Manufacture and characterization of natural fiber biocomposites for automotive application

Cindu Annandarajah
Iowa State University

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Manufacture and characterization of natural fiber biocomposites for automotive application

by

Cindu Annandarajah

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Agricultural and Biosystems Engineering

Program of Study Committee:
David Grewell, Co-major Professor
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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2020

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DEDICATION

To my husband Guido
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<td>Agave Fiber</td>
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<td>CAFE</td>
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<td>p-p</td>
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In response to environment and sustainability issues, the materials science field has shown a growth and increasing interest in natural fiber biocomposites as an alternative to synthetic fillers such as glass fibers and talc powder. Albeit many years of research, the greatest challenge with working with natural fiber reinforced plastic composites is their large variation in properties and characteristics as well often required pretreatment and cleaning. These issues have limited the commercial products produced from natural fiber composites. In more detail, natural fiber composite properties are variable and influenced by many parameters such as fiber type, growing conditions, processing methods, and any modification of the fiber. Additional challenge of incorporating natural fibers arises when agricultural byproduct is looked into as a potential source of natural filler because fiber pretreatment to remove impurities has to be taken into consideration before processing. Currently, there is an existing market for agave fiber bagasse and thermoplastic biocomposites in the automotive industry with potential interior applications for storage bins, coin trays, battery and fuse cover, to name a few.

This research aimed develop a technology that would enable commercialization of agave fiber bagasse plastic composites, and to optimize the interfacial adhesion to improve the mechanical properties of these composites for structural application. The research is initially studied hybrid fibers (cellulose and glass) to investigate the properties
of recycled polyamide-6 (rPA6) and recycled polypropylene (rPP) blends and served as a baseline for performance specifications, such as specific strength. While adding glass fiber alone enhanced the mechanical properties, incorporation of cellulose fibers into the composite enables use less glass fibers while retaining similar mechanical (small loss) properties which correlated to a weight reduction. However, the addition of cellulose fibers increased the composites stiffness and rPA6/rPP composites were optimized at loading levels of 15 wt.% glass and 10 wt.% cellulose fibers. These properties from the research findings were considered as a baseline performance target of the automotive industry requirements while creating eco-friendly composites in automobile industry.

Biobased composite with polypropylene and agave fiber filler at different loading levels (0-40 wt.%) were investigated. Surface treatments studies on natural fibers to maximize the bonding strength as well as the stress transferability in the composites were also conducted. Treatments using chemicals such as sodium hydroxide, sodium chlorite and acetylation were carried out to improve the bonding at the fiber polymer interface. All the treatments significantly enhanced the tensile and stiffness properties of the composites compared to the control sample (no treatment), but to varying degrees. Among the various treatments, acetylation treatment of fiber reported maximum interfacial interactions.

To further investigate the potential of compounding agave fiber biocomposites, talc-filled thermoplastic olefin (TPO), a polymer matrix commonly used in the
automotive industry was studied. The composites were prepared with three different compatibilizers and their thermomechanical, morphological, and water absorption properties were characterized. The compatibilizers had significant improvement on the tensile, flexural strengths, and water absorption; however, no considerable effect on impact strength, elastic or flexural moduli was observed. The composite comprised of TPO, Washington Penn Plastic (WPP) compatibilizer, and agave fibers exhibited the best mechanical properties. The addition of agave fiber increased the elastic and flexural moduli but reduced the elongation to failure and impact strength. Overall, average TPO-agave fiber biocomposites exhibited comparable mechanical properties to pristine TPO and its components as used in automotive industry, while offering environmental and economic advantages.

Talc-filled thermoplastic olefin (TPO) reinforced with agave fiber composites were prepared with three different compatibilizers and their thermal-mechanical, morphological, and water absorption properties were characterized. The objective of this study was to investigate the use of agave fibers as a reinforcing agent in TPO composites. The effects of addition of 20 wt.% agave fiber and compatibilizers (WPP, Adicco 9320, and maleic anhydride grafted polypropylene, PPgMA) on the properties of the TPO-agave fiber composites were comparatively studied. The compatibilizers had a significant improvement on the tensile, flexural strengths, and water absorption; however, no considerable effect on impact strength, elastic or flexural moduli was observed. The
composite comprised of TPO, WPP, and agave fibers exhibited the best mechanical properties. The addition of agave fiber increased the elastic and flexural moduli but reduced the elongation and impact strength. Overall, average TPO-agave fiber biocomposites exhibited comparable mechanical properties to pristine TPO and its components as used in automotive industry, while offering environmental and economic advantages.

Because the renewable resources used in this study are agricultural byproducts, pretreatment of the fibers was necessary to remove sugars and impurities that could be damaging to the processing equipment. Traditional washing, a commonly used method for agave fiber bagasse conditioning uses a large amount of resources such as water, time and energy. Ultrasonication experiments in batch-scale were conducted to test the feasibility of potentially substituting the washing method. The results showed that the optimum ultrasound pretreatment conditions for maximum reducing sugar yield was an amplitude of 160 µm for 7.5 min of treatment at 23 °C. Under these conditions, 100% of maximum sugar removal through washing was achieved. Improvement in thermal properties is also observed for ultrasound-treated agave fibers. The substantial reduction in pretreatment time, temperature, energy with improved efficiency is the most attractive features of the ultrasound pretreatment.
CHAPTER 1. GENERAL INTRODUCTION

1.1. Background and Motivations

Over the past few decades, the efforts to find more environmentally friendly materials have spurred as a result of persistence of plastics in the environment, landfill space shortage and depletion of petroleum resources. Growing environmental problems has become a major influence on government policy in many countries by encouraging “greener” materials research. These driving forces have motivated industries and academicians to search and develop new materials derived from more sustainable resources, to meet the need of these new markets for biobased products.

Natural fibers, by definition embody eco-friendly raw products has been emerging as a viable alternative to glass fibers and talc powders as well as other non-biobased fillers for various applications in automotive, construction and packaging materials. Natural fiber biocomposites has become an extensive and rapidly developing area of materials science because of their prospective advantages that make them attractive as a potential substitute to the synthetic (glass and carbon) fibers. For example, natural fibers possess advantages of lower cost ($200-1000/ton) and energy to produce (4 GJ/ton) compared to synthetic fillers such as glass fibers (cost: $1200-1800/ton and energy to produce: 30 GJ/ton) and carbon fibers (cost: $12500/ton and energy to produce: 130 GJ/ton)[1]. In addition, when compared to synthetic fibers, natural fibers offer competitive specific mechanical properties (strength/density), low density, relatively non-abrasiveness, CO₂
sequestration, recyclability and biodegradability. Thus, these properties make natural fibers attractive as a reinforcement element in a plastic matrix for high volume commodity products.

Similar to other industries, the automotive industry continues to search for new sustainable materials such as biocomposites that could reduce the weight of automobile, improve fuel economy, and alleviate the use of petrochemicals and decrease the overall impact of vehicles on the environment. Fiber reinforced composites have gained importance in the automotive sector where high mechanical properties and dimensional stability must be coupled with light weight. Concurrently, these fiber-based composites can contribute to an automotive cost reduction of 20% and weight reduction of 30%. Some of the successful applications in the industry include flax, jute, kenaf, wheat straw, cellulose, wood, coconut fiber and rice hull [2], [3]. Agave fiber bagasse, a byproduct of the tequila industry has been considered as a possible reinforcement fiber for the development of sustainable materials. Utilizing agricultural waste requires the characterization of the physical, mechanical and thermal properties of these materials in order to develop sustainable new materials. This also avoids the hazards from burning the fibers or leaving them to deteriorate in the field.

However, there are concerns of fiber quality, consistency of growth and post-harvest conditions; and low thermal stability reducing upper processing temperature limits (200 °C). In addition, the application of natural fibers has had limited industrial
acceptance as they are moisture sensitive and form weak bonding with polymer matrices. Typically, these problems could be overcome by suitable fiber treatments and optimization of processing parameters. Thus, optimization of the compounding process of natural fiber biocomposites and investigation of the feasibility of large-scale production must be performed to increase the feasibility to launch agricultural byproduct biocomposites on the market.

This dissertation discusses the feasibility of using agave fiber bagasse, a byproduct of the tequila industry as reinforcement filler for the automotive industry. In order to measure the level of success, long studied biobased composite fillers, namely cellulose, will be considered a baseline marker.

1.2. Scope and Objectives

This project was sub-part of a project entitled “Natural Fiber Biocomposites” funded by the NSF Center for Bioplastics and Biocomposites (CB2) with collaboration of Ford Motor Company. The overall objectives of this project were to develop knowledge for increased adoption of plant fiber biocomposites from agricultural waste, to provide technology and guidelines to the automotive industry enabling them to increase usage of sustainable composites, and to develop new composites based on thermoplastic matrices. The detailed objectives of the dissertation and brief description of the approach to the research are as follow:
To investigate the effect of hybrid glass and cellulose fibers on characterization and material properties of recycled polyamide-6 (rPA6)/recycled polypropylene (rPP) blends for under-the-hood application. Their thermal, mechanical, morphological, and water absorption properties were characterized and use these findings as a baseline for agave fiber composites.

To determine the effect of various compatibilizers on agave bagasse fibers in thermoplastic olefin (TPO) composites. Their thermal, mechanical, morphological, and water absorption properties were characterized.

To examine the optimization of agave fiber bagasse and polypropylene biocomposites through filler ratios. The investigation also included chemical treatments to improve the interfacial adhesion between the agave fiber bagasse and polypropylene matrix. Mechanical, chemical morphological, and thermal properties were characterized.

To evaluate the feasibility of ultrasonication as a pretreatment to remove residual sugar from agave fiber bagasse. The sugar removal analysis involved a comparison ultrasonication process and traditional as pretreatment methods in agave fiber conditioning.

1.3. Dissertation Outline

This dissertation is organized into seven chapters. Chapter 1 “Introduction” presents the general background and identifies the specific issues that need to be addressed to expand agave fiber bagasse biocomposites into the automotive industrial
market. It also outlines the scope of research and the main objectives. **Chapter 2**

“Literature Review” provides an overview of the previous work on natural fiber composites, focusing on the overall performance of biocomposites. A review of the current state-of-the-art in natural fiber composite in automotive industry is also presented. The following four chapters consist of four manuscripts prepared for publication in various journals. The first manuscript has been published in Materials in September 2019, while the second manuscript was submitted to Journal of Industrial Crops and Products in October 2019. The third and fourth manuscript will be submitted to Composites Part B: Engineering, Ultrasonics Sonochemistry, respectively.

**Chapter 3**, “Hybrid Cellulose-Glass Fiber Composites for Automotive Applications” examines the introduction of natural fiber into the recycled polymer blends composite of polypropylene (rPP), Nylon 6 (rPA6) and glass fiber blends, for under-the-hood application. This chapter also evaluates loading level optimization of the hybrid fibers to improve mechanical properties.

**Chapter 4**, “Chemical Modification of Fiber to Increase Interfacial Bonding in Agave Fiber Polypropylene Biocomposites,” evaluates the effect of surface treatments on natural fibers to maximize the bonding strength as well as the stress transferability in the composites.

**Chapter 5**, “Effect of Compatibilizers On Agave Fiber-Reinforced Thermoplastic Polyolefin (TPO),” reports on studies of the effects of three different compatibilizers on
the natural fiber and polymer matrix composite. This paper discusses the effect of modification on the overall thermal-mechanical properties, morphological, and water absorption were characterized.

**Chapter 6, “Sonication of Agave Fiber Bagasse: A Potential Pretreatment to Enhance Sugar Release,”** discusses the effects of high-powered ultrasonics on the removal of sugar from agave fiber bagasse in batch scale and compared to the traditional washing method. The sugar concentration in the rinsate and the morphology of the fiber is discussed in this paper.

Finally, **Chapter 7 “Conclusions & Future Work”** summarizes the main findings of the dissertation and suggestion for future works for the development of agave fiber biocomposites for automotive application is provided.
CHAPTER 2. LITERATURE REVIEW

2.1. Natural Fiber Biocomposites

The use of natural fiber with another material to form composites is not a new idea and have been used for hundreds of years such as clay, reinforced with straw for housing applications in ancient Egypt around 4000 B.C. [4]. Natural fibers have also been used to make ropes, beds, bags and etc. for centuries. With tremendous growth of the petrochemical industry in the 20th century and development of more resilient materials i.e. metals, the interest in natural materials vanished as man-made materials were easier to process, durable, high yield and also low in cost [5]. However, increasing environmental awareness, global waste problems, initiation of ecological regulations and legislations and the depletion of fossil fuels are responsible for the increasing interest in renewable resources in various industries such as construction, aerospace, automotive and sports. Natural fiber biocomposites has become an extensive and rapidly developing area of materials science, especially with polymers over the past few decades. Global availability of natural fibers and other abundantly accessible agricultural byproduct provide impetus for this new polymer science and engineering research for a sustainable technology. Agricultural products form a foundation for novel industrial products to be made from renewable resources. Plant fibers have been historically used for various applications, depending on their composition and physical properties. Some of the examples are pulp, paper, ropes, twines, textiles and geotextiles, insulation materials,
fleece, nonwoven materials and much recently as polymer reinforcements [6]–[10]. The life cycle of these natural fibers of all walks of life is shown in Figure 2.1.

Figure 2.1 Life cycle of bio-composites [11].

The main intention of incorporation of natural fibers were to introduce low cost and light weight composited by replacing traditional high-density fillers. Natural fibers have a lower density (1.2–1.6 g/cm$^3$) than that of glass fiber (2.4 g/cm$^3$) and talc (2.76 g/cm$^3$), which ensures the production of lighter weight composites while maintaining higher specific strength compared to glass fiber and a similar specific modulus [12]. These biocomposites present many other advantages such compared to synthetic fibers, such as flexibility during processing, low tool wear, low costs (on a volumetric basis), availability, and biodegradability [2], [11]. The aim of this section is to give a general overview and to introduce short fiber biocomposites, especially of agave fiber bagasse which is the main theme of this work.
2.2. Polymers and Biocomposites

Both biobased and petroleum-based polymers are common matrices for biocomposites applications. Petroleum-based plastics represent a vast majority of the matrices used for natural fiber biocomposites with commodity thermoplastics (polyolefins, polystyrene, polyvinyl chloride) and thermosets (polyester, epoxy, vinyl esters) used extensively in current application. Biobased polymers that are commonly used include cellulose polymers, starch polymers, aliphatic polyesters (PLA, PHA and PHB) and protein and vegetable oil-based polymers. Generally defined, biocomposites are composite materials made by combination of natural fiber and petroleum-based polymer such as polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC) or biopolymers such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA). Composites materials prepared by biopolymers and synthetic fibers such as glass and carbon fibers also fall under biocomposites category [10]. Biocomposites derived from biobased plastic and natural fibers (plant) are commonly termed as ecofriendly or “green composites”.

It is important to note that not all biobased polymers are degradable, and some petroleum-based polymers can be biodegradable via microorganisms, photo degradation, oxo-degradation and hydrolysis. Biodegradable polymers are commonly defined as plastics that undergo decomposition process induced by microorganisms in composting or anaerobic digestion process. The biodegradation process is closely
associated to the molecular structure of the polymer and independent of the origin of the material. For example, soy oil-based resins and biobased polyolefins are non-biodegradable polymers. In contrast, poly(ε-caprolactone) and aliphatic polyesters are common examples of petrochemical biodegradable polymers [13].

Hybrid biocomposites includes combination of fibers with a polymer matrix in which the fiber or matrix can be biobased, petroleum-derived or a blend of both. There has been a particular interest in the hybrid combination of polymer matrices as they offer interesting cost-performance properties and provide a compromise between fully fossil-based plastic matrices and fully biobased materials by limiting the moisture absorption or increasing the impact strength [9]. An overview of the natural fiber composite types and their related compounds is shown in Figure 2.2.

![Figure 2.2 Natural fibers, biopolymers and biocomposites [13].](image-url)
2.3. Plant Fiber Composition and Structure

Natural fibers are subdivided based on their origins they are derived from, i.e. plants, animals, or minerals. The most common classification for natural fibers is by botanical type. By this system, the plant fibers can be categorized into six types including bast (or stems), leaf, seed, fruits, wood, cereal, straw and other grass fibers as shown in Table 2.1.

Table 2.1. Six general types of natural fibers [13].

<table>
<thead>
<tr>
<th>Bast</th>
<th>Leaf</th>
<th>Seed Fibers</th>
<th>Pod</th>
<th>Husk</th>
<th>Fruit</th>
<th>Hulls</th>
<th>Core</th>
<th>Grass</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemp</td>
<td>Pineapple</td>
<td>Cotton</td>
<td>Kapok</td>
<td></td>
<td></td>
<td></td>
<td>Rice</td>
<td>Kenaf</td>
<td>Wheat</td>
</tr>
<tr>
<td>Ramie</td>
<td>Sisal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Oat</td>
<td>Jute</td>
<td>Oat</td>
</tr>
<tr>
<td>Flax</td>
<td>Agave</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wheat</td>
<td>Hemp</td>
<td>Barley</td>
</tr>
<tr>
<td>Kenaf</td>
<td>Henequen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rye</td>
<td>Flax</td>
<td>Rice</td>
</tr>
<tr>
<td>Jute</td>
<td>Curaua</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bamboo</td>
</tr>
<tr>
<td>Mesta</td>
<td>Banana</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bagasse</td>
</tr>
<tr>
<td>Urena</td>
<td>Ababca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Corn</td>
</tr>
<tr>
<td>Roselle</td>
<td>Palm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coir</td>
<td>Oil palm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cabuja</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rape</td>
</tr>
<tr>
<td></td>
<td>Albardine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rye</td>
</tr>
<tr>
<td></td>
<td>Raphia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Esparto</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sabai</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Canary</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Grass</td>
</tr>
</tbody>
</table>

The structure and chemical composition of fibers are influenced by various factors i.e. growing atmosphere, age and the digestion process [12]. Natural fibers are primarily composed of rigid, crystalline cellulose, hemicellulose, lignin and a small portion of and waxes [35–38]. Cellulose is known to be a linear homopolymer of D-glucopyranose (C₆H₁₁O₅) rings that are connected by α-1,4 glycosidic linkages with high degree of
crystallinity. It is also the main structural component of cell walls (Figure 2.3). Hemicelluloses are made from five and six carbon sugars (hexoses and pentoses) and the sugar composition varies from species to species.

The hemicellulose sugars are held together by glycosidic linkages and are more accessible to chemical and physical attack. Lignin is an amorphous component of the cell wall and is a strengthening constituent, penetrating the fibrils during development. The components of the cell wall are interlinked by hydrogen bonds and glycosidic linkages; therefore, separation requires chemical treatment [18].

![Figure 2.3. Structural hierarchy in agave plant (modified from [19])](image)

The chemical composition of fibers varies from plant to plant, and within different parts of the same plant. Table 2.2 summarizes the chemical composition, as well as the structure of natural plant and synthetic fibers.
Table 2.3 shows the range of the average chemical constituents for a wide variety of plant types. Plant fibers are generally non-abrasive when compounded in standard industrial mixing and molding equipment, which can contribute to significant equipment maintenance cost reductions. They also present safer handling and working conditions compared to synthetic reinforcements, such as glass fibers. Their processing is offer better working conditions than glass fibers and therefore, a reduction in risk of dermal or respiratory problems. An interesting aspect of natural (plant) fibers is their positive environmental impact compared to non-biobased fibers. Natural fibers are renewable resources, where they are biodegradable, and their production requires little energy.

Table 2.2. Chemical composition of some common natural fiber.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Cellulose (wt%)</th>
<th>Hemicellulose (wt%)</th>
<th>Lignin (wt%)</th>
<th>Waxes (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abaca</td>
<td>56–63</td>
<td>20-25</td>
<td>7-9</td>
<td>3</td>
</tr>
<tr>
<td>Agave</td>
<td>73.6</td>
<td>-</td>
<td>21.1</td>
<td>-</td>
</tr>
<tr>
<td>Bagasse</td>
<td>55.2</td>
<td>16.8</td>
<td>25.3</td>
<td>-</td>
</tr>
<tr>
<td>Bamboo</td>
<td>26–43</td>
<td>30</td>
<td>21-31</td>
<td>-</td>
</tr>
<tr>
<td>Coir</td>
<td>32-43</td>
<td>0.15-0.25</td>
<td>40-45</td>
<td>-</td>
</tr>
<tr>
<td>Curaua</td>
<td>73.6</td>
<td>9.9</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td>Flax</td>
<td>71</td>
<td>18.6-20.6</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Hemp</td>
<td>68</td>
<td>15</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>Jute</td>
<td>61–71</td>
<td>14-20</td>
<td>12-13</td>
<td>0.5</td>
</tr>
<tr>
<td>Kenaf</td>
<td>72</td>
<td>20.3</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>Oil palm</td>
<td>65</td>
<td>-</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>Pineapple</td>
<td>81</td>
<td>-</td>
<td>12.7</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>68.6–76.2</td>
<td>13-16</td>
<td>0.6-0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Rice husk</td>
<td>35–45</td>
<td>19-25</td>
<td>20</td>
<td>14-17</td>
</tr>
<tr>
<td>Rice straw</td>
<td>41–57</td>
<td>33</td>
<td>8-19</td>
<td>8-38</td>
</tr>
<tr>
<td>Sisal</td>
<td>65</td>
<td>12</td>
<td>9.9</td>
<td>2</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>38-45</td>
<td>15-31</td>
<td>12-20</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.3. Characteristic values for the density, diameter, and mechanical properties of (natural) plant and synthetic fiber [3].

<table>
<thead>
<tr>
<th>Fibers</th>
<th>Density (g cm(^{-3}))</th>
<th>Diameter (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abaca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agave bagasse</td>
<td>0.74-1.34</td>
<td>435-426</td>
<td>49-58</td>
<td>2.6-2.9</td>
<td>6-9</td>
</tr>
<tr>
<td>Coir</td>
<td>1.15-1.46</td>
<td>100-460</td>
<td>131-220</td>
<td>4.6</td>
<td>15-40</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.5-1.6</td>
<td>12-38</td>
<td>287-800</td>
<td>5.5-12.6</td>
<td>7-8</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>40-600</td>
<td>345-1500</td>
<td>27.6</td>
<td>2.7-3.2</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.47</td>
<td>25-500</td>
<td>690</td>
<td>70</td>
<td>1.6</td>
</tr>
<tr>
<td>Henequen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jute</td>
<td>1.3-1.49</td>
<td>25-200</td>
<td>393-800</td>
<td>13-26.5</td>
<td>1.16-1.5</td>
</tr>
<tr>
<td>Kenaf</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nettle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil palm EFB</td>
<td>0.7-1.55</td>
<td>150-500</td>
<td>248</td>
<td>3.2</td>
<td>25</td>
</tr>
<tr>
<td>Oil palm mesocarp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PALF</td>
<td></td>
<td>20-80</td>
<td>413-1627</td>
<td>34.5-82.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.55</td>
<td>-</td>
<td>400-938</td>
<td>61.4-128</td>
<td>1.2-3.8</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.45</td>
<td>50-200</td>
<td>468-700</td>
<td>9.4-22</td>
<td>3-7</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.55</td>
<td>&lt;17</td>
<td>3400</td>
<td>73</td>
<td>2.5</td>
</tr>
<tr>
<td>Kevlar</td>
<td>1.44</td>
<td>-</td>
<td>3000</td>
<td>60</td>
<td>2.5-3.7</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.78</td>
<td>5-7</td>
<td>3400-4800</td>
<td>240-425</td>
<td>1.4-8</td>
</tr>
</tbody>
</table>

2.3.1. Agave Fiber Bagasse

Blue agave (also termed as Agave tequilana, A. palmaris or A. Americana L) is a large desert succulent that grows radially and up to 2m tall belonging to the family Agavaceae [20]. A native to Mexico, blue agave plant is mainly used to produce distilled spirit tequila [21]–[23]. The most commonly grown species of agave are Agave americana, A. angustifolia, blue agave (A. tequilana) and A. attenuata. The Mexican Law allows only the agave with intense blue color (Agave tequilana Weber var. Azul) to be harvested and used for tequila production (Figure 2.4(a)). The harvested agave head is then brought to an artisanal production plant, locally referred to as ‘palenque’. Tequila is prepared by cooking the
core or commonly known as ‘piná’ by steaming followed by shredding, milling and extracting the agave juice. Relatively large amounts of blue agave bagasse that is mainly composed of heterogeneous fibers and pith that vary in length and non-fibrous organic material in the form of fine particles are produced as a byproduct of this process (Figure 2.4 (b)). The bagasse are often underutilized and have caused accumulation and disposal problem [24]–[27]. The milled fibrous waste called agave bagasse is produced represent 40% of the total weight [28]. Considering the 2018 agave consumption, reported by the Tequila Regulatory Council, approximately 455,520 tons of bagasse were generated in that year alone [29]. Currently, the byproducts are underutilized as they are accumulated in large areas and used for compost, ruminant feed, burned to generate electricity or sent to a landfill [23], [30]. These materials can be acquired for a relatively low cost and can help automotive manufacturers to replace high-density fillers such as glass to produce more sustainable, lightweight products as well as new markets and revenue streams for farmers.

Figure 2.4. (a) Mexican agave ‘tequilana’ (blue agave) heart harvesting process. (b) cooked agave bagasse piled up in a traditional “palenque.” [31].
2.4. Benefits and Limitation of Natural Fibers

In general, industries that have adopted and established sustainable policies by incorporating natural fibers are mainly looking for weight savings. Ford vehicle currently uses 20–40 pounds of renewable materials and their continued investment in lightweighting technologies is helping them reduce overall vehicle weight and improve fuel economy [14, 15]. These fiber based composites have the advantage to meet design requirements with a 30% weight reduction and a cost reduction of 20% because natural fibers are more cost effective compared to the traditional synthetic fibers [16, 17]. Figure 2.5 shows the cost comparison between glass and natural fibers. The fuel consumption and CO₂ emission can also be reduced by lowering the weight of a car. On average, for every 100 kg weight reduced from a car, fuel consumption is lowered by approximately 0.2 liters per 100 km and CO₂ emissions can be decreased by around 10 g/km [36].

![Figure 2.5. Cost comparison between glass and natural fibers (a) by per weight [kg] and (b) by per unit length [m]. Adapted from [37].](image)
Natural fiber composites have low density materials which often have good sound dampening, the acoustics of the vehicles can also be improved and parts with coupled with the enhanced strength, it is possible to produce parts with additional functionality [19]. Application of natural fibers are also desirable for their less abrasive damage to processing equipment and low manufacturing hazard such as irritation to eyes and skin. Increasing awareness to reduce greenhouse gasses such as CO$_2$ added with the limited availability of fossil fuel created the need for development of materials from renewable resources. Natural fibers are also attractive for their low emission of toxic fumes when subjected to heat and during incineration at end of life [3], [39]–[41]. While glass fibers are widely used in the automotive industry, they offer several disadvantages when compared to natural fibers as detailed in Table 2.4 [1].

Table 2.4. Properties comparison between glass and natural fibers for automotive industry.

<table>
<thead>
<tr>
<th></th>
<th>Glass fibers</th>
<th>Natural fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health risk when inhaled</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Cost</td>
<td>~ $1.20±1.50/kg</td>
<td>~ $0.30±0.55/kg</td>
</tr>
<tr>
<td>Recyclability</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Renewability</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Disposal</td>
<td>Not biodegradable</td>
<td>Biodegradable</td>
</tr>
<tr>
<td>Distribution</td>
<td>Wide</td>
<td>Wide</td>
</tr>
<tr>
<td>Fiber emissions</td>
<td>Glass fiber (/kg): Energy 48.3 MJ</td>
<td>China reed fiber (/kg): Energy 3.4 MJ</td>
</tr>
<tr>
<td>Separation</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>Shatter resistance</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Weight reduction</td>
<td>2.5-2.8 g/cm$^3$</td>
<td>1.2-1.5 g/cm$^3$</td>
</tr>
<tr>
<td>Sound-absorbing properties</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
However, there are challenges with natural fiber as a reinforcement material, mainly because of their hydrophilic nature that lowers the adhesion between fiber and matrix because of moisture absorption. The incompatibility is also caused by the polarity differences as some thermoplastics that are used in the automotive industries are hydrophobic [21, 24]. Another challenge are their the high variability of natural fiber quality that are controlled by growing conditions year-to-year, fiber processing techniques and shortage of established storage and handling systems to prevent natural fiber degradation during storage for a long period [10]. There is a need for quality assurance protocols that need to be established for natural fibers. These natural fibers also display low impact strength and durability due to high fiber defects added in the material during processing [43]. Lower processing temperatures limiting matrix option owing to the possibility of lignocellulosic degradation add to the limitation of the application of natural fibers [27, 28].

2.5. Markets and Driving Force

Currently, natural fiber biocomposites industry is valued at $4.5bil and is growing at a Compound Annual Growth Rate (CAGR) of 11.68% [44]. The automotive sector has the second highest applications of natural fiber biocomposites revenue owing to its excellent technical properties such as high strength, stiffness, excellent fatigue and abrasion resistance coupled with light weight (Figure 2.6). These properties help the
original equipment manufacturers (OEMs) of vehicles to meet the requirements to reduce vehicle weight, emissions and improve fuel economy.

The construction (42%) and automotive (25%) industries will be leading the markets for fiber composites revenue followed by aerospace, electrical & electronics, sport and other accounting for 9, 10, 7 and 7% of the revenue respectively [44], [45]. The use of natural fiber composites in the automotive industry is growing by more than 20% annually, with the full market projected to reach $6.5 billion by 2021, at a compound annual growth rate of 11.7% between 2016 and 2021 [10, 11].

Automakers are searching for new materials to remain competitiveness in the market and to meet new standards and regulations by continuously optimizing the cost versus quality. The current Corporate Average Fuel Economy (CAFÉ) standard that mandates light duty vehicles to have an average corporate fuel economy of 54.5 mpg by
2025 [9, 10]. The legislation in the United States have formulated specific guidelines for the end-of-life of vehicles that have also resulted in increased use of natural fibers. The National energy policy of the 2002 farm bill in which biomass research and development is a national priority also played an important role in the growth of natural fiber application. According to an estimate from IHS Automotive, carloads must be reduced by 30% in order to meet the standard set by the Federal Law in the United States [1].

2.6. Application in the Automotive Industry

In the early 1900s, biobased resources started to make a comeback as a prospective material within the automotive industry. For example, in the 1930s and 1940s, Henry Ford strongly advocated and established leadership role in the research and the use of natural materials, including hemp, producing reinforced soy resin composites in the manufacture of exterior body panels. This includes the discovery of the viability of soybean oil to be used as high quality paint enamel and also plastic molded parts with exceptional shock resistance. However, this trend failed to be executed for production as these materials required long cure time and difficulty in molding [39], [51].

The implementation of natural fiber reinforced composite was established first in Europe when body of East German “Trabant” car was built using cotton fiber and polyester composite around 1950-1990. Europe has already established in the development and application of natural fiber biocomposites way ahead of North America especially in the automotive sector. This advancement is driven by various
environmental and logistics reasons. Over the course of several decades, there have been numerous attempts to incorporate natural materials into automotive components and some efforts were more effective than others. Some of the successful applications in today’s automotive industry is summarized in Table 2.5.

Table 2.5. Automotive parts containing natural fibers [3], [5–7].

<table>
<thead>
<tr>
<th>Car manufacturer</th>
<th>Natural fillers</th>
<th>Automotive parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Audi</td>
<td>Flax/sisal</td>
<td>Door trim panels</td>
</tr>
<tr>
<td>BMW</td>
<td>Sisal</td>
<td>Interior door panel</td>
</tr>
<tr>
<td>Fiat</td>
<td>Castor</td>
<td>Fuel line</td>
</tr>
<tr>
<td></td>
<td>Wheat</td>
<td>Filler</td>
</tr>
<tr>
<td></td>
<td>Soybean</td>
<td>Seats</td>
</tr>
<tr>
<td></td>
<td>Kenaf</td>
<td>Door panels</td>
</tr>
<tr>
<td></td>
<td>Castor</td>
<td>Instrument panels</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>Seatbacks, cargo floor</td>
</tr>
<tr>
<td></td>
<td>Flax</td>
<td>Trim</td>
</tr>
<tr>
<td>General Motors</td>
<td>Cotton</td>
<td>Acoustic insulator</td>
</tr>
<tr>
<td></td>
<td>Kenaf</td>
<td>Ceiling liner</td>
</tr>
<tr>
<td></td>
<td>Hemp, flax, kenaf</td>
<td>Interior door panel, seatbacks</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>Floor area parts</td>
</tr>
<tr>
<td>Honda</td>
<td>Corn</td>
<td>Interior fabrics</td>
</tr>
<tr>
<td>Hyundai</td>
<td>Castor</td>
<td>Seat frames</td>
</tr>
<tr>
<td>Mazda</td>
<td>Corn</td>
<td>Seat fabrics/ console</td>
</tr>
<tr>
<td></td>
<td>Flax/sisal/wood</td>
<td>Door panels</td>
</tr>
<tr>
<td></td>
<td>Jute</td>
<td>Interior door panels</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>Instrument panel support</td>
</tr>
<tr>
<td></td>
<td>Leather</td>
<td>Seat coverings</td>
</tr>
<tr>
<td>Mercedes-Benz</td>
<td>Coconut</td>
<td>Seat backrest</td>
</tr>
<tr>
<td></td>
<td>Cotton</td>
<td>Trunk panel</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>Insulation</td>
</tr>
<tr>
<td></td>
<td>Flax</td>
<td>Molding rod</td>
</tr>
<tr>
<td></td>
<td>Banana</td>
<td>Floor panels</td>
</tr>
<tr>
<td>Nissan</td>
<td>Corn</td>
<td>Floor mats</td>
</tr>
<tr>
<td></td>
<td>Corn</td>
<td>Instrument panels/ AC vent</td>
</tr>
<tr>
<td></td>
<td>Kenaf</td>
<td>Floor mats/ spare tire cover</td>
</tr>
<tr>
<td>Toyota</td>
<td>Potatoes/sugarcane</td>
<td>Interior component</td>
</tr>
<tr>
<td></td>
<td>Castor</td>
<td>Radiator end tank</td>
</tr>
<tr>
<td></td>
<td>Bamboo</td>
<td>Luggage compartment</td>
</tr>
</tbody>
</table>
Table 2.5. Continued

<table>
<thead>
<tr>
<th>Car manufacturer</th>
<th>Natural fillers</th>
<th>Automotive parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volkswagen</td>
<td>Flax, sisal</td>
<td>Interior door panel</td>
</tr>
<tr>
<td>Volvo</td>
<td>Soybean</td>
<td>Seats</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>Cargo floor tray</td>
</tr>
<tr>
<td>Volkswagen</td>
<td>Flax, sisal</td>
<td>Interior door panel</td>
</tr>
</tbody>
</table>

2.7. Processing Technologies for Natural Fiber Composites

2.7.1. Extrusion

The extrusion process is the most common component of all polymer processing equipment used in the plastics industry. Plastic extrusion relies on the use of pressure to push a heated and melted substance towards a die. Various type of profile shapes can be created such as rods, fibers, tube, film and sheets. The extrusion process incorporates multiple functions including melting (plasticizing), mixing, compounding and pressurizing [1]. Both single and twin-screw extruders that operates by co- or counter rotating may be used for the process.

Twin screw extruder (Figure 2.7) leads to better fiber dispersion and wetting and is generally used for more intensive mixing process than single screw extruder [3]. Single screw extruders are used when the mixing effects are critical and larger scales are needed. Owing to the excellent mixing effect of the twin-screw extruder the natural fiber materials can be homogenously distributed and wetted in the thermoplastic melt. A few studies have focused on the composite preparation with agave fiber. Biocomposite film was made via extrusion by using various polymers and agave fibers blended in a Leistritz
27mm co-rotating twin-screw extruder with a barrel – l/d ratio of 25:1. The extrusion temperatures for the compounding process were varied between 70 – 210°C at a screw speed of 225 RPM. The agave fiber compositions were varied from 0-30 wt.% [55]. PP-agave fiber composite was also produced in another study using a ThermoHaake Rheomex Model PTW25 twin-screw extruder with barrel temperatures that ranged from 160 to 180 °C [56].

An important issue during extrusion of natural fiber is dimensional change of fibers during compounding. Berzin et al. conducted a series of studies on lignocellulosic fiber breakage in a molten polymer and reported that the natural fibers are subjected to reduction of their diameter by separation of the bundles and a reduction in their length by breakage. Besides, processing conditions such as screw profile, barrel temperature, screw speed and feed rate greatly affects the fiber changes [57], [58].

Figure 2.7. Schematic representation of twin screw extruder and processing of hot melt extrusion [59].
2.7.2. Injection Molding

Injection molding is a process that is able to produce products with high dimensional tolerances, complex geometry components and varying wall thickness in very short-cycle time. It includes five main steps of heating and melting material (extruder), mixing and homogenization of melt (screw), injection of melt into mold, cooling and part ejection (Figure 2.8). When compared to compression molding, injection molding process offers multiple advantages such lower production costs, minimal warping and shrinkage, high function integration and use of recycled materials [60]. This process is governed by a few parameters: filling time, melting temperature, molding temperature, and packing pressure. Injection molding of natural fiber composites is especially relevant to the automotive industry because the majority of polymeric vehicle components are produced via injection molding techniques [34]. After extrusion of agave fiber and PP, the materials were granulated using a lab-scale grinder/chopper, and then dried in a conventional oven for 12 h at 60 °C to reduce the moisture content. The chopped materials were then molded into test specimens with a Boy Machines Model 80M injection molding machine with barrel temperature ranging from 175 to 185 °C and mold temperature of 26 °C [56]. Samples were molded for flexural and tensile tests according to ASTM D 790 and ASTM D 638 standards, respectively [61], [62].
Figure 2.8. Schematic representation of injection molding equipment.
CHAPTER 3. HYBRID CELLULOSE-GLASS FIBER COMPOSITES FOR AUTOMOTIVE APPLICATIONS

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   USA

3.1. Abstract

In the recent years, automakers have been striving to improve the carbon footprint of their vehicles. Sustainable composites, consisting of natural fibers, and/or recycled polymers have been developed as a way to increase the “green content” and reduce the weight of a vehicle. In addition, recent studies have found that the introduction of synthetic fibers to a traditional fiber composite such as glass filled plastics, producing a composite with multiple fillers (hybrid fibers), can result in superior mechanical
properties. The objective of this work was to investigate the effect of hybrid fibers on characterization and material properties of recycled polyamide-6 (rPA6)/recycled polypropylene (rPP) blends. Cellulose and glass fibers were used as fillers and the mechanical, water absorption, and morphological properties of composites were evaluated. The addition of hybrid fibers increased the stiffness (tensile and flexural modulus) of the composites. Glass fibers reduced composite water absorption while the addition of cellulose fibers resulted in higher composite stiffness. The mechanical properties of glass and cellulose filled PA6/PP composites were optimized at loading levels of 15 wt% glass and 10 wt% cellulose, respectively.

Keywords: composites; hybrid fibers; cellulose; glass fiber; automotive; compatibilizer

3.2. Introduction

Increasing global industrialization has resulted in environmental deterioration, including land and air pollution, leading to more global environmental awareness and promoting the investigation of environmentally friendly and sustainable materials. In addition, new legislation in large industrial markets, such as the European Union, has driven the automotive industry to prioritize global sustainability. Even though there is no federal law governing extended producer responsibility (EPR) in the United States, “product stewardship” practices call for shared responsibility among manufacturers and consumers to reduce product impact on the environment [1]. Currently, about 50% of the volume of materials in the cars are made of polymeric materials.
The average usage of plastics in automotive in developed countries and globally averages are 120 kg and 105 kg, respectively, accounting for 10–12% of the total weight of a vehicle [2–4]. The Corporate Average Fuel Economy (CAFE) estimates that a reduction of 10% of an automobile’s weight will reduce its fuel consumption by 6–8% [3]. In attempts to lightweight and decrease the carbon footprint of vehicles, automakers have expressed increased interest in bio-based materials, especially natural-fiber reinforced polymer composites including kenaf, hemp, sisal, jute, and flax [5,6]. Automobile manufacturers have incorporated these natural fibers as the reinforcing phase for polymer composites in door panels, seat backs, headliners, package trays, dashboards, and interior parts. Use of these materials not only increases the “green content” of each vehicle, but can also contribute to reduction in weight, cost, carbon footprint, and lead to less dependence on foreign and domestic petroleum-based fuels [2,5]. These fiber-based composites have the advantage to meet diverse design requirements with a 30% weight reduction and a cost reduction of 20% [7]. Development of hybrid composite reinforced with more than two types of fibers in matrix provides a more favorable balance of material properties. In hybridization, the formulation is made so that the fibers are able to support the loads while the matrix adheres the fiber together for efficient load transfer in the composite [8]. The properties of a hybrid composite are dependent on several factors, such as the nature of matrix; the nature, length, and relative composition of the reinforcements, fiber–matrix interface, and hybrid design [9]. For instance, Kalaprasad et
al. studied the hybrid composited of sisal/glass reinforced polyethylene (SGRP) and reported that the mechanical properties were increased with increase in volume fraction of glass fibers [10]. In another study, Langhorst et al. found that increased fiber loading level in agave fiber filled polypropylene composite enhanced the stiffness of the material [11]. Joseph et al. investigated the mechanical properties and water sorption behavior of phenol-formaldehyde (PF) hybrid composites reinforced with banana fiber and glass fiber. It is found that the tensile, impact, and the flexural properties of the banana fiber-PF composites have been increased by the hybridization of glass fibers [12]. In another study, Kahl et al. reported that the glass fiber content helped in significant increase of the tensile strength and compared to cellulose fiber composites at an overall 16% vol. ratio [13]. The automotive industry has been looking into adapting polymer blends, such as the polypropylene (PP) and Nylon 6 (PA6) blends, for “under-the-hood” applications where thermal stability is a key parameter. PP is commonly used for automobile parts because it is inexpensive, highly processable, and exhibits high water/chemical resistance. However, the relatively low modulus and poor heat resistance of PP makes it unsuitable for use in under-the-hood components [14]. PA6, on the other hand, exhibits high heat resistance, tensile strength, modulus, resistance to corrosive chemicals, and has attractive surface appearance, but readily absorbs moisture resulting in dimensional instability. Thus, blends of PP and PA6 yield intermediate properties that can be suitable for engine covers, air intake manifolds, cooling, and heating components, and cylinder
head cover [15,16]. On the contrary, the opposing polarities of PP and PA6 causes phase separation in the blend and could result in poor mechanical properties [16–18]. In order to improve the mechanical properties and the morphology of PP/PA6 blends, PP grafted maleic-acid anhydride (PPgMA) has been used as a reactive compatibilizer [17,19]. Many studies have investigated the use of polymers blends of PP/PA6 along with compatibilizing agents [20–23]. In addition, there are also works done on the use of short glass fiber as a filler or reinforcement in these polymer blends [24–26]. However, to the authors’ best recollection, there are no studies that have been published investigating the mechanical properties of natural fiber reinforced PA6/PP blends or even cellulose-glass fiber reinforced PP/PA6 composites via injection molding, a technique that is used in the automotive industry. The main objective was to study the dispersion of cellulose and glass fibers in recycled PP/PA6 blends, and to examine the fiber hybridization effect on the mechanical, morphological, and water absorption properties of these polymer blends.

3.3. Materials and Methods

3.3.1. Procurement

Post-consumer recycled polyamide 6 (PA6) and polypropylene (PP) were supplied by Wellman Advanced Materials (Johnsonville, SC, USA). Maleic anhydride-grafted-polypropylene (PPgMA) with a grafting level of 0.5 wt% maleic-anhydride (Fusabond P613) was supplied by DuPont (Wilmington, DE, USA). Cellulose fiber (~150 µm × 20 µm × ~2 µm) and glass fiber (~6–10 mm) were obtained from International Paper (Memphis,
TN, USA) and PPG Industries Inc. (Pittsburgh, PA, USA), respectively. The supplied PP and PA6 had melting points of approximately 160 °C and 220 °C, respectively.

### 3.3.2. Extrusion and Injection Molding

Nine samples were produced, and their formulations are shown in Table 3.1. Each formulation consisted of a 70:30 wt% ratio of PA6: PP and, 6 wt% PPgMA. All composites contained 15–30 wt% glass fibers and 10–30 wt% cellulose fibers. Control groups consisting of an unfilled PA6/PP blend, a 30% glass filled PA6/PP blend, and a 30% cellulose filled PA6/PP blend were produced.

Table 3.1. Experimental design for the preparation of recycled polypropylene and Nylon 6 blends with hybrid fibers composites.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>PA6 (wt%)</th>
<th>PP (wt%)</th>
<th>PPgMA (wt%)</th>
<th>Glass (wt%)</th>
<th>Cellulose (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6/ PP/ PPgMA (Blend)</td>
<td>65.8</td>
<td>28.2</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Blend + 30% Glass fiber</td>
<td>44.8</td>
<td>19.2</td>
<td>6</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Blend + 30% Cellulose</td>
<td>44.8</td>
<td>19.2</td>
<td>6</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Blend + 15% Glass fiber + 10% Cellulose</td>
<td>48.3</td>
<td>20.7</td>
<td>6</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Blend + 15% Glass fiber + 15% Cellulose</td>
<td>44.8</td>
<td>19.2</td>
<td>6</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Blend + 20% Glass fiber + 10% Cellulose</td>
<td>44.8</td>
<td>19.2</td>
<td>6</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Blend + 20% Glass fiber + 15% Cellulose</td>
<td>41.3</td>
<td>17.7</td>
<td>6</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

Extrusion was completed using a twin-screw laboratory extruder (ThermoHaake Rheomex Model PTW25, Fisher Scientific, MA, USA). Prior to extruding, the materials were dried for at least 12 hours at 60 °C in a conventional oven to reduce the moisture content to less than 1% in the fibers and the possibility of hydrolysis the nylon in the blend. The blend pellets and the hybrid fibers (cellulose and glass fiber) were separately...
starve-fed into the extruder using K-Tron gravimetric feeders (Coperion, Germany), and the extruded samples were immediately immersed into a room-temperature water bath. Extruder temperatures ranged from 205 to 220 °C from the hopper to the die. The compounded materials were pelletized using a lab-scale chopper. Pellets were dried in a conventional oven for at least 12 hours at 60 °C to reduce moisture content less than 1% before being injection molded into test specimens using a Boy Machine model 80M injection molding machine (BOY, Exton, PA, USA). Molding occurred using barrel temperatures ranging from 175 to 185 °C, with a mold temperature of 26 °C.

3.4. Test Procedures

3.4.1. Mechanical Testing

Tensile, flexural, and impact tests were performed according to ASTM D638-10 (2010), ASTM D790-10 (2010), and ASTM D256-10 (2010), respectively. All samples were tested in an environmentally conditioned room maintained at 23 °C and 50% relative humidity. Tensile tests were performed on an Instron 3366 machine (Instron, Norwood, MA, USA) using a 5 kN load cell, 50 mm extensometer, and extension rate of 5 mm/min. Three-point bend flexural tests were performed using a 50 mm wide support span and were run at a crosshead speed of 1.25 mm/min. Notched Izod impact tests were performed using a TMI machine (model 43-02-03), (Testing Machines Inc., New Castle, DE, USA) fitted with a 2 lb pendulum. At least six tensile, five flexural, and ten impact test specimens were tested for each formulation. The ultimate tensile strength, yield
strength, elongation at break, and Young’s modulus were determined from the tensile stress-strain curves, while flexural strength and flexural modulus were determined from the flexural stress-strain curves. The impact strength was determined from the notched Izod impact tests.

3.4.2. Water Absorption Test

Water immersion tests were performed according to ASTM D570. At least six specimens of each formulation were pre-conditioned in a 50 °C oven for 24 h to remove all moisture. All the samples were cooled at room temperature for 30 min and then weighed to the nearest 0.001 g. The conditioned samples were then immersed completely in a container of distilled water at 23 °C. The samples were weighed again to the nearest 0.001 g after 24 h, seven days, 21 days, and 35 days until the increase in weight for 3 consecutive weighing averages less than 1%.

3.4.3. Microscopy

The fractured surfaces of the tensile specimens were mounted vertically on sample holder to expose the composite’s cross-section perpendicular to the injection molding flow direction. The cross-sections of samples were observed using a FEI Quanta FEG 250 field emission SEM (Thermo Fisher Scientific, (Waltham, MA, USA). A 10 keV beam was used and backscatter electron images were collected. The low vacuum mode was used with 60 Pa water vapor environments. The working distance was set at approximately 10 mm.
3.4.4. Statistical Analysis

Results were analyzed by ANOVA using SAS (version 9.2; SAS Institute Inc., Cary, SC, USA) and XLStat (version 2013.4; Addinsoft, New York, NY, USA). A significance level of $\alpha = 0.05$ with Tukey adjustment for multiple comparisons was used to determine significant differences and to look at the data in more detail.

3.5. Results and Discussion

3.5.1. Mechanical Properties

3.5.1.1. Strength and Elongation

Figure 3.1 shows the tensile strength and strain at maximum load for the composites. The 30% glass fiber control sample exhibited the highest tensile strength (64% more than unfilled control) while the unfilled control exhibited the highest elongation at the ultimate strength. Contrary to cellulose being a high elongation fiber [6], the 30% cellulose control exhibited the lowest elongation at the ultimate strength. The significant reduction in both tensile strength and elongation may have been caused by agglomeration of cellulose fibers at high loading levels as well as poor adhesion between fiber and matrix. This result is in agreement with Sukri et al., who reported that extension was reduced by 63% when kenaf fiber loading levels were increased from 0 to 30% in rPP/rPA6 blends [17]. Santos et al. also reported that the tensile strength and extension of PA6 and Curaua fiber composites (with fiber content from 20 to 40%) was lower compared to the PA6 control sample [18].
No significant differences were observed in tensile strength and elongation of composites containing 15 or 20% glass fibers. It is speculated that the effect of the glass fiber reinforcement in these composites is maximized near 15% loading level. In more detail, strength as a function of glass content asymptotically approaches a maximum level around 15% filler levels. The increment of filler ratio could also cause more fiber ends to act as stress generators during deformation of composites and this results in causing earlier fiber-matrix debonding and crack development during deformation [27,28]. This assumption is supported by a study by Mishra et al. in which the tensile strength of sisal/glass hybrid polyester composites did not increase with the addition of glass fibers beyond 5.7 wt%. Similarly, the author reported that the tensile strength of a pineapple leaf/glass hybrid polyester composite decreased by about 10% when loaded with more than 12.9% glass fiber [9]. This result is also in line with the studies by Franciszczak et al. in which, addition of 14 vol% glass fiber with PP gave merely 27% further increase in composite's tensile strength [28]. In general, as the cellulose content in the composites increased, the tensile strength and elongation was reduced. While cellulose is a high elongation fiber [6], this reduction may be attributed to the decreased strength of cellulose compared to glass fiber. The glass fiber, relatively stiff, failed first which caused the transfer of the applied load to the cellulose fibers. The hybrid composite exhibited medium elongation (higher compared to the cellulose control but lower compared to the glass control) compared to the individual fiber reinforced composites [12].
Figure 3.1. Tensile strength and elongation at maximum load of unfilled polymer blends and cellulose + glass fiber hybrid reinforced composites.

The results of flexural strength and impact strength for PP, PA6, PPGMA, cellulose, and glass fiber composites are shown in Figure 3.2. The 30% glass fiber control and 30% cellulose control samples exhibited the largest and smallest flexural and impact strengths, respectively. Results from composites containing 15% glass fiber suggest that increasing cellulose loading-levels reduced the flexural and impact strength of the hybrid composites. The impact strength of fiber-reinforced composites depends on many factors, including the nature of the constituents, fiber/matrix adhesion, construction, and geometry of the composites, and test conditions. It is possible that cellulose fiber
agglomeration resulted in the formation of stress concentrations, reducing the energy
needed to initiate crack propagation.

Additionally, replacement of cellulose fiber with glass fiber resulted in an increase
in flexural and impact strength. For example, 15% glass + 15% cellulose composites (30% total fiber content) exhibited lower flexural and impact strength compared to 20% glass +
10% cellulose composites (30% total fiber content) (Figure 3.2).

![Figure 3.2. Flexural and impact strength of unfilled polymer blends and cellulose and glass fiber reinforced composites.](image)

This is consistent with previous studies that reported an increase in impact
strength with glass fiber content. For example, Misra et al. observed a 34% increase in impact strength by the addition of 8.5% glass fiber to sisal-fiber-reinforced polyester composites. In a three-point flexure test, failure occurred as a result of bending failure
and shear failure [9]. It is possible that higher glass fiber content prevents shearing, resulting in an increase in flexural strength.

### 3.5.1.2. Stiffness

Figure 3.3 shows the Young’s and flexural moduli for the composites. The 30% glass composites exhibited the highest moduli of all tested composites. It is also important to note that the hybrid composite of glass and cellulose fiber results in higher flexural strength than the tensile strengths implying the composite has better response to compression stress than tensile. In general, Young’s and flexural moduli increased with increasing cellulose and glass fiber content and these results are in agreement with the Rule of Hybrid Mixture (ROHM). This result is in agreement with Kahl et al., who reported the increase in tensile modulus with increasing content of glass fibers in the PP/glass fiber and cellulose composite due to the higher modulus of glass fiber [13]. Several mechanisms, such as compression, shearing etc., take place together during the stiffness test [29]. The significant increase in stiffness is due to the reinforcement effect of the cellulose and the increased resistance to shearing with the addition of glass fiber. This result is supported by a study of Sukri et al. who studied rPP, rPA6 and kenaf fiber by varying the fiber content from 10 to 30% [17]. Lei et al. also found a 50% increase in modulus by adding 30 wt% of bagasse to recycled high density polyethylene (rHDPE) [30].
3.5.1.3. Water Absorption

The water absorption of PA6/ PP/ PPGMA composites is shown in Figure 3.4. The highest and lowest water absorptions during a 3-week period was exhibited by 30% cellulose control (5.5%) and 30% glass fiber (2.89%), respectively. The hydrophilic OH groups on the surface of the cellulose crystallites or in the amorphous region may be available for bonding with water if there is no crosslinking with other OH groups. The water bonding at the amorphous region and the free water in the cellulose cavities cause an increase in absorption [31]. Among the composites, there was no significant difference in water absorption with increasing cellulose content. However, increasing the
composite’s glass fiber content from 15 to 20% significantly reduced water absorption. The water enters through the interface and can diffuse through the porous structure of the fibers. Water penetration and diffusion mainly occur at the fiber–matrix interface and through the fibers via capillary mechanism [31]. When glass fiber was incorporated, the water uptake decreased, as the diffusion of water is not possible through glass fiber, as shown in Figure 4. In more detail, it is seen that in general, water absorption is inversely proportional to glass content. Similar observation has been seen by Joseph et al. who reported that the incorporation of a small amount of glass fiber (12%) increased the resistance of banana/PF composites to water sorption very effectively [12].

Figure 3.4. Water absorption of unfilled polymer blends and cellulose and glass fiber reinforced composites.
A summary of the mechanical results is shown in Table 3.2. Incorporation of glass fibers increased the strength and moduli of the PA6/PP/PPgMA blend composites. The cellulose control group reduced the strength, elongation, stiffness, and increased water absorption of the polymer composites. On average, the composites with glass/cellulose fiber mixtures showed only increased Young’s modulus and flexural modulus of the composite and a reduction in tensile strength and elongation compared to the unfilled control. It has no effect on the flexural, impact strength and water absorption (for 10 and 15% only). The addition of glass and cellulose fibers improved the stiffness of the polymer blend, but all composites showed lower strength and elongation compared to the unfilled polymer blend. In this study, 15% glass + 10% cellulose composites exhibited the best balance in properties. Sreekala et al. analyzed the tensile, elongation, and stiffness properties of phenol formaldehyde reinforced with glass and oil palm fibers composites as a function of fiber composition. The author reported that 40 wt% fiber loading, composites with 0.74 volume fraction of oil palm fiber (29.6% oil palm fiber, 10.4% glass fiber) exhibited the highest tensile properties among the hybrid composites as excellent dispersion of the fibers and increased oil palm fiber/glass compatibility occurs at this composition [29].
Table 3.2. Details of mechanical properties for PP, PA6, and hybrid fibers (cellulose and glass fibers) composites. Samples containing the combination of one or both fibers were compared to their unfilled control, lacking the hybrid fibers. Boxes labelled (+) exhibited property improvement, white boxes with (o) experienced no significant property change, and boxes (-) experienced property degradation.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Single Filler Composites</th>
<th>Dual Filler Composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glass Fiber</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Strength</td>
<td>Tensile</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Flex</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Impact</td>
<td>+</td>
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<tr>
<td>Elongation</td>
<td>Tensile</td>
<td>-</td>
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<tr>
<td></td>
<td>Young’s Modulus</td>
<td>+</td>
</tr>
<tr>
<td>Stiffness</td>
<td>Flexural Modulus</td>
<td>+</td>
</tr>
<tr>
<td>Absorptivity</td>
<td>Water Absorption</td>
<td>o</td>
</tr>
</tbody>
</table>

3.5.2. Morphological Properties

Scanning Electron Microscopy

SEM images in Figure 3.5 show morphological differences between the control polymer blends and composite containing the blend and the glass and cellulose fibers. The micrograph of Figure 1a illustrates the well dispersion of glass fibers in the polymer blend matrix. Figure 1b shows cellulose fibers within a polymer blend matrix (cellulose fibers are circled). The matrix surrounding the cellulose fibers is cracked, suggesting that adhesion between the fiber and matrix is weak and this is in line with the low tensile strength achieved in the results. The micrographs of blend + 15% glass fiber + 10% cellulose fiber suggests that the area of the cellulose fibers is surrounded with glass fibers, which effectively reinforces the fiber and matrix together, leading to good interfacial
adhesion between the two and this in result brings the tensile property of this formulation close to the one of neat blend formulation.

Figure 3.5. SEM images of the fracture surfaces of (a) blend + 30% glass fiber; (b) blend + 30% cellulose fiber (circled); and (c and d) blend + 15% glass fiber + 10% cellulose fiber at 150× and 500× respectively.

3.6. Conclusion

This study determined the effects of adding cellulose and glass fibers on the mechanical, morphological, and water absorption properties of PP/PA6/PPgMA composites. In general, the mechanical properties were enhanced by addition of glass
fibers alone: tensile strength, Young’s modulus, flexural modulus, flexural strength, and Izod impact strength were increased at 30% glass fiber load. Even though the composites with hybrid (cellulose and glass) fibers did not perform better than the control PP/PA6 blend, increasing the cellulose content from 10 to 20% increased the Young’s and flexural modulus and water absorption, while flexural strength and elongation was reduced. In addition, when the glass fiber content was increased from 15 to 20% in the composite, the flexural strength, Young’s modulus and impact strength improved as well. There are no significant differences observed in the different loading levels from 10 to 30%. The 15% glass + 10% cellulose fiber composite showed the best properties among the composites with hybrid (cellulose and glass) fibers as the modulus and percentage elongation at break was the highest. Effect of fiber reinforcement on thermal properties and effect of compatibilizer should also be studied in the future to learn more about the thermal stability, crystallinity, compatibility, and to improve the properties of these composites.


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Conflicts of Interest: The authors declare no conflict of interest.

3.7. References


CHAPTER 4. AGAVE FIBER - POLYPROPYLENE BIOCOMPOSITES: EFFECT OF CHEMICAL MODIFICATION TO INCREASE INTERFACIAL BONDING

Modified from a manuscript to be submitted to Composites Part B: Engineering

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4.1. Abstract

There has been a rapid growth in research and innovation in the area natural fiber composites over the last few years because of their advantages such as low cost and low environmental impact. However, the major limitation of using natural fibers are their high degree of moisture absorption, pretreatment and wide variation in properties. This paper investigates the effect of surface treatments on natural fibers to maximize the matrix/fiber interfacial strength as well as the stress transferability in the composites. The effect of chemical treatment on the tensile properties of agave fiber reinforced polypropylene (PP) composites was investigated. Treatments using chemicals such as sodium hydroxide, sodium chlorite and acetylation were conducted to improve the
bonding at the fiber polymer interface. All the treatments significantly increased the tensile and stiffness properties of the composites compared to the control sample (no treatments), but to varying degrees. Among the various treatments, acetylation treatment of fiber reported maximum interfacial interactions.

Keywords: composites; natural fibers; blue agave; automotive; chemical treatments

Introduction

Global environmental factors such as depletion of petroleum resources and plastic waste, sustainability principles and green chemistry together with growing awareness are acting synergistically to provide the impetus for new materials and products that are eco-friendly while reducing our dependence on petroleum. Composite materials, especially biocomposites are well aligned this new paradigm shift. Composite materials are also appealing to the market as they combine properties that are not found in a single material. Natural fibers have specifically become crucial in composite applications because of the demand for recyclable and reduction of raw material use. This change in trend toward greater utilization of this biocomposites materials has not only been driven by environmental factors but also economic factors. The natural fiber composites market is a multibillion-dollar business. This market was worth $3.36bil in 2015 and is projected to reach $6.5bil in 2021 at a Compound Annual Growth Rate (CAGR) of 11.68% [46].

Transportation is one of the sectors with a relatively fast growing end-use segments adopting biocomposites application because of their specific high strength [44].
In the United States, the current Corporate Average Fuel Economy (CAFÉ) standards require that automakers increase the fuel economy of their cars to be on average of 54.5 mpg by 2025 [40], [63]. Thus, high specific strength materials are important to reduce vehicle weight and efficiency. Most of the natural fiber biocomposites are used in non-structural components such as storage bins, coin trays, battery and fuse cover and interior panels to replace traditional synthetic fibers such as e-glass and talc. Natural fibers have the potential to be superior to glass fiber composites in because of their lower environmental impact during production, competitive performance thus reducing polymer content and most importantly, it the end of life incineration of natural fibers results in recovered energy and carbon credits [64]. The integration of natural fibers not only help in weight and cost reduction but may also lower the possibility of injury to passengers in case of an accident because of their relatively high impact strength.

Some of the common biobased materials that are used usually derived from renewable agricultural feedstocks such as plant fibers, wood, grasses and agricultural byproducts. In Mexico, tequila industry represents an important economic activity. Tequila has a recognized Appelation of Origin (AOC) meaning that it is covered by and named after a specific geographical region i.e. Jalisco and that its characteristics are derived from the location, climate and cultural traditions of that specified area [65]. Only plants with intense blue color (*Agave tequilana* Weber var. *Azul*) are allowed to be harvested and used for tequila production by the Mexican Law. According to the
National Tequila Regulatory Chamber (CNIT), a total of 309 million liters of tequila was produced in 2018 from 1,138,800 tons of agave stem (pina) resulting in second-highest volume ever recorded [29], [66]. After the pina is cooked, crushed and milled, a byproduct called agave bagasse is produced that represent 40% of the total weight [28]. In 2018 alone, approximately 455,520 tons of bagasse were produced from the tequila production. The agave fiber bagasse is accumulated in large areas and are used for composting, burned to generate electricity or sent to a landfill [23], [30]. However, it is important to consider the use of this blue agave (A. tequilana) for a higher value product, such using them as a prospective reinforcing agent in biocomposites.

Several scientific studies have been conducted on blue agave fiber bagasse as a filler or reinforcing agent in both biobased and petroleum based polymeric matrices [27], [55], [56], [67]–[69]. In addition to blue agave bagasse, there are also other works on fiber biocomposites within the agave genus but different species such as Agave sisalana, Agave Americana and Agave fourcroydes that has been studied [51], [70]–[74]. According to the work by Langhorst et al., the chemical compositions and the mechanical properties of the single fiber varies between different species of agave plant. For instance, Agave tequilana, Agave sisalana and, Agave Americana have cellulose composition of 64.9, 47-62 and 63.19 respectively. Alternatively, whether the raw fiber could enhance the mechanical properties of polymers as fillers effectively is also of interest, especially in the automobile manufacturing enterprise. In addition, this is the only published work that has evaluated
the mechanical behavior of injection molded blue agave fiber, a relevant manufacturing process especially in the automotive industry [56].

This study evaluated the application of raw agave fiber with surface treatment in order to determine whether it could effectively enhance the mechanical properties of polymer composites applied in the automotive industry. Polypropylene (PP) was chosen as the polymer matrices because it has been widely applied in automotive vehicles. Composites with various agave fiber loading contents (up to 40 wt %) and chemical treatments (alkaline, acetylation and sodium chlorite) were prepared by extrusion and injection molding, and their mechanical and thermal properties were studied. The raw agave fibers were washed to remove residual sugars prior to testing. Preliminary tests from the washing showed that about 0.8 (g/g.d.m.) amount of residual sugar per unit of fiber can be removed from the washing step.

4.2. Materials and Methods

4.2.1. Materials

A polypropylene (PP) resin was used for the experimental work, manufactured by RheTech Products, namely P100-00. The resin had a density of 0.905 g/cm³. The melt indices (MI) of 20g/10min (230 °C). The melt density and thermal conductivity were approximately (@ 230 °C) 0.739 g/cm³ and 0.20 W/(m °K), respectively. Agave fibers were obtained from Diageo Corporation in blue agave bagasse form.
4.2.2. Preparation of Agave Fibers

Agave fiber bagasse was separated into heterogeneous fibers of varying lengths and the pith, a non-fibrous spongy organic material in the form of fine particles [10]. The raw fiber was then milled on a H28 Pilot Scale Circ-U-Flow hammer mill with a 4.76mm screen to separate the fiber-fiber entanglement and mineral contaminants. Milled agave fibers and water were placed at a 1:4 (solid:liquid) volume ratio in a 250-liter Feldmeier jacketed tank and stir-agitated with a Lightnin prop-type variable speed mixer. The mixture was heated to 70°C and stirred for 24 hours, after which the fibers were removed with a filter. For three wash cycles, this process was repeated two more times, totaling to 72 hours of agitation. Following the wash process, the fibers were then strained and dried in a Humboldt H-30135 convection oven (Elgin, IL, USA) at 105 °C for approximately 48 hours. The dry fibers were then chopped using a with an Ingento paper cutter to approximately 10mm. Short fiber enabled easier processing. Figure 4.1 shows a photograph of the raw, milled and chopped fiber.

Figure 4.1. Raw, milled and chopped agave fiber bagasse
4.2.3. Extrusion and Injection Molding

Prior to extruding PP and AF, the resins and the agave fiber were dried for 12 hours at 85 °C in conventional oven to reduce moisture. The fiber and PP were then hand-fed according to formulations in Table 4.1 into the Leistritz 18 mm co-rotating twin-screw extruder (Nuremberg, Germany) with a barrel – l/d ratio of 25:1. The screw speed was set at 240 RPM. Extruder temperature was set at 195, 205, 210, 210, 215, 220, and 210 °C from zone 1 (hopper) to zone 8 (dye). Following extrusion, the extruded composites went through a water bath and were then fed into a pellet chopper. The pellets were dried for 16 hours at 60 °C to reduce moisture content before injection molded into test specimens using BOY 22S, 28-mm injection molding machine (Exton, USA). The temperature profiles utilized were 180, 190, 200, 195 and 190 °C from zone 1 (hopper) to zone 5 (dye), with a mold temperature of 52 °C. The dog bone specimen conditioned at room temperature for a week prior to tensile testing.

Table 4.1 Formulation details of PP and agave fiber composites.

<table>
<thead>
<tr>
<th>PP Resin (wt.%)</th>
<th>Agave Fiber (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>
4.2.4. Chemical Treatments of Agave Fibers

4.2.4.1. Alkaline Treatment

For the fibers that were alkaline pretreated, the milled agave fibers (no prior washing) were soaked 5% NaOH solution at 30°C maintaining a liquor ratio of 1:20. The fibers were immersed in the alkali solution for 4h. The fibers were then removed and washed with water to remove excess NaOH on the fiber surface. Fibers were then neutralized with dilute acetic acid and washed with water again until a final pH of 7 was reached. The fibers were then dried in oven at 50°C for 24h.

4.2.4.2. Acetylation Treatment

For the fibers that were acetylated, the alkali-treated fibers were soaked in glacial acetic acid for 1 h at a liquor ratio of 1:20. Fibers were separated by decanting and soaked in acetic anhydride containing 2 drops of concentrated H$_2$SO$_4$ for 2 min. The fibers were then removed, washed well with water and dried in an oven at 50°C for 24 h.

4.2.4.3. Sodium Chlorite Treatment

The alkali-treated fibers were soaked in sodium chloride at a liquor ratio of 1:20 at a temperature of 70°C for 2h, washed with distilled water and dried in the dryer at 70°C for 24 h.

4.3. Test Procedures

4.3.1. Mechanical Testing

Tensile tests were performed according to ASTM D638-10 (2010) [60]. All the samples were tested in an environmentally conditioned room maintained at 23°C and
50% relative humidity. The tensile tests were performed on an Instron 3367 machine (Instron, Norwood, USA) using a 30 kN load cell and extension rate of 5 mm/min. At least ten tensile test specimens were tested for each sample. The ultimate tensile strength, yield strength, elongation at break and Young’s modulus were calculated from a constant cross head displacement.

4.3.2. Density Test

The average densities of the composites were determined from dry initial weights and immersion of thermally compounded pelletized samples. Dry convection oven sample weights were measured and recorded. Samples were then submerged into 2-propanol and volumetric displacement measured within a graduated cylinder. The average density was calculated as defined in Equation 1, where \( \rho_c \) is the composite density, \( m \) is the dry mass of the composite sample, \( V_i \) is the initial volume, and \( V_f \) is the final volume measured within the graduated cylinder after composite was inserted.

\[
\rho_c = \frac{m}{V_f - V_i} \tag{1}
\]

4.3.3. Fourier-Transform Infrared Spectroscopy (FTIR)

FT-IR spectra of bio-filler reinforced thermoplastic films were recorded in the range of 4000–650 cm\(^{-1}\) (Frontier Optica FT-IR spectrometer equipped with UATR accessory, Perkin-Elmer, Waltham, MA, USA).
4.3.4. Thermogravimetric Analysis (TGA)

To determine the degradation temperature of the agave fibers after surface modification, the rate of weight change in the treated fibers as a function of increasing temperature were measured with a TA instrument Q50 V20.13 (New Castle, DE) thermal gravimetric analyzer under nitrogen atmosphere. Each sample of 10 mg was placed in a ceramic pan and heated from 10 to 200 °C at a heating rate of 5 °C/min, and the degradation profile was analyzed. These results were used to determine the thermal stability for the fibers during melt extrusion processing with PP.

4.3.5. Statistical Analysis

Results were analyzed by ANOVA using SAS (version 9.2; SAS Institute Inc., Cary, NC) and XLStat (version 2013.4; Addinsoft, New York, NY). A significance level of $\alpha = 0.05$ with Tukey adjustment for multiple comparisons was used to determine significant differences.

4.5. Results and Discussion

4.5.1. Effect of Fiber Loading Level

The effect of fiber loading on the tensile strength and the maximum elongation of the agave fiber -PP composites is shown in Figure 4.2. The composites are compared with the mechanical properties of neat PP resin in order to study the reinforcement effect of the fiber. The agave fiber content is varied from 20 to 40 wt%. There were small statistically significant differences between the tensile strength of neat PP (0% AF) and the composites with agave fiber as the addition of agave fibers slightly reduces the tensile
strength of the composite. The addition of 20, 30 and 40% agave fiber reduced the composite strength by 18, 18 and 22% and the elongation by 29, 33 and 45% respectively. The data is supported by the studies conducted by several authors who found reduction of tensile strength and elongation on non-compatibilized natural fiber-PP composites [24, 25]. Li et al. produced biocomposites with flax fiber content from 10 to 30 wt.% with high-density polyethylene (HDPE) via extrusion and injection molding and reported increase in tensile properties but reduction in elongation as the fiber loading level increases [77]. The reduction in elongation as the fibers increased could be as a result of fiber agglomeration and created void in the composites [78]. Generally, the tensile properties of the composites are known to significantly improved by adding fiber reinforcement to the polymer matrix since fibers have much higher strength and stiffness values than the polymer matrix. In this study for instance, the single strand agave fiber has a tensile strength value of 59.3 MPa, 21% higher compared to the PP matrix with a tensile strength of 37.9 MPa [55]. However, the discrepancies in the result may be mainly due to incompatibility between hydrophilic natural fibers and hydrophobic polymer matrices, thermal degradation, fiber length, orientation and breakage during processing, poor fiber wetting by matrix. In a study by Bourmaud et al, the authors reported that higher microfibrillar angle of the fiber induces a decrease in their mechanical properties [79]. The increase in void content in the polymer matrix could be another reason of reduction of tensile strength when the fiber loading level is increased [42]. The chemical
modification the fiber surfaces, use of compatibilizers or coupling agents are normally required to improve the interfacial adhesion between fiber and matrix [33], [51], [80], [81].

![Graph](image)

Figure 4.2. Tensile strength of agave fiber-PP composites at different fiber loading level.

In general, the specific strengths are inversely proportional to the addition of agave fiber at levels between 0 and 40% in Figure 4.3. However, the specific strengths between 20% and 30% agave fiber concentration are comparable. This trend is expected as the specific strength were calculated as the ratio of ultimate tensile strength to density. However, from Figure 4.4, it can be observed that the specific stiffness of the composite increases as the agave fiber level increased from 0 to 40% loading level. The addition of agave fiber helps in the reduction of the density of the composite that is crucial in meeting the goal of weight reduction by replacing the traditional fillers. Even though the tensile strengths and Young’s moduli of natural fibers are lower than the fillers such as e-glass
or talc, but their specific properties i.e. stiffness are comparable making natural fiber an ideal replacement to produce lightweight automotive parts [10].

Figure 4.3. Specific strength of agave fiber-PP composites at different fiber loading level.

Figure 4.4. Specific stiffness of agave fiber-PP composites at different fiber loading level.
4.5.2. Effect of Surface Modification

The effect of different types of surface modifications i.e. alkaline treatment, acetylation and sodium chlorite of agave fiber the tensile strength and Young’s modulus of the composite made with 20 wt.% agave fiber is shown in Figure 4.5. The milled and chopped agave fiber (no treatment) composite is used as a control for comparison. All the chemical treatments showed improvement in both tensile strength and modulus. In this case, sodium hydroxide treatment showed to have the highest tensile strength (33.07 MPa). The improvement is potentially caused by the removal of impurities, wax, partial hemicellulose from surface which increases the fiber surface roughness and preventing the moisture absorption via the removal of the coat of OH groups of fiber. This results in better bonding between the fiber and matrix. Similar observation is found in other studies which have reported that tensile properties increased with alkaline [72], [82], [83]. The composite with acetylation-treated fibers showed a higher increase in Young’s modulus than that of alkali treated fibers. During acetylation, the hydroxyl groups on the fibers are replaced with an acetyl functional group that makes the fiber more hydrophobic. Besides, the removal of lignin and extractables slightly increases cellulose content and a small portion of hemicellulose converting to acetylated hemicellulose. Bledzki. et al. reported similar observation of increase in tensile strength of flax fiber-polypropylene composites with increasing degree of acetylation up to 18%. The improvement in mechanical properties can be attributed to the removal of outer surface of fiber, increase
in cellulose content and effective surface area, increase interfacial adhesion and physical and chemical changes induced by fiber [84], [85]. Sodium chlorite treated fiber has also shown improved mechanical properties compared to the control sample as found in another study in which composite made with LLDPE and bleached flax fiber showing an increase in tensile strength [86].

Figure 4.5. Tensile strength and Young’s modulus of chemical treated PP and 20% agave fiber biocomposites.

4.5.3. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to examine the chemical changes of the agave fibers. Figure 4.6 shows the FT-IR spectra of raw agave fibers, and chemically treated (sodium
hydroxide, acetylation and sodium chlorite) agave fibers. Similar to all lignocellulosic fiber, agave fiber bagasse presents the typical signals of cellulose and lignin combination. FTIR spectrum of raw agave fiber illustrates a broad peak at 3339 cm\(^{-1}\), which correlates to the stretching vibrations of hydroxyl groups from the cellulose in the agave fiber bagasse. The peak at 2923 cm\(^{-1}\) correlates to C–H group while peak at 1738 cm\(^{-1}\) corresponds to the C=O group of hemicellulose, waxes, pectin, and lignin [87]. The peak at 1617 cm\(^{-1}\) was due to H–O–H group stretching of absorbed moisture and for lignin C-H deformation. The milder peaks at 1375 cm\(^{-1}\) to 1427 cm\(^{-1}\) were attributed to –CH, –CH\(_2\), or –CH\(_3\) groups [55]. The peak at 1318 cm\(^{-1}\) was due to the –CH group from the cellulose. The peak at 1229 cm\(^{-1}\) corresponds to C–O–C and C=O groups of lignin [70]. The peak at 1028 cm\(^{-1}\) was attributed to C–O stretching vibrations of the cellulose. The peak at 893 cm\(^{-1}\) was due to β–glycosidic linkage of the agave fiber [55].

As shown in the sodium hydroxide and sodium chlorite treatments, the efficiency of the treatment is verified by the disappearance of peak located at 1724 cm\(^{-1}\) due to the presence of conjugated carboxylic C=O group in ester linkages or due to the removal that are associated to the lignin or wax in natural fats [88]. The bands related to lignin aromatic ring (guaiacyl and syringyl rings) vibrating at 1602 cm\(^{-1}\) decreased. The peak around the range 1250 cm\(^{-1}\) originated from the C–O stretching in guaiacyl ring was also significantly decreased [89]. The band at 1467 cm\(^{-1}\) was attributed to reduction of methyl group deformation and the aromatic ring vibrations [90]. For the acetylation treatment, there is
also a slight presence of three acetyl bands at the 1724 cm\(^{-1}\) for C=O ester, –C–CH\(_3\) at 1379 cm\(^{-1}\) and for –C–O– 1267 cm\(^{-1}\) [18, 43].

Figure 4.6. FTIR spectra of chemically treated agave fibers

4.5.4. Thermogravimetric Analysis (TGA)

The thermal properties of agave fibers are important to be examined to evaluate their applicability in biocomposites processing with TPO and other thermoplastics, where the temperature increases above 200 °C. Figure 4.7 shows the TGA curves of the untreated (raw) and chemically treated (alkaline, acetylation and sodium chlorite) agave fibers. The fibers show a three-step decomposition profiles. The first one, a small weight loss (< 10%) for fiber samples is observed from 35-100 °C range due to the moisture evaporation in the fibers. The hydrophilicity nature of fibers subject them to a
dehydration process in which the crystal or the water absorbed during the processing. The weight of the fibers remained relatively constant up to 230 and 260 °C for untreated and treated fibers, respectively indicating thermal stability of the blue agave bagasse fiber that could be due to high value of crystallinity (70%) and high lignin content [22]. The second step corresponds to hemicellulose and glucosidic link depolymerization, starts at about 300 °C; and the third step by the thermal degradation of α-cellulose occurs between 380 and 420°C. Lignin, on the other hand presents a broad peak through the range, decomposing between 280 and 500°C [92], [93]. The TGA graph also suggests that all these fibers can be used safely up to the maximum temperature of 230 °C but with chemical treatments, the fibers can be used for processing temperature up to 260 °C.

The degradation temperatures in all three steps for the treated fibers are higher compared to the one of raw fiber, demonstrating that chemical treatments had a substantial effect on the thermal degradation profile of fibers. The increase in thermal stability can be attributed to the removal of volatile substances, organic and inorganic residues which decompose earlier than the major components and reduction in lignin and hemicellulose percentages during the treatment in the fiber [94]. Similar increments in thermal stability have been found for esterification of blue agave fiber [27], mercerization and bleaching of coir fibers and dewaxing, alkali treatment and methyl methacrylate grafting on sisal fibers [95].
Figure 4.7. TGA curves of chemically treated agave fibers.

4.5.5. Microscopy

Scanning electron microscopic images of the untreated and chemically treated fibers are shown in Figure 4.8. Even though it is rather difficult to quantify the efficiency of the treatment, it is necessary to run the SEM analysis since the surface modifications did not only modify the chemical nature of the fiber but also their morphology as shown in the images. The raw fiber on Figure 8(a-c) reveals the agave fiber strands gathered in a bundle with some inorganic crystals, cracks and microvoids on the surface at different magnifications. Non uniform patches on the fiber surface are also present probably due to the waxy and fatty acid components on the fiber. Similar observation is also seen with
Sansevieria cylindrica fibers [96]. Water transport unit in spiral tracheids and amorphous waxy cuticle layer is also found on untreated Agave Americana L. fiber [70]. After chemical treatments, all the fibers are moderately free from the fiber strand bundle due to the slight removal of the pectic substances that act as cementing materials for the fibers. These chemical treatments amount of cellulose and helical fibrils exposed on the fiber surface by removing some amount of lignin, wax and oils covering the external surface of the fiber cell wall [97]. From the SEM images, the treatment used affected the surface morphology of the fibers. For sodium hydroxide on Figure 8(d-f), a less uneven superficial morphology and a better defined cellulose microfibrils is observed compared to the untreated indicating removal of waxy and fatty acids residues. Ben Sghaier et al. has also reported removal of the parenchyma cells with this treatment [94]. Acetylation (g-i) showed different degrees of cellulose microfibrils separation rest of lignocellulosic material in the natural fiber. Complete defibrillation can be observed for the sodium chlorite treatment demonstrating the more prominent removal of hemicellulose and lignin that interconnects the cellulose fibrils through the bleaching process [98].
Figure 4.8. SEM images of untreated and treated agave fibers: (a,b,c) untreated; (d,e,f) sodium hydroxide; (g,h,i) acetylation; and (j,k,l) sodium chlorite.
4.6. Conclusion

The agave fiber-PP biocomposites were successfully prepared in order to investigate the effect of fiber addition on mechanical properties on the composites at various fiber loading level between 0 and 40 wt.%. The tensile strength and elongation of the composite were inversely proportional to the loading level of agave fiber content. The composite with 20 wt.% loading level had better mechanical properties (strength and stiffness) compared to the other composites. The addition of agave fiber also helped in increasing the specific stiffness because of the reduction of the density of the composite. This factor is crucial in meeting the goal of weight reduction by replacing the traditional fillers. Chemical treatments of the agave fiber were investigated for 20 wt.% agave fiber composite and it was observed that all the chemical treatments improved in both tensile strength and Young’s modulus, especially the acetylation pretreatment. This enhancement in interfacial bonding could be attributed to the removal of lignin, pectin and other impurities that helps the PP matrix to bond better to the fiber. The FTIR spectra suggested that the efficiency of the chemical interaction occurred on the agave fiber. Because there were new chemical bonds created as a result of chemical treatments, the thermal properties of the agave fiber did change by the various chemical treatments. Future studies will investigate water absorption, crystallinity of the composite and compatibilizer effect to learn more about the to improve the properties of these composites. A fiber-debonding test will also be performed to better quantify fiber-matrix
adhesion. In summary, blue-agave and PP composites have the potential to replace traditional filler components, resulting in a lower part density and lower overall vehicle carbon footprint.

4.7. References


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CHAPTER 5. AGAVE FIBER REINFORCED THERMOPLASTIC OLEFIN (TPO) COMPOSITES: EFFECTS OF COMPATIBILIZATION

Modified from a manuscript under review in Industrial Crops and Products

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5.1. Abstract

Talc-filled thermoplastic olefin (TPO) reinforced with blue agave fiber composites were prepared with three different compatibilizers and their thermal-mechanical, morphological, and water absorption properties were characterized. The objective of this study was to investigate the use of blue-agave bagasse fibers as a reinforcing agent in TPO composites. The effects of addition of 20% agave fiber and compatibilizers (WPP, Adicco 9320, and maleic anhydride grafted polypropylene, PPgMA) on the properties of
the TPO-agave fiber composites were comparatively studied. Samples were produced with a twin-screw extrusion and injection molding. The compatibilizers have significant improvement on the tensile, flexural strengths, and water absorption; however, no considerable effect on impact strength, elastic or flexural moduli was observed. The composite comprised of TPO, WPP, and agave fibers exhibited the best mechanical properties. The addition of agave fiber increased the elastic and flexural moduli but reduced the elongation and impact strength. Overall, average TPO-agave fiber biocomposites exhibited comparable mechanical properties to pristine TPO and its components as used in automotive industry, while offering environmental and economic advantages.

Keywords: Composites; Natural fibers; Blue agave; Automotive; Compatibilizer

5.2. Introduction

Biocomposites material are of great importance to the automotive industry to meet the consumer needs and regulatory requirements on being sustainable and on reducing the dependence on petroleum resources. Besides that, natural fiber biocomposites industry is growing at a Compound Annual Growth Rate (CAGR) of 11.68% and is estimated to reach $6.5bil in 2021. The automotive sector plays a huge role as one of the highest application of biocomposites [46]. Automakers are always in search of adopting new materials to meet the current Corporate Average Fuel Economy (CAFÉ) standard that mandates light duty vehicles to have an average corporate fuel economy of 54.5 mpg
by 2025 [50], [63]. According to an estimate from IHS Automotive, carloads must be reduced by 30% in order to meet the standard set by the Federal Law in the United States. Many automakers (Ford vehicle currently uses 20–40 pounds of renewable materials) have adopted and established sustainable policies to emphasize the corporations’ environmental responsibilities and their continued investment in light weighing technologies is helping them reduce overall vehicle weight and improve fuel economy [32], [33].

Natural fibers are attractive because of their low density, easy of processing, low cost, enhanced energy recovery, CO$_2$ neutrality, biodegradability and non-abrasiveness [5], [99]–[101]. The use of natural fiber composites in the automotive industry is growing by more than 20% annually, with the full market projected to reach $6.5 billion by 2021, at a compound annual growth rate of 11.7% between 2016 and 2021. [46], [47], [62]. Furthermore, these fiber based composites have the potential of contributing greatly to the automotive manufacturer’s final goal of a 30% weight reduction and a cost reduction of 20% [35], [100]. Cellulose, kenaf, flax, hemp, jute are just few of the fibers that have shown to be potential alternatives to traditional fillers [102]–[104].

Blue agave (also termed as *Agave tequilana*, *A. palmaris* or *A. Americana L*) is a large desert succulent that grows radially and up to 2m tall [20]. A native to Mexico, blue agave plant is mainly used to produce distilled spirit tequila. The Mexican Law allows only the agave with intense blue color (*Agave tequilana Weber var. Azul*) to be harvested and used
for tequila production. Tequila is prepared by cooking the core or commonly known as ‘pinā’ followed by shredding, milling and extracting the agave juice. Relatively large amounts of blue agave bagasse (with fiber and pith) are formed as a byproduct of this process are often underutilized and have caused accumulation and disposal problem [24]–[27]. These materials can be acquired for a relatively low cost and can help automotive manufacturers to replace high-density fillers to produce more sustainable, lightweight products as well as new markets and revenue streams for farmers.

One of the most common plastics used by the automotive industry is thermoplastic polypropylene (PP). Polypropylene was first synthesized in 1950s and remains popular for its features of being inexpensive, easy processability, excellent mechanical and electrical properties, and also good dimensional stability and impact strength [43], [51]. Thermoplastic olefin (TPO) is typically produced by blending PP with uncured ethylene-propylene rubber (EPR) and additional fillers and additives. Thermoplastic olefin is similar to impact toughened PP or a thermosetting rubber depending on the ratio of PP and EPR. The automotive industry represents the largest single market of TPO compounds as it can be processed as other thermoplastics while exhibiting higher impact strength and elasticity properties than polypropylene [105]. In addition, TPO offer many benefits such as lightweight, recyclable, inexpensive, and easily molded into complex geometries [43], [106]. Talc filled TPO’s are commonly used in automotive applications, including instrument panels, console substrates, hard trim, and appliques. The addition
of 20 and 40% talc in a polymer is shown to increase stiffness more than 0.33 and 0.5 times respectively [107]. Previous studies have investigated the use of blue-agave fibers as reinforcing agents in polypropylene matrices [56]. However, these studies showed that the resulting composites exhibited low impact strength and flexural moduli. The objective of this study was to improve the impact strength and flexural modulus of blue-agave fiber reinforced composites. This study investigates the properties of a hybrid TPO composite containing agave fiber and talc reinforcement.

5.3. Materials and Methods

5.3.1. Procurement

Thermoplastic olefin (TPO) containing 5 wt% talc was supplied by Washington Penn Plastic (WPP), Pennsylvania. The polymer had a density of 0.93 g/cm³ and a melt flow index (MI) of 26.7 g/10 min. Agave fiber was supplied by BioSolutions, Mexico. Three different compatibilizers were obtained from commercial sources; Washington Penn Plastic (Pennsylvania, USA) provided a proprietary compatibilizer, AddiCo 9320 (Mexico) provided a styrene-co-methyl methacrylate-co-glycidyl methacrylate) (MMA-GMA) copolymer compatibilizer, and DuPont (Wilmington, USA) provided polypropylene grafted maleic anhydride compatibilizer (PPgMA; Fusabond P613). These compatibilizers will labeled as C1, C2 and C3 respectively throughout the paper. The experimental design of the study is shown in Table 5.1 below.
Table 5.1. Experimental design for the preparation of agave fiber and talc reinforced thermoplastic olefin (TPO) composites with different compatibilizers composites

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Formulation</th>
<th>Final Composition</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>TPO [wt%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Talc [wt%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agave [wt%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Compat. [wt%]</td>
</tr>
<tr>
<td>TPO</td>
<td>TPO + 5% Talc</td>
<td>95</td>
</tr>
<tr>
<td>TPO + AF</td>
<td>TPO + 5% Talc + 20% agave</td>
<td>76</td>
</tr>
<tr>
<td>TPO + C1 + AF</td>
<td>TPO + 5% Talc + 2% WPP + 20% agave</td>
<td>74.1</td>
</tr>
<tr>
<td>TPO + C2 + AF</td>
<td>TPO + 5% Talc + 2% Adicco 9320 + 20% agave</td>
<td>74.1</td>
</tr>
<tr>
<td>TPO + C3 + AF</td>
<td>TPO + 5% Talc + 2% PPgMA + 20% agave</td>
<td>74.1</td>
</tr>
</tbody>
</table>

5.3.2. Extrusion and Injection Molding

Prior to compounding, the agave fiber, compatibilizers the resins were dried overnight at 60 °C in conventional oven to reduce moisture. Ten ASTM tensile tests samples were produced, and the formulations (total of eight) that were studied are detailed in Table 1. Extrusion was completed using a twin-screw laboratory extruder (ThermoHaake Rheomex Model PTW25, Sigma Aldrich, St. Louis, USA) with barrel temperatures ranging from 180-195 °C. The talc filled TPO, compatibilizers, and agave fiber were separately starve fed into the extruder using K-Tron gravimetric feeders (Coperion, Stuttgart, Germany). Extruded samples were cooled in a room temperature water bath and pelletized using a lab scale grinder/chopper. Compounds were dried in conventional oven for 12 hours at 60 °C to reduce moisture content before being injection molded into test specimens using a Boy Machines Model 80M injection molding machine (Exton, USA) with barrel temperatures ranging from 175 to 185 °C, mold temperature: 26°C.
5.4. Test Procedures

5.4.1. Mechanical Testing

Tensile, flexural and impact tests were performed according to ASTM D638-10 (2010) [60], ASTM D790-10 (2010) [11] and ASTM D256-10 (2010) respectively. All the samples were tested in an environmentally conditioned room maintained at 23 °C and 50% relative humidity.

The tensile tests were performed on an Instron 3366 machine (Instron, Norwood, USA) using a 50 mm extensometer and extension rate of 5 mm/min. The three-point bend flexural tests were performed using a 50mm wide support span and were run at a crosshead speed of 1.25 mm/min. The Izod impact tests were performed using a TMI machine (model 43-02-03, New Castle, USA) along with a 2lb pendulum. At least six tensile, five flexural and ten impact test specimens were tested for each sample.

The ultimate tensile strength, yield strength, elongation at break and Young’s modulus were determined from the tensile stress-strain curves. The flexural strength and flexural modulus were determined from the flexural stress-strain curves. The impact strength was determined from the notched Izod impact tests.

5.4.2. Water Absorption Test

Water immersion tests were performed according to the ASTM D570. At least six specimens of each sample were conditioned by drying in the oven at 50 °C for 24 hr. All the samples then cooled at room temperature for approximately 30 min and the samples
were immediately weighed to the nearest 0.001 g. The conditioned samples were then immersed in distilled water at 23 °C. The samples were weighed again to the nearest 0.001 g after 24 h, 7 days, 21 days and 35 days until the increase in weight for 3 consecutive weighing averages less than 1%.

5.4.3. Microscopy

The fractured surfaces of the tensile specimens were mounted vertically on sample holder to expose the composite’s cross-section perpendicular to the injection molding flow direction. The cross-sections of samples were observed using a FEI Quanta FEG 250 field emission SEM (Thermo Fisher Scientific, OR, United States). A 10 keV beam was used and backscatter electron images were collected. The low vacuum mode was used with 60 Pa water vapor environment and thus the surfaces were not metalized prior to SEM examination. The working distance was set at approximately 10 mm.

5.4.4. Statistical Analysis

Results were analyzed by ANOVA using SAS (version 9.2; SAS Institute Inc., Cary, NC) and XLStat (version 2013.4; Addinsoft, New York, NY). A significance level of α = 0.05 with Tukey adjustment for multiple comparisons was used to determine significant differences.
5.5. Results and Discussion

5.5.1. Mechanical Properties

5.5.1.1. Strength and Elongation

The tensile, modulus and impact properties are presented in Figure 5.1-5.3, below for all the samples. The mechanical property requirements for thermoplastic polyolefin elastomer (TPO) mineral filled, high impact molding compound, were based on Ford material specifications for interior applications (specification numbers WSS-M4D550-A10). These requirements (Table 5.2) must be met by testing the specimens at 23 °C after injection molding with a one-end gated mold that was used in this study.

Figure 5.1 shows the result of tensile strength and strain at failure for TPO and agave fiber composites made with different compatibilizers. The addition of agave fibers in TPO results in a reduction of the tensile strength compared to the neat TPO. This result is in disagreement with the general tensile properties in which it is improved with the addition of natural fibers to a polymer matrix as a result of fibers possessing much higher strength and stiffness than the TPO used for this study. Agave fiber bagasse has an average tensile strength of 50-58MPa [22], 57% higher strength than the TPO used in this study (20.6 MPa). This discrepancy can be attributed to a few factors such as fiber degradation and improper processing and mainly incompatibility between matrix and fibers [81]. Natural fibers are usually polar and have inherently low compatibility with non-polar, hydrocarbon matrices such as PP, PE and TPO. This incompatibility tends also
cause fiber agglomeration and uneven distribution of fibers in the polymer matrix during processing. Another reason could be as a result of poor fiber wetting by TPO matrix that caused weak interfacial adhesion [108]–[110]. As a result, the stress transfer efficiency from the matrix to the reinforcing fibers is reduced. The addition of compatibilizer, however improved the tensile strength in all of the composite, especially the composite with C1 compatibilizer resulted in similar tensile strength to the one of the control sample TPO. This result is consistent with other studies which found that the addition of PPgMA improves the mechanical properties of natural fiber composites [72], [76], [104]. In contrary, the elongation at break of the composites showed the reverse trend as depicted in Figure 1. The elongation of the composite is reduced compared to the neat TPO as agave fiber has lower elongation than the polymer matrix [86]. A lower tensile elongation indicates a higher tensile modulus because a high tensile modulus. This also means that the material is rigid - more stress is required to produce a given amount of strain. Therefore, the tensile modulus of biocomposites can be increased with increased fiber content. On the other hand, the addition of agave fiber reduces the elongation compared to the TPO control sample, and addition of compatibilizers does not have any changes in the maximum strain.
Figure 5.1. Tensile strength and elongation at maximum load of TPO and agave fiber with different compatibilizers composites.

The results of flexural strength for TPO and agave fiber with different compatibilizers composites are shown in Figure 2. The addition of agave fiber slightly reduced the flexural strength by 0.5% but there were no significant differences. However, with compatibilization, TPO + C1 + AF sample presents highest flexural strength value and has significant difference in flexural strength between the rest of the samples that were tested. The increase in flexural strength of these composites can be attributed to a well-formed interface due to the presence of the C1 compatibilizer that allows better stress transfer from matrix to the natural fibers. This flexural strength results are in agreements with findings by Suzuki et al, in which the authors reported that adding maleic-anhydride-grafted polypropylene (MAPP) and cationic polymer using primary
amine (CPPA) as coupling agents in MFC-reinforced polypropylene (PP) have drastically improved the interaction between the fiber and matrix [111].

However, for the impact strength shown in Figure 3, the addition of agave fiber shows lower impact strength than the control TPO sample as has been reported in other works [27], [112]. Possibility of poor interfacial adhesion between the agave fiber and TPO could have caused weak interfacial regions as shown in the fracture surface SEM on Fig.5. Besides, the smooth rod like shape of the fiber may act as a small stress concentrator thus contributing to the reduction in impact strength. The image shows deboned fibers and also micro cracks on the TPO matrix. During the impact test, crack is initiated and propagates through the polymer, the weak interfacial regions that may be formed as a result of poor adhesion and then the fiber and so on until a complete fracture. The poor adhesion causes fiber debonding before it could resist crack propagation as effectively as the polymer region, resulting in lower impact strength. [113][85]. The addition of compatibilizers slightly reduces the impact strength of the composite. This may be because the polymer matrix was softened [56].
Figure 5.2. Flexural strength of TPO with 5% talc and 20% agave fiber with different compatibilizers composites.

Figure 5.3. Impact strength of TPO with 5% talc and 20% agave fiber with different compatibilizers composites.
5.5.1.2. Stiffness

Figure 5.4 shows both the Young’s and flexural moduli for the composites. The addition of agave fiber in the composite is shown to have a slight increase in the stiffness. However, by adding compatibilizer, no change the stiffness of the composite is observed. The addition of agave fiber along with the compatibilizers also increased the flexural modulus of the composites when compared to the control TPO sample. The significant increase in the stiffness can be attributed to the reinforcement effect of the agave fiber as the fibers act as rigid fillers that increases stiffness. This result is in agreement with several other studies that tested the mechanical properties of natural fiber-polymer [104], [114], [115]. The sample compatibilized with C1 showed the highest Young’s modulus and flexural modulus.

![Graph showing Young's modulus and flexural modulus](image)

Figure 5.4. Young’s modulus and flexural modulus of TPO, agave fiber and talc with different compatibilizers composites
5.5.1.3. Water Absorption

The water absorption results are shown in Figure 5.5. The results from the graph below suggests that the control TPO sample has no significant water absorption (~0.1%) over 3 weeks. It can be observed that water absorption is higher in the composite with agave fiber than the samples without the fibers. Agave fibers are hydrophilic in nature due to the presence of large hydroxyl groups and this property assist the water absorption process. Up to week 1, there were no significant differences in absorption between the compatibilized and compatibilized samples. This occurrence suggests that the majority of the absorption is occurring within the fiber bulk, not the interface [56]. On week 3, there is a significant difference in water absorption in the uncompatibilized TPO + agave fiber sample and the composites compatibilized with C1, C2 and C3 samples. It is postulated that the compatibilizers are creating a better fiber-matrix bond via reactions with fiber hydroxyl groups (see higher strengths in the mech properties section), resulting in less free hydroxyls on the agave fiber surface to bond with water.

The average tensile, flexural, and impact properties are presented in Table 5.2 and compared to the Ford requirement of material specifications for interior application (specification numbers WSS-M4D550-A10) assuming it is the common requirement used in the automotive industry. The agave fiber-TPO biocomposite meets the Ford requirement for tensile strength and modulus properties, but the flexural modulus and impact strength did not attain the requirement values.
Figure 5.5. Water absorption of TPO-agave fiber composite with different compatibilizers soaked in water for a week.

Table 5.2. Summary of the material properties of TPO-agave composites compared to Ford’s requirement.

<table>
<thead>
<tr>
<th>Property</th>
<th>WSS-M4D550-A10 Requirement</th>
<th>20% Talc TPO Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler Content (%)</td>
<td>16-22</td>
<td>20</td>
</tr>
<tr>
<td>Tensile Strength at Yield (MPa)</td>
<td>18</td>
<td>20.7</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>1.6</td>
<td>1.93</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>Report Value</td>
<td>32.5</td>
</tr>
<tr>
<td>Flexural Modulus (GPa)</td>
<td>1.8</td>
<td>1.48</td>
</tr>
<tr>
<td>Impact Strength at 23°C (kJ/m²)</td>
<td>24</td>
<td>8.18</td>
</tr>
<tr>
<td>Elongation at Yield (%)</td>
<td>Report Value</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Overall, the addition of the PPgMA compatibilizer to the composites resulted in a relatively small increase (< 10%) on the mechanical properties of TPO polymers. The addition of agave fiber in the composites did reduce the tensile strength elongation and impact strength as reported by other studies [60], [114]. However, the Young’s modulus,
flexural modulus and strength are enhanced by the addition of agave fiber in the composites.

5.5.2. Morphological Properties

Scanning Electron Microscopy

![SEM images](image)

Figure 5.6. SEM images of the fracture surfaces of (a) TPO control sample (b) TPO + 20% agave fiber and (c) TPO + C1+ 20% agave fiber.

SEM images are seen in Figure 5.6. In Figure 5.6(a) that there is good dispersion of talc within the TPO sample. Without the compatibilizer, there are is debonding between the agave fibers and resin as seen with voids at the interface as can be suggested in Figure 5.6(b). In Figure 5.6(c), matrix and the agave fiber do not show evidence of voids which suggests that adhesion between the fiber and matrix is relatively strong. This is in agreement with the tensile strength (Figure 5.1) in which the composite strength with no compatibilizer is 18.5 MPa and with the addition of to a compatibilizer (C1) the strength increase to 20.8 MPa. This trend is also seen in the balance of the results in the improved mechanical properties with the addition of compatibilizer C1.
5.6. Conclusion

1. The mechanical properties and morphologies of agave fiber- TPO/ compatibilizers composites were investigated. Addition of agave fiber caused a reduction in the strength and elongation at break but increased the stiffness.

2. The addition of compatibilizers have a significant improvement on the tensile and flexural strengths but no considerable effect for strain, impact and flexural modulus.

3. Water absorption within TPO - agave fiber composites increased with the addition of agave fiber but addition of compatibilizers does help in reduction of water absorption in week 3.

4. When compared to the Ford requirement, average TPO-agave fiber biocomposite meets the requirement tensile strength and modulus and optimization to improve the flexural modulus and impact strength need to be looked into for future work. This can be done by optimization of interfacial adhesion through surface modification, processing conditions and investigating the effect of hybrid fibers to enhance the synergy of the properties.

5. In short, agave fiber has advantageous properties such as being sustainable material and has the potential to reduce TPO content in the final components that can help in achieving lower density parts and lower carbon footprint.
5.7. References


N. Ramli et al., “Natural fiber for green technology in automotive industry: A brief review.”


CHAPTER 6. SONICATION OF AGAVE FIBER BAGASSE: A POTENTIAL PRETREATMENT TO ENHANCE SUGAR RELEASE

Modified from a manuscript to be submitted to *Ultrasonics Sonochemistry*

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6.1. Abstract

Ultrasound pretreatment of agave fiber bagasse to remove residual sugar was conducted and the sugar yield was compared to the traditional washing method. Thermogravimetric Analysis (TGA) and microscopy were also conducted to analyze the effect of sonication on the thermal properties and morphology of the fiber. The optimum ultrasound pretreatment conditions for maximum reducing sugar yield was an amplitude of 160 µm with a treatment time of 7.5 min at 23°C. Under these conditions, 100% of maximum sugar removal through washing is achieved. Improvement in thermal properties is also observed for ultrasound-treated agave fibers. The substantial reduction
in pretreatment time, temperature, energy with improved efficiency is the most attractive features of the ultrasound pretreatment.

6.2. Introduction

_Agave tequilana_ is a perennial arid succulent plant that is native to Mexico and is mainly used to produce the distilled spirit tequila [1–3]. Only plants with intense blue color (_A. tequilana_ Weber var. Azul) are allowed to be harvested and used exclusively for the spirit production under the Mexican Law. During the tequila production process, the ‘pina’ is steamed, crushed and shredded to extract the juice. The milled fibrous waste called agave bagasse is produced that represent 40% of the total weight [28]. Considering the 2018 agave consumption, reported by the Tequila Regulatory Council, about 455,520 tons of bagasse were generated in that year alone [29]. Currently, the byproducts are underutilized as they are accumulated in large areas and used for compost, ruminant feed, burned to generate electricity or sent to a landfill [3, 6]. These fibers have mechanical properties competitive to synthetic fibers such as e-glass, making them a prospective reinforcing agent to be used in automotive applications [7, 8]. However, several major technical considerations such pretreatment of the agave fiber bagasse to remove the pith, soluble substances i.e. reducing sugars, large particle suspensions, agglomerate and fiber foreign sediments is required. The removal of the surface contaminants from the fiber allows the ease of processing via extrusion and injection molding to enable widescale acceptance of these fibers to be used in biocomposites.
Literature suggests that thermal washing with water is the only used method to remove the impurities from the agave fiber bagasse. A patent on the conditional process of the bagasse suggests washing in heated stirred tanks at an agave fiber concentration ranging from 10 to 40% and the process is repeated until sugar content below 0.5% is achieved [116]. Most studies on agave fiber conditioning have been limited to thermal washing [7, 8, 10, 11]. However, the thermal process demands high-energy consumption, limiting their profitability. The novelty of this research is that it focuses on potential of the utilization of ultrasonic energy to enhance residual sugar release from agave fiber bagasse. Ultrasound is defined as sound waves with frequencies beyond the human hearing threshold, (> 20 kHz). When ultrasound is applied in a fluid medium, the sound waves propagate in alternate compression and rarefaction pressure regions alternately to create cavitation. Cavitation is the formation of vapor-filled cavities or microbubbles in liquid when it is subjected to negative pressures. These microbubbles grow unstable as they increase in size and collapse drastically, releasing extreme energy density with localized temperatures of 5000 K and pressures of 500 atm. During ultrasound propagation in liquid, continuous displacement of liquid movement generates acoustic streaming that helps in mixing and enhances energy distribution in the medium [11, 12]. This process also generates high power hydro-mechanical shear forces in the bulk liquid that helps in disintegrating nearby particles by extreme shear forces [121].
Ultrasonics has been widely used in various biological and chemical applications. Islam et al. studied the ultrasonic treatment of kenaf fiber and reported that 57% increase in tensile strength and also removal of lignin, pectin, hemicelluloses, and other surface impurities at optimized parameter of 95 C and at 100% power [122]. Montalbo-Lomboy et al. reported the use of ultrasonic treatment to enhance sugar release of sugar-2-corn showed increased yield compared to the conventional jet cooking [121]. Sánchez-Madrigal et al. investigated the extractions of fructans from A. tequilana plants of 6 and 7 years and reported enhancement of fructan yield at power density of 120 mW/mL and 1:2 solid: liquid ratio [123]. Other studies also investigated the application of ultrasound on food and bioprocessing and reported processing times reduction, and therefore, decreasing energy consumption. [15–17].

Even though ultrasound treatment is used for many applications, a particular emphasis has been given in this article to examine the potential and optimization of exposing agave fiber bagasse to high-power ultrasonics to enhance residual sugar removal. The objectives of the study were to determine the efficacy of ultrasound treatment in releasing residual sugar in agave fiber bagasse and to compare ultrasonication treatment to conventional washing method.
6.3. Materials and Methods

6.3.1. Procurement

Polypropylene (PP) resins were used for the experimental work, supplied by RheTech Products, namely P100-00. The resin had a density of 0.905 g/cm$^3$. The melt indices (MI) of 20 g/10 min (230 °C). The melt density and thermal conductivity at about 230 °C were 0.739 g/cm$^3$ and 0.20 W/(m °K) respectively. Agave fibers were obtained from Diageo Corporation in blue agave bagasse form. The density of agave fiber is 1.39 g/cm$^3$.

6.3.2. Preparation of Agave Fibers

Agave fiber in bagasse form was separated into heterogeneous fibers of varying lengths and the pith, a non-fibrous spongy organic material in the form of fine particles through hammer milling [11]. The raw fiber was then milled on a 428 Pilot Scale Circ-U-Flow hammer mill with a 1/8$^{th}$ inch screen to separate the fiber-fiber entanglement and mineral contaminants. The fibers were then chopped using a with an Ingento paper cutter to approximately 10 mm lengths to promote easier processing.

6.3.3. Conventional Washing Process

Agave fibers and water samples (50 ml) were prepared at 20:80 ratio respectively in an Erlenmeyer flask with a rubber stopper to mimic the large-scale washing tank. The flasks were maintained in a Fisher Scientific 2340 water bath (Fisher Scientific, Waltham, MA USA) at 70 °C for 24 hours. After 24 hours, the fiber samples were removed and the rinsate (water with the residual sugar) were saved for sugar analysis. A new batch of water was added to the flask with the same fiber samples and this process is repeated up
to 7 days to ensure the maximum residual sugar removal process. When there are no changes in the sugar levels, maximum sugar level is reached. In order to compare washing process with ultrasonics, similar sugar analysis procedure was followed. A 0.04mL extracts were added to 0.21mL of DI water and 0.25mL of 5% phenol solution. Then, 1.3mL of concentrated sulfuric acid (18M) were added to the solution and stirred vigorously in a vortex mixer and cooled at room temperature for 20 min before the absorbance reading.

6.3.4. Ultrasonic Batch Experiment

Agave fiber and water samples (50 ml) were prepared at 20:80 ratio respectively. The samples were then sonicated using a Branson DCX Series (Branson Ultrasonics, Danbury, Connecticut, USA) bench-scale ultrasonic unit (Figure 6.1 (a)) for treatment times of 0 (control group), 2.5, 5 and 7.5 min. The ultrasonic treatments were conducted in a 100ml Branson sonifier continuous flow rosette cooling cell (Figure 6.1 (b)) using three different amplitudes (power): low (16 µm peak-to-peak(p–p)), medium (80 µm p–p), and high (160 µm p–p). The corresponding average power output of the three amplitudes were 11.4 W (low), 56.9 W (medium), and 113.7 W (high). The system had the capacity to operate at a maximum power output of 1.25kW and a frequency of 20 kHz. The ultrasonic booster (Branson Ultrasonics, Danbury, CT) was a booster with 1:1 gain and the horn was a standard 20-kHz half-wavelength catenoidal titanium with a flat 13-mm diameter face.
(gain = 1:8). All experiments and analytical procedures were conducted in duplicate and triplicate, respectively.

![Schematic diagram of ultrasonics equipment used in the experiment](a)
![Branson continuous flow rosette cooling cell](b)

Figure 6.1 (a) Schematic diagram of ultrasonics equipment used in the experiment (b) Branson continuous flow rosette cooling cell

### 6.3.5. Sugar Content Analysis

The total sugar content analysis was performed according to the phenol-sulfuric acid colorimetric method by Dubois et al [127]. Extracts from each treatment (0.04mL) were added to 0.21mL of DI water and 0.25mL of 5% phenol solution. Then, 1.3mL of concentrated sulfuric acid (18M) were added to the solution and stirred vigorously in a vortex mixer and cooled at room temperature for 20 min. Aliquots of 1 mL of the mixture obtained were transferred into a disposable VIS semi-micro cuvette. The absorbance of the samples was measured at 490nm using a GENESYS™ 30 Spectrophotometer (Thermo Scientific, IL, USA). To obtain the control curve, ten known glucose concentration of 0.1% glucose solution were prepared by using D-(+)-Glucose ≥ 99.5% (Sigma Aldrich, Saint Louis, USA) and tested as shown in Table 6.1.
Table 6.1. Glucose concentrations for control curve and its respective absorbance at 490nm

<table>
<thead>
<tr>
<th>Glucose concentration [µg]</th>
<th>Absorbance @ 490nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.179</td>
</tr>
<tr>
<td>10</td>
<td>0.377</td>
</tr>
<tr>
<td>15</td>
<td>0.473</td>
</tr>
<tr>
<td>20</td>
<td>0.475</td>
</tr>
<tr>
<td>25</td>
<td>0.916</td>
</tr>
<tr>
<td>30</td>
<td>1.142</td>
</tr>
<tr>
<td>40</td>
<td>1.401</td>
</tr>
<tr>
<td>50</td>
<td>1.698</td>
</tr>
<tr>
<td>60</td>
<td>2.120</td>
</tr>
</tbody>
</table>

6.3.6. Thermogravimetric Analysis (TGA)

To determine the degradation temperature of the agave fibers after surface modification, as a function of increasing temperature were measured with a TA instrument Q50 V20.13 (New Castle, DE) thermal gravimetric analyzer under nitrogen atmosphere. Each sample of 5 mg was placed in a ceramic pan and heated from 10 to 600 °C at a heating rate of 20 °C/min, and the degradation profile was analyzed. These results were used to determine the thermal stability for the fibers during melt extrusion processing with polymers.

6.3.7. Fourier-Transform Infrared Spectroscopy (FTIR)

FT-IR spectra of bio-filler reinforced thermoplastic films were recorded in the range of 4000–650 cm⁻¹ (Frontier Optica FT-IR spectrometer equipped with UATR accessory, Perkin-Elmer, Waltham, MA, USA).
6.3.8. Microscopy

The fractured surfaces of the tensile specimens were mounted vertically on sample holder to expose the composite’s cross-section perpendicular to the injection molding flow direction. The cross-sections of samples were observed using a FEI Quanta FEG 250 field emission SEM (Thermo Fisher Scientific, OR, United States). A 10 keV beam was used and backscatter electron images were collected. The low vacuum mode was used with 60 Pa water vapor environment and thus the surfaces were not metalized prior to SEM examination. The working distance was set at approximately 10 mm.

6.4. Results and Discussion

6.4.1. Sugar Content Analysis

The phenol-sulfuric acid colorimetric method was used to quantify the amount of residual dissolvable sugars and polysaccharides within the agave fibers after pretreatment. A linear fit regression equation (Equation 2) was initially obtained by conducting the control glucose solution tests as shown in Figure 6.2 below. The equation was then used to quantify the amount of residual sugar that has been removed from the agave fiber bagasse through both the conventional washing and the ultrasonication methods. For this test, the conditions of linearity were satisfied (R2 ≥ 0.98) and thus the phenol-sulfuric acid colorimetric methods established by Dubois et. al [127] were assumed applicable.

\[ y = 0.035x - 0.0225 \] (2)
Because agave fiber bagasse is primarily composed of residual sugars from the cooking and extraction process, D-glucose was used as the standard reducing sugar assay in this study. The sugar content was expressed as g/100g.d.m. Figure 6.3 shows the sugar yield of agave fiber bagasse that underwent traditional water washing process. The process was conducted up to 7 days to ensure maximum sugar removal from the fibers. The total residual sugar that were removed from the 7 days of washing was 22.7 mg/g.d.m. and this value was assumed to be the maximum (100%) of the residual sugar present in the agave fiber bagasse (Table 6.2). The graph below also suggests that washing is an effective process to remove the sugars because approximately 91% of the sugar is removed after 3 wash cycles. However, this process requires long processing time, energy and water consumption as the water needs to be replaced and heated up to 70 °C for every 24-hour wash cycle.
Figure 6.3. Sugar yield from traditional washing method at 70 °C for 7 cycles. Note: Each wash cycle is for a day long and water is replaced for every new wash cycle.

Table 6.2. Washing treatment setting, energy used and sugar yield.

<table>
<thead>
<tr>
<th>No. of washes</th>
<th>Time (hr)</th>
<th>T\textsubscript{i} (°C)</th>
<th>T\textsubscript{f} (°C)</th>
<th>Energy (kJ)\textsuperscript{i}</th>
<th>Mean Energy Density (kJ/L)</th>
<th>Sugar yield per wash (mg/g\textsubscript{d.m.})</th>
<th>Total Sugar yield (mg/g\textsubscript{d.m.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>70</td>
<td>70</td>
<td>11.1</td>
<td>278.4</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>70</td>
<td>70</td>
<td>22.3</td>
<td>556.7</td>
<td>4.1</td>
<td>16.5</td>
</tr>
<tr>
<td>3</td>
<td>72</td>
<td>70</td>
<td>70</td>
<td>33.4</td>
<td>835.1</td>
<td>2.1</td>
<td>18.6</td>
</tr>
<tr>
<td>4</td>
<td>96</td>
<td>70</td>
<td>70</td>
<td>44.5</td>
<td>1113.5</td>
<td>1.6</td>
<td>20.1</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>70</td>
<td>70</td>
<td>55.7</td>
<td>1391.8</td>
<td>0.8</td>
<td>21.0</td>
</tr>
<tr>
<td>6</td>
<td>144</td>
<td>70</td>
<td>70</td>
<td>66.8</td>
<td>1670.2</td>
<td>0.8</td>
<td>21.8</td>
</tr>
<tr>
<td>7</td>
<td>168</td>
<td>70</td>
<td>70</td>
<td>77.9</td>
<td>1948.6</td>
<td>0.8</td>
<td>22.7</td>
</tr>
</tbody>
</table>

\textsuperscript{i}Note: 40ml of water= 0.004kg; \( C_p = 4.186 \text{kJ/kg°C} \)

Figure 6.4 shows the sugar yield of agave fiber bagasse as a function of sonication time at different amplitudes. The temperature was maintained at room temperature instead of heating it up to 70 °C, as done in washing process. A sonication amplitude of 0 µm indicates the control group that had the same time in the water bath as the other
treatment groups with no sonication. The samples treated with sonics produced a 3 to 4-fold increase in the removal of sugar compared to the control group during the test period (Table 6.3). Sugar yield ranged from 6 mg/g<sub>d.m.</sub> for the control group to approximately 23 mg/g<sub>d.m.</sub> for the sonicated groups. The sugar yield was proportional to time and power (amplitude) level [121]. The result is consistent with previous studies [128] that shows increased extraction of fructans, total carbohydrates and reducing sugars with increasing ultrasonic power. These results can be attributed to particle size reduction and streaming effects on the fibers that enhanced mass transport.

The shortest traditional washing for 24hrs resulted in the lowest sugar yield at 12.5 mg/g<sub>d.m.</sub> by using 11.1 kJ energy while about the same amount of sugar (12.0 mg/g<sub>d.m.</sub>) can be removed in sonicating for only 5 minutes at 80 µm by using lesser energy than washing of only 3.4 kJ. In order to remove the maximum amount of sugar (~23 mg/g<sub>d.m.</sub>), sonication at 160 µm for 7.5 min is needed (5.1 kJ energy). When compared to traditional washing method to remove the maximum sugar, ultrasonication saves time by nearly 99% (7.5 min vs. 168 hr), 93% energy (5.1 kJ vs. 77.9 kJ) and 86% water (1 vs. 7 replacement). This result proves the efficiency of ultrasound to replace traditional washing method in terms of time and water. Velmurugan et al, reported similar result of producing higher reducing sugar yield by using ultrasound-assisted alkaline pretreatment of sugarcane bagasse (SCB) for fermentable sugar production compared to commercial alkaline pre- treatment [129].
Figure 6.4. Sugar yield from ultrasonication pretreatment at room temperature at 4 different amplitudes. Note: The control group here is indicated as 0µm is the control group in which no sonication treatment is applied.

Table 6.3. Sonication treatment settings, average temperature before and after treatment, and average energy density and sugar yield.

<table>
<thead>
<tr>
<th>Amplitude (µm)</th>
<th>Time (min)</th>
<th>Power (W)</th>
<th>Ti (°C)</th>
<th>Tf (°C)</th>
<th>Energy (kJ)</th>
<th>Mean Energy Density (kJ/L)</th>
<th>Total Sugar yield (mg/g d.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>N/A</td>
<td>23.0</td>
<td>23.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.9</td>
</tr>
<tr>
<td>7.5</td>
<td>5</td>
<td>11.4</td>
<td>24.9</td>
<td>24.3</td>
<td>1.7</td>
<td>85.3</td>
<td>7.3</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>56.9</td>
<td>26.2</td>
<td>26.2</td>
<td>5.1</td>
<td>127.9</td>
<td>9.5</td>
</tr>
<tr>
<td>160</td>
<td>5</td>
<td>113.7</td>
<td>44.5</td>
<td>44.5</td>
<td>3.4</td>
<td>85.3</td>
<td>12.0</td>
</tr>
<tr>
<td>160</td>
<td>7.5</td>
<td></td>
<td>48.0</td>
<td>48.0</td>
<td>5.1</td>
<td>127.9</td>
<td>15.3</td>
</tr>
<tr>
<td>160</td>
<td>2.5</td>
<td></td>
<td>53.3</td>
<td>53.3</td>
<td>1.7</td>
<td>42.6</td>
<td>18.6</td>
</tr>
<tr>
<td>160</td>
<td>7.5</td>
<td></td>
<td>61.1</td>
<td>61.1</td>
<td>3.4</td>
<td>85.3</td>
<td>17.9</td>
</tr>
</tbody>
</table>
6.4.2. Thermogravimetric Analysis (TGA)

The thermograms of sonicated agave fibers are shown in Figure 6.5 indicating the mass loss or the decomposition of the samples. Sonicated agave fiber samples were dried in convection oven at 85°C to remove water and excess moisture for 12 hours and then was evaluated with TGA. The samples were heated from room temperature to 20 to 600 °C at a heating rate of 20 °C/min. All sonicated fibers exhibited ~10 °C increase in degradation temperature (temperature at 10 and 50% mass loss), indicating that sonication improved the thermal stability of the agave fibers along with the sugar removal (Figure 6.5, Table 6.4). There was no difference in thermal stability of fibers sonicated at 80 and 160µm. Thermal stability is crucial in the automotive industry as it can lead to issues of odor and fogging in a vehicle. Having high thermal stability lowers the risk of these issues.

![Thermal gravimetric analysis (TGA) of the agave fibers with and without sonication treatment.](image-url)
Table 6.4. Thermal gravimetric analysis (TGA) of the agave fibers with and without sonication treatment

<table>
<thead>
<tr>
<th>Sonication Amplitude (µm)</th>
<th>Temp at 10% Mass Loss (°C)</th>
<th>Temp at 50% Mass Loss (°C)</th>
<th>T_d,max (°C)</th>
<th>Residue (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>312</td>
<td>390</td>
<td>415</td>
<td>13.94</td>
</tr>
<tr>
<td>16</td>
<td>320</td>
<td>395</td>
<td>420</td>
<td>14.53</td>
</tr>
<tr>
<td>80</td>
<td>325</td>
<td>400</td>
<td>425</td>
<td>13.14</td>
</tr>
<tr>
<td>160</td>
<td>325</td>
<td>400</td>
<td>425</td>
<td>14.01</td>
</tr>
</tbody>
</table>

6.4.3. Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-Transform Infrared Spectroscopy (FTIR) spectroscopy is an appropriate technique in determining the variations in fiber chemical composition introduced as a result of sonication. Figure 6.6 shows the FT-IR spectra of untreated (0 µm) agave fibers, and sonicated agave fibers at different amplitudes (16, 80 and 160 µm). Similar to all lignocellulosic fiber, agave fiber bagasse presents the typical signals of cellulose and lignin combination. The FTIR spectrum of untreated agave fiber illustrates a broad peak around 3400 cm\(^{-1}\), which correlates to the stretching vibrations of hydroxyl groups from the cellulose in the agave fiber bagasse. The peak was still observed in the sonicated agave fibers, although the intensity reduced, indicating protection of free hydroxyl group. The peak at 2881 cm\(^{-1}\) correlates to C–H group stretch and is present in all fiber [130]. After the sonication treatment, the peak at 1731 cm\(^{-1}\) that corresponds to the ester linkage of the C=O groups of the ferulic and p-coumeric acids of hemicellulose, pectin, and lignin or wax in natural fats disappeared when compared to the untreated sample. This indicates the removal of hemicellulose and waxes from the fiber surface [87], [88], [131]. The peak at 1617 cm\(^{-1}\) on the untreated sample was due to H–O–H group stretching of absorbed
moisture and the C=O bonds of hemicellulose. This result supports the theory of the removal of hemicellulose from the fiber [130]. The peaks at 1589 and 1450 cm$^{-1}$ shows the presence of benzene ring stretching and CH2 deformation of lignin. The sonicated agave fiber samples are missing the specified peaks, an indication of complete or partial removal of the cementing components in the agave fiber [122].

Figure 6.6. FTIR spectra of ultrasonic treated agave fibers at different amplitudes.

### 6.4.4. Morphological Properties

**Scanning Electron Microscopy**

The SEM images of agave fiber morphology without any treatment, fibers that has been washed for 7 days and fibers with ultrasonic treated for 5 mins are shown in Figure 6.7. The images in the left column were magnified 50× whereas the images on the right were magnified 150×. In the control samples of untreated agave fibers (Figure 6.7A and
B), the all the inorganic crystals and the voids are still intact. In comparison, washed fibers (Figure 6.7C and D), displayed surface smoother with fewer weak dissolvable cellulosic structures with more porous surfaces possibly as a result of water transfer within the fiber cells during washing for a long time. In contrast, as seen in 5 min ultrasonic treated sample (Figure 6.7E and F), the fiber surface appears rougher with exposed fibrils and some strands were partially ruptured. The sonication process also shown to break the inorganic crystals that were intact in the untreated and washed fibers verifying the efficiency of the process to remove residual sugar and inorganic compounds as supported by the result in Table 6.3.

Figure 6.7. SEM images of control samples (A and B), washed samples for 7 days (C and D) and sonicated for 5min samples (E and F). The images on the left column were magnified 50x while images on the right were magnified 150x.

6.5. Conclusion

This study evaluated the effects of high-power ultrasonics in removing residual sugar in agave fiber bagasse that could be used as filler in biocomposites for automotive
application. The efficiency of the sonication was compared to the traditional washing method. Assuming 100% of the sugar is removed with 7 wash cycles, about 23 mg/g_{d.m.} of sugar is removed after 168 hrs of washing at 70 °C and the same amount of sugar is achievable through ultrasonication 160 µm for 7.5 min at room temperature. Ultrasonication process in saves time, energy and water by almost 99, 93 and 86% respectively, proving that ultrasonics are not only efficient to remove residual sugars but also more efficient that washing method. The SEM images confirmed that the ultrasonic treatments showed uneven and defined cellulose microfibrils was observed indicating removal of waxy and fatty acids residues. It was also observed that under excessive treatment conditions, i.e. an exposure of 5 min at 160 µm, the highest amplitude, the ultrasonication had an adverse effect on the agave fibers. The ultrasonication process also resulted in increased thermal stability of the agave fiber bagasse.

Future studies will analyze the mechanical properties, thermal properties and crystallization kinetics of sonicated agave fiber composite. To have better understanding of the chemical changes occurring on the fiber as a result of washing and sonication, fiber surface chemistry via FTIR spectroscopy will also be conducted. Understanding these chemical and mechanical properties will enable the optimization of composite performance without significant mechanical property loss.
6.6. References


[38] N. Ramli et al., “Natural fiber for green technology in automotive industry: A brief review.”


CHAPTER 7. GENERAL CONCLUSION

Natural fiber biocomposites are gaining industry interest over the past few decades for various advantages over synthetic fibers (glass, aramid and carbon fibers) such as processing advantages, competitive specific mechanical properties, low density, relatively non-abrasive, CO₂ sequestration, recyclability and biodegradability. In the automotive industry especially, the goal of increased fuel efficiency coupled with environmental awareness are leading to growing development of natural fiber composites. The industry is searching for cost effect and eco-friendly materials substitute for synthetic fillers that are commonly used. The success of the natural fiber biocomposites research would help in solving the growing environmental and fossil fuel depletion issue.

This thesis focused on key aspects for the development for the automotive industrial application by exploring novel fiber source, i.e. agave fiber bagasse, fiber pretreatment before processing and suitable surface treatments to increase interfacial adhesion between fiber and matrix. The challenge of homogenizing fiber into polymers, adhesion between fiber and matrix, moisture repellence properties were studied in depth in this study. Manufacturing with different fiber loading levels, including hybrid fibers and recycled polymer blends were also conducted along with characterization of fibers and composites after pretreatment.
7.1. Conclusion

In Chapter 3, study of hybrid fibers (glass and cellulose) composite by using recycled polymer blends (rPP/ rPA6) was investigated and used as a baseline to create a light weight and eco-friendly composites in automobile industry. The selected thermoplastics composite component had the potential to be used for used in areas that are thermally challenging, such as under-the-hood applications. Cellulose fibers were added to produce a sustainable component and reduce the weight of a vehicle.

The addition of hybrid fibers increased the stiffness (tensile and flexural modulus) of the composites. Glass fibers reduced water absorption in the composite while the addition of cellulose fibers resulted in higher composite stiffness. The mechanical properties of glass and cellulose filled rPA6/rPP composites were optimized at loading levels of 15 wt.% glass and 10 wt.% cellulose, respectively. The findings suggested a pathway of material design to reduce the weight and cost as well as environmental stewardship.

A further investigation using agave fiber bagasse, a new natural reinforcement filler was also explored as a potential component for interior applications such as coin trays, storage bins, fuse and battery covers was discussed in Chapter 4. Polypropylene was chosen as the matrix and the effect of fiber loading level and chemical treatment on agave fiber is explored to maximize the bonding strength as well as the stress transferability in the composites. Without any pretreatment and compatibilizers added,
20 wt.% agave fiber and PP produced the best mechanical properties. Additional chemical pretreatments using sodium hydroxide, sodium chlorite and acetylation resulted in significantly enhanced the tensile and stiffness properties of the composites compared to the control sample (no treatments), but to varying degrees. Among the various treatments, acetylation treatment of fiber reported maximum interfacial interactions.

Talc-filled thermoplastic olefin (TPO) were investigated as new matrix to be compounded with agave fiber bagasse as TPO offers better mechanical properties than regular neat PP. Three different kinds of compatibilizers were tested and all the compatibilizers exhibited significant improvement on the tensile, flexural strengths, and water absorption; however, no considerable effect on impact strength, elastic or flexural moduli was observed. The addition of agave fiber increased the elastic and flexural moduli but reduced the elongation and impact strength. Compared to the Ford requirement, average TPO-agave fiber biocomposites meet the requirement tensile strength and modulus and optimization to improve the flexural modulus and impact strength is needed.

Agave fiber bagasse pre-treatment was necessary to remove sugars and impurities that could be damaging to the processing equipment. The process is traditionally completed with a hammer milling and washing the fibers multiple cycles. In order to justify ultrasonics as a potential pretreatment method in Chapter 6, it was compared with
the current washing method. The optimum ultrasound pretreatment conditions for maximum reducing sugar yield was an amplitude of 160 µm for 7.5 min at 23 °C. Under these conditions, 100% of maximum sugar removal through washing for 7 days is achieved. The substantial reduction in pretreatment time, temperature, energy with improved efficiency is the most attractive features of the ultrasound pretreatment.

Based on these results above, the study concluded that agave fiber bagasse has the potential to be used as a filler/ fiber reinforcement for polymeric material in the automotive industry as well as an alternative natural fiber source. The interfacial adhesion of agave fiber can be improved through chemical treatments and with the addition of compatibilizers relevant to the matrix. Moreover, ultrasonication has also been proven to be an effective method to be used for agave fiber bagasse fiber conditioning. In short, incorporation of agave fibers into the composite enables usage of less materials, have potential weight reduction and improve fuel economy meet while meeting certain of the automaker’s material requirements.

7.2. Future Work

- This study is mainly focused on optimizing manufacture of biocomposites using agave fiber bagasse as a filler/ fiber reinforcement for polymeric material in the automotive industry. Due to the limitations in the laboratory, uniform fiber length was difficult to produce, and fiber length offers critical value in determining the
mechanical properties in short-fiber composite. Thus, it is recommended that effects of fiber length on the composites’ properties should be investigated.

- The ultrasonic pretreatment study exhibited promising pretreatment method that is effective and efficient. However, these studies were conducted in batch system in lab-scale experimental set up. This worked well for batch system considering agave fibers have higher density than water and tends to settle during processing, but this may complicate the continuous process. Hence, further studies on ultrasonication for potential scale-up is proposed.

- The study used limited polymer matrices that are commonly used in the automotive industry i.e. PP, TPO and PA6. The success of manufacturing agave fiber thermoplastic composites to meet automotive requirements shows promising outcomes to use the same filler for other applications; structural, packaging etc. So, studies with other petroleum based/ biobased matrices should be investigated.

- A major problem of successful global application of these biocomposites is the aging properties. Effect of temperature, hygrothermal and UV exposure that results in deterioration, discoloring and deformation are crucial and should be investigated for improved biocomposites development.