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Properties of agave fiber reinforced thermoplastic composites

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Properties of agave fiber reinforced thermoplastic composites

by

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Program of Study Committee:
Reza Montazami, Co-Major Professor
David Grewell, Co-Major Professor
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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ABSTRACT

Biocomposites have attracted a great deal of interest in research and industry sectors because they are typically lightweight, sustainable, environmentally friendly, and their thermomechanical properties can be designed to fit specific applications by tuning of their composition. In this study, mechanical properties of natural-fiber reinforced thermoplastic composite films were explored. Thermoplastic resins (linear low-density polyethylene, high-density polyethylene, and polypropylene) reinforced with various ratios of agave fibers were prepared and characterized in terms of mechanical, thermal, and chemical properties as well as their morphology. The morphological properties of agave fibers and films were characterized by scanning electron microscopy, Fourier-transform infrared spectroscopy was used to analyze variations in chemical interactions between the filler and matrix materials. No significant chemical interaction between the filler and matrix was observed. While addition of natural fillers did not affect the thermal properties of the composite materials, elastic modulus and yielding stress were generally proportional to fiber content. The level of the effect on yield stress and modulus of the fibers varied over the range of the different matrix materials.

CHAPTER 1

BACKGROUND AND LITERATURE REVIEW

1.1 Introduction

In the past decades, conventional petroleum-based plastics have resulted in environmental and sustainability issues [1, 2]. The abundance, low cost and sustainability of biocomposites have brought them to the center of attention of polymer industries, especially for automotive, packaging and construction applications [1-5]. Bio-based composites with thermomechanical properties which were either similar or superior to their petroleum-based equivalents.

As the significant component of biocomposites, natural plant fibers have experienced rapid growth in the bio-renewable marketplace in recent years. Natural plant fibers have various advantages compared to traditional fibers, including lower density, prevalence, ease of processing, and low environmental impact [6, 7]. There are some powerful evidences of the rising interest of bio-materials from research and industry. The growing number of publications including books [8-12] and reviews [1, 13-19] show the importance of the new biocomposites. In the market, the production of natural fibers around the world was approximately 45.5 million tons in 2013 [19] and the worldwide capacity of bio-based plastics and continues to grows.

However, the matrix dominates composites' shape, surface appearance and durability. In the polymer market, there are approximately 80% consuming materials

produced from the petroleum-based plastics [1]. The effects of natural fibers in petroleum-based thermoplastics and thermoset matrices have been extensively studied. Thermoplastic materials, as an important plastic type of polymer, are commonly used in production of consumer products. This research aims to study the effect of thermoplastics reinforced by those have been widely used natural fibers. Polyethylene (PE) and polypropylene (PP) were used for thermoplastic matrices for natural fiber reinforced polymer composites.

1.2 Fiber Types

Natural fibers have been classified into different types. Natural fibers including ●bast fibers (flax, hemp, jute and ramie), ●leaf fibers (abaca, sisal and pineapple leaf), ●seed fibers (coir), ●core fibers (kenaf), ●grass/reed fibers (rice husk) and ●other types (wood and roots) reinforced composites have been extensively reported in the past decades.

1.2.1 Flax

Flax, Linum usitatissimum, is a member of the genus Linum in the family Linaceae, belongs to the bast fibers.

Various literature researches of flax fiber reinforced thermoplastic composites have been completed. The mechanical properties of unidirectional and multidirectional composites flax/polypropylene composites have been studied by K. Van de Velde and P. Kiekens [20]. They reported the influence of various process parameters and found the combination of boiled flax with maleic acid anhydride modified PP produced the best mechanical properties. Menghe Miao also reported a highly aligned composite structure

could be produced from flax fibers using a modified nonwoven process. This composite structure achieved the similar tensile and flexural strengths as the composites made from unidirectional woven fabrics, but the manufacturing process was much simpler and cheaper [21]. The influence of different fiber content on properties of flax fiber/HDPE composites was studied by X. Li [22]. They reported the HDPE with flax fiber content from 10 to 30 wt% processed by extrusion and injection molding. The results showed that compared to tensile and flexural strength of biocomposites, the tensile and flexural modulus was more dependent on fiber content. The trend was the mechanical properties increased when the fiber content was increasing. However, the water absorption increased with increased fiber content was a disadvantage of flax fiber reinforced composites. Researchers have also investigated the comparison of natural fiber thermoplastic mat (NMT) and conventional glass fiber thermoplastic mat (GMT) [23]. Investigation revealed that NMT composites had a high stiffness compared to the pure PP and for 50 wt% flax fiber content the NMT composites showed a better stiffness than the GMT composites. This result showed that NMT composites had a potential to replace the conventional GMT composites.

The effects of different chemical treatments modified flax fibers, such as mercerization, peroxide treatment, benzoylation and peroxide treatment [24] and maleic anhydride, maleic anhydride-polypropylene copolymer and vinly trimethoxy silane treatment [25] also have been investigated.

1.2.2 Hemp

Hemp belongs Cannabis sativa plant species and is one of the fastest growing plants. There are many studies focused on biocomposites reinforced by hemp. Different

research groups worked on the mechanical and thermal properties of thermoplastic composites with hemp fibers. P. Wambua's group investigated the mechanical properties of hemp reinforced PP composites and they found the tensile strength and modulus increased with increasing fiber volume fraction [26]. PP composites reinforced with hemp fibers and modified by means of grafting reactions with glycidyl methacrylate (GMA) were also examined [27]. The modified fibers and the modified PP matrix, as well as various compatibilizers were used to improve the fiber/matrix interaction. Compared to the untreated PP/hemp composites, the composites after modified showed improved fiber dispersion in PP matrix and higher interfacial adhesion because of the new chemical bonding between the fiber and the matrix. The thermal stability was more dependent on the fiber and matrix modification. All modified composites exhibited higher tensile modulus. In another study, A. Etaati et al. [28] studied the static and dynamic mechanical and viscoelastic properties of short hemp reinforced PP composites in a temperature range of 25- 150 ℃. The matrices were modified with maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted poly (ethylene octane) (MAPOE) and reinforced by up to 40 wt% short hemp fiber content. The results showed both storage modulus and tensile strength of the composites improved by the coupling agents because of improved interfacial adhesion between fiber and matrices.

Another group reported the PP/hemp composites showed recyclability [29]. The PP/hemp fiber composites after recycling still exhibited good mechanical properties with injection cycles.

1.2.3 Jute

Jute is a long, soft, shiny fiber and is produced from plants in the genus Corchorus. Jute is one of the most affordable natural fibers in the world.

The dynamic mechanical and thermal properties of jute reinforced high density polyethylene (HDPE) composites were studied considering the effect of using maleic anhydride grafted polyethylene (MAPE) as coupling agent [30]. Various mechanical properties such as tensile, flexural and impact strengths and storage and loss modulus were investigated in this study. The outcomes of the study concluded that the mechanical and thermal properties of HDPE matrix with MAPE treated jute fiber reinforcement was improved compared with untreated composites. Moreover, it was observed that the optimum mechanical strengths of the composites achieved at the composites with 30 wt% fiber loading and 1 wt% MAPE. Compared to the neat polymer, the tensile, flexural and impact strength were increased 38%, 45%, and 67%, respectively.

In another study, J. Gassan et al. [31] introduced the effect of fiber treatment on the mechanical properties of jute/PP composites. The maleic anhydride and graft copolymer of PP were applied as coupling agents in this case. The results revealed that the mechanical properties such as flexural strength, flexural modulus and dynamic strength of the composites with treated fibers was higher than the untreated composites. The trend was the strength increased with fiber loading up to 40%. This study also proved that using the coupling agent was able to reduce the progress of damage.

1.2.4 Kenaf

Kenaf is in the genus Hibiscus, belongs to the Malvaceae family. Kenaf fibers shows similar characteristics with jute.

R. M. Rowell et al. [32, 33] studied the mechanical properties of kenaf/PP composites and did a comparison between biocomposites and conventional composites. The maleic anhydride grafted polypropylene (MAPP) as a coupling agent was introduced to the matrix to improve the interfacial property of the composites. The results presented the mechanical properties of biocomposites improved and compared to the conventional composites, the specific tensile and flexural modulus of 50 wt% of kenaf/PP composites had advantages to a 40 wt% glass fiber reinforced PP composites, where the specific tensile modulus and flexural modulus of 50 wt% kenaf/PP composites were 7.8 GPa and 7.3 GPa respectively, and the specific tensile modulus and flexural modulus of 40 wt% glass fiber/PP composites were 7.3 GPa and 6.2 GPa respectively.

M. Zampaloni et al. [34] also have proved that the layered sifting of a microfine PP powder and chopped kenaf fibers is a favorable fabrication method for compression molding process to manufacture the kenaf/PP composites. In this case, 3 wt% Epolene G3015 was used to improve the adhesion of fiber/matrix. The strength of PP powder increased when the fiber content was at both 30 wt% and 40 wt%.

Another group has reported that the electron beam irradiation could change the thermal and mechanical properties of the kenaf fiber reinforced PP composites [35]. The result showed the thermal conductivity and the tensile strength changed and became

minimum when the dose of electron beam was 10kGy, which was important for energy savings in automobiles.

1.2.5 Sisal

Sisal is a species of Agave and produces a stiff fiber used in making various products.

K. Jayaraman et al. [36] introduced a simple manufacturing method for producing sisal fiber reinforced polypropylene composites. They sprinkled the fibers down a drop feed tower onto a substrate to make loose fiber mats. This method could allow the fibers avoid the processing degradation. The sisal fiber mats was introduced into the PP matrix by vacuum forming or hot-pressing to make composites. The optimum mechanical properties of composites were achieved when the fiber length was greater than 10 mm and the fiber loading was in the range 15-35 wt%.

In another study, sisal/PP composites investigated the influence of fiber treatment on the performance [37]. Various fiber loading of volume percent, the maleic anhydride coupling agent concentration and fiber treatment time were studied in the research. The optimum mechanical strength of the composites was observed when the fiber content was at 21% volume percent and the concentration of maleic anhydride grafted polypropylene was at 1%. Specifically, the tensile, flexural, and impact strength, increased to 64%, 119%, and 123%, respectively.

K. Josseph and coworkers did a series of studies on sisal fiber reinforced PE composites. They evaluated the influence of the processing method and the effect of fiber content, fiber length and orientation on mechanical properties of the low density

polyethylene-based composites. The results showed the tensile properties of the biocomposites increased with fiber content and got the maximum properties at the fiber length around 6 mm, specifically, the tensile strength and modulus were 34.27 MPa and 3328 MPa respectively. They also investigated the surface treatment on various properties of short sisal fiber reinforced PE composites and proved that chemical treatment could improve the mechanical properties [38, 39] and electrical properties [40] of the composites. In addition, they studied the effect of ageing on mechanical properties of untreated and cardanol derivative of toluene diisocyanate (CTDIC) treated sisal/LDPE composites. Investigation revealed that CTDIC treated composites exhibited excellent mechanical properties and dimensional stability as compared to untreated composites.

1.2.6 Abaca

Abaca fiber is from the banana plant and is the strongest of the cellulose fibers on the market.

Various fiber loadings (20, 30, 40 and 50 wt%), different fiber lengths (5, 25 and 40 mm) and three different compounding processes (mixer-injection molding, mixer-compression molding and direct compression molding process) for abaca fiber reinforced PP composites was investigated by Bledzki and coworkers [41, 42]. It was observed that, the tensile, flexural and Charpy impact strengths increased with fiber content up to 40 wt% and the optimum fiber loading was 40 wt%, specifically, the tensile and flexural strength increased 30 to 80%. It was also learned that the tendency of the tensile and flexural strengths was increased with increasing the fiber length but not significantly. Moreover, the results exhibited that the mixer-injection molding process exhibited a better mechanical performance (tensile strength was around 90%).

Different fiber treatment methods used to enhance the fiber/matrices have been reported. M. R. Rahman et al. [43] studied the abaca fiber was treated with Benzene diazonium salt. It showed that abaca fibers treated with benzene diazonium salt could reduce the hydrophilicity of the cellulose present in the filler. The tensile strengths of the composites for both treated and untreated abaca were found to decrease as increasing fiber loading. The optimum tensile properties of treated abaca fiber reinforced composites was observed with the fiber loading at 15 wt%. However, other mechanical properties such as Young's modulus, flexural strength, flexural modulus, impact strength and hardness values were showed the trend of increasing with the fiber content increased. Bledzki et al. [44] also reported the abaca fibers were modified by nature enzyme. The results showed that this modification of fibers could reduce 20-45% moisture absorption of the abaca/polypropylene composites. Meanwhile, the mechanical properties of the biocomposites were improved.

1.2.7 Pineapple leaf fiber

The pineapple is a tropical plant and the most affordable plant in the Bromeliaceae family. The pineapple leaf fiber is inexpensive and abundantly available.

George et al. [45] studied on the effect of fiber length, fiber loading and orientation on the mechanical properties of pineapple leaf fiber (PALF) reinforced low density polyethylene (LDPE) and the viscoelastic properties of PALF/LDPE composites also have been reported [46]. Longitudinally oriented composites showed the better mechanical performance than randomly and transversely oriented composites. Dynamic storage and loss modulus increased with fiber content and leveled off beyond 20% due to fiber-to-fiber interactions. The dynamic viscoelastic results showed that the optimum

fiber length for reinforcement was at 2 mm [46]. However, considering the overall mechanical properties and processing characteristics, it was found that 6 mm was the optimum fiber length for reinforcement in LDPE [45]. Furthermore, the water absorption behavior of PALF/LDPE composites has been investigated with referring to fiber loading, fiber/matrix interface and temperature [47]. Because of good interfacial adhesion, the chemically modified fiber composites exhibited a reduction in water absorption. They also studied the flexural strength and modulus of composites after exposure to UV light and found that PALF did not have any significant effect on UV resistance.

Sanjay K. et al. [48, 49] have investigated the influence of fiber length on mechanical, thermal and morphological properties of modified pineapple leaf fiber reinforced PP composites. They studied that the alkali treatment of the fibers improved the fiber/matrix interface by enhancing fiber aspect ratio, fiber wetting and impregnation and further improved by the action of maleic anhydride grafted polypropylene (MAPP) compatibilizer. They obtained a 73% increase in impact properties, 37% increase in flexural modulus, 33% increase in the flexural strength and 14% in Vicat Softening Temperature at 10 vol% PALF loading and 6mm fiber length in the longitudinally oriented composites.

1.2.8 Ramie

Ramie, commonly known as China grass, is a flowering plant and belongs to the family Urticaceae. Ramie is one of the strongest natural fibers.

Ramie fiber reinforced PP composites were fabricated with a hybrid method-blending and injection molding method [50]. Different fiber loading, fiber length, and fiber pre-treatment method on mechanical properties of ramie/PP composites were investigated in this study. The results showed that the tensile strength, flexural strength, and compression strength increased with fiber length and fiber content increased, specifically, the tensile, flexural, and compression strength increased about 45%, 14%, and 10% respectively when the fiber loading was 20 wt%, but the impact strength decreased, of ramie/PP composites. The optimum fiber loading was observed between 15-20 wt%.

The properties of epoxy-silicone oil treated natural ramie fiber reinforced PP composites have also been reported [51]. The results showed that this modification method improved the compatibility between fiber and matrix but without changing the crystalline type of the ramie fiber. Compared to untreated ramie/PP composites, the modified ramie/PP achieved better mechanical and thermal properties.

1.2.9 Coir

Coir or coconut fiber, is a thick and coarse fiber obtained from the husk of coconut.

The effects of treated coir fiber on the physico-mechanical properties of coir reinforced PP composites were reported [52-54]. The coir fiber was treated with o-hydroxybenzene diazonium salt. The results revealed that the mechanical properties of the chemical modified coir fiber reinforced PP composites were much better than those untreated one, the tensile, flexural, and impact strength increased at least 6.8%, 8.6%, and 3.9% respectively, and the optimum set of mechanical properties was achieved at 30 wt%

fiber loading. In addition, the treated coir fiber/PP composites obtained a lower water absorption compared to untreated one.

In another study, Rozman et al. [55] investigated the influence of lignin as a compatibilizer on mechanical properties of coir fiber/polypropylene composites. The results demonstrated that the biocomposites with lignin as a compatibilizer achieved higher flexural properties and lower water absorption and thickness swelling compared to the neat composites, but there was not a significant change in tensile properties. In addition, the results also showed that the fiber size irregularities and fiber distribution might dominate the properties of the composites, which might overtake the influence of improved compatibility.

The coir fiber reinforced PE composites also have been reported. Enriquez et al. [56] fabricated the high density polyethylene composites with coconut fiber and stearic acid (SA) as the coupling agent. The results showed that after SA treated coconut fiber improved the mechanical properties and the thermal stability of the composites. It also exhibited the better aging resistance of the composites when they were exposed to aqueous, acidic, and alkaline environments. Prasad et al. [57] also investigated the effects of different fiber loading, fiber treatment, and compatibilizer on properties of coir/low density polyethylene composites. The results showed that the mechanical properties of composites with alkali and acrylic acid treated fibers decreased. The reason of this phenomenon was the alkali treatment removed part of cementing materials from the fiber and impurities from the fibers surface and resulted poor fiber/matrix interfacial adhesion. On the other hand, the compatibilizer (maleic anhydride grafted polypropylene) did improve the mechanical properties and water resistance of the biocomposites.

1.2.10 Bamboo

Bamboo is an evergreen perennial flowering plants and is an abundant natural resource in Asia. It is one of the best natural engineering materials in the world.

Chen et al. [58] studied the mechanical properties of bamboo fiber reinforced PP composites. The results revealed that the bamboo fiber reinforced maleic anhydride grafted polypropylene (MAPP) composites obtained better interfacial adhesion between fiber and matrix compared to the untreated composites. The optimum mechanical properties, the tensile strength was 32-36 MPa which was more than three times higher than those commercial product and the tensile modulus was 5-6 GPa, of the modified composites were achieved at around 50 wt% fiber content.

Several groups worked on bamboo fiber reinforced PE composites. Han et al. [59] investigated the compounding characteristics, clay dispersion, HDPE crystallization, and mechanical properties of the bamboo fiber/PP composites. The results showed that by adding 5% clay, the storage modulus and loss modulus was obtained the maximum; for the composites, the tensile strength increased with the increase of the maleic anhydride grafted polyethylene content. In another study, Ren and coworker studied the mechanical and thermal properties of HDPE composites reinforced by bamboo pulp fibers (BPF) and the comparison between BPF composites and bamboo flour (BF)/HDPE composites [60]. The results observed that the optimum mechanical properties of the composites with BPF was obtained at 30 wt% fiber content and higher than the composites reinforced with 50 wt% BF. And the thermal properties of BPF/HDPE composites was better than BF/HDPE composites as well.

1.2.11 Rice husk

Rice husk is a byproduct from the rice mill. Because of their large availability many studies have been investigated by using the rice husk as a thermoplastic composites reinforcement.

Permalal et al. [61] investigated the comparison of mechanical properties between the polypropylene composites reinforced with rice husk powder (RHP) and talc reinforced polypropylene composites. The results showed that the untreated talc composites exhibited higher yield strength, Young's modulus, flexural modulus and impact resistance compared to the raw RHP composites. Rice husk/PP composites were investigated regarding the effect of compatibilizing agents on biocomposites with various fiber loading [62], mechanical and morphological [63]. The results showed that the compatibilizing agent (maleic anhydride polypropylene) improved the tensile strength and modulus but there was no positive effect on Izod impact strength.

Rahman et al. [64] also investigated the effect of rice husk size and composition on injection molding of the rice husk/high density polyethylene composites. They observed that the most proper size as the biocomposite filler was the fiber size between 250~500 µm, the rice husk improved the mechanical properties of HDPE based composites and the optimum impact strength was obtained at 30 wt% rice husk content.

The thermal stability of the rice husk flour reinforced PP and HDPE composites was also investigated [65]. The results showed that the thermal stability of the composites decreased with the filler content increased.

1.2.12 Oil palm

Oil palm, Elaeis, contains two species of palm family. Abundance of oil palm has the great potential for polymer reinforcement.

Rozman et al. [66] investigated the flexural and impact properties of oil palm empty fruit bunch (EFB) reinforced PP composites. The EFB fiber modified with maleic anhydride (MA). The composites with treated EFB exhibited higher flexural and impact strength than the one with neat EFB due to there were new chemical bonding between fiber and matrix. In another study, Ramli and coworks suggested that the PP composites with 30 wt% oil palm fiber loading was the best formulation for biocomposites to obtain better young's modulus, processing compatibility, and good thermal stabilities [67]. Suradi et al. [68] studied the effects of alkali fiber treatment and coupling agents on properties of EFB/PP composites. The alkaline peroxide treatment helped EFB to separate lignin and hemicelluloses and it led to improvement of porosity, effectiveness of surface charge, and crystallinity index of fibers and addition of maleic anhydride polypropylene as coupling agent resulted a better interfacial adhesion between fiber and matrix compared to composites with raw EFB. In addition, a comparative study of EFB/PP composites and oil palm derived cellulose/PP composites were reported [69]. The results suggested that cellulose reinforced composites had a better mechanical properties compared to traditional oil palm fibers.

Oil palm reinforced PE composites was also studied by different groups. Arif et al. [70] studied that the effect of EFB fiber shape on the tensile and flexural properties of high density polyethylene composites. It showed that the EFB short fiber was the better choice compared to particulate system to reinforce HDPE composites on mechanical

properties. The tensile strength and modulus, flexural properties had a better performance in short fiber system compared to the particulate composites, specifically, the tensile and flexural modulus increased up to 50% and 82%, and the flexural strength increased up to 36%. Moreover, the dynamic mechanical properties of oil palm fiber/linear low density polyethylene (LLDPE) composites was investigated [71]. The results showed the storage modulus increased as fiber loading increased, the loss modulus also increased with fiber content increased except at 10% fiber loading; the glass transition temperature of neat LLDPE was increased from -145 ℃ to -128 ℃ when the fiber content was at 40%.

1.2.13 Bagasse

Bagasse is the fibrous matter that remains after sugarcane stalks are crushed to extract their juice.

Luz et al. [72] investigated that the effect of different processes on producing the bagasse fiber reinforced PP composites. Compared to compression molding process, the injection under vacuum provided a better performance for processing the biocomposites. This method led to composites with homogeneous distribution of fibers and without blisters. Although poor interfacial adhesion was observed between fiber/matrix, the mechanical properties of composites was improved by bagasse fiber.

The influence of various fiber treatment methods on the mechanical properties of bagasse fiber reinforced PP composites was also investigated [73]. The isocyanate, acrylic acid, mercerization, and alkaline solution were applied to bagasse fiber in order to improve the fiber/matrix interface. The results showed that the composites with fiber using mercerization treatment was achieved the better mechanical properties which the

storage modulus increased about 59%. The optimum results were obtained with the composites with 12 wt% mercerized bagasse fiber.

In another study, Darabi et al. [74] evaluated that the high density polyethylene composites reinforced with bagasse fiber after accelerated weathering followed by biodegradation. The results proved that bagasse fiber did reduce the discoloration of weathered composites. Although bagasse fiber reinforced HDPE composites obtained high resistance ability to against biological attack, the weathering triggers attack by termites and fungi on the surface and caused surface quality decreased.

1.2.14 Lignin

Lignin is a natural polymer based on phenylpropane derivatives and is found in wood and other lignin cellulosic materials. It is one of the most abundant biopolymer on earth.

The effect of lignin reinforced PE and PP on physical properties was studied [75]. The composites with lignin loading up to 30 wt% were prepared by extrusion molding. The results showed that the tensile strength decreased with lignin content increasing was very similar for both lignin/LDPE and lignin/PP composites. Toriz et al. [76] studied the effect of the coupling agent on mechanical properties of biocomposites. Maleic anhydride grafted polypropylene as a coupling agent improved strength properties especially at high lignin loading. It also showed that the flexural and tensile modulus were slightly improved.

1.2.15 Agave fiber

Recently, plant-based byproducts, such as agave fibers, have has received considerable attention from the industry sector. As the world's leading automobile manufacturing enterprises, Ford researched the use of sustainable materials for their vehicles since 2000 [77]. Currently, Ford uses eight bio-based materials in their vehicles, including soy foam, kenaf fiber, cellulose, wood, coconut fiber, rice husk, castor oil, and wheat straw. Today, Ford is exploring agave-based parts for every single vehicle in their fleet. Agave fiber comes from Agave Americana, belonging to the Agavaceae family, and the fibers used are a co-product of agave tequila production [78]. Similar to other natural fibers, agave fibers are light, low cost, and reproducible [79]. Despite abundance of agave fibers and desirable properties of agave fiber-based composites, there is only limited published information on agave fiber-based polymer composites. Singha and Rana studied the effects of different fiber concentrations and surface modification on mechanical properties of polystyrene (PS)/agave-fiber composites. Their investigations revealed that PS composites reinforced with 20% fiber loading by weight exhibited the best mechanical properties and that the mechanical properties of biocomposites reinforced with modified fibers were superior to those reinforce with raw fiber [6, 80]. Moscoso et al. reported that with PS and agave-fiber composites and foams the specific stiffness and strength where enhanced[81]. In another study, Pérez-Fonseca investigated the effect of hybridization of two natural fibers on the mechanical properties of high-density polyethylene-(pine/agave) composites and observed that the addition of agave fibers improved the mechanical properties of the composites [82]. Several fiber pretreatment methods have been reported; for instance, López-Bañuelos and Moscoso

reported on rotational molded agave fiber/linear medium density polyethylene composites, where alkali was used to pre-treat the agave fibers [79]. The outcomes of the study concluded that the composites reinforced with treated fibers exhibit a slightly higher tensile, compression, flexural and impact strength than the one with raw fibers, specifically, the tensile and flexural modulus increased up to 65% and 21%, and the tensile and flexural strength did not change significantly. A.A. Pérez-Fonseca and C. Gómez reported another chemical treatment method. They discovered the composites of high-density polyethylene and agave fibers coated with chitosan exhibited high adsorption capacity. The high adsorption ability could make the composites as a good treatment material of contaminated effluents [83]. The study concluded that composites reinforced with treated fibers exhibited slightly higher tensile, compression, flexural and impact strength than composites reinforced with raw fibers. When maleated polyethylene (MAPE) was used as the matrix and dry-blended with agave fibers, an increase in several mechanical properties (impact, tensile and flexural strength and tensile and flexural modulus) was reported [84, 85]. Corral et al. [86] investigated plasma treatment to improve adhesion between agave fiber powder and polyethylene matrix, reporting an increase of 21.7% in Young's modulus over composites with untreated filler. In general, short agave fibers (< 3 mm) exhibit better adhesion with epoxy resin matrices [78].

1.3 Summary

Extensive studies were carried out and introduced in the literature and reviewed in this paper, showing the great possibilities of using natural fiber to enhance the thermoplastics. In this study, we investigated the properties of biocomposite films containing different fiber loading ratios in linear low-density polyethylene (LLDPE),

high-density polyethylene (HDPE), and polypropylene (PP) matrices. Composite films with various agave fiber contents (up to 30 wt%) were prepared by extrusion molding and their mechanical and thermal properties were studied. This study evaluated the use of agave fibers that were not pretreated in order to determine if "raw" fibers could be used to effectively as fillers to enhance mechanical properties. The only pretreatment that was studied was washing to remove residual sugars. It is envisioned that these sugars could be used to produce additional co-products through fermentation.

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CHAPTER 2

MODIFICATION OF NATURE FIBERS

Low cost, easy to process, and ease of recycling are the main advantages of natural fibers. Many studies have reported that natural fiber reinforced polymer-based composites. A good fiber/matrix interface bond is critical for composites with high mechanical properties. However, the high moisture absorption and lack of adhesion between fiber and polymer matrix are the major disadvantages of nature fibers. Therefore, natural fibers modifications are the important methods to improve the properties of the composites. There are two main methods to modify the natural fibers, physical modifications and chemical modifications.

2.1 Physical modifications

Physical methods involve stretching [1], calendaring [2], thermos-treatment, electronic discharge (corona, plasma), and the production of hybrid yarns. The purposes of physical modifications are changing the structure and surface properties of the fibers without changing their chemical composition. Physical treatments improve the interface adhesion between fiber and matrices by increased physical bonding in the composites.

2.1.1 Corona treatment

Corona treatment is a surface oxidation activation techniques. The corona discharge treatment results that the fiber and matrix adhesion improved by increasing of the fiber surface energy by introducing polar groups on the surface [3]. Corona treatment

is an effective method to improve the compatibility between hydrophilic fibers and hydrophobic matrix [4].

Pizzi et al. investigated that the properties of composites of natural fibers and resin matrices [5]. The flax and hemp fiber mats were treated by corona method and the optimum length and time (10 mins) of corona treatment determined to improve the mechanical properties of the biocomposites. After the corona treatment, the fibers were shown a rougher surface because of the raising surface layers compared to untreated fibers. In addition, it was proven that the modulus of elasticity tensile property was increased up to 67% with increasing the corona treatment time while the tensile break force decreased.

Ragoubi et al. reported that the effect of corona treated hemp fiber on mechanical properties of PP based composites [6]. Fibers were treated in a corona discharge treatment device based on a dielectric barrier technique for 15 mins. The results proved that the property of composites with treated fiber was improved about 30% in Young's modulus.

2.1.2 Plasma treatment

As another physical treatment, plasma surface modification removes the current contaminants on the surface and improve the surface energy to make the surface more suitable for further processing. Plasma treatment can be used to treat surfaces of various materials before any coating and bonding processes.

The effects of plasma treatment on the performance of wood fiber/PP composites has been reported [7]. A radio-frequency generated cold plasma system was used to

modify the pine wood fibers for 30s. The results proved that the surface roughness of wood fiber increased after plasma treatment and the higher interfacial contact and better mechanical interlocking improve the tensile strengths and modulus of wood fiber/PP composites.

Sever et al. [8] studied that the effects on mechanical properties of HDPE composites reinforced with oxygen plasma treated jute fibers. The jute fibers treated by two different plasma systems, low frequency (LF) and radio frequency (RF), at various plasma powers (3, 60, and 90 W) for 15 mins were observed. In general, RF plasma treated jute fiber/HDPE composites achieved the best improvements in mechanical properties. The optimum parameter for oxygen plasma treatment was plasma power at 90 W for 15 mins.

Flax fibers were treated in different atmospheric plasma systems (argon and air) under various plasma powers to increase the interface adhesion between the flax fiber and HDPE matrix. The composites with treated fibers was obtained higher interlaminar shear strength value and a rougher surface compared to the composites with untreated fibers. In addition, a new functional group (O-C=O) were observed on the flax fiber surface [9].

2.2 Chemical modifications

The goal of chemical modification of natural fibers is improving the adhesion with the polymer matrix. The chemical composition of natural fibers include cellulose, hemicellulose, lignin, pectin, waxes, and moisture. The chemical composition of various natural fibers are shown in **Table 1** [10]. There is large amount of hydrophilic group in cellulose which leads the natural fiber hydrophilic properties. The hydrophilic nature of

natural fibers causes poor interface between natural fiber and matrix [11]. Chemical

treatments may activate hydroxyl groups or introduce some new groups that can enhance

the bonding between fibers and the matrix. Basically, the functions of chemical coupling

agents are activating the hydroxyl groups of cellulose in the fiber and the functional

groups of the matrix.

Table 1. Chemical composition of various natural fibers [10]

Fiber name	Cellulose (%)	Lignin (%)	Hemi-cellulose (%)	Wax (%)	Moisture (%)
Abaca	56-63	7-9	20-25	3	-
Agave fiber	68.42	4.85	4.85	0.26	7.69
Bamboo	26-43	1-31	30	-	9.16
Coir	37	42	-	-	11.36
Flax	64.1-71.9	2.0-2.2	64.1-71.9	1.7	8-12
Hemp	70.2-74.4	3.7-5.7	17.9-22.4	0.8	6.2-12
Jute	61-71.5	11.8-13	17.9-22.4	0.5	12.5-13.7
Kenaf	45-57	21.5	8-13	0.8	6.2-12
Oil palm	65	17.5	10.12	4	-
Ramie	68.6-91	0.6-0.7	5-16.7	-	-
Rice husk	38-45	-	12-20	-	-
Sisal	78	8	10	2	11

2.2.1 Alkaline treatment

Alkaline treatment or mercerization in one of the most widely used chemical

treatment for natural fibers when used to reinforce polymers. The modification of

alkaline treatment is the disruption of hydrogen bonding in the network structure, thus

increasing surface roughness. This treatment reduces the amount of lignin, wax and oils

covering the external surface of the fiber cell wall [12]. The reaction of sodium hydroxide

with natural fiber is shown below:

Fiber-OH + NaOH → Fiber-O-Na + H_2O
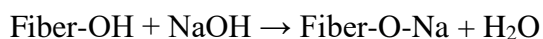
Huda et al. [13] investigated the effect of alkali treatment of pineapple leaf fiber on interfacial and mechanical properties of poly(lactic acid) (PLA) based composites. They found that alkali-treated fiber reinforced composites exhibited excellent mechanical properties including higher storage modulus and flexural modulus compared to the composites with untreated fiber. It was also found that with modified fiber surfaces, the interfacial properties of the composites improved significantly.

2.2.2 Silane treatment

Silane is an inorganic compound with chemical formula SH_4. Silane coupling agents are known as efficient coupling agents widely used in composites and adhesive formulations. This type of agents is used as adhesion promoters or substrate primers which offer strong adhesion.

Xie et al. [14] reported that in the case of aminosilanes, the amino groups cannot react with the hydrocarbon backbone of PP or PE, however, the natural fibers and thermoplastic-based composites modified with APS was exhibited a better mechanical properties than untreated composites.

Cantero et al. [15] studied that the effects of various fiber treatments on wettability and mechanical properties of the flax/PP composites. The maleic anhydride (MA), maleic anhydride-polypropylene copolymer (MAPP) and vinyl trimethoxy silane (VTMO) were used as coupling agents in this research. They observed that the composites with MAPP treated fibers achieved the highest mechanical properties, meanwhile there was no significant change in the value of composites containing the MA and VTMO treated fibers compared to the untreated one.

2.2.3 Maleated coupling

Maleated coupling agents are extensively used to enhance natural fibers reinforced composites. Compared to other chemical modifications, maleic anhydride (MA) can be used to modify both the fiber surface and the polymer matrix to obtain better interfacial adhesion between fiber and matrix and improve the mechanical properties of composites. There are plenty of studies related to this topic especially for PE or PP based composites reinforced with natural fibers.

Yang et al. [16] reported the effect of MAPP coupling agents on rice-husk flour reinforced PP composites. The tensile strength and modulus were improved with the addition of MAPP coupling agent while there was no significant change on Izod impact strength. The morphological study also proved the positive influence of the coupling agents on interfacial adhesion.

Gassan et al. [17] investigated the effect of MAPP modification on fiber/matrix bonding in jute fiber reinforced PP-based composites and on the material properties. It obtained that a strong interface is connected with a higher dynamic modulus and reduction in stiffness degradation with increasing load cycles and applied maximum stresses due to using MAPP modified the fiber surfaces. Moreover, the loss-energy for non-penetration impact tested composites reduced about 30% because of the better fiber/matrix interface. Mohanty et al. [18] also reported using MAPP as a coupling agent for fiber modification on properties of jute/PP composites. It observed that the mechanical properties of treated composites were improved due to better fiber matrix adhesion.

In addition, Liu et al. [19] investigated that the properties of abaca (banana) fiber reinforced composites based on high density polyethylene (HDPE)/Nylon-6 blends. Maleic anhydride grafted styrene/ethylene-butylene/styrene triblock polymer (SEBS-g-MA) and maleic anhydride grafted polyethylene (PE-g-MA) were used to improve the interfacial adhesion between fiber and matrix. The results showed that using SEBS-g-MA as coupling agents modified abaca fibers obtained a positive influence on the Nylon-6 component in the composites. The effect of MA treated various fibers (including banana, hemp and sisal fibers) reinforced polymer composites was reported [20]. The MA as the coupling agent reduced the water absorption and steam absorption to a significant extent. The MA modified composites obtained a greater mechanical properties including Young's modulus, flexural modulus, hardness and impact strength.

2.2.4 Acetylation

Acetylation is a widely studied modification method of cellulosic fibers to make them more hydrophobic. Acetylation is to react with hydroxyl groups of fiber to change their hydrophilic properties to more hydrophobic.

Bledzki et al. [21] investigated the effect of acetylation on properties of flax fiber reinforced PP composites. The results showed: 1) the flax fiber surface morphology improved significantly after the acetylation; 2) the moisture absorption properties decreased with increased of acetyl content of fiber; 3) before the acetyl content was 18%, the degree of polymerization slowly decreased with increased degree of acetylation, after 18% acetyl content, the polymerization decreased rapidly; 4) the thermal stability improved with increasing the acetylation degree; 5) compared to untreated composites,

the tensile and flexural strengths of composites with acetyl treated fiber increased with increasing the acetyl content up to 18%.

Favaro et al. [22] reported that the effects of acetyl treated sisal fiber reinforced recycled HDPE composites. For sisal fiber surface modification, the fibers were treated with NaOH solution then acetylated with acetic acid and sulfuric acid. The results showed that the flexural and impact properties of composites with both treated and untreated fiber were improved. Nonetheless, this modification was not good for oxidation of the HDPE.

The influence of acetylation on properties of cellulose and cellulignin fibers from bagasse reinforced PP composites was studied [23]. However, for this study, acetylation was not a good modification method for cellulose and cellulignin fibers from sugarcane bagasse. The acetylation changed the morphology of fibers, led to agglomerates with globular form. The results revealed that the mechanical properties of the acetylation of fibers reinforced composites decreased.

2.2.5 Enzyme technology

Enzyme technology is becoming more popular, especially for modifying textile and natural fibers. It has various benefits involving environmental friendly, the reactions catalyzed are very specific with a focused performance as a result, cost reduction, energy and water saving [24].

The properties of enzyme treated abaca fiber reinforced PP composites was investigated [25]. The fibers were treated by fungamix and natural enzyme. After modification, the fiber surface became smooth compared to the surface of untreated fiber.

The tensile strength of the composites with enzyme treated fibers increased 5-45%. The moisture absorption of the treated composites was reduced. The modified fiber reinforced composites also exhibited a better acid and base medium resistance. The MAPP coupling agent modified abaca fiber composites was also studied in this research. The enzyme treated abaca composites showed a comparable or better performance in moisture absorption, mechanical and rheological properties compared to the MAPP treated composites.

2.3 Modifications of agave fiber

Like the other natural fibers, the agave fiber contains cellulose, hemi cellulose, lignin, wax, ash etc. and the cellulose dominates the chemical composition of it. In order to obtain a better interfacial bonding between the fiber/polymer matrices, it is necessary to modify the fiber. Currently, there are limited studies and publications on agave fiber reinforced polymer-based composites, especially on agave fiber modifications. Based on those published studies, alkali treatment [26, 27] and maleated treatment [28, 29] were the common chemical modification methods for agave fiber. Other chemical method such as graft copolymerization of methyl methacrylate onto agave fiber [30] and coated with chitosan [31] were also investigated. In addition, Corral et al. [32] reported the effect of plasma treatment of agave fiber power on properties of PE composites. All those researches proved that modification of agave fiber had the positive influence on the performance of the biocomposites.

2.4 Summary

Various studies showed the importance of the modification of natural fibers to improve the interfacial properties of the composites. For those physical treatments, they may create a hydrophilic or hydrophobic fiber surface by changing the surface energy, without changing the hygroscopic characteristics of fiber, to improve the interfacial adhesion in the composites. Chemical modifications are more and more popular than physical methods. The alkaline treatment, silane treatment, and maleated coupling agents are the most commonly used chemical treatments. Compared to the physical treatments, the chemical modifications may make the fiber walls more dimensionally stable, reduce water sorption, or increase resistance against fungal decay, however, there may be an associated reduced dynamic strength such as impact strength due to embrittlement [14]. Furthermore, the cost of chemical treatment is higher than physical treatment and disposal of chemical after modification should be concerned.

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CHAPTER 3

AGAVE FIBER REINFORCED THERMOPLASTIC FILMS

In this chapter, agave fiber reinforced thermoplastic composite films were prepared using extrusion molding method and their mechanical and thermal properties were investigated. The linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and Polypropylene (PP) are selected as matrices. In this study, the fibers and matrices were mixed directly and no coupling agent was used to produce the composites. The study presented in this chapter is submitted for publication.

3.1 Experimental

3.1.1 Materials

Polymer matrices were created using LLDPE, HDPE or PP, all in pellet form. The LLDPE had a melt flow index of 20 g/10 min at 190 °C and a density of 0.925 g/cm^3 (ExxonMobil Chemical Corporation, Texas). The HDPE had a melt flow index of 20 g/10 min at 190 °C and a density of 0.952 g/cm^3 (Chevron Phillips Chemical Company LP, Texas). The PP had a density of 0.868 g/cm^3 (Formosa Plastics Corporation, Texas). Agave fibers were obtained from Byogy Renewables, Inc.

3.1.2 Preparation of agave fibers

Agave fibers and water were placed in a 70-liter tank (Feldmeier Equipment, INC., USA) at a 2:3 (solid:liquid) volume ratio. The solution was heated to 70 °C and stirred for 24 hours, the fibers were then removed from the water using a filter. This wash cycle was repeated 6 times. After the washing cycles, the agave fibers were laid onto

drying trays, the thickness of the layer of fibers was less than 1.5" and dried at 105 °C for 18-24 hours. **Figure 1** shows photo of Feldmeier 70-liter tank (a) and agave fiber during the wash treatment. **Figure 2** shows photo of the raw agave fiber before (a) and after (b) wash treatment. The washing removed the residual sugars in the fiber and the dust on the surface, which resulted in the color of the agave fibers after washing as seen in a lighter color compared to the raw fibers.

Figure 1. Photos of (a) Feldmeier 70-liter tank and (b) agave fiber during the wash treatment
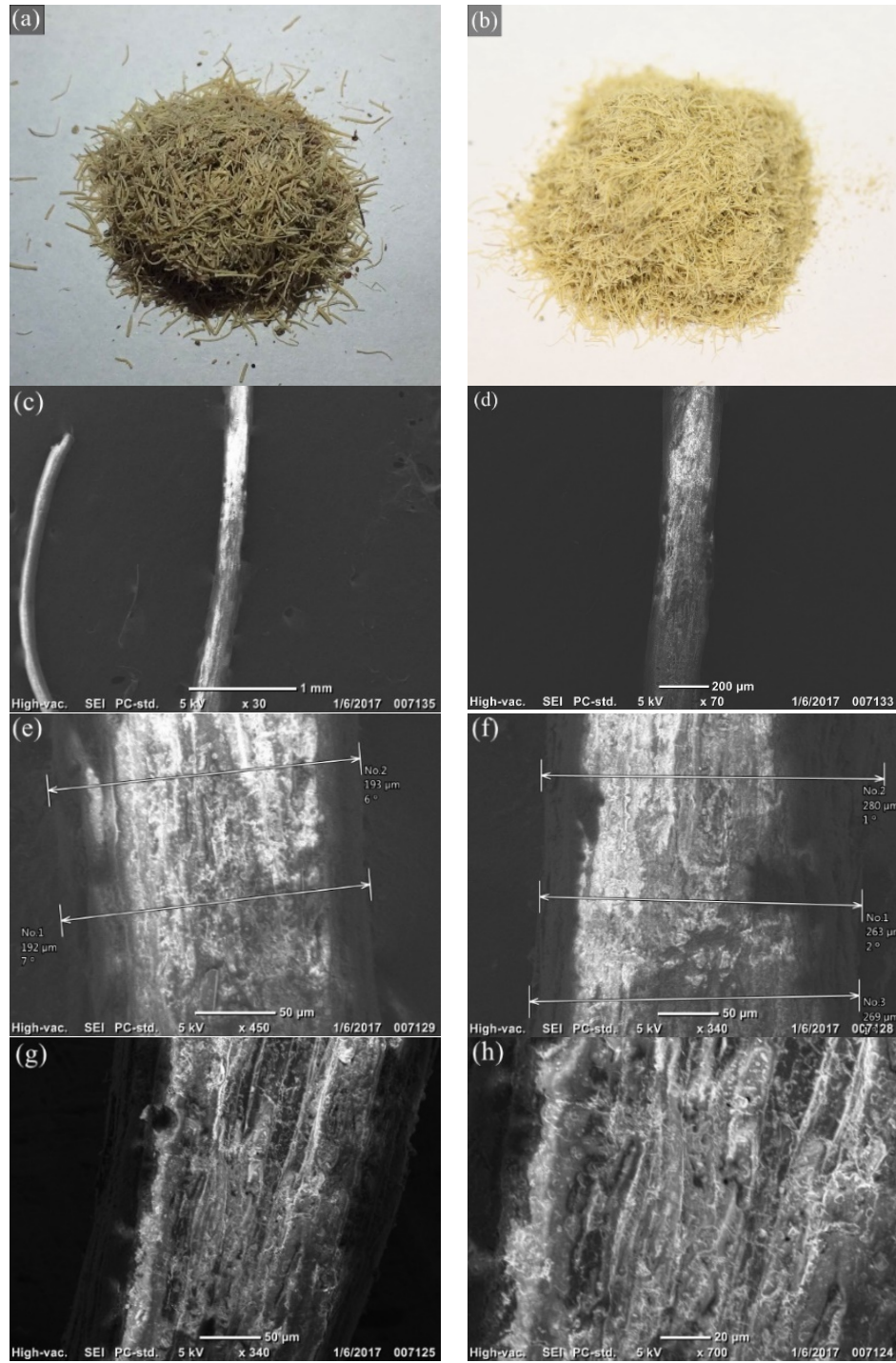
Figure 2. Agave fibers: (a) before and (b) after washing treatment; SEM images of agave fibers: (c) 1 mm, (d) 200 µm; fiber diameter varies: (e) and (f) 50 µm; Surface roughness of agave fiber: (g) 50 µm, and (h) 20 µm.

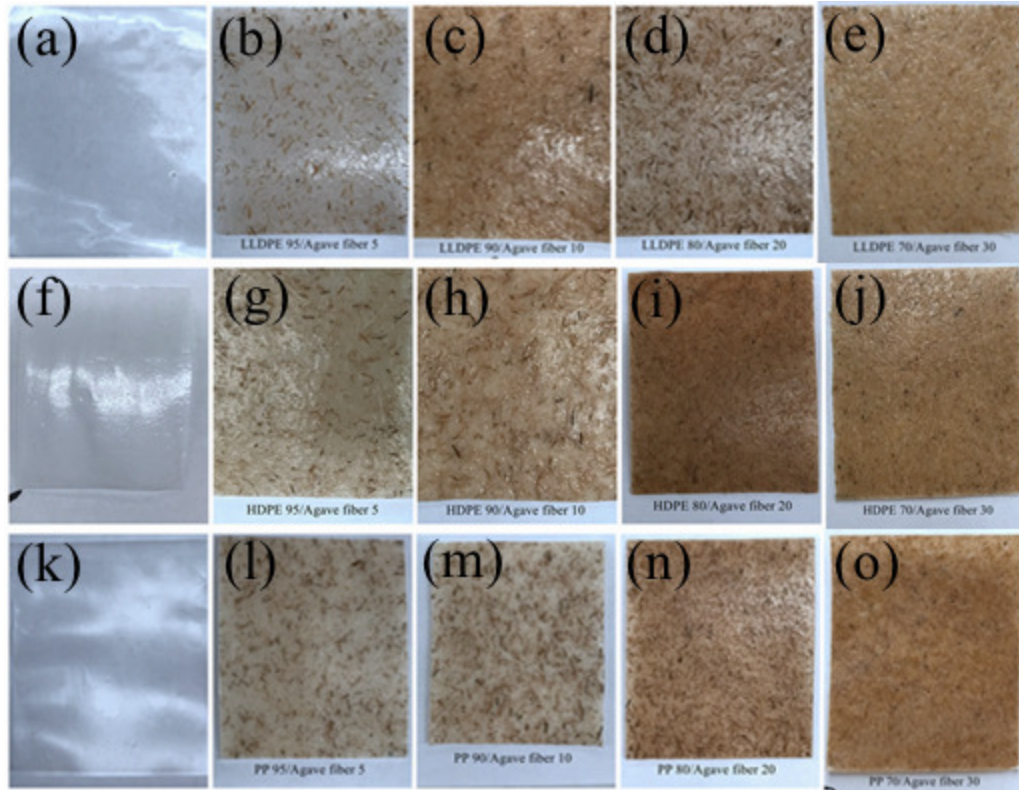**3.1.3 Test for density stop**

    The density of the agave fiber was determined by the ethanol displacement method. The fibers were completely submerged in ethanol and the volumetric displacement was measured.

3.1.4 Preparation of biocomposite film

    Polymers and agave fibers were blended in a Leistritz 27mm co-rotating twin-screw extruder. The extrusion temperatures parameters of compound processing are detailed in **Table 2**. In total, four agave fiber compositions were integrated: 0, 5, 10, 20 and 30 wt%. The screw speed was set to 225 RPM. When blending was complete, the extrudates were pelletized. Table 1 also details the temperatures of the Brabender 18mm single extruder from the feeder to the die for creating films. The screw speed was set to 75 RPM. **Figure 3** shows images of all film samples.

Table 2. The extrusion temperature (℃) parameters of extrusion for compounding and films

The extrusion temperature(°C) parameters of extrusion for compounding (twin screw extrude)												
Heating zone		1 (feeder)	2	3	4	5	6	7	8	9	10	11 (die)
Resin	LLDPE	70	160	165	170	175	180	170	175	170	165	165
	HDPE	70	165	170	175	170	185	185	180	175	170	165
	PP	70	170	195	200	210	215	215	210	205	200	190
The extrusion temperature(°C) parameters of extrusion for films (single screw extruder)												
Heating zone		1 (feeder)		2		3		4		5 (die)		
Resin	LLDPE	90		165		180		175		165		
	HDPE	90		175		185		180		170		
	PP	90		150		190		180		180		

Figure 3. Images of agave fiber reinforced thermoplastic composite films. a-d), LLDPE reinforced with agave fiber at 0 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt%; f-j), HDPE reinforced with agave fiber at 0 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt%; k-o), PP reinforced with agave fiber at 0 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt%.

3.2 Characterization

3.2.1 Scanning electron microscopy

The morphology of the prepared fibers and the cross-sections of the biocomposite films were investigated using SEM (NeoScopo, JCM-6000 Benchtop SEM). Before SEM measurements, the samples were freeze-fractured with liquid nitrogen to reveal cross-sections.

3.2.2 Mechanical analysis

Tensile test was conducted with a DMA machine, which was using a Mettler Toledo instrument, model DMA 1. All measurements were performed at room temperature (25 °C) at a force rate of 0.5 N/min. The thickness of the film was measured at three positions for each sample. The thickness of the film varied depending on the extrusion molding conditions. The thickness of biocomposite films with LLDPE, HDPE and PP resins are 0.41-0.63 mm, 0.34-0.54 mm and 0.31-0.47 mm respectively. The length and width of all samples were 10 mm and 2 mm.

3.2.3 Differential scanning calorimetry (DSC)

DSC was conducted using a Mettler Toledo polymer differential scanning calorimeter. The samples of both LLDPE and HDPE with agave fiber were heated from 25 °C to 150 °C at a rate of 10 °C /min. The samples of PP/agave fiber were heated from 25 °C to 200 °C at a rate of 10 °C /min.

3.2.4 Fourier-transform infrareds

FT-IR spectra of bio-filler reinforced thermoplastic films were recorded using a Perkin-Elmer FT-IR Spectrometer in the range of 4000-650 cm^{-1}.

3.3 Results and Discussion

Different types of biocomposite films were prepared and the elastic modulus, the melting point, and the fiber-matrix interface were characterized for each sample. The density of agave fiber is 1.348 g/cm^3 and the length of agave fibers are between 3 to 7 mm. the length distribution of fibers was not investigated in this studied.

3.3.1 Morphology

The SEM of a single agave fiber is seen in **Figure 2**. The fiber diameter and surface morphology for different fibers have been studied. Agave fiber has a visibly rough surface and varying diameter.

Prior to SEM analysis, the films were fractured following an axis perpendicular to the extruding direction. **Figure 4** shows SEM cross-sectional images of PP: agave fiber; LLDPE and HDPE with agave fiber are similar. **Fig. 4(a)** is the PP control group film. **Fig. 4(b, c, d, e)** and **(f)** show the variations of fibers in the polymer matrix for 80:20 wt% PP-agave fiber film. The cross-sectional of agave fiber is shown in **Fig. 4(e) and (f)**. This image shows random morphology and distribution of agave fibers in the polymeric blends. In **Fig. 4(c)**, it is apparent that there are three voids at the bottom part of the image. These voids are likely air bubbles. One explanation for their presence is that although those pellets were went through the drying process for more than 24 hours, there was still a small amount of moisture, less than 0.34%, in the pellets. The moisture could cause the steam during the extrusion processing. The steam could be trapped in the film as well.
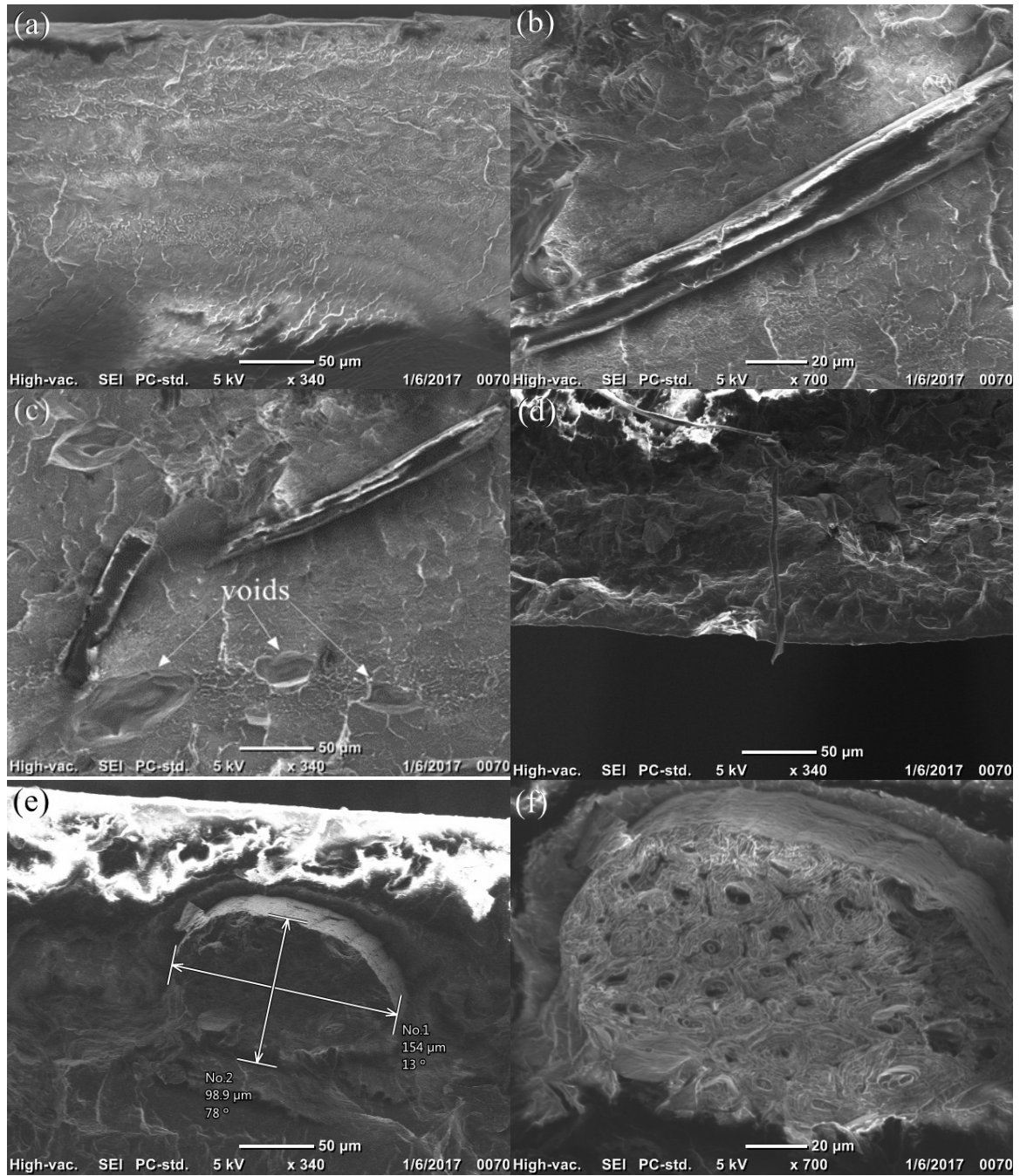
Figure 4. Cross-sectional SEM micrographs of PP/agave fiber films: (a) PP control group, (b)-(f) PP:agave fiber 80:20 wt%.

3.3.2 FT-IR analysis of polymeric films

FT-IR spectroscopy was used to examine the interactions between the thermoplastic matrix and the agave fibers. **Figure 5** (a) shows the FT-IR spectra of pure agave fibers, an LLDPE control group, and a 80:20 wt% LLDPE:agave fiber composite. FTIR spectrum of pure agave fiber showed a broad peak at 3331 cm^{-1}, which was due to the stretching vibrations of hydroxyl groups from the cellulose in the agave fiber. The peak at 2923 cm^{-1} was assigned to C-H group. The peak at 1732 cm^{-1} was corresponding to the C=O group of hemicellulose, waxes, pectin, and lignin [2]. The peak at 1616 cm^{-1} was due to H-O-H group stretching of absorbed moisture and for lignin C-H deformation. The peak at 1517 cm^{-1} was due to the lignin aromatic ring vibration and stretching. The milder peaks at 1375 cm^{-1} to 1427 cm^{-1} were attributed to -CH, -CH2-, or -CH3 groups [3]. The peak at 1317 cm^{-1} was due to the –CH group from the cellulose. The peak at 1238 cm^{-1} was assigned to C-O-C and C=O groups of lignin [4]. 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 [3].

The LLDPE control group showed peaks at 2915 cm^{-1} –2849 cm^{-1}, 1473 cm^{-1} – 1463 cm^{-1}, and 730 cm^{-1} –719 cm^{-1}. These variations where the peaks at 2915 cm^{-1} –2849 cm^{-1}, 1473 cm^{-1} –1463 cm^{-1}, and 730 cm^{-1} –719 cm^{-1},are assigned to the symmetrical stretching vibration of the C–H bonds. However, the LLDPE composites reinforced with agave fibers exhibited additional peaks: 1) a broad peak between 3600 cm^{-1} and 3200 cm^{-1} was due to the –OH group in the cellulose of agave fiber; 2) the peak at 1712 cm^{-1} was assigned to C=O group of hemicellulose; 3) the peak at 1614 cm^{-1} was due to H-O-H stretching; 4) the peak at 1376 cm^{-1} was attributed to –CH2– group; 5) the peak at 1271

cm^{-1} was due to C-O-C stretching; 6) the milder peaks at 1165 cm^{-1} and 1125 cm^{-1} were attributed to O-C-O asymmetric stretching of the cellulose; 7) the peak at 998 cm^{-1} was assigned to C-O stretching vibrations of the cellulose.

Figure 5 (b) shows the spectra of pure agave fiber, an HDPE control group, and a 80:20 wt% HDPE:agave fiber composite. The results for HDPE composites were similar to those for the LLDPE composites. Compared to the neat HDPE, there were several additional peaks exhibited in the composites. The explanations of those additional peaks were the same as the LLDPE composites.

Figure 5 (c) shows the spectra of agave fiber, neat PP, and a 80:20 wt% PP:agave fiber composite. Both neat PP and the PP composites showed four peaks in the wavenumber range between 3000 cm^{-1} and 2800 cm^{-1}: the peaks at 2950 cm^{-1} and 2868 cm^{-1} were assigned to $-CH_3$ asymmetric and symmetric stretching vibrations, respectively; the peaks at 2918 cm^{-1} and 2839 cm^{-1} were caused by $-CH_2$ asymmetric and symmetric stretching vibrations, respectively [5-7]. The peak at 1456 was assigned to $-CH_2-$ or $-CH_3$ groups, while the peak at 1376 cm^{-1} was caused by $-CH_3$ groups. Various small peaks also appeared in the wavenumber range between 1200 cm^{-1} and 700 cm^{-1}: the peak at 1168 cm^{-1} was attributed to C–C, $-CH_3$ and C–H groups. The peak at 998 cm^{-1} was assigned to $-CH_3$ groups, while the peak at 973 cm^{-1} was attributed to $-CH_3$ or C–C groups. The peak at 841 cm^{-1} was assigned to the $-CH_2-$ group [7]. However, the PP composites reinforced with agave fibers showed additional peaks: 1) a broad peak between 3600 cm^{-1} and 3200 cm^{-1} was due to the –OH group in the cellulose of agave fiber; 2) the peak at 1712 cm^{-1} was assigned to C=O group of hemicellulose; 3) the peak at 1610 cm^{-1} was due to H-O-H stretching; 4) the peak at 1376 cm^{-1} was attributed to –CH2– group; 5) the peak at 1275

cm^{-1} was due to C-O-C stretching; 6) the peak at 1166 cm^{-1} was attributed to O-C-O asymmetric stretching of the cellulose; 7) the peak at 998 cm^{-1} was assigned to C-O stretching vibrations of the cellulose; 8) the peak at 900 cm^{-1} was due to –β glycosidic linkage of the agave fiber.

From the FT-IR spectrum, neither LLDPE, HDPE, nor PP composites have new chemical bonds at the interface between polymer and fiber.

3.3.3 Mechanical properties

Tensile test was conducted with a DMA machine. Based on the stress-strain curves obtained, **Figure 6** shows the elastic modulus (E) and **Figure 7** shows yield stress (σ) of the thermoplastic control group films and composites films. The physical and mechanical properties of all agave fiber and biocomposite films are summarized in **Table 3**. It is seen from **Table 3** that for LLDPE, neat LLDPE films exhibited elastic modulus of 88.4 MPa whereas LLDPE composites reinforced with agave fibers exhibited an elastic modulus of 241.5, 266.7, 370.7 and 324.2 MPa at 5 wt%, 10 wt%, 20 wt% and 30 wt% fiber loading respectively. Similarly, for HDPE, neat HDPE exhibited an elastic modulus of 435.1 MPa while HDPE composites reinforced with agave fibers exhibited an elastic modulus of 617.6, 657.6 736.0 and 640.3 MPa at 5 wt%, 10 wt%, 20 wt% and 30 wt% fiber loading respectively. Moreover, it has been observed that PP control group films exhibited an elastic modulus of 560.4 MPa whereas PP composites showed an elastic modulus of 766.7, 829.7, 882.7 and 738.8 MPa when reinforced with agave fibers at 5 wt%, 10 wt%, 20 wt% and 30 wt% respectively.
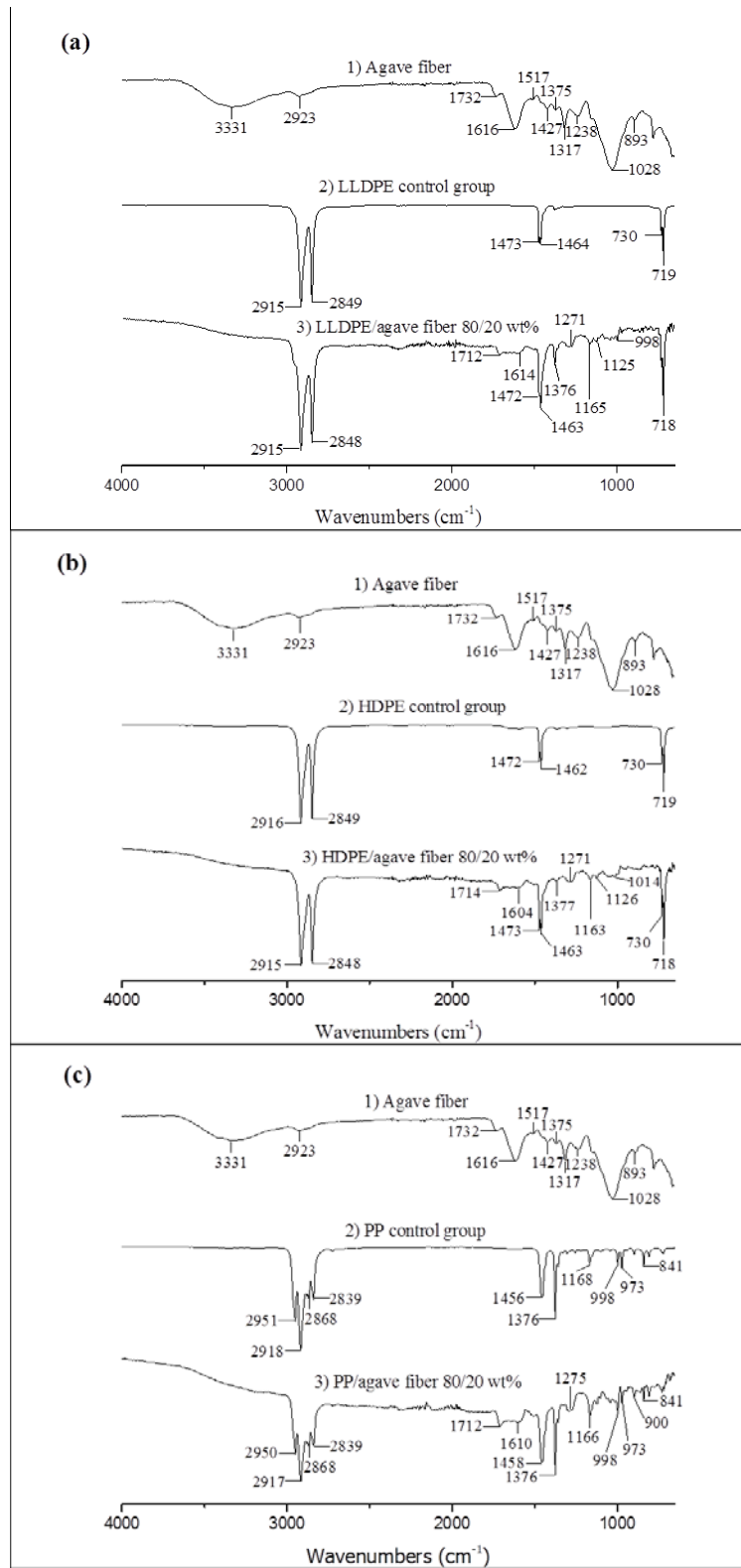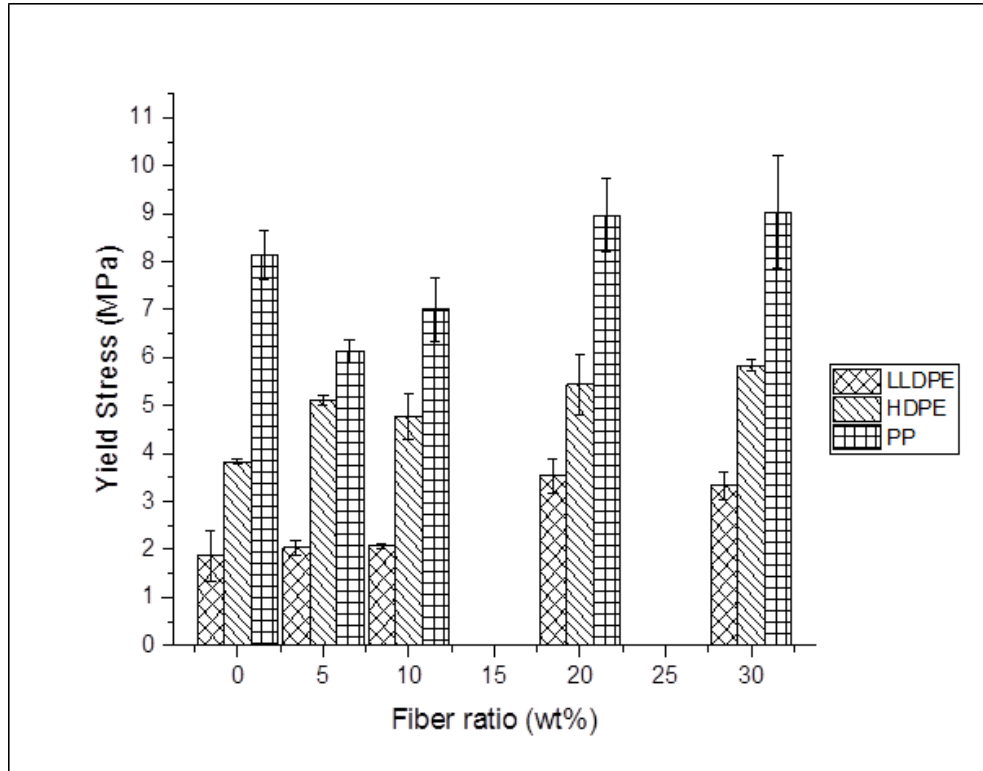
Figure 5. FT-IR spectra of agave fiber reinforced thermoplastic-based composite films:

(a) LLDPE with agave fiber, (b) HDPE with agave fiber, (c) PP with agave fiber.
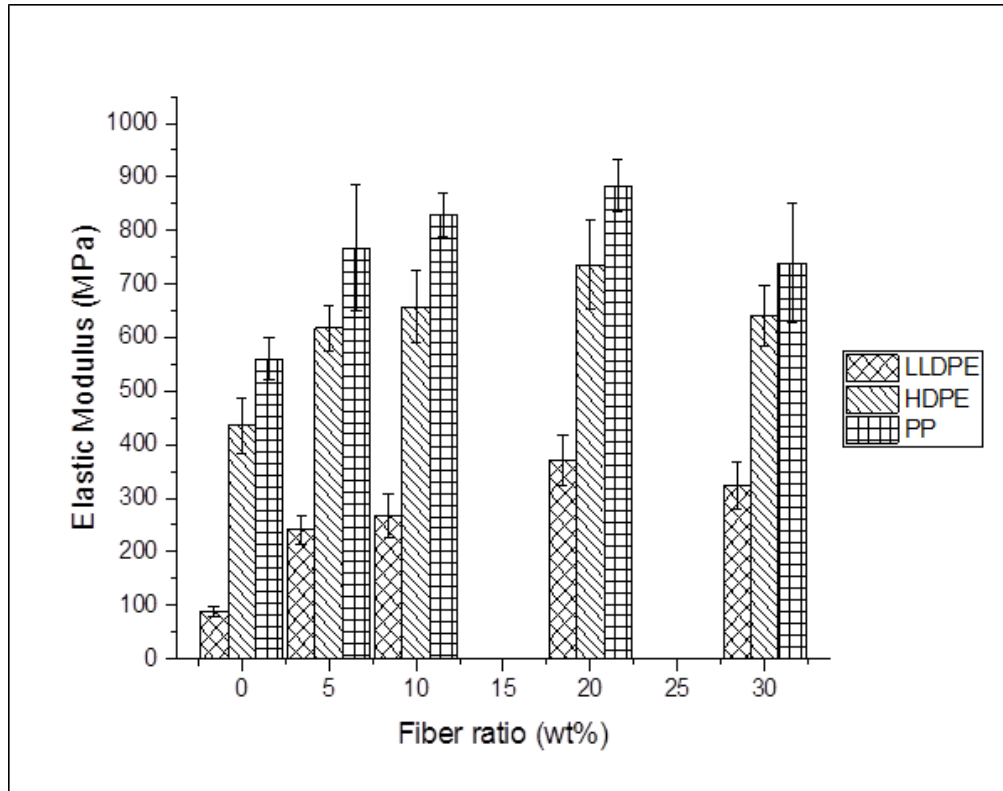
Figure 6. Elastic modulus (E) of biocomposite films

Figure 7. Yield stress (σ) of biocomposite films

Figure 7 shows the yield stress (σ) of LLDPE, HDPE and PP composites reinforced with agave fibers. The results from **Figure 7** and **Table 3** show that the yield strength of agave fiber reinforced LLDPE films increased with fiber loading increased and the highest yield strength was achieved at 20 wt%. For the HDPE reinforced with agave fiber, compared to the neat polymer the yield strength of composites with all fiber contents was improved and the highest yield strength was achieved at 30 wt%. For agave fiber reinforced PP composites, the highest yield strength was achieved when the fiber loading was at 30 wt%. However, the yield strength decreased when the fiber loading were at 5 wt% and 10 wt%, compared to neat polymer. This might be because of it was not ensured that there were enough fibers forming a 'network' to reinforce the composites, when the composites was at a lower fiber content. Specifically, neat LLDPE film exhibited a yield strength of 1.7 MPa while LLDPE composites reinforced with agave fibers exhibited yield strength of 2.0 MPa, 2.1 MPa, 3.5 MPa and 3.3 MPa at 5 wt%, 10 wt%, 20 wt%, and 30 wt% fiber loading, respectively. Similarly, neat HDPE film exhibited a yield strength of 3.8 MPa whereas HDPE composites reinforced with agave fibers exhibited yield strength of 5.1 MPa, 4.8 MPa, 5.4 MPa and 5.8 MPa at 5 wt%, 10 wt%, 20 wt%, and 30 wt% fiber loading, respectively. In addition, neat PP film exhibited a yield strength of 8.1 MPa while PP composites reinforced with agave fibers exhibited yield strength of 6.1 MPa, 7.0 MPa, 9.0 MPa and 9.1 MPa at 5 wt%, 10 wt%, 20 wt%, and 30 wt% fiber loading, respectively.

In addition, the specific yield strength was also investigated and the results was shown in **Table 3**. The neat LLDPE film exhibited a specific yield strength of 1.83 kN·m/kg while LLDPE composites reinforced with 20 wt% agave fibers loading achieved the highest specific yield strength of 3.55 kN.m/kg; compared to the neat LLDPE film,

the specific yield strength of LLDPE composites was increased with fiber loading increased. The HDPE film exhibited a specific yield strength of 3.99 kN.m/kg whereas HDPE composites reinforced with 30 wt% agave fibers loading achieved the highest specific yield strength of 4.03 kN.m/kg; the specific yield strength of with all the fiber contents composites was improved compared to the neat polymer. Moreover, compared to the neat PP film, the PP composites reinforced with 20 wt% agave fibers exhibited the highest specific yield strength of 9.63 kN.m/kg.

3.3.4 Thermal analysis

The samples of thermoplastics and composites reinforced with agave fibers were subjected to heating, cooling and second heating cycles in DSC analysis to determine the variations of samples' melting temperature (T_m). The DSC results are shown in **Figure 8.** There are no significant changes in T_m between control groups and composites.

Table 3. Mechanical properties of biocomposite films

	Fiber ratio (wt%)	Elastic modulus (MPa)	Standard deviation numbers	Yield stress (MPa)	Standard deviation numbers	Specific yield strength (kN·m/kg)
LLDPE:agave fiber	0	88.4	9.29	1.9	0.51	1.83
	5	241.5	27.16	2.0	0.15	2.13
	10	266.7	41.65	2.1	0.06	2.09
	20	370.7	46.55	3.5	0.35	3.55
	30	324.2	43.64	3.3	0.29	3.23
HDPE:agave fiber	0	435.1	50.83	3.8	0.06	3.99
	5	617.6	42.58	5.1	0.10	5.28
	10	657.6	68.23	4.8	0.47	4.89
	20	736.0	82.06	5.4	0.64	5.34
	30	640.3	56.38	5.8	0.12	5.68
PP:agave fiber	0	560.4	40.04	8.1	0.51	9.33
	5	766.7	118.18	6.1	0.23	6.90
	10	829.7	40.73	7.0	0.65	7.78
	20	882.7	48.31	9.0	0.76	9.63
	30	738.8	113.43	9.1	1.17	9.36
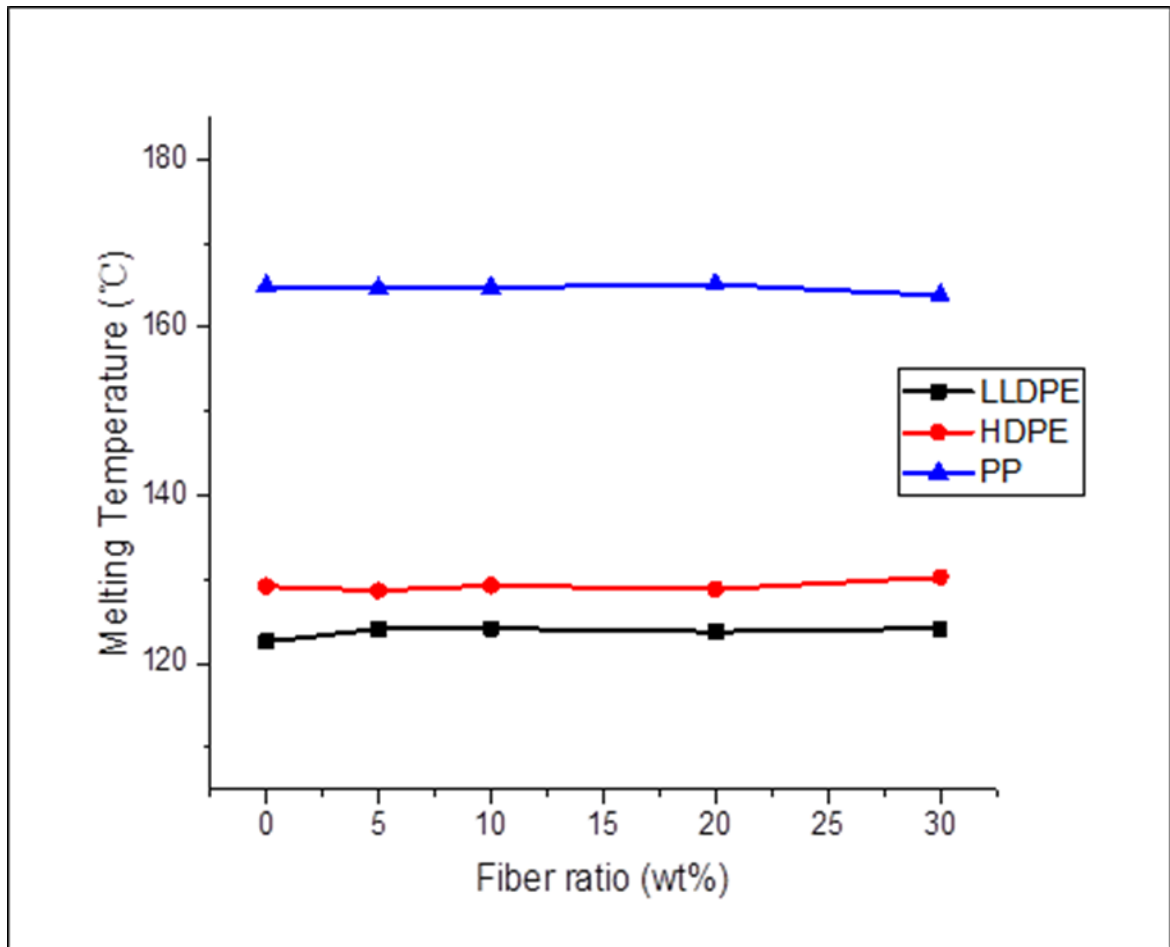
Figure 8. Melting temperatures of biocomposites

3.4 References

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CHAPTER 4

CONCLUSION AND FUTURE WORK

4.1 Conclusion

Biocomposite films made of thermoplastic (LLDPE, HDPE and PP) matrices and agave fiber reinforcement were successfully prepared in order to investigate the effect of fiber addition on chemical structure and mechanical and thermal properties. The level of fiber loading was varied between 0 and 30 wt%. SEM images of the freeze-fractured biocomposite samples revealed a good distribution of the agave fibers. Compared to control films, the elastic moduli of composites reinforced with agave fibers exhibited improvement as fiber content increased. . The highest elastic modulus was observed when the fiber concentration was at 20 wt%. For LLDPE composites, the highest yield strength was observed when fiber loading was at 20 wt%; for HDPE and PP composites, the highest yield strength was observed when fiber concentration was at 30 wt%. The specific strength of agave fiber reinforced biocomposite film was also investigated and it was observed that the specific yield strength of LLDPE, HDPE, and PP reinforced with agave fiber was improved. However, the interfacial adhesion between bio-fillers and matrices was poor. The FT-IR spectra suggested that the bonding between fibers and matrices was solely physical and no chemical interaction occurred. Because there were no new chemical bonds created, the thermal properties of the composites were dominated by the matrix resin. The melting temperature of biocomposites did not change significantly by the addition of agave fibers compared to neat thermoplastic films. The results combining mechanical and thermal properties of biocomposites showed that agave

fibers have a great potential as an excellent substitutable nature filler for thermoplastics reinforcement and the composites with 20 wt% fiber loading was the optimum formulation.

4.2 Future work

In the current study, we have successfully manufactured agave fiber reinforced thermoplastic-based composite films, which achieved a significant improvement in mechanical properties compared to those neat thermoplastics. In the future, there still has lot of works to do on study of composites with agave fiber.

1) Modification of fibers and polymer matrix

Although good mechanical properties were obtained in this study, poor fiber/matrices interfacial bonding was observed by both SEM and FTIR investigations. To achieve a better mechanical and thermal properties, we should treat the fiber surface and modify the polymer matrix. Based on the extensive studies, it suggested that the alkali treatment [1, 2] and maleated treatment [3, 4] methods are more efficient for modifying the agave fiber reinforced composites.

2) Study on the durability of biocomposite films

The agave fiber reinforced composites have been got the attention from the industry, the industrial giant, like Ford motor company [5], have tried to use this sustainable material to replace those conventional petroleum-based polymer parts. As a very practical research, the durability of the material is important. In the future, we could investigated the reliability of the biocomposites including the UV durability, accelerating aging test, corrosion resistance, and so on.

3) Other possible modification works on agave fiber reinforced composites

Owing to the nature of agave fiber and polymers, some odor would associate with the final products. Eliminated the odor will make the bio-products more environment friendly.

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