting liquid-like due to a reduction in molecular weight, melt flow rate with reduced strain, stress, and energy at break [3,71-73]. These observations in reprocessing cycles of polyolefins are seen in Figure 1.9.

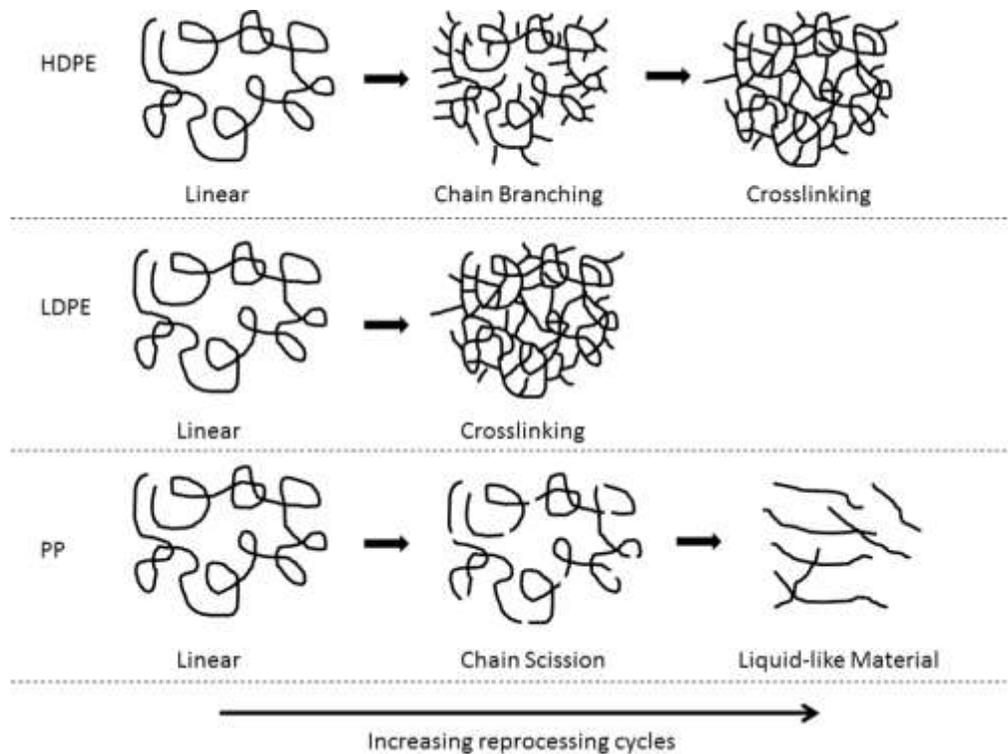


Figure 1.9: Stages of thermal degradation of HDPE, LDPE and LLDPE polyolefins [3]

To resolve the issues of thermo-oxidation reactions in degradation, the use of additives called antioxidants, heat stabilizers, lubricants, fillers (natural and synthetic) have been employed to reduce the effect of thermal stress on polyolefin matrices [51, 59, 74].

## 1.2 Rice Hulls Polyolefin Composites

RHPC which are engineered materials containing phases of rice hulls and a polymer matrix with distinct properties and a defined boundary, has proven to satisfy the gap left by pure polymers over the years due to their hybrid characteristics [75]. This is a result of their recyclability, improved properties, no toxic by-products when burnt, low CO<sub>2</sub> emission, better strength, and stiffness [76, 77]. They also have a high resistance to termite attack when compared to wood plastic composites [78]. Continuous research is still done that involves the reinforcing of polyolefins of PP and PE with rice hulls with positively enhanced composite properties. RH-PE composites have been studied by many researchers [25, 26, 28, 75–77, 79–81], amongst many with different research goals of improving properties by fiber loading,

characterization, and surface modification. PP reinforced with RH have also been investigated [78, 82-90].

Recently, the focus on using RH for fillers in recycled polyolefins has become popularly embraced in support of a greener environment and sustainability. A case study done on the life cycle assessment of recycled HDPE and PP combined with RH showed that recycled based composites had a reduced environmental impact compared to virgin thermoplastics [91]. Chen et al, [92] characterized recycled thermoplastic RH composites using HDPE and polyethylene terephthalate (PET) blends via a two-step extrusion and hot/cold pressing technique. They used a high fiber loading of 50 to 80% and reported an increase in thermal stability and modulus with maximum values of tensile strength. Srebrenkoska et al. [93], compared the properties of composites from recycled PP with virgin PP reinforced with rice hulls/kenaf fibers, prepared using melt mixing and compression molding. Flexural and thermal degradation tests showed similar values proving the importance of reusing of recycled PP in place of neat ones. A similar study which involved recycled PP-RH composites that were subjected to five cycles of grinding and reprocessing yielded recycled composites of less water absorption compared to the original composites. It was claimed that this could have been due to the change in chemical and physical structure of the polyolefin during recycling [94]. These studies show the importance recycling polyolefins, their similarity to virgin grades and its efficiency in composite production.

### **1.2.1 Processing Techniques for RHPC**

Manufacturing of RHPC involves the steps of compounding and further sample processing into pellets or end products. Different parameters affect the processing of RHPC from temperature, fiber type and volume fraction. Several techniques are employed in the manufacturing of RHPC from injection molding, compression molding and extrusion. These techniques require the use of specific processors like extruders which come in different types with exit dies to form final shapes of the composites [13, 95]. Extruders could either be a single screw for just formation of final shapes of composites, or a twin-screw extruder which performs the dual function of compounding and composite shaping. The screws used in these extruders are mainly of three types: intermeshing co-rotating, counter-rotating, and non-intermeshing counter rotating screws [96].

### **1.2.1.1 Compression Molding**

This process has been used since the 90s for thermoplastic composites and it involves the compression of preheated materials in a mold under pressure. This pressure is held constant until the composite solidifies. Several factors to be considered whilst using this process includes time for solidification, amount of sample added, and pressure applied to mold [97]. Compression molding requires high volume and pressure with low cost for more complex composite parts. It also runs in fast set up times with efficient uniformity, requiring less trimming and nice surface finishes. It is mostly applied when molding automotive parts, furniture, and housing components. Different types of compression molding under sheet molding are thick molding compound, bulk molding compound and wet lay-up compression molding [25, 97]. RHPC has also been manufactured using this process in several studies [98-100].

### **1.2.1.2 Injection Molding**

Injection molding is mostly used for specially shaped (3-dimensional) composites with molten polymers from heating zones injected into a mold where it cools down into a solid. Although the process sounds simple, it is more challenging than that. The concepts of heat transfer and pressure flow are essential. High pressure is required to push the highly viscous composite through the barrel into the mold [56]. Due to its ability to maximize composite flow, it has been applied in several RHPC production [84, 87, 101-104]. A typical injection molding unit has a feed hopper where samples are fed in, an injection unit where the composite is heated into a homogenous melt and injected into a mold and a clamp unit for holding molds during injection of composite melt and closing/opening mold valve. There are different forms of the injection molding unit from a single to a two-stage ram and single to two stage screw. The single and double stage ram are not efficient with heating, mixing and pressure distribution. The single stage screw is the most popularly use system with the multitask concept of combining heating, mixing and injection. The screw has heating zones and a barrel for feeding, melting, and conveying the composites [57].

### 1.2.1.3 Extrusion

Extrusion which is a continuous process is the most common approach for processing composites. It is more preferred due to the higher strength and stiffness of the produced composites [51]. Due to its low production costs, the application of this method is seen in most studies of RHPC [75, 76, 95]. One or more screws are involved in the heating and pressurizing of the composites in the heating barrel called “the extruder”. The melted product is forced through a die after which a final product is formed. The most important determinant of an extruder is the screw, which is responsible for feeding, transporting, melting, compounding and homogenizing the composites as it moves to the die. The two types of extruders are the single screw and twin-screw extruder [56, 57, 105]. The single screw extruder (Figure 1.10) consists of a hopper for feeding in samples, a motor driven screw within a close-fitted barrel which has cooling and heating modes and a die for purging downstream.

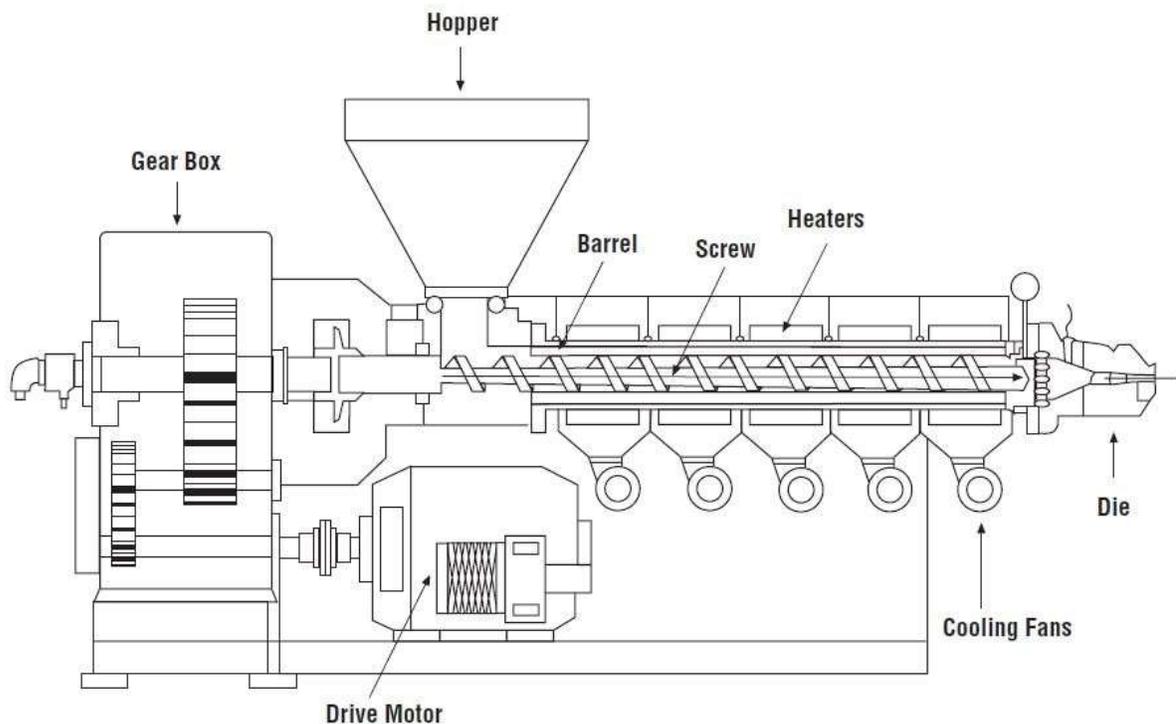


Figure 1.10: A typical single screw extruder [106]

Although the single screw extruder is popular, the twin-screw extruder is more suitable for producing a more homogeneity/fiber dispersion during mixing and the presence of counter-rotating or co-rotating screws for proper compounding of the mixtures [105].

Twin screw extruders have oriented screws in the same horizontal plane that can move either counter-rotating or co-rotating. A twin-screw extruder has three major zones comprising of the conveying, melting, and metering zones [107]. Samples fed into the hopper move into the conveying zone where compounding and compacting occurs, then into the melting zone and a second phase of added mixing in the metering zone before extrusion through the die. Some extruders also have more than two screws (quad screws) but are not popularly used [57].

### **1.2.2 RHPC Performance**

Several factors affect the behavior of composites prior to and during production ranging from aspect ratio, interaction between filler and plastic matrix, type of compatibilizer used, fiber size and orientation. After production, environmental (moisture effects, radiation, climate conditions), biological (microorganisms and insects), thermal and chemical factors inevitably become a thing of concern and must be factored into consideration whilst processing is ongoing to promote a long shelf life for RHPC [103, 108, 109].

### **1.2.3 Effect of Compatibilizers in RHPC**

For further improvement and reactivity of the interface between a polymer and fiber matrix homogenous composite, the use of different compatibilizers have been researched with each having its advantages and disadvantages. These compatibilizers and coupling agents help increase the extent of crosslinking expected between the hydrophobic polymer and the hydrophilic fiber [110]. Coupling agents can react with both the natural fiber and polyolefin surface to create a better chemical bridge at the interface whilst reducing agglomerates and enhancing filler dispersion. They improve surface chemical bonds and interactions by enhancing rigidity, dimensional stability, chemical resistance and surface hardness. The popularly used methods for improving composite matrices include silane coupling agents and maleic anhydride grafted polyolefins [60, 110].

Chemical coupling agents of maleated polyolefins are synthesized by grafting the monomeric anhydrides of polar maleic acid unto the hydrophobic polyolefin surface. The

hydroxyl group reaction in the amorphous region with maleic anhydride causes a coating of the fibers with long chain polymers leading to an interlocking interface [111]. Examples of coupling agents are maleated grafted polymers of polyolefins: maleated polypropylene (MAPP) (Figure 1.11) and maleated polyethylene (MAPE)(Figure 1.12).

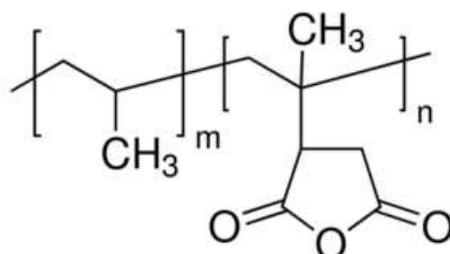


Figure 1.11: Maleated anhydride polypropylene structure (MAPP)

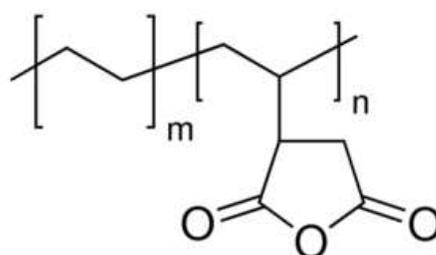


Figure 1.12: Maleated anhydride polyethylene structure (MAPE) [112]

Studies have shown the effective influence of maleated polyolefins in composites for tensile strength and mechanical properties improvement [refs]. In a study by Yang *et al.* [102], to determine the effect of MAPP and MAPE in rice hulls polyethylene composites produced via injection molding. Addition of MAPE showed a better performance due to its compatibility with PE. This study confirms that maleated polyolefins used will be more responsive to corresponding polyolefins. Another study used MAPE in proportions of 0, 3 and 6 wt.%, and improved physical and mechanical properties were obtained with the 6 wt.% of the MAPE [113]. A lower percentage of MAPP (3 wt.%) was confirmed to be more efficient with improved interfacial bonding and tensile properties in another study using 1, 3 and 5 wt.% in rRH-PP composites [114]. An optimum amount of 1% MAPP in a study was also concluded to be more effective in composite performance [115] but a 5 wt.% of MAPP was effective in another study using a 40% RH loading for PP composites [88]. These studies

above show that it is quite unclear what the proper amount of maleated copolymer should be because variations are seen in fiber loading and processing types.

Silane coupling agents promote the mechanical properties of RHPC by creating a siloxane link between the fiber and polymer matrix. One end of the silanol reacts with the cellulose hydroxyl group and the other, with the polyolefin functional group by condensation reaction forming a continuous hydrocarbon chain along the RHPC [97]. A silane coupling agent ( $\gamma$ -aminopropyltriethoxysilane (KH-550) ) is seen in study of RH-HDPE composites using a twin-screw extruder and results showed crosslinking with the hydroxyl group in the fiber with improved flexural strength and water resistance [116]. A similar trend was observed in the characterization of white RH-PP/natural rubber composites using 3-aminopropyl triethoxysilane [117].

Modification of natural fibers is also a way to improve compatibility prior to compounding of composites. The cell wall of rice hulls has hydroxyl groups which permit the modification of dimensional stability with the polyolefins. This modification could either be physical or chemical [95].

Physical methods include stretching, calendaring, heat treatment and can require treatment by laser, gamma ray or plasma to produce hybrid yarns without changing the chemical properties of the fiber [118]. They are cleaner and simpler than chemical methods but also depend on different duration. Surface modification of the natural fibers occur with plasma treatment with controlled pressure and flow. Ultraviolet laser treatments make the fiber surface more polar to improve proper wetting and improved strength whilst heat treatment increases the surface area with better interlocking and defibrillation of fibers [119, 120]. The removal of hemicelluloses by the steam explosion method also improves adhesion with polyolefins. Fibers are exposed to high pressure steam over a period leading to subsequent decomposition of hemicelluloses.

Chemical treatments, depending on fiber and matrix kind, could either be benzoylation, acetylation, mercerization (alkali treatment) [25]. Benzoylation has shown to decrease the hydrophilicity of rice hulls whilst improving tensile strength and stiffness [121]. Reactive surface of the fibers is exposed with the removal of lignin, waxes and oils and the hydroxyl groups on the surface is replaced with benzoyl groups. Acetylation introduces an acetyl group into the fibers causing them to be more hydrophobic [122]. An esterification

reaction occurs between the hydroxyl and carboxylic/anhydride groups of the fibers resulting in smooth fiber surface due to the removal of wax and cuticle on the fiber surface. Research has shown that more acetyl content reduced moisture absorption [25, 121, 122].

Mercerization, which is one of the simplest and effective approaches, removes most of the oils, lignin, and waxes from the fiber surface cell wall with mercerized fibers showing improved surface roughness with adhesion characteristics. This method requires the use of sodium hydroxide for increased fiber fragmentation by creating amorphous regions which are filled with water molecules. The alkali sensitive hydroxyl groups get replaced by the (-O-Na) group decreasing the hydrophilicity of the fiber surface and increasing its resistance to moisture [25, 95].

Isocyanates have also shown to react with the hydroxyl groups on the fiber surface to create a urethane (-N=C=O) linkage. This linkage increases moisture resistance in the fibers due to the strong covalent bonds [95]. Amidst all, a moderate amount of treatment of fibers is expected because an increase will cause the weakening of fibers leading to loss in strength and stability.

#### **1.2.4 Effect of Aspect Ratio, Rice Hulls Loading and Particle Size**

Fiber aspect ratio plays an important role in composite strength. RH have a wide range of aspect ratios but with a small amount of fiber ratio comes a low composite strength and vice versa. A fiber is expected to have a length bigger or equal to the vertical length  $L_c$  to be able to carry the maximum applied load during tensile testing before they break, and this varies with different fibers [123]. This critical length is responsible for the stress transfer between the fibers and the polyolefin matrix. Whilst fiber length enhances tensile break properties, an overly long fiber will cause entanglements and cause poor fiber dispersion in the composite [124].

Different RH loadings from 5 to 70 wt.% have been studied in thermoplastic composites, and in most cases, a higher loading accounts for increased tensile strength [88, 98, 108, 114, 115]. On the contrary, a few researchers have stated otherwise [101, 125] These negative responses could be due to the agglomerates that form during processing from the non-uniform dispersion of the fibers [126]. Since tensile and flexural modulus is highly dependent on the fiber, an optimum amount should be used in composite preparation.

Ground or raw RH are mostly used during composite preparation which could come in a range of sizes. Smaller sizes with their high surface area have shown to result in better dispersion, mechanical properties and thermal stability compared to larger sizes [127, 128], but some studies state the contrary [129]. Rahman et al. studied the effect of rice hulls filler sizes below 500  $\mu\text{m}$  in HDPE and claimed that the larger sizes influenced the best impact strength and dispersed uniformly in the matrix [101]. Similar results were observed in another study using rice hulls sizes between 60 and 100  $\mu\text{m}$  [130] and larger fiber sizes had higher energy at break.

### **1.2.5 Mechanical Properties**

Mechanical properties of the RHPC depends on filler/matrix type and adhesion, filler concentration, fiber dispersion and orientation. These properties studied are tensile strength and modulus, energy at break, flexural strength and modulus and have been reported to increase with high fiber loadings with a few contradicting results. The interfacial compatibility of the fiber and polyolefin surface also plays a major role in enhancing the mechanical properties of a composite [95]. To improve this, different fiber/matrix treatments and modifications have been studied. Fiber dispersion also promotes a better interfacial bonding reducing voids and causing the complete immersion of the fiber in the matrix. Dispersion can be affected by processing temperatures, pressure and presence of additives. A higher mechanical property is also attained with aligned fibers with the best results attained when the fiber is parallelly aligned to the direction of the load [131].

### **1.2.6 Thermal Properties**

Processing temperatures for RHPC depends on the polymer matrix used but studies show that RHPC can be processible at temperatures exceeding 200  $^{\circ}\text{C}$  when compared to wood plastic composites that typically degrade within that temperature [132]. Under high temperature exposure for a long time, RHPC undergoes thermal degradation and expansion leading to its inefficiency and non-applicability in external conditions. Thermal degradation of rice hulls which breaks down the hemicellulose and lignin layers in the fiber, is an important issue during processing leading to adverse effects on the physical and chemical structure of RHPC [129]. To understand the issues associated with thermal degradation,

characterization techniques of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), have been used to study the reaction of RHPC under high temperatures. Properties of melting, crystallization, glass transition, softening and degradation temperatures are all determined for the composite.

### **1.2.7 Rheology**

This is the scientific study of flow and deformation of polymer under applied force and stress. The effect of reprocessing polyolefins contributes to the melt flow viscosity of corresponding composites causing an increase or decrease in molecular weight. Composites which act like non-Newtonian fluids, also exhibit viscous and elastic responses and different parameters are needed to understand how they react. Amongst these parameters are creep, phase angle, dynamic moduli, and shear viscosity [133]. Rheology also accounts for non-Newtonian fluids and determining the relationship between the shear strain and shear stress the polymer matrix undergoes with corresponding temperatures. These experiments are done in “rheometers” under varying experimental modes like frequency sweep, creep recovery, steady shear rate, isothermal and temperature ramps [134]. Two main types of rheological setups used are capillary and dynamic or rotational rheology.

#### **1.2.7.1 Capillary Rheology**

A capillary rheometer is mostly of a vertical setup consisting of a barrel, into which polymer and composite samples are fed into, at thermal equilibrium, a plunger under applied force is used to push out the melt through a die at the end of the barrel (Figure 1.13). The plunger is pushed by a load cell at varying speeds. The experiment occurs at higher frequency or shear rates when compared to dynamic rheology. Advantages to using a capillary rheometer include, flow rate and geometry and shear rates are like extrusion processes, barrel is easier to fill with samples and extrudates can be studied for melt fractures. The main disadvantages are that the shear rate varies with radial position within the barrel and there are several corrections used to get the accurate shear rate and viscosity values [135].

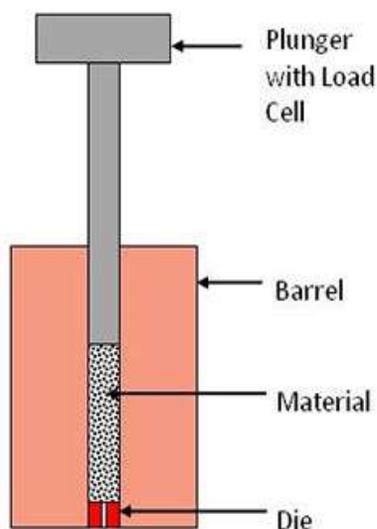


Figure 1.13: Capillary rheology setup [136]

The extracted data of pressure force and velocity is used to determine the apparent shear rate and stress, apparent and true viscosity of the samples. The data is also corrected for pressure drop using the Bagley correction, and the Weissenberg-Rabinowitsch for apparent shear rate to true shear rate corrections [135].

It is important to know that die geometries have effects on melt flow results. A larger die length helps reduce extrudate swell as the melt relaxes and restores its continuity inside the die. Also, a longer die length yields a pressure increase in the die entrance causing a flow shift at a steady flow rate. A smaller die diameter is also preferred to accommodate smaller sized samples. Two types of fracture occurs as a polymer is being extruded from a die: a stick-slip fracture due to instability from discontinuity in the flow curve yielding rough/smooth surface extrudates, and gross melt fracture which occurs at high shear rates in an irregular manner causing distortions in an irregular manner [134, 135].

### 1.2.7.2 Dynamic Rheology

Dynamic oscillatory rheology is used in the characterization of a polymer matrix to determine the relationship between the fiber and polyolefin matrix and its dependence on frequency indicated via the storage modulus. This experiment is mostly used for lower shear rates or frequency. Different geometries are available for this experiment from cone-plate, concentric cylinders to plate-plate. The plate-plate geometry which is mostly used for

composite flow characterization is setup as seen in Figure 1.14. the sample is placed between two parallel plates with the bottom plate in stationary position and the top plate moving at a constant rate parallel to the lower plate at a defined shear stress and shear rate. The sinusoidal stress  $\tau(t)$  applied to the sample at fixed angular frequency  $\omega$ , yields a sinusoidal deformation shift. The behavior of the polymer melt can further be described by the tangent of the phase angle ( $\tan\delta$ ). Other results gotten from the data are the storage modulus  $G'$ , loss modulus  $G''$  and complex viscosity ( $\eta^*$ ) [135, 138].



Figure 1.14: Parallel plate rheology setup [139]

A minimum constant gap between plates is used to ensure uniform distribution of temperature and constant shear rate throughout sample. A major disadvantage is the presence of slip with increasing shear rate, distortion with the shape of the free surface edge of the sample [135].

### 1.2.8 Moisture Effects

Moisture or water absorption in composites increases when there is high fiber loading due to the presence of increased hydroxyl groups in cellulosic wall that react with water. This absorption is governed by different factors from capillary transport in interface gaps resulting from poor wetting, diffusion of water into micro gaps to transport of micro-cracks due to swelling. [139]. The presence of moisture in RHPC can also lead to biological attacks from microbes. Water absorption in RHPC has also been observed to be the lowest when compared

to particle boards and wood plastic composites. Diffusivity coefficients of the composites can also be obtained depending on different molecular diffusion behaviors and models [139, 140].

### **1.3 Research Objectives**

The overall objective of this study involves the composite characterization of mechanically recycled polyolefins isotactic polypropylene (iPP) and high-density polyethylene (HDPE) reinforced with rice hull fibers of different sizes which will be compared to virgin polyolefin and wood plastic composites. The influence of rice hulls particle size will be ascertained.

In detail, the physical properties of water absorption and thickness change will be determined. Surface chemistry, morphological change of the recycled polyolefins and corresponding composites will be obtained using Fourier Transform Infrared Spectroscopy (FTIR), the flow behavior of the rice hulls composites will be analyzed using rheological experiments of capillary and dynamic rheology. Thermal analysis using DSC, TMA and TGA of the composites will be evaluated. Tensile testing will be conducted to determine the mechanical properties with respect to particle size.

Chapter 2 lists and details out the materials used in this research, the experimental procedures used for the manufacturing of composites, preparation of samples, methods of mechanical, thermal, and rheological or flow characterization for composites.

Chapter 3 presents the discussion and investigation of acquired data and results from the methods in chapter 2. Statistical analysis on analyzed results were also done to determine the correlation and significant relationship between the effect of rice hulls particle size on the mechanical, water absorption and thermal properties, respectively.

Chapter 4 describes the summarized findings of this research, a few limitations encountered and recommendations for future research work.

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## Chapter 2: Materials and Methodology

### 2.1 Materials

This chapter which discusses and investigates the materials and testing procedures used for recycled rice hulls polyolefin composites manufacturing, also describes the statistical relationships between the effect of rice hulls sizes on composite properties. Detailed steps of composite manufacturing and testing are also discussed with correlating ASTM standards. Materials used were commercial BREWCRAFT Briess rice hulls, purchased from Tristate at Tristate Outfitters, Moscow, ID, USA, milled into different sizes, recycled/waste HDPE milk jugs, and PP (bottle caps, yoghurt containers) obtained from the Moscow Recycling Center, ID, USA. Commercially sourced maleated polymers of MAPE (Polybond 3029), and Honeywell MAPP AC950, were used as coupling agents.

### 2.2 Methodology

Prior to compounding, purchased whole rice hulls were milled using a Thomas Wiley mill through mesh screens into particle sizes of  $<1$  mm and  $<0.5$  mm as seen in Figure 2.1. Milled rice hulls were subjected to drying in an oven at  $104$  °C for 24 h to reduce moisture content and physically characterized for aspect ratios and density.



Figure 2.1: Screened rice hulls of (a)  $<1$  mm and (b)  $<0.5$  mm Particle sizes

Since the lignin and hemicelluloses in RH are lower than that of wood; and a similar cellulose content, higher processing temperatures can be used for RHPC than wood plastic

composites. Due to previously reported limited effect of finely grounded and coarser fibers on composite properties, the particle sizes  $<1$  mm and  $<0.5$  mm, were chosen for optimum composite properties results [1-4].

The recycled/waste polyolefins were washed, rinsed with water, and dried for 24 h. A plastic granulator (Sterling BP608) was used to shred the dried recycled polyolefins to  $<6$  mm sizes as shown in Figure 2.2. The screened RH and milled polyolefins were further compounded in batches before extrusion.



Figure 2.2: Granulated recycled polyolefins (a) HDPE and (b) PP

T-test for mean of paired two samples statistical analysis was performed on results using Excel to determine the relationship and effect of fiber particle size on composites. A level of significance of 0.05 was defined to determine statistical differences between particle sizes and strength properties.

### 2.2.1 Composites Manufacturing

Oven dried rice hulls (50 wt%) were mixed with rHDPE or rPP (48 wt%) and corresponding maleated polyolefins; MAPE or MAPP (2 wt%), in 500 g batches. The individual batches were fed at 0.5 kg/h and compounded/extruded into ribbons via a Leistritz ZSE18 co-rotating twin screw extruder (LD ratio 40, 200 rpm) [5]. Feed from hopper into screws had with zone temperatures of 160 °C for rHDPE and 200 °C for rPP composites. In these zones, melting, mixing, and conveying of composite mixtures are achieved [6]. The extruded ribbons were cut into 150 mm lengths, slowly hot pressed using a PHI 30 ton press

at the individual polyolefin melting temperatures; 140 °C for rHDPE and 160 °C for rPP, to further create flat surfaced ribbons of 3.2 mm thickness for sample preparation.

## **2.2.2 Composites Characterization**

Performance characterization on the recycled polyolefins and composites to determine physical, thermal, mechanical, rheological properties, tensile strength, and conformation.

### **2.2.2.1 Density, Aspect ratio and Particle Size Measurement**

Aspect ratios via measured length and width for 200 particles each of the milled rice hulls (<1 mm and <0.5 mm), were determined using a 40x magnification on an Olympus BX51 optical microscope. Images were analyzed using the Olympus Micro Suite software (version 3.2). Density which shows the mass per unit volume of rice hull particle sizes and composites were determined using an ultra-pycnometer.

### **2.2.2.2 Melt Flow Rate (MFR) and Differential Scanning Calorimetry (DSC)**

MFR is a quick technique used to determine molecular weight and the flow properties of a material under pressure. The basic principle behind the MFR procedure requires the heating of a material which will be forced out of a cylinder through a capillary die with a piston loaded with weights up to 21.6 kg [7,8]. Capillary dies used in this process are mostly of a fixed diameter. MFR of composite samples (4 g) was measured in triplicate using a CEAST Modular Melt Flow Indexer at 190 °C according to ASTM D1238-01e1 [9] through a standard die (8 mm × 2.0955 mm Ø). A load of 2.16 kg was used for recycled polyolefins and 15 kg for composites. Chopped samples were fed into the mini barrel, and plunger dropped in, preheated and load was applied onto plunger. Melted material purges out until the maximum height coded by the digital piston is reached. Average melt flow rate and viscosity were obtained from the maximum of 40 measurements recorded from each test.

DSC is used to ascertain a materials' melting and crystalline temperatures, heat of enthalpy, glass transition temperature ( $T_g$ ) and percent crystallinity.

DSC analysis was determined using polyolefin and composite duplicate samples (4-6 mg) in TA sealed aluminum pans. A Q200 DSC TA Instruments with refrigerated cooling and purged nitrogen (20 mL/min) was used with scanning performed within -50 °C to 220 °C.

Samples had 3 cycle scans as follows: equilibration at 40 °C (3 min) and then ramped to 180 °C (rHDPE) or 220 °C (rPP) (cycle 1) at 10 °C/min (held for 3 min), cooled to -50 °C (cycle 2) at -10 °C /min and reheated to corresponding temperatures (cycle 3). Percent crystallinity was calculated using the equation below.

$$X_c = \frac{\Delta H_m}{\Delta H_0 \times W_f} \times 100\%$$

$\Delta H_m$  is the calculated melting enthalpy from the area under peak,  $W_f$  is the weight fraction of polyolefin in composites (50%) and  $\Delta H_0$  is the theoretical enthalpy of fusion for polypropylene (207.1 J/g) and polyethylene (293 J/g).

### 2.2.2.3 Thermogravimetric Analysis (TGA)

TGA is used to study the thermal degradation, stability of a material and measuring the onset temperature at which this begins. A derivative thermogravimetric (DTG) curve enables the detailed degradation stages of the material. The TGA for the recycled polyolefins and corresponding composites were performed on 4-5 mg samples using a Perkin-Elmer TGA-7 instrument under nitrogen (30 mL/min) at 20 °C/min from 30 °C to 900 °C.

### 2.2.2.4 Thermomechanical Analysis (TMA)

Since many materials will deform under stress with temperature, TMA is used to determine a material softening temperature [10]. Softening temperature ( $T_s$ ) and melting temperature ( $T_m$ ) of polyolefin and composite samples (2 mm ( $l$ )  $\times$  1.5 mm ( $w$ )  $\times$  1 mm ( $h$ )) were determined using a PerkinElmer TMA-7 instrument (Shelton, CT, USA) under nitrogen (20 mL/min) with refrigerated cooling, an applied force of 10 mN with a penetration probe mode from -30 to 180 °C at a rate of 5 °C/min. Data was analyzed using the Pyris v13.3 software.

### 2.2.2.5 Tensile tests

Tensile tests were performed using an Instron 5500R-1132 universal testing machine (5 kN load cell and cross head speed of 5 mm/min) coupled to an extensometer (Epsilon model 3542) on composite and polyolefin-machined dog bone samples as seen in figure 2.3 (nine replicates) according to the ASTM D638 [11] standard, and at room temperature.



Figure 2.3: Extruded cut dog-bone samples

Data of thickness, width, tensile strength, and tensile modulus were collected and analyzed using Bluehill v3 Instron software.

#### 2.2.2.6 Dynamic Mechanical Analysis (DMA)

DMA has been an important tool used to determine the viscoelastic property and bonding characteristics of a composite with respect to its storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan \delta$  as it resists deformation under applied strain and stress. The storage modulus is related to stiffness, energy stored and shape recovery during a heating cycle while the loss modulus shows how much energy is lost through molecular motions and instability.  $\tan \delta$  which is the loss factor and a ratio of the  $E''$  to  $E'$ , plays a major role in the interfacial bonding of composites. It is used to measure the damping capability and amount of energy dissipated or absorbed by a material [12].

DMA tests were performed using a 15mm span, 3-point bending mode on a Perkin-Elmer DMA-7 instrument for replicate rectangular samples ( $2.5 \times 4.5 \times 15 \text{ mm}^3$ ) at a frequency of 1Hz, from  $-50 \text{ }^\circ\text{C}$  to  $140 \text{ }^\circ\text{C}$  at  $3 \text{ }^\circ\text{C}/\text{min}$  with refrigerated cooling ( $20\text{mL}/\text{min}$ ). Data was analyzed using the Pyris v13.3 software.

#### 2.2.2.7 Dynamic Rotational Rheology

Due to the exhibition of viscoelastic properties by polymer melts, several parameters are needed to understand their flow characteristics. In other to achieve that, shear viscosity, dynamic moduli amongst others will help to describe the materials rheological properties. Several experimental modes like frequency sweep, creep recovery and steady shear can be used [13].

Frequency sweep which is widely used especially with a parallel plate geometry, requires the oscillatory motion of the upper plate with recorded displacement or stress values. The strain values could either be within the linear viscoelastic region or non-viscoelastic region and can be used to determine the  $G'$ ,  $G''$  and  $\eta^*$ . Dynamic rheological measurements ( $\tan \delta$ , viscous modulus ( $G''$ ), elastic modulus ( $G'$ ) and complex viscosity ( $\eta^*$ )) on polyolefin and composite samples (2.5 mm ( $h$ )  $\times$  25 mm  $\varnothing$ ), (Figure 2.4) were acquired on a Bohlin CVO 100 N rheometer with 25 mm  $\varnothing$  serrated parallel plates.



Figure 2.4: Extruded cut circular discs

A plate gap of 2000  $\mu\text{m}$ , 0.5% strain, and frequency range of 0.01 Hz to 100 Hz, were used at 190  $^{\circ}\text{C}$  to minimize further degradation of recycled polyolefin and composite samples. Samples were loaded on the bottom plate of the rheometer, top plate was closed onto the sample to melt and keep gap at 2000  $\mu\text{m}$ , excess material was removed from the sides and temperature is equilibrated before the run begins.

#### 2.2.2.8 Capillary Rheology

Shear viscosity was determined using a INSTRON Model 3213 capillary rheometer at 190  $^{\circ}\text{C}$  connected to a Instron 5500R-1137 universal testing machine (5 kN load cell) and operating at cross head speeds of 0.6, 2, 6, 20, 60, and 100 mm/min. The barrel diameter was 9.5504 mm and two capillary dies were used (lengths of 14 mm and 27 mm with diameter of 1.4 mm  $\varnothing$ ) to determine the effect of shear rate on the viscosity of polyolefin and composite samples. Bagley correction was also used since the L/D ratio was  $<200$ , to correct the influence of pressure drop on measurements. Loaded samples (7 g) were thermally equilibrated for approximately 10 min with a heating temperature variance of  $\pm 0.2$   $^{\circ}\text{C}$ . Each sample was run in triplicate and data was analyzed using Bluehill v3 Instron software in

conformation to the ASTM D3835-02 [14] standard. Extrudate swell diameters were measured using a digital caliper.

According to the ASTM standard used for analysis for non-Newtonian fluids, the Bagley correction which is used for pressure drop calculations ensures the calculation of the true stress applied on the sample in the barrel. This is achieved with two dies of same diameter and different length. A plot of pressure or force versus L/D ratio for the two dies and the equation below is used for the true shear stress ( $\tau$ ).

$$\tau = \frac{(P - P_c)D}{4L} = \frac{(F - F_c)D}{4LA_B}$$

Where P is the melt pressure, F is the plunger force,  $P_c$  and  $F_c$  are the pressure and force intercepts from plot respectively, D is the die diameter, L is the die length and  $A_B$  is the cross-sectional area of the barrel.

Corrections for true shear rate ( $\gamma$ ) from the apparent shear rate ( $\gamma_a$ ) was attained using the Weissenberg Rabinowitsch parameters and equation below.

$$\gamma = \frac{(3n + 1)}{4n} \gamma_a$$

The tangent slope of the logarithmic true shear stress vs logarithmic apparent shear rate curve plot is represented by  $n$ . the apparent shear rate is calculated using the equation below.

$$\gamma_a = \frac{4Q}{\pi r^3}$$

The radius of the barrel is signified by  $r$  and Q represents the volumetric flow rate ( $m^3$ ) of the sample, calculated from the product of the crosshead speed and cross-sectional area of the barrel. To determine the apparent viscosity ( $\eta_a$ ) and true viscosity ( $\eta$ ), the equations were used, respectively.

$$\eta_a = \frac{P\pi r^3}{8LQ}$$

$$\eta = \frac{\text{True shear stress } (\tau)}{\text{True shear rate } (\gamma)}$$

### 2.2.2.9 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR is used to observe the surface chemistry changes of recycled composites with the addition of varying rice hulls particle sizes, FTIR Spectra (duplicate) of polyolefin and composite samples were obtained on a Thermo-Scientific Nicolet-iS5 with an attenuated total reflectance (ATR) accessory (iD5, ZnSe). An average of 64 scans were obtained in the range of 400-4000  $\text{cm}^{-1}$ . Spectra were averaged and baseline corrected using the OMNIC v9.0 software.

### 2.2.2.10 Water Soak

Moisture absorption of circular polyolefin and composites samples (2.5 mm ( $h$ ) by 25 mm  $\emptyset$ , 5 replicates) were determined after continuous soaking in water for a maximum of 100 days at 22 °C. Diffusivity was calculated using equation below:

$$D_f = \pi \left( \frac{h}{4M_f} \right)^2 \left( \frac{M}{\sqrt{t}} \right)^2$$

where  $M_f$  is the maximum moisture content at the end of the test,  $h$  is the sample thickness in meters,  $M/\sqrt{t}$  is the initial slope from the plot  $MC$  vs  $\sqrt{t}$ . Sample weights were recorded before and after soak daily to determine weight gained. The process continued until there was an acceptable saturation limit.

## 2.3 References

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## Chapter 3: Results and Discussion

This chapter discusses the experimental results obtained in Chapter 2 with focus on the physical, surface chemistry, mechanical, thermal, and rheological properties.

### 3.1 RH Properties

RH were milled into two particle size classes (<0.5 mm and <1 mm) and were analyzed for size by optical microscopy (Figure 3.1). Optical micrographs show a significantly mixed morphology of round-rectangular shaped fibers when compared to wood. The micrographs also show a range of large and fine particles. The respective average lengths of the <1 mm and <0.5 mm screened particles were  $266 \pm 332 \mu\text{m}$  and  $174 \pm 155 \mu\text{m}$ . The widths of the <1 mm and <0.5 mm screened particles were  $152 \pm 170 \mu\text{m}$  and  $109 \pm 89 \mu\text{m}$ , respectively. The calculated aspect ratios for the <1 mm and <0.5 mm screened particles were 1.8 and 1.6, respectively. These aspect ratios are slightly higher than the reported average values of 1.2 by Raghu et al. [1] and promote better properties of the fiber as a filler.

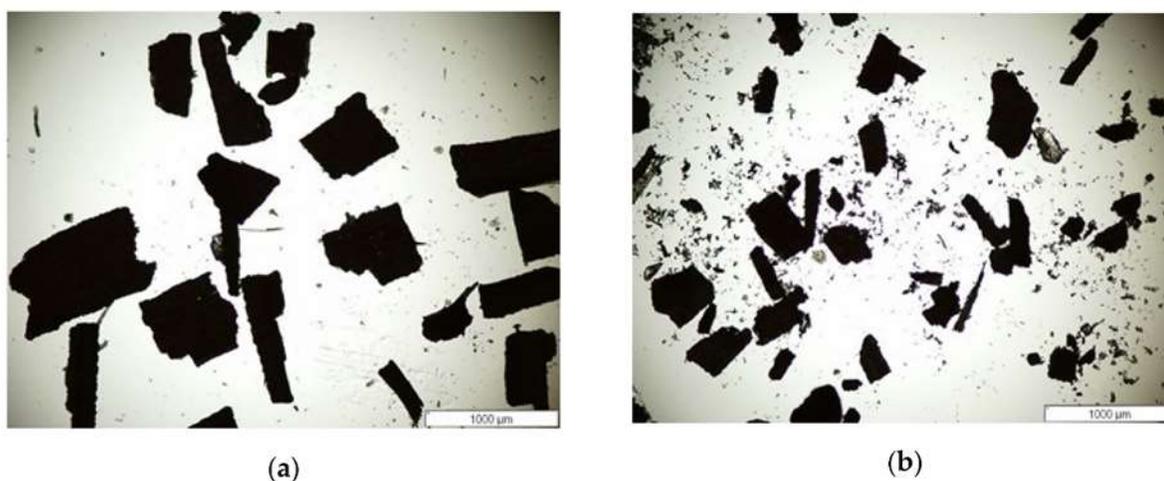


Figure 3.1: Optical micrographs of screened (a) <1 mm and (b) <0.5 mm rice hull particles (40 $\times$ , scale bar 1000  $\mu\text{m}$ ).

The measured density for the <1 mm and <0.5 mm rice hull particle sizes were 1508  $\text{kg}/\text{m}^3$  and 1535  $\text{kg}/\text{m}^3$ , respectively (Table 3.1). Density for <1 mm and <0.5 mm rHDPE composites were 1157  $\text{kg}/\text{m}^3$  and 1110  $\text{kg}/\text{m}^3$ , respectively, as compared to 1123  $\text{kg}/\text{m}^3$  and 1109  $\text{kg}/\text{m}^3$  for the respective rPP composites. The presence of rice-hulls reinforcing fibers

increased the density of the composite as compared to the raw polyolefins. The lower density of the <0.5 mm composites were perhaps a result of differences in packing during extrusion causing some interstitial spaces between fiber and polyolefins [2]. The detailed density results can be seen in Table 3.1. With the addition of rice hull fibers, statistically significant differences were observed in the density of the composites with p values lower than 0.05 and varying sizes of the rice hulls.

Table 3.1: Density of the recycled polyolefins and rice hull composites

Polyolefin	Composite particles	Density kg/m <sup>3</sup>
rHDPE	-	978 (0.002) <sup>c</sup>
	<1 mm	1157.4 (3.1) <sup>a</sup>
	<0.5 mm	1109.9 (1.1) <sup>b</sup>
rPP	-	912 (0.001) <sup>b</sup>
	<1 mm	1122.6 (5.9) <sup>c</sup>
	<0.5 mm	1109.3 (1.7) <sup>a</sup>

Note: Standard deviations are in parentheses. Each polyolefins' sample with different superscript letters (<sup>a, b, c</sup>) are statistically different ( $p < 0.05$ ) via a one-tailed *t*-test.

### 3.2 Composite Mechanical Properties

Tensile properties (strength, modulus, and energy at break (EAB)) for polyolefins and RH composites are given in Table 3.2. Tensile strength and modulus properties of rHDPE were significantly higher than the values recorded by Wang et al. [3] for HDPE ( $21.1 \pm 0.4$  MPa,  $0.6 \pm 0.0$  GPa). The 23.8% and 83% increase in tensile strength and modulus of the rHDPE were perhaps due to different plastic grades and processing conditions, resulting in different properties. Tensile strength of the <1 mm and <0.5 mm rHDPE composites were respectively  $25.1 \pm 2.9$  and  $26.3 \pm 2.0$  MPa. The tensile moduli for the composites were  $2.7 \pm 0.1$  GPa (<1 mm) and  $3.1 \pm 0.5$  (<0.5 mm) GPa. Chen et al. [4] obtained a lower strength value of 10.9 MPa and a modulus value of 1.446 GPa for 50 wt% RH fiber with a mix of rHDPE and recycled polyethylene terephthalate (rPET) matrix. The tensile strength for the rPP composites were,  $14.5 \pm 0.3$  MPa (<1 mm) and  $16.7 \pm 0.9$  (<0.5 mm) MPa. The tensile moduli for the rPP composites were  $2.9 \pm 0.5$  GPa (<1 mm) and  $3.5 \pm 0.2$  GPa (<0.5 mm).

The tensile strength for the rPP/rice hulls composites were lower than the rHDPE/rice hull composites, possibly due to thermal degradation after extrusion [5]. A similar trend is observed in the tensile modulus (2.5 – 3.0 GPa) and tensile strength (10 MPa – 15 MPa) for 50 wt% RH filled PP composites [6]. The tensile modulus and tensile strength for the rPP composites were also higher than the recorded values Razavi-Nouri et al [7] (1.1GPa) for chopped RH/PP composites, probably due to the high surface area of the RH fibers and better matrix interaction.

Table 3.2: Tensile properties of the polyolefins and rice hull composites.

Polyolefin	Composite particles	Strength (MPa)	Modulus (GPa)	EAB (J)
rHDPE	-	26.0 (0.5) <sup>a</sup>	1.1 (0.1) <sup>b</sup>	3.64 (0.4) <sup>c</sup>
	<1 mm	25.1 (2.9) <sup>a</sup>	2.7 (0.1) <sup>a</sup>	0.65 (0.22) <sup>a</sup>
	<0.5 mm	26.3 (2.0) <sup>a</sup>	3.1 (0.5) <sup>a</sup>	0.64 (0.16) <sup>b</sup>
rPP	-	14.3 (1.9) <sup>b</sup>	1.7 (0.2) <sup>b</sup>	0.16 (0.06) <sup>c</sup>
	<1 mm	14.5 (0.3) <sup>a</sup>	2.9 (0.5) <sup>a</sup>	0.12 (0.02) <sup>b</sup>
	<0.5 mm	16.7 (0.5) <sup>a</sup>	3.5 (0.2) <sup>a</sup>	0.19 (0.05) <sup>a</sup>

Note: Standard deviations are in parentheses. Each polyolefins' sample with different superscript letters (<sup>a, b, c</sup>) are statistically different ( $p < 0.05$ ) via a one-tailed *t*-test.

The EAB values for the rHDPE composites (0.64 J and 0.65 J) decreased significantly by 82% when compared to the rHDPE (3.64 J), showing a lower toughness (Table 3.2). The lower EAB for rPP and its composites could be attributed to an increase in brittleness as compared to rHDPE and composites. The <0.5 mm rPP composite exhibited a higher EAB showing a stronger matrix as compared to the <1 mm composite due to improved interfacial bonding. Statistically significant differences were observed with an increase in strength and a decrease in energy at break (EAB) for polyolefin composites at a significant level of 0.05. There were no statistical differences in moduli between the composites made with <0.5 mm and <1 mm fiber size for each polyolefin type.

In comparison to wood plastic composites (WPC), alike to lower tensile properties have been observed for wood/HDPE composites with significant particle size effect [8-10]. Yi studied wood/HDPE composites; 50 to 70% fiber content in different particle sizes with MAPE as a coupling agent and observed a tensile modulus and tensile strength of 4.6 GPa and

30.2 MPa respectively with no particle size effect [11]. Equal weight composition of recycled and virgin HDPE wood composites was also studied by Adhikary et al, and tensile properties were compared. rHDPE/wood composites showed higher tensile properties (Modulus: 1.7, Strength:12.3 MPa) when compared to the virgin composites and this was attributed to stiffer polymer grades in the recycled plastic [12]. These values in comparison to rHDPE/RH composites are evidently low possibly due to the fiber properties and orientation [13]. Several wood/PP composites of varying compositions and fiber size have also been studied with similar or higher tensile properties to the RH/rPP composites depending on the fiber specie, and type of polyolefin grade used [14 -17].

DMA analysis which was used to determine the load bearing tolerance of the corresponding recycled polyolefins and composites showed an increase of storage modulus with the addition of the rice hull fibers and reduced particle size [18]. Values of  $E'$  at 30 °C are seen in Table 3.3 and Figure 3.2 shows thermograms of the recycled polyolefins, their corresponding composites and their response to  $E'$  with increase in temperature. A higher  $E'$  for the <0.5 mm composites as seen in figure 3.2, was observed due to the probable large surface area of the rice hulls fiber, better interaction in the matrix which resulted in lower mobility during bending. The presence of the maleated coupling agents (MAPE and MAPP), and increase in stiffness of the matrix caused by the rice hull fibers also contributed to this  $E'$  increase [19]. rHDPE composites showed better  $E'$  properties when compared to rPP composites due to a better reinforcing effect by the fibers and dense crosslinked recycled polyolefin structure which created a higher degree of stress transfer [20].

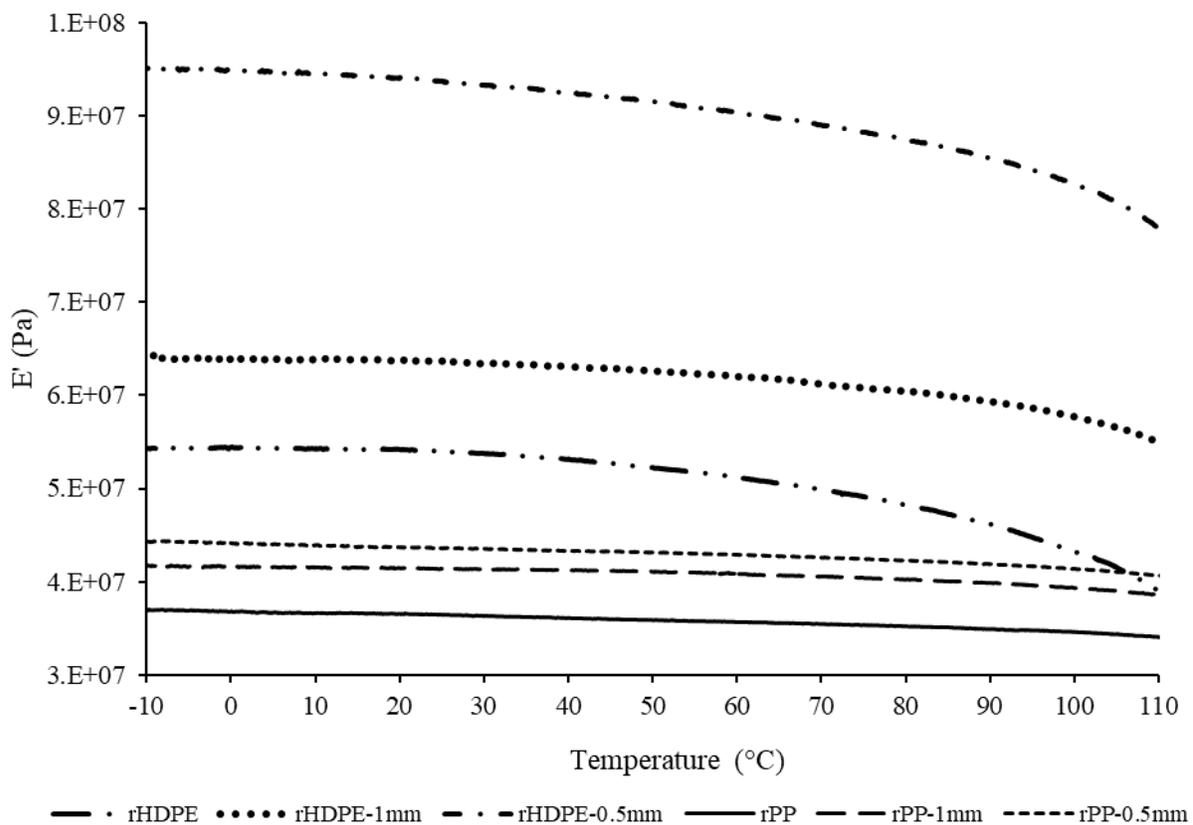


Figure 3.2: DMA plots for recycled polyolefins and composites

Table 3.3: Storage modulus of polyolefin and composites at 30  $^{\circ}\text{C}$

Polyolefin	Composite particles	$E'$ (Pa) at 30 $^{\circ}\text{C}$
rHDPE	-	$5.4 \times 10^7$
	<1 mm	$6.3 \times 10^7$
	<0.5 mm	$9.3 \times 10^7$
rPP	-	$3.6 \times 10^7$
	<1 mm	$4.1 \times 10^7$
	<0.5 mm	$4.4 \times 10^7$

### 3.3 Thermal Properties

To determine the melting ( $T_m$ ) and crystallization ( $T_c$ ) temperatures, DSC was performed on polyolefin and composite samples (Figure 3.3). Values for the melting and crystallization shift are given in Table 3.4. The thermograms for rHDPE and rPP are shown in (Figure 3.3 a and b). The observed  $T_m$  for rHDPE was 135.1 °C and a slightly lower value of 133 °C for <0.5 mm composites. Wang et al. observed a similar melt temperature for pure HDPE at 131 °C [21]. The  $T_c$  for rHDPE and <0.5mm composites were respectively 118.9 °C and 119.6 °C. The presence of small fibers could be attributed to a slightly faster crystallization [22]. Enthalpy of crystallization also decreased with the addition of the rice-hull fibers which restricted the movement of the polymer matrix. This contrasts the findings of reduced crystallinity with increased wood fiber content by Cui et al. [23] and agrees with the notion of a shift in crystallinity with increased temperature by Ndiayi et al. [24]. The above results also contrast with the study done by Lei et al [25] using rHDPE and natural fibers showing a recycled polyolefin melting peak of 130.8 °C which increased with the addition of different fibers.

In the case of rPP, two melting and crystallinity peaks were seen, signifying either a structure change, the presence of a copolymer or impurities. The earlier (minor)  $T_m$  and  $T_c$  peaks for rPP were 125.1 °C and 112.3 °C, respectively. The main (major)  $T_m$  and  $T_c$  peaks for rPP were respectively at 163.8 °C and 123.75 °C. Also, the addition of <0.5 mm rice-hulls reduced the  $T_m$  and  $T_c$  of the composite and showed a slight shift compared to rPP. With comparison to wood/rPP composites studied by Ghahri et al [26], the virgin PP used had a melting peak of 162 °C, with the two times and five times rPP showing melting peaks within the same range. Multiple peaks were also recorded during processing and DSC characterization of the rPP which had also been recorded for different types of PP and probably attributed to stereo irregularities, molecular weight inhomogeneity, partial melting, and recrystallization [27, 28]. According to a study also done on wood rPP composites, DSC melting peaks remained constant with the addition of wood flour fibers, and increase was seen in crystallinity. This constant melting peaks demonstrated that the wood fibers did not affect the crystallization structure of the PP but modified the crystallization rate [29].

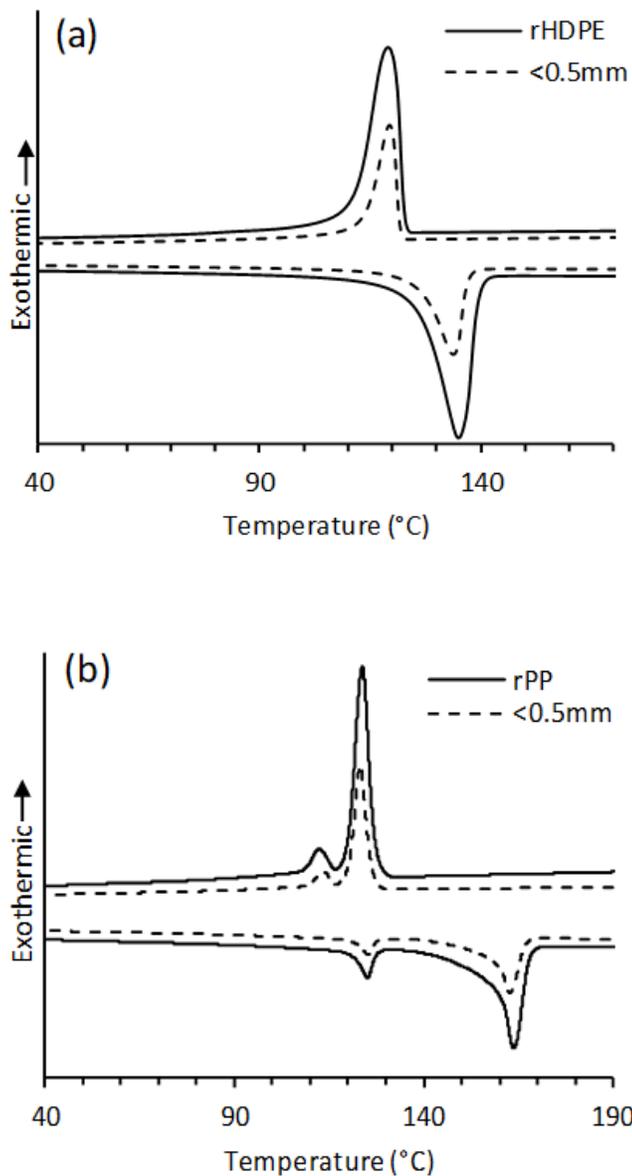


Figure 3.3: Differential scanning calorimetry (DSC) thermograms of recycled polyolefin composites for (a) recycled high-density polyethylene (rHDPE), (b) recycled polypropylene (rPP)

DSC scan peaks ( $T_m$ ) fell within the range of the TMA softening temperature ( $T_s$ ) values as shown in Table 3.4 for both polyolefins and composites. The more responsive TMA analysis (Figure 3.4 a and b) shows a decrease in height and yielded  $T_s$  values of 130.1 °C and 156.4 °C, respectively, for rHDPE and rPP, while the <0.5 mm composites remained more stable at <1mm before softening at 131.3 °C and 161.2 °C for their composites. Glass

transition temperature ( $T_g$ ) for rPP was seen at  $-2.2$  °C by TMA.  $T_s$  increased slightly for the composites compared to the raw polyolefins because of an increase in reinforcement from the rice hull fibers.

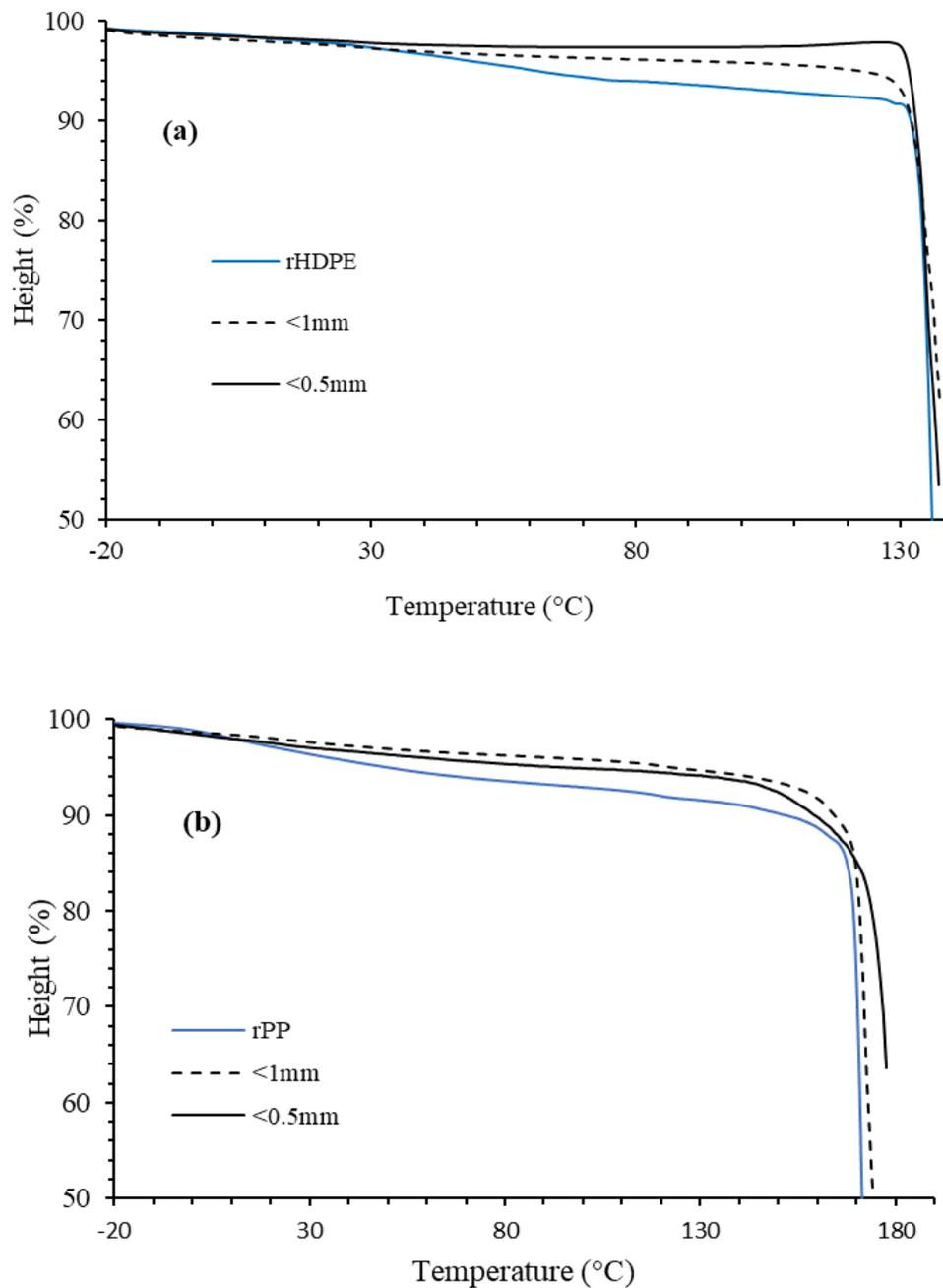


Figure 3.4: Thermomechanical analysis (TMA) thermograms for (a) rHDPE and composites (b) rPP and composites.

Table 3.4: Thermogram Peak data for polyolefins and corresponding rice hull composites.

Polyolefin	Composite particles	DSC				TMA
		T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	X <sub>c</sub> (%)	ΔH <sub>c</sub> (J/g)	T <sub>m</sub> or T <sub>s</sub> (°C)
rHDPE	-	135.1 (0.14)	118.9 (0.16)	69.0 (1.00)	203.2 (2.65)	130.1
	<1 mm	134.0 (0.09)	119.3 (0.04)	71.6 (0.89)	99.2 (2.76)	130.2
	<0.5 mm	133.0 (0.73)	119.6 (0.21)	61.9 (0.82)	85.4 (1.42)	131.3
rPP	-	125.1 (0.08) <sup>a</sup>	112.3 (0.04) <sup>a</sup>	-	-	-
		163.8 (0.06) <sup>b</sup>	123.8 (0.06) <sup>b</sup>	31.5 (0.26)	67.0 (0.41)	156.4
	<1 mm	125.3 (0.05) <sup>a</sup>	113.6 (0.02) <sup>a</sup>	-	-	-
		162.9 (0.04) <sup>b</sup>	123.2 (0.05) <sup>b</sup>	33.3 (0.29)	33.7 (0.39)	157.7
	<0.5 mm	125.4 (0.11) <sup>a</sup>	113.9 (0.03) <sup>a</sup>	-	-	-
	163.2 (0.09) <sup>b</sup>	123.4 (0.09) <sup>b</sup>	32.2 (0.27)	32.1 (0.72)	161.2	

Note: Standard deviations are in parentheses. <sup>a</sup> minor peaks and <sup>b</sup> major peaks

The thermal degradation of composites was determined by TGA as shown in Figure 3.5. The differential thermogravimetric (DTG) thermograms are shown in Figure 3.6. The thermal degradation transition temperatures are given in Table 3.5. Significant total degradation occurred in one step for rPP composites due to radical chain mechanics and rapid chain scission [30] as compared to the four peaks for rHDPE composites. The complete decomposition of the polymer matrix of both polyolefins can be seen in the peaks within the range of 454 °C to 540 °C for rHDPE composites and 430 °C to 506 °C for rPP composites.

The rice hull composites made with <0.5 mm fibers degraded at slightly higher temperatures, showing that they were more thermally stable. The small weight loss at the beginning of the rPP plots could possibly represent the breakdown of rice-hulls components from 345 °C to 420 °C. Raghu et al. [1] observed the breakdown of virgin polypropylene between 400 °C and 480 °C and increased degradation in the composite at about 500 °C. The weakening of the cellulosic fibers of the rHDPE can be seen in the peak range between 317 °C to 423 °C with the possible presence of volatile impurities at the small peak at 303 °C and 299 °C for <0.5 mm and <1 mm, respectively.

For WPCs, lower ranges of decomposition temperatures have been observed in several studies due to the presence of hemicellulose, lignin and structural components that break degrade fast [31-33].

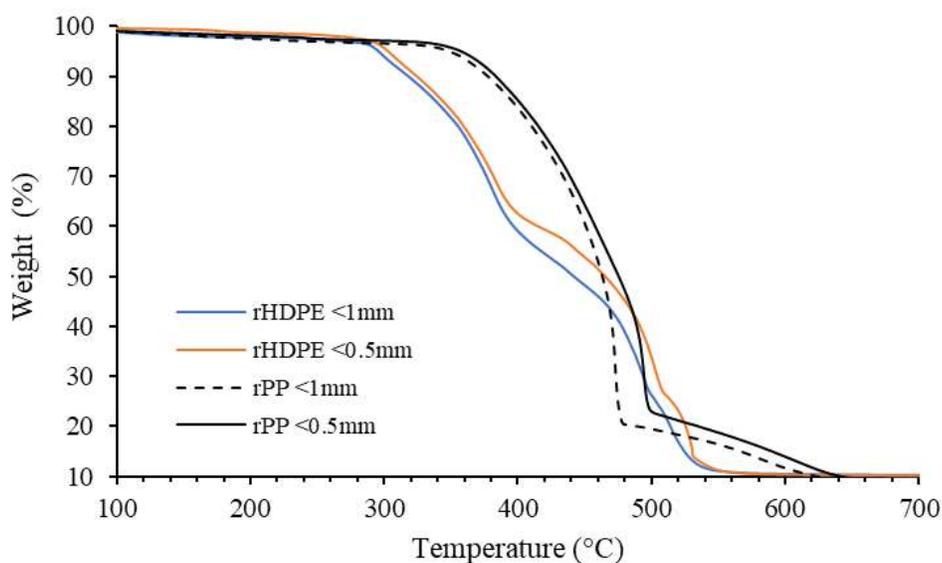


Figure 3.5: Thermogravimetric analysis (TGA) for RHPC

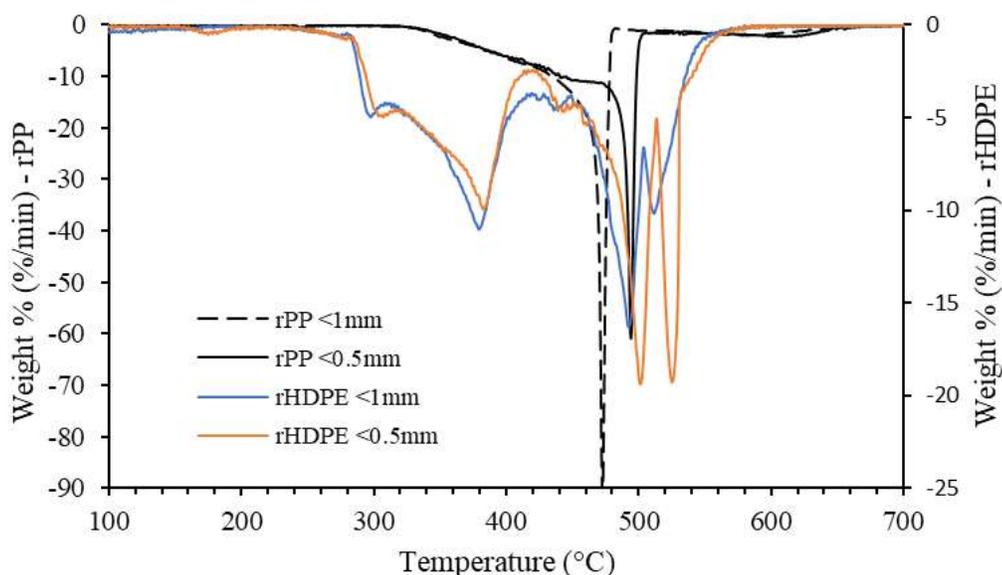


Figure 3.6: Differential thermogravimetric (DTG) curves for RHPC

Table 3.5: Thermal degradation behavior of polyolefin composites.

Polyolefin	Composite particles	Onset (°C)	1 <sup>st</sup> Peak (°C)	2 <sup>nd</sup> Peak (°C)	3 <sup>rd</sup> Peak (°C)	Final decomposition (°C)
rHDPE	<1 mm	278	299	380	502	512
	<0.5 mm	276	303	383	493	525
rPP	<1 mm	322	-	-	-	472
	<0.5 mm	320	-	-	-	493

### 3.4 Rheological and Melt Flow Properties

Due to the reprocessing of the polyolefins, a minimal temperature of 190 °C was used to reduce the thermal degradation bracket and chain breaking as studied by Oblak et al. [34]. The melt flow rate (MFR), which is an industrial test, was determined and compared to rheology results (Table 3.6). Under the applied temperature, load conditions of 2.15 kg and 15 kg for polyolefins and composites were determined, respectively. The MFR for rHDPE composites were 4.6 and 3.9 g/10 min with corresponding viscosities of 15.9 and 18.6 kPa.s

for <1 mm and <0.5 mm particles, respectively. The MFR of rHDPE <0.5 mm particle size is comparable with the MFR of corn cob composites as reported by Adefisan and McDonald [35]. In the presence of natural fiber fillers, there is the resistance to flow and sliding between the intermolecular layers, causing an increase in melt viscosity [36]. rPP composites MFR were significantly higher, with values of 125 and 109 g/10 min and concomitant lower viscosities of 0.35 and 0.41 kPa.s for <1 mm and <0.5 mm particles, respectively. rPP experienced a high displacement during the MFR process due to the reduction in entanglements and molar mass [34].

Dynamic rheology tests were performed to study the influence of shear rate on the melt (Figure 3.7). An increase in viscous modulus ( $G''$ ) for polyolefins and composites with frequency was observed, indicating good viscoelastic liquid behaviors of the polyolefins in the blend and strong-structured matrices. The probability of energy storage in the composites is observed via the elastic modulus ( $G'$ ) [37]. The addition of the rice hulls also caused an increase in the  $G'$  and  $G''$  and reduced the spacing for rPP at lower frequency.

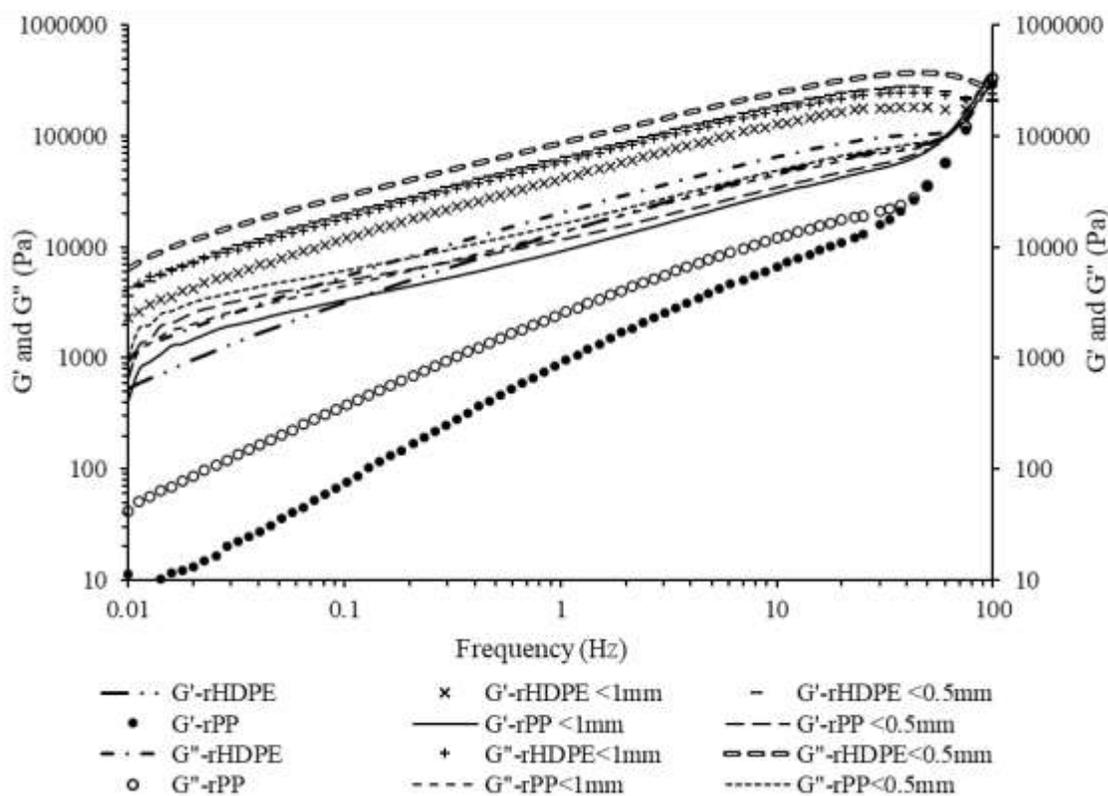


Figure 3.7: Dynamic rheological measurements ( $G'$  and  $G''$ ) of polyolefins and rice hull composites.

Differences in  $G'$  are also observed with each composite due to the varying particle sizes and polymer matrices. rPP composites exhibited the lowest  $G'$ – $G''$  curves in comparison to the rHDPE composites. Complex viscosity ( $\eta^*$ ) also decreased (Figure 3.8) from low to high frequency for all samples as a result of shear thinning [38]. rPP and its composites had a lower  $\eta^*$  than rHDPE, which had a better cross-linked structure in composite melts [39]. With multiple extrusion and processing cycles for PP, a rapid decrease in  $\eta^*$  was experienced [40]. The highest  $\eta^*$  of the <0.5 mm for each case of composite was due to the high surface area and better interactivity in the composites. This increase in  $\eta^*$  for the <0.5mm composites also corresponded with the results from the MFR. With the heat applied to the materials, the higher  $\eta^*$  of the composites occurred because of lower heat transfer in the insulating-like rice hulls as compared to the polyolefins [41]. Melt flow rate, apparent and complex viscosity also conform statistically to measured results showing a significant difference with the addition of different sized fibers as seen in Table 3.6.

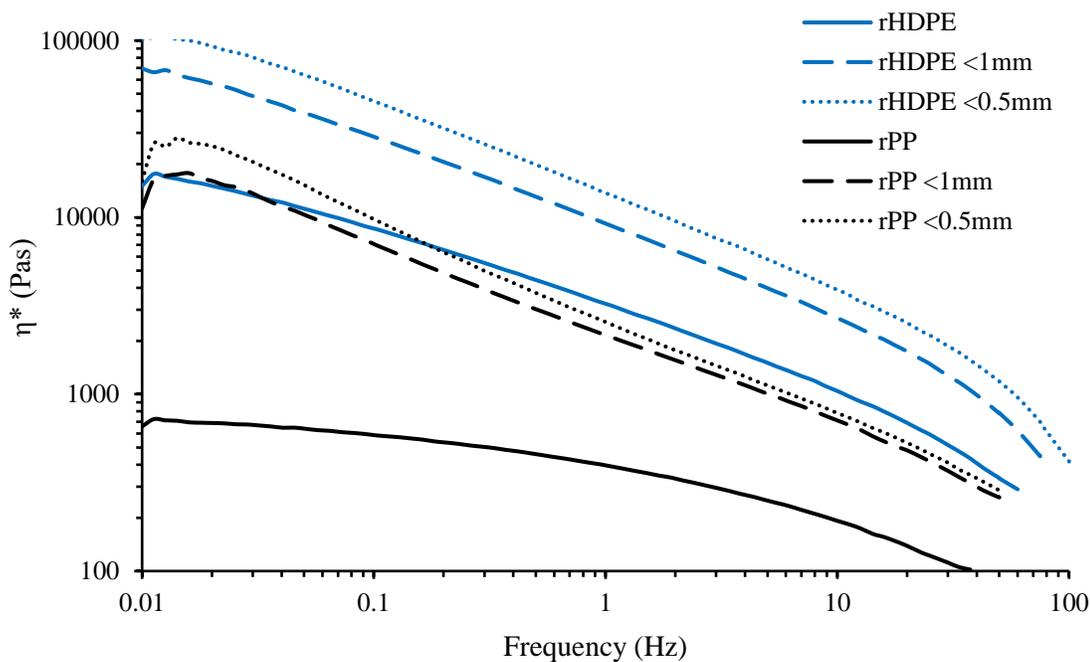


Figure 3.8: Flow curves of complex viscosity ( $\eta^*$ ) of polyolefins and rice hull composites with frequency.

In contrast to dynamic rheology, which runs at lower frequencies, capillary rheology was used to study the flow behavior and the response of polymer matrices to higher shear rates [42]. Shear rates applied were in the range of  $2.9 \text{ s}^{-1}$  to  $580 \text{ s}^{-1}$  for both polyolefins and composites. A gradual decrease in shear viscosity was observed with increased shear rates due to shear thinning behavior which also seen in the dynamic rheology results. Data was Bagley and Rabinowitch corrected, according to ASTM D3835-02, for both dies used to reduce the effects of shear thinning and to improve viscosity results. This yielded corresponding results of true viscosity for both dies. True shear viscosity vs. shear rate plots are shown in Figure 3.9 for polyolefins and composites. Shear viscosity values were within  $10^2$ – $10^4 \text{ Pa}\cdot\text{s}$  for rHDPE and composites and  $10^2$ – $10^3 \text{ Pa}\cdot\text{s}$  for rPP composites. A lower range of results ( $10^1$ – $10^3 \text{ Pa}\cdot\text{s}$ ) were attained by Mazzanti et al. [43].

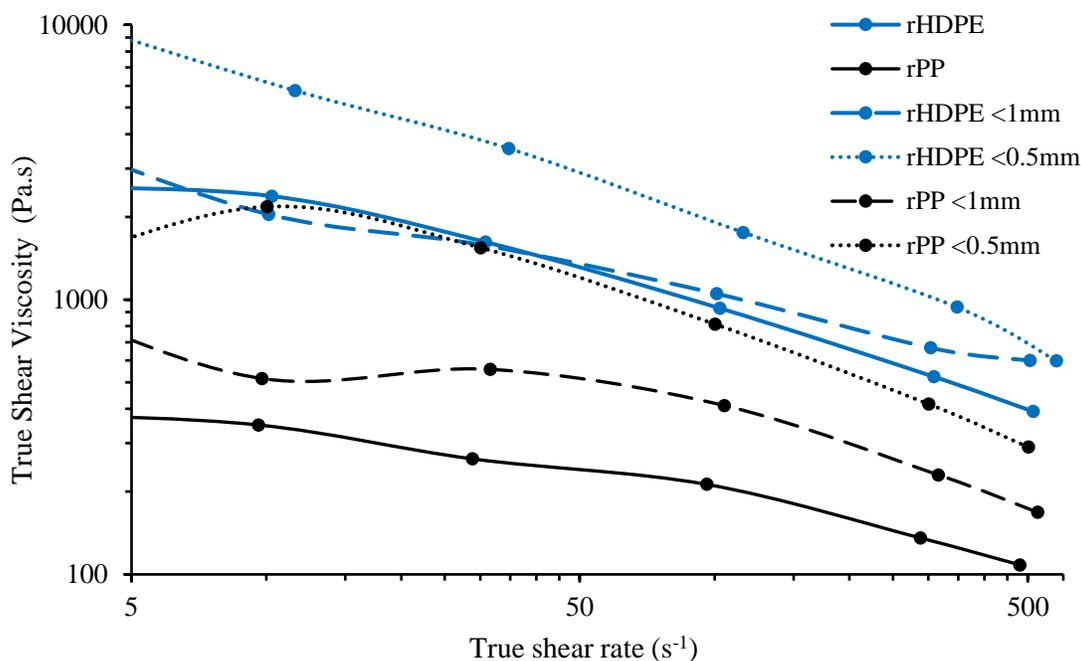


Figure 3.9: Flow curves of true shear viscosity versus true shear rate by capillary rheology of polyolefins and rice hull composites.

Table 3.6: Melt flow rate and Rheology results

Polyolefin	Composite particles	MFR (g/10 min)	Apparent viscosity (kPa.s)	$\eta^*$ at 1.06 Hz (kPa.s)	Dynamic	Capillary
					Apparent viscosity at 30 s <sup>-1</sup> (Pa.s)	True viscosity at 30 s <sup>-1</sup> (Pa.s)
rHDPE	-	0.961 (0.023) <sup>c</sup>	10.91 (0.260) <sup>c</sup>	3.17 (1.32) <sup>c</sup>	2387	1621
	<1 mm	4.592 (0.021) <sup>b</sup>	15.91 (0.073) <sup>a</sup>	8.95 (0.816) <sup>b</sup>	7091	1580
	<0.5 mm	3.919 (0.010) <sup>a</sup>	18.65 (0.039) <sup>b</sup>	13.34 (1.56) <sup>a</sup>	6148	3548
rPP	-	25.0 (2.318) <sup>c</sup>	0.38 (0.032) <sup>b</sup>	0.39 (0.014) <sup>c</sup>	376	263
	<1 mm	124.9 (1.278) <sup>a</sup>	0.35 (0.004) <sup>b</sup>	2.09 (0.300) <sup>a</sup>	850	557
	<0.5 mm	109.4 (0.062) <sup>b</sup>	0.41 (0.006) <sup>a</sup>	2.48 (0.240) <sup>b</sup>	808	1544

Note: Standard deviation in parentheses. Each polyolefins' sample with different letters (a, b, c) are statistically different (p <0.05) via a one-tailed t-test

Rice hulls (<0.5 mm)/rHDPE composite registered the highest viscosity when compared to other composites and polyolefins due to density effects, surface area and thermal stability. At low crosshead speeds, rPP composites experienced breaking, which accounted for the non-linear results attained. A brittle effect from cooled extrudate of rPP composites was observed, which could have been caused by the continuous degradation from multiple extrusion cycles [44]. The shear viscosity from capillary rheology in both cases were significantly higher than that from dynamic rheology when both were compared. A similar trend is also seen in the study done by Mazzanti et al. [43].

Extrudate swells were also measured, and the 27 mm die extrudates were smaller in diameter for all composites and polyolefins in comparison to the 14 mm die. There was a minimal increase in swell ratio of the polypropylene composites at increased crosshead speed.

### 3.5 Surface Chemistry

The FTIR spectra of the rice husk fiber are shown in Figure 3.10. The spectrum shows the presence of the hydroxyl group (-OH) in cellulosic fibers with a stretched medium intensity broad band at  $3334\text{ cm}^{-1}$ , C-H stretching bands at  $2921\text{ cm}^{-1}$  and  $2851\text{ cm}^{-1}$  associated with lignin and lipids, and two bands at  $1603\text{ cm}^{-1}$  and  $1513\text{ cm}^{-1}$  assigned to aromatic skeletal vibrations of lignin [4]. A high intensity band at  $1048\text{ cm}^{-1}$  is assigned to the C-O stretching of cellulose and hemicellulose [45]. The rice hull (<0.5mm) /rHDPE composite spectra (Figure 3.11) shows bands at a lower intensity than the pure rice hulls due to dilution.

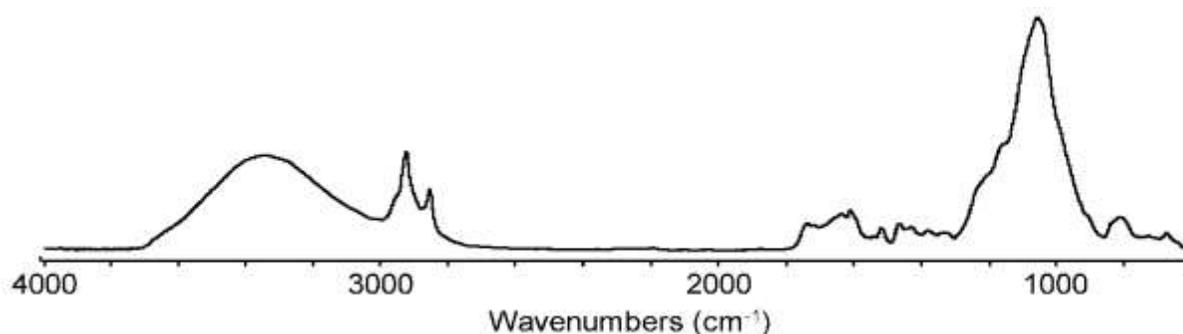


Figure 3.10: Fourier-transform infrared spectroscopy (FTIR) spectrum of rice hulls.

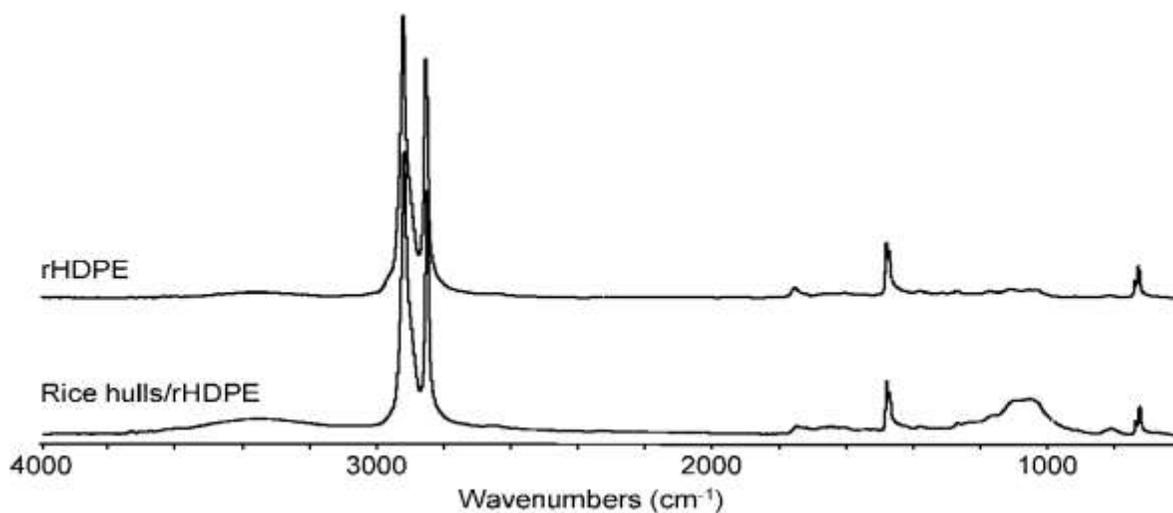


Figure 3.11: FTIR of recycled HDPE (top) and rice hulls (<0.5 mm)/rHDPE composite (bottom).

Major bands for rPP (Figure 3.12) were between 2866 and 2949 cm<sup>-1</sup> assigned to C-H stretching vibrations. In addition, bands for -CH<sub>2</sub> and -CH<sub>3</sub> groups were observed at 1454 cm<sup>-1</sup> and 1375 cm<sup>-1</sup> respectively and are characteristic for the propylene unit. The band at 803 cm<sup>-1</sup> was assigned to a C=C bond that could be due to some thermal degradation [46]. This band could help explain the presence of the minor peak found in the DSC analysis for rPP. After extrusion and compounding of the rice hulls with rPP, the C=C band was shown to decrease (Figure 3.12).

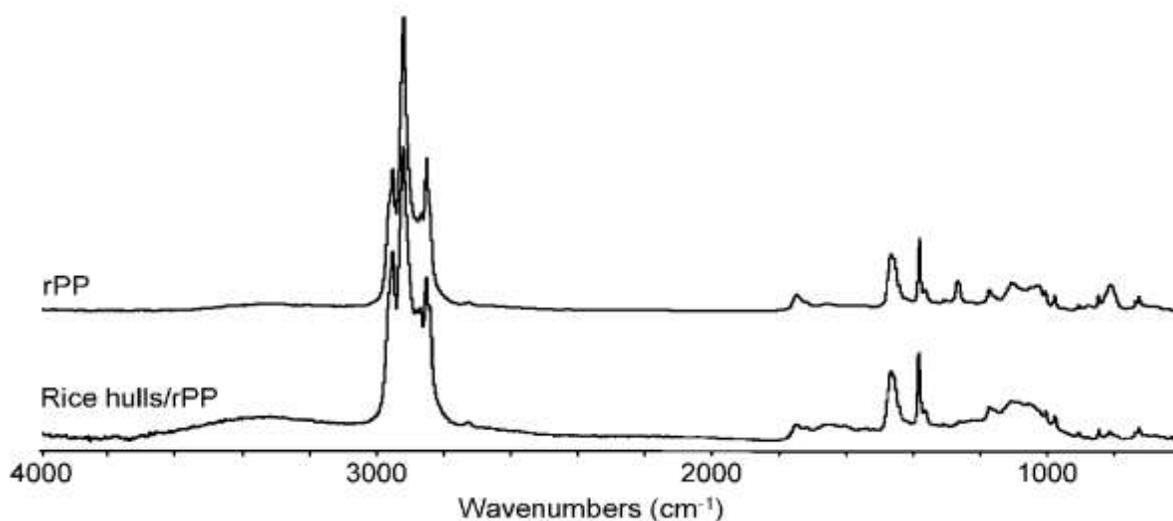


Figure 3.12: FTIR spectra of recycled PP (top) and rice hulls (<0.5 mm)/rPP composite (bottom).

### 3.6 Water Absorption

The relationship of water uptake with time for the composites was analyzed based on Fick's diffusion behavior [47] and, an initial increase in water absorption was observed for both composites as seen in Figure 3.13 with corresponding diffusivities. The respective WA for rice hulls <1 mm and <0.5 mm composites were 9.9% and 7.8% for rHDPE and 13.2% and 11.7% for rPP (Table 3.6). The presence of the large <1mm particle size created a larger exposed hydrophilic surface with the potential for more voids which would absorb more moisture over time [32]. The  $D_f$  for the <1 mm and <0.5 mm composites were  $3.2 \times 10^{-11} \text{ m}^2/\text{s}$  and  $3.5 \times 10^{-11} \text{ m}^2/\text{s}$  for rHDPE and  $6.1 \times 10^{-11} \text{ m}^2/\text{s}$  and  $7.0 \times 10^{-11} \text{ m}^2/\text{s}$  for rPP, respectively. Since a higher diffusivity signifies a shorter time to approach equilibrium absorption [48], <0.5 mm composites for polypropylene will absorb less water over more time. The relationship between water absorption and fiber size for both composites were significantly different.

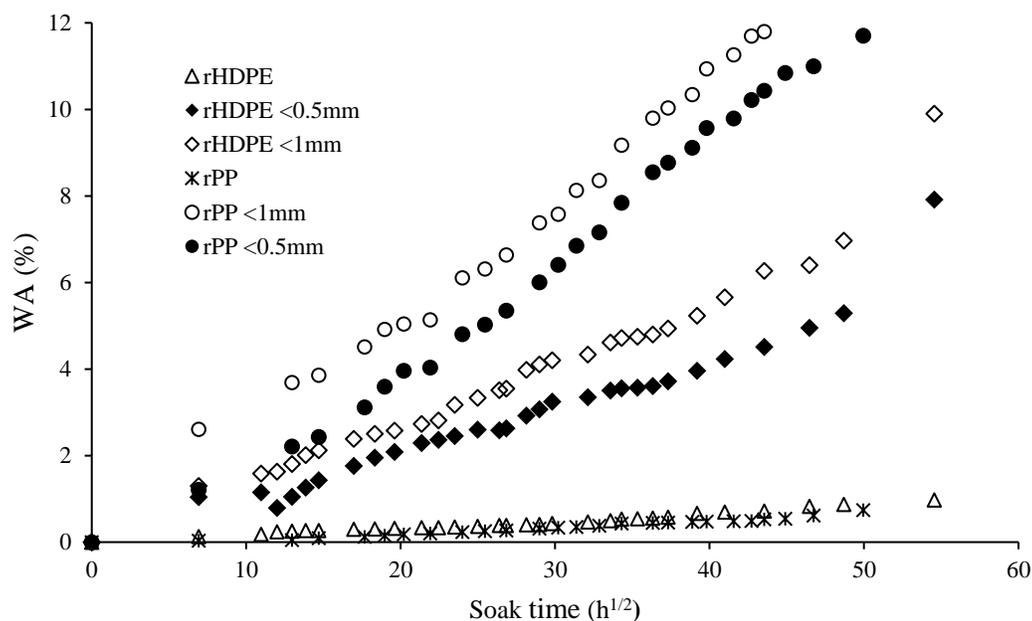


Figure 3.13: Water soak of polyolefin composites as a function of time.

Table 3.7: Water soak properties of polyolefin composites.

Polyolefin	Composite particles	WA (%)		Diffusion Coefficient $\text{m}^2/\text{s} (10^{-11})$
		2 days	100 days	
rHDPE	<1 mm	1.3 (0.3) <sup>a</sup>	9.9 (5.5) <sup>b</sup>	3.2
	<0.5 mm	1.1 (0.3) <sup>a</sup>	7.8 (0.9) <sup>a</sup>	3.5
rPP	<1 mm	2.6 (1.1) <sup>a</sup>	13.2 (0.6) <sup>a</sup>	6.1
	<0.5 mm	1.2 (1.1) <sup>a</sup>	11.7 (1.3) <sup>b</sup>	7.0

The resistance and reduced water intake by the <0.5 mm fibers are due to the better interaction between the rice hulls fibers which prevents interstitial spaces that absorb water. The addition of the coupling agents is a possible advantage which helps reduce the amount of water intake by the lignocellulosic fiber [49].

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## Chapter 4: Conclusion

### 4.1 Conclusion

Rice remains a primary source of food worldwide and a major source of the affordable and available agricultural by-product, RH. The chemical constituents of RH, which is a lignocellulosic material, makes it a potential substitute in composite manufacturing especially with the present issues of deforestation and scarce wood products worldwide. RHPC are in continuous growing demand for different applications in automotive industries, furniture and building industries which all require long term property efficiency in outdoor environments. Hence the different approaches to stabilize and extend the life span of these composites which includes, the use of coupling agents, effective optimization of fiber size, fiber treatments, reuse and recycling of non-biodegradable polyolefins, waste fibers etc.

Rice hulls natural fiber of <1 mm and <0.5 mm particle sizes were successfully compounded with recycled polyolefins, rHDPE and rPP, using a twin-screw extruder to form extruded profiles. Rheology, mechanical, and thermal characterization were used to analyze the composites, and were shown to have a performance comparable to WPC, and hence could be a direct substitute. Mechanical properties of the rice hulls composites are similar or in some cases higher or lower than the virgin polyolefin and WPC composites studied. It was evident that the proportion of the 2% maleated coupling agents used enhanced the properties of the composites. Rheology was performed via dynamic and capillary methods with a minimum temperature of 190 °C to reduce the adverse effect of thermal degradation.

Although the densities of the smaller particle-sized composites were low, stability results were not negatively affected. The <0.5 mm composites of rHDPE possessed better thermal stability and tensile properties when compared to rPP composites and raw recycled polyolefins, due to the size and incorporation of rice-hull fibers. This study affirms the importance of upcycling plastic waste and natural fiber residues into sustainable composite products for industrial and residential applications.

This study also clearly suggests the efficient use of recycled polyolefins in composites as they match up closely to their virgin forms in properties and stability.

## 4.2 Limitations and Future Recommendations

While this study covered an ample research gap, limitations were still encountered. Sorting out polyolefins which ensures cleaner material characterization and property determination, was still a concern during composite manufacturing. Other manufacturing processes i.e. injection molding, compression molding etc., can be considered when working with recycled composites to ascertain their effectiveness in property characterization in consequent studies. Mechanical property characterization using the tan delta was not factored in and should be considered in future work. The use of two common polyolefins HDPE and PP were employed in this study with significant results. Thus, other available polyolefins and plastics which constitute to the enormous landfill and waste can be continually used to manufacture composites to aid their biodegradation and improve sustainability in the future. Natural fiber particle sizes should also be considered during composite manufacturing since they have proven to improve properties and act as good fillers for composites.