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SUSTAINABLE COMPOSITE MATERIALS FROM RENEWABLE RESOURCES FOR AUTOMOTIVE APPLICATIONS

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Master of degree in Science

Material Science and Engineering

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SUSTAINABLE COMPOSITE MATERIALS FROM RENEWABLE RESOURCES FOR AUTOMOTIVE APPLICATIONS

By

Arief Cahyo Wibowo

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

SUSTAINABLE COMPOSITE MATERIALS FROM RENEWABLE RESOURCES FOR AUTOMOTIVE APPLICATIONS

By

Arief Cahyo Wibowo

As part of an ongoing program on the development of biocomposites from renewable resources, e.g. cellulosic fibers and cellulosic plastics, to produce more ecofriendly/green automotive parts, this thesis deals with the development of a cellulose acetate (CA) biopolymer. Through plasticization, CA was found to be processable at 170-180°C, approximately 50°C below the melting point of neat CA. Eco-friendly green/biocomposites were fabricated from chopped hemp fiber and cellulose ester biodegradable plastic through two process engineering approaches: powder impregnation through compression molding (Process I) and extrusion followed by injection molding (Process II). Cellulose acetate plasticized with 30% citrate plasticizer proved to be a better matrix compared to polypropylene (PP) for hemp fiber reinforcements in terms of flexural and damping properties. In addition to plasticized CA, we used cellulose acetate butyrate plastic (CAB) as matrix in developing the biocomposites. Both matrices had good interaction (hydrogen bonds) with hemp fibers with CAB having higher strength. The addition of a small amount of compatibilizer (maleic anhydride functionalized CAB) into the system led to formation of ester linkages (covalent bonds) between hemp fibers and the matrix to improve the adhesion and to enhance their thermomechanical properties.

In dedication to GOD, my mother, father, wife, daughter, and all of my family back home in Indonesia. Your love and support is unquestionably cherished. Thank you.

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INTRODUCTION

Sustainability, industrial ecology, eco-efficiency and green chemistry are guiding the development of the next generation of advanced materials, products and processes. Biodegradable polymers and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, ecoefficient products. These products can capture markets currently dominated by products based exclusively on petroleum feedstock ¹⁻⁸. Cellulose is attracting interest as a substitute for petroleum feedstock in making plastics (cellulosic plastic - - cellulose esters) for the consumer market¹. Natural cellulose fibers are one of the most abundant renewable resources throughout the world with high potential as reinforcing element in structural composite application. In this project, we are investigating various issues that are components of the structure-property relationships of cellulose esters-short natural fiber biocomposite materials in order to identify potential 'green' applications in automotive parts. The results of this research have been drafted into research papers which have been submitted for publication to leading journals in the field. They make up the main content of this thesis.

The first paper describes biomatrix development and characterization, i.e. plasticization of cellulose acetate with environmentally friendly plasticizer, using different processing methods necessary to make them suitable for biocomposites fabrication. The second paper focuses on the fabrication and characterization of the biocomposites utilizing the developed matrix with the main emphasis on optimization of the method of processing of the biocomposites. The third paper compares the mechanical

and damping properties of different cellulose esters (CE) as matrices for biocomposites, including their comparison to petroleum based polypropylene (PP).

The fourth and the fifth papers describe the synthesis and characterization of a compatibilizer suitable to improve adhesion between cellulose ester matrix and fibers and fabrication as well as characterization of compatibilized biocomposites utilizing our synthetic compatibilizer, respectively. Finally, this thesis addresses issues and challenges that need to be faced in the future in order to implement the biocomposites in SMC (sheet molding compound).

LITERATURE REVIEW



1. Cellulose Fibers for Reinforcement

Hemicellulose joining two microfibrils

Figure 1. Schematic representation of cellulose fiber (one cell wall) -- http://www.bath.ac.uk/mecheng/biomimetics/HV01.pdf

Cellulose fibers were used as reinforcement material since ancient times when mud bricks were reinforced by grass and straw ⁹. The automotive industry had extensively used coconut fiber/natural rubber latex ¹⁰ in a few applications, however, the usage, was decreased during 1970's and 1980's due to the innovation of synthetic fibers with better performance. In the past few years the interest of using natural fiber has been renewed due to increasing cost of plastics and environmental concerns regarding non-degradable, petroleum based plastics and fibers ¹¹.

1.1. Utilization of cellulose fibers: opportunities and limitations

Natural cellulose fibers are abundant renewable resources found throughout the world with the potential to function as reinforcements in structural composite applications. Depending upon the plant source from which cellulose fibers are obtained, they can be classified as:

- 1. Grasses and reeds (from the stem): such as bamboo and sugar cane ⁹.
- Leaf fibers (from the leaves, lengthwise): sisal, henequen, abaca, and esparto, are most commonly used as reinforcing material⁹.
- 3. Bast fibers (from inner bark of the stem): jute, hemp, kenaf^{9, 12}.
- 4. Seed and fruit hairs (from seed-hair and flosses): cotton and coconut 10, 12.
- 5. Wood fibers (from hardwood and softwood trees): maple, yellow poplar, and spruce.

The above fibers can be extracted using different techniques such as: retting, scrapping and pulping ¹².

Cellulose fiber generally is built from lignocellulosic containing helically wound cellulose microfibrils (run along the length of the fiber) held together by an amorphous matrix of lignin and hemicellulose (Figure 1). Different chemical compositions and variations of internal fiber structure among natural fibers are dependent on their location in the plant.^{10, 13}. In general, the best natural fiber used as a reinforcing element is the one with a high cellulose content (more than 60%) and low microfibrillar angle (between 7- 12^{0})¹³.

Natural fibers have several advantages including: their abundance, their renewability ^{14, 15}, low cost, relatively high specific properties due to low density ^{9, 15, 16, 17, 18, 19}, their flexibility and toughness i.e. will not fracture when processed over sharp curves ¹¹, non abrasive (thus permits high volume fraction and prevents machine wear problem) as compared to glass and ceramic. They are non-toxic whereas glass fibers can cause skin irritation and respiratory disease when fibrous dust is inhaled ²⁰. Their surfaces can be modified to increase the interfacial adhesion with the matrix ¹⁴, they require processing with a lower expenditure of energy ^{9, 14}, and biodegradable ^{9, 15, 21} are other advantages of these natural fibers.

There are, however, some drawbacks of cellulose fibers when using as reinforcement in composites including thermal stability is limited to 200^oC ^{9, 14-16, 19, 22}. Agglomeration of fibers can occur in the resulting composites due to strong hydrogen bonding between fibers ^{14, 18}. The inherent polarity and hydrophilicity of natural fibers results in lower compatibility with non-polar, hydrophobic olefin thermoplastics. High moisture absorption causes swelling of the fiber and the resulting composites, which leads to a reduction in dimensional stability ^{11, 16} and mechanical properties. Another

weakness of natural fibers is the limitation of service life when exposed to outdoor environment. This is due to the hydrophilic nature and the fact that they are highly biodegradable. Another factor that may restrain the use of natural fibers in plastic based composites is the difficulty in getting natural fibers with high and uniform quality due to collection and storage methods are not yet mechanized and standardized.

1.2. Chemical modification of cellulose fibers

Processing cellulose fibers at high temperature (200^oC and up) for long periods of time will result in degradation indicated by the formation of a tar-like product and



Figure 2. Typical coefficient of thermal expansion (CTE) curve of cellulose acetate plastics (CAP) and CAP biocomposites (30wt% hemp fiber content)

pyrolysis acid that could damage processing equipment and the resulting composite properties ²³. High moisture absorption of cellulose fibers, due to formation of hydrogen bonding between water and hydroxyl groups of cellulose cell wall, will cause swelling of

the fibers and the resulting composite (fiber-matrix interface)^{9, 11}. The swelling affects the dimensional stability of the cellulose based composites. The coefficient of thermal expansion (CTE) is defined as the change in dimension when a material is subjected to a temperature increment with constant pressure and can be measured using thermomechanical analyzer (TMA). Shrinkage of bio-based material (hydrophilic material) starting from about 80^oC during CTE measurement using the TMA is explained by the reversible and irreversible swelling of the composites ^{9, 24, 25}. Increasing temperature releases moistures inside the composites and hence shrinkage of the tested composites is observed (Figure 2).

Swelling of the composites also affects the fiber matrix adhesion and thus the mechanical properties as well. Lee et al ²⁴ found the reduction of mechanical properties after weathering of jute-polyester composites. Surface crazing and debonding between resin and jute fiber occurred due to adsorption and desorption of moisture by the composites, which resulted in high shrinkage. The hydrophilic nature of cellulose fibers affects the composite processing, namely formation of voids during compounding ²². The voids would cause stress concentration, which could lead to early failure of the composite during loading.

Acetylation of cellulose fibers was reported to overcome these drawbacks of natural fibers. Rana et al reported that acetylated jute fibers had higher thermal stability compared to those of untreated jute fibers ²⁶. Replacing hydroxyl groups on the cellulose fibers dramatically reduced moisture absorption of both fibers and resulting composites. Acetylation, ^{9, 11, 13} or grafting a vinyl monomer such as acrylonitrile ¹⁰, were some

examples of fiber surface treatments suitable for handling the hydrophilic nature of cellulose fibers.

Agglomeration of cellulose fibers when incorporated inside synthetic polymer is often due to differences in polarity and strong hydrogen bonding between the fibers. These clumps of fibers will be the center of stress concentration, which will initiate cracks during loading and hence will lead to mediocre mechanical properties. Fibers coated by the matrix ²⁷ and the addition of a dispersion aid (stearic acid and mineral oil) ²⁸ were reported to improve the separation of individual fibers inside the matrix and fiber wetting, thus enhancement of mechanical properties was observed.

Non-compatibility between polar, hydrophilic cellulose fibers and non polar, hydrophobic polyolefins leads to the formation of porosity, and poor interfacial adhesion. The use of coupling agents or compatibilizer and fiber surface treatment are widely used to improve the wetting of this system. Isocyanates and silanes are coupling agents that work as a bridge forming a chemical bond between fiber and matrix ²⁹, which results in an improvement of interfacial adhesion suggested by increase in mechanical properties. Gatenholm et al observed an improvement in mechanical properties of polypropylene based composites with cellulose fibers treated with maleic anhydride grafted polypropylene (MAPP). The improvement observed was due to enhanced fiber wetting (formation of covalent and hydrogen bonds across the interface – proved by FTIR analysis), and fiber dispersion as observed in SEM micrographs ³⁰.

Lignocellulosic material can be easily degraded when exposed to nature in different ways: biological, thermal, aqueous, photochemical, and mechanical means of

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degradation. Retardation of biodegradability, by acetylation, is required to obtain fiberbased composites with long service life ^{25, 31}.

1.3. Factors influencing the performance of short fiber composites

Properties of short fiber-reinforced composites depend on the following factors ²³. ²⁷):

1. Fiber dispersion

Good fiber dispersion means fibers are individually separated homogeneously and surrounded by the matrix, such that stress transfer from matrix to fiber is efficient. Lack of fiber dispersion leads to resin rich areas (weak area) and fiber rich areas (vulnerable to microcracking), which results in lower mechanical properties. The extent of fiber dispersion depends on two major factors, fiber to fiber interactions (such as hydrogen bonds), and fiber length ³². A critical length of the fiber is a very crucial factor for homogeneous fiber dispersion. If fiber is too long then it may get entangled with other fibers, whereas less effective reinforcement effect will be observed if the fiber length is too small. Effective fiber (nylon, rayon, polyester fiber) dispersion can be achieved by using 0.4 mm fiber length. The fiber dispersion problem can be solved by several methods including fiber surface modification such as acetylation, use of dispersing agent such as compatibilizer, stearic acid and mineral oil ²⁸, and increase of shear force and mixing time ^{9, 11, 21, 32}.

2. Fiber-matrix adhesion

In short fiber based composites system, effective stress/loading transfer from matrix (low modulus) to fiber (high modulus) requires good adhesion at the fiber-matrix interface.

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This good interfacial adhesion can be achieved by the use of coupling agents, polymer coating materials, fiber surface treatments, and chemical grafting. Selke et al ³² reported a promising improvement in fiber-matrix adhesion reflected by the increase in mechanical





properties of wood fiber/high density polyethylene composite with addition of MAPP, and ionomer modified polyethylene.

3. Fiber aspect ratio

The critical length to diameter ratio of a fiber or 'aspect ratio' is inversely proportional to interfacial shear stress (based on shear slip analysis ³³):

$$\sigma_{fu} = 2\tau_i m(s) \tag{1}$$

$$\tau_i = \frac{\sigma_{fu}}{2m(s)} \tag{2}$$

where: σ_{fu} = ultimate tensile strength of fiber

 $\tau = interfacial shear stress$

s = aspect ratio (=l/d)

m = slippage length

Composites should have a higher fiber aspect ratio, i.e. fiber should be longer than its critical fiber length to achieve its ultimate fiber strength – Figure 3, such that interfacial shear stress is low and thus maximum stress transfer to fiber can be accomplished. Altering the interfacial shear stress of the fiber can be achieved by modifying the surface of the fiber by chemicals such as coating agents. High performance short fiber reinforced composites can be obtained if the fiber aspect ratio after processing can be maintained in the range of 100-200.

4. Fiber orientation

In a short fiber system, the mechanical properties also depend upon the fiber orientation with respect to the loading axis ³⁴. Higher mechanical properties resulted from composites with fibers oriented parallel to the test direction ^{35, 36}. The polymer melt experiences elongational, extensional and shear flow, which helps in fiber alignment during processing.

5. Fiber volume fraction

The rule of mixtures can predict the mechanical properties of a composite with various fiber contents. At low fiber volume fraction, dilution of the matrix and flaws at the fiber ends can lead to a high stress concentration, which causes interfacial failure between fiber and matrix ³⁷. At higher fiber content, the stress is more evenly distributed, i.e. reinforcement effect compensates for the dilution effect.

2. Cellulose Ester

In the middle of 19th century, a cellulose derivative namely nitrocellulose, was first employed as a synthetic plastic for applications such as film and cast objects. It was, however, flammable, hence cellulose acetate (CA) took over in early 20th century due to lower flammability and it is easy formability. This ester derivative of cellulose, in addition to cellulose ether, has persisted in their intended application of coatings and films since their development about half century ago. Photographic film, in particular, is an example of the long product life cycle of cellulose triacetate. However, the innovation of synthetic, petroleum-based polymers in the middle of 20th century has substituted CA due to relatively low cost and good properties.

Cellulose ester plastics, despite requiring larger equipment per amount produced and higher capital cost, continued to satisfy the market and to attract more interest. Mixed acetyl and longer acyl side chain polymers were introduced in the 1930's and 1940's as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). They are tougher versions of CA and thermally processable with little or no plasticizer. General features of cellulosic plastics are stiffness, moderate heat resistance, high moisture vapor transmission, grease resistance, clarity and appearance, and moderate impact resistance. Some unfavorable properties include the need of plasticizer to widen the window of processing due to relative lability of the polysaccharide backbone at high temperature, tendency to creep under load, inelasticity because of the rigid rod nature of cellulose backbone. Cellulosic plastics are gradually reclaiming interest as a result of their biodegradability.

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2.1. What is Cellulose Ester (CE)?

Cellulose ester (CE) is derived from cellulose and is considered to be a semi-synthetic



Figure 4. Structure of cellulose comprised of cellobiose repeat unit with alternate anhydroglucose containing three active OH groups at position 2, 3, and 6.

material due to the fact that some of its basic characteristics (upper molecular weight, polydispersity, etc) are inherent from its base polymer cellulose, which predominantly depend upon its tree species (source). Cellulose, as depicted in Figure 4, is a linear polysaccharide composed of cellobiose repeat units

linked at the β -1 \rightarrow 4 positions ³⁸. A cellobiose consists of two anhydroglucose repeat units with opposite orientation (in terms of hydroxyl groups' locations) from each other. These β -1 \rightarrow 4 linkages lead to materials with relatively low water solubility and low thermal stability. Excessive heat during processing will break this linkage hence chain degradation occurs. In general, cellulose extracted from natural resources is a high molecular weight non-branching polysaccharide and has a conformation with a great tendency to form intermolecular hydrogen bonding. Extensive hydrogen bonding formation produces cellulose fibers which are highly insoluble and relatively impermeable to liquids ³⁹. The inherent rigidity of cellulose originates from hydrogen bonding of the free hydroxyl groups in the anhydroglucose repeating unit within and between chains. The stability of the structure, thus mainly depends upon the ability to form hydrogen bonds. As a consequence, cellulose is not a thermoplastic but degrades on heating before the theoretical melting point is reached. Breaking the hydrogen bonds by solubilizing and reacting the free hydroxyl groups yields a thermoplastic, such as cellulose ethers and cellulose esters.

A convenient basis for nomenclature is the degree of polymerization (DP) and the degree of substitution (DS) of the anhydroglucose unit, $C_6H_{10}O_5$, the building block of cellulose. DP can be defined as the average number of anhydroglucose repeat unit per



Figure 5. Structure of Cellulose esters (Cellulosic Plastics): R = H (Cellulose), acetyl (Cellulose acetate), acetyl and propionyl (Cellulose acetate propionate), or butyryl (Cellulose acetate butyrate).

molecule. In natural form, cellulose has DP ranging from 4,000 - 20,000 for different species of plants ³⁹. During the extraction of cellulose and during manufacturing of cellulose ester, DP loss due to chain degradation will inevitably occur. Typically, DP falls in the range of 800-1,500 for the commercially available

CE.

In one anhydroglucose unit, there are three hydroxyl groups which, in theory, can be esterified. The location of these hydroxyl groups (2, 3, and 6 according to IUPAC nomenclature) is schematically represented in Figure 4. If all three are replaced by acyl groups (acetyl, propionyl, butyryl, etc), then the degree of substitution (DS) is three. Figure 5 represents the general chemical structure of commercially available esterified cellulose including mixed CE (cellulose acetate propionate-CAP, and cellulose acetate butyrate-CAB). Figure 6 shows a simplified processing scheme of esterification of cellulose (adopted from Eastman Chemical Company). In general, 4.78 pounds of wood chips are



Figure 6. Simplified processing scheme of esterification of cellulose (adopted from Eastman Chemical Company).

required to produce 1 pound of cellulose. Esterification of extracted cellulose (high quality, high-alpha cellulose, part of a cellulosic material that is insoluble in a 17.5% solution of sodium hydroxide at 20° C) is achieved using reactive organic anhydrides in the presence of catalysts such as sulfuric acid. As

much as 0.59 pound of cellulose is needed to obtain 1 pound of cellulose ester. Careful derivatization is done on relatively high molecular weight (MW) cellulose focusing on controlling the inevitable MW breakdown (DP loss) that occurs during industrial scale processing. To date, an economically feasible technique to make a non-randomized substitution pattern of CE similar to the stereoregular polyolefins has not been discovered.

2.2. Cellulose ester and its applications

Research and development on esterified cellulose during the past 20 years is reviewed in this part. Polysaccharide cellulose is altered to its organic esters for two main reasons:

- 1. Cellulose is not very soluble in common solvents and is not melt processable hence it decomposes before it undergoes melt flow.
- 2. This conversion to cellulose ester can greatly change the physical properties of the parent polysaccharide, which greatly expands its application.

This part of paper contains the review on understanding the structure-property relationship of cellulose ester (CE) and the performance of cellulose ester in modern coatings, plastics (biodegradable plastics), composites and laminates. The fundamental understanding of how esterification of cellulose impacts the overall properties, which then leads to performance vs. application requirements, is discussed ⁴⁰.

2.2.1. Modern coatings applications

Cellulose esters, such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB), have played crucial roles in solvent borne coatings for over 50 years. By using CE in coatings applications, one can obtain: improved flow and leveling, reduced cratering, reduced dry time, stable carrier for metallic pigments, polishability, UV stability, resistance to yellowing, improved sprayability, cold-crack resistance, solvent-craze resistance, reduced plasticizer migration, viscosity control, pigment-dispersion medium, and redissolve resistance. One can control structural, physical, and chemical characteristics by manipulating the polymer structure (CAB for example) mainly by the degree of substitution (DS), hydroxyl content,

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and chain length ⁴⁰. By increasing the butyryl content, flexibility, solubility, hydrocarbon tolerance, and compatibility increase. Increasing DS leads to a decrease in chemical and grease resistance as well as hardness. Increasing chain length or ester molecular weight decreases the compatibility and solubility. Toughness and melting point increase with increasing chain length. Moisture resistance and toughness both decrease with increasing hydroxyl content.

CE improves metal flake orientation and is used as basecoat for metallic appearance in automotive coatings. The high viscosity of CE restricts the mobility and orientation of metal flakes so that they are aligned parallel to the metal surface by film shrinkage during drying. By adding CE to the basecoat formulation, the dissolution of the basecoat will be prevented by the relatively high molecular weight.

In the mid 1960's, the U.S. government regulations reduced the amount of VOC released during coating applications. Solvent borne high solid coatings, waterborne coatings, and radiation curable coatings are examples of new coating technology with less VOC which can be achieved by modifying the traditional CE to improve the compatibility with resins and solvents.

Modern coatings technologies

To minimize the amount of VOC release, volatile organic solvents have been replaced by exempt solvents such as water (waterborne coatings). In addition, radiation curable coating is another method adopted for modern coatings using CE. In general, radiation curable coatings typically use non volatile monomers as reactive solvents. Upon exposure to UV radiation, a hard coating is formed due to crosslinking of monomers and

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associated resins with essentially no VOC emission. A common strategy to impart water dispersibility and radiation curability is accomplished by grafting of alternative functional groups onto CE 40 .

A. Waterborne coatings

Several methods were adopted to implement easy dispersion in water:

1) Dispersion of conventional CE in water.

CE with higher hydroxyl content imparts greater hydrophilicity and thus leads to more stable dispersion than that of conventional CE. Das and coworker ⁴¹ developed an aqueous dispersion of conventional CE with at least two vinyl monomers using a high shear technique. In this method shear and cavitation provided by a microfluidizer enabled micro dispersion. This basic composition, CE with at least two vinyl monomers, is the aqueous dispersion medium for metallic pigments for automotive coatings. Aqueous coating compositions are claimed with good flow and leveling, a high resistance to mottling, acceptable humidity resistance, good appearance, improved adhesion, and chip resistance when used in low bake repair processes.

2) Introduction of carboxylate functionality to CE.

The methods included:

a) The radical-initiated grafting of acrylate monomers.

The grafted products contained a copolymer of cellulosic backbone and carboxylcontaining branches. The anionic aqueous dispersion can be achieved by

neutralizing the carboxylic functionality with tertiary amine, ammonia, or ammonium hydroxide 40 .

b) The esterification with cyclic anhydrides of dicarboxylic acids.

Examples of esterification with cyclic anhydrides of dicarboxylic acids were cellulose acetate phthalate (CAP) and cellulose acetate butyrate succinate (CAB-SU). Both result in improved water dispersibility. CAP was used in leather coating and pharmaceutical enteric coating applications. CAB-SU improved the metallic appearance by playing an important role in aluminum flake orientation ⁴⁰.

c) Preparing oxidation products of CE (XAB/XAP)

Treatment of CAB with ozone resulted in carboxylic acid containing CE and pendant peroxide groups. Grafting other functional groups was possible through the formation of a radical due to the decomposition of formed peroxide. The hydroxyl groups could be the crosslinking site with melamine formaldehyde, urea formaldehyde, or isocyanate resins. The product led to improved alcohol tolerance and resin compatibility, rheology control agents (XAB and XAP), and improved metal flake orientation. In addition, with proper thixotropy agent, the lower MW XAB allowed an increase in the solid content from 16.7% to about 31% in solventborne coating method at constant spray viscosity ⁴⁰.

d) Esterification of carboxymethyl CE (CM-CAB).

Allen et al ⁴² prepared carboxyalkyl CE by esterification of carboxyalkyl celluloses with the following benefits: good metallic flake orientation, good face brightness, excellent substrate wetting and good adhesion. The carboxyl group of CM-CAB is more hydrolytically stable than that of CAB-SU since the carboxyl

group is attached through an ether linkage whereas the latter is attached through an ester linkage.

e) Cellulose acetoacetate esters: Edgar et al 43 treated cellulose or CE with diketene. It was readily crosslinkable through enamine formation, Michael addition, and reaction with melamine or isocyanates. Improved hardness and solvent resistance were observed as well as water resistance for the product (up to DS = 0.61).

B. Radiation curable coatings

Introduction of pendant branches, readily crosslinkable upon radiation curing or sometimes with addition of crosslinking agent and/or photoinitiator, into CE formed a hard, scratch resistant, and solvent resistant surface after UV curing. The presence of CE gave advantages such as a quick drying as well as workable lacquer. Most of these pendant-carboxyl containing branches were esterified form of α , β unsaturated compounds, readily crosslinkable upon exposure of UV radiation. Some examples were: cellulose carboxylate/glycidyl methacrylate derivatives. cellulose ester/urethane/methacrylates. Some benefits included enhancement in cure speed, adhesion, and impact strength (Jaylink®). Wood coating application was observed for cellulose ester urethane. Improved crosslinking efficiency with the reduction of the reactive diluents needed, improved stain resistance, scratch resistance, and adhesion were the properties of CE urethane acrylates. Greater improvements in hardness and solvent resistance as well as pot life were observed for CE modified with both methacrylate and isocyanate. Maleated CE was prepared by UV radiation of alkali-catalyzed maleation of CAP in the presence of vinyl crosslinking agent and photoinitiator. CAP-maleate can be

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used in waterborne and solventborne UV curable coatings, which provided coatings with desired level of resistance and hardness as well as excellent pot life ⁴⁰.

C. Modification of conventional CEs for solventborne coatings.

Transesterification of mono or di-ester of maleic or fumaric acid led to formation of maleate and fumarate derivatives of mixed CE. These compounds were then copolymerized with α , β -ethylenically unsaturated monomers to give increased viscosity due to poor compatibility with resins ⁴⁰.

2.2.2. CE in plastics applications

Mixed acetyl and longer acyl side chains than acetyl were introduced in the 1930's and 1940's as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). They are tougher versions of CA and are thermally processable with little or no plasticizer. General features of cellulosic plastics are stiffness, moderate heat resistance, high moisture vapor transmission, grease resistance, clarity and appearance, and moderate impact resistance. Some unfavorable properties include the need of plasticizer to widen the window of processing due to relative lability of polysaccharide backbone at high temperature, tendency to creep under load, inelasticity because of the rigid rod nature of cellulose backbone. Cellulosic plastics have been proven to be biodegradable, opening up new interest to a societal need for better plastic waste management ⁴⁰.

A. Long Chain Ester of Cellulose (LCCEs)

The main objective to synthesize cellulose esters with longer chain acids than those of CA, CAP, and CAB is to avoid the use of external plasticizer. Plasticizer leads to volatilization, which causes change in material properties ⁴⁰. There are two combinations successfully used as solvents in making LCCEs. First is N, N-dimethylacetamide and lithium chloride (DMAC/LiCl). A homogeneous reaction of cellulose with acid chlorides or long chain anhydrides in DMAC/LiCl with acid or base catalyst results in CEs with any desired degree of substitution (DS) and very long chain length (C_{12} - C_{20}). In general, glass transition temperature, Tg decreases as ester chain length increases. DMAC/LiCl combination, however, has inherent disadvantage in recycling the expensive lithium salt. Thus, as the second combination, the use of DMAC as solvent with titanate catalyst (Ti/DMAC method) in reacting cellulose with carboxylic acid anhydrides produces partially substituted LCCEs. These are soluble in common solvents and are thermally processable. A comparison between externally plasticized CE with LCCEs shows that both have similar mechanical properties with the latter having lower viscosity evaluated at the same temperature and thus having lower processing temperature. In addition, Tg and flexural modulus vary linearly as a function of solubility parameter, hence the values can be predicted.

B. Blends of cellulose esters with other polymers

Blending of cellulose esters with other polymers has been done to compensate for detrimental properties. For cellulose esters, in particular, blending is one strategy to improve toughness in both low and high temperature applications, to avoid fugitive plasticizer and property degradation issue, to improve biodegradability, elasticity and

heat deflection temperature, as well as to reduce cost. In general, an immiscible blend with a well dispersed rubbery phase with diameter of about 10 μ m will significantly improve the toughness of CE blend. An example of improvement in toughness and elasticity is the work done by Light et al ⁴⁶ where they used a copolymer of methyl acrylate and butyl acrylate to blend with CAB (DS Butyryl = 1.76, Acetyl = 1.03). An immiscible blend of 25% copolymer (50:50) resulted in 260% enhancement in impact resistance. Lee et al ⁴⁷ blended CAB with a low percentage of polyestercarbonate (PEC) and reported it to be biodegradable. Another polymeric plasticization was done by Alberts and coworkers ⁴⁸ using a series of graft polymers containing ethylene/vinyl acetate and vinyl monomers to improve softening temperature and impact strength.

In most cases, among different compositions adopted, partially miscible blends can be achieved when blending CE with other polymers due to the presence of hydroxyl and carbonyl groups which form hydrogen bonds. In addition, similarity in solubility parameter, δ will lead to smaller enthalpy (Δ H) value since

$$\Delta H = x_1 x_2 (\delta_1 - \delta_2)^2 \tag{1}$$

where x_1 and x_2 are volume fraction of component 1 and 2, respectively (detailed example of the use of solubility parameter is shown in APPENDIX 2). This will give negative Gibbs free energy of mixing, ΔG_m which is the main requirement of miscibility. ^{49, 50, 51} The entropy, ΔS is generally small and positive ⁵²:

$$\Delta G_m = \Delta H - T \Delta S \tag{2}$$

One exception is blending CA with poly(vinylphenol) (PVP). All composition ranges were found to be miscible judging from the clarity of film, DSC and DMA analysis.

Landry et al ⁵³ explained that it is due to strong interaction potential between the acidic phenolic hydroxyl group and hydroxyl/carbonyl groups of CA.

2.2.3. Biodegradation of CE

Biodegradation or mineralization is the microbial catalyzed conversion of a polymeric substrate in a biologically active environment to biogas (CO₂ under aerobic conditions), biomass, and other biological by products. Biodestructability, in contrast, is measured by the weight loss, film or fiber disintegration, or loss in physical properties ⁴⁰ (Both definitions are depicted in Figure 7). Cellulose acetate (CA) with a degree of



Figure 7. Simplified biodegradation/biodestructability mechanism of cellulose ester. substitution (DS) less than 2.5 is inherently biodegradable. In general, as the DS decreases the rate of biodegradation increases. CA with a DS below 2.1 has a degradation rate similar or in excess of other known biodegradable polymers. In this part, discussion about the mineralization and/or biodestructability of CE under aerobic, and composting conditions was presented. Effect of blending CE with other polymers or plasticizers on biodegradation rate was also investigated using the composting method.

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A. Aerobic biodegradation

Buchanan et al ⁵⁴ used enriched culture obtained from activated sludge inoculum to determine the biodestructability of CA film and fibers with DS 1.7 and 2.5, respectively. Mineralization of CA was also performed by a biologically mediated pathway using an enrichment assay where the carbonyl carbon of the acetyl substituent of CA was labeled carbon-14. Deacetylation of CA resulted in a conversion of acetate to CO_2 ; as much as 68% conversion for CA with DS of 1.85.

In general, as the DS and the acyl chain length increased, the degradation rate decreased. CA needs to have a DS less than 2.5 to be considered biodegradable. According to Komarek et al results 55 , CA with a DS of 1.85 released more than 80% CO₂ in 14 days, whereas CA with DS 2.07 to 2.57 yielded only 60% of CO₂ in 14-31 days period.

B. Composting

A method to conserve metabolic heat by putting organic matter into piles or heaps, which will accelerate the natural degradation of a material, is known as composting 40 . It produces humus, heat, biomass, CO₂, and water. There were two methods of bench scale composting utilized in this review paper. Method 1 utilized a compost bioreactor with natural dynamic progression common to municipal composting. Method 2 used controlled composting conditions, typically at 53^oC and 60% moisture.

In method 1, CA with a DS 2.97 and 2.52 underwent minimal weight loss and the film remained intact. 38% weight loss was observed for CA with DS of 2.21 and

complete disintegration was found for CA with DS of 2.01. Method 2 had a biodestruction rate higher than Method 1. CA with DS 2.5 only needed 18 days for film disintegration. Again, the disappearance of the film was due to a biologically mediated process. Mineralization of CA required about 24 days and 60 days for DS of 1.7 and 2.5, respectively.

In general, biodegradation of CA involved an attack by cellulase enzymes (microorganisms) on the unsubstituted residues (free OH groups) in the polymer backbone as depicted in Figure 7 40 .

C. Effect of plasticizer on biodegradation of CA

Using composting Method 1, plasticized CA (CA with DS = 2.05 + triethyl citrate) films were broken up into chips after 12 days (Buchanan et al ⁵⁶). They found that the remaining chips underwent possible internal chain cleavage. As the amount of citrate plasticizer increase, the biodegradation rate was increased for plasticized CA (with CA of DS = 2.5) exposed to Method 2 (Ghiya et al). Hence, a slower degrading CA can be altered into a faster degrading CA with addition of triethyl citrate plasticizer. The accelerated degradation is due to synergistic effect of plasticizer on CA. Rapid mineralization was observed as well after addition of plasticizer into CA ⁵⁷.

D. Effect of polyester on biodegradation of cellulose ester

Buchanan and coworkers ⁵⁸ blended cellulose acetate propionate (CAP) with poly(ethylene glutarate) (PEG), poly(tetramethylene glutarate) (PTG), poly(hydroxyl butyrate) (PHB), and poly(lactic acid) (PLA) which formed, in general, a stable, optically

clear, amorphous blend. They used composting method 1 and found a general trend such that when the amount of PEG and PTG increased and as DS of CAP decreased, the weight loss increased. When PEG was the continuous phase and CAP DS was lower than 2.15, maximum weight loss was observed. CAP/PHB and CAP/PLA blend were more resistant to microorganisms as compared to CAP/PEG and CAP/PTG blends. The authors mentioned that the PHB degradation mechanism was similar to that of cellulose where it required the attachment of an extracellular enzyme, whereas PEG, PTG and PLA underwent hydrolytic degradation to form monomer or short chain oligomers prior to being disintegrated by microorganisms. In addition, at fixed DS of CAP, the rate of composting and weight loss increased as the PEG amount increased. Initial degradation was due to chemical hydrolysis of PEG which depended upon the temperature of composting and DS of CAP. Blend of CA (DS = 2.5)/poly(ethylene succinate) (PES) with CA being the continuous phase revealed the degradation rate similar to CA and thus the blend's (75% CA and 25% PES) degradation rate was dominated by CA.

E. Effect of polysaccharide on biodegradation of cellulose ester

Mayer et al ⁵⁹ observed that blending starch into a CA matrix with propylene glycol as a plasticizer decreased its degradation rate due to starch dispersion inside the slower degrading CA. A synergistic effect on biodegradation was found when making nonwoven fabrics containing cotton and CA fibers. The addition of CA with DS of 2.0 into CA with DS of 2.5 was proven to increase the biodestructability of the latter in composting method 1. The rate was further increased by addition of PEG plasticizer in the formulation (Buchanan et al 60).

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F. Future work of biodegradation of CE

It would be desirable to develop or find plasticizers or polymers which would accelerate the biodegradation rate of the highest volume current commercial products yet slow the degradation of CA (DS = 2.5) to an acceptable level, lower the cost, and enhance the properties. The mechanism of biodegradation and biodestruction of cellulose ester should be thoroughly investigated and defined. One way is to isolate and characterize the enzymes responsible for the disintegration of cellulose ester.

2.2.4. CE in composites and laminates

Good adhesion can be observed between cellulose esters and natural fillers due to their similar structure. Several applications in composites and laminates include paper applications, polymer-polymer laminates for packaging material and food contents, , structural and utility applications ⁴⁰.

A. Cellulose ester in laminate and composite paper applications

A low level of CA (1-5%) can be incorporated into paper to increase the tensile strength of the paper, and the ability for print inclusion. A higher level of CA tends to decrease tensile strength.

B. Polymer-polymer laminates containing cellulose esters

The residual hydroxyl groups on cellulose esters help to compatibilize it with other polymers such as polyurethane and PVC. CA sandwiched between PVC resulted in a light-transmitting, insulating panel for potential building and construction applications (Rankle et al ⁶¹). CA can be used as a protective layer to prevent migration of different materials into each other, mainly due to the inherent grease resistance of CA. Lu et al ⁶² of Mobil Corporation made a microwavable laminate food container with an inner protective layer of CAP which prevents direct contact between the food and the bulk container plastic.

C. Cellulose ester as structural and utility applications

Duckett et al ⁶³ described the use of 25-75% cellulose acetate (DS 2.5) with cotton fibers to make a nonwoven composite fabric. They pretreated them with acetone vapor so that the cotton fiber and CA can be thermally bonded at lower temperature (90-140^oC) as compared to non-solvent assisted bonding (176-190^oC). The resulting fabrics were of higher tensile strength and were proven to be biodegradable.

Warth and coworkers ⁶⁴ worked on compatibilization of cellulose/cellulose ester composites. They emphasized reactive extrusion with hydroxyl containing plasticizer and fillers (starch and lignin) in the presence of a lactone for grafting reactions on available hydroxyl groups.

Glasser et al ⁶⁵ utilized cellulose acetate butyrate (CAB) as a matrix for continuous cellulose fibers (yellow poplar wood fiber and regenerated cellulose – Lyocell fibers) reinforced material. In their first paper, they investigated the effect of different methods of processing on the performance of the composites.

Lyocel fiber is regenerated from cellulosic solutions of N-methyl morpholine-Noxide/water. Cellulose acetate butyrate (CAB) is particularly promising as a matrix

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material. Its thermoplastic flow and fiber wetting characteristics have resulted in composites with high fiber content (>60%) and high modulus (>20GPa). An unusual occurrence was observed for Lyocel fiber/CAB which had brittle matrix failure at strain considerably below the value of lyocel fiber strain. Generally, composites fail when their fibers have reached their ultimate tensile strain, since matrix strain is greater than that of fiber.

In their research, they used CAB 381-20 and they encountered problems such as uniformity of matrix and fiber distribution that were inherent in the prepregging technique. The solvent removal technique was responsible for extensive void formation in the matrix, and difficulties with fiber wetting by liquid matrix were found, especially in the film stacking technique.

Depositing powdered matrix from turbulent air assisted by the electrostatic charge different between fiber and particle led to uniform surface coverage and adequate adhesion. Usually smaller matrix with particle size about 600nm (<10mm) was good for fiber reinforcement. Oversized matrix particles led to insufficient (gap filling) melt flow, and resulted in void formation.

The film stacking method had a non-uniform fiber distribution problem. They attempted to remove excess matrix by the use of pressure and temperature during consolidation and the results were a material with extensive discoloration.

After all methods had been investigated, they concluded that solution prepregging provided the most uniform matrix application to fiber surfaces and was most repeatable. It utilized most common solvents for cellulose: acetone and methyl ethyl ketone (MEK) to coat the fibers with the matrix and to tailor fiber volume content to desired level. Note

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here that modulus did not depend upon the method of manufacturing or void content. Tensile strength could not be predicted by rule of mixtures since it depended upon fibermatrix stress transfer and fiber-matrix orientation.

Lyocel fiber reinforced composites failed at 3 to 4% strain due to matrix failure. The finer fibers, however, continued to carry on load and remained intact. This indicated interfacial delamination problems were present. In SEM images, plenty of fiber pullouts were observed indicating lack of adhesion between fiber and matrix. Note here that fibers might have suffered molecular or macroscopic damage during processing which resulted in decreased tensile strength. Cellulose fiber mechanical property measurements depended upon moisture content. With low moisture content, the strength could be unrealistically high. Lower strain values of composites compared to that of pure matrix and pure fiber were due to inadequate fiber-matrix wetting or adhesion.

The second part of Glasser et al paper discussed the fiber surface modification and consolidation conditions of CAB based biocomposites ⁶⁶. Acetylated lignocellulosic fibers had considerably stronger adhesion to a thermoplastic cellulose ester compared to the unmodified fiber. Continuous Lyocel fiber reinforced composites, however, did not show a significant increase in tensile strength and modulus. SEM showed no significant decrease in interfacial failure (fiber pull outs).

Theory of Agarwal and Broutman relating aspect ratio and optimum stress transfer from matrix to fiber for short fiber composites (similar to that of shear slip analysis):

$$\frac{l_c}{d} = \frac{\sigma_{\max}}{2\tau}$$

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Where $l_c =$ fiber critical length, by definition it is a minimum fiber length at which the maximum fiber stress (σ_{max}) occurs at the breaking strength of the fiber itself or in between the fiber and matrix; d = diameter of fiber, and τ = fiber matrix interface. The theory suggests that increasing the amount of stress transfer between the matrix and fiber lowers the fiber critical length to an optimum length. As a result, it will increase the efficiency of short fiber reinforcement due to increased interfacial adhesion, which leads to increased tensile strength and modulus. If the fiber is too long, however, the amount of stress transferred from matrix to fiber will remain constant at the breaking stress of the fiber, thus changes in interfacial stress transfer are undetected. They did not observe any increase in strength proving that interfacial stress transfer was not a limitation in this system.

Melt consolidation studies showed that two methods seemed to produce the lowest void content. The conditions were: 200° C, 81.4 kPa for 13 minutes and 200° C, 163 kPa for 8 minutes. Maximum strength was achieved with above consolidation conditions: 246 MPa in tensile strength and about 21.6 GPa for tensile modulus.

SEM images indicated that fiber pullouts were present in relatively small amounts. Cohesive failure of the matrix was observed in that bundle of fibers with extensive amounts of fractured matrix particles adhering to the fiber surface, i.e. matrix spread over the fiber and adhered to the surface.

Matrix embrittlement sometimes results from matrix transcrystallization on fiber surfaces indicating the comparison between sized and unsized fibers are important. In plasticization, void content is also recognized to influence ultimate strength but not stiffness. By plasticization, the material will have superior melt characteristics. The effect

of fiber sizing will occur in composites interfacial properties (adhesion fiber to matrix). Acetylation has failed to produce significant strength gains in lyocel/cellulose ester.

Composites made from unsized fibers gave higher ply thickness, and hence gave double void contents, which led to lower ultimate tensile strength. Sized fibers were easy to handle and reduced per-ply-thickness, and produced composites with superior strength and low void content.

The third part of Glasser et al discussed the effect of fiber type on the properties of CAB based composites. Rayon, for example is less organized and less costly ⁶⁷. It has fewer filaments in a yarn and thus adheres to the matrix more uniformly. Rayon composites gave lower void content indicating better consolidation behavior. Alternating unidirectional plies gave lower properties than that of unidirectional. In fiber stacking, they observed lower strength and stiffness due to reduced interply adhesion and thicker composites with the possibility of more defects. Rayon composites exhibited the usual strain failure mode (fiber<matrix) and thus it gave greater composite failure at strains than lyocel composites.

Gatenholm et al investigated the effect of furfuryl alcohol on the performance of CAB biocomposites ⁶⁸. Furfuryl alcohol (FA) is a product of the acid-thermal transformation of biomass-based pentoses, such as xylan whose traditional applications include foundry cores and molds, polymer concretes, coating for corrosion resistance, wood adhesives and binders, materials with low flammability and smoke release, and graphitic electrodes from carbonaceous products. FA polymerizes under acid conditions and heat and ultimately yields crosslinked resins. Cellulose acetate butyrate used here is CAB-553-0.4 supplied by Eastman Chemical Co.

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Flax reinforced CAB/FA was prepared by mixing the required amount of FA with CAB while stirring to achieve a homogeneous clear solution or paste. Composites with flax fiber content of 50wt% were prepared by the addition of CAB/FA mixtures, catalyst, and acetone (evaporated afterward under vacuum) to improve the impregnation of the flax mat. The composite was prepolymerized in an oven followed by curing in compression molding with applied pressure.

The melt viscosity of CAB is dramatically decreased after introducing FA, which acted as a CAB solvent and facilitated the impregnation of the flax fiber mats. Modulus and maximum fiber stress (strength) of flax composites was observed to increase linearly with decreased toughness with addition of FA into CAB. DMA showed that CAB/poly(furfuryl alcohol) (PFA) matrices were miscible because the glass transition temperature (T_g) in the resulting blend occurred between the T_g of homopolymers. This indicates a good combination between thermoplastic and thermoset because of the miscibility and affinity. Increasing the FA content, resulted in the improvement of storage modulus. The flexural strength and modulus of the composites were about 70 MPa and 6 GPa with addition of 25wt% FA into CAB/Flax composites.

3. Conclusion

Cellulose esters (CEs), as have been illustrated above, have much potential in many applications. In this particular project, we examined the potential of CEs reinforced by natural fibers to replace/substitute petroleum based glass reinforced polypropylene for automotive parts. The structure and property relationships of cellulose esters, namely cellulose acetate (CA) and cellulose acetate butyrate (CAB), starting from matrix development for biocomposites until the development of the "engineered biocomposites" for "greener" automotive and structural applications were discussed.

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I. Development of Renewable Resource Based Cellulose Acetate Bioplastic: Effect of Process Engineering on the Performance of Cellulosic Plastics

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1. Abstract

As part of an ongoing program on the development of biocomposites from renewable resources, e.g. cellulosic fibers and cellulosic plastics, to produce more ecofriendly/green automotive parts, this paper deals with the development of a cellulose acetate biopolymer. Plasticization of this biopolymer under varying processing conditions so as to make it a suitable matrix polymer for biocomposite applications was studied. In particular, cellulose acetate was plasticized with varying concentrations of an ecofriendly triethyl citrate (TEC) plasticizer, versus a conventional, petroleum derived phthalate plasticizer. Three types of processing were used to fabricate plasticized compression molding, extrusion followed by compression cellulose acetate parts: molding, and extrusion followed by injection molding. It was found that processing mode affected the physico-mechanical and thermal properties of this cellulosic plastic. Compression molded samples exhibited the highest impact strength tending towards the impact strength of a thermoplastic olefin (TPO), while samples that were extruded then injection molded exhibited the highest tensile strength and modulus values. Increasing the plasticizer content in the cellulosic plastic formulation improved the impact strength and strain to failure while decreasing the tensile strength and modulus values. The coefficient of thermal expansion (CTE) of the cellulose acetate increased with increasing amounts of plasticizer. Through plasticization, this cellulose acetate was found to be processable at $170-180^{\circ}$ C, approximately 50° C much below the melting point of neat cellulose acetate.

Keywords: Cellulose acetate, plasticization, citrate plasticizer, compression molding, extrusion and injection molding, thermo-mechanical properties.

2. Introduction

Sustainability, industrial ecology, eco-efficiency and green chemistry are guiding the development of the next generation of advanced materials, products and processes. Biodegradable polymers and biobased polymer products based on annually renewable

Cellulose esters



Figure 1. Structure of Cellulose esters (Cellulosic Plastics): R = H (Cellulose), acetyl (Cellulose acetate), acetyl and propionyl (Cellulose acetate propionate), or butyryl (Cellulose acetate butyrate).

can form the basis for a portfolio of sustainable, eco-efficient products that can capture markets currently dominated by products based exclusively on petroleum feedstock ¹⁻⁸. Cellulose from trees is attracting interest as a substitute for petroleum feedstock in making

agricultural and biomass feedstock

plastics (cellulosic plastic - - cellulose esters) for the consumer market ¹.

Cellulosic plastics (Figure 1) like cellulose acetate (CA), cellulose acetate

propionate (CAP), and cellulose acetate butyrate (CAB) are thermoplastic materials produced through the esterification of cellulose. A variety of raw materials such as: cotton, recycled paper, wood cellulose and sugarcane are used in making cellulose ester biopolymers in powder form. Such cellulose ester powders combined with plasticizers and additives are extruded to produce various grades of commercial cellulosic plastics in pelletized form. The phthalate based plasticizers, currently used in commercial cellulose ester plastics, is under environmental scrutiny and perhaps poses a health threat, raising concerns about their long-term use. One of our objectives is to replace phthalate plasticizers with an eco-friendly plasticizer based on citrate and blends of citrate and derivatized vegetable oil when designing sustainable cellulosic plastics for biocomposite applications. Besides material selection, processing plays a vital role in the design of new biobased polymers. Most commercial cellulose acetate products are clear, strong and stiff and have a broad range of applications. Some of the applications of cellulose ester biopolymers are film substrates for photography, toothbrush handles, selective filtration membranes in medicine, and automotive coatings⁹. In general, those cellulose acetates, which have an acetyl substitution number of 2.2 or less, are biodegradable in soil and marine environments as well as being suitable for composting. Higher substitution numbers ranging from 2.2 to 3.0 are less biodegradable. The main drawback of cellulose acetate is that its melt processing temperature is very close to its decomposition temperature, as determined by the structure of its parent cellulose ¹⁰. This requires that cellulose acetates should be plasticized if they are to be used in thermoplastic processing applications. The plasticization of cellulose acetate, although reported by Ghiva et al.¹¹ has not been studied in terms of its effects on processing-properties in detail.
Citric acid esters are non-toxic and have been approved as plasticizers for many applications such as additives in medical plastics, personal care, and food contact and are useful in a variety of polymers. Since citrate esters are a derivative of natural compounds, it is of interest to determine their effect on plasticization with special reference to processing parameters. The effects of TEC plasticizer on the physico-mechanical properties and thermal behavior of the resulting cellulosic plastics with varied processing conditions were studied.

The development of cellulose plastic as a matrix polymer in biocomposites requires that properties such as: percent elongation, flexibility and impact behavior can be tailored to meet the needs of the application. Our recent research results ¹²⁻¹⁴ have demonstrated that natural fiber reinforced polypropylene (PP) composites have potential to replace glass fiber-PP composites. With the goal to replace or substitute Polypropylene with cellulosic plastic when designing more eco-friendly and sustainable biocomposite materials, our fundamental studies focus on structure-processing-property relationships. This paper gives a detailed analysis of the effect of material selection and processing conditions on the performance of cellulose ester bioplastics.

3. Experimental

3.1. Materials

Powdered cellulose acetate (CA) free from any plasticizer or additives was supplied by Eastman Chemical Co., (Kingsport, TN) for the present study. The degree of substitution of the cellulose acetate was approximately 2.5. The triethyl citrate (TEC) plasticizer was provided by Morflex Inc., (Greensboro, North Carolina). The CA powder was dried overnight in vacuum oven at 80°C before processing.

3.2. Processing

Three types of processing commonly used for thermoplastics were used to make test specimens of plasticized cellulose acetate so as to study the effect of processing conditions on the physico-mechanical properties of the corresponding cellulosic plastics.

I. Compression Molding: A specific amount of liquid plasticizer was added drop-wise onto dried cellulose acetate powder and the mixture stirred mechanically in a kitchen mixer for 30 minutes. The mixture was compression molded using a three-piece picture-frame mold in a Carver Press SP-F 6030 at three different temperatures 170, 180 and 190^oC. During compression molding at a specific temperature, for the first ten minutes the materials were kept at a constant pressure of 1.1 MPa and then held at 2.67 MPa for last five minutes. The samples were cooled while maintaining the pressure.

II. Extrusion Followed by Compression Molding: In this process, the cellulose acetate powder and TEC plasticizer in the desired proportions were pre-mixed mechanically and then extruded as thermoformable sheets. The resulting thermoformable sheets were then compression molded to make the test specimens. In this case, the cellulose acetate with TEC plasticizer was fed into a twin-screw extruder ZSK 30 (Werner-Pfleiderer). The temperature profile of extruder from Zone 1 through Zone 6 was kept between 170 to 180^oC and the exit die temperature was 190^oC. The extruder was operated at two different rpm screw speeds (100 rpm and 200 rpm). The resultant thermoformable sheets were compression molded at 180^oC and 1.1 MPa for 10 minutes and at 2.67 MPa for 5 minutes and then cooled down while maintaining the pressure.

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III. Extrusion Followed by Injection Molding: The samples were extruded as described above (subsection II) and instead of collecting thermoformable extruded sheets, through proper die arrangement, the thin strands of plasticized cellulose acetate were pelletized and stored for future injection molding. The injection-molding machine used was an 85-ton Cincinnati-Millacron press. The molding conditions were as follows: temperatures on zones 1 to 3 as well as the die were held between 180 to 190 ^oC with 45 seconds cooling time, the fill, hold and pack pressures were maintained at 8.2, 4.8 and 5.5 MPa, respectively. In addition, the optimum processing temperature for injection molding was determined to be between 180 and 190 ^oC. The resulting dumbbell shaped products were used appropriately for mechanical properties based on ASTM standards.

3.3. Analysis and Testing

Differential scanning calorimetry (2920 Modulated DSC, TA instruments, USA) and thermogravimetric analysis (Hi-Res TGA 2950, TA instruments, USA) were used for the thermal analysis of cellulose acetate plastics. In DSC measurements, the pure and plasticized cellulose acetate samples (10 mg) were sealed in aluminum pans and heated from 25 to 200° C at a rate of 10° C/min (cpm), held at 200° C for 5 min, then cooled down to -60° C before a second heating scan at 10 cpm from -60 to 300° C. A nitrogen purge (50 ml/min.) was maintained throughout the test. Dimensional stability of the materials as a function of temperature were measured as per ASTM D 696 using Thermo-mechanical Analyzer (TMA) 2940 from TA instruments, USA. The heating rate was 4 cpm over a temperature range of 25 to 100° C. The coefficient of thermal expansion (CTE) at 80° C was determined with respect to 25° C as the reference temperature from



Figure 2. Effect of processing conditions on the tensile strength and tensile modulus of plasticized (30% TEC) cellulose acetate, A = compression molded (CM) at 190 $^{\circ}$ C, B = CM at 180 $^{\circ}$ C, C = CM at 170 $^{\circ}$ C, D = extruded at 180 $^{\circ}$ C (100 rpm) and CM at 180 $^{\circ}$ C.

the samples for impact measurements was maintained at around 3.15 mm for compression molded test specimens and 3.3 mm for injection molded test specimens. Samples were notched using a TMI Notching Cutter, model TMI 22-05, and were left for one day at ambient equilibrate prior temperature to to pendulum capable testing. Α of delivering impact energy of 6.8 J was used for these experiments.

the resulting plot in units of μ m/m⁰C.

Tensile strength and elongation at break (EB) were determined using a United Calibration Corporation test frame, model SFM-20 as per ASTM D 638. Test conditions were: a crosshead speed of 5.1 mm/min, 0.9 kg preload and a 454 kg capacity load cell. The impact resistance testing was carried out with an Impact tester from Testing Machines Inc., model 43-OA-01, according to IZOD method (ASTM D 256). The thickness of



Figure 3. Effect of processing conditions on the impact strength and elongation at break of plasticized (30% TEC) cellulose acetate, A = compression molded (CM) at 190 $^{\circ}$ C, B = CM at 180 $^{\circ}$ C, C = CM at 170 $^{\circ}$ C, D = extruded at 180 $^{\circ}$ C (100 rpm) then CM at 180 $^{\circ}$ C.

Environmental scanning electron microscope (ESEM) images were taken using a Phillips Electroscan 2020. The specimens were fractured after cooling in liquid nitrogen



Figure 4. ESEM images of: (a) pure cellulose acetate (CA) powder with particle size of 5-10 mm (500X, scale bar 100 μ m), (b) extruded followed by compression molded CA plastic with 30% Triethyl citrate plasticizer (1500X, scale bar 30 μ m) and were gold sputtered before taking the images.

4. Results and Discussions

Cellulose acetate (CA). renewable resource based plastic, has excellent potential replace to polypropylene as a matrix polymer in composite formulations to design eco-15-17 friendly biocomposite materials Recently, several of world's leading chemical companies have announced maior new businesses based on bioresources instead of petrochemicals 18, biopolymers move into the mainstream^{20, 21}. Biopolymers were not developed by nature to be plastics, but to act as cellular components to build the structure of an organism to survive in the environment. Biopolymers need to be modified so as to make them suitable matrix polymers for commercial composite applications. The main drawback of cellulose



Figure 5. Effect of plasticizer content on the tensile strength and tensile modulus of extruded followed by compression molded cellulose acetate plastics.

acetate plastic is that its melt processing temperature is close to its decomposition temperature. Cellulosic plastics may be developed either by blending with another suitable polymer or being plasticized with a miscible plasticizer for specific applications. Cellulose ester polymers are blended with different polymers for film and molding applications ²²⁻²⁴. Plasticizers are widely

used in plastics industry to increase the processibility, flexibility, and ductility of polymeric materials.

4.1. Comparison of Properties of Plasticized Cellulose Acetates - · Compression Molding vs. Extrusion followed by Compression Molding: The effect of the above processing conditions, on the tensile strength, modulus and impact strength of plasticized cellulose acetates



Figure 6. Effect of plasticizer content on the impact strength and elongation at break of extruded followed by compression molded cellulose acetate plastics.

containing a fixed amount of TEC plasticizer (30 wt.%) is illustrated in Figures 2 and 3. The samples A, B and C are obtained through compression molding (CM) of the mixture



Figure 7. Stress Strain plots for varied amount of plasticizer of extruded followed by compression molded cellulose acetate plastics.

of pure cellulose acetate powder and TEC plasticizer at temperatures of 190, 180 and 170^oC respectively. As can be observed, the sample processed at 170^oC ("C") exhibited superior tensile and impact strengths over the samples processed at higher temperatures. The plasticized cellulose acetate as obtained through extrusion followed by

compression molding ("D") exhibited better tensile properties versus compressionmolded samples. All of the plasticized cellulose acetates had elongation at break (Figure 3) in the range of 24 to 34%. If we compare the tensile properties of the compressionmolded sample ("B") versus the extruded followed by compression-molding sample ("D") we find a 48 and 13% enhancement of the tensile strength and modulus respectively of the latter material. The superior strength of the extruded material is attributed to the better mixing of cellulose acetate and TEC plasticizer during high shear extrusion processing. The lower impact strength of the extruded followed by compression molding material versus the compression molding material suggests that cross-linking of cellulose acetate with TEC may have occurred during the melt extrusion processing, which exposes the material to shear stresses during processing. This observation is supported by the environmental scanning electron microscope images in Figure 4. As can be seen, homogeneity of the blended mixture was observed indicating that it will serve as a good polymer matrix. Similar reduction in the elongation at break for sample "D" is also observed as shown in Figure 3. The plasticized cellulose acetate obtained through compression molding exhibits superior impact properties as contrasted with samples obtained through extrusion followed by compression molding. The main motivation of this research is to develop cellulose ester plastics to replace polypropylene in biocomposite applications. Although PP has adequate tensile and flexural properties, its low impact strength, necessitated the invention of thermoplastic olefins (TPO) - - known as extended polypropylene which is industrially produced through incorporation of an elastomeric component into the virgin polypropylene. The impact strength of plasticized cellulose acetate under various processing conditions ranges from 173 J/m to 419 J/m (Figure 3), which approaches to impact strength value of TPO ²⁵. Such high-impact plasticized cellulosic acetate can be used as a suitable matrix for biocomposites in automotive applications that require superior impact strength.

4.2. Comparison of Properties of Plasticized Cellulose Acetates - - Extrusion Followed by Compression Molding vs. Extrusion Followed by Injection Molding: Plasticized cellulose acetate fabricated through extrusion followed by injection molding showed better tensile properties and lower impact properties over its counterpart obtained through extrusion followed by compression molding. As can be seen in Table 1a, when using injection molding versus compression molding, we get a significant increase in tensile strength and modulus by about 40 and 60%, respectively. The additional shear force applied during injection molding may have enhanced the cross-linking between the



Figure 8. TGA results of weight loss versus temperature with varying amounts of plasticizer of extruded followed by compression molded cellulose acetate plastics.

cellulose acetate and TEC plasticizer, thereby increasing the stiffness of the injectionmolded material. As expected, the increased stiffness sacrifices the impact strength of the injection-molded material (Table 1a).

Table 1a*. Effect of optimized processing conditions on the tensile strength and the tensile modulus of plasticized (30% TEC) cellulose acetate

Processing	Tensile	Tensile	Elongation at	IZOD Impact
	Strength (MPa)	Modulus (GPa)	Break (%)	(J/m)
E-CM at 180 ⁰ C	26 ± 1.1	1.3 ± 0.1	24 ± 0.0	173 ± 35
E-IM at 190 ⁰ C	36 ± 0.4	2.1 ± 0.2	13 ± 1.7	68 ± 15

Table 1b*. Effect of temperature variation for extruded – injection molding CA plastics (30% TEC)

Processing	Tensile	Tensile	Elongation at	IZOD Impact
	Strength (MPa)	Modulus (GPa)	Break (%)	(J/m)
E-IM at 180°C	27 ± 3.2	2.1 ± 0.0	8.3 ± 3.2	241 ± 0.0
E-IM at 190°C	36 ± 0.4	2.1 ± 0.2	13 ± 1.7	68 ± 15

Table 1c*. Effect of varying rpm of extruder for extruded – injection molding CA plastics (30% TEC)

Processing	Tensile	Tensile	Elongation at	IZOD Impact
	Strength (MPa)	Modulus (GPa)	Break (%)	(J/m)
E-IM at 190°C,	36 ± 0.4	2.1 ± 0.2	13 ± 1.7	68 ± 15
100 rpm				
E-IM at 190 ⁰ C, 200	32 ± 3.8	2.1 ± 0.1	14 ± 1.2	88 ± 21

*E-CM = Extruded followed by Compression Molding;

E-IM = Extruded followed by Injection Molding.

Note: Reported are mean values along with its standard deviation (\pm)

Different processing temperatures in the injection molding experiments were used to study the effect of temperature on the properties of the resulting cellulosic plastics (Table 1b). Increasing the injection molding temperature from 180 to 190^oC enhanced the tensile strength by about 32%, whereas the impact strength decreased by about 75%. Hence, a 190^oC processing temperature was utilized. To study the effect of extruder screw rpm on properties, we used the plasticized cellulosic acetates fabricated through extrusion followed by injection molding processing for comparison. We found that material processed at 100-rpm exhibited better mechanical properties than that processed at 200-rpm (Table 1c). This means that the longer resident time (lower rpm) gave better mixing between the CA powder and the TEC plasticizer, which led to a stiffer product as cross-linking was enhanced. In all of our previous descriptions on extrusion, we had processed the materials at 100 rpm.

4.3. Effect of Plasticizer Content on Performance of Cellulose Acetate Plastic: In our above-mentioned discussions on processing-property evaluations of plasticized cellulose acetate, we had kept the plasticizer content at 30wt.%. In order to investigate the effect of varying the amount of TEC plasticizer on the performance of cellulosic plastics (Figs. 5-7) we have prepared samples fabricated through extrusion followed by compression molding. It was not possible to process the cellulose acetate with plasticizer content of 10 and 15 wt.%. With an increase of plasticizer content from 20 to 40wt.%, the tensile properties decreased while impact strength and percent elongation increased (Figs. 5 and 6). The plasticized cellulose acetate containing 30 wt.% plasticizer shows tensile strength

about 45% less and impact strength about 86% more over plasticized cellulose acetate with 20 wt.% plasticizer. In order to obtain cellulosic plastic with an optimum balance of strength and stiffness, 30 wt.% plasticizer content cellulose ester is quite appropriate for biocomposite applications. Again, it is easier to process cellulose ester with 30 wt.% plasticizer over 20 wt.% plasticizer. Although 40 wt.% plasticized cellulose ester would



Figure 9. TMA results of the coefficient of thermal expansion for varied amounts of plasticizer of extruded followed by compression molded cellulose acetate plastics.

be processed easily, the tensile strength of such plastic would be too low for any structural applications, especially in composite area. As much as 21 and 63% improvements in impact strength and elongation at break respectively were found in 40 wt% plasticizer content cellulose ester plastic as compared to 30 wt% plasticizer content cellulose ester

plastic (Figure 6). In stress-strain plot (Figure 7), 40 wt% plasticizer content cellulosic plastic sample covers a larger area under the curve indicating that it is a ductile material, and hence it has the highest impact strength and elongation at break as shown in Fig.6.

4.4. Thermal and Thermomechanical Behaviors of Plasticized Cellulose Acetates:

The plasticized cellulose acetates fabricated through extrusion followed by compression moldings were studied via thermal analysis. The TGA curves of pure and plasticized cellulose acetates (with 20, 30 and 40% TEC plasticizer) show overall addition of plasticizer shifts the maximum degradation temperature towards the higher temperature range (Figure 8). Pure cellulose acetate shows a smooth weight loss curve as contrasted with plasticized cellulose esters. We observe that as the plasticizer content increases, the maximum decomposition temperature of CA plastics also increased as can be observed in Figure 8. Additionally, the thermal stability of the materials shows that as the plasticizer content increases, the coefficient of thermal expansion (CTE) increased as well (Figure 9). It is well known that the CTE of the low molecular weight TEC plasticizer is greater than the cellulose acetate polymeric matrix and thus with increase of plasticizer content in the formulations, the CTE of the resulting plasticized cellulose acetate increases, as shown in Figure 9. The presence of plasticizer limits the crystallinity in the matrix and increases the free volume present in the system. Thus, increasing the amount of



Figure 10. DSC curves for varied amounts of plasticizer of extruded followed by compression molded cellulose acetate plastics.

plasticizer in the formulation gives a more flexible material. The increase of CTE with decrease of rigidity of polymeric materials also has been observed by Tyan et al. ²⁶.

The sharp crystalline melting peak of pure cellulose acetate also disappears upon plasticization as observed from

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the DSC curves (Figure 10) confirming the shift of properties of the CA from rigid to ductile. Similar observations from DSC have also been noted by Ghiya et al. ¹¹, which indicates that the resulting plasticized CA is an amorphous material.

5. Conclusions

Cellulose acetate, a renewable resource based bioplastic has excellent potential to replace petroleum based polyolefins as matrix polymers when designing green, ecofriendly biocomposites for a new millennium. It is encouraging to see that with control of plasticizer content the cellulosic plastic can exhibit the stiffness and toughness properties comparable to either PP or TPO. Through plasticization of cellulose acetate by an environment friendly citrate plasticizer, the cellulose acetates are processable at 170-180°C much below the melting point of cellulose acetate (233°C). Extrusion allows better mixing of cellulose acetate and plasticizer due to the high shear of extrusion processing as shown by ESEM images. The material processed at lower extruder screw rpm (100 rpm) exhibited better mechanical properties over its counterpart processed at higher extruder rpm (200 rpm). The extruded sample showed lower elongation at break, thus it is a stiffer material and showed least impact strength where as the compression molded sample exhibited highest elongation at break, thus was a tougher material and exhibited the highest impact strength. Extrusion followed by injection molding processed materials exhibited better properties as compared to extrusion followed by compression molding as additional shear forces applied during injection molding resulted in stiffer product. Cellulosic plastics fabricated through injection molding at higher temperature $(190^{\circ}C)$ exhibited better tensile properties over their counterpart that was injected molded at a comparatively lower temperature (180°C). Thus, processing parameters played a vital role in designing cellulosic plastics with the desired properties for biocomposite applications.

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II. Effect of Process Engineering on the Performance of Natural Fiber Reinforced Cellulose Acetate Biocomposites

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1. Abstract

Eco-friendly green/biocomposites were fabricated from chopped hemp fiber and cellulose ester biodegradable plastic through two process engineering approaches: powder impregnation through compression molding (Process I) and extrusion followed by injection molding (Process II). Cellulose ester e.g. cellulose acetate (CA) plasticized with 30 wt. % citrate plasticizer (CAP) was used as the matrix polymer for biocomposite fabrication. Intimate mixing due to shear forces experienced in Process II produced superior strength biocomposites over their counterparts made using Process I. Biocomposite fabricated through Process II containing 30 wt.% hemp natural fiber showed an improvement of storage modulus by 150% over the virgin matrix polymer. The coefficient of thermal expansion (CTE) of the said biocomposite decreased from the CAP polymer by 60% whereas the heat deflection temperature improved by 30% versus the virgin bioplastic, indicating superior thermal behavior of the biocomposite. Plasticized cellulose acetate is proved to be much better matrix than non-polar polypropylene (PP) for hemp fiber (HF) reinforcements because of the better interaction of polar cellulose ester with the polar natural fiber. Fabricated through Process II and with same content of hemp (30 wt.%) the CAP-HF based biocomposite exhibited flexural

strength of 78 MPa and modulus of elasticity (MOE) of 5.6 GPa as contrast to 55 MPa and 3.7 GPa for the corresponding PP-HF based composite. The experimental findings of tensile modulus of the biocomposites are compared with the theoretical modulus using the rule of mixture (ROM). The fiber-matrix adhesion is evaluated through Environmental Scanning Electron Microscopy (ESEM) studies.

Keywords: A. Cellulose Acetate; A. Natural hemp fiber; E. Powder impregnation; E. Extrusion/Injection/Compression Molding; B. Physico-mechanical and thermal characteristics.

2. Introduction

There is a growing urgency to develop and commercialize biobased composite materials those can reduce the widespread dependence on petroleum and the same time can enhance the environment and economy. The manufacture, use and removal of traditional composite structures, usually made of glass, carbon or aramid fibers reinforcing nonbiodegrable polymers like epoxies, unsaturated polyester resins, polyurethanes, phenolics etc. are considered critically ¹. *Eco*-friendly green composites from plant derived fiber and crop-derived plastics are novel materials for the 21st century and can be of great importance to the materials world ². Biocomposites are emerging as a viable alternative to glass fiber reinforced composites especially in automotive applications ³. While they can deliver the same performance for lower weight, they can also be 25-30 percent stronger for the same weight ⁴. Moreover, they exhibit a favorable non-brittle fracture on impact, which is another important requirement in the passenger compartment. Interior parts from natural fiber – polypropylene and exterior parts from

natural fiber – polyester resins are already in use 5° . Johnson Controls, Inc. has started production 6° of door-trim panels from natural fiber and polypropylene.

Advantages of natural fibers over man-made glass fiber are: low cost, low density, competitive specific mechanical properties, reduced energy consumption, carbon sequestration and biodegradability. Auto companies are seeking materials with sound abatement capability as well as reduced weight for fuel efficiency. Natural fibers possess

Cellulose esters



Figure 1. Structure of Cellulose esters (Cellulosic Plastics): R = H (Cellulose), acetyl (Cellulose acetate), acetyl and propionyl (Cellulose acetate propionate), or butyryl (Cellulose acetate butyrate).

excellent sound absorbing efficiency and are more shatter resistant and have of better energy management characteristics than glass fiber reinforced composites. In automotive parts, compared to glass composites, the composites made from natural fibers reduce the mass ⁷ of the

component and can lower the energy needed for production by 80%. In Europe, renewable materials are of increasing interest ⁸ because of a directive of the European Parliament that an automotive material recycling rate should be greater than 80% by the year 2006. This directive is an opportunity to introduce materials from renewable resources.

Cellulose from trees and cotton is used in place of petroleum as a feedstock to make cellulosic plastics ⁹. Cellulose esters are considered as potentially useful biodegradable polymers. The structures of cellulose esters include cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), are illustrated in

Figure 1. The production of cellulose esters from recycled paper and sugarcane has also been demonstrated ¹⁰. Some of the applications of cellulose ester biopolymers are film substrates for photography, toothbrush handles, selective filtration in the medical field, automotive coatings, etc. ¹¹. In an ongoing project, we are investigating various processing issues to study the structure-property relationship of cellulose esters-natural fiber biocomposite materials to find their applications in green automotive parts. As a part of our current investigation, this communication describes the effect of process engineering on performance of hemp fiber-cellulose ester biocomposites.

3. Experimental

3.1. Materials

Powder Cellulose Acetate (CA 398-30) free from any plasticizer and additives was supplied by Eastman Chemical Co., (Kingsport, TN). The degree of substitution of the cellulose acetate used was 2.5. The triethyl citrate (TEC) plasticizer was procured from Morflex Inc., Greensboro, North Carolina. The chopped raw hemp fiber (1/4 inch) was kindly supplied by Hempline, Canada.

3.2. Hemp Fiber Density and Tensile Modulus Measurements

Pre-dried raw hemp was used for both the measurements. The density of raw hemp was measured using Archimedes method with ethanol using ASTM D 3800. The average density (20 measurements) of hemp fiber was found to be 1.29 gram/cm³. The tensile modulus of hemp fiber was measured using United Calibration Corp. SFM-20 with load cell of 20 lbs and speed rate of 0.05-in/sec. Single fiber tests were conducted with 20 trials. The average tensile modulus of hemp was found to be 42 GPa.

3.3. Spectral, Thermal, and Morphological Analysis of Hemp Fibers

The Fourier Transform Infrared (FTIR) spectrum of raw chopped hemp in KBr pellets was measured using a Perkin-Elmer Spectrum® 2000 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere using Hi-Res. TGA 2950 Thermogravimetric Analyzer at heating rate of 10^oC/min to 600 ^oC. Environmental scanning electron microscopy (ESEM) was carried out at 20 kV and chamber pressure of 3 Torr using a Phillips Electroscan 2020.

3.4. Composite Fabrication Processing

Two different types of processing are adopted in fabricating the biocomposites: Process I: Novel Powder Impregnation Processing (compression molding of the mixture of chopped hemp natural fiber and powder cellulose acetate along with liquid plasticizer)

A premeasured amount of triethyl citrate plasticizer was added drop wise on to pre-dried cellulose acetate (CA) powder and the mixture was stirred mechanically in a kitchen mixer for 30 minutes. The investigated cellulosic plastic composition contained 30 wt. % of TEC plasticizer. The vacuum dried chopped hemp was added according in the desired weight percentage to the CA + TEC mixture. The mixture was then mechanically mixed for another 20 minutes. The resulting mixture was compression molded using a picture-frame mold in a Carver Press SP-F 6030 at temperature 195^oC under pressure. During compression molding at specified temperature, for the first 12 minutes the materials were kept at contact pressure of 1.1 MPa and then held at a pressure of 2.67 MPa for three minutes followed by cooling under pressure. The fabricated biocomposites were then cut into the required shapes and were kept sealed inside zip lock bags for 2 days (at room temperature) prior to physico-mechanical property evaluation.

Process II: Extrusion followed by injection molding

Two-step extrusion was carried out in this process. In the 1st extrusion step, cellulose acetate plastic (CAP) pellets were made by pre-mixing cellulose acetate powder with 30 wt. % TEC plasticizer. In the 2nd step, CAP pellets as obtained through 1st process; were fed into the twin-screw extruder (ZSK-30 from Werner-Pfleiderer with L/D = 30 and six temperature controlled zones) while feeding the chopped hemp (~ 1/4 inch) into the last zone of the extruder. The temperature profiles along the barrel were 190° C with die temperature held at 195° C. A screw speed of 150-rpm was used with ~ 40% torque reading, the resulting output was 65 to 70 grams/minute. The thin strands of composites were pelletized and stored for further injection molding. The injection molding (85-ton Cincinnati-Milacron press) conditions used were: temperatures in zones 1 through 3 were ~195°C, mold at 60°C, 40 sec. cooling time, 25 sec. extruder delay, fill pressure of 1500 psi, pack pressure and hold pressures were 1500 and 1200 psi, respectively. The thermo-mechanical properties were determined following ASTM standards. The test specimens for the thermo-mechanical properties were cut in the desired shapes from the injection molded tensile coupons and were kept for two days inside zip lock bags (at room temperature) prior to properties evaluations.

3.5. Analysis and Testing

The flexural strength and modulus of elasticity (MOE) of virgin cellulose acetate plastics and their biocomposites as fabricated through above mentioned two processing

approaches were determined using a United Calibration Corp. SFM-20 as per ASTM D 790. Similarly, the tensile strength and modulus were measured using the same machine



Figure 2. ESEM micrograph of raw hemp fiber (100 μm scale bar, 600X). between hemp fiber and cellulose acetate plastic (CAP) matrix. The fractured impact specimens were gold sputtered prior to examination.

Dimensional stability measurements were made following ASTM D 696 using a thermomechanical analyzer (TMA) 2940 from TA instruments, USA. The heating rate was 4°C/minutes (cpm) starting at room temperature to 120 °C. The coefficient of thermal expansion (CTE) was calculated

following ASTM D 638. The notched Izod Impact strength was carried out with an Impact tester from Testing Machines Inc. (model 43-OA-01) according to ASTM D 256. Environmental scanning electron microscope (ESEM) photo micrographs of impact fractured samples were taken at 20 kV and chamber pressure of 3 Torr using a Phillips Electroscan 2020 to evaluate the adhesion



Figure 3. Flexural properties of powder processing (Process 1) and extrusion followed by injection molding (Process II): A = CA Plastics (CAP) of Process I, B = CA Plastic Biocomposites (30wt% hemp) of Process I, C = CA Plastic of Process II, D= CA Plastic Biocomposites (30wt% hemp) of Process II.

from the slope of the curve of dimension change vs. temperature. The heat deflection temperature (HDT) and storage modulus of virgin CAP bioplastic matrix and biocomposites were determined using a TA dynamic mechanical analyzer (DMA) 2980 at a heating rate of 2 cpm for HDT measurements and 4 cpm for storage modulus measurements. The material was heated from room temperature to 100°C. A modified





Figure 4. ESEM micrographs of impact fractured samples: A = CA Plastic Biocomposites (30wt% hemp) of Process I --150 µm scale bar (300X), B = CA Plastic Biocomposites (30wt% hemp) of Process II -- 200 µm scale bar (250X).

ASTM D 648 was used for HDT measurement since the DMA could only handle a smaller size of specimen as compared to that of ASTM D 648.

4. Results and Discussion

In an on-going project to develop ecofriendly biocomposites from various natural fibers like hemp, kenaf, jute, flax etc. and cellulose ester bioplastics to design and engineer greener automotive parts, the present investigations report the effect of two processing approaches on the physicomechanical and thermo-mechanical properties of the resulting hemp fiber based biocomposites. Besides fiber surface modification, matrix modification and the use of compatibilizer during composite fabrication

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to get optimum fiber-matrix adhesion, different processing approaches also affect the over all properties of the resulting composite ². Powdered cellulose esters are obtained through a proprietary (Eastman Chemical Co.) acetylation process. The cellulose ester powder in combination with different additives and plasticizer is extruded into cellulose ester pellets for commercialization. In cellulose acetate plastic formulation, the major plasticizer used in the industry now is dioctyl phthalate (DOP), which is under environmental scrutiny. In our investigations we are using an eco-friendly citrate plasticizer. We obtained cellulose ester powder from the Eastman Chemical Company and combined the plastic with the citrate plasticizer for biocomposite applications. We are targeting to fabricate the biocomposite pellets through one-step extrusion process by adding powder cellulose ester, liquid plasticizer and chopped natural fiber followed by injection molding to the desired shape.

Hemp is an important ligno-cellulosic natural fiber and has attracted much attention of auto-parts manufacturer in Europe and North America. Hemp fiber is a bast fiber, meaning it is attained from the stem of the plant. As reported in the literature ¹ hemp contains (by weight) 70.2-70.4% cellulose, 3.7-5.7% lignin, 17.9%-22.4% hemicellulose, 0.9% pectin, 0.3% wax and 10.8% moisture. The hemp fiber used under the present studies is characterized through FTIR, ESEM and TGA analysis. The broad absorption band in the region around 3500 cm⁻¹ is the characteristic of hydrogen bonded O-H stretching. The characteristic carbonyl peak at 1740 cm⁻¹ of the fiber is due to lignin and hemicellulose components, which exists in the hemp fiber. The hemicellulose contains groups that absorb in the carbonyl region. The ESEM micrograph (Figure 2) of raw hemp fiber shows the presence of natural waxy substances on the fiber surface. Such

waxy substances contribute to ineffective fiber-matrix bonding and poor surface wet-out. Although the present investigations deal with raw hemp fiber based composites we are also investigating the effect of various surface treatments of hemp fiber to improve fibermatrix adhesion of the resulting biocomposites for superior performance. The results of such investigations will be reported in our subsequent communications. The low temperature resistance of natural fibers does not allow an arbitrary choice of thermoplastic as matrix material. For the manufacture of biocomposites with thermoplastic matrix systems, it is important to know about the degradation of mechanical properties when the fibers are exposed to manufacturing temperature for a certain time. The TGA analysis (Figure is not shown) indicates that the raw hemp fiber starts to decompose at 300°C and its maximum rate of thermal decomposition as indicated by the derivative of the weight curve vs. temperature was found to be 396°C. In





the present studies, during composite fabrication used a maximum we processing temperature of $\sim 195^{\circ}$ C, well below the decomposition temperature of the hemp fiber.

The main objective of the present investigation is to study the effect of two different process engineering approaches of biocomposite fabrication on the performance of the resulting biocomposites. In Process I, the powder impregnation

processing approach through compression molding is followed and in Process II

extrusion followed by injection molding is adopted in fabricating the hemp-cellulose ester plastic based biocomposites. Recently, powder impregnation processing through compression molding for biocomposite fabrications from chopped henequen natural fiber and powder polypropylene has been reported ¹². Most work on natural fiberthermoplastic composites is based on melt mixing of short length natural fiber and polymer pellets through extrusion followed by injection molding processing. Such processing exposes the natural fibers to high shear forces, which can break or otherwise damage the fibers, decreasing their aspect ratio. It is well known that the lower the aspect ratio the lower stress transfers across the length of the fiber. However, one of the main advantages of extrusion-injection molding processing is the intimate mixing of fiber and matrix, which plays a vital role in giving the requisite performance. In comparison to the powder impregnation process, although the fibers are free from high shear, thus avoiding fiber damage unlike the extrusion-injection molding technique, the lack of intimate



Figure 6. Stress-strain plot of: A = virgin cellulose acetate plastics (CAP) and B = CAP biocomposites (30wt% hemp).

mixing sometimes adversely affected the over-all properties of the resulting biocomposites.

The flexural properties of biocomposites fabricated through the abovementioned processes are presented in Figure. 3. The flexural strengths (FS) of cellulose acetate plastic (CAP) and its biocomposites show superior performance when fabricated through process II as contrasted to Process I. The FS of CAP matrix polymer made through process II is 33% more than CAP as made through Process I. The corresponding biocomposites (30 wt.% hemp) exhibit a FS variation of ~ 30%, processing II thus showing superior strength over processing I. As expected; the impact strengths of both CA plastic (CAP) and CAP based biocomposites fabricated through Process II showed lower values when compared to their counterparts



Figure 7. Comparison between tensile modulus of Rule of Mixture (ROM), modified ROM, and experimental Tensile Modulus with density of raw hemp (ρ)= 1.29 g/cc, Tensile Modulus of hemp fiber (E_f) = 42 GPa, E_m = 2.1 GPa.

made through Process I (Data is not shown). The variation of properties is attributed to the fact that in Process I, we adopt powder processing and lack of shear force is applied whereas in process II the extrusion and injection molding processing exert sufficient shear forces for the intimate mixing of powder polymer, liquid plasticizer, and raw hemp fibers. This observation is supported by Environmental Scanning Electron Microscope (ESEM) images of fractured

impact sample taken for Process I (Figure 4 A) and Process II (Figure 4 B). Process II shows a lesser amount of fiber pull out indicating better adhesion between hemp fiber and CAP matrix as compared to that of Process I. In contrast, plenty of longer fiber pull-outs are observed in Process I and thus they can be easily distinguished from CAP matrix, thus indicating poor fiber-matrix adhesion. Therefore, non-uniformity of fiber distribution could be found in some parts of the sample. As a result, modulus of elasticity (MOE) of

the biocomposite of Process I has a lower value than its counterpart made through Process II. Much better performance of biocomposites made through powder processing approach is targeted through better consolidation processing by the use of a new coupling agent. The use of the right coupling agent is expected to improve the wetting and fibermatrix adhesion, since the fiber length remains intact the resulting biocomposites are poised to show much improved performances. Such investigations are in progress and will be reported in our future communications.

In order to study the effect of fiber content on the performance of these composites, the usual extrusion and injection molding processing (Process II) was used in making the biocomposite samples. Both the flexural strength and MOE increase with



Figure 8. Heat Deflection Temperature (HDT) data comparison of A = CAP (0wt% hemp), B = 15wt% hemp, C = 30wt% hemp content.

increasing of fiber content from 15 to 30 wt.% (Figure 5). We target to further increase the fiber content to 40 and 50 wt. % in our biocomposite system; however such investigations are beyond the scope of the present study. Flexural strength and MOE of virgin cellulose acetate plastic (CAP) enhance by 75 and 200% respectively on reinforcements with 30 wt% hemp fibers. The tensile stress vs.

strain curves of cellulose acetate plastic and hemp-CAP based biocomposite (30 wt. % hemp) are showed in Figure 6. It is well observed that natural fiber reinforcement improved the stiffness and decreased the elongation of the virgin CAP matrix.

Although a number of models have been developed to study the mechanical properties of a fiber-reinforced polymer, the simplest and reasonable equation for prediction of these is given by the rule of mixtures (ROM). The modified ROM ¹³⁻¹⁵ for determining the tensile modulus of a composite is shown in equation 1. A comparison between the theoretical modulus value from Rule of Mixtures, modified Rule of Mixtures and experimentally determined values is shown in Figure 7. The Rule of Mixtures estimates the composites stiffness by a weighted mean of the moduli of the two components -- matrix and fiber -- depending upon the volume fractions of the components ¹⁶. This equation is valid for long fibers, assuming they have equal strain. Since short fibers (1/4 inch long) with a random orientation were used in this experiment, a constant k^{13-15} is used in fiber part of ROM (modified ROM) to compensate non-equality of fiber strain that causes the inferiority of tensile modulus of experimental composites as compared to tensile modulus of ROM. The *k* value can be calculated from modified ROM as:



Figure 9. Coefficient of Thermal Expansion (CTE) data comparison of A = virgin cellulose acetate plastics (CAP) and B = CAP biocomposites (30wt% hemp).

$$E_c = kV_f E_f + V_m E_m$$

Where: $E_c = Modulus$ of resulting composites

k = "Empirical factor" representing the reinforcing efficiency dependent on the orientation of the fibers and the stress transfer between the matrix and the fibers. V_f = Fiber Volume Fraction (ρ of hemp = $E_f = Modulus of fiber (E_f = 42 GPa)$

 V_m = Matrix volume fraction

 $E_m = Matrix modulus (2.1GPa)$

In this experiment, k=0.40 (k_1) is obtained for ~10vol% hemp fiber-CAP biocomposite



Figure 10. Flexural properties comparison of: A = CAP, B = CAP -30wt% hemp composites, C = PP, D =PP-30wt% hemp composites.

whereas in ~20vol% hemp fiber-CAP biocomposites k = 0.3 (k_2). Curve fitting method is done among the experimental data, hence it yields k = 0.35, or it simply the average between k_1 and k_2 in this particular case.

Thermomechanical properties namely storage modulus, heat deflection temperature (HDT) and coefficient of thermal expansion (CTE) of hemp fiber

reinforced CAP biocomposites (fabricated through Process II) were evaluated. The storage modulus represents the ratio in-phase stress to the applied strain, which further is related to the mechanical energy stored per cycle of deformation ¹⁷. The storage modulus (at 30° C) of virgin CAP bioplastic was enhanced by ~ 150% when reinforced with 30 wt. % of hemp fiber (Data not shown). The heat deflection temperature (HDT) is widely used in automotive applications and represents the temperature at which the material deflects by 0.25 mm at an applied force (three point bending arrangement) of 66 psi (ASTM D 648). After incorporating the hemp fiber into the CAP matrix, the stiffness of the resulting biocomposite was enhanced thereby improving the HDT (Figure 8). The HDT

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of virgin the CAP matrix improved by 13 and 30% respectively at reinforcement loadings of 15 and 30wt% of hemp fibers. Enhancement of stiffness means reduction in free volume presented in the system. This fact will not only affect storage modulus and HDT, but also it will reduce the coefficient of thermal expansion (CTE) of the material. The CTE is defined as the dimension change with respect to initial dimension per degree of temperature change (normally measured below or above the glass transition temperature of material). Two sampling methods were adopted when measuring the CTE, based upon flow direction during processing; they are machine (flow direction -- 0^{0}) and transverse direction (perpendicular to flow direction -- 90^{0}). In this paper we evaluate CTE from room temperature up to the CAP glass transition temperature (~80 0 C). Figure 9 shows a dramatic reduction of CTE for both directions (64% reduction for machine and 54% reduction for transverse direction) of CAP-hemp based biocomposites in respect to virgin CAP. The above explanation clearly demonstrates that the thermomechanical properties of cellulose ester plastic improve upon reinforcement with hemp fibers.

We are targeting to replace/substitute PP with the cellulose ester bioplastic and synthetic glass fiber with natural fibers to design eco-friendly biocomposites for greener automotive parts. The comparative reinforcement effect of hemp fiber on both the matrices e.g. cellulose acetate plastic (30 % citrate plasticizer) and commercial PP as regards to flexural properties of 30wt% fiber based composites fabricated through Process II is represented in Figure 10. The flexural strength and MOE of hemp-CAP based biocomposite are superior by about 40 and 50% respectively over the hemp-PP based composite counterpart. Natural fiber and cellulose ester both being polar; binds to each other more effectively in the composite structure unlike PP, which is a non-polar polymer.

5. Conclusions

Two types of processing e.g. powder impregnation processing through compression molding (Process I) and conventional extrusion followed by injection molding (Process II) were successfully applied in making the biocomposites from chopped hemp fiber and cellulose acetate plastics. Biocomposites fabricated through Process II showed better strength over their counterparts made through Process I. This is due to sufficient shear forces for the intimate mixing of powdered polymer, liquid plasticizer and fibers. The ESEM examination of impact fractured surfaces proved that biocomposites made through Process I show poor adhesion and lack of fiber dispersion as compared to Process II. In thermomechanical properties, enhancements of 150% and 30% are observed for the storage modulus (at 30^oC) and heat deflection temperature, respectively, of CAP based biocomposite (30wt% hemp content fabricated through Process II) as compared to its base line data (0wt% hemp content). The coefficients of thermal expansions (CTE) of CAP based biocomposites are decreased as much as 64% and 54% for machine and transverse direction respectively. Between non-polar polypropylene (PP) matrix and 30% plasticized polar cellulose acetate plastic (CAP) the latter proved to be a much better matrix for hemp fiber (polar in nature) and thus exhibited improved physico-mechanical properties. Fabricated by the same processing method (Process II, extrusion and injection molding) with the same content of hemp fiber (30wt%) the CAP-hemp based biocomposite exhibited a FS of 78.3 MPa and MOE of 5.6
GPa as contrasted to 55.3 MPa and 3.7 GPa for the corresponding PP-hemp based composite. The incorporation of a high content of natural fiber say up to 50wt% or even more in the biocomposite system along with suitable surface treatments of natural fibers along with the use of coupling agents during composite fabrications, which are currently under investigations are poised to generate superior performance biocomposites.

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III. Chopped Industrial Hemp Fiber Reinforced Cellulosic Plastic Biocomposites: Thermomechanical and Morphological Properties

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1. Abstract

Biocomposites, i.e. biopolymers reinforced with natural fibers offer an environmentally benign alternative structural material for automotive applications. Cellulose esters (bioplastic made from cellulose) are potentially useful biosourced polymer. By embedding inexpensive plant-based cellulosic fibers (chopped hemp fiber) into a biopolymeric matrix (cellulose ester) novel biocomposites have been made utilizing two different processing approaches: (Process I) powder impregnation and (Process II) extrusion followed by injection molding. The resulting biocomposites have been evaluated for their physico-mechanical and thermomechanical properties. Cellulose acetate plasticized with 30% citrate plasticizer proved to be a better matrix compared to polypropylene (PP) for hemp fiber reinforcements in terms of flexural and damping properties. Biocomposites with 30 wt% of industrial hemp fiber processed through extrusion and injection molding exhibited a flexural strength of ~78 MPa and modulus of elasticity of ~5.6 GPa. Cellulose acetate butyrate plastic (CABP) proved to be a better matrix than plasticized cellulose acetate (CAP) for biocomposite applications. The fiber-

matrix adhesions are evaluated through Environmental Scanning Microscopy (ESEM) analysis.

Keywords: cellulose ester, natural fiber, biocomposites, thermo-mechanical properties.

2. Introduction

Eco-friendly biocomposites from plant derived fiber (natural/biofiber) and cropderived plastics (bioplastic) are novel materials for the 21st century and can be of great importance to the materials world, not only as a solution to growing environmental threats but also as a solution to alleviating the uncertainty of the petroleum supply ^{1,2}. There is a growing urgency to develop *eco-friendly* biobased polymers and composites and other innovative technologies that can reduce the widespread dependence on fossil fuel. Natural/biofiber composites (biocomposites) are emerging as a viable alternative to

Cellulose esters



Figure 1. Structure of Cellulose esters (Cellulosic Plastics): R = H (Cellulose), acetyl (Cellulose acetate), acetyl and propionyl (Cellulose acetate propionate), or acetyl and butyryl (Cellulose acetate butyrate)

glass fiber reinforced composites especially in automotive applications ³. While they can deliver the same performance for lower weight, they can also be 25-30 percent stronger for the same weight ⁴. Moreover, they exhibit a favorable non-brittle fracture on impact,

which is another important requirement in the passenger compartment. Interior parts from natural fiber-polypropylene and exterior parts from natural fiber-polyester resins are already in use ⁵. For example, Johnson Controls, Inc; has started production ⁶ of door-trim panels from natural fiber and polypropylene.

Studies of the American market identify the potential impact and opportunities for natural fiber composites 2,7 . It is estimated that ~75% of a vehicle's energy consumption is directly related to factors associated with a vehicle's weight. To reduce vehicle weight; a shift away from steel alloys towards aluminum, plastics and composites has





predicted that in near future polymer and polymer composites will comprise ~15% of a car weight ⁸. Weight reduction is critical to producing safe and cost-effective light-weight vehicles. Auto companies are also seeking materials with sound abatement capability as well as reduced weight for fuel efficiency. Natural fibers possess excellent

sound absorbing efficiency and are more shatter resistant and have better energy management characteristics than glass fiber based composites. In automotive parts, compared to glass fiber composites, biocomposites made from natural fibers reduce the mass ⁹ of the component and can lower the total energy consumed in producing this material by 80%. The main motivation for using natural/biofibers like kenaf and hemp to replace glass fibers is the low cost (~1/3 of E-glass fiber), low density (~ $\frac{1}{2}$), acceptable specific mechanical properties, enhanced energy recovery, CO₂ sequesterization, and biodegradability ².

Plant-based materials for transportation are the wave of the future. Using natural fibers with polymers (plastics) based on renewable resources will allow many environmental issues to be solved. Natural fiber–PP (thermoplastic base) or natural fiber–polyester (thermoset base) composites are not sufficiently eco-friendly due to the petroleum-based source as well as non-biodegradable nature of the polymer matrix. By embedding biofibers like hemp, kenaf, pineapple leaf fiber, henequen, corn straw fibers and grasses with renewable resource based biopolymers such as cellulosic plastic, combased plastic, starch plastic and soy-based plastic, green biocomposites with acceptable mechanical properties are being developed at Michigan State University. This paper relates to the fabrication as well as thermo-mechanical property evaluation of biocomposites from natural fiber and cellulose ester biopolymers for the 21st century 'green' car.

Cellulose esters are considered as potentially useful biosourced polymers for the future¹⁰. As shown in Figure 1, R of cellulose esters is replaced by acyl groups (RCO-). The hydroxyl and carbonyl groups thus have good potential to form hydrogen bonding

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with hydroxyl groups of cellulose fibers as represented in Figure 2. We are focusing on two kinds of cellulose ester, they are cellulose acetate (CA), where acetyl groups are replacing the R groups in the chemical structure, and cellulose acetate butyrate plastic (CABP) in which not only acetyl groups are present but also a moderate content of butyryl groups (37%) in the chain. The CABP polymer processes easier without the need for a plasticizer and has higher moisture resistance compared to CA. CABP possesses excellent surface hardness and good strength in comparison to CA besides lower viscosity at 195 °C due to the presence of these higher functional groups, which can act as an internal plasticizer. In contrast, CA needs an external plasticizer to be added in order to enhance its flow and allow processing below its degradation temperature (230 °C), which is near the lower portion of its typical melting range.

3. Experimental

Powdered cellulose acetate (CA 398-30) and cellulose acetate butyrate plastic (CABP = CAB 381-20) free from any plasticizer and additives were supplied by Eastman Chemical Co., Kingsport, TN. The degree of substitution of acetyl groups in the CA is approximately 2.45. CABP 381-20 has a butyryl content of 37%, acetyl content of 13.5%, hydroxyl content of 1.8%, with melting and glass transition temperatures of 195° C and 141° C, respectively. The triethyl citrate (TEC) plasticizer was obtained from Morflex Inc., Greensboro, North Carolina. Chopped industrial hemp fiber of length ~1/4 inch (hence forward, chopped industrial hemp fiber will be written as only hemp fiber after this section) was supplied by Hempline, Ontario, Canada.

Two different types of processing methods were employed in fabricating the green/biocomposites:

3.1. Process I: Powder Impregnation Process followed by Compression Molding

A specific amount of liquid plasticizer (triethyl citrate, TEC) was added drop wise to pre-dried CA powder and the mixture was stirred mechanically in a kitchen mixer for 30 minutes. Vacuum dried, chopped hemp fiber was added in the required weight



Top View

Figure 3. Fabrication procedure of hemp fiber reinforced cellulose acetate biocomposites using Process I: powder impregnation process followed by compression molding

percentage into the CA powder premixed with 30 wt% of TEC plasticizer (plasticized CA – CAP). The mixture (total of 60 grams) was mechanically mixed for another 20 minutes. The resulting mixture was compression molded using a picture-frame mold, as pictured in Figure 3, in a Carver Press SP-F 6030 at temperature 195 $^{\circ}$ C under pressure. A bed lay up of the mixture of 30 wt% hemp fibers + 70 wt% matrix (CAP) with total of 60 grams was fitted into picture frame mold with dimension of 18cm (length) * 14cm (width) * 0.15cm (thickness). This amount surpasses the volume defined by picture frame mold and the platens so that hydrostatic pressure is applicable. The resulting compression

molded plaque has thickness of 0.18±0.003 cm. An image of cross section of the compression molded sample was taken using optical microscope showing a compacted sample is achieved (Figure 4).

During compression molding at the specified temperature, the materials were kept at contact pressure of 1.1 MPa for 12 minutes and then compacted at a pressure of 2.67 MPa for three minutes followed by cooling under pressure. The fabricated samples were cut to desired shapes for physico-mechanical properties evaluations.

3.2. Process II: Extrusion followed by Injection Molding



Figure 4. Cross sectional image of compression molded hemp reinforced cellulose acetate based biocomposites (50X magnification, 1mm scale bar)

A two-step extrusion was carried out in making CAP-hemp biocomposites in contrast to a one step extrusion step in making the CABP-hemp biocomposites. The first step was to produce CA plastic granules from CA powder and 30 wt% TEC plasticizer. In the 2nd step, CA plastic granules were fed into a twin-screw extruder

(ZSK-30 Werner Pfleiderer, co-rotating, intermeshing, with L/D = 30) while feeding the chopped hemp (~ 1/4 inch) in the 2nd to last port of the extruder. The temperature profiles were ~190°C with a die temperature ~195°C. A 150-rpm screw speed was used with ~ 40% machine torque reading and a resulting extrudate output of about 65–70

grams/minute. For CABP-hemp biocomposite pellet production, both CABP powder and chopped hemp fibers in the requisite amounts were fed into the extruder under similar conditions for extrusion. The thin strands of composites were granulated and stored for further injection molding. The injection-molding machine used was an 85-ton Cincinnati-Milacron press. The injection molding conditions used were: temperatures on zone 1 to 3 were at 195°C, die at 60°C with 40 seconds cooling time, 25 seconds extruder delay, fill pressure was 1500 psi, pack pressure and hold pressure were 1500 and 1200 psi, respectively. All of the physico-mechanical properties were determined through ASTM standards.

3.3. Analysis and Testing

Flexural strength and modulus of elasticity (MOE) were determined using United Calibration Corp. SFM-20 as per ASTM D 790. Similarly, tensile strength and modulus properties were measured using the same machine following ASTM D 638. The notched Izod Impact strength was carried out with an Impact tester from Testing Machines Inc. 43-OA-01 according to ASTM D 256. Environmental scanning electron microscope (ESEM) micrographs of impact and tensile fractured samples were taken using Phillips Electroscan 2020 (at 20 kV and chamber pressure of 3 Torr) to evaluate the adhesion between hemp fiber and CA matrix. The fractured specimens were gold sputtered before taking the images.

Storage, loss modulus, and damping (tan delta) of a material can be determined using DMA. In DMA, a sample is exposed to a sinusoidal strain input and the output



Figure 6. Impact properties of powder processing (Process I) and extruded followed by injection molding (Process II): A = CA Plastics (CAP) of Process I, B =CA Plastic Biocomposites (30wt% hemp) of Process I, C = CA Plastic of Process II, D= CA Plastic Biocomposites (30wt% hemp) of Process II.

measured. The stress is portion of this output stress represents energy stored (Storage Modulus, E') by the material elastic or component of the material, which is in phase with the sinusoidal applied strain input. The viscous component or the remainder of the output stress that is out phase represents the of amount of energy dissipated

by the material (Loss Modulus, E"). The relationship between the two is given by:

$$E^* = E' + E''$$

where E^* is the complex modulus. The ratio between E" and E' is the phase lag or tan delta or damping factor. The peak of loss modulus (E") where the storage modulus (E') decreases rapidly is generally the glass transition (Tg) of a material.

Besides storage, loss modulus and tan delta, one can get damping characteristics



Figure 7. ESEM micrograph of impact fractured samples: A = CAP Biocomposite (30wt% hemp) Process I (100X and 450 µm scale bar), B = CAP Biocomposite (30wt% hemp) of Process II (95X and 450µm scale bar) using DMA. The temperature step / frequency sweep method using a single cantilever clamp in DMA (TA dynamic mechanical analyzer, DMA model 2980) was used in determining the damping factor (tan delta) of the materials at temperatures around the glass transition (Tg) of CAP with frequency ranges from 0.01 to 100 Hz. Sample dimensions for damping characteristics are 17.18mm long, 12.76mm wide, and 3.18mm thick.

4. Results and Discussion

4.1. Processing Approaches Vs. Performance of Biocomposites





Figure 8. Comparison between rule of mixtures (ROM), modified ROM, and experimental tensile modulus of CAP Biocomposites.

can be observed from Figure 5; the flexural strengths (FS) and modulus of CA plastics and their biocomposites show superior performance when fabricated through process II as contrast to Process I. The FS of CAP made through process II is 33% greater than CAP plastic made through Process I. Similarly the corresponding biocomposites (30 wt% hemp) exhibit a FS variation of ~ 31% - - process II thus show superior strength over process I. As expected, the impact strengths of both of CA plastic (CAP) and CAP based biocomposites fabricated through Process II, showed a lower value as compared to their counterparts as made through Process I. The variation of properties is attributed to the fact that in Process I; we adopt powder processing and lack of shear force is applied whereas in process II the extrusion and injection molding processing exert sufficient shear forces for the intimate mixing of powder polymer, hemp and liquid plasticizer. This phenomenon is supported by Environmental Scanning Electron Microscope (ESEM) images of fractured impact sample taken for Process I (Figure 7 a) and II (Figure 7 b). Process II shows a smaller amount of fiber pull out indicating better adhesion between hemp fiber and CA matrix as compared to that of Process I. In addition, it is difficult to distinguish between fiber and CA matrix in Process II as the fiber is chopped to smaller size during pelletizing, which might improve adhesion with CA matrix, and give better



contrast, the long fiber in Process I can be easily distinguished from CA matrix -- indicating poor adhesion -- as it does not undergo sufficient shear force and chopping during the processing. Therefore, non-uniformity of fiber distribution could be found in some parts of the

dispersion.

In

fiber

Figure 9. Comparison between rule of mixtures (ROM), modified ROM, and experimental tensile modulus of CABP Biocomposites

sample. As a result, the modulus of elasticity (MOE) of CAP-based biocomposite of Process I has a slightly lower value than its counterpart made through Process II.

4.2. Fiber Contents Vs. Performance of Green/Biocomposites

In order to study the effect of the variation of fiber content on the performance of the composites, the usual extrusion and injection molding processing (Process II) was utilized. Comparison between the theoretical modulus values from Rule of Mixtures (ROM), modified ROM and experimental tensile modulus is shown in Figures 8 and 9. A least squares fit of the experimental values in Figures 8 and 9 with respect to rule of mixture equation yields a constant k value of 0.35 and 0.45 for CAP biocomposites and CABP biocomposites, respectively, in the following equation:

$$E_c = kV_f E_f + V_m E_m$$

Where: $E_c = modulus$ of resulting composites

k = constant value (fiber orientation parameter) used to fit experimental tensile modulus data with theoretical modified ROM

$$V_f$$
 = fiber's volume fraction (using ρ of hemp = 1.29 gm/cm³)¹¹

 $E_f = modulus of hemp = 42 GPa^{11}$

 V_m = matrix's volume fraction

 $E_m = modulus of the matrix$

The variation of theoretical and experimental modulus (Figures 8 and 9) value seems reasonable since the fiber orientation is random throughout the samples, and there is no modification on the surface of the fiber or no compatibilizer is used to make natural fiber and matrix become more compatible (improvement in adhesion).



4.3. Hemp Fiber Reinforced Cellulose Acetate Vs. Hemp Fiber Reinforced Polypropylene Composites

Figure 10. Flexural properties: CAP, CAP Biocomposites, PP, and PP-30wt% composites

Our ultimate goal is to replace existing synthetic glass fibers with natural fibers as reinforcements and also petroleum-based polymers with renewable resourcebased biopolymers as matrices in designing and engineering biocomposite materials. of With this in mind, the flexural properties of un-sized hemp-

polypropylene (PP-Hemp) composites were compared with CAP-Hemp based biocomposites. Both samples contain 30 wt% fibers and are extruded and injection molded (Process II). Figure 10 shows a higher flexural strength -- by 42% -- for CAP-Hemp based biocomposites than that of PP-Hemp based biocomposites.

Besides mass, stiffness, and dimensional stability, NVH (noise, vibration, and harshness) is another crucial factor in automotive world for passenger comfort. Preliminary studies have shown that certain natural fiber reinforced thermoplastics gain similar or improved damping characteristics as compared to petroleum-based, glass fibers-reinforced thermoplastics. Damping characteristics of these biocomposites were



measured using the temperature step / frequencies sweep method (DMA) and were evaluated at the temperature interest of 80^oC, since both CAP and PP are in their rubbery states. As can be seen in Figure 11,

Figure 11. Damping properties: CAP, CAP-Hemp Biocomposites, PP, and PP-Hemp composites

both CAP and its biocomposites have better damping characteristics (higher tan delta values for all frequencies applied) and thus better sound absorption and less vibration as compared to PP and its biocomposites. Thus, CAP can be a green alternative for replacing PP in

plastic composites for automotive applications.

4.4. Hemp - CAP based Biocomposites Vs. Hemp - CABP based Biocomposites

Besides CAP based biocomposites, a 2nd type of promising cellulose ester matrix, cellulose acetate butyrate plastic, CABP is also evaluated for the biocomposites applications. One main advantage of CABP as compared to CAP is that CABP does not need plasticizer in order to be processed. The longer acyl substituted groups present in the CABP chain may act as internal plasticizers so that its processing window is wider as



compared to CAP. By adopting the 2nd processing approach e.g. extrusion followed by injection molding (Process II); we evaluated their stress-strain behavior and morphological properties.

In Figure 12, the inherent higher energy absorption capacity and higher strength of CABP

Figure 12. Stress-strain comparison between CAP, CAP Biocomposites, CABP, and CABP Biocomposites

biocomposites compared to CAP biocomposites was observed as the larger area under the stress-strain curve was obtained for the former. Further, a rougher tensile fracture surface is produced with CABP biocomposites (Figure 14A). Good interaction between hemp fiber and cellulose ester matrix (both fiber and matrix are polar) can be observed in the tensile fractured samples as depicted in Figure 13 and 14. Fiber pull out micrographs, especially for CABP biocomposites (Figure 14B), show that individual fibers are covered by the matrix as a result of hydrogen bonds formed between matrix and fibers.

5. Conclusions

Eco-friendly green composites from plant derived fibers and plant derived plastics

are new, emerging "green" materials for automotive applications. Cellulose acetate,



Figure 13. ESEM micrograph of tensile fractured samples of CAP Biocomposites (Process II): A = 200X with 250 μ m scale bar, B = 1000X with 45 μ m scale bar.

plasticized with eco-friendly citrate plasticizer, and cellulose acetate butyrate plastic,



Figure 14. ESEM micrograph of tensile fractured samples of CABP Biocomposites (Process II): A = 200X with 250 μ m scale bar, B = 1500X with 30 μ m scale bar. CABP (without additives or plasticizers) can be successfully used as matrix polymers in

fabricating the green composites. Comparing the plasticized (30%) cellulose acetate (CAP) with neat CABP, CABP is a better matrix as far as composite processing and physico-mechanical properties are concerned. Comparing the non-polar polypropylene (PP) matrix and the 30% plasticized polar cellulose acetate plastic (CAP), the CAP proved to be a much better matrix for hemp fiber (polar in nature) and thus exhibited improved flexural and damping properties. Both CABP and CAP matrix have good interaction with hemp fibers as shown by fiber pull out micrographs, with the former being the better, and thus it leads to higher strength.

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IV. A Solvent free Graft Copolymerization of Maleic Anhydride onto Cellulose Acetate Butyrate Bioplastic by Reactive Extrusion

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1. Abstract

Interfacial adhesion between fibers and matrix is crucial factor for effective stress transfer from matrix to fiber to enhance composite properties especially in short fiber composite system. The use of a chemical compatibilizer is a way to achieve such adhesion. We have synthesized maleic anhydride grafted cellulose acetate butyrate (CAB-g-MA), which can be used as compatibilizer in biocomposite fabrication. The research was directed at maleation of cellulose acetate butyrate (CAB) to study the effect of initiator, monomer – maleic anhydride (MA) concentration and processing conditions on grafting efficiency. CAB-g-MA was characterized by FTIR and titration methods. This compatibilizer was also produced under optimized conditions on a large scale extruder. The unique feature of this process is its solvent-free approach to grafting of maleic anhydride onto CAB, without hydroxyl group protection.

Keywords: Functionalization of biopolymers, extrusion, FT-IR.

2. Introduction

With the growing importance of environmental concern, there is increasing development of eco-friendly materials. Sustainable biocomposites can be fabricated using biopolymers derived from biomass as matrix and natural plant fibers (PF) as reinforcing materials. A potentially useful biodegradable, biobased polymer that is compatible with polar plant fibers (PF) is cellulose ester (CE). Our initial work has shown that cellulose esters particularly plasticized cellulose acetate (CAP) and cellulose acetate butyrate (CAB) have better mechanical and damping properties as compared to those of non-polar, petroleum based polypropylene matrix in composites prepared from industrial hemp (a bast natural fiber) as reinforcing material ^{1.2}. The polar-polar interaction between the PF and CE produces good interfacial adhesion and thus better stress transfer from matrix to fibers, resulting in high performance bio-composites.

In order to compete with petroleum based glass-reinforced polypropylene for structural applications, the interfacial adhesion between PF and CE has to be improved further. To improve adhesion the addition of a suitable coupling agent would be an economically feasible option as an alternative to surface treatment of fibers. Significant enhancement of mechanical properties was achieved for polypropylene based composites after addition of maleated polypropylene (PP-g-MA)^{3,4}. Currently, a number of maleated polypropylenes with varying acid numbers and molecular weights are commercially available ⁵. No report is yet available to the literature on grafting of MA onto cellulose ester bioplastics. The mechanism of maleation onto polar bioplastic is quite different to that of nonpolar plastic; the main motivation of the present investigations. In this study, maleic anhydride grafted CAB (CAB-g-MA) has been synthesized as a compatibilizer by reactive extrusion and characterized with FTIR and acid base titration. Initiator and

monomer concentrations were optimized based on the FTIR and titration results using a microextruder. Reaction conditions (temperature, rpm) in a twin-screw extruder were optimized to obtain similar acid number and percentage MA grafting values as obtained using the microextruder.

3. Experimental

3.1. Materials

Cellulose acetate butyrate (CAB 381-20) free from any plasticizer and additives, was supplied by Eastman Chemical Co., Kingsport, TN, with a butyryl content of 37 %, acetyl content of 13.5 %, hydroxyl content of 1.8 % and has melting and glass transition temperatures of 195 °C and 141 °C, respectively. Maleic anhydride (MA), acetone, and 0.1011 N methanolic KOH were purchased from Aldrich Chemical Co and liquid initiator: 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (Luperox 101) was obtained from Akzo Nobel, USA. Sodium hydride (NaH), sodium hydroxide (NaOH) were purchased from Aldrich Chemical Co as well.

3.2. Instrumentation

The FTIR spectra of neat CAB and CAB-g-MAs were recorded in absorbance mode from compression molded thin films using a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer.

3.3. Synthesis of maleic anhydride grafted CAB (CAB-g-MA).

Two processing techniques were adopted for the synthesis of CAB-g-MA:

Process I: Small-scale extrusion using DSM micro extruder. Pre-measured amounts of CAB, MA (all in powder form) were mixed in small beaker. Liquid initiator was added



Figure 1. FTIR curve showing unreacted maleic anhydride (MA) peak before putting in vacuum oven (A) and after putting in vacuum oven at $80-90^{\circ}$ C for overnight (B), and (C) is neat CAB.

dropwise using a syringe while stirring. The resultant mixture (about 12 grams total) was fed into a DSM Research 15cc Micro Extruder, DSM research, Netherlands, under the following conditions: temperatures in zone 1, 2, and 3 were kept between 195 to 205°C, screw speed was 100 rpm, cycle time was 3 minutes. Thin strand (extrudate) was collected and pelletized into granules.

Process II: Large-scale extrusion using ZSK-30 twin-screw extruder. Premeasured CAB,

MA (all in powder form) were mixed in kitchen mixer. Liquid initiator was added drop wise while stirring. The resulting mixture (about 1500 grams total) was hand fed into

ZSK-30 twin screw extruder with the following optimized conditions: temperatures in zone 1 to 6 were kept between 190 to 195 °C with die temperature of 200 °C, 150 rpm screw speed and 50 % torque reading. Extrudate was collected and pelletized.

3.4. Characterization of CAB-g-MA by FTIR (qualitative)

The pellets as obtained by Process I and II were vacuum dried overnight at 80 to 90 °C to remove unreacted maleic anhydride. Disappearance of unreacted maleic anhydride (MA) after granulated samples were put inside vacuum oven at 80-90°C for overnight is shown in Figure 1. A relatively small peak at 1850cm-1 was initially present as unreacted MA. Once the sample was heated at 80-90°C (as melting points of MA is about 53°C) in vacuum condition, this unreacted MA was emitted. Hence the corresponding peak was disappeared.

Some of the vacuum dried CAB-g-MA was compression molded (in a Carver Press SP-F 6030) into thin films at 197 °C for FTIR measurements. Here, anhydride groups belonging to MA were assigned to a peak value of 1786 cm⁻¹ whereas carbonyl groups of neat CAB were designated by 1778 cm⁻¹ peak. Similarly, Silverstein et al. reported that grafting MA onto the ester showed band at 1788cm⁻¹ corresponding to the symmetric C=O stretch of a saturated cyclic five membered anhydride ⁶.

3.5. Characterization of CAB-g-MA by titration (quantitative)

A part of purified CAB-g-MA was used to determine acid number (AN) and percentage MA grafting (% MA) using titration method. Following procedure was adopted in this quantitative measurement: 0.2 g of Maleic Anhydride grafted CAB was dissolved in hot acetone (~200 ml) using magnetic stirrer. The hot solution was then titrated against 0.1011 N methanolic KOH adding 5 drops of thymol blue in DMF (1 %) as an indicator. Appearance of stable yellow color was considered as the visible end point. Acid number (AN) and grafting percentage (% MA) were calculated using the following equation:

AN =
$$\frac{V_{KOH}N_{KOH}(EW)}{\text{weight of sample}} \left(= \frac{\text{mg KOH}}{\text{g of sample}} \right)$$

%MA = $V_{KOH}N_{KOH}(EW)$ (g of sample) (100%)
where EW = $\frac{MW}{\text{number of H}^{+} \text{ or OH}^{-} \text{ donor}}$

where, V, N, EW are volume, normality, and equivalent weight, respectively. Blank titration was done as well on neat CAB. However, the details of this procedure are available elsewhere 7 .

4. Results and Discussion

Cellulose is a linear polysaccharide comprises of cellobiose repeat units linked at β -1 \rightarrow 4 position ⁸. A cellobiose consists of two anhydroglucose repeat units with opposite orientation (in terms of hydroxyl groups' locations) from each other. This β -1 \rightarrow 4 linkages lead to material with relatively low water solubility. In general, cellulose extracted from natural resources are high molecular weight non-branching polysaccharides and are having conformational with great tendency to form intermolecular hydrogen bonding. Extensive hydrogen bonding formations produce cellulose fibers with high insolubility and relatively impermeable to liquids ⁹. The

inherent rigidity of cellulose originates from hydrogen bonding of the free hydroxyl groups in the anhydroglucose repeating unit within and between chains. The stability of the structure, thus mainly depends upon the ability to form hydrogen bonds. As a consequence, cellulose is not a thermoplastic but degrades on heating before the theoretical melting point is reached. Breaking the hydrogen bonds by solubilizing and reacting the free hydroxyl groups yields a thermoplastic, such as cellulose ethers and cellulose esters.

Free hydroxyl groups are normally expected to react with anhydrides under suitable reaction conditions leading to anhydride ring opening reactions. Thus, grafting of maleic anhydride onto cellulose esters would require hydroxyl group protection in order to avoid the reaction with anhydride. We allowed these OH groups in cellulose acetate butyrate (CAB) to react with NaH, NaOH, and maleic anhydride to determine their reactivity with the following procedures:

1. Procedure of NaH reaction:

NaH + R-OH -----> R-ONa + H₂ dry acetone

We added NaH into dissolved CAB according to the following calculation:

1 mole equivalent OH (CAB) = 1 mole equivalent NaH $\frac{1.8(0.1)}{17} = 0.0105 \text{ mole equivalentOH}$ = 0.0105(23+1) = 0.254 gm minimum of NaH needed

The mixture was heated while stirring until it dissolved. Obtaining CAB-ONa was done by precipitation using methanol. The precipitate was vacuum dried for overnight at 80^oC prior to FTIR analysis.

2. NaOH reaction procedure:

R-OH + NaOH -----> R-ONa + H₂O Heat

> CAB+MA+hitiator CAB+MA CAB+NaH CAB+NaOH CAB+NaOH CAB+NaOH CAB 3600 3400 3200 3000 2800 cm⁻¹

Into DI water (T = $60-70^{\circ}$ C), we added CAB such that free OH groups ready to react, i.e.

Figure 2. FTIR analysis of OH protection on cellulose acetate butyrate (CAB) using different materials: NaOH, NaH, and MA with and without initiator.

effective swelling agent (water) is needed to encounter the strong hydrogen bonds between cellulose chains, which creates hindrance during reaction ¹⁰. Aqueous NaOH (20wt%) was added into it while stirring. The mixture was left for stirring for 6 hours. Collecting CAB-ONa powder was done by Buchner filtration. The recovered powder was vacuum dried for overnight at 80^oC prior to FTIR analysis.

3. Extruded CAB+MA and CAB+MA+Initiator

These experiments were conducted also to investigate whether MA reacts with the free

I. Initiation R-O-O-R $\xrightarrow{\Delta}$ 2R-O •

II. Propagation + Termination



Figure 3. Proposed mechanism of maleic anhydride grafted cellulose acetate butyrate (CAB-g-MA).

OH groups or not. Pre-measured amounts of CAB, MA (all in powder form) were mixed in small beaker. Liquid initiator, for the second experiment, was added dropwise using a syringe while stirring. The resultant mixture (about 12 grams total) was fed into a DSM Research 15cc Micro Extruder, DSM research, Netherlands, under the following conditions: temperatures in zone 1, 2, and 3 were kept between 195 to 205°C, screw speed was 100 rpm, cycle time was 3 minutes. Thin strand (extrudate) was collected and pelletized into granules. All samples were put in vacuum oven for overnight at 80-90^oC to eliminate unreacted MA at ~1850cm⁻¹ peak. This vacuum dried samples were compression molded (in a Carver Press SP-F 6030) into thin films at 197 °C for FTIR measurements.

FTIR spectra (Figure 2) of these reacted CAB did not show any changes in the intensity of OH peak, indicating that almost all reactive (primary and secondary)



Figure 4. FTIR analysis of varying initiator (I) concentration (0, 0.5, 0.9, and 1.4wt%) with 5wt% MA content kept constant.

hydroxyl groups are esterified in CAB. The remaining free hydroxyl groups are either hindered or docile and do not react with maleic anhydride. Thus, free radical grafting of MA onto CAB could be carried out without OH group protection. The proposed mechanism of CAB maleation is schematically represented in Figure 3. The process involves free radical generation on the CAB backbone using a peroxy radical initiator. The free radicals on the polymer chains react with the MA to give CAB-g-MA (Note:

Material	Description	AN	StDev	% MA	StDev
CAB, neat	100% CAB powder 381-20	-	-	-	-
CAB-g-MA1	0.5wt% Initiator + 5wt% MA + 94.5wt% CAB, neat	12.8	0.0	0.6	0.0
CAB-g-MA2	0.9wt% Initiator + 5wt% MA + 94.1wt% CAB, neat	19.7	1.1	0.8	0.2
CAB-g-MA3	1.4wt% Initiator + 5wt% MA + 93.1wt% CAB, neat	18.2	0.0	0.8	0.0
CAB-g-MA4	0.9wt% Initiator + 7.5wt% MA + 91.6wt% CAB, neat	31.7	1.5	1.8	0.4
CAB-g-MA5	0.9wt% Initiator + 10wt% MA + 89.1wt% CAB, neat	24.2	0.0	1.2	0.0

Table 1. Effect of initiator concentration (CAB-g-MA1, 2, and 3) and effect of MA concentration (CAB-g-MA2, 4, and 5) on acid number (AN) and % MA grafting.

hydrogen abstraction is from the CAB backbone). It was found that the residence time of the polymer melt in the extruder did not affect the grafting reaction significantly. Optimized compositions of process I yielding the best results of grafting were chosen for process II (with optimized temperature and rpm) in order to get similar acid number and percentage grafting.

The initiator concentration was varied as follows: 0.5, 0.9, and 1.4 wt% while keeping 5 wt% MA constant with the following nomenclature: CAB-g-MA 1, 2, and 3, respectively (Figure 4 and Table 1). The increase in the anhydride peak intensity with initiator concentration is apparent in the FTIR spectra. As initiator amount increased, acid number and % MA increased up to 0.9 wt % initiator and then leveled off due to the lack of free radicals on the CAB backbone. From above results, 0.9wt% was set as optimum amount for initiator for this system.

The initiator amount of 0.9 wt % was kept constant while varying MA concentration from 5 to 10 wt %. Figure 5 and Table 1 shows that acid number and %

MA increases with the amount of MA in the reaction mixture. Maximum grafting was



Figure 5. FTIR analysis of varying maleic anhydride (MA) concentration (0, 5, 7.5, and 10wt%) with 0.9wt% initiator content kept constant

observed for 7.5 wt% of MA in the reaction mixture and reached steady state due to

limited free radicals on the CAB backbone. This result is supported by the increase in the

Table 2: Acid Number and Maleic Anhydride percentage (% MA) comparison between samples obtained from Process I (DSM micro extruder) and Process II (ZSK-30 large extruder).

Material	Description	Process I (DSM extruder)				Process II (ZSK-30 extruder)			
		Acid Number	StDev	% M A	StDev	Acid Number	StDev	% M A	StDev
CAB-g-MA2	0.9wt% Initiator + 5wt% MA + 94.1wt% CAB, neat	19.7	1.1	0.8	0.2	18.8	1.7	0.8	0.1
CAB-g-MA4	0.9wt% Initiator + 7.5wt% MA + 91.6wt% CAB, neat	31.7	1.5	1.8	0.4	33.2	1.4	1.5	0.1

intensity of the anhydride peak in CAB-g-MA samples. Based upon FTIR, AN, and %

MA results, compositions for CAB-g-MA 2 and CAB-g-MA 4 (Table 1) were chosen for higher quantity scale up.

One of the aims of this research was to develop a commercially and industrially feasible process for the production of CAB-g-MA with predetermined acid number and % MA content. This was achieved by optimizing the reaction conditions of Process II on the basis of Process I while keeping compositions (CAB-g-MA 2 and 4) constant. With such conditions described in experimental part for Process II, we have successfully developed products as shown in Table 2 in which equivalent values of acid number and % MA (considering the overlapping error bars) were observed for Process II as compared to those of Process I.

5. Conclusions

We have successfully synthesized maleated cellulose acetate butyrate (CAB-g-MA) with controlled acid number by a solvent free process in order for it to be used as compatibilizer in cellulose ester based biocomposites. OH group protection could be avoided since the reactivity of the hydroxyl groups on the CAB backbone was low. The effects of initiator and maleic anhydride (MA) concentration on the synthesis of CAB-g-MA were studied by Process I (DSM Micro Extruder – small scale). Acid numbers of the maleated CAB increased with the MA and the initiator concentrations. However, the effect of residence time on the product was negligible. Using optimized reaction conditions and reagent compositions, the grafting reaction was reproduced by Process II in a large-scale fabrication facility using ZSK-30 Twin Screw Extruder – to achieve similar acid numbers and percentage grafting to those of Process I. The effect of CAB-g-MA compatibilizer on adhesion of cellulose fiber based biocomposites will be presented in future publications.

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V. Effect of Compatibilizer on Thermomechanical and Morphological Properties of Hemp Fiber Reinforced Cellulose Ester Biocomposites

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1. Abstract

Biocomposites are emerging as a viable alternative to glass fiber reinforced composites especially in structural and automotive applications. By embedding inexpensive natural cellulosic fibers into biopolymeric matrices, 100% biobased composite materials (biocomposites) can be made. Cellulose esters e.g. cellulose acetate (CA) and cellulose acetate butyrate (CAB) plasticized with 25-30 wt.% plasticizer have been successfully reinforced with chopped hemp fiber using an extrusion–injection molding process to produce a potential alternative to glass fiber/polyolefin composites for automotive applications. The addition of a small amount of suitable compatibilizer (CAB-g-MA) into these systems had been shown to improve the adhesion of the hemp fiber to the biopolymer matrix as well as their thermomechanical properties.

Keywords: composites, biofibers, adhesion, extrusion-injection molding,

thermomechanical properties, morphological properties.

2. Introduction

Cellulose ester is one biobased polymer that has been produced for decades (Eastman Chemical Company). This environmentally benign plastic has outstanding clarity, high surface gloss, toughness and durability, good chemical resistance, ease of processing and molding, and colorability. As a result it is commonly used in such common everyday items such as hair brushes, tooth brushes, sunglasses frames, tool handles, toys, packaging applications, automobile trim, and so forth. The objective of this research is to utilize cellulose ester as a biomatrix and reinforce it with inexpensive natural fibers, with a goal of improving the interfacial adhesion between matrix and fiber; in order to provide a biobased alternative to glass fiber reinforced polypropylene for automotive applications. Previously completed research has shown that cellulose esters (particularly plasticized CA (CAP) and CAB) are much better matrices in terms of mechanical and damping properties compared to non-polar polypropylene matrix in using natural fiber, such as hemp, as a reinforcing material ^{1,2}. The natural polar-polar interactions between these constituents produce good interfacial adhesion and thus better stress transfer from the low modulus matrix to the high modulus natural fibers resulting in high performance biocomposites.

To compete with petroleum based glass filled polypropylene for structural applications, however, the interfacial adhesion between natural fiber and cellulose esters matrix has to be improved further. Grafting a polar group (maleic anhydride) onto polymer matrix, for example maleic anhydride functionalized polypropylene (PP-g-MA), is widely used as one method to improve compatibility in polymer blends, to improve adhesion of glass and carbon fibers, and is used as processing aid for recycling plastic waste ^{3,4,5}. Enhancement of tensile strength and impact strength has been observed after

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adding PP-g-MA into cellulose-polypropylene (PP) composites ^{6,7,8}. Gatenholm et al have proposed that the formation of entanglements at brushlike interfaces in cellulose-PP composites is responsible for the improvement of adhesion between PP-g-MA treated cellulose fibers and PP.

Based on this approach, CAB-g-MA has been produced ⁹ by reactive extrusion as a compatibilizer for cellulose esters based biocomposites and their thermomechanical, and morphological properties have been evaluated.

3. Experimental

3.1. Materials

Powdered cellulose acetate (CA 398-30) free from any plasticizer and additives and plasticized cellulose acetate butyrate (Tenite Butyrate 485E3720016) were supplied by the Eastman Chemical Co., Kingsport, TN. The degree of substitution of the acetyl groups in the CA was approximately 2.45. The supplied Tenite Butyrate (TEB) was composed of about 72% cellulose acetate butyrate (CAB), ~25% bis(2-ethylhexyl) adipate (DOA) plasticizer, and ~7% additives. Triethyl citrate (TEC) plasticizer was obtained from Morflex Inc., Greensboro, North Carolina. Chopped industrial hemp fiber (1/4 inch) was supplied by Hempline, Delaware, Ontario, Canada. CAB-g-MA granules (with acid number of ~33 and ~18) were made following the procedure described in earlier paper ⁹. CAB-g-MA with acid number ~33 and ~18 have been used in this research and are subsequently identified as compatibilizer 1 (C1) and compatibilizer 2 (C2), respectively.

3.2. Biocomposites Processing

A two-step extrusion process was utilized in making the plasticized CA-hemp biocomposites in contrast to a one step extrusion step in making the TEB-hemp biocomposites. All biocomposites produced were of 30 wt% fiber content. Note that CA, TEB, compatibilizer, and hemp were vacuum dried overnight at 80 °C prior to processing. The first step was to produce CA plastic granules from CA powder and 30 wt% TEC plasticizer. In the second step, CA plastic granules with or without compatibilizer were fed into a twin-screw extruder (ZSK-30 Werner Pfleiderer, corotating, intermeshing, with L/D = 30) while feeding the chopped hemp (~ 1/4 inch) in the next to last port of the extruder. The temperature profiles were ~190 °C with a die temperature of ~195 0 C. A 150-rpm screw speed was used with ~ 40% machine torque reading and a resulting extrudate output of about 65-70 grams/minute was obtained. TEB pellets with or without compatibilizer and chopped hemp fibers in the requisite amounts were fed into the extruder under similar conditions of extrusion to produce the biocomposites. The thin strands of composites were granulated and stored for subsequent injection molding. The injection-molding machine used was an 85-ton Cincinnati-Milacron press. The injection molding conditions used were: temperatures on zone 1 to 3 were at 195 °C, die at 60 °C with 40 seconds cooling time, 25 seconds extruder delay, fill pressure was 1500 psi, pack pressure and hold pressure were 1500 and 1200 psi, respectively. All of the physico-mechanical properties were determined through ASTM standards.

3.3. Plastics Fabrication using Micro Compounder

Pre-measured quantities of TEB with CAB or compatibilizer were mixed in small beaker. Similarly, CAP granules (made on the ZSK-30) with CAB or compatibilizer were mixed in a small beaker. The above compounds (about 10 grams per batch) were fed separately into a DSM Micro 15 cc compounder (DSM research, Netherlands) under the following conditions:



Figure 1. Effect of addition C1 (acid number ~33), C2 (acid number ~18), on tensile properties of plasticized cellulose acetate butyrate (Tenite Butyrate, TEB) – hemp biocomposites.

temperatures in zone 1, 2, and 3 were kept between 195 to 205 0 C, screw speed was 100 rpm, and cycle time was 3 minutes. This extruder is equipped with a screw of length 150 mm, L/D of 18, and net capacity of 15 cm³. In order to obtain the desired specimen samples required for various measurements and analysis, the molten plastics samples were transferred after extrusion in a preheated cylinder to the mini injection molder, which is pre-set with desired temperature (mold temperature of 50 0 C), pressure (~100 psi) and cooling.



Figure 2. Effect of addition of C1 (acid number ~33), C2 (acid number ~18), on flexural properties of TEB hemp biocomposites.

3.4. Characterization and analysis



Figure 3. Effect of addition of C1 and C2 on impact properties of TEB hemp biocomposites.



Figure 4. Effect of addition of C1 (acid number ~33), C2 (acid number ~18), on storage moduli of TEB hemp biocomposites.

The tensile and flexural properties of the composite specimen were measured with a United Testing System (SFM-20) testing machine according to ASTM D638 and ASTM D790, respectively. The Notched Izod impact strength was measured with a Testing Machines Inc. 43-02-01 Monitor/Impact machine according to ASTM D256. The storage modulus and tan delta of the composite specimen were measured as function of temperature (from room temperature to 140°C) using a TA instruments 2980 Dynamic Mechanical Analyzer (DMA) with the frequency of 1 Hz at a heating constant rate of 4°C /min (cpm). The heat deflection temperature (HDT) of the samples was determined using the same machine at a heating rate of 2 cpm. HDT is widely used in automotive applications and represents the temperature at which the material deflects by 0.25 mm at an applied force (three point bending arrangement) of 66 psi (ASTM D 648). A modified ASTM D 648 was used for HDT measurement since the DMA could only handle a smaller size of specimen as compared to that of ASTM D 648. Environmental scanning electron microscope (ESEM) micrographs of tensile fractured samples were taken using Phillips Electroscan 2020 (at 20 kV and chamber pressure of 3 Torr) to evaluate the adhesion between hemp fiber and matrix. The fractured specimens were gold sputtered before taking the images.



Figure 5. Comparison between rule of mixtures (ROM), experimental tensile modulus data of TEB – hemp biocomposites with and without compatibilizer: C1 (acid number \sim 33), and modified ROM.

4. Results and Discussion

Interfacial adhesion between hemp fibers and cellulose ester (CE) matrix was investigated in this study by the addition of a small amount compatibilizer (C1 or C2) made by grafting maleic anhydride onto cellulose acetate butyrate (CAB-g-MA)⁹. In optimizing the amount of compatibilizer needed, we have found (Figure 1) that between 5



Figure 6. ESEM micrographs of compatibilized TEB-hemp biocomposites using compatibilizer: C1 (acid number ~33). A = 450µm, 105X, B = 100µm, 490X



Figure 7. ESEM micrographs of compatibilized TEB-hemp biocomposites using compatibilizer: C2 (acid number ~18). A = 450µm, 105X, B = 100µm, 500X and 10 wt% of C1, the latter amount is sufficient to get considerable improvement of adhesion between hemp fibers and TEB matrix.

As can be seen in Figure 1, the addition of 10 wt% of C1 into the TEB-hemp system improved the tensile strength about 20% and tensile modulus about 45%. Similar trends were observed when adding 10 wt% of C2 into the system, i.e. a 25% increase in



Figure 8. ESEM interographs of non-compatibilized TEB-nemp biocomposites. $A = 450 \mu m$, 105X, B = 100 μm , 500X flexural strength (Figure 2). Correspondingly, 20 % increase in storage modulus at 40 ⁶C and 80 ⁶C were also obtained for compatibilized TEB-hemp biocomposites as compared to the non-compatibilized one (Figure 4). There was, however, no improvement in impact properties (Figure 3), glass transition temperature and heat deflection temperature (HDT) of the biocomposites.



Scheme 1. Proposed mechanism of how grafted maleic anhydride (CAB-g-MA) interacts with biofibers (alcoholysis reaction).

A number of models have been developed to predict the mechanical properties of a fiber-reinforced polymer composite. A useful relationship for predicting the mechanical properties of unidirectional composites is the rule of mixtures (ROM). The modified ROM ^{7,10,11} for determining the tensile modulus of a short fiber composite is

Matrix System	Description	Material	OH Content
CAB	Cellulose Acetate Butyrate	CAB 381-20	1.8wt%*
ТЕВ	Plasticized CAB	CAB 381-21	1.8wt%*
		DOA (Dioctyl Adipate)	Owt% ^a
САР	Plasticized Cellulose Acetate	CA 398-30	[*] 3.5wt% ^a
		TEC (Triethyl Citrate)	Plenty

Table 1. OH content of cellulose acetate butyrate (381-20), dioctyl adipate (DOA), cellulose acetate (CA 398-30), and triethyl citrate (TEC).

^a Eastman Chemical Company (www.eastman.com)

shown in equation 1. A comparison between the theoretical modulus value from Rule of Mixtures, modified Rule of Mixtures and experimentally determined values is shown in Figure 5. The Rule of Mixtures estimates the composites stiffness by a weighted mean of the moduli of the two components -- matrix and fiber -- depending upon the volume fractions of the components 12 . This equation is valid for long and parallel aligned fibers. Since short fibers (1/4 inch long) with a random orientation were used in this experiment, a constant $k^{7,10,11}$ is used in the fiber part of the ROM (hence named modified ROM) to compensate for the non-equality of fiber strain that causes the reduction of tensile modulus of the experimental composites as compared to the tensile modulus predicted by the ROM. The k value, representing the reinforcing efficiency dependent on the orientation of the fibers and the stress transfer between the matrix and the fibers, can be calculated from modified ROM as:

$$E_c = kV_f E_f + V_m E_m \tag{1}$$

....

Where: $E_c =$ Modulus of resulting composites

 V_f = Fiber Volume Fraction (ρ of hemp = 1.29 gm/cm³)^a

 $E_f = Modulus of fiber (E_f = 42 GPa)^a$

 $V_m = Matrix$ volume fraction

 $E_m = Modulus of matrix.$

^aValue is taken from earlier paper¹.

In this experiment, k=0.3 is obtained for non compatibilized TEB-hemp biocomposite whereas in compatibilized TEB-hemp biocomposite k=0.42. The increase of reinforcing efficiency suggests an improvement in fiber dispersion resulting in improvement of stiffness of the biocomposites.

Such major improvements in tensile and storage modulus properties are due to the



Dioctyl Adipate (DOA)

Figure 9. Chemical structure of cellulose ester, triethyl citrate (TEC) plasticizer, dioctyl adipate (DOA) plasticizer.

improved dispersion and adhesion between hemp fibers and TEB matrix. As presented in Figures 6 and 7, smaller fiber pull out lengths, more fiber fibrillation and individual fibers covered with TEB matrix, are indications of an improvement in adhesion after adding C1 or C2. This improvement is believed to be due to alcoholysis reaction between grafted maleic anhydride (C=O groups) with OH groups of hemp fibers forming esters as



Figure 10. Effect of addition of C1 and C2 on tensile properties of CAP – hemp biocomposites.

proposed in Scheme 1. In contrast, lower quality adhesion was observed for noncompatibilized TEB-hemp biocomposites such as: longer fiber pull outs and wider gap between hemp fibers and TEB matrix after tensile fracture (Figure 8).

A lower content of OH groups on TEB matrix (Table 1 and Figure 9) makes it easier for grafted maleic anhydride to be reacted with OH groups of fibers without significant competition from OH groups of TEB matrix during reactive extrusion. This nucleophilic substitution leads to ester linkage formation on the fibers resulting in better adhesion between matrix and fibers. In addition, the similar CAB backbone used in the compatibilizer and matrix may give good entanglement necessary to improve interfacial adhesion.

In the plasticized cellulose acetate (CAP)-hemp biocomposites system, after adding compatibilizer there was no significant improvement in either tensile, flexural or impact properties (Figures 10,11,12, respectively). A possible reason for this result is the





existence of available OH groups on the CAP matrix. As depicted from their chemical



Figure 12. Effect of addition of C1 and C2, on impact properties of plasticized cellulose acetate (CAP) – hemp biocomposites.

structure (Figure 9), CA and TEC have plenty of OH groups (Table 1), which can compete with OH groups of fibers in reacting with the grafted maleic anhydride during



Figure 13. Effect of addition of C1 and C2 on storage moduli of CAP – hemp biocomposites at 40 0 C.

reactive extrusion. Hydrogen bonds on the matrix and on the fibers are broken due to heat ¹³ during reactive extrusion making OH groups free to react.

Grafting the compatibilizer (C1) onto the fibers by dissolving C1 into hot acetone followed by immersing the fibers for 15 minutes was utilized to avoid competition among OH groups of CAP matrix and fiber. The resulting biocomposites which utilized the treated hemp fibers were named 'trt-HP'. Gelation of the solution, however, was a problem during the reaction forcing the use of a very dilute solution (1wt%) compared to the optimum concentration (~7wt% of solution). Therefore, low C1 grafting and low distribution of C1 on the fiber might be responsible for the zero change of mechanical properties observed when using the treated fiber (Figures 10, 11, 12). In the future, the gelation problem can be solved by using higher miscible solvents.

The storage moduli of CAP biocomposites at 40 ^oC do not improve after addition of the compatibilizer (Figure 13). This result retaliates with the modulus data obtained



Figure 14. Effect of addition of different compatibilizer: C1 (acid number \sim 33), C2 (acid number \sim 18), on storage moduli of plasticized cellulose acetate (CAP) – hemp biocomposites at 100 $^{\circ}$ C.

from the flexural test. There was significant improvement, however, in storage modulus



Figure 15. Effect of addition of C1 and C2 on glass transition temperature (peak of tan delta curve) of plasticized cellulose acetate (CAP) – hemp biocomposites.

especially at high temperature (100 °C). An improvement of storage modulus of about





260% was obtained at 100 6 C (Fig.14). This fact is probably due to inclusion of more thermally stable compatibilizer into the CAP-hemp biocomposites system. An enhancement of ~20 6 C in glass transition temperature (from tan delta peak results – Figure 15) and heat deflection temperature (HDT – Figure 16) was observed to support the fact that inclusion of more thermally stable compatibilizer into the system led to reduction in polymer segmental motion inside CAP backbone.

A thorough investigation to find out whether CAB-g-MA functioned as filler or as compatibilizer in TEB or CAP based biocomposites system was conducted using DMA analysis. As described in experimental section, compatibilizer (C1) was not only added into both systems (TEB and CAP) but also neat CAB was included to investigate the real cause of improvement in each case (addition of 10wt% of CAB or C1). Figure 17 showed that there was no improvement in storage modulus after addition of either compatibilizer



or neat CAB into TEB from room temperature to about 100 °C. This proved that CAB-g-

Figure 17. Effect on storage modulus: A = TEB, B = A + 10wt% neat CAB, C = A + 10wt% C1.

MA acted as compatibilizer enhancing interfacial adhesion between TEB matrix and hemp fiber as well as improving the hemp fiber dispersion and fibrillation as suggested in the earlier section. The CAP based system, in contrast, showed an increase of storage modulus at high temperature (starting from about 70-80^oC: CAP's glass

transition temperature, as depicted in tan delta curves – Figure 19) after addition of both CAB and C1 (Figure 18). This supported the assumption about inclusion of more thermally stable materials (CAB based) into CAP based systems (for both plastic and biocomposites systems).

5. Conclusions

Interfacial adhesion between hemp fibers and cellulose ester matrices can be enhanced by the addition of small amount of a suitable compatibilizer. By the addition of ~10 wt% compatibilizer (CAB-g-MA) into plasticized cellulose acetate butyrate (TEB)-Hemp system we found an improvement in tensile strength of about 20%, a 45% enhancement in tensile modulus, and a 25% increase in flexural strength. A 20% increase



Figure 18. Effect of inclusion of CAB or C1 into CAP system on storage modulus: A = neat CAP, B = A + 10wt% neat CAB. C = A + 10wt% C1.

in storage modulus at 40 °C 80 and was also obtained for compatibilized TEB-hemp biocomposites compared as to noncompatibilized ones. Comparison with ROM and DMA analysis showed that these improvements were predominantly due to the effectiveness of the

compatibilizer in improving

the fiber dispersion and fibrillation well as as increasing the interfacial TEB adhesion between matrix and hemp fibers. Enhancement in CAP based biocomposites, in contrast, has been shown to be due to insertion of the more thermally stable CAB-g-MA



Figure 19. Effect of CAB or C1 into CAP system on Tg (peak of tan delta curve): A = neat CAP, B = A + 10wt% neat CAB, C = A + 10wt% C1.

into the CAP based system. This filler improved storage modulus of CAP biocomposites

by about 260 % at 100 $^{\circ}$ C. A ~20 $^{\circ}$ C increase in glass transition temperature and heat deflection temperature was observed to support the 'inclusion effect' statement.

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CONCLUSION and FUTURE WORK

Sustainability, industrial ecology, and green chemistry are challenging today's society. Rapid growth in technology can result in over dependence on petroleum feedstocks, increased energy consumption and increased carbon dioxide emission. Issues such as global warming, shortage of petroleum feedstock, and limited landfill space are becoming more important considerations and causing scientists and engineers to consider the increased use of environmentally benign materials for many applications. Renewable resources made primarily from carbon dioxide, can be a potential solution to achieve equilibrium between consumption and emission of carbon dioxide. Recyclability and biodegradability are common features of these renewable resources and their products.

Many plants therefore are grown to collect their fibrous materials such as hemp, jute, kenaf (from stem), henequen, pineapple (from leaf), and cotton (from seed). On the other hand, agriculture based plants, which also lignocellulosics, are mostly getting wasted and solely used as source of energy by burning them. The cellulose fibrils in many lignocellulosics are potential biobased reinforcements. Extraction of these nanofibrils can be achieved by chemical/mechanical processes. These bio-sourced nano reinforcements would be compatible with a biomatrix (matrix derived from renewable resources such as cellulose esters, poly(hydroxy alkanoates)) and thus will result in a biobased composite with superior properties. The modification of the nanofibrils either by adding or subtracting functional group/s can tune the interfacial properties as desired.

For example, hemp fibers interact with a cellulose ester matrix through hydrogen bonding. Stronger interaction can improve the resulting composite properties. Formation of covalent bonds through ester linkages between maleic anhydride functionalized

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cellulose acetate butyrate (CAB-g-MA) and hemp fibers was accomplished to improve adhesion and fiber distribution resulting in improvement of thermomechanical and morphological properties. [Refer to: A. Wibowo, A. K. Mohanty, M. Misra, L. T. Drzal, "Effect of Compatibilizer on the Thermomechanical and Morphological Properties of Hemp Fiber Reinforced Cellulose Ester Biocomposites", *Ind. Eng. Chem. Res.* (to be published)]. When using plasticized cellulose acetate (30wt% plasticizer content) as the matrix in the biocomposites formulation, the addition of CAB-g-MA produces a matrix with better thermal properties than the CAP matrix. Advantage of the reaction of hydroxyl groups on the biofober surface with the carbonyl groups of CAB-g-MA can be gained by increasing the surface area of the hemp fibers (by for example doing alkali treatment) such that more OH groups are exposed on the surface for easier reaction.

In attempt to replace/substitute petroleum based glass fiber reinforced polypropylene composites by natural fiber reinforced cellulose ester biocomposites, several issues still need to be addressed including improvement in impact strength, reduction of moisture absorption and better fiber distribution when using sheet molding compound (SMC) in fabricating the biocomposites. Impact strength can be improved by addition of rubberized materials, which induce phase separation, which leads to improvement in impact fracture. Inclusion of leaf fibers in addition to hemp (bast) fibers can improve the impact strength as well. Moisture absorption can be reduced by blocking most of the functional groups that can form hydrogen bonds with water. Such protection can be done by, for example silane grafting or blending with hydrophobic polymer, which is miscible or partially miscible with cellulose ester. Finally better fiber dispersion for any process with lacking of applied shear force can be achieved by optimizing the

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fiber length so as to have minimum fiber entanglement with optimum fiber 'aspect ratio'. Another crucial parameter is to alter the fiber surface tension to be higher than the surface tension of the matrix to get good wetting by addition of compatibilizer or by suitable surface treatment.

APPENDIX 1



Figure 5. Flexural properties of powder processing (Process I) and extruded followed by injection molding (Process II): A = CA Plastics (CAP) of Process I, B = CA Plastic Biocomposites (30wt% hemp) of Process I, C = CA Plastic of Process II, D = CA Plastic Biocomposites (30wt% hemp) of Process II.

APPENDIX 2

In this project, we utilized cellulose acetate (CA) as one of the matrix in developing biocomposites for future automotive parts. CA needs to be plasticized in order to increase its flowing capability due to its thermal decomposition temperature is close to its melting temperature. Plasticizer selection was conducted using equation 1 (Introduction section page 22) to get similar value of solubility parameter for a miscible blend. Hildebrand solubility parameters (δ) of several plasticizer and CA with DS of 3.0 and 2.5 were calculated based upon the knowledge of their chemical structures (Barton, Allan F. M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters, Boca Rotan, CRC Press, 1991) using the following equation:

$$\delta = \sqrt{\frac{\sum U}{\sum V}}$$

Where δ = Hildebrand solubility parameter (MPa^{0.5})

U = group contribution to the molar vaporization energy (J/mol)

V = group contribution to the molar volume at 25 $^{\circ}$ C (cc/mol)

Table 1 shows that CA (DS = 3.0 and 2.5), Triethyl Citrate (TEC) plasticizer, Diethyl

Material	δ (MPa ^{0.5})	δ ((cal/cc) ^{0.5})
Cellulose acetate DS = 3.0	22.8	11.1
Cellulose acetate DS = 2.5	24.0	11.7
Triethyl citrate	22.5	11.0
Glycerol	37.0	18.1
Diethyl phthalate	21.6	10.5

Table 1. Calculated Hildebrand Solubility values close among one another.

Thus, TEC can replace DEP in CA bioplastic formulation for more environmentally benign

Phthalate (DEP) plasticizer have δ

plasticizer. Detailed discussion on the effect of the TEC plasticizer and process engineering in developing CA bioplastic suitable for biocomposite application is

Parameter (δ) based upon the chemical structure

described on part I of this thesis.

