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Development and Characterization of Renewable Resource-based Structural Composite Materials

A Thesis submitted in partial satisfaction of the requirements
for the degree Master of Science

in

Structural Engineering

by

Andrea Gillian Cutter

Committee in charge:

Professor Vistasp M. Karbhari, Chair
Professor Francesco Lanza di Scalea
Professor Yu Qiao

2008

The Thesis of Andrea Gillian Cutter is approved and it is acceptable in quality and form for publication on microfilm:

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Chair

University of California, San Diego

2008

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LIST OF ABBREVIATIONS

AN	acrylonitrile
AFO	animal feeding operations
ASTM	American society for testing and materials
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CNSL	cashew nut shell liquid
CO_2	carbon dioxide
DMTA	dynamic mechanical thermal analysis
DP	degree of polymerization
DS	degree of substitution
DSC	differential scanning calorimetry
ESO	epoxidized soybean oil
F/M	fiber/matrix
FRP	fiber reinforced polymer
GL	gage length
GFRP	glass fiber reinforced polymer
HDPE	high density polyethylene
HT	Halpin-Tsai
IM	injection molded
L/D	cell aspect ratio (length to diameter)
LDI	lysine-based diisocyanate

LDPE	low density polyethylene
LCA	life cycle assessment
MA	maleic anhydride
MAPP	maleic anhydride grafted polypropylene
MEK	methyl ethyl ketone
MMA	methyl methacrylate
MROM	modified rule of mixtures
MW	molecular weight number
NFRP	natural fiber reinforced polymer
OH	hydroxyl
PALF	pineapple leaf fiber
PBS	polybutylene succinates
PCL	polycaprolactone
PE	polyethylene
PET	polyethylene terephthalate
PHA	polyhydroxyalkanoates
PHB	polyhydroxybutyrate
PHBV	polyhydroxybutyrate-valerate
PLA	polylactic acid
PP	polypropylene
PS	polystyrene
PVA	polyvinyl alcohol
RH	relative humidity

ROM	rule of mixtures
RTM	resin transfer molding
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
THC	tetrahydrocannabinol
UPE	unsaturated polyester
USDA	United States department of agriculture
UTS	ultimate tensile strength
UV	ultraviolet
VOC	volatile organic compound

LIST OF SYMBOLS

A_c	cross-sectional area of composite
A_f	cross-sectional area of fiber
A_m	cross-sectional area of matrix
α	twist angle of fibers in yarn
E	elastic modulus
E_α	modulus of twisted yarn
E_b	elastic bending modulus
E_c	elastic modulus of composite
E_f	elastic modulus of fiber
E_m	elastic modulus of matrix
E_o	modulus of straight yarn
E_T	transverse composite modulus
E'	storage modulus
E''	loss modulus
f_α	strength of twisted yarn
f_o	strength of straight yarn
M_w	average molecular weight number
P_c	load carried by composite
P_f	load carried by fiber
P_m	load carried by matrix
ρ_c	density of composite
ρ_{ce}	theoretical density of composite

ρ_{ct}	experimental density of composite
ρ_f	density of fiber
ρ_m	density of matrix
ε_c	strain in composite
ε_f	strain in fiber
ε_m	strain in matrix
SCF	stress concentration factor for Halpin-Tsai model
σ	tensile strength
σ_c	tensile strength of composite
σ_f	tensile strength of fiber
σ_m	tensile strength of matrix
σ_{mu}	ultimate tensile strength of matrix
σ_{Tu}	ultimate transverse tensile strength of composite
$\tan \delta$	tangent delta (loss factor)
T_g	glass transition temperature
v_c	volume of composite
v_{ce}	experimental volume of composite
v_f	volume of fiber
v_m	volume of matrix
v_v	volume of void
V_f	volume fraction of fiber
V_{fe}	experimental volume fraction of fiber

V_m	volume fraction of matrix
V_{me}	experimental volume fraction of matrix
V_v	volume fraction of void
w_c	weight of composite
w_{ef}	weight of end fibers
w_f	total weight of fiber
w_{f1}	weight of fibers in layer one
w_{f2}	weight of fibers in layer two
w_m	total weight of polymer matrix
w_{m1}	weight of matrix in layer one
w_{m2}	weight of matrix in layer two
W_f	weight fraction of fiber
W_m	weight fraction of matrix
δ	solubility parameter

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ABSTRACT OF THE THESIS

Development and Characterization of Renewable Resource-based Structural Composite Materials

by

Andrea Gillian Cutter

Master of Science in Structural Engineering

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Professor Vistasp M. Karbhari, Chair

Current building materials and practices in the construction industry cause the depletion of natural resources and simultaneously result in large amounts of waste material and green house gas emissions. In recent years, concerns over such economic and environmental problems have initiated research efforts into the development of materials derived from quickly renewable resources, such as biocomposites. Most of the research to date in the field of biocomposites has, however, been directed at applications

involving non-structural elements. This is largely attributed to previous research efforts showing that these materials do not possess the properties necessary to make them useful for structural applications.

Through the development and characterization of a novel biocomposite system, this project aims to overcome some of the challenges currently in place for biocomposite application. Unidirectional-aligned hemp fiber reinforced cellulose polymer composites were manufactured for this study using selected processing procedures to allow for efficient fiber reinforcement and an increase in overall composite performance. For composites with a fiber volume fraction of 0.51, tensile and flexural strengths of 224 and 133 MPa and elastic tensile and bending moduli of 25 and 22 GPa, respectively, were achieved. The experimental results of this study confirm the potential for biocomposites to be used as secondary structural elements; however, these properties were below the predicted values for the biocomposite system using the rule-of-mixtures and Halpin-Tsai methods. This discrepancy was attributed to high void content and poor adhesion between the fiber and matrix for both of which potential solutions were identified.

1. INTRODUCTION TO RESEARCH

1.1 Background and Motivation

In the built environment, there is continual interest and demand for new materials that are stronger, stiffer, and lighter-weight than their predecessors. The scientific and industrial path of fiber reinforced polymer (FRP) composites was successful primarily because these materials were able to offer higher structural efficiency and strength to weight ratios over tradition materials such as metals, plastics, and wood. These technologies offer exceptional performance; however, in recent years there have been growing concerns regarding the depletion, and simultaneously increasing costs, of petroleum resources which serve as feed-stocks for these polymer matrix materials. Additionally, there has been increased awareness regarding the environmental impact of synthetic materials during their manufacture, use, and end-life. Scientists have been faced with the difficult challenge of lowering the human impact on their surroundings while maintaining or even bettering the quality of life. The potential environmental and economic benefits of using natural renewable resource-based materials have, therefore, led to increased interest in the development of novel biocomposite materials.

Biocomposites are broadly defined as materials that are either partially or totally derived from bio-based or biodegradable materials. Over the span of civilization, man has developed technology that utilizes natural resources as structural materials. One example of this is the progression from early civilization’s use of grasses and straw in mud bricks, to straw bale housing, to fiber reinforcements in polymer matrix composites. However, the tailored use of natural fiber reinforcements in biocomposites has been relatively limited until the last several decades.

The use of natural fibers as reinforcement in bio-based resin not only increases the mechanical properties over those of neat resin, but can also reduce the cost of the resulting product. Over the course of the last two decades, the biocomposites industry has experienced continual growth as a result of technological advancements and increased applications for these materials. The production of chemicals and materials from bio-based resources is expected to continually increase from approximately 12% in 2010 to 25% in 2030 [1]. Currently, biocomposites have found application in the transportation, packaging, building, biomedical, and consumer goods industries. Most of the technology to date in the field of biocomposites has focused on the use of short, randomly aligned fiber reinforcements. Additionally, due to performance requirements, the polymer matrix of these composites is often synthetic or petroleum derived. To truly optimize the economic and environmental benefits of biocomposite materials the development of aligned natural fiber-reinforced biopolymers with good performance characteristics is needed.

There are several key factors that serve as motivation for the further development of biocomposite materials. Firstly, biocomposite materials offer high strength and stiffness at lighter weights than most traditional materials such as metals, glass fiber reinforced polymer (GFRP) composites, and wood products. The seemingly endless supply of agricultural resources to serve as feedstock for biocomposite materials also allows for lower costs and makes them less subject to economic fluctuations. From an environmental and sustainability standpoint, bio-based composites from renewable resources are superior to traditional FRP composites as they do not contribute to the depletion of the world's natural resources, require less energy and chemicals to produce [2-5], emit less greenhouse gasses and toxins during their production, use, and disposal [2,3], and have the potential to be biodegradable, recyclable or used for energy harvesting upon incineration [3,5].

1.2 Goals of the Research

In the past, products used in the building industry have typically been made from materials such as timber, metals, concrete, masonry and plastics. Although these materials have good performance characteristics, they are often very inefficient. Additionally their use contributes to the accumulation of waste that is rapidly filling the world's landfill space. Biocomposites have been used as an alternative to traditional building materials in applications that require minimal load bearing capabilities, however, the widespread application of these materials has been limited by the relatively immature state of the material development and lack of knowledge regarding their long-term durability.

This project builds upon the previous work done by researchers in the area of natural fiber reinforced biocomposites. The project objectives were to develop a novel biocomposite system that is derived entirely from renewable resources and has adequate performance to be used in secondary load bearing applications thereby offering potential implementation in sustainable building practices. Various composite manufacturing techniques were investigated with the aim of developing a manufacturing process that would allow for high performance characteristics and the most efficient use of the material constituents. Particular focus was put on fabricating composites with high fiber volume fractions and good fiber alignment as these characteristics were considered paramount to achieve the best composite performance. Through experimental testing, the performance of these composites under various loading conditions was evaluated to determine their potential as structural materials. Additionally, this study identified key process variables and material parameters that negatively impact the performance characteristics of biocomposites and enabled suggestions to be made on how to overcome the current factors that are limiting biocomposite performance and implementation.

1.3 Scope of Project

Various combinations of natural fiber reinforcements and bio-based polymers were examined for their potential as composite constituents. After a review of the literature (Chapter 2), two forms of hemp fiber reinforcement and two plasticized cellulose-based polymers were chosen to be used as biocomposite constituents. The materials used in this study were strategically chosen based on their environmental advantages, anticipated mechanical performance, affordable costs, availability, and their anticipated compatibility as composite constituents. The mechanical and processing characteristics of the hemp fibers and cellulose polymers were then determined through experimental testing (Chapter 3) and their optimal processing conditions were used as a basis for the development of a robust composite processing window.

The determination of an optimized manufacturing procedure for the biocomposite system was achieved through a process of parameter identification and process characterization (Chapter 4). The effect of natural fiber reinforcements on the mechanical performance of biocomposites was maximized through unidirectional alignment of the fibers. Controlled alignment was achieved through the use of continuous yarn structures and a custom built fiber winding machine. Additionally, several application methods for the thermoplastic polymer matrix were investigated including powder impregnation, thin film stacking and solution impregnation. The solution impregnation process yielded composites with the best combination of high fiber volume fraction and fiber wet-out. The matrix impregnated yarns were then hot pressed using the previously determined processing window to optimize polymer melt flow and composite consolidation. The composite processing scheme determined to result in composites with the highest fiber volume fractions, most controlled fiber alignment and best combination of physical and mechanical properties was chosen as the standard processing scheme for the remaining portion of the study.

Four composite systems incorporating the hemp fibers and cellulose polymers were manufactured under the defined processing scheme (Chapter 4). The performance of the four composite systems under tension, flexure, impact and thermal testing was determined though experimental testing (Chapter 5). An optimized composite system was determined based on the analysis of these test results. On the basis of a comparison of performance characteristics with traditional wood and GFRP composites used in the building industry as well as other published results for natural fiber reinforced composite systems, the composites manufactured in this study were seen to be competitive, particularly on the basis of strength-to-weight.

Additionally, key parameters that should be controlled during composite manufacture for the development of even high performance biocomposites including, high fiber content, low void content, good fiber alignment and fiber wet-out, and good fiber/matrix adhesion were identified. Suggestions for further research regarding the improvement of the currently developed hemp fiber reinforced cellulose polymer composite system are presented (Chapter 6). Further testing and characterization, particularly relating to environmental and moisture sensitivity and long term behavior of these composites systems, are identified as needed research efforts before large scale adoption of these materials as structural components for the building industry can be expected.

1.4 <u>References</u>

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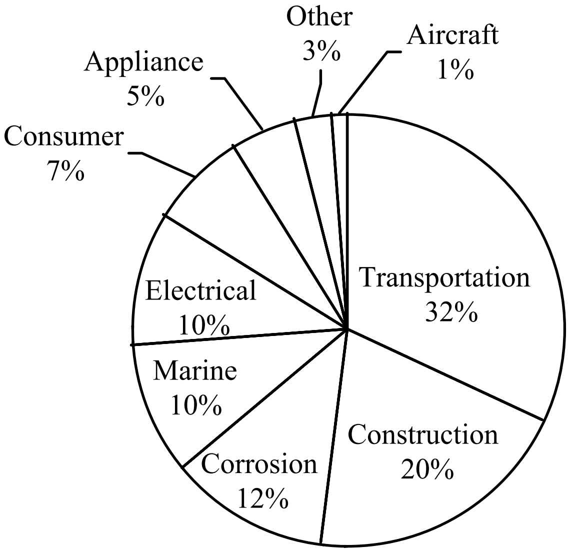
2. LITERATURE REVIEW

2.1 Introduction to Biocomposites

The fiber-reinforced composites market is a multi-billion dollar business with applications in the automotive, construction, marine, electronics, sporting goods, appliance, aerospace, and consumer product industries. These materials are attractive because of their unique ability to combine the properties of various materials to produce a high-performance, easily tailored and efficient system that is not found in nature. As a result the market for composite materials is fast growing and lucrative. The establishment of the fiber reinforced polymer (FRP) composites industry dates back to the early 1900s when cellulose fibers were first combined with phenolic resins and later reached commodity status during the 1940s with the development of glass-fiber reinforced unsaturated polyester [1]. Since then, the FRP industry has seen a steady increase with glass-fibers being the dominant reinforcing material in use [1]. A breakdown of the major industries in the glass fiber reinforced polymer (GFRP) market is shown in Figure 2.1. Not surprisingly, the demand for composite materials continues to grow as new applications are found.



GFRP shipments estimated at 4 billion lbs. for 2004

Figure 2.1: Breakdown of GFRP applications by industry (Adapted from [2])

In recent years, there have been growing economic concerns regarding the depletion of petroleum resources as well as an increased awareness of the environmental effects of producing, using and disposing of synthetic materials. Additionally, in the past decade several government based initiatives such as the Energy Policy Act of 2005 (U.S. Public Law 109-058), Biomass Research and Development Act of 2000 (U.S. Public Law 106-224), the Farm Security and Rural Investment Act of 2002 (U.S. Public Law 107-17), and presidential executive orders 13134 (Developing and Promoting Biobased Products and Bioenergy, August 12,1999) and 13101 (Greening the Government Through Waste Prevention, Recycling, and Federal Acquisition, September 14, 1998) have offered economic incentive to consider biobased alternatives to petroleum based materials [1].

Economic and environmental concerns coupled with these government initiatives have encouraged research into more environmentally benign alternatives to common glass and petroleum-derived composites. Much of this research has focused on the development of biocomposites and other natural renewable materials.

Biocomposites can be broadly defined as a composite material that makes use of one or more environmentally friendly materials such as natural fiber reinforcements or biopolymers. Biocomposites have varying levels of environmental friendliness based on their constituent materials and their ability to biodegrade. A schematic of these categories of composites under the current definition of biocomposites is shown in Figure 2.2. Composites that incorporate both natural fiber reinforcements and biopolymers are termed ‘green’ composites [1]. Depending on the type of polymer used, these composites can also be entirely biodegradable, suggesting the highest level of economic and environmental benefits.

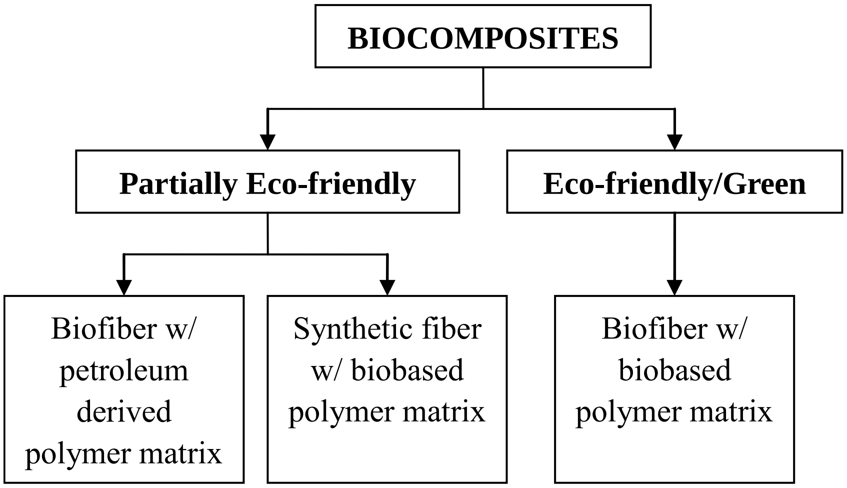


Figure 2.2: Classification of biocomposites based on material constituents

For the class of biocomposite materials to be successful and long-lasting it is important that their development follow a promising economical route. Glass fibers and petroleum-derived polymers both have well developed manufacturing processes which ensure that the resulting GFRPs are produced at relatively low cost. Although most biopolymers currently cost more than traditional petroleum-based polymers, it is expected that increased demand and further technological developments will reduce the cost of these materials. Furthermore, the low cost of natural fiber reinforcements can help to bring down the overall composite costs. Several researchers have shown that the energy consumption required to produce a natural fiber mat (9.7 MJ/kg), including cultivation, harvesting, and fiber digestion, is less than a quarter of the energy required to produce a comparable glass fiber mat (54.8 MJ/kg) [3]. Furthermore, the density of most plant fibers is also around 40 percent lower than that of glass fibers. This allows for additional cost savings where product weight is of concern such as in transportation (automotive) applications. From the above reasons, it is clear that biocomposites offer many potential advantages over traditional synthetic composites.

Biocomposites with high mechanical properties are the target for many research efforts; however, the immature state of biopolymers, variability in fiber properties, and difficulties in composite processing have limited their performance preventing their ability to compete with traditional synthetic composite materials. Nevertheless, the clear advantage of biocomposites from an environmental standpoint has encouraged further efforts to develop new materials as well as characterize and improve the properties of currently developed biocomposite materials. It is anticipated that a high-performance, environmentally friendly and economically stable biocomposites industry is possible with such continued advancements.

2.2 Natural Fiber Reinforcements

Cellulosic fibers can be used to reinforce both thermoplastic and thermosetting resins from petroleum or natural feed stocks. As in traditional composites, natural fibers in bio-composites serve as the reinforcing phase thereby increasing the performance of the resulting composite material. Mechanical properties such as strength and stiffness are typically increased, while weight is often decreased, allowing for more efficient systems. In traditional structural composite materials, fibers such as glass, carbon, and aramid are the most common reinforcement. These fibers are chosen largely because of their high mechanical properties and their good resistance against environmental degradation. Although these fibers offer many opportunities as reinforcements in composites, growing environmental and economic concerns regarding the manufacture, use, and disposal of these materials have encouraged research in the development of composites utilizing natural fibrous reinforcement materials such as those derived from renewable agricultural crops and other fast growing plants.

2.2.1 Advantages of Natural Fibers

The majority of natural fibers that have been investigated for composite reinforcement are lignocellulosic materials, or those derived from plants. The strengths of plant fibers have long been recognized and utilized. Roping, textiles, tools, and even housing materials are just some of the past and present applications that take advantage of the unique mechanical properties of plant fibers. In addition to their good mechanical properties, there are several other advantageous qualities that plant fibers have over traditional composite fiber reinforcements. These fibers are typically derived from fast-growing renewable plants and therefore are not only significantly cheaper and much less subject to economic fluctuations, but also reduce environmental concerns associated with the depletion of natural resources. Additionally, the density of cellulose based fibers can be as much as half that of traditional reinforcing fibers such as those made from glass [4]. The resulting natural fiber reinforced polymer (NFRP) composites can therefore be lighter than traditional composites allowing for more efficient systems and reduced costs associated with material transportation. Natural fibers are also non-toxic materials making them occupationally safer than glass fibers which produce glass particles during processing that can cause allergic reaction, skin irritation, or irritation to the respiratory system if inhaled. Plant fibers are also known to be less abrasive than traditional fibers allowing for less damage to the equipment required to process them.

Composites made with natural fibers are alleged to have considerably improved life cycle assessments (LCA) as they require less energy and have a lower carbon footprint than those made with glass fibers [5-7]. This is in part due to the fact that only the amount of carbon dioxide that a plant assimilates during its growth phase is released during its degradation or combustion, thereby making plant fibers a carbon neutral material [5]. Additionally, the energy consumption to produce a natural fiber mat (9.55 MJ/kg), including cultivation, harvesting, and fiber digestion, is less than a quarter of the energy required to produce a comparable glass fiber mat (54.7 MJ/kg) [5]. A study by Patel and co-workers [6] performed LCAs for several current biocomposite systems and determined that the potential environmental benefits of biocomposites are significant and can be expected to be a valuable contributor toward a more environmentally friendly and sustainable world. Additionally, a study by Joshi et al. [5] defined four general drivers for the superior environmental performance of natural fiber reinforced composites as compared to glass fiber reinforced composites for automotive applications; (i) the production of natural fibers has lower environmental impact, (ii) substitution of base polymers by higher volume of natural fibers, (iii) lower energy use during lifecycle as a result of reduced material weight, (iv) biodegradation or energy and carbon credits from end life incineration. This study determined that in most cases natural fiber composites are likely to be environmentally superior to glass fiber composites. Table 2.1 highlights some of the main beneficial characteristics of natural fibers as compared to glass fibers.

Table 2.1: Comparison between natural and glass fibers (adapted from [8])

	Natural Fibers	**Glass Fibers**
Density	Low	~Twice that of natural fibers
Cost	Low	Low to high
Distribution	Wide	Wide
Energy Consumption	Low	High
Renewable	Yes	No
Recyclable	Yes	No
CO_2 Neutral	Yes	No
Abrasion to Machines	No	Yes
Health risk when	No	Yes
Disposal	Biodegradable, energy harvesting	Incineration, land-filled

2.2.2 Disadvantages of Natural Fibers

The transition from conventional fibers like glass, carbon, and aramid to plant based fibers for composite reinforcement faces some difficulties. Firstly, the processing and manufacture of natural fibers is different from that of traditional fiber reinforced polymers (FRP). This can act as an obstacle for widespread implementation of natural fiber reinforced composite technology as it may require companies to develop new machines and methods for manufacture of broad goods and fabrics. Additionally, conventional fibers can be repeatedly produced with a defined range of properties. In contrast, the properties of natural fibers are subject to a higher level of variability. Some factors affecting fiber properties, such as chemical composition and physical structure, are inherent to the fiber. Other factors like growing conditions, harvesting and processing techniques, and even storage are more variable and therefore can change the properties of fibers from one batch to the next. Perhaps the most serious problem with using natural fibers in composites is their moisture sensitivity. Their hydrophilic nature causes the fibers to take on water causing degradation and swelling potentially leading to fiber/matrix interface problems. For biocomposite technologies to be successful, it is necessary that weakness be thoroughly researched and addressed in terms of efficient resolution.

2.2.3 Properties of Natural Fibers

2.2.3.1 Chemical and Molecular Structure

Plant fibers are lignocellulosic in nature. The major constituents are cellulose, hemicellulose, and lignin. The amount and location of these constituents depends on a fiber's species and age and are important contributors to the overall fiber properties. Cellulose is the essential component of plant fibers. Cellulose is a semi-crystalline polymer containing many hydroxyl functional groups along its long chain macromolecular structure. These hydroxyl groups are capable of forming hydrogen bonds with other hydroxyl groups along the chain as well as with other cellulose chains in fibers [9]. The amorphous and crystalline regions of cellulose are similar in structure; however, the amorphous regions have a lower frequency of interchain hydrogen bonding making then more open to water molecules. In these regions the hydroxyl groups will hydrogen bond with water vapor in the air making the cellulose naturally hydrophilic. The chemical structure of cellulose is the same for all natural fibers; however, the degree of polymerization (DP) or length of the polymer chains of the cellulose varies. The DP of cellulose has a significant affect on the mechanical properties of a fiber as it is directly related to the molecular weight (MW) [4]. When the structure of cellulose has a high DP and MW, the fiber will likely have greater strength properties. In general, bast fibers, such as flax, hemp, jute, ramie and kenaf, have high cellulose contents and commonly show the highest DP among natural fibers, explaining their good use in composite materials [10].

Hemicellulose is a fully amorphous branched polymer with a selection of sugar molecules as monomeric units. Unlike cellulose, the constituents of hemicellulose differ between plant species and crops. The open structure of hemicellulose, containing many –OH and acetyl groups, allows it to absorb significant amounts of water. In addition, the DP of hemicellulose is much lower than that of cellulose making it a weaker polymer [11]. Lignin is a complex cross-linked polymer with a chemical network that is still not completely understood. It functions as a structural support material in plants by filling the spaces between the cellulose and hemicellulose regions cementing them together. Mechanical properties of lignin are lower than that of cellulose [12]. Additionally, the aromatic nature of lignin, high carbon and low hydrogen content, makes it hydrophobic [4,11].

2.2.3.2 Physical Structure

Plant fibers are characterized by a cellular structure consisting of cellulose regions connected via lignin and hemi-cellulose fragments. A single cell consists of a series of cell walls, typically with a hollow center, giving the overall fiber a porous structure (Figure 2.3) [12]. The microfibrillar angle of a plant fiber is an important characteristic and can be defined as the deviation in alignment of the microfibrils to the parallel axis of the fiber. The cell aspect ratio of a fiber (L/D) is defined as the relationship between the fiber cells length and diameter, with higher values therefore representing long thin fibers. In addition to the chemical composition of a fiber, the structural parameters including microfibrillar angle and cell aspect ratio (L/D) have been suggested to be the most significant properties affecting the values of fiber strength, stiffness and elongation. It has also been shown experimentally that in general the smaller the fiber angle, i.e., the more parallel the microfibrils are to the fiber axis, the higher the mechanical properties of the fiber [10]. Theoretical models predicting fiber properties, such as modulus, based on these parameters have been demonstrated [13].

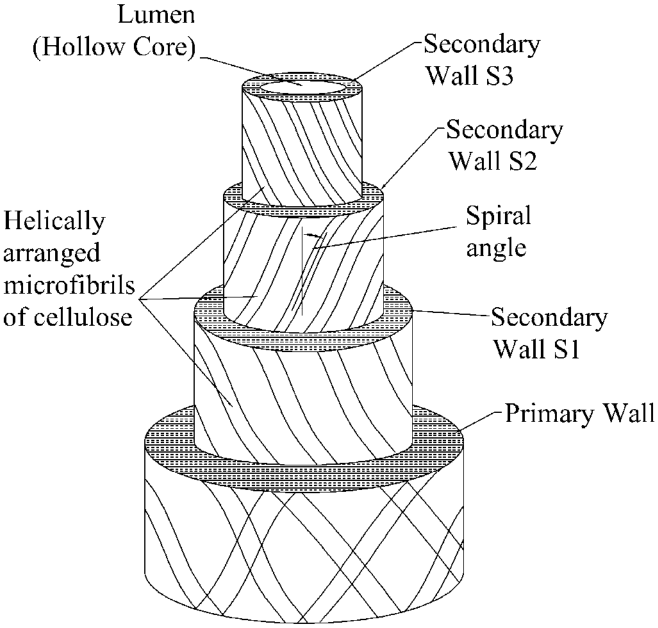


Figure 2.3: Structure of an elementary plant fiber cell showing spiral angle of the microfibrils, where the secondary cell wall, S2, makes up about 80% of total cell thickness (adapted from [14])

2.2.3.3 Durability/Environmental Sensitivities

Plant fibers have varying sensitivities to thermal, environmental and chemical exposures. Research has suggested cellulosic fibers exhibit a loss in properties when subjected to extended thermal exposure, particularly at temperatures above 200°C [15,16]. Plant fibers have varying levels of resistance to environmental conditions such as moisture, UV radiation, and attacks by microorganisms and bacteria. Environmental sensitivities are inherent to many natural fibers and aid in their ability to degrade upon disposal; however, these sensitivities must be considered when using materials incorporating natural fibers in applications that could require periods of environmental exposure. Some natural fibers are also known to exhibit a reduction in mechanical properties when exposed to chemical mediums such as alkaline or acids [14]. Although brief exposure to these mediums has been strategically used by researchers to enhance the properties of natural fibers [17], in general, uncontrolled or extended exposure can be expected to greatly reduce the properties of natural fibers.

2.2.3.4 Engineering Properties of Natural Fibers

The mechanical properties of plant fibers are very good and in some cases are comparable to those of glass fibers. Although the tensile strengths of these fibers are below than that of glass fibers, the lower density of the natural fibers give them comparable values of specific strength. Depending on the species of plant fibers, the fiber elongation to break can be above or below the range for traditional glass fibers, allowing for easily tailored composite properties through selection of natural fibers. Additionally, the hollow tubular structure of natural fibers provides better insulation against heat (low thermal conductivity properties of between 0.29-0.32 /m-K) and noise [18,19]. As explained in the previous sections, the mechanical properties of natural fibers are highly dependent on the chemical and physical characteristics of the fibers. Several experimental research efforts have demonstrated these trends. Research by

Mukherjee et al. [20], on several bast, leaf, and fruit fibers determined that high ultimate tensile strength (UTS) and low elongation are typically correlated with high cellulose, low fiber angles, and high cell aspect ratios (L/D) in fibers. Similarly, low UTS and high elongation values were found in fibers with lower cellulose content, high fiber angles, and low L/D values [20]. It is important to note, however, that the correlation between strength and the above parameters is weaker than for elongation and stiffness values as fiber strengths are strongly affected by the presence of defects [12]. By understanding the effect of different chemical and structural parameters of fibers on their mechanical properties, the choice of fibers for composite reinforcement can be better tailored to meet the application needs of the composite. Some mechanical properties of natural fibers commonly used for composite reinforcement in comparison to conventionally used fibers are shown in Table 2.2. Table 2.3 provides relative data on the chemical and physical structural of natural fibers. A comparison between the mechanical properties in Table 2.2 and chemical/physical properties in Table 2.3 is useful when determining an ideal natural fiber for use as reinforcement in a composite.

Table 2.2: Physical and mechanical properties of natural fibers [4,7,14,21,22]

Material Type	**Type**	**Density (g/cm^3)**	**Diameter (μm)**	**Tensile Stength (Mpa)**	**Elastic Modulus (Gpa)**	**Elong. at break (%)**	**Price range ($)/kg**
Glass	Mineral	2.5-2.55	5-25	1800-3500	70-73	2.5-3.0	1.30-2.00
Flax	Bast	1.4-1.5	20-600	345-1500	27.6-80	1.2-3.2	0.40-1.50
Hemp	Bast	1.45-1.5	25-2000	550-900	70	1.6	0.40-1.80
Jute	Bast	1.3-1.49	25-200	393-800	10-30	1.16-1.8	0.35-0.55
Ramie	Bast	1.5-1.55	10-25	400-938	44-128	1.2-3.8	0.44-2.50
Kenaf	Bast	1.193	90-100	375-930	22-53	1.5-1.6	0.40-0.55
Coir	Seed/Hair	1.15-1.46	100-460	131-220	4-6	15-40	0.25-0.55
Cotton	Seed	1.5-1.6	12-38	287-800	5.5-12.6	7-8	0.44-0.55
Sisal	Leaf	1.33-1.45	50-390	468-700	9.4-38	2-7	0.40-0.70
PALF	Leaf	1.44-1.53	20-80	413-1627	34.5-82.5	1.6-2.4	0.40-0.55
Curaua	Leaf	1.4		500-1150	11.8	3.7-4.3	0.6
Hardwood	Wood	0.6-0.9		90-110*	11-13*		0.44-0.60
Softwood	Wood	0.3-0.7		60-90*	8-14*		0.44-0.60

*Elastic properties of wood samples at 12% moisture content

Table 2.3: Chemical compositions and structural properties of natural fibers [4,9,14,23-26]

Type of Fiber	**Cellulose (wt. %)**	**Lignin (wt. %)**	**Hemi-cellulose (wt. %)**	**Microfibril/ spiral angle (degree)**	**Moisture content (wt. %)**	**Cell length to diameter ratio (L/D)**
BAST						
Flax	71	2.2	18.6-20.6	5-10	8-12	1687
Hemp	70.2-78	3.7-5.7	17.9-22.4	2-6.2	6.2-12	906
Jute	61-71.5	12-13	13.6-20.4	8	12.5-13.7	110
Ramie	68.6-83	0.6-0.7	13.1-16.7	7.5	7.5-17	3500
Kenaf	31-57	8-19	21.5			130
FRUIT						
Coir	32-43	40-45	0.15-0.25	30-49	8	35
SEED						
Cotton	85-90		5.7		7.85-25	1250
LEAF						
Sisal	67-78	8-14	10-14.2	10-22	10-22	100
Pineapple	70-82	5-12.7		14	11.8	450
WOOD						
Hardwood	44-50	20-30	20-25		3-7	30
Softwood	44-50	20-30	20-25		8	164

2.2.4 Fiber Types [27]

Plant fibers used for composite reinforcement are commonly categorized by their origin: (1) bast fibers, obtained from the fibrous bundles within the inner bark of a plant stem; (2) leaf fibers, obtained from fibers running the length of plant leaves; (3) seed fibers; (4) reeds and grass stems; (5) fruit fibers; and (6) wood fibers from the core of trees. The plants within these categories that are most researched for uses in bio-composites are shown in Figure 2.4. The majority of research in the field of natural fiber composite reinforcements has been conducted using plant fibers from the bast and leaf categories. These fibers, also known as hard fibers, are the most common in natural fiber composites because of their combination of high strength and stiffness as well as low elongation to break. Bast fibers are also of particular interest because of their long lengths, providing for easier fiber alignment and relatively low moisture uptake, reducing fiber swelling and consequently giving better fiber/matrix adhesion in humid environments [11]. The intrinsic properties of bast plant fibers described above suggest their potential to serve as efficient composite reinforcements. Therefore, an overview of the characteristics, processing methods, and applications of these fibers including flax, hemp, jute, kenaf, and ramie as biocomposite reinforcement will be the focus of this work.

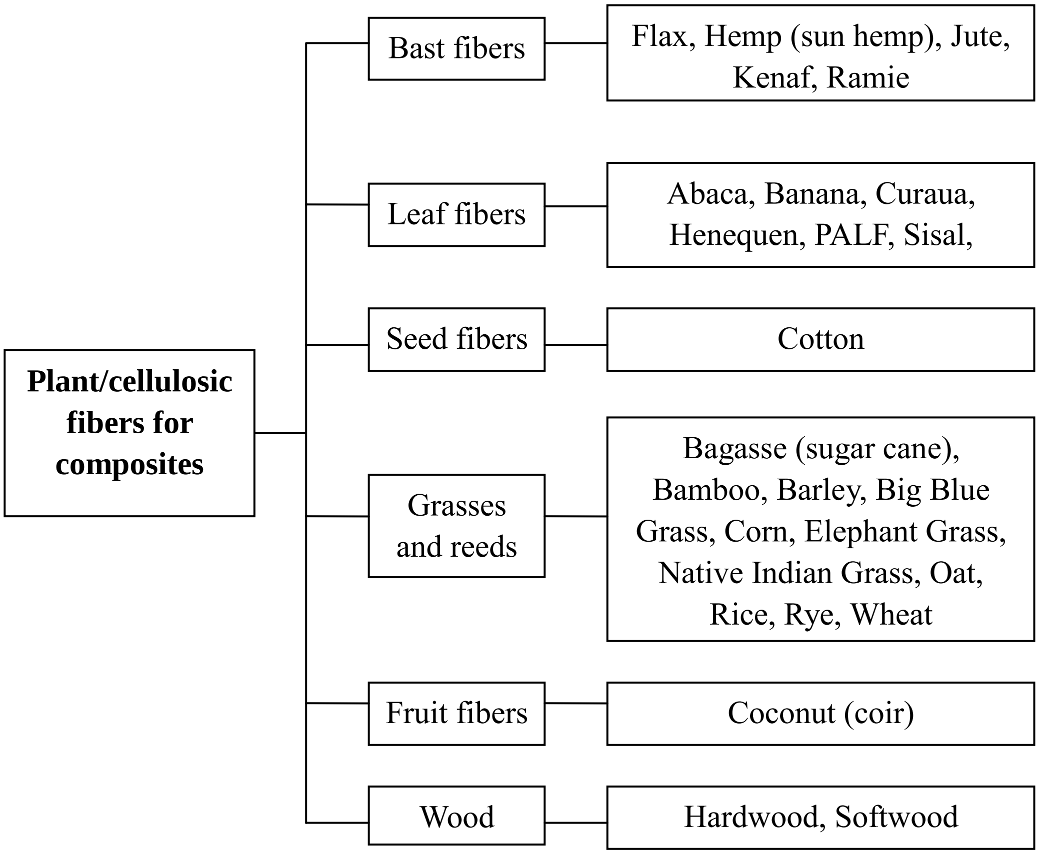


Figure 2.4: Cellulosic fibers and their origins used for natural fiber composites [18]

2.2.4.1 Bast Fibers

Bast fiber crops have rigid stalks with nodes regularly spaced along their length. Between each node, the stalks have a hollow core followed by a thick woody pith layer, a cambium transition layer, a phloem with short chlorophyll-containing cells and long bast fiber cells, and lastly a thin protective layer consisting of the cortex and epidermis [14]. The bast fibers of interest for composite reinforcement are the long fibers which run lengthwise in the phloem regions, just inside of the protective bark. Although the shape and size of the stem of various bast fiber crops are different, the structure of the individual bast fibers is similar. High yields of the long individual fibers or fiber bundles can be obtained from bast fiber crops at relatively low cost.

A review depicting the unique characteristics of the various bast stalk and fiber structures as well as their properties was recently published by Bismark et al. [14] and hence will not be repeated in detail, here. A summary of the most commonly used bast fibers for natural fiber reinforcements as well as their geographic origins, physical characteristics, and corresponding mechanical properties are described in the following sections.

2.2.4.1.1 Flax [14]

Flax (*Linum usitatissimum L., Linaceae*) is typically grown in temperate regions such as southern Europe, Argentina, India, and China and has been cultivated for nearly 10,000 years. Common uses of flax plants are to provide important products such as oil seed, paper and pulp, and textile yarns and fabrics. Flax plants are quite fast growing and can grow to heights of 80 to 150 cm in less than 110 days. The bast fibers come from the central portion of the plant and are in bundles between 60 and 140 cm long with diameters ranging from 40 to 80 μm. Additional dimensional properties and chemical compositions for flax fibers are shown in Table 2.3. Flax fibers are one of the strongest and stiffest plant fibers; however, they have relatively low longitudinal extension to failure when subjected to tensile loads.

2.2.4.1.2 Hemp [14]

Hemp (*cannabis sativa L., Cannabaceae*) is typically grown in moderate climates such as those of Central Asia and Northern America. Although it has been cultivated for more than 12,000 years, its cultivation has been limited by strict legislation as a result of its physical resemblance to the narcotic drug, marijuana. Hemp cannot be used as a narcotic, however, as it produces less than 1% of the narcotic 9-Δ tetrahydrocannabinol (THC) in comparison to 3-20% produced by marijuana. There are a wide variety of products made from hemp plants including specialty paper, textiles, construction materials, plastics and composites, food, medicine, and fuel. Hemp crops are advantageous to other fiber crops in that they are very resilient crops requiring no or minimal herbicides, fungicides, pesticides, and fertilizers. Hemp plants also have quick growth rates reaching heights of up to 5 m with bast fiber contents between 28 and 46 percent. The fiber strands have lengths of 1.8 m or longer with elementary fibers averaging 13 to 25 mm in length. Hemp fibers, although hygroscopic, are highly resistant to moisture degradation and rot very slowly in water. Hemp fibers also have excellent mechanical properties such as strength and stiffness, with low elongation to break as a result of their low cellular microfibril angle.

2.2.4.1.3 Jute [14]

Jute (*Corchorus capsularis, Tiliaceae*) plants thrive in hot humid environments and although it originated in the Mediterranean it spread to the Near and Far East. Today it is grown mostly in the delta formed by the Ganges River and Bramhaputra River in India and Bangladesh as well as in Thailand, China and Brazil. The use of jute plants by humans dates back to prehistoric times. These annuals grow to heights between 2 and 3.5 m, with stalk diameters ranging from 2 to 3 cm. Unlike flax and hemp, jute plants are grown entirely for its fibers which are between 1.5 and 3 m in length. These bast fibers vary widely in size and although they are strong, their tensile properties are lower than those of other bast fibers such as hemp and flax. Additionally, they are fairly brittle and exhibit low elongation to break as a result of high lignin content. Jute fibers are resilient to attacks by microorganisms; however, they are quite hygroscopic and are sensitive to moisture as well as chemical and photochemical attack

2.2.4.1.4 Ramie [14]

Ramie (*Beohmeria nivea L. and Boehmeria viridis, Urticaceae*) is a hardy perennial crop that is cultivated primarily in Indonesia, China, Japan, and India. The plants grow to heights of 1.2 to 2.5 m and can be planted and harvested up to six times per year. Ramie fibers are primarily used in textile industries as they are very fine (diameters from 10 to 25 μm) and silk-like as well as strong. They also have very good resistance to bacteria, mildew and insect attack. Unlike flax, hemp, and jute fibers they are also stable in both alkaline media and mild acids. Ramie fibers also have excellent strength and stiffness properties which is most likely a result of their high cellulose content (Table 2.3). A disadvantage of ramie fibers is their often high cost in comparison to other natural fibers.

2.2.4.1.5 Kenaf [14]

Kenaf (*Hibiscus cannabinus L., Malvaceae*) is an annual cane-like crop originating in Asia and Africa. Kenaf plants are fast growing and reach heights of 2.4 to 6 m in 5 months. Products made from kenaf plants include paper, textiles, and composites. The kenaf plant has both short and long fibers within its stalks; however the elementary fibers are quite short, having lengths of 1.5 to 6 mm. The fibers have a striated surface as well as an irregular shape. Additionally, the fibers are coarse and brittle and can be difficult to process. Their mechanical properties are similar to those of jute fibers; however, the density of kenaf fibers is typically less than that of jute as a result of the lower cellulose content. Kenaf plants are the newest of the bast crops reviewed and therefore it is anticipated that many new applications will be found for the stalks and fibers of these plants. Kenaf has also been said to have the highest carbon dioxide absorption of any plant making it a valuable tool in the reduction of CO_2 contents in the atmosphere.

2.2.5 Worldwide Supply and Crop Yields

The application of natural plant fibers is an important contribution to the global goal of a more sustainable world. Growing and using these plants contributes to recycling of carbon dioxide in the atmosphere. Bast fiber plants are grown in regions throughout the world and have a seemingly inexhaustible supply. Based on data from studies conducted in 1994 by animal feeding operations (AFO) and independent researchers, the estimated annual worldwide availability of agro-based crops was 76 million metric tonne (mt) with bast plant crops accounting for approximately 20 percent or between 13 and 16 million mt [28]. A more updated estimate of the worldwide production of bast fibers was approximately 6 million mt in 2000 [29]; however, only a small portion of these fibers are used in industrial applications reflecting the huge growth potential for applications of this natural resource. The properties of bast fibers depend on the variety of the plants, growing conditions, and the methods of processing. Therefore, it is imperative that proven cultivation, harvesting, and processing techniques are established for these plants to ensure consistent high quality materials.

2.2.6 Cultivation and Harvesting Procedures

Cultivation and harvesting procedures for bast fiber crops can vary depending on the plant species and variety. Cultivation techniques are employed so as to produce the highest quantity crop yields with the least impact on the surrounding environment. For example, crop rotations, advanced soil tilling and optimized use of fertilizers, herbicides, and pesticides are all desirable cultivation techniques. The timing of harvesting bast fiber crops is highly dependent on whether the plant products will be used for one or multiple purposes. Some plants, such as jute, are planted for the sole purpose of fiber use. Optimized harvesting times for these crops typically depend on when the highest bast fiber yields are expected. For other plants, such as flax and hemp, where both the seeds and fibers are useful products, harvest times for the crops will vary. Optimizing harvest times to obtain maximum quantity and quality yields for multi-purpose crops can therefore be difficult. In general, the development of bast fibers increases with plant age;

however the beneficial increase in fiber properties over time can compete with the detrimental lignification of the stalk [14]. Rowell et al. [26], have reviewed the changes in fiber properties with respect to the stage of plant growth for several cellulosic fiber crops. The useful bast fibers are typically in the outer portion of the stalk and therefore must be separated from the inner woody tissue. Decortication and separation of the fibers from the woody core and one another gets more difficult when the plants are left to grow beyond optimal ripeness.

Currently, bast fibers are harvested by either pulling or mowing of the plant towards the base of the stalk to preserve the length of the bast fibers. The stalks are then left in the field for typically 3 to 4 weeks to allow the process of retting to occur [30]. Several reviews of various retting techniques such as dew retting, water retting, enzyme retting and chemical or mechanical retting, exist [31,32]. For dew retting, the most common of the retting processes, the cut or pulled plant stalks are left in the field to allow for proper drying. The actual retting process is initiated by changes in temperature and moisture, such as from dew or rain, during which point aerobic and anaerobic fungi and bacteria attack the stalks dissolving the lignin and pectin that hold the fibers together and to the woody core [29]. The dried stalks of fibers are then baled and stored until further separation and processing of the elementary fibers can be done in a factory.

Although dew retting is easily implemented in humid climates and allows for the most natural separation of the fibers from the stalks, this process requires down time in the field between crop growing cycles and also is subject to fluctuations in temperature and humidity causing variability in the quality of the resulting fibers. Dodd et al [31] examined the use of water, enzyme, and chemical retting as alternate methods to dew retting. Duralin®, a hygrothermal retting process, has also been investigated as an alternative to field retting. This process was seen to result in better separated fibers, increased yields and more consistent fiber qualities over dew retting [11]. Although these technologies show promise, they are still in the research and development stages and therefore have not yet been optimized and made cost effective for large production quantities and commercial use. Naturally some plant species allow for the use of better cultivation and harvesting techniques than others. Therefore, it is imperative that the advantages and disadvantages of each plants cultivation needs are considered in the overall comparison between fiber materials.

2.2.7 Processing of Natural Fiber Plants

After retting, drying, and storage of the plant stalks, the bales are opened up, the straws are cut to a workable length (typically between 300 and 400 mm) and any impurities introduced during the retting and harvesting processes such as stones, metals, leaves and seeds are removed. The elementary bast fibers can then be extracted from the woody shives through a process known as decortication. Decortication is typically a mechanical separation technique with common methods including the use of breaking rollers and hammer mills with and without integrated cleaning effects. The advantages and disadvantages of the various decortication methods are well presented in the literature [29]. The decorticated fibers are then further cleaned and processed until the desired fiber quality is achieved. Bast fibers are cleaned in several steps involving a scutching turbine for coarse cleaning, a step cleaner for fine cleaning, and a comb shaker for the final cleaning [29].

2.3 Biopolymers

The plastics industry has been continually thriving due of the seemingly endless applications for these materials in industries such as packaging, automotives, building products, furniture, and consumer goods. Traditionally the majority of these materials are derived from petroleum feed-stocks because of their high mechanical properties and durability. Biocomposites made from traditional synthetic and petroleum derived polymers have been developed extensively in the last few decades. Thermoplastic polymers such as polypropylene (PP) and polyethylene (PE) as well as thermosetting polyester, epoxy and polyurethane polymers are the most common matrix materials used in natural fiber reinforced composites. The incorporation of natural fiber reinforcements in these resins clearly makes then better from an environmental perspective to traditional glass-fiber reinforced polymer (GFRP) composites; however, they do little to solve the problems of diminishing petroleum resources and landfill space.

The petroleum supply is not renewable and has also been shown to be unreliable in recent years making the cost of these materials rise appreciably. Additionally, petroleum derived plastics do not degrade which means they must either be incinerated, causing harmful emissions, or disposed of in diminishing landfill space. Research interests in biopolymers, broadly defined as polymers which are biodegradable and/or derived from renewable resources [1], have increased worldwide in the last several decades. Biodegradable petroleum derived plastics are some scientist's response to concern regarding the accumulation of non-degradable plastics waste. These polymers have offered scientists a possible alternative to the waste disposal problems typically associated with traditional petroleum derived polymers often times without having to sacrifice the exceptional properties of non-degradable plastics. However, this does not address the issue of rising costs of plastics due to fossil fuel shortages. The instability of the petroleum supply and environmental issues related to its products has led many researchers to look into alternate feed stocks for plastics, the majority of which are renewable and agricultural based. Biopolymers derived from renewable resources offer a similar solution to waste disposal, but have the added advantage of reducing dependence on the diminishing petroleum resources.

Clearly, both can be seen as advantageous in advancing and sustaining the technology of environmentally friendly materials. For this study, it was of interest to develop a biocomposite that optimized properties of environmental friendliness and high performance, therefore, only biopolymers with good properties and biodegradable capabilities were investigated for use as composite matrix materials. Mohanty and co-workers [4] reviewed the state of biopolymer technologies and presented structures, synthesis and properties of many of the common biodegradable polymers from synthetic and renewable resources. Since the time of this review, however, several notable research efforts have been reported on new biopolymer materials for composites. Figure 2.5 shows a broad breakdown of the emerging technologies in the field of biopolymers. An overview of the previous review as well as current findings in biopolymer technology is presented below.

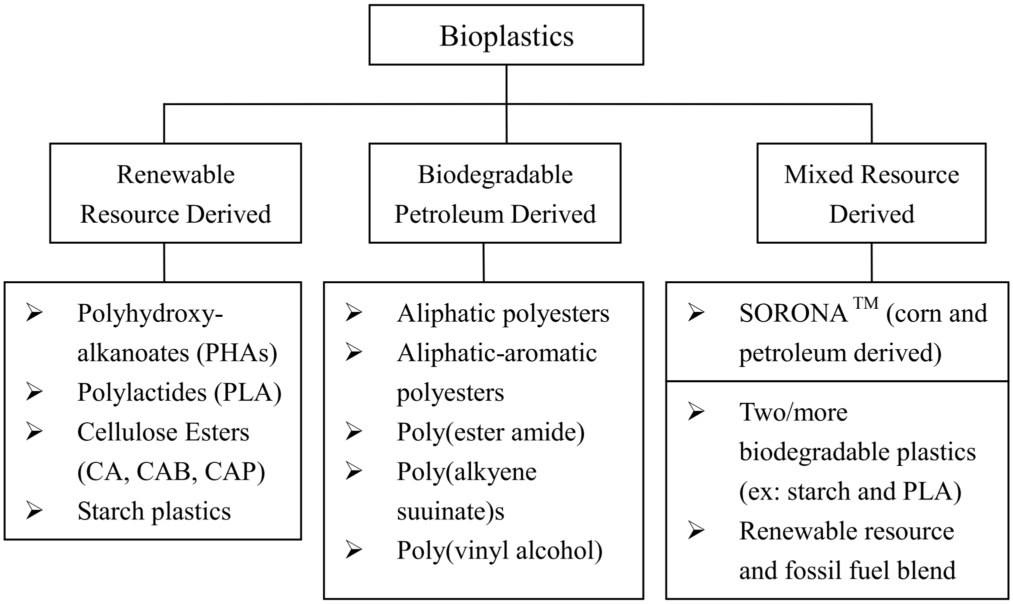


Figure 2.5: Broad classification of materials termed ‘bioplastics’ (adapted from [1])

2.3.1 Biodegradable Petroleum Based Polymers

There are currently a great number of commercially available biodegradable polymers derived from petroleum resources [4]. In particular, aromatic polyesters such as PCL and PBS, aliphatic-aromatic polyesters such as Eastman’s Eastar Bio® and BASF’s Ecoflex®, and polyester amides such as Bayer’s BAK 1095 and 2195, are the most recognized biodegradable polymers [1]. These biodegradable polymers exhibit mechanical properties similar to those of traditional petroleum derived polymers which can be beneficial when attempting to use them in place of conventional polymers. It is important to consider the processing parameters for these polymers when selecting them for a specific application, as they can vary greatly.

Poly(ε-caprolactone), PCL, is a tough and semi-rigid semicrystalline thermoplastic polymer with a modulus between that of low- and high-density polyethelylene [4]. PCL has a glass transition of -60°C, a low melting point around 60°C, and low viscosity making it easily melt processed. As a result of its low melt temperature it is typically blended with other polymers. Additionally, PCL possess good resistance to water, oil, solvents, and chlorine.

Commercially available polybutylene succinates, PBS, have been developed by Showa Highpolymer under the trade name Bionelle®. These materials are reportedly high molecular weight white semicrystalline thermoplastic polymers with a glass transition temperature between -45 and -10°C and a melting point of about 90 to 120°C [4]. These polymers have a density around 1.25 g/cm^3 and tensile strength and stiffness properties between PE and PP, and LDPE and HDPE, respectively.

Polyester amides were first introduced in 1995 by the Bayer Corporation under the name BAK 1095, two years later the injection molding grade polyester amide, BAK 2195, was introduced. These polymers are noted for their high toughness and tensile strain at break with mechanical and thermal properties similar to those of polyethylene. The BAK 1095 and 2195 have melting points of 125 and 175°C, respectively [1]. These polymers are unique in that they break down into water, carbon dioxide, and biomass under aerobic conditions at rates comparable to other compostable materials.

2.3.2 Bio-resource Derived Polymers

It has been recognized that plastics derived from biobased renewable resources offer both economic and environmental advantages for the United States. Firstly, by utilizing renewable resources such as agricultural crops the country's dependence on foreign petroleum supplies will be reduced. Additionally, the use of natural materials is in line with increasing support for environmentally friendly alternatives in science and technology. In the past decade several government based initiatives have offered economic incentive to consider biobased alternatives to petroleum based materials [4]. Some of the most developed technologies in biobased plastics are aromatic polyesters such as PHAs from bacterial fermentation and PLA from corn as well as polymers derived from renewable resources such as cellulose (cellulose acetates), starches, (starch esters), and proteins or oils from plants such as soybeans. Demand for these materials is expected to increase by more than 20% a year along with improved economics as production and sales increase [1].

2.3.2.1 Polyhydroxyanlanoates (PHAs)

PHAs are biodegradable polyesters that are formed through bacterial fermentation. PHA polymers are synthesized in the bodies of bacteria fed with glucose in a fermentation plant. The first PHA discovered was polyhydroxybutyrate (PHB), a linear semicrystalline polymer, and since then over one hundred compositions have been reported in the literature [4]. PHAs were commercialized by ICI Zeneca in the late 1980's under the commercial name Biopol®. These polymers are typically highly crystalline with melting and glass transition temperatures similar to those of PP. Reported values for PHB include a glass transition of 9°C, melting point of 175°C, tensile strength of 45 MPa, elastic modulus of 3.8 GPa and elongation at break of 4 percent [33]. The actual and potential uses for the PHB polymers and PHBV copolymers have been reviewed [34,35]. Additionally, the specific use of bacterial polyesters in biocomposites has been reviewed [33]. As a result of their ease of biodegradation and processing they are a likely candidate for commercialized development, however, their high cost, low impact resistance, and small difference between melting and degradation temperatures has prevented large commercial application [33].

2.3.2.2 Polylactic Acid (PLA)

PLA polymers are not a new technology. The manufacture of polyester from lactic acid, the basic building block of PLA, was developed by Carothers, DuPont, and Ethicon starting in the 1930s. PLA was used almost exclusively in the biomedical industries until the late 1980s when more economical manufacture of the monomer of PLA from agricultural products placed this material at the forefront of the biopolymer industries [1]. Until recent years the production of PLA resulted in low yield polymers with limited molecular weight and as a result the costs were still quite high (>$2/lb). In recent years, however, Cargill Dow LLC has developed a continuous process to increase production and reduce the cost of lactic acid-based polymers. The PLA polymers produced through this process embody the principles of green chemistry, require the use of significantly less fossil fuel and can be recycled, degraded or incinerated with very low environmental impact [36].

PLA is unique in that it processes like PET but has performance similar to PP. General properties and characteristics of PLA polymers are well known [36-39]. Polylactide is a rigid thermoplastic polymer that can be semicrystalline or totally amorphous. Glass transition temperatures of PLA are reported between 40 and 63°C with a melting range of 130 to 230°C for the semicrystalline polymer form. Processing temperatures should be kept below 200°C, however, as thermal degradation can occur [40]. A wide range of mechanical properties can be seen for PLA polymers. For high molecular weight PLA, Garlotta [38] reports ultimate tensile strength of 47.6 to 53.1 MPa, elastic modulus values of 3.45 to 4.0 GPa, and elongation at break of 3.1 to 5.8 percent, respectively. In contrast, for lower molecular weight PLA polymers strength, modulus, and elongation values were reported around 60 MPa, 1.2 GPa and 3.1 percent, respectively. The good properties seen for PLA are expected to increase the demand for agricultural products. The versatility of PLA biopolymers as well as the fact that they can be entirely derived from renewable resources like corn offers a cost-effective alternative to traditional petroleum derived polymers.

2.3.2.3 Starch Based Polymers

Starch is produced in plants such as corn, potato, wheat and rice, and is one of the least expensive biodegradable materials available in the world market today. Reports from the 1990s estimated the annual production of starch in Europe was almost 7 million tons with between 20 and 50 percent being used in non-food applications [4,41]. When starch is converted to a thermoplastic material it offers an interesting alternative for petroleum polymers where long-term durability is not a requirement. Properties and applications of starch and starch plastics have been reviewed [42-44]. Thermoplastic starch alone is mainly used in soluble compostable foams several the trade names include Bioplast®, Bioflex®, and Biopur® all developed by BIOTEC of Germany. This is because of starch polymers sensitivity to water and its ability to rapidly degrade. Starch therefore, is typically blended with other natural and synthetic polymers for longer term applications. Starch-based polymer blends as well as starch based composites have also been reviewed [45]. On a commercial level, Novamont of Italy produces several forms of biodegradable polymers which are a blend of starch and various synthetic polymers under the Mater-Bi trademark. Mater-Bi polymers have mechanical properties similar to those of conventional polymers like polyethylene and polystyrene and have been certified compostable [4]. A notable advancement in starch-based polymers was the USDA's development of a starch/PVA blend wood adhesive which can be used in place of traditional formaldehyde-based resins, a known carcinogen [46]. Although, applications for starch-based polymers are increasing, many biodegradable products based on starch still have disadvantages as compared to common thermoplastics as a result of their highly hydrophilic character.

2.3.2.4 Soy Based Polymers and Blends

The first soybeans crops were grown for food purposes in the US in the early 1800s and are still, to this day, a major source of fats, oils, and proteins used for food and feed in the US. Although protein levels as high as 55 percent have been observed, typical soybeans contain 20 percent oil and 40 percent protein. Petrovic and co-workers [47] report good mechanical properties and water resistivity from biopolymers derived from cross-linked soy oils such as epoxidized soybean oil (ESO). Wool and Khot [48] report processing and mechanical properties for several polymers derived from soy oil. By incorporating various types and contents of chemical groups, such as anhydride or maleic acid, the properties of the plant oil based polymers were seen to improve greatly, but still were often below the values for traditional synthetic polymers. These polymers, similar to synthetics polymers, are not able to readily break down at their end life; therefore, their use is limited to applications not requiring biodegradability [48].

Soy protein concentrates and isolates, the purified forms of soy protein flour, have also been considered as alternatives to petroleum derived polymers in the manufacture of adhesives, plastics, and packaging materials. General characteristics of soy protein-based polymer technologies including the structure, composition, production and processing methods, applications, and biodegradability have been reviewed [4,49]. Soy protein-based polymers are typically prepared by injection molding or compression molding. Control and optimization of the mechanical properties and water resistivity of soy protein plastics has been achieved through plasticization and changes in processing parameters [50]. Additionally, further enhancement of the soy protein polymer properties can be achieved through blending with other polymers. These soy-based polymers utilize natural polymers such as starch, cellulose, or lignin as well as biodegradable polymers with similar processing windows to soy such as polyester amide, PCL, PLA, Biomax, and Eastar Bio. Mohanty and co-workers [50] report tensile strength and modulus values for several soy-based polymer blends with values in the range of 10 to 15.5 MPa and 0.22 to 0.27 GPa, respectively.

2.3.2.5 Cellulose Based Polymers

Cellulose ester derivatives are produced from biopolymer cellulose, a linear polysaccharide. Cellulose biopolymer is a readily available biomass, extracted from wood species and other lignocellulosic plants, and as a result has been considered as a potential feedstock for the development of environmentally friendly polymers. Although cellulose esters such as cellulose acetate (CA) have many current applications including adhesives, tool handles, eyeglass frames, packaging materials, coatings and films, only a few studies have been reported that examine the use of cellulose based polymers as matrix materials in composites [15,51-57]. There has been much debate regarding the biodegradation potential of cellulose esters. It has been clearly demonstrated that cellulose acetates with a degree of substitution (DS) less than 2.5, as well as several other plasticized cellulose esters, are biodegradable under aerobic and anaerobic conditions and many are readily compostable [58].

For cellulose esters to be used as thermoplastic matrix materials in fiber composites they must be plasticized as they have degradation temperatures at or below their melt processing temperatures [4]. Common plasticization techniques use acetates, propionates, and butyrates resulting in various derivates of cellulose acetate (CA) such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). The physical, mechanical, and processing characteristics have been shown to be highly dependent on the content of plasticizer [4,55,59-64]. Cellulose esters are either readily degradable, can be 'triggered' to biodegrade, or can be burned cleanly without producing harmful toxins [55]. Cellulose esters can be processed using most common techniques for thermoplastic polymers with processing temperature typically between 180 and 240°C. These polymers also exhibit good chemical and UV light stability, moisture resistance, and dimensional stability. They are, however, quite susceptible to attack by strong acids or alkalis and are dissolved or swollen by alcohols, esters, ketones, and aromatic and chlorinated hydrocarbons [55].

2.4 Bio-composites: Past, Present, Future

In recent years there has been an increase in research efforts to develop biocomposites that can compete with traditional non-renewable materials such as petroleum derived polymers and synthetic fiber reinforced composites. This chapter has outlined many natural fiber and biopolymer materials available to be used in the manufacture of biocomposites. Several reviews of the biocomposite technologies utilizing these materials are available [4,12,19]. Although it is beyond the scope of this work to review all research efforts in the field of biocomposites, an overview of the more notable studies is presented (Table 2.4). Studies that have utilized bast fiber reinforcements and renewable resource based biopolymers as composite constituents will be the focus of this work as these incorporate good mechanical properties in addition to low environmental impact. Key parameters for achieving superior composite performance such as tailored processing techniques and the use of fiber surface treatments for increased fiber/matrix adhesion will be reviewed as well. Lastly, an overview of the current and potential future applications for biocomposites will be presented.

Table 2.4: Summary of currently published natural fiber-reinforced composites

Polymers	**Bast Plant Fibers**				
	Hemp	**Flax**	**Jute**	**Ramie**	**Kenaf**
Soy protein/oil	[48,65-68]	[42,48,68-77]	-	[78,79]	[80]
Poly-lactic acid	-	-	[81]		[82,83]
Starch	[15]	[15]	[84]	[15]	[85]
Cellulose	[15,51,52, 56,57,86]	[15,54]	-	[15]	-
Plant oil	[87,88]	-	-	-	[87]
PHA	[89]	[15]	[90]	[15]	
Polypropylene	[8,52, 91-96]	[92,96-99]	[8,81,100, 101]	-	[8,22,102, 103]
Polyethylene	[104,105]	-	-	-	-
Nylon	[106]	-	-	-	-
Polyester	[107-115]	[108,110,116]	[109,113]	-	[107]
Epoxy	[92,117]	[92,116-119]	-	-	-

2.4.1 Key parameters for Biocomposite Performance

The mechanical and physical properties of constituent materials are important parameters to consider when choosing the constituents to be used for fiber reinforced polymer (FRP) composites. However, to fully exploit the properties of composite constituents, reinforcement parameters must be carefully considered when designing a composite processing system. The key reinforcing parameters known to affect the performance of a natural fiber reinforced biocomposite are similar to those identified as key parameters for traditional composite performance: fiber volume fraction, fiber aspect ratio, fiber dispersion and orientation, and fiber/matrix adhesion [120]. The fiber aspect ratio, i.e. the ratio of fiber length to diameter, and fiber volume fraction are parameters that can be determined and easily controlled before and during composite manufacturing. The control of fiber orientation and dispersion is also possible through the selection of proper composite processing technologies. Good adhesion, and therefore effective stress transfer, between the fiber and matrix constituents is more difficult to control, however improvements in the fiber/matrix adhesion through fiber surface modifications have shown promise [12].

2.4.1.1 Biocomposite Processing Technologies

The processing parameters for biocomposites depend largely on the type of polymer being used as a matrix material. Thermoplastic polymers, often with high melt viscosity, require the application of heat and pressure to ensure good melt flow and consolidation of the polymer around the fiber reinforcements. Thermosetting polymers, however, generally have low viscosity prior to curing which allows for easier fiber wet-out, therefore the application of heat and/or pressure to these composites is typically used to initiate cure reactions in the polymer. A known challenge for processing of natural fiber composites is to keep processing temperatures below 200°C as temperatures above this point have been shown to cause degradation of natural fibers [16,121,122]. An increasing number of biopolymers that require lower processing temperatures such as plasticized starch, cellulose and soy-based polymers have, however, offered greater a selection of composite matrix materials such that the detrimental effects of high temperature composite processing can be avoided.

Composite processing techniques are also chosen based on the desired structure of the fiber reinforcements. Natural fibers come in the ‘raw’ unprocessed form or, after varying levels of mechanical and/or chemical processing, result in more refined and purified structures. Natural fiber reinforcements can range in length from short to long lengths and can be in a random or highly oriented structure. For short fiber reinforced composites where random orientation is desired, injection molding (IM), resin transfer molding (RTM) and various hot press techniques have all been shown to yield composites with good physical and mechanical properties (Table 2.5). However, when long fiber reinforcements with high levels of orientation are desired composite processing techniques such as pultrusion, filament winding and prepreg formation followed by compression molding are typically implemented (Table 5.16). As a result of the wide variety materials and desirable performance characteristics in biocomposites, highly tailored processing techniques are not uncommon for the production of specific biocomposite systems.

Table 2.5: Variation in properties of randomly oriented hemp fiber-reinforced composite with processing procedure

Processing Procedure	**Composite Constituents (Fiber/Matrix)**	**Composite Properties***	**[Ref.]**
Injection Molding	Glass/PP	$V_f = 0.4$, TS = 61, E = 4.3	[94]
	Hemp/PP	$W_f = 0.4$, TS = 48, E = 6.4	[95]
	Hemp/plasticized CA	$W_f = 0.3$, FS = 78, Eb = 5.6	[57]
	Hemp/PHB	$W_f = 0.3$, TS = 28, E = 4.5	[89]
RTM	Hemp/Polyester	$W_f = 0.36$, FS = 112, Eb = 7.5	[115]
Hot Press	Hemp/PP	$V_f = 0.4$, TS = 52, E = 7, FS = 55, Eb = 5	[8]
	Hemp/plasticized CA	$W_f = 0.3$, FS = 60, Eb = 4.7	[57]
	Hemp/Polyester	$V_f = 0.6$-0.65, FS = 100, Eb = 9.5	[107]

**Values for tensile strength (TS) in MPa, flexural strength (FS) in MPa, elastic modulus (E) in GPa, and bending modulus (Eb) in Gpa*

2.4.1.2 Fiber Surface Modifications

The effective use of natural fibers as reinforcement in composite materials requires strong adhesion between the fibers and the matrix. It is suggested that the hydrophilic nature and poor surface conditions of plant fibers as well as the chemical mismatch between many fiber and matrix materials are the root causes for poor fiber/matrix adhesion in biocomposites [11,24,123]. Therefore the development of efficient natural fiber reinforced composite materials with superior mechanical properties requires modifications be made to improve fiber/matrix interfaces. Research into technologies that help improve the fiber/matrix adhesion for natural fiber reinforced composites has been conducted by some researchers [1,9,12,17,18,24,118,123-125]. In general, the modification methods used focus on changing the physical or chemical structure of the fiber, thereby improving upon one or more of the reasons for poor adhesion between the fiber and matrix. Optimization of these surface modifications is necessary such that an increase in the composite processing time and cost of natural fibers is minimized.

2.4.1.2.1 Physical Fiber Modification

Physical methods such as such as steam explosion, thermotreatment, fiber fibrillation and electric discharge change the structural and surface properties of the fiber and thereby influence the mechanical bonding of the fibers and polymer matrix in a composite [24]. Wet oxidation and hydrothermal treatments have been investigated to remove impurities from the surface of natural fibers resulting in natural fibers with higher cellulose contents, increased surface roughness and a more fibrillated structure [126]. Additionally, the steam explosion process has been used on wood products [127,128] and plants [126,129,130] to extract fibers with decreased lignin contents and increased surface roughness leading to increased adhesion between the fiber and matrix. Surface modifications by discharge methods such as plasma, sputtering, and corona discharge are of interest for improving the functional properties of natural fibers. Corona discharge is used for fiber surface oxidation activation and works by changing the surface composition and therefore surface properties of composite components typically increasing bonding ability between the fiber and matrix. Similarly, during plasma treatment [131] the fiber surface energy can either be increased or decreased depending on the type and nature of the gasses used [12] making these fibers more compatible with polymers of different chemical or polar nature.

2.4.1.2.2 Mercerization

Mercerization is an old method of cellulose fiber modification that involves the alkaline treatment of cellulose fibers. Alkali treatments gradually remove the cementing hemicellulose and lignin portions of natural fibers which in turn cause fibrillation of the fiber bundles thereby increasing the surface area of the fibers [17,124,125,132]. The dissolution of hemicellulose and lignin result in a more purified cellulose fiber with increased surface roughness. The efficiency of the treatment has been shown to depend on the type and concentration of the alkaline solution as well as the length and temperature of the treatment [17]. Although the removal of cementing materials can improve the alignment of the fiber microfibrils, reductions in fiber strengths and stiffness by as much as 50 to 70 percent, respectively, have been reported [92,121]. Some studies [92,121] have found that by stressing fibers during mercerization losses in fiber strength can be diminished. Additionally, it was found [121] that thorough rinsing of the fibers with water or acid solutions following mercerization is required to prevent further degradation of the fiber properties.

Some authors have also reported a change in the cellulose crystallinity as well as changes in thermal stability of natural fibers through alkaline treatment [92,95,132-135]. Alkali treatments on natural fibers have been extensively used to increase the properties of composites with traditional petroleum-based polymers [17,92,95,107,111,136,137] and biopolymers [84,87,103,138-145] through better fiber/matrix adhesion. The improved adhesion is hypothesized to be a result of changes in fiber surface roughness allowing for better mechanical interlocking. In general, composites with alkali treated fibers show improved strength properties, whereas stiffness and impact strengths were shown to either increase or decrease depending on specifics of constituent materials and mercerization conditions. Increased strength and stiffness as well as decreased impact strengths (toughness) are attributed to good transfer of stresses between the constituents resulting in composite failure controlled by fiber fracture. However, reductions in the fiber stiffness allowing for greater fiber elongations at failure have also been attributed to decreases in composite stiffness and increased impact strength.

2.4.1.2.3 Acetylation

Another surface treatment for natural fibers known as acetylation describes a reaction resulting from the introduction of acetyl functional group into an organic compound. Chemical modification with acetic anhydride substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, making the polymers hydrophobic [125]. As a result, acetylation is commonly used to reduce the hygroscopic nature of natural fibers thereby improving the dimensional stability and fiber matrix interface of composites. Increased fiber/matrix adhesion as a result of acetylation on natural fibers such as abaca [103], sisal [142,146], PALF [142], coir [144], banana [136], kenaf [147], and jute [148] has been reported. In addition, increased thermal stability of natural fibers as a result of acetylation has been reported [148]. In general, however, the mechanical properties of these composites did not increase significantly. This may be a attributed to reduced mechanical interlock between the fiber and matrix as a result of bulking action of the acetyl groups on the fiber cell walls causing a smoother fiber surface [148]. Fiber acetylation can, however, be challenging because the fibers must be free of moisture for the reaction to occur. Additionally, because the hydrophobicity of the fibers increases with increased acetyl content, long treatment time and the use of a catalyst or solvent are sometimes necessary to ensure that all available polymer hydroxyl groups are reached and able to be replaced with the acetyl groups [12].

2.4.1.2.4 Chemical Modifications

All natural plant fibers are hydrophilic in nature, which lowers their compatibility with hydrophobic polymers. The incompatibility and weak interface between polar natural fibers and non-polar polymer matrix materials, due to their dissimilar chemical nature, is a shortcoming in natural fiber composites. Several chemical modifications have been shown to enhance the fiber/matrix adhesion in natural fiber reinforced composites by introducing a third material that has properties intermediate of the other two [9,12]. Chemical coupling agents, such as silanes acrylonitrile, isocyanates, and maleates, improve interfacial adhesion by treating the fiber surface or polymer with a compound that form a bridge of chemical bonds between the fiber and matrix materials [9].

The use of silanes as coupling agents for glass fiber reinforced polymer composites is extensive [149]. Silane coupling agents have also been used to modify the surface and increase fiber/matrix adhesion of several natural fibers including big blue grass [52], banana [104], bamboo [147], PALF [136], sisal [150], henequen [151], kenaf [83], hemp [111], and jute [12]. In general, these studies reflected little or no change in the physical properties of the fiber surface, but instead saw increased fiber/matrix adhesion through increased chemical bonding and decreased fiber swelling as a result of moisture uptake in the fibers. Improvements in the thermal stability of the fiber and composite were seen [83]. Many of these studies compared the effect of silane treatments to alkaline treatments and found the chemical bonding of the silane treatment to have a greater influence on the composite properties than the increased mechanical interlocking offered by alkaline treatments.

The effect of grafting acrylonitrile (AN) on natural fibers has been studied by several researchers [75,103,111,135,142]. The graft polmerization of AN on sisal fibers, studied by Mishra et al. [142] showed decreased moisture absorption and increased tensile properties of the treated fibers. Similarly, AN treatment of flax fibers [75] in an soy oil-based resin has been reported to increase composite strength and decrease moisture absorption. In a study by Mehta et al. [111] on the effect of various fiber surface treatments on hemp fiber reinforced UPE composites, AN grafting was shown to yield the best improvement in composite mechanical properties. In contrast, the use of AN coupling agent on abaca fiber PLA and PBS reinforced composites resulted in little improvement of composite properties [103]. In general, the effectiveness of AN grafting on natural fiber composites was shown to be highly dependent on the characteristics of the treatments such as reaction medium, treatment time, initiatior, AN concentration, and even fiber loading [142].

For thermoplastic fiber reinforced composites, maleated coupling agents are commonly used on fibers and polymers to increase compatibility between the two constituents [17,22,92,94,95,129,146,149,152]. The most common use for maleic anhydride (MA) is with PP where the MA is grafted onto the backbone of the polymer chain. Fibers are then treated with the heated MAPP copolymer and covalent bonds form across the interface [125]. Studies on the use of MAPP for glass [149,153,154], bamboo [129], kenaf [17,22], henequen [17], sisal [146,155], flax [92,96], jute [100], and hemp [93-96] fibers have reported an increase in adhesion between the polar fibers and non-polar polymer matrices. The increase in fiber/matrix adhesion was also seen to correspond to increases in composite properties; in particular the tensile strength was seen to increase as much as 77 percent for natural fibers [94]. The use of maleated coupling agents in natural fiber reinforced PE [17,115], PHB [89], CAB [56], and soy oil-based polymers [68] has also been shown to improve the fiber/matrix adhesion suggesting that the successful use of these agents is not limited to composites with a PP matrix.

Methyl methacrylate (MMA) grafted onto coir [144] and sisal [156] fibers resulted in increased properties of polyester amide biocomposites. For MMA grafted coir fibers, composite properties exceeded those using AN grafted fibers, whereas for sisal fiber reinforced composites the AN grafted composite properties were superior. Joseph et al. [146] studied the effect of coupling agents, such as MA and isocyantes, on moisture absorption of sisal/PP composites. Coupling agents decreased the hydrophillicity of natural fibers and increased bonding between the fibers and matrix resulting in significant reductions in composite moisture absorption. The reduction in moisture absorption is expected to increase long term performance of natural fiber reinforced composites. Similar results were seen for a study using bio-based coupling agents such as lysine-based diisocyanate (LDI) in natural fiber reinforced composites [157].

2.4.2 Applications for Biocomposites

Even with increased research efforts in bio-based materials over the last several decades, the biocomposite industry still faces many challenges. Most of these challenges are as a result of difficulties in composite processing, and inherent susceptibilities of some natural fibers and biopolymers to moisture, thermal and environmental attack. Additionally, the long-term durability of these materials has not yet been characterized. Many advances have been made to improve upon these inherent issues such as new techniques to enhance adhesion between the fiber and matrix, the development of novel bio-based polymers, and a better understanding of the effect of reinforcement and processing parameters on composite properties. It is therefore expected that as the science of biocomposites advances, new applications for these materials will be developed. Biocomposite materials are already seeing application in industries such as geotextiles, transportation, building/housing, packaging and consumer products [3,18,19,30,48,72,73,113,158-163].

2.4.2.1 Transportation/Automotive

As a result of their good mechanical properties, large thin walled interior and exterior automobile parts have been made from glass fiber reinforced polymer (GFRP) composites. However, the technological, economical, and ecological benefits of natural fiber reinforced polymer (NFRP) composites over GFRPs provide many opportunities for these materials in the automotive industry. There are several useful publications on the current and potential uses of biocomposite in the automotive industry [3,7,18,30,159]. In

1996, the use of natural fibers in the European automotive industry was reportedly around 4,300 mt. By 1999 that number had increased to over 24,000 mt and is projected to continue increasing to more than 100,000 mt by 2010 [30]. Initial applications were for interior door panels and trunk liners; however in recent years automotive applications for biocomposites have expanded to both interior and exterior applications. Interior composite parts using natural plant fibers typically include door panels, instrument panels, and glove boxes, whereas exterior applications are predominately floor panels [3]. DaimlerChrysler achieved the first global introduction of flax fiber reinforced polyester composites as engine and drive train covers for Travego busses and Mercedes passenger cars and has since increased the number of automotive parts containing natural fibers [3]. The Ford Company, whose use of biocomposite materials in car parts dates back to the 1940s when the hemp fiber reinforced ‘soy based car’ was being advertised, recently unveiled a Model U concept vehicle that uses PLA for the canvas roof and carpet mats [40]. Additionally, soy based materials are already in commercial use for composite parts on John Deere tractors [47,48].

Table 2.6: Use of natural fiber reinforced materials in the automotive industry (Adapted from [3])

INTERIOR PARTS	**Model year**	**No. of parts**	**Weight (kg)**
Mercedes-Benz			
C Class	2000	33	22
S Class	1998	32	24.6
E Class	1995	21	20.5
A Class	1997	27	11.9
C Class	1992	30	18.3
Other manufacturers			
BMW Series 3	1998	-	12
Audi A4 (B6)	1999	-	10
VW Passat	1997	-	2
Audi A4 (B5)	1993	-	1.5
EXTERIOR PARTS			
Mercedes-Benz			
Travego	2000	3	12.3
TopClass	2000	3	14.1

2.4.2.2 Building/Housing

Lignocellulosic composite materials in the form of laminated lumber, veneers, fiberboards, particleboard and molded particulate reinforced plastics, are commonly used for structural and non-structural applications in the building and housing industries [18]. The United States alone consumes over one billion pounds of formaldehyde-based resins every year in the manufacture of particleboard, oriented strength board, and plywood [42]. The toxic nature of these resins has initiated research into replacement adhesive systems derived from bio-based sources such as starches and plant oils. Additionally, in many cases these traditional wood based composites can be replaced by biocomposites derived from renewable plant fibers [18,162]. Biocomposite panel binders may be synthetic or bio-based polymers.

Youngquist et al. [162] reviewed the use of nonwood plant fibers for building materials and panels. More recently, Kozlowski et al. [18], have reported that composite boards made from fibers and shives of non-wood lignocellulosic sources such as hemp, flax and kenaf are competitive with traditional wood based materials. Although in some cases the properties of the products were competitive with traditional wood based composites, further studies to improve the performance and investigate the durability and weatherability of these materials is clearly needed. Their uses include doors, door and window frames (fenestration products), floor, ceiling or wall boards, and even furniture. In addition to being lighter than many conventional materials, biocomposites have also been shown to have excellent insulation properties due to the cellular structure of the fibers or fillers.

2.4.2.3 Packaging

The packaging industry is one of the most widely known uses for fibrous materials. Paper-based packaging is centered around the use of cellulose pulps, whether they be from wood or other agro-based resources [164]. It is clear then that molded containers with complex or simple shapes as well as lightweight packaging fillers all have the potential to be made from biocomposites [159]. NEC Corporation has developed a fully biodegradable flax fiber reinforced PLA composite which is anticipated to see use in electronics packaging [165]. The use for biopolymers and biocomposites in the food packaging industry has also seen increased interest in recent years. Most notable was the introduction of PLA based biodegradable plastic bags and containers by Dow Cargill under the NatureWorks™ trademark [40]. For packaging materials, the ease of biodegradation of bio-based materials proves advantageous in reducing abundant waste material.

2.4.2.4 Consumer Products

Through various molding techniques, biopolymers and natural fiber reinforced biocomposites can be processed to meet the needs of consumer products, often at lower costs and lower weights [159]. It is expected that virtually any injection molded part currently made by neat synthetic polymers and those with inorganic fillers could be replaced by biocomposites made in a similar fashion. Examples of such applications for consumer goods already being replaced by biopolymer and biocomposite materials include tool handles, clothing hangers, food trays, compostable planting cups, hygiene products, laptop computer casings, and furniture such as tables and chairs [19,40,159,165].

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3. MATERIALS AND CHARACTERIZATION METHODS

3.1 Material Selection

The level of environmental friendliness of biocomposites ranges from those with small portions of renewable resource based materials to those that are not only entirely based on renewable resources, but are also entirely biodegradable; the latter of which is optimal. Although biocomposites show great promise in achieving the goals of a more environmentally friendly world, widespread application and use of these materials has been limited by their relatively low properties in comparison to traditional composite materials. The vast majority of research to date on biocomposites has focused on randomly-aligned fiber reinforced composites with low to moderate strengths. The limited amount of research that has been done on unidirectional natural fiber-reinforced biocomposites has shown immense promise for the development of higher strength biocomposites. Recent research has shown that with the proper selection of material constituents and processing methods, higher strengths can be achieved in biocomposites.

The goal of the research reported in this thesis was to develop high strength biocomposites based entirely on renewable resources. Research efforts in the area of polymers derived from natural renewable resources are rapidly increasing. As a result of these research efforts, technological advancements have led to an increase in the number of commercially available biopolymers having properties competitive with traditional petroleum derived polymers. In the initial stages of the study a review of the literature using biopolymers as a composite matrix material was conducted (see Chapter 2). As was shown in this review, several researchers have investigated the use of cellulose esters and its conjugates as the matrix material in biocomposites [1-10]. Cellulose is a naturally occurring and abundant material, making it an attractive substitute for the diminishing petroleum resources traditionally used as base materials for the production of polymers. The general chemical structure of cellulose esters is shown in Figure 3.1. As shown, the R of cellulose esters is replaced by acyl groups (RCO-), thus allowing the carbonyl and hydroxyl groups good potential to form hydrogen bonds with the hydroxyl groups of cellulosic fibers (Figure 3.2). Research results show cellulose based polymers to have properties competitive to commonly used thermoplastic polymers such as polypropylene used for composites, making their potential for the use in biocomposites evident [10].

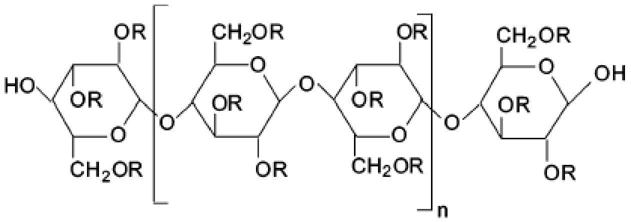

Figure 3.1: Chemical Structure of cellulose esters: R = H (cellulose), actyl (cellulose acetate), acetyl and propionyl (cellulose acetate propionate), or acetyl and butyryl (cellulose acetate butryate) [10]

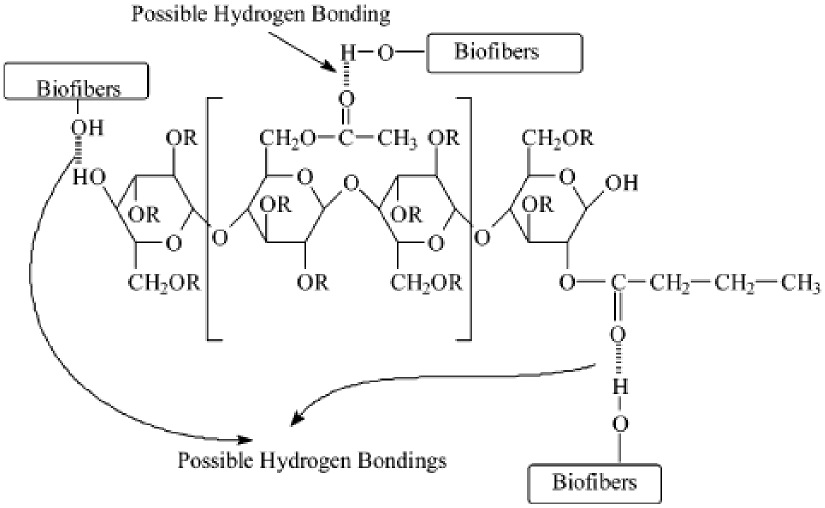

Figure 3.2: Possible hydrogen bonds that can be formed between natural fibers and cellulose ester matrix [10]

To further achieve the goal of developing renewable resource based composites, several types of natural fiber reinforcements were investigated including hemp, flax, jute, and ramie. In the initial stages of the study a review of the literature using these various plant fibers as composite reinforcement was conducted (see Chapter 2). Based on the findings of this review, bast fibers, specifically hemp, were chosen as the biocomposite reinforcement in the current study. The hemp fibers were ultimately chosen for their high mechanical properties, resistance to moisture and environmental attack, low costs, and their crop characteristics including fast growth, high yields, and the ability to be grown and processed in a wide range of geographic regions including the United States. Prior work within the research group had attempted to use raw 'uncut' hemp fibers as the reinforcing material in unidirectional-aligned biocomposites [11]. However, alignment of the hemp fibers proved extremely time consuming and overall fiber volume fractions were found to be too low to achieve the desirable strength levels. Additionally, the strength of the raw hemp fibers was lower than desired due the presence of degraded or damaged areas. Hemp yarns, traditionally used in textile applications, were therefore investigated as the reinforcing material for unidirectional-aligned biocomposites. Such natural fiber yarns consist of many micro-scale filaments spun together to form a continuous bundle of material. The resulting yarns can be spun to diameters lower than those of raw natural fibers allowing for greater fiber packing, and correspondingly higher possible fiber volume fractions, in composites.

3.1.1 Cellulose Acetate Butyrate (CAB) Resin

Two plasticized cellulose ester resins, CAB-381-20 (further referred to as resin A) and CAB-381-2 (further referred to as resin B), were obtained in powdered form from Eastman Chemical, Kingsport, Tennessee, USA. In these polymers, acetyl groups as well as a moderate amount of butyryl groups (~37%) replace the R groups in the chemical structure of cellulose acetate (Figure X). The butyryl groups lower the melt viscosity, allowing for easier polymer processing over traditional cellulose acetate (CA). In addition, the CAB polymers possess excellent surface hardness and good strength in comparison to CA polymers. The two CAB formulations were chosen for use in natural fiber composites based on the manufacturer provided mechanical and processing characteristics shown in Table 3.1. It can be seen that the acetyl, butyryl, and hydroxyl contents of the two resins are nearly identical; however, the viscosity and melt characteristics of the two resins differ greatly. The effect of these differences on polymer performance in a biocomposite will be investigated in this study.

Table 3.1: Manufacturer provided properties of cellulose acetate butyrate resins

Resin	Butyryl content (avg. wt %)	Acetyl content (avg. wt %)	Hydroxyl content (avg. wt %)	Viscosity (poises)	Melting Range (°C)	Specific gravity	Glass transition temp (°C)	Molecular weight (Mn)
A	37	13.5	1.8	76	195-205	1.2	141	70,000
B	38	13.5	1.3	7.6	171-184	1.2	133	40,000

3.1.2 Hemp Fiber Reinforcement

The goal of the project was to manufacture high strength unidirectional hemp reinforced composites. Industrial grade wet spun long fiber hemp yarns of varying sizes were obtained through Hemp Traders, Los Angeles, CA, USA. The yarns used were industrial weaving grade, size 16N, in both single- and double-ply form. Specific values needed for composite manufacture such as linear density, cross sectional area, twist angle, or mechanical properties of the hemp yarns were not provided by the manufacturer.

Investigation into these properties was therefore necessary to sufficiently characterize the yarns for the purpose of composite reinforcement.

3.2 **Test Methods**

3.2.1 Resin Characterization

3.2.1.1 Processing Parameters

Specific information regarding the optimal processing parameters for compression molding of the CAB resin was not provided by the manufacturer. Preliminary experimentation showed that the melting range temperatures for either resin system could not be directly used as a processing window for compression molding. Therefore, a series of experiments involving compression molding of powder resin under varying temperatures were performed to determine a processing window for each resin system. The tested temperature range for each set of CAB formulations was chosen based on manufacture provided data for melt temperature and results from previous published works [1,9,10,12-14].

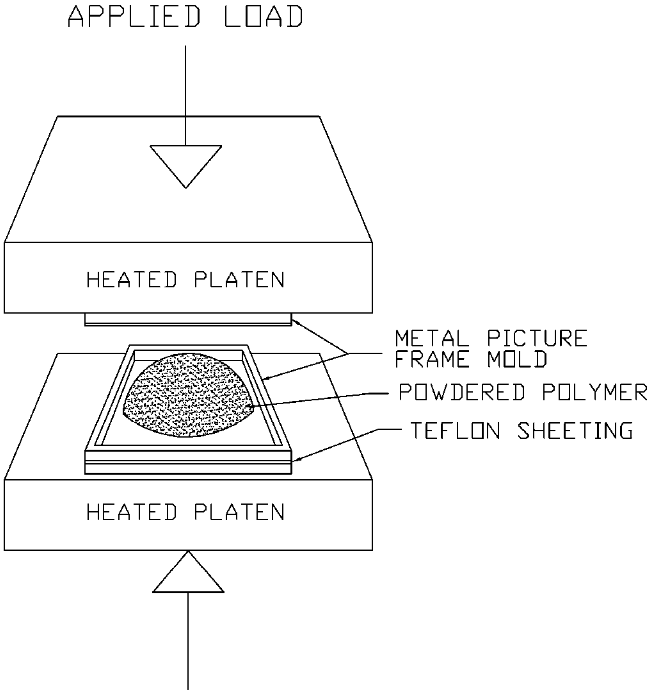

Figure 3.3: Schematic of resin sheet formation using a picture frame mold

Neat resin sheets of approximately 127 mm (5 in.) square were made by compression molding a defined amount (30 g) of the CAB in powder form in a picture frame mold (Figure 3.3). The compression molding process involved first heating the powdered resin in the mold for 5 minutes under constant temperature and no pressure. A pressure of 13.8 N/mm^2 (2000 psi) was then applied to the mold and held for 10 minutes under constant temperature. The mold was then removed from the hot press and cooled under 13.8 N/mm^2 (2000 psi) of pressure for a minimum of 10 minutes or until ambient temperature was reached.

3.2.1.2 Mechanical Properties

Mechanical properties of the CAB resins were not provided by the manufacturer. Additionally, the review of the literature found that published mechanical values for CAB resins varied greatly between research groups [1,9,10,12-14]. Therefore, preliminary tests were conducted to determine the required strength and stiffness values for the neat resin systems to be used in this study. Tension tests were performed, according to ASTM D 638 [15] at a cross-head speed of 5 mm/min, to determine mechanical properties of the resin and the relationship of these properties to the resin processing temperature. Rectangular shaped specimens of approximately 127 mm x 13 mm x 1.5 mm were machined using a wet tile saw from the compression molded neat resin sheets. The specimens were dried in an oven for 1 hour at 40°C to remove any excess moisture that may have been absorbed during the machining process. The samples were then conditioned according to the ASTM standard for a minimum of 40 hours prior to testing. The overall gage length of the test specimens was 75 mm and an extensometer was used during testing with a gage length of 25.4 mm. At least five specimens were tested from each processing temperature and the results were then averaged to produce mean values.

3.2.2 Fiber Characterization

3.2.2.1 Fiber and Yarn Dimensions

Diameters, and cross sectional areas of both the hemp fibers and corresponding yarns were determined using an optical microscope and image analysis. Samples of hemp yarn reinforced composites (see Chapter 4) were suspended in a 2-part acrylic resin. The resin was allowed to cure for 24 hours before polishing. The surface of the specimen perpendicular to the fiber direction was wet polished using a combined Streurs RotoPol-22 and RotoForce-4 unit. Settings for the polishing procedure were 300 RPM, at 25 N pressing force, for 5 minutes each at 800, 1200, and 2400 grit silicon carbide grinding paper. The polished surface was then cleaned with deionized water and dried with pressurized air. Cross-sections of the yarn were observed using a Mitutoyo Series FS60 optical microscope at various magnifications. Digital images of the cross sections were taken using as Sony DKC-5000 Catseye^{TM} digital still camera mounted on the optical microscope. All analysis of the images was done using Java based ImageJ software.

3.2.2.2 Linear Density of Yarn

The linear density of the fiber reinforcement was needed to accurately gauge the expected weight percentages of fibers in the unidirectional composites. In addition, the linear density can be used in combination with the cross-sectional area to estimate an average value for the density of the solid region of the hemp yarns. Linear density values for the two yarns were determined from dry weights of 10 m yarn samples. A minimum of 5 samples were used from various parts of the yarn spools and average values were reported in the standard unit of tex (g/1000m).

3.2.2.3 Fiber Twist Angle

Scanning electron microscopy (SEM) images (100x magnification) of both yarns were obtained using an FEI Quanta 600 instrument. Image analysis was then performed using ImageJ software to determine the yarn twist angle. The twist angle was determined by taking the angular deviation of the surface fibers from the overall yarn longitudinal axis. Twist angles were taken at different points along the yarns with results including both a range and average twist value.

3.2.2.4 Mechanical Properties

Yarn tension tests were performed to determine mechanical properties of the single- and double-ply hemp yarns. Tension tests were performed using an Instron testing machine Model 5565 with a 2 kN load cell and cross-head speed of 5 mm/min. All yarns were kept at standard conditions of 23 ± 2°C and 50 ± 5% relative humidity prior to testing. Yarn specimens of 75 mm were cut and weighed to determine average linear density of each tested yarn specimen. Values for approximate yarn cross-sectional area were then back-calculated using the measured linear density of each sample and the previously determined density of the hemp fibers. The specimens were loaded in tension until failure and values of tensile strength, modulus, and elongation were calculated. The yarns were tested at two gage lengths of 5 and 10 mm. The longer gage length allowed for fiber slippage in the yarns, resulting in uncharacteristically low mechanical properties in the yarns. The data from the 5 mm gage length tests was regarded as standard for the yarns; therefore, this data was used for the remainder of the study on composite analysis. However, the comparative data is useful as an indication of loss in fiber efficiency due to slippage within the twisted yarn bundles.

3.3 Results of Constituent Characterization

3.3.1 Cellulose Acetate Butyrate (CAB) Polymer Matrix

The mechanical properties and processing parameters for the cellulose resin systems were evaluated based on their use in a natural fiber reinforced composite. The molecular weight of a polymer is directly proportional to the length of its polymer chains. Typically, the longer the polymer chains the greater the level of chain entanglement, and therefore the better the polymer mechanical characteristics such as tensile strength. It has been suggested that the minimum molecular weight required for a polymer to have good physical and mechanical properties is around 25,000 g/mol [16]. It is expected that both cellulose resins in this study will have sufficient mechanical properties for use as a matrix in natural fiber composites as both have average molecular weights well above this value, with manufacturer provided values of 70,000 and 40,000 g/mol for resins A and B, respectively. However, the difference in molecular weight values between the two resin systems is expected to have an effect on their respective processing parameters and mechanical properties.

In the melt state, polymer chain entanglements cause the viscosity to be raised significantly [16]. The melt flow characteristics, or viscosity of the resin under temperature and pressure, is an important parameter to consider when using a thermoplastic polymer for composites. For fiber reinforced composite applications, lower viscosity resins are typically advantageous as they allow for better impregnation of the reinforcing fibers. In addition, this results in lower void content in the composite and better bonding between the fiber and matrix. Mechanical properties including strength, stiffness, and elongation of a polymer resin are also important parameters to determine when using it as a matrix in composites as these properties will directly effect the overall mechanical properties of the final composite product.

3.3.1.1 Physical Effects of Processing Conditions

For resin system A, temperatures of 180, 185, 190, 195, and 200°C were used during the compression molding process. At temperatures of 180°C or lower it was found that the viscosity of the resin was high, therefore, compression molding required the application of excessive pressure to get adequate resin flow to fill the mold. In contrast, at processing temperature of 195°C or higher resin flow was very good, however, discoloration (Figure 3.4) and odor was present in the final resin sheets suggesting that degradation of the polymer was occurring at these high temperatures. These physical results suggest that an optimal processing window for compression molding of cellulose resin system A exists between 185-190°C.

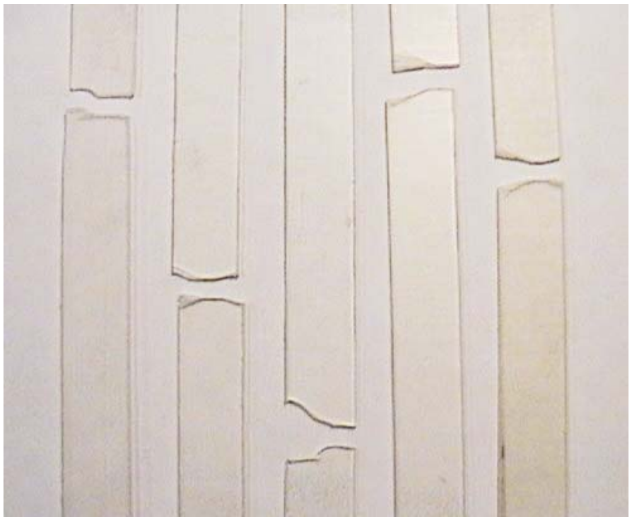

Figure 3.4: Physical appearance of neat resin A samples processed at various temperatures (samples from left to right processed at 180, 185, 190, 195 and 200°C)

For resin system B, temperatures of 180, 185, and 190°C were used during the compression molding process. Based on the results from resin A, it was expected that resin B would show some signs of degradations at the chosen processing temperatures as they are on the high side of the manufacturer provided melting range. However, no discoloration or odor was noticed at the lower temperatures and only slight discoloration (Figure 3.5) and odor was present in the sheet processed at 190°C. The melt flow properties of resin system B in the chosen temperature range were very good. However, when processing temperatures below 180°C were investigated; inadequate transverse flow of the resin was found even under excess pressure. The resulting resin sheets were therefore thick and did not fill the entire mold. Based on necessary melt flow characteristics and to avoid the possibility of polymer degradation optimum processing temperatures of resin system B were determined to be between 180-185°C. It was therefore found from the preliminary processing tests that the two cellulose resins have very similar processing windows for compression molding.

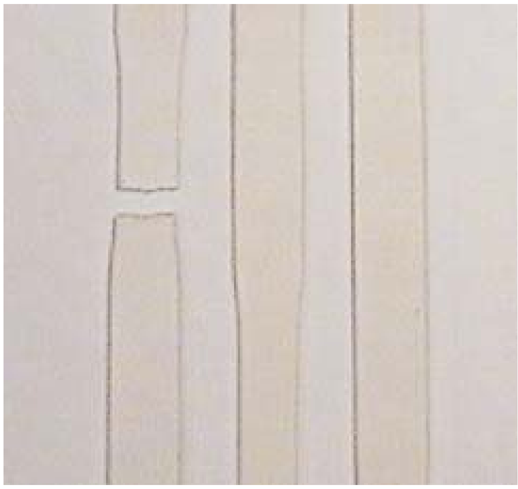

Figure 3.5: Physical appearance of neat resin B samples processed at various temperatures (samples from left to right processed at 180, 185 and 190°C)

Although the two CAB polymers are virtually identical in chemical structure, the manufacturer reported average molecular weights of resin A and B differed from 70,000 to 40,000, respectively. The difference in molecular weight between polymer A and B was believed to influence the viscosity of the two polymers during melt processing, where the melt viscosity was lower for resin B, with the lower average molecular weight. Although the lower melt viscosity of resin B was expected to be advantageous for composite processing, the exact impact of this characteristic on final composite performance was unknown.

3.3.1.2 Mechanical Effects of Processing Conditions

Tension tests were performed on the resin samples processed at the different temperatures considered. A minimum of 5 samples at each processing temperature for resin systems A and B were tested and the averaged results are shown in Table 3.2 and compared in Figures 3.6-8. Trends in test data show the effect of varying processing temperature on mechanical properties of the cellulose resin. These results were then used to define an optimized composite processing window for the resin system.

Table 3.2: Mechanical Properties of CAB Resins

Resin System	Processing Temperature °C	Tensile Strength MPa (Stdev)	Tensile Modulus GPa (Stdev)	Ultimate Elongation % (Stdev)
A	180	37.96 (1.25)	1.82 (0.09)	11.09 (8.09)
	185	42.43 (2.02)	2.08 (0.05)	12.91 (12.75)
	190	43.33 (0.86)	2.15 (0.09)	6.38 (0.77)
	195	36.08 (4.76)	2.15 (0.09)	3.98 (2.07)
	200	29.04 (3.91)	2.07 (0.09)	2.19 (0.53)
B	180	43.53 (0.96)	1.89 (0.26)	22.3 (2.33)
	185	41.9 (2.41)	2.09 (0.10)	36.2 (29.89)
	190	40.84 (1.40)	2.05 (0.14)	17.79 (9.50)

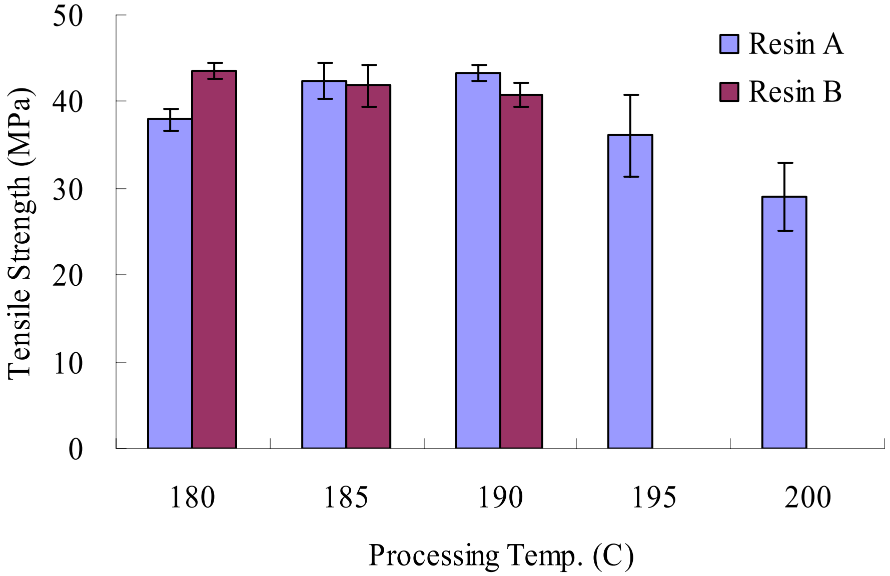

Figure 3.6: Effect of Processing Temperature on Neat Resin Tensile Strength

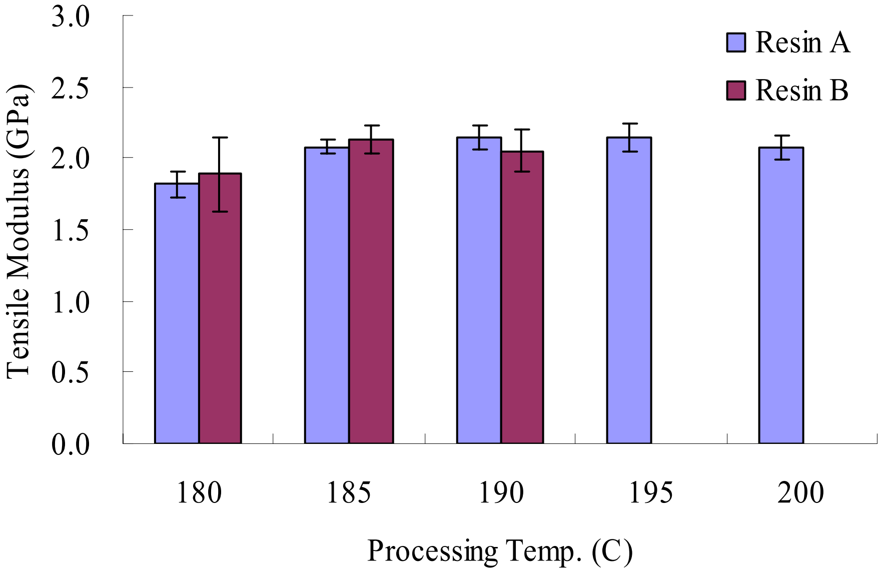

Figure 3.7: Effect of Processing Temperature on Neat Resin Tensile Modulus

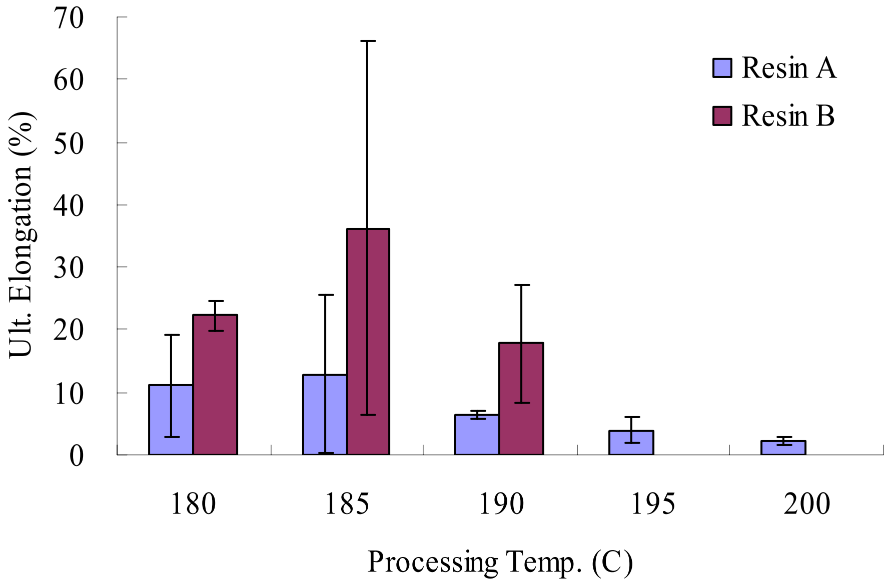

Figure 3.8: Effect of Processing Temperature on Neat Resin Ultimate Elongation

The tension test results for the resin samples processed at each temperature are shown in Table 3.2. For resin A, average tensile strengths are highest for the samples processed between 185-190°C with a noticeable reduction in tensile strength in the samples processed at temperatures above 190°C. The decrease in tensile strength values for resin system A processed at temperatures above 190°C seem to verify the existence of polymer degradation as was suggested by discoloration of the polymer sheets after processing. Modulus values for the resin samples processed at temperatures of 185°C or above are relatively similar, with the highest values obtained in resin samples processed between 190-195°C. The trend in this data suggests that at temperature above 200°C the modulus of the polymer would decrease.

For resin B, average tensile strengths were highest for the samples processed at 180°C with a reduction in tensile strength being seen in the samples processed at temperatures at 185°C or above. This trend suggest that at temperature above the processing range used, strength values would continue to decrease, similar to the trend seen in the strength data for resin A at higher temperatures. The modulus data for resin B also has a peak value of 2.09 GPa occurring at 185°C. The test results in combination with visual observations suggest that temperatures resulting in significant degradation of the polymer were not used. However, further testing of samples processed above 190°C was not performed as this temperature was believed to be on the threshold of optimal processing conditions as suggested by the slight discoloration in the resin sheets processed at this temperature and the downward trends of both the strength and modulus data.

Mechanical properties of the two CAB polymers investigated in this study were found to be similar. Although, there were not significant differences in polymer mechanical performance, resin A did exhibit slightly higher average values of strength and stiffness and lower elongations during mechanical testing. The slightly lower mechanical properties of resin B were expected to be detrimental to composite performance. Since the relative impact of polymer parameters on the final composite performance was unknown it was decided that both resin A, with the higher viscosity and mechanical properties, and resin B, with the lower viscosity and mechanical properties, would be used to fabricate the biocomposites. Additionally, it was expected that manufacturing composites with both resins could provide valuable insight about the importance of these resin properties on composite performance that could be of assistance during future materials selection.

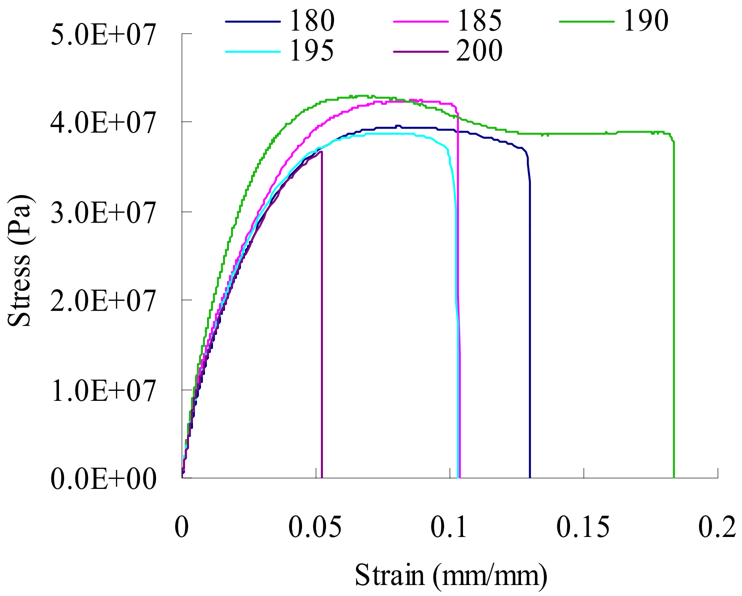

Figure 3.9: Effect of processing temperature on typical stress-strain curves for resin A

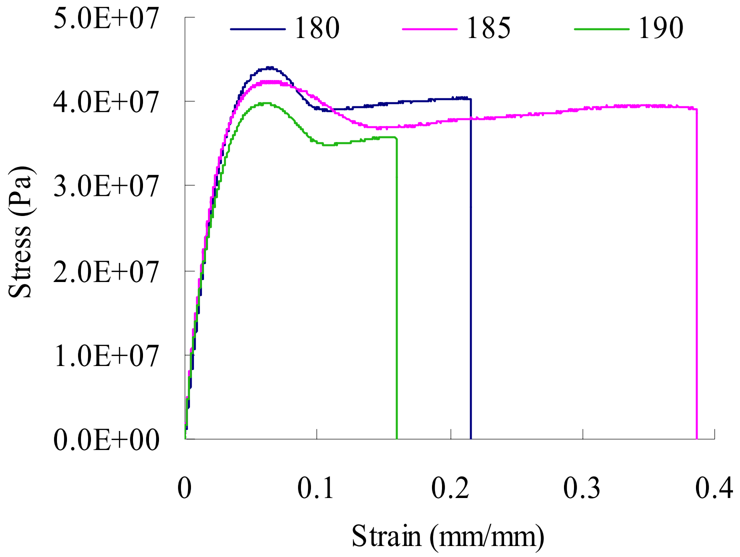

Figure 3.10: Effect of processing temperature on typical stress-strain curves for resin B

Previous literature has shown similar cellulose resin systems to be amorphous polymers [13]. Typical stress-strain curves for the CAB polymers used in this study (Figure 3.9 and 3.10), exhibit a clear initial linear elastic range and then yielding as a result of material necking, often times followed by ductile elongation. Changes in stiffness and elongation properties of the resins processed at various temperature profiles suggest that changes in the polymer orientation and structure occur. When the cellulose polymers are processed at temperature below melting, complete flow of the material is not obtained resulting in residual internal stresses. These internal stresses are the likely explanation for lower mechanical properties. As the processing temperature is increased to allow for adequate flow, internal stresses between the polymer chains are released and chain entanglement is increased allowing for increased mechanical properties. When processing temperatures of the natural polymers are further increased, however, degradation of polymer covalent bonds occurs. This results in the formation of polymers with smaller chain segments (lower molecular weight) and likewise a reduction of the materials' mechanical properties. This can be seen in both resins, where at higher temperatures the polymers exhibit discoloration and lower values of strength, modulus, and elongation before break.

3.3.2 Hemp Fiber Reinforcement

By definition, a yarn is a linear assemblage of fibers formed into a continuous strand having textile-like characteristics including substantial tensile strength and flexibility [17]. Yarns are typically classified by their type of filaments and assembly structure (Figure 3.11). Monofilament (a) or multifilament (b-c) yarns consist of one or more continuous fibers, respectively, and can be either twisted or untwisted. Spun yarns (d) on the other hand are composed of many discontinuous staple fibers and require a substantial amount of twist or entanglement to form a functional yarn and to resist slippage of the fibers. Additionally, two or more yarns can be twisted together to form plied yarns. The properties of yarns greatly depend upon the physical properties of the constituent fibers as well the structure of the yarn itself.

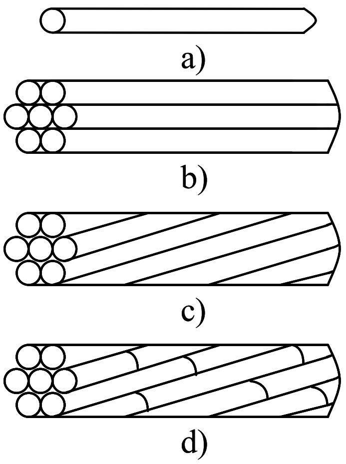

Figure 3.11: Idealized models of a) monofilament, b-c) multifilament, and d) spun yarns

3.3.2.1 Physical Characteristics

The degree of fiber twist in yarns is an important characteristic to know when using them for composite reinforcement. The angled fibers in each yarn make the overall fiber orientation of the composite non-unidirectional. The composite can therefore be expected to be weaker in the longitudinal direction than a true unidirectional aligned fiber composite, but more resistant to shear loading. To determine the fiber twist angle in the single- and double-ply yarns used in this study, SEM images were taken of the yarn surfaces and the fiber angles were measured relative to the longitudinal axis of the yarn. It can be seen in Figures 3.12 and 3.13 that the single-ply yarns exhibited a Z-twist structure, whereas the double-ply yarns exhibited an S-twist structure resulting from the combination of two Z-twist single-ply yarns [18]. This is an important distinction to be made between the single- and double-ply yarns as this twist structure will affect the twist angles of the individual fibers within the yarn.

Results from SEM image analysis confirm the difference in fiber twist angles between these two yarns. Figure 3.12 shows the fiber twist angles within the single-ply yarns. The angle of twist of these fibers relative to the longitudinal axis of the yarn ranged from 8 to 18 degrees. Figure 3.13 of the double-ply yarns, however, showed very different results. In this case the angle of the fibers relative to the longitudinal yarn axis is much smaller, between 3 and 5 degrees. The ply twist angles, however, are between 15 and 30 degrees, which overlap with the range of values seen for the fiber twist angle in the single-ply yarn. For spun yarns like the ones used in this study the interior fibers are nearly parallel to the yarn axis with an increasing angle of twist moving from the inner to outermost fibers in the yarn. A model to predict average fiber twist can be used which suggests that mean twist angle is related to the surface twist angle by a factor of 0.7 for yarns with surface twist of less than 40 degrees [18]. Based on this model, the mean fiber twist angles for the single- and double-ply yarns can be estimated at approximately 9 and 16 degrees, respectively. These values correspond well to those reported by Madsen [19] for similar single-ply hemp yarns where exterior fiber twist values between 15-16 degrees and mean yarn twist values of 11 degrees were found. The yarn twist structures are expected to affect the mechanical properties of the yarns, however, estimates of the effect are difficult to predict.

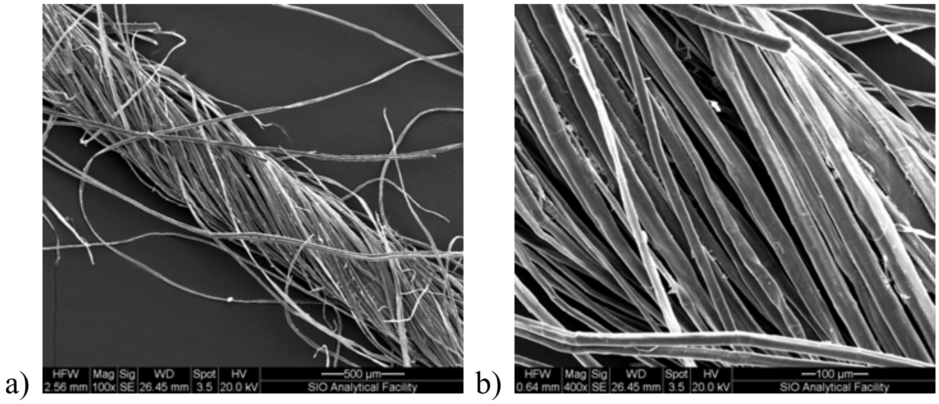

Figure 3.12: SEM images of single-ply hemp yarn, a) magnification 100x, b) magnification 400x

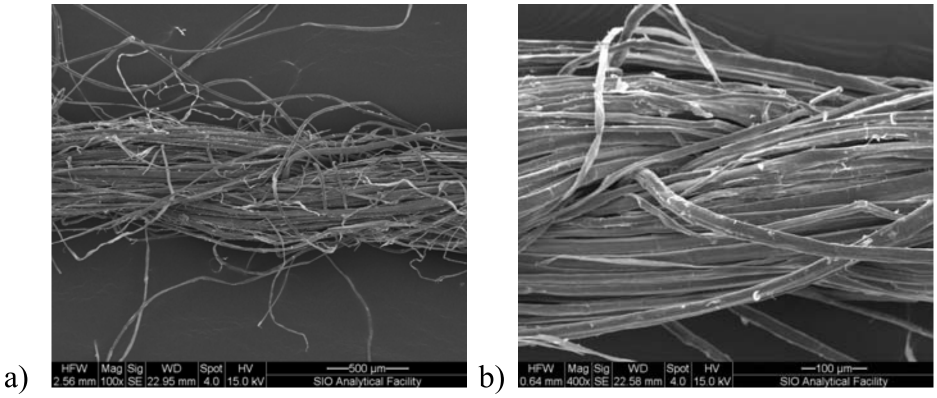

Figure 3.13: SEM images of double-ply hemp yarn a) magnification 100x, b) magnification 400x

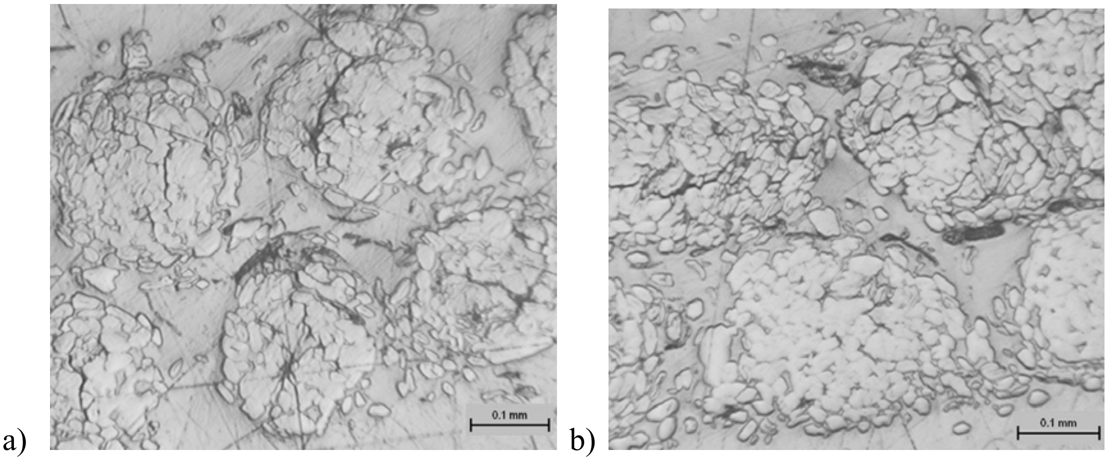

Figure 3.14: Optical Microscope pictures of yarn cross-sections embedded in CAB polymer matrix, a) single-ply, b) double-ply

Optical microscope images of the yarn cross-sections (Figure 3.14a-b) were analyzed to determine average values for diameters and cross sectional areas of individual hemp fibers and hemp yarns. Samplings of 100 individual hemp fibers were measured for diameter and cross-sectional area. The hemp fibers had significant variation in size. Diameters ranged from 6 to 42 μm with an average fiber diameter value of 18 μm (Figure 3.15). Cross-sectional areas for the hemp fibers ranged from 24-919 μm^2 with an average value of 239 μm^2 (Figure 3.16). Diameters (100 samples) and cross-sectional areas (30 samples) of the single- and double-ply yarns were also measured using the optical microscope images. Single-ply yarn diameters ranged from 141 to 391 μm with an average yarn diameter of 239 μm (Figure 3.17). The cross sectional area for these yarns was found to be between 0.028 and 0.061 mm^2 ($28\text{-}61 \times 10^3\ \mu m^2$) with an average value of 0.043 mm^2 ($43 \times 10^3\ \mu m^2$) (Figure 3.18). Similarly, double-ply yarn diameters ranged from

301 to 645 μm with an average yarn diameter of 417 μm (Figure 3.19). The cross sectional area for these yarns was found to be between 0.038 and 0.093 mm^2 (38-93 x 10^3 μm^2) with an average value of 0.060 mm^2 (60 x 10^3 μm^2) (Figure 3.20).

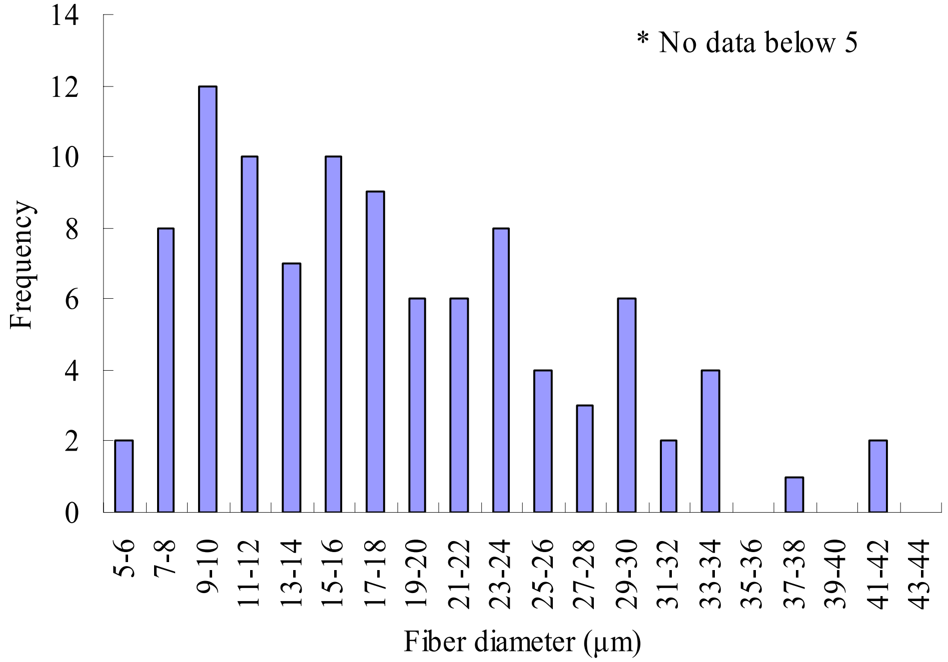

Figure 3.15: Statistical distribution of measured hemp fiber diameters

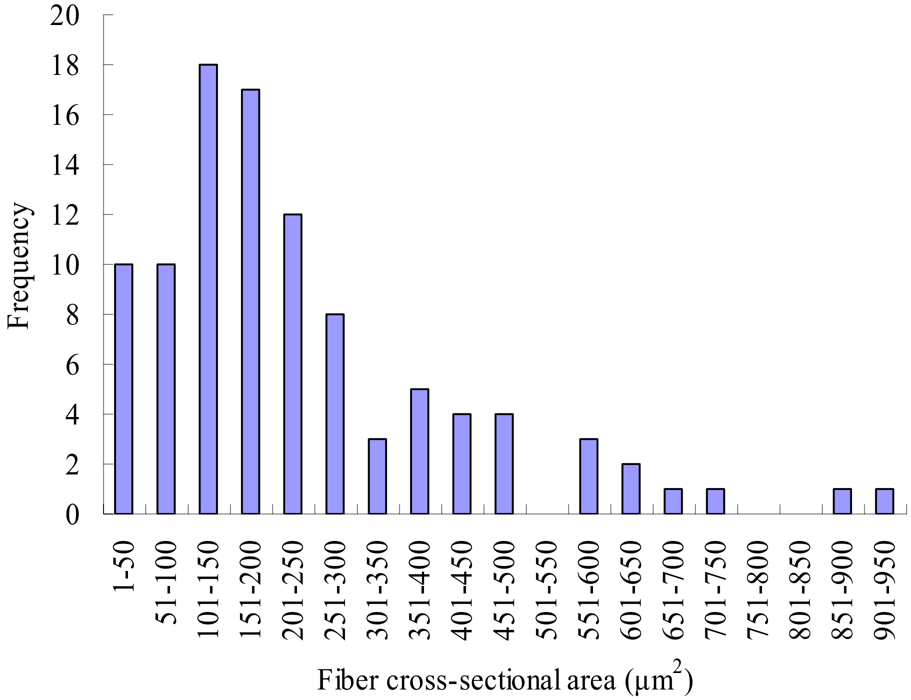

Figure 3.16: Statistical distribution of measured c-s areas of hemp fibers

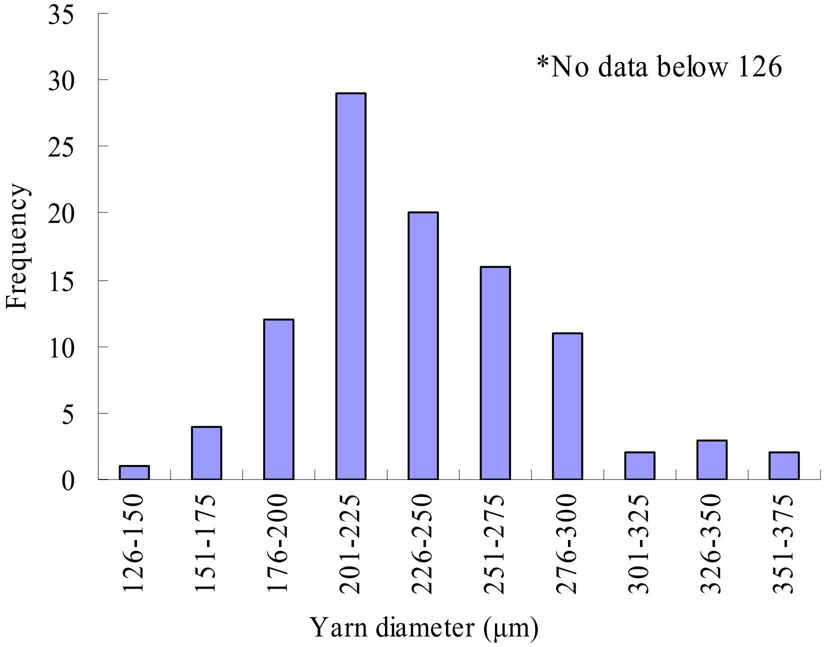

Figure 3.17: Statistical distribution of measured diameters of single-ply hemp yarns

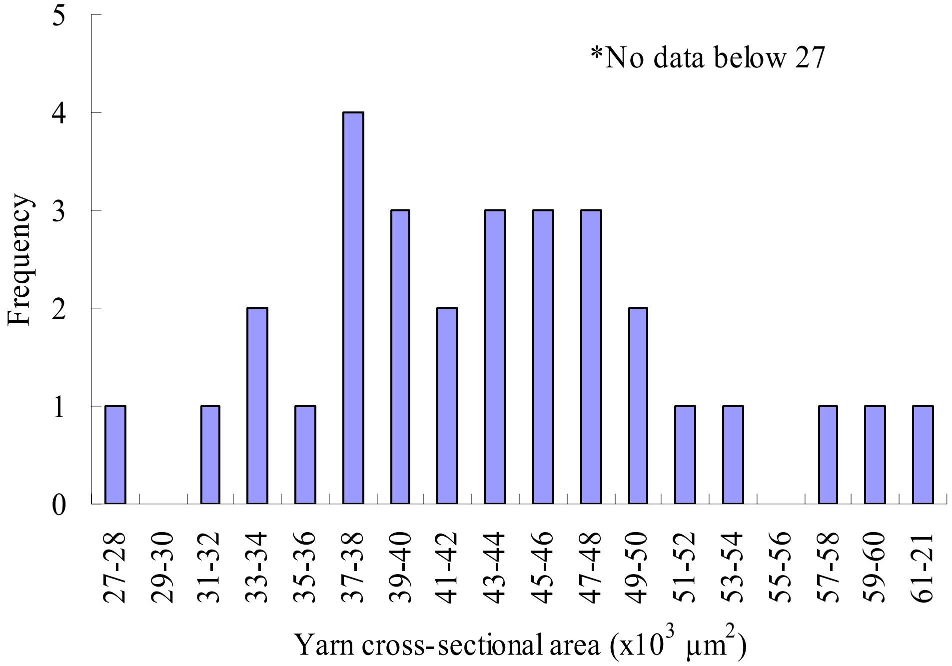

Figure 3.18: Statistical distribution of measured c-s areas of single-ply hemp yarns

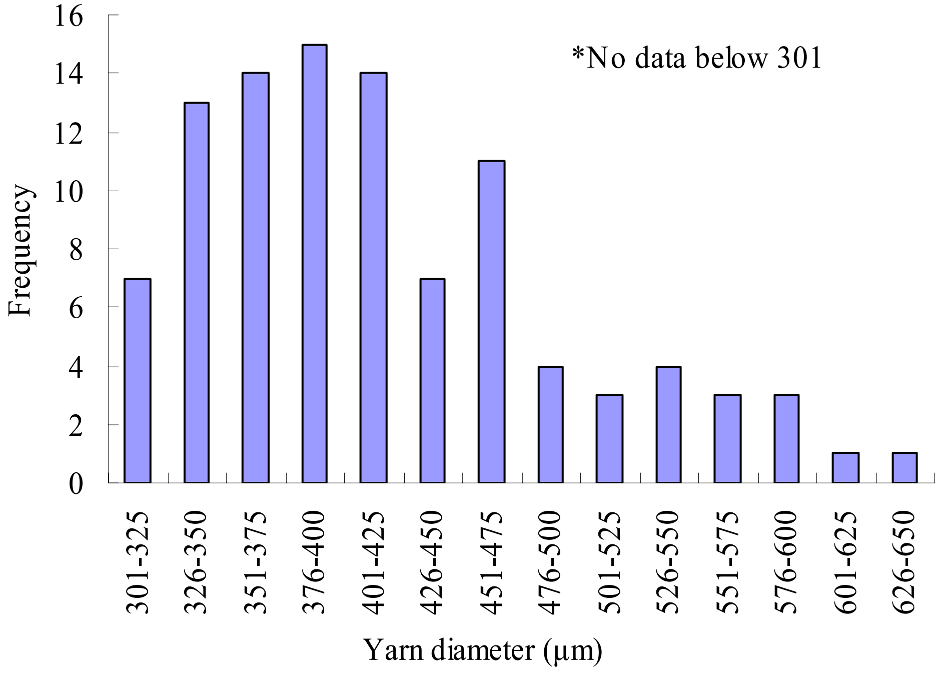

Figure 3.19: Statistical distribution of measured diameters of double-ply hemp yarns

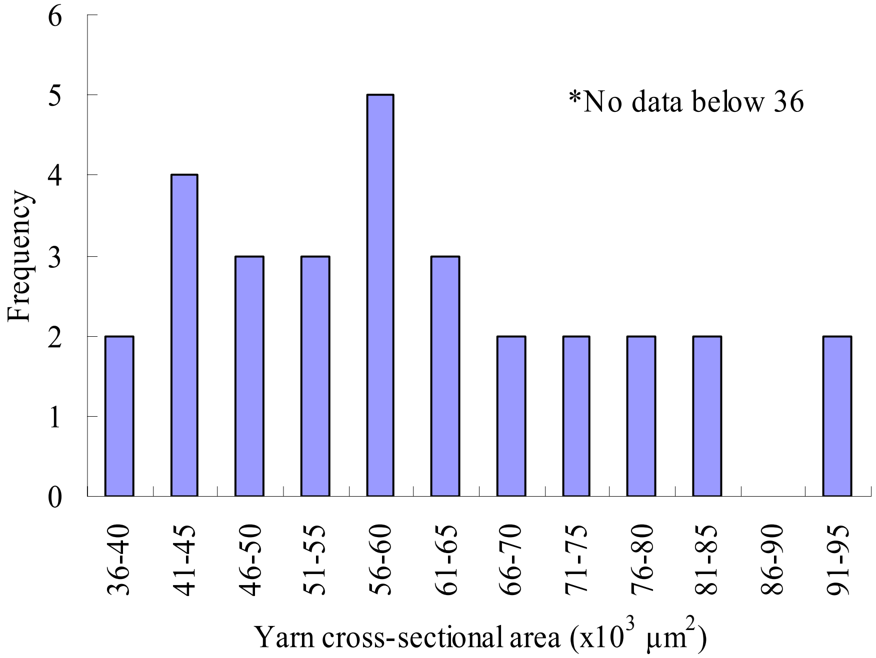

Figure 3.20: Statistical distribution of measured c-s areas of double-ply hemp yarns

Five 10 m long samples were measured and cut from each spool of yarn conditioned under ambient conditions (23 ± 2°C and 50 ± 5% RH). The linear density of the single-ply yarn ranged from 54.1 to 64.6 tex (g/1000m) with an average value of 58.1 tex. Values for the double-ply yarn ranged from 113.8 to 125.6 tex with an average value of 120.4 tex. Not surprisingly, the linear density values for the double-ply yarn are slightly greater than twice the values for the single-ply yarn. This can be attributed to the fact that the double-ply yarn is two single-ply yarns twisted together leading to a higher fiber density per unit length than if the two single-ply yarns were run parallel to one another.

Ideally, the density values for both the single- and double-ply yarns should be identical as they are both made from the same hemp fibers. By taking the average linear density of each yarn and dividing it by its corresponding average cross-sectional area, an estimated average density of the hemp yarns was determined to be 1.53 g/cm^3. Findings by Madsen et al. [19], show the density of hemp fibers used in similar industrial grade yarns to be between 1.58 and 1.6 g/cm^3.

The yarn density value in this study is higher than the commonly published value for hemp fibers of 1.47 g/cm^3 [20]. This value is, however, based on raw hemp fibers having a reported cellulose content of 70-74 wt%. Common chemical and physical pre-treatments used in the production of hemp textile yarns are known to reduce the content of hemicellulose, lignin, and non-cell wall materials (e.g. pectin and waxes) in raw hemp fibers. This results in an increase of cellulose content from 70-74 wt% in raw field retted hemp fibers to 83–90 wt% in treated fibers used for textiles [21]. Additionally, a study by Thygesen et al. [22], found the degree of crystallinity of cellulose in comparable hemp yarn fibers to be 90-100 %. Pure crystalline cellulose has been found to have a density of 1.64 g/cm^3 [19]; therefore, this density can be assumes to be the upper limit value that can be expected for plant fibers. The relatively high density values found for the hemp fiber yarns used in this study can therefore be explained by their chemical and physical pre-treatments resulting in increases in both the cellulose content and its degree of crystallinity.

3.3.2.2 Mechanical Properties

The fibers used for composite reinforcement in this study were industrial grade hemp yarns developed for the textile industry. As a result, mechanical characterization data provided by the manufacturer for the two hemp yarns was difficult to correlate when predicting composite properties. To determine the necessary mechanical properties for this study, tension tests were performed on the single- and double-ply hemp yarns. At least five samples of each type of yarn were tested and the results were used to determine average tensile strength, modulus and elongation values.

For mechanical testing, yarn specimens of 75 mm were cut and weighed and the linear densities and corresponding cross-sectional areas of the samples were determined for further calculations. The single-ply yarn specimens had linear densities ranging from 37 to 66 tex (g/1000m) with an average linear density for the sample lot of approximately 50 tex. Similarly, the double-ply yarn specimens had linear densities ranging from 80 to 127 tex with an average linear density for the sample lot of approximately 102.5 tex. Using the previously determined hemp yarn density of 1.53 g/cm^3 (See section 3.3.2.1), cross-sectional areas of each yarn specimen were estimated to be 0.0327 and 0.0667 mm^2 (32.7 and 66.7 x 10^3 μm^2), respectively. These area values were used in conjunction with the maximum load values from tensile testing to calculate tensile strength of the hemp yarns specimens.

While conducting preliminary test experiments to establish an optimized cross-head speed for testing the two yarn systems, it was found that when the hemp yarns were tested at gage lengths (GL) of 10 mm, the tensile strengths and modulus of the yarns (Figure3.21) were much lower than values reported in the literature [20,23]. These uncharacteristically low properties of the yarns were attributed to failure of the yarn by fiber slippage rather than fiber breakage. To account for this discrepancy in the fiber properties, the testing procedure was adjusted to use a minimum possible specimen gage length of 5 mm. This resulted in a greater ability to grip both ends of the staple fibers that make up the yarn. The difference in mechanical properties between the yarn specimens tested at a 10 mm gage length versus a 5 mm gage length, shown in Table 3.3 and Figure 3.19, clearly reflects the presence of fiber slippage at longer test gage lengths.

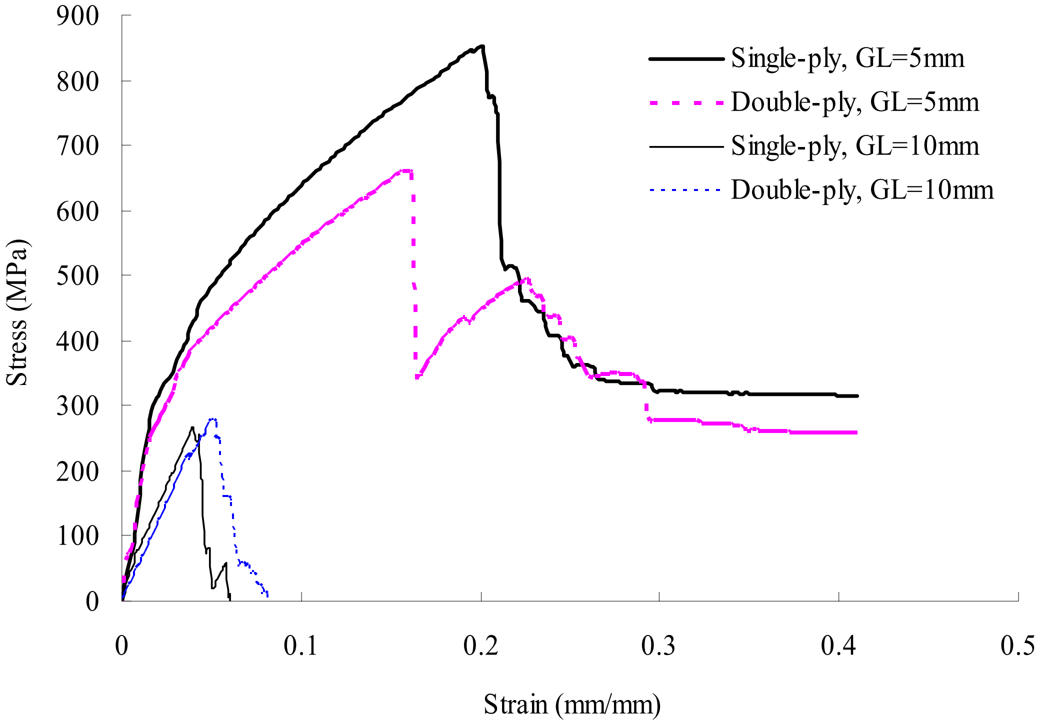

Figure 3.21: Typical tensile stress-strain relationships seen for yarns tested at varied gage lengths

Table 3.3: Mechanical properties of hemp yarns tested at various gage lengths

Yarn Sample		**Tensile Strength (MPa)**		**Elastic Modulus (GPa)**		**Elongation at Break (%)**	
		Average	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
5mm GL	Single-ply	869.43	91.05	9.43	2.57	15.95	2.51
	Double-ply	564.84	69.48	6.56	0.68	15.17	1.88
10mm GL	Single-ply	281.53	28.25	9.32	3.08	4.08	1.05
	Double-ply	298.22	44.40	7.35	1.04	5.37	0.57

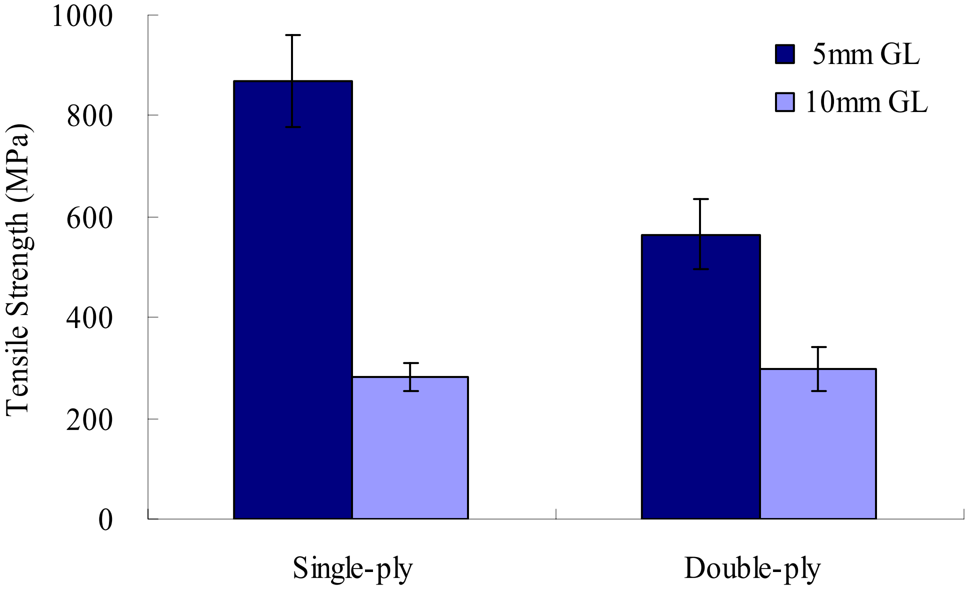

Figure 3.22: Comparison of tensile strength properties for single- and double-ply yarns tested at varying gage lengths

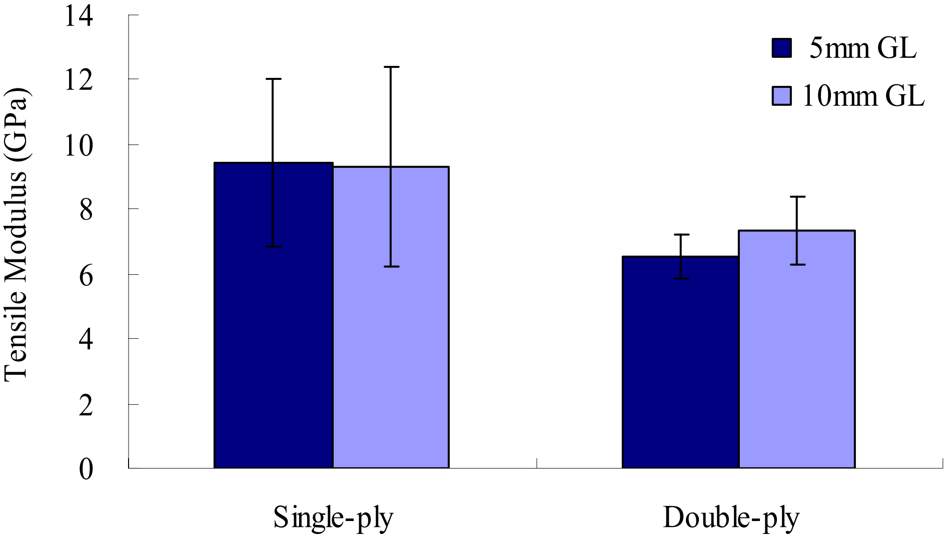

Figure 3.23: Comparison of elastic modulus properties for single- and double-ply yarns tested at varying gage lengths

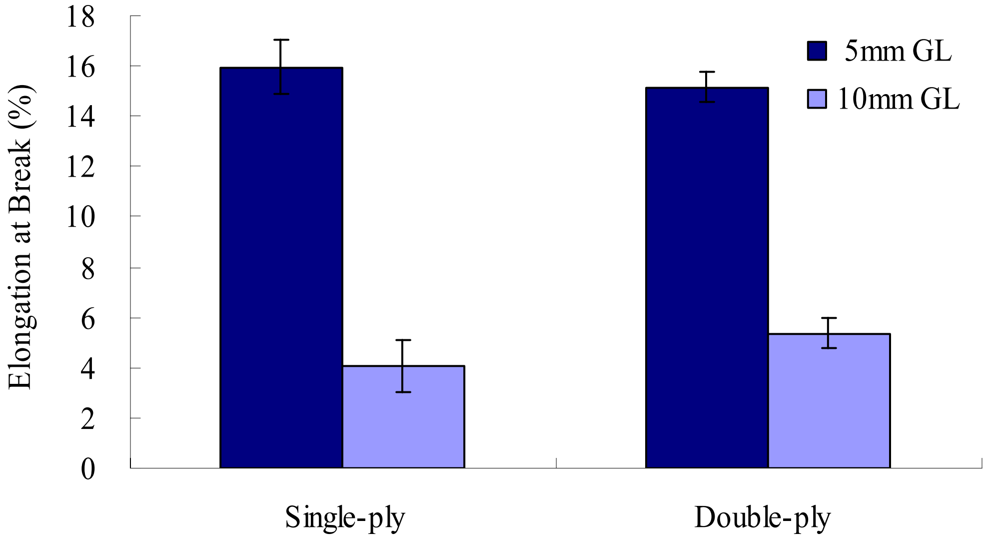

Figure 3.24: Comparison of breaking elongations for single- and double-ply yarns tested in tension at varying gage lengths

As shown in Table 3.3 and Figures 3.22-24, average strength and modulus values for the single-ply yarns tested at 5 mm gage lengths were 869.73 MPa and 9.43 GPa, respectively. Similarly, for the double-ply yarns tested at 5 mm gage lengths the average strength and modulus values were 564.84 MPa and 6.56 GPa, respectively. For both yarn types the strengths and modulus of samples tested at 5 mm gage lengths exceeded those samples tested at a gage length of 10 mm. Additionally, the ultimate elongations of the yarns tested at 5 and 10 mm were significantly different. These results can be explained by a change in failure mode of the yarn samples from fiber fracture to fiber slippage when switching between 5 and 10 mm gage lengths, respectively.

As expected, for yarn samples tested at 5mm gage lengths, the single-ply yarns with lower twist had significantly higher average values of strength and modulus than the higher twist double-ply yarns. This validates the hypothesis that fiber twist has a detrimental effect on the translation of fiber properties to yarn properties when fiber slippage is not an issue, such as in the case of filament yarns or spun yarns tested at short gage lengths. In contrast, when the specimens were tested at a longer gage length, the average strengths of the double-ply yarns exceeded those of the single-ply yarns. These results are likely attributed to the greater mechanical interlocking and frictional forces in yarns with higher fiber twist angles.

It has been shown that yarn structure, which can vary greatly in level of fiber twist and entanglement, plays a dominant role in the translation of fiber properties into yarn properties [17]. There are several ways that fiber twist can affect the properties of a spun yarn, like those used in this study. The effect of fiber slippage on staple yarn properties is a highly researched topic because of its consequence on yarns used in the textile industry. When a twisted yarn is put under axial tension, the twist causes transverse forces (hoop stresses) to develop, which in turn generate frictional forces between the fibers holding them together and giving the yarn its axial strength [23]. The greater the twist angle, the greater the hoop stresses when the yarn is under tension. For this reason, the effect of fiber slippage in spun yarns with high twist is minimal, and therefore they are commonly modeled like filament yarns where the strength of the yarn largely depends on the breaking strength of the fibers. In contrast, for low twist spun yarns fiber slippage and fiber pull-out are the predominant modes of failure.

In contrast to the previous relation, increased twist angles can also have a negative effect on the longitudinal mechanical properties of yarns. When high twist angles are introduced in fibers the longitudinal strength of the overall yarn is generally reduced, as the fibers are no longer loaded along their strong axis. Although the packing ratio and cross-sectional area of the yarns are generally increased, the strength of the yarns have been shown to decrease. This negative influence of high twist angles has been best shown for continuous fiber or filament yarns.

Several researchers have studied the relationship between filament twist angles and mechanical properties for the resulting yarns [17,23,24]. Simplified fiber to yarn strength translation efficiencies of various yarn structures are shown in Table 3.4, where the efficiencies mainly reflect the fiber twist angle, or orientation of the fibers relative to the yarn axis, and fiber entanglement [17]. As shown, the fiber strength efficiencies for spun yarns are significantly lower than for filament yarns. Additionally, the contrasting detrimental effect of increasing twist on filament yarns and beneficial effect of increasing twist on spun yarns is clear.

Table 3.4: Fiber to yarn strength translation efficiencies [17]

Yarn Structure	Strength translation efficiency (%)
Monofilament	100
Multifilament	
Untwisted	98
Slightly twisted	95
Spun	
Soft twisted	45
Hard twisted	67

More rigorous analytical methods including force-deformation analysis, energy analysis, and finite-element analysis have been used by researchers to model the mechanics of twisted staple yarns [23,25-27]. However, these works have found that the translation of properties from fibers to twisted yarns that are not inclined to fail by fiber slippage can generally be explained by the relation:

$$\frac{E_\alpha}{E_o} = \frac{f_\alpha}{f_o} = \cos^2 \alpha \tag{3.1}$$

where, E_α and E_o are the modulus of the twisted yarn and straight yarn, respectively; f_α and f_o are the strengths of the twisted yarn and straight yarn, respectively; and α is the twist angle of the outer fibers relative to the longitudinal axis of the yarn. In Table 3.5, typical properties for hemp fibers reported in the literature [28-31] are compared to the values found for the hemp yarns in this study. Additionally, the table includes predictions for the fiber strength and stiffness values based off of the relationship in Equation 3.1. These predictions were made using the average fiber twist angles determined for the single- and double-ply hemp yarns in Section 3.3.2.1. It can be seen that the strength values for both yarns are within the range of values published in the literature for hemp fibers. The modulus values, however, are significantly lower than the reported values.

Table 3.5: Comparison of hemp fiber properties

Property	**Strength (MPa)**	**Modulus (GPa)**
Published Values	550-900	40-70
1-Ply Experimental	869	9.5
1-Ply Theoretical* (α=8-18)	518-847	37-65
2-Ply Experimental	565	6.6
2-Ply Theoretical** (α=15-30)	466-763	34-60

*based off $\sigma_{th} = \sigma * \cos^2\alpha$

**based off $E_{th} = E * \cos^2\alpha$

High twist angles have also been shown to change the mode of failure for multifilament and spun yarns from gradual or quasi-ductile failure to catastrophic or instantaneous failure. It is typically assumed that the central fibers in yarns have little or no twist to them, putting them under the highest tensile stresses and strains during loading [23]. For this reason, these fibers typically break first when they have reached their ultimate strains, followed by gradual breakage of the fibers from center of the yarn outwards as they are strained to failure. This breaking pattern gives the yarns greater tenacity, allowing them to absorb more energy during failure. However for higher twist yarns, the transverse stresses in the fibers as a result of loading increase the friction between the fibers making them act like a homogeneous material subjected to uniform stresses and strains. As a result, when the breaking strain of the inner fibers is reached the entire yarn breaks in a brittle and instantaneous manner [23]. This failure usually occurs at stresses similar to those of low twist yarns; therefore, it is not so much the strength but the tenacity or toughness of the yarns that is reduced when high twist angles are present.

3.4 References

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4. COMPOSITE PROCESSING AND TEST PROCEDURE

4.1 Composite Constituent Selection

As described in Chapter 3, two versions of Cellulose Acetate Butyrate (CAB) were selected for use as the resin in a hemp fiber reinforced thermoplastic composite. The reinforcement was in the form of single- and double-ply industrial grade spun yarns. Details related to the manufacturer reported characteristics and results of tests carried out as part of the current investigation were reported in Chapter 3. Four composite systems, referred to as systems A1, A2, B1, and B2, were thus developed based on the combinations of the two CAB polymers and two hemp fiber yarns.

Table 4.1: Outline of hemp fiber-reinforced cellulose polymer composite systems

Composite System	CAB-381-20	CAB-381-2	Single-ply hemp yarn	Double-ply hemp yarn
A1	X		X	
A2	X			X
B1		X	X	
B2		X		X

4.2 Composite Processing Method

The ultimate goal of this project was the development of natural fiber reinforced biopolymer composites that could replace traditional synthetic or non-renewable materials used as non-primary load bearing building materials. A review of the current state of biocomposites technology suggested that the limited use of these materials is largely due to the lack of biocomposite materials currently developed with the level of mechanical performance necessary to carry significant load. Wood based materials, plastics, and glass fiber reinforced polymer (GFRP) composites were the most likely candidates for replacement with biocomposites. Therefore, the properties of these materials were used as the benchmark for evaluation of the biocomposites performance.

The successful manufacture of a composite material is dependent on several conditions. Selection of constituent materials with the necessary mechanical properties is initially very important. However, once the appropriate constituent materials have been selected, the selection of an appropriate manufacturing procedure is crucial for superior composite performance. For reinforcing fibers, mechanical properties, length, and orientation are the major factors that contribute to the mechanical performance of a composite [1]. For the most part, mechanical properties of a fiber are intrinsic to the chosen material and cannot be controlled or changed. However, other fiber characteristics such as length and orientation within the composite can be manipulated to meet performance needs as they are largely dependent on the method of composite manufacture. The matrix features most important for composite performance are its ability to encapsulate the fibers thereby stabilizing and protecting them and its ability to effectively transfer load to the reinforcing fibers [1]. While each class of polymer has a set of attributes, the actual performance characteristics are highly dependent on the method of manufacture and processing conditions. Processing methods and parameters, therefore, play a key role in the translation of constituent properties to composites properties.

To maximize the properties of the hemp fiber and cellulose polymer used in this study, control of parameters including even distribution and alignment of the reinforcing fibers, high fiber content, and good matrix impregnation of the yarns, were considered when designing the biocomposite fabrication process. The cellulose resin used in the study was a thermoplastic, therefore, typical processing techniques for thermoplastic plastics were used a basis in the design of the biocomposite manufacturing procedure for this study. Additionally, previous studies of natural fiber thermoplastic biocomposites were consulted [2-20], the majority of which used injection molding and compression molding. The custom designed processing procedure used to manufacture the hemp/CAB biocomposites in this study combined two composite processing procedures; (a) filament winding of the fibers for controlled alignment and (b) compression molding for overall consolidation.

4.2.1 Fiber Alignment

The majority of research to date on natural fiber reinforced thermoplastics use injection or compression molding manufacturing techniques. Both of these techniques mold a thermoplastic polymer and randomly oriented fibers into a composite using elevated temperatures and pressures. While composites can be made quickly using these methods their properties are limited by the random alignment of fibers.

Although their specific strengths have been shown to be competitive with commonly used chopped fiber GFRP composites, it was expected that with controlled fiber alignment the properties could exceed those of randomly aligned GFRPs. In a previous study done at the University of California, San Diego [21] biocomposites reinforced with raw ‘uncut’ hemp fibers were fabricated, and it was found that alignment of the hemp fibers was arduous and time consuming and control of the alignment during processing was limited. Therefore, for this study, other forms of hemp fibers were investigated to promote well-aligned composite reinforcement and reduce processing times.

Hemp yarns, used in the textile industry made by wet spinning mechanically separated long hemp fibers, were investigated. The yarns offered the benefits of continuous structure, smaller fiber diameters, higher purity, i.e. higher cellulose contents, and the use of oriented fibers over raw ‘uncut’ hemp.

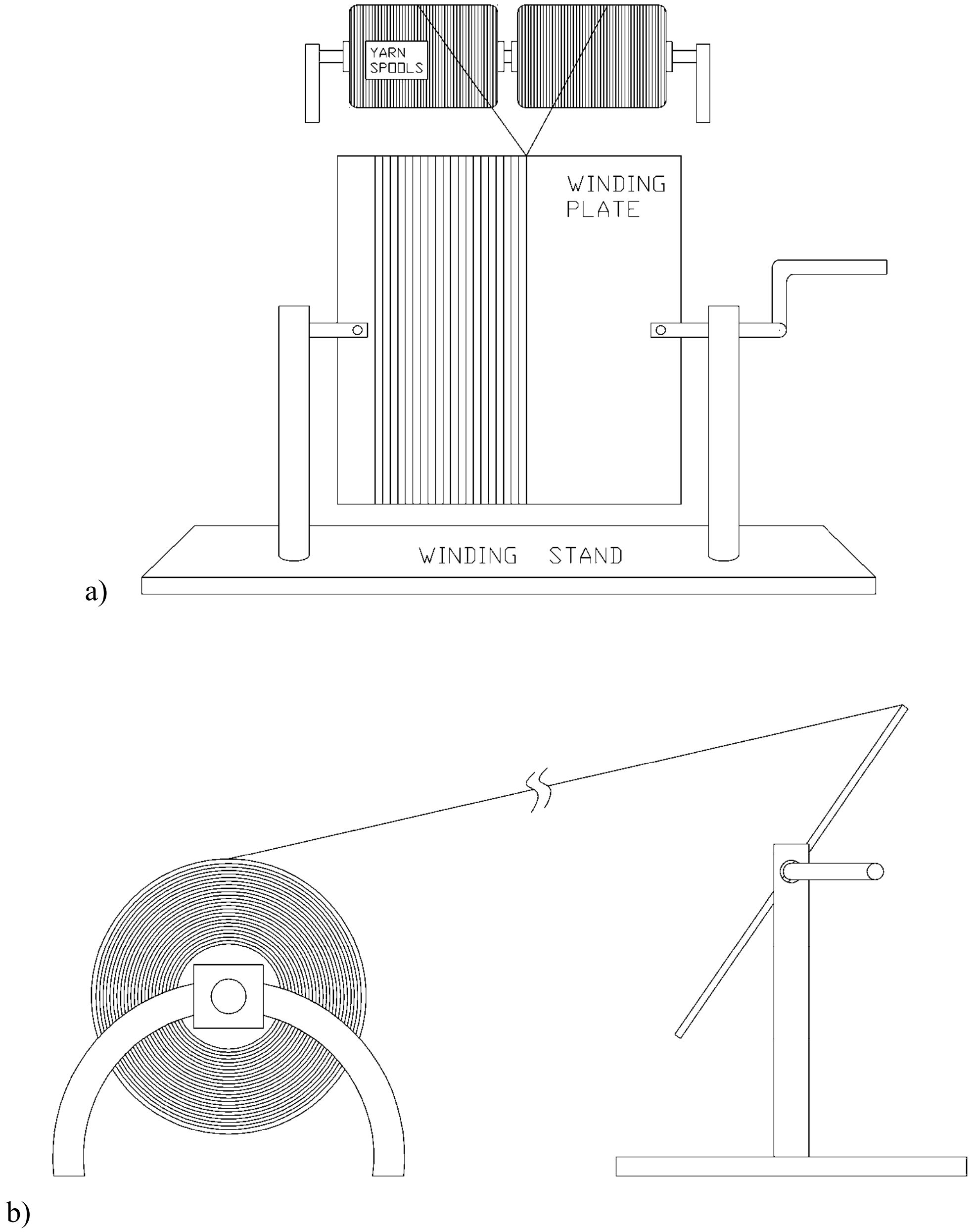

Figure 4.1: Schematic of the yarn winding system developed for controlled fiber alignment a) front profile, b) side profile

A simple winding system was developed for this study to allow for controlled fiber alignment. A schematic of the winder developed for this study can be seen in Figure 4.1. Hemp yarns from freely rotating spools were guided through a die and fastened to a steel plate. The steel plate, covered in thin Teflon sheeting, was manually rotated on a frame. With each rotation the hemp yarns were wrapped around the steel plate and systematically guided down and back the width of the plate to ensure that even distribution of the yarns on the plate was achieved. After several layers of yarn were wound onto the plate, the plate was removed from the winding frame and prepared for resin impregnation.

The tension induced in the yarns during the winding process was essential as it served to secure the fiber alignment through future processing steps. Separate plates were wound with several layers of single- and double-ply yarns. During the winding process it was noticed that fibers in the single-ply yarns had a tendency to slip past one another causing the yarn to break. This was problematic to the continuity of the winding processes as it required frequent stops to re-feed the broken yarns. In contrast, the double-ply yarns were able to take the level of tension produced during winding with minimal breaks as a result of the significant amount of twist in the double-ply structure.

4.2.2 Composite Matrix Application

It is noted that composite properties are negatively influenced by poor resin dispersion and fiber wet-out. The level of composite performance desired in this study was high; therefore, high fiber volume fractions as well as good fiber wet-out were vital.

Most studies on natural fiber reinforced composites have shown that at high fiber volume fractions (>0.5), good fiber wet-out and matrix adhesion are often difficult to obtain. Therefore several methods of applying resin to the reinforcing fibers including thin film stacking, powder impregnation and solution impregnation were investigated to determine which would yield composites with the best resin dispersion and fiber wet-out.

4.2.2.1 Thin Film Stacking

The cellulose resins used in the study were supplied in powdered or thin sheet form from the manufacturer. Powdered resin was purchased for this study and was pressed into thin sheets between 0.35 and 1.0 mm thick for mechanical characterization following the procedure outlined in Section 3.2.1.1 of this report. These thin films were then alternately stacked with layers of aligned hemp fibers and heated and compressed following the optimized processing procedures outlined for the CAB resins in Chapter 3. A schematic of this process and the resulting biocomposites are shown in Figure 4.2.

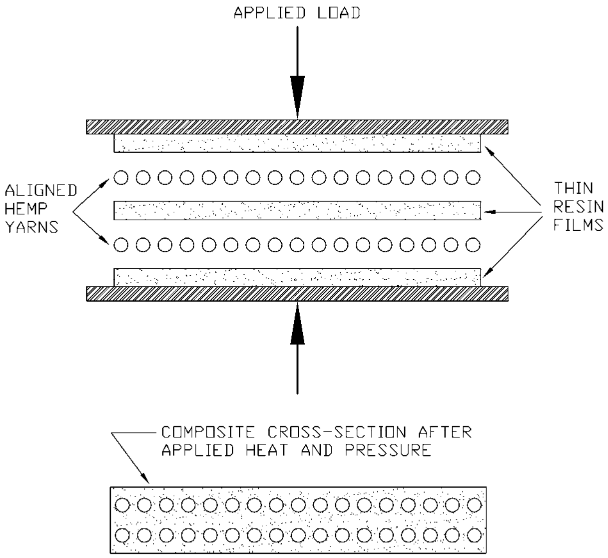

Figure 4.2: Schematic of thin film resin impregnation system and resulting composite cross-section

Although melt flow of the resin sheets was good enough to adequately impregnate the yarns, even dispersion of the yarns throughout the composite cross-section was poor. As shown in the schematic, the resulting composite had a structure with defined fiber rich and resin rich layers. Similar difficulties with fiber distribution were reported by Seavey and co-workers [12,22], when using a thin film stacking technique. Although the use of thinner resin films was investigated in an attempt to minimize the thickness of resin rich layers, resin films with thicknesses below 0.3 mm were difficult to produce and handle.

4.2.2.2 Powder Resin

The powdered particulates of resin were believed to be small enough to allow for good application and even distribution within the reinforcing yarns. The resin application technique using this powdered resin, shown in Figure 4.3, involved distributing a pre-determined weight of the powdered cellulose polymer over aligned hemp fibers and hot pressing the two constituents into a single composite material following the optimized processing procedure outlined for the CAB resins in Chapter 3.

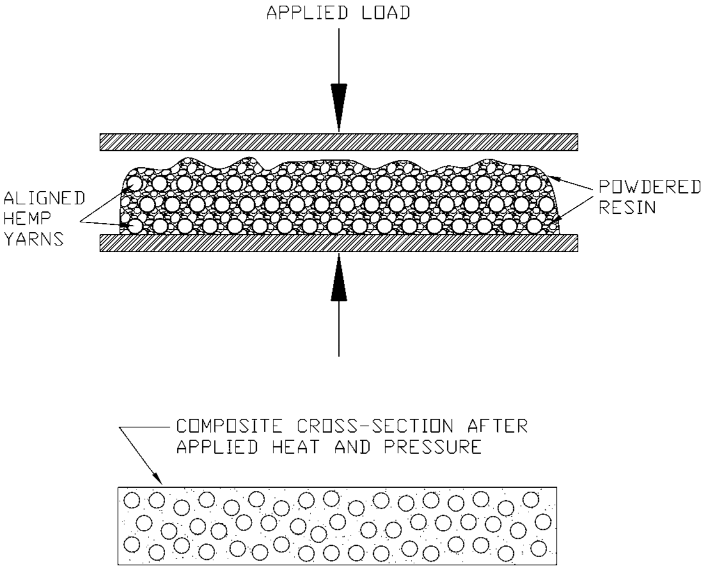

Figure 4.3: Schematic of powder resin application system and resulting composite cross-section

The amount of polymer was chosen based on the desired final weight and/or volume fractions of the constituents. High composite mechanical properties were the goal of the study; therefore, high fiber volume fractions of 0.5 or greater were desired.

At high fiber volume fractions, i.e. low resin fractions, even distribution of the polymer matrix was difficult to attain. The final composite after heating and consolidation exhibited a variable thickness as well as noticeable dry patches on the surface of the composite suggesting poor fiber wet-out. Upon examination of the composite under an optical microscope it was discovered that resin distribution was poor leading to areas of poor fiber wet-out throughout the composite cross-section. At higher resin contents, the dry patches were significantly reduced. This addition of extra powdered resin, however, meant lower than desired fiber volume fractions. Additionally, controlled distribution of resin was difficult and resulted in irregular dispersion of fibers through the composite cross-section. Seavey and co-workers [12], using a powdered resin also reported difficulty in obtaining composites with high fiber volume fractions, even matrix distribution, and good surface finish. In this study, difficulties were attributed to the fact that the resin particulates were too large to uniformly fill the gaps between fiber reinforcements.

4.2.2.3 Solution Impregnation

The processing procedures outlined above using resin in the thin film or dry powder forms resulted in biocomposites with low fiber volume fractions. Although biocomposites with low fiber volume fractions typically have adequate properties for low-strength applications, higher fiber volume fractions were desired for this study. Additionally, in both processing methods described above uniform fiber dispersion was difficult to achieve. The forces applied on the fibers during melt and consolidation of the resin can be high as a result of low melt flow of the polymer. Therefore, if even distribution of the resin throughout the composite is not obtained prior to heating and consolidation non-uniform forces on the fibers can push them out of alignment.

The use of all chemicals, including solvents, was initially avoided during composite manufacture for environmental reasons. However, in an attempt to improve the overall quality of the final biocomposites, the use of solvents was investigated. A resin solution system was therefore developed to minimize the effects of poor resin melt flow and uneven resin dispersion on the fiber alignment and wet-out in the final biocomposites. Figure 4.4 shows a schematic illustration of this process.

Solvents capable of dissolving the powdered resin into a low viscosity fluid, including acetone and methyl ethyl ketone (MEK), were investigated based on an estimated solubility parameter, δ, of approximately 13 $(\mathrm{cal/cm^3})^{1/2}$ for the CAB polymers [23]. Acetone was selected as it provided good solvent capabilities with minimal release of volatile organic compounds (VOCs) and low costs. Solutions with polymer weight percentages from 8 to 20 percent were created to determine the highest possible resin to acetone ratio that would yield a workable solution. At 20 weight percent the polymer took several hours to dissolve and resulted in a high viscosity solution that was not workable and resulted in significant entrapped air voids. At lower weight percents the polymer quickly dissolved in the acetone, however, the resulting solution was very low viscosity and required several applications to obtain a sufficient amount of resin coating on the fibers. Solutions with 10 to12 weight percentage CAB polymer had the best combination of solution viscosity and fiber coating properties and therefore were used for the remainder of the study.

For composite preparation, acetone/CAB solutions were placed in a sealed glass beaker with 10 to 12 wt% of dry CAB polymer and allowed to dissolve on a hot plate maintained at 60°C for one hour. The prepared resin solution was poured onto the plates of aligned fibers and allowed to dry until the solvent portion of the solution was evaporated off. The resulting product, composed of reinforcing fibers lightly coated in a dried polymer matrix, was similar to a prepreg used in traditional fiber reinforced polymer (FRP) composite applications. By impregnating the yarns with a solution form of resin, an even coating of resin on the fibers could be achieved prior to the heating and consolidation process. This allowed for good fiber wet-out and dispersion in the final biocomposites even at higher fiber volume fractions.

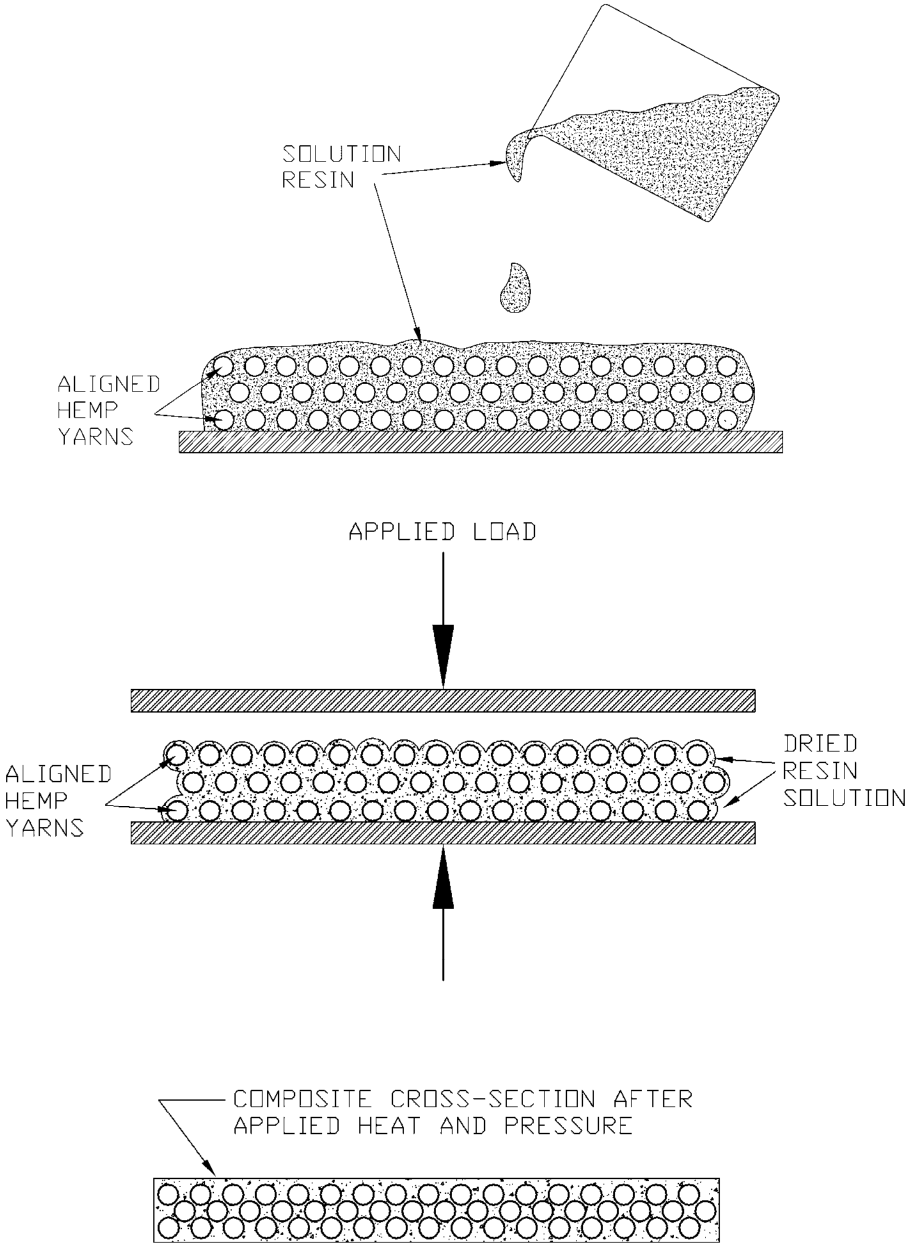

Figure 4.4: Schematic of two-step solution resin application system and resulting composite cross-section

The composites produced through the solution resin application processes had very good consolidation, fiber dispersion and fiber wet-out properties. This process did, however, show visible voids in the final composites as a result of entrapped air during the solvent evaporation and composite consolidation phases. Based on existing studies in the literature [12,22], it was expected that the use of a vacuum during consolidation would reduce the void content of final composites. Additionally, the use of a solution resin required additional composite processing time as it was necessary to allow the solvent to evaporate before heating and consolidation.

4.2.3 Hot-press Consolidation

As previously mentioned, the aligned and resin coated fibers were placed between rigid metal plates and hot-pressed using a Carver model 4391 hydraulic press with heated platens as shown in Figure 4.5. Preliminary experiments were conducted to determine the ideal processing window to be used in the hot-press procedure and all samples used for the characterization of the hemp/CAB biocomposites were manufactured according to this processing procedure.

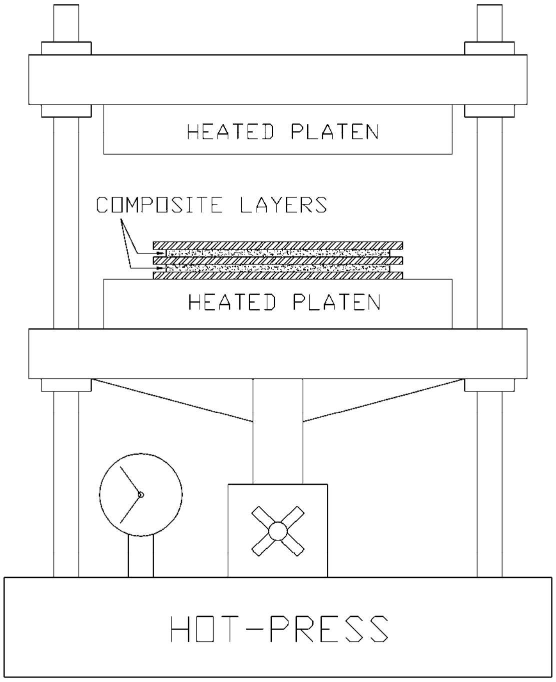

Figure 4.5: Schematic of biocomposite in the hot-press for consolidation

4.2.3.1 Determination of Ideal Processing Window

An ideal processing window was established for each resin by determining the best combination of processing and mechanical properties. This required the optimization of temperature, pressure, and processing time during hot-pressing that would permit adequate resin flow for consolidation without loss of fiber wet-out or degradation of the material constituents. Previous research has demonstrated the detrimental effects of elevated thermal conditions on the mechanical properties of natural fibers [20,24-26]. In comparison to traditional composite reinforcements like glass fibers, natural fibers have low thermal stability. Degradation of some mechanical properties of flax fibers at elevated temperatures is well documented

[24,26]. Work done by Madsen [25] on hemp yarn reinforced PP composites reflects similar effects of elevated temperatures on the ultimate strength capacities of natural fibers. In general, the results of these studies have shown that natural fibers kept at elevated temperatures (>160°C) for extended periods of time will have a gradual loss of mechanical properties. Additionally, when the natural fibers are subjected to processing temperatures at 200°C or higher for even short periods of time, significant fiber degradation can occur.

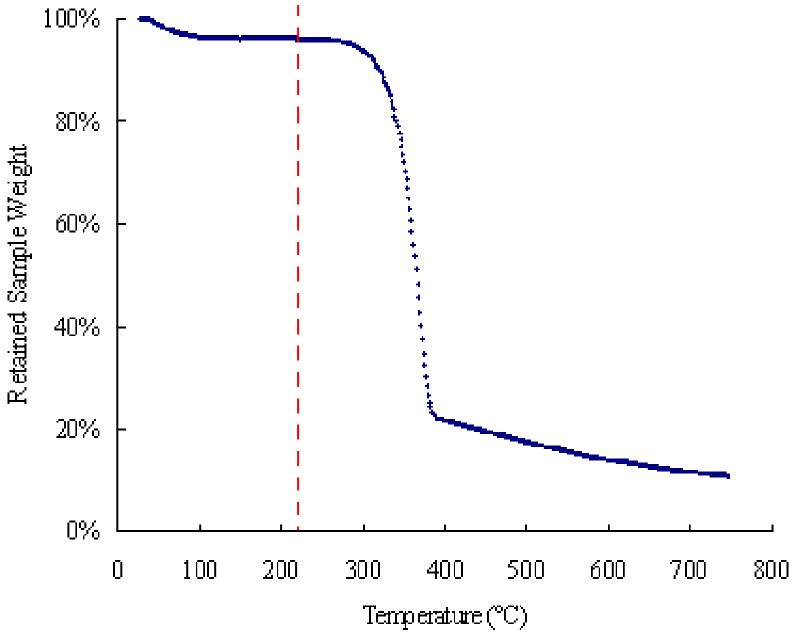

Figure 4.6: TGA analysis of hemp yarn

Thermogravametric analysis (TGA) of the hemp fibers used in this study suggest that fiber degradation begins at temperatures of about 220°C, represented by the dotted vertical line in Figure 4.6, marked by the onset of sample weight loss outside of moisture loss. However a study by Weilage et al. [26], suggests that the onset of fiber weight loss does not necessarily correlate to the onset of degradation of fiber mechanical properties. The comparison between thermal and mechanical test data for flax fibers in their study identified the presence of substantial loss in fiber mechanical properties before temperatures resulting in weight loss were reached in the thermal analysis. The thermal degradation of cellulosic fibers is explained by the scissions of the cellulose chains also regarded as an increased number of 'broken bonds' [24]. Therefore, to avoid the potentially detrimental loss of mechanical properties in the hemp yarns used in this study, processing temperatures were kept below this threshold while still allowing for good resin melt flow. As discussed in Chapter 3, preliminary characterization of the two resin systems had determined that at temperatures of 185°C, both CAB polymers showed good melt flow characteristics without physical or mechanical degradation. This temperature is also below the suggested upper limit for short term processing natural fibers of 200°C [24,26], therefore it was expected that composite processing temperatures of 185°C would not negatively affect composite performance.

It was found that when the resin coated fibers were placed between the heated platens of the hot press and pressure was immediately applied, crushing of the fibers occurred and good resin distribution was difficult to achieve. To avoid fiber crushing and achieve maximum resin impregnation of the reinforcing fibers, therefore, it was necessary to ensure the CAB polymer matrix achieved complete melt before applying pressure to the composite materials. It is also important for economical composite manufacturing to minimize overall processing times. A study was therefore performed where resin coated fibers were placed in a oven preheated to 185°C and checked periodically to determine the time necessary to achieve complete polymer melt. After approximately five minutes in the oven, the resin impregnated fiber material began to display good melt properties. When pressure was applied to the specimen at this point the melted resin was consolidated around the fibers giving increased resin impregnation and less fiber crushing. After the composite specimens were heated between the platens for five minutes without applied pressure, a compressive pressure between 2 to 3 tons was then applied for five additional minutes. This pressure allowed for complete resin melt through the composite thickness allowing for good composite consolidation and a more even thickness of the finished composite samples.

The consolidated composites were held under pressure until they reached ambient temperatures. The entire alignment, resin impregnation, and consolidation procedure was repeated in thin layers until the desired composite thickness was reached. In most instances, the processing cycle was only repeated two times before composite thickness was adequate for mechanical testing. The composite samples were then removed from the rigid steel plate and specimens were machined and conditioned according to individual testing procedures. Optical microscope images of the cross-sections of the composites are shown in Figure 4.7a-b. In general, the images show good resin impregnation of the hemp fiber yarns for composites made through the described manufacturing procedure. Not surprisingly, the tighter packed 2-ply yarns show worse impregnation towards the center of the yarns. Poor resin impregnation resulting in a weak fiber/matrix interface is generally known to affect the load transfer between the fiber and matrix materials, resulting in reduced composite properties. Therefore, the difference in impregnation between the single- and double-ply yarns needs to be considered when comparing the tested composite properties.

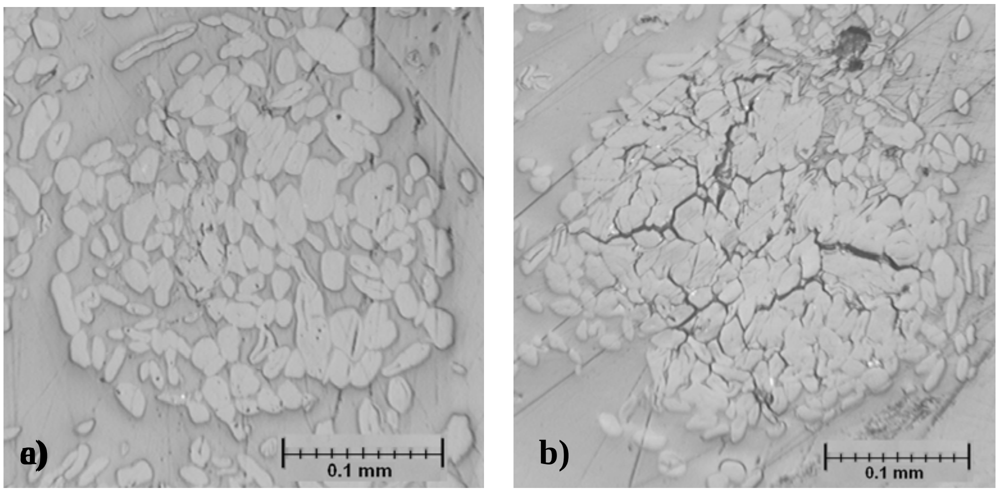

Figure 4.7: Optical images of composite cross-sections showing fiber/resin interface. a) single-ply yarn and b) double-ply yarn

4.2.4 Degree of Repeatability in Composite Manufacturing

Once a good composite manufacturing procedure was chosen, it was important to determine the degree of repeatability in the process. The properties of fiber reinforced composites are known to be highly dependent on the fiber volume fractions; therefore, the ability to control the fiber and resin fractions in the composites was very important in the assessment. By controlling the fiber volume fractions of the composite specimens to around 0.5 it was possible to compare the results from mechanical, impact, and thermal characterization of the four composite systems manufactured in this study.

The system used to determine the ability to repeatedly produce composites with consistent fiber to resin content ratios was based on a series of controlled biocomposite manufacturing experiments. The experiments involved taking gravimetric measurements of the composite system after each stage of the composite processing procedure. Initially, the weight of the winding plate with Teflon coating was recorded. After each layer of fiber and resin were applied to the plate, the entire plate and composite system was weighed. Lastly, after the finished composite was removed from the winding plate, the end yarns, or those that wrapped around the ends of the plates that were not impregnated with resin, were trimmed and weighed. The removed end fiber weight, w_{ef}, was recorded and subtracted from the total weight of fibers, w_{f1} and w_{f2}, wound onto the plate. This allowed for more accurate values of fiber weight and volume fractions to be determined for each composite specimen.

From the weight measurements described above, total fiber and resin weights, w_f and w_m, in each composite sample could be determined and the corresponding fiber and matrix weight fractions, W_f and W_m, of each composite sample were calculated according to Equation 4.1 and 4.2, respectively. The previously determined fiber density of 1.53 g/cm^3 (Section 3.3.2.1) and manufacturer provided CAB polymer density of 1.2 g/cm^3 were used to compute the total fiber and matrix volumes in the composite specimens. Additionally, theoretical fiber and matrix volume fractions, V_f and V_m, were calculated according to Equation 4.3 and 4.4, respectively. These theoretical volume fractions, however, should be used for comparison purposes only as they assume an idealized zero void content in the composite specimens. Visual observation of the composite's surface and cross-section confirm this assumption is inaccurate as voids in the matrix are clearly present (Figures 4.8a-b).

$$W_f = \frac{w_f}{w_c} = \frac{w_f}{(w_f + w_m)} \tag{4.1}$$

$$W_m = \frac{w_m}{w_c} = \frac{w_m}{(w_f + w_m)} \tag{4.2}$$

$$V_f = \frac{v_f}{v_c} = \frac{v_f}{(v_f + v_m)} \tag{4.3}$$

$$V_m = \frac{v_m}{v_c} = \frac{v_m}{(v_f + v_m)} \tag{4.4}$$

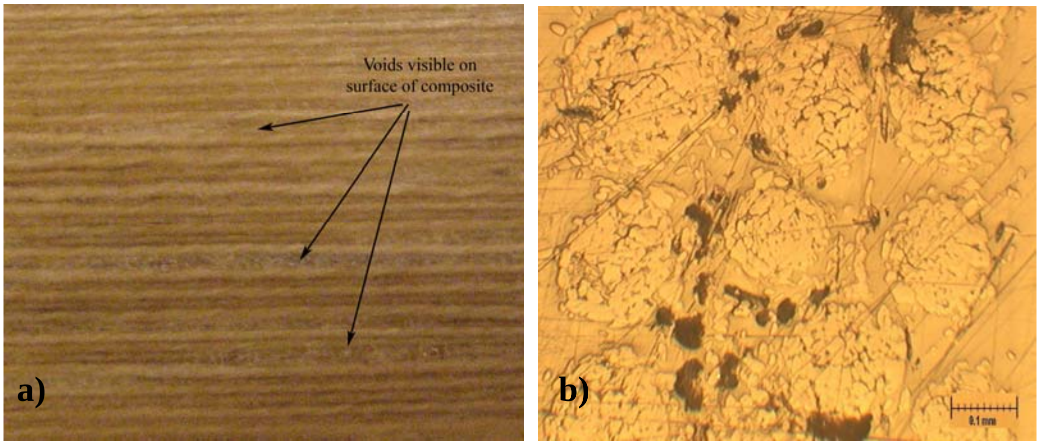

Figure 4.8: Digital and optical pictures of the a) outer surface and b) cross-section of manufactured hemp/cellulose composite showing voids formed during manufacturing

Table 4.2: Summary of weight measurements recorded during experimental controlled manufacturing studies

Manufactured composite panel weights (grams)				
	A1	**B1**	**A2**	**B2**
Plate and teflon	1223.2	1223.4	1221.3	1223
+ fiber layer 1	1248.7	1249.3	1251.3	1250.4
Fiber weight 1 (w_{f1})	**25.5**	**25.9**	**30**	**27.4**
+ resin layer 1	1267.3	1267.6	1270	1269.5
Matrix weight 1 (w_{m1})	**18.6**	**18.3**	**18.7**	**19.1**
+ fiber layer 2	1298.5	1297.7	1300.9	1301.3
Fiber weight 2 (w_{f2})	**31.2**	**30.1**	**30.9**	**31.8**
+ resin layer 2	1320	1319.7	1321.4	1323
Matrix weight 2 (w_{m2})	**21.5**	**22**	**20.5**	**21.7**
End-fiber weight (w_{ef})	**2.71**	**2.8**	**3.15**	**2.74**

Table 4.3: Summary of weight-based calculations to determine fiber and matrix fractions in biocomposite systems

Composite Weight-based Calculations	A1	B1	A2	B2
Total fiber weight: $w_f = w_{f1} + w_{f2} - w_{ef}$	53.99	53.20	57.75	56.46
Total matrix weight: $w_m = w_{m1} + w_{m2}$	40.10	40.30	39.20	40.80
Total composite weight: $w_c = w_f + w_m$	94.09	93.50	96.95	97.26
Fiber weight fraction (W_f)	**0.57**	**0.57**	**0.60**	**0.58**
Matrix weight fraction (W_m)	**0.43**	**0.43**	**0.40**	**0.42**

Table 4.4: Summary of volume-based calculations to determine fiber and matrix fractions in biocomposite systems

Composite Volume-based Calculations	A1	B1	A2	B2
Total fiber volume (cm^3)*: $v_f = w_f/\rho_f$	35.29	34.77	37.75	36.90
Total matrix volume (cm^3)*: $v_m = w_m/\rho_m$	33.42	33.58	32.67	34.00
Fiber volume fraction (V_f)**	**0.51**	**0.51**	**0.54**	**0.52**
Matrix volume fraction (V_m)**	**0.49**	**0.49**	**0.46**	**0.48**

* assuming fiber density = 1.53 g/cm^3 and resin density = 1.2 g/cm^3

** theoretical values based on zero void content

Weight measurements obtained during the experimental controlled manufacturing studies of the four prepared biocomposite systems are shown in Table 4.2. Composite fiber and matrix weights and weight fractions were calculated for the four composite systems and the results are summarized in Table 4.3. Similarly, composite fiber and matrix volumes and volume fractions were calculated and the results are summarized in Table 4.4. When manufacturing the composite specimens, 0.5 was used as a target value of fiber volume fraction. Results show that all four composite systems prepared in the study had fiber volume fractions close to the desired 0.5 target value, suggesting good control of composite constituents. Additionally, comparison of the results for the four biocomposite systems, A1, B1, A2, and B2, show that there is a relatively good degree of repeatability during composite manufacture. Sections of the composite samples were inspected for surface quality, fiber dispersion, resin impregnation, and void content using optical microscope. Although there were slight differences in the visual observations for the four composite systems, these differences resulted more from the difference in physical structure of the reinforcing yarns and melt parameters of the polymers resins, rather than the composite processing technique. For example, composites made with the double-ply yarn exhibited slightly higher void content and worse fiber wet-out as compared to the composites made with the single-ply yarn reinforcements.

4.3 Composite Test Methods

The composite systems prepared under the above manufacturing procedure were put through a detailed testing procedure to determine their mechanical, impact, and thermal performance characteristics. These tests were performed to determine the potential for hemp fiber reinforced CAB polymer biocomposites for use as secondary structural materials. Additionally, comparison of the performance properties of the four composite systems under various loading conditions was expected to help determine the influence of the physical and mechanical properties of composite constituents on the resulting composite performance.

4.3.1 Mechanical Testing

4.3.1.1 Tension

Tension tests were performed on the unidirectional hemp reinforced composites using an Instron mechanical testing machine model 5583 with a 150 kN load cell and a cross-head speed of 2 mm/min. Rectangular shaped composite specimens of approximately 203 mm x 15 mm x 1 mm were cut from compression molded composite panels. The specimens were conditioned at 23 ± 2°C and 50 ± 5% relative humidity for a minimum of 40 h prior to testing. The overall gage length of test specimens was 127 mm, with fibers aligned along the length, and an extensometer was used during testing with a gage length of 25.4 mm. At least five specimens were tested for each material and the results were then averaged to produce mean values. Strength, elastic modulus, and elongation values for the composites were obtained following the procedures of ASTM D 3039 [27].

4.3.1.2 Flexure

Flexure tests were performed on the unidirectional hemp reinforced composites according to ASTM D 790 [28]. The tests were performed using an Instron mechanical testing machine model 5583 with a 150 kN load cell. A cross-head speed of 0.672 mm/min was chosen based of the requirements of testing procedure A of

ASTM D 790. Rectangular shaped composite specimens of approximately 50.8 mm x 12.7 mm were cut from compression molded composite panels having thickness varying from 1.0 -1.6 mm. The specimens were conditioned at 23 ± 2°C and 50 ± 5% relative humidity for a minimum of 40 h prior to testing. The samples were tested in 3-pt bending with a span length of 25.4 mm allowing for the minimum required span to depth ratio of 16:1 to induce proper flexural failure. At least five specimens were tested for each material. Values for flexural strength and bending modulus were obtained for each specimen and the results were averaged. These values were used to compare the flexural mechanical performance of the various composites and to determine the effect of the material properties of the composite constituents on composite performance in out-of-plane loading conditions.

4.3.2 Impact Testing

Un-notched Charpy impact tests were performed according to standard ISO 179 [29] using an Instron Dynatup 9250 testing system with a 50 J capacity. Thicker composite sheets were made by stacking preprocessed composite sheets in a picture frame mold and compression molding the samples at 185°C for 10 minutes under a pressure of 2 ton. Specimens with 80 mm length, 10 mm width and approximately 3 mm thickness were machined from composite sheets, and the specimen edges were carefully polished using a Streurs RotoPol-22 and 1200 grit silicon carbide grinding paper to allow for an even impact surface during testing. The specimens were tested edgewise (perpendicular to the compression molding direction) under pendulum type impact with an impact energy of 6.21 J and impact velocity of 3.4 m/s to insure failure of the composite specimens. A minimum of four samples of each composite system were tested and their impact strengths, bending modulus, and failure modes were determined following procedures outline in ISO 179.

4.3.3 Thermal Characterization

4.3.3.1 Dynamic Mechanical Thermal Analysis (DMTA)

A Rheometric Scientific dynamic mechanical thermal analyzer was applied to perform single- and multi-frequency DMTA tests in single cantilever mode. For the multi-frequency tests, frequencies 0.3, 1, 3, 10 and 30 Hz were selected, whereas the single frequency tests were performed at a frequency of 1 Hz. For both test procedures, a tension strain of 0.0025% was used. A heating rate of 3°C/min from -10°C to 200°C was adopted, and the dimensions of the specimens were 30 x 8~10 mm with a gauge length of 8 mm.

4.3.3.2 Thermogravametric Analysis (TGA)

TGA was performed with a Mettler Toledo instrument (TGA/SDTA 851e). The initial weight of each TGA specimen was around 10 mg. Dry nitrogen gas was introduced into the test furnace at a rate of 25 mL/min to ensure an inert testing atmosphere. The sample was heated at a 10°C/min rate between 25 and 750°C.

4.3.3.3 Differential Scanning Calorimetry (DSC)

DSC tests were performed in a Rheometric Scientific DSC machine. The weight of specimen was in the range of 10 mg - 20 mg. Samples were put in aluminum pans, and heated in an inert nitrogen gas environment at a rate of 10°C/min between -10 and 250°C. The flow rate of nitrogen gas was controlled at 10 ml/min.

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5. COMPOSITE THEORETICAL ANALYSIS, RESULTS AND DISCUSSION

Several composite systems, referred to as A1, A2, B1, and B2, were produced in this study under a set of specific manufacturing procedures and with target constituent fractions. The four composite systems fabricated for this study are all classified as unidirectional composite laminates, consisting of zero degree layers only. The composites were put through a rigorous characterization program including tensile, flexural, impact and thermal testing. The results of these tests were analyzed to determine the potential of the systems for application as load bearing structural materials. Additionally, the test results were compared to predicted composite properties from theoretical models as well as results from similar studies on biocomposites found in the literature. Evaluation of the test data makes clear the effect of the physical and mechanical constituent properties on the final composite performance under the defined manufacturing procedure. From this comparison several key parameters necessary for increased composite performance were identified.

5.1 Determination of Composite Properties

One of the most important factors for determining the properties of unidirectional composites are the relative proportions, either weight or volume fractions, of the matrix and the reinforcing fibers. The definitions of the constituent volume and weight fractions were explained in Section 4.2.4 of this report. As previously explained, the weights of the fiber and matrix materials were controlled during composite manufacture allowing for the determination of their respective weight and volume fractions in the composite. By substituting the known fiber and polymer density values into Equation 5.1 a relation can be developed to calculate the theoretical composite density (ρ_{ct}) in terms of volume fractions as shown in Equations 5.3.

$$w_c = w_f + w_m \tag{5.1}$$

$$\rho_c v_c = \rho_f v_f + \rho_m v_m \tag{5.2}$$

$$\rho_{ct} = \rho_f \frac{v_f}{v_c} + \rho_m \frac{v_m}{v_c} = \rho_f V_f + \rho_m V_m \tag{5.3}$$

Where the subscripts, *c*, *f*, and *m* denote the composite, fiber and matrix, respectively and *w*, *v*, and ρ represent the values for weight, volume, and density, respectively. Additionally, ρ_{ct}, represents the theoretical density of the composite; and W_f, W_m, V_f, V_m represent the weight and volume fractions of the fiber and matrix constituents, respectively. Similarly, the density of the composite could be derived in terms of constituent weight fractions as shown by Equations 5.4-5.6.

$$\frac{w_c}{\rho_{ct}} = \frac{w_f}{\rho_f} + \frac{w_m}{\rho_m} \tag{5.4}$$

$$\frac{1}{\rho_{ct}} = \frac{\left(\dfrac{w_f}{\rho_f} + \dfrac{w_m}{\rho_m}\right)}{w_c} \tag{5.5}$$

$$\rho_{ct} = \frac{1}{\left(\dfrac{W_f}{\rho_f} + \dfrac{W_m}{\rho_m}\right)} \tag{5.6}$$

Although constituent weight fractions are easier to obtain in an experimental setting, volume fractions are exclusively used in the theoretical analysis of composites. Using the theoretical composite density, the following expressions (Equation 5.7-5.10) can be developed to covert between weight and volume fractions which will aid in the ability to correlate experimental composite results to theoretical predictions.

$$W_f = \frac{\rho_f}{\rho_c} V_f \tag{5.7}$$

$$W_m = \frac{\rho_m}{\rho_c} V_m \tag{5.8}$$

and inversely,

$$V_f = \frac{\rho_c}{\rho_f} W_f \tag{5.9}$$

$$V_m = \frac{\rho_c}{\rho_m} W_m \tag{5.10}$$

The constituent fractions for the composite panels fabricated in this study using the two hemp fiber yarns and two cellulose polymers were previously determined to assess the degree of repeatability during composite manufacture. The results are summarized in Tables 4.3 and 4.4 in Section 4.2.4. The equations used to derive these constituent fractions, however, are based off of an assumption that the volume of the composite is equal to the volume of the fiber and matrix constituents only. For most composite materials there are at least a small amount of voids present. With the presence of voids the volume of the composite will be larger than was theoretically calculated based off of the constituent weights. This increased volume, however, does not result in an increase in composite weight. Therefore, it can be seen that the true composite density will be lower than the theoretical composite density that would be calculated from either Equations 5.3 or 5.6.

An experimental buoyancy procedure based off of Archimedes principle can be used to determine the true or experimental composite density using Equation 5.11. Knowing that the true volume of the composite is equal to the sum of the fiber, matrix and void volumes (Equation 5.12), the theoretical and experimental composite densities can then be compared by Equations 5.13 and 5.14, to determine the volume and volume fraction of voids in the composite, respectively.

$$\frac{w_c}{\rho_{ce}} = \frac{w_c - w_{c\,\text{in water}}}{\rho_{\text{water}}} \tag{5.11}$$

$$v_{ce} = v_f + v_m + v_v \tag{5.12}$$

$$\frac{w_c}{\rho_{ce}} = \frac{w_f + w_m}{\rho_{ct}} + v_v = \frac{w_c}{\rho_{ct}} + v_v \tag{5.13}$$

$$V_v = \frac{\rho_{ct} - \rho_{ce}}{\rho_{\text{ct}}} \tag{5.14}$$

$$V_v = \frac{v_v}{v_{ce}}, \quad V_{fe} = \frac{v_f}{v_{ce}}, \quad V_{me} = \frac{v_m}{v_{ce}} \tag{5.15a-c}$$

$$V_{fe} + V_{me} + V_v = \frac{\left(v_f + v_m + v_v\right)}{v_{ce}} = 1 \qquad (5.16)$$

Where, ρ_{ce} and ρ_{water} represent the experimental density of the composite and density of water, respectively; v_{ce} represents the experimental volume of the composite when including the volume of voids, v_v; and V_v, V_{fe}, V_{me} represent the volume fraction of voids and the experimental volume fractions of the fiber and matrix constituents, respectively.

It has been shown by several researchers that the void content of a composite can significantly affect some of its mechanical properties and overall performance [1-4]. Composite properties in shear and compression can be affected by void contents of 1% or lower; however, when greater than 5% void content is present in composites, general composite properties are expected to be reduced significantly. High void contents in composites usually result in reduced fatigue resistance, lower shear strength and stiffness, greater variation in strength properties, and increased susceptibility to water penetration and weathering [1]. Table 5.1 shows the calculated values of theoretical and experimental densities as well as the volume of voids and correspondingly the void fraction of the composites used in this study.

Void contents of the composites in this study were seen to vary from 9 to 17 percent. These high void contents are thought to be a result of the evaporation during composite processing of solvent from the polymer matrix and residual moisture in the hemp fibers. As seen in Figures 5.1a-b, it is clear from optical images of the cross sections of the composites that megavoids are present in the resin layers around and between the reinforcing fibers. Additionally, some portion of void content in these composites is expected to be a result of the hollow cellular nature of the hemp fibers used as the reinforcement (Figure 5.3).

Once the void content was determined for each composite system, adjusted experimental fiber and matrix volume factions of the composites could be calculated (Equations 5.15b-c) such that the relation in Equation 5.16 was satisfied. The calculated values for fiber, matrix, and void contents will be used later in this report to study the effect of voids on the composite properties as well as to back-calculate the effective fiber properties.

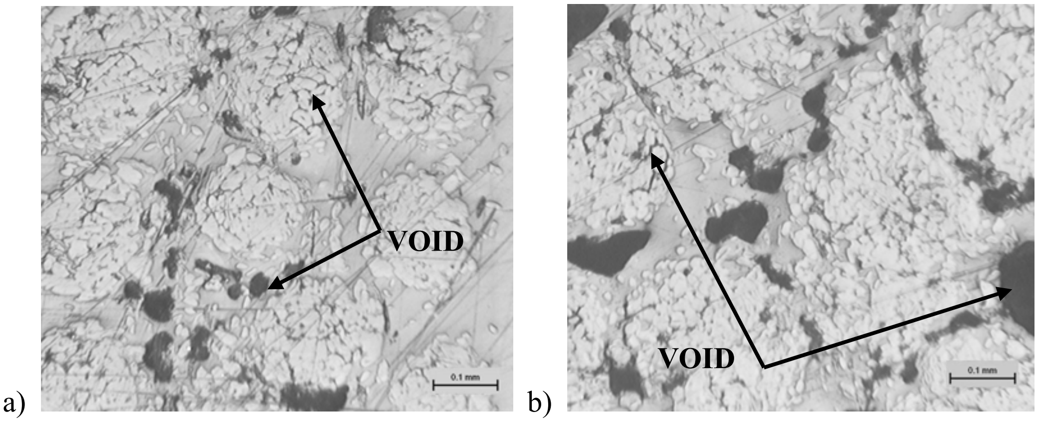

Figure 5.1: SEM images of composite cross-sections showing yarn impregnation and voids in a) single-ply and b) double-ply yarns

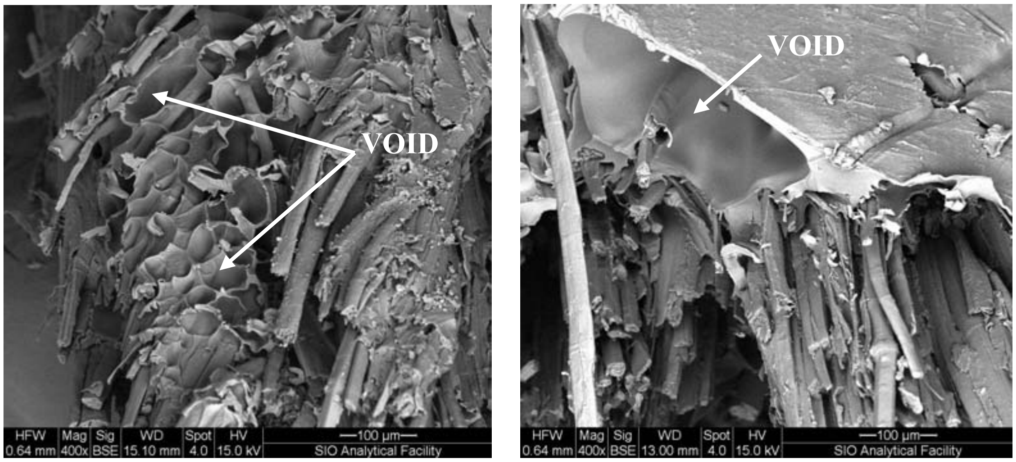

Figure 5.2: SEM images showing voids in the matrix of the hemp/CAB composites

Figure 5.3: SEM images showing voids in the hemp/CAB composites as a result of hollow fiber structure

Table 5.1: Summary of physical properties of manufactured composite panels

Experimental Density and Composite Constituent Calculations	**Average Sample Values**			
	A1	**B1**	**A2**	**B2**
Theoretical composite density (g/cm^3): ρ_{ct}	1.37	1.37	1.38	1.37
Exp. composite density (g/cm^3): ρ_{ce}	1.25	1.19	1.15	1.17
Volume fraction of voids: V_v	0.09	0.13	0.17	0.15
Exp. Volume fraction of fibers: V_{fe}	0.47	0.44	0.45	0.44
Exp. Volume fraction of matrix: V_{me}	0.44	0.43	0.39	0.41

The properties of a composite material mainly depend on the properties and contents of the constituents as well as the orientation and distribution of them within the composite volume. The determination of composite properties can be simply and directly achieved through experimental testing. For a composite with defined materials, produced through a consistent manufacturing procedure, fabrication and testing is a viable means for determining the composite properties. However, this process can be very time consuming when trying to develop and analyze a variety of composite systems resulting from changes in constituent volumes and processing parameters. For this study, two hemp fiber yarns and two CAB polymers were investigated for the use in unidirectional biocomposites. During the material characterization phase of the project, the mechanical properties for these constituent materials were determined. The constituent properties were then used in conjunction with known models to theoretically predict the properties of the hemp/CAB biocomposites in this study.

The following equations (Equations 5.17-5.22) are used to predict the longitudinal composite properties for the unidirectional hemp fiber reinforced composites, where, the subscripts c, f, and m denote composite, fiber and matrix, respectively; and variables ε, σ, and E represent the material strain, stress and stiffness in the direction of applied load, respectively; P, represents the load carried by the material; and A, represents the area of the material in the composite cross-section perpendicular to the loading direction. Equation 5.20 and 5.22, known as the *rule of* *mixtures* (ROM), indicates that the contributions of the fiber and matrix constituents to the overall composite material properties are proportional to their volume fractions.

$$\varepsilon_f = \varepsilon_m = \varepsilon_c \tag{5.17}$$

$$P_c = P_f + P_m \tag{5.18}$$

$$\sigma_c A_c = \sigma_f A_f + \sigma_m A_m \text{ or } \sigma_c = \sigma_f \frac{A_f}{A_c} + \sigma_m \frac{A_m}{A_c} \tag{5.19}$$

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \tag{5.20}$$

$$\frac{d\sigma_c}{d\varepsilon} = \frac{d\sigma_f}{d\varepsilon} V_f + \frac{d\sigma_m}{d\varepsilon} V_m \tag{5.21}$$

$$E_c = E_f V_f + E_m V_m \tag{5.22}$$

The transverse composite modulus, E_T, can be predicted using the Halpin-Tsai equation (Equation 5.23). Where η is defined as shown in Equation 5.24 and ξ is a measure of reinforcement characteristics including fiber geometry, packing geometry, and loading conditions. For circular or square fiber cross-sections ξ is generally assumed to equal 2. Predictions for the ultimate transverse tensile strength of the composite, σ_{TU}, are based on the strength of materials approach (Equation 5.26), where, σ_{mu} represents the matrix ultimate strength and *SCF* is a stress-concentration-factor defined by Equation 5.25.

$$\frac{E_T}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \tag{5.23}$$

$$\eta = \frac{(E_f/E_m)-1}{(E_f/E_m)+\xi} \tag{5.24}$$

$$SCF = \frac{1-V_f\left[1-(E_m/E_f)\right]}{1-(4V_f/\pi)^{1/2}\left[1-(E_m/E_f)\right]} \tag{5.25}$$

$$\sigma_{TU} = \frac{\sigma_{mu}}{SCF} \tag{5.26}$$

5.2 Predicted Values for Unidirectional Hemp/CAB Biocomposites

All predictions were made for composites with fiber volume fractions between 0.2 and 0.6. This fiber volume fraction range was chosen as it was expected that below 20 percent fiber volume content the high fiber properties would not be efficiently used, and at fiber volume content greater than 60 percent poor fiber impregnation in the natural fiber reinforced composites was expected to result in high voids and significant reductions in composite performance [1,5]. A few studies [6-9] on composites with unidirectional natural fiber reinforcement have, however, manufactured composites with fiber volume contents between 60 and 77 percent having very good properties.

For the composite predictions, two different data sets of mechanical properties were used for the hemp fiber reinforcements. This was done because of the large variation seen between some of the mechanical properties determined experimentally in this study and those reported in the literature for hemp fibers. In particular, the elastic modulus values determined for the hemp yarns was significantly below common reported values for hemp fibers [10-12]. Madsen [13] saw similar low modulus values when performing tensile tests of hemp yarn and determined these properties to be a poor estimation of composite performance. The translation of these unique yarn characteristics when embedded in resin to overall composite performance is not easily determined; therefore, both experimentally determined yarn properties and commonly reported properties were used to predict composite performance.

For the single- and double-ply hemp fiber yarns, average experimental strength values were approximately 870 and 565 MPa, and elastic modulus values were approximately 9.5 and 6.6 GPa, respectively. The values for strength and modulus of hemp fibers reported in the literature, however, are 550–900 MPa and 40–70 GPa, respectively. If the effects of fiber twist angles are applied to the values reported in the literature, the expected strength and modulus values for the two hemp yarns are slightly reduced. As was shown in Section 3.3.2.2 of this report, for the single-ply yarns with an average twist angle of 15 degrees, the strength and modulus values are expected to be in the range of 518 to 847 MPa and 37 to 65 GPa, respectively. Similarly, for the double-ply yarn with a slightly higher average twist angle of 22.5 degrees the strength and modulus values are expected to be in the range of 466 to 763 MPa and 34 to 60 GPa, respectively. Clearly, it can be seen that the strength values determined experimentally fall within the range of values reported in the literature, whereas the experimentally calculated modulus values are significantly lower than reported values.

Although, there were distinct differences in mechanical properties for the two fiber reinforcement systems, the strength and stiffness properties were nearly identical for the two CAB polymer resins processed at 185˚C. Additionally, these values were analogous to the range of values reported in the literature for similar plasticized cellulose polymers [14,15]. Preliminary tensile tests showed the hemp fiber reinforced composites to fail at an average strain of approximately 0.035 mm/mm. From the polymer stress-strain diagrams, the stress in the matrix, σ_m, at a strain of 0.035 was determined to be 36 and 37 MPa for polymer A and B, respectively. Therefore, these matrix properties were used in the prediction of composite longitudinal properties. For transverse properties, however, the maximum tensile strength of the matrix of 42 MPa was used. For both longitudinal and transverse predictions, an elastic modulus of 2.1 GPa was used for the cellulose polymers. It is also important to note that although the matrix is known to be an isotropic material, such that the properties are independent of the material axis, the structure of the fiber reinforcements most likely implies the fibers are a non-isotropic material. Therefore, the variation in fiber properties must be accounted for when predicting the transverse composite properties.

5.2.1 Predicted Longitudinal Properties

Theoretical longitudinal strength and stiffness values for the unidirectional hemp reinforced CAB polymer biocomposites manufactured in this study were based on the strength-of-materials approach shown in Equation 5.20 and 5.22. Composite predictions were made using the experimentally calculated fiber and matrix strength and stiffness values as well as an average of the values reported for hemp fibers with the twist angle accounted for as shown in Table 5.2. Using Figure 5.4 and 5.5, a comparison of the composite predictions using the different fiber properties can be made (Table 5.3).

Table 5.2: Summary of fiber and polymer properties used for longitudinal composite strength and modulus predictions

Material	**Modulus (GPa)**		**Strength (MPa)**	
	E_E *	**E_R ****	**σ_E ***	**σ_R ****
Single-ply	9.5	51.0	870	683
Double-ply	6.6	47.0	565	615
Resin A	2.1	-	36	-
Resin B	2.1	-	37	-

* Experimentally determined material properties

** Average reported fiber properties with twist angles

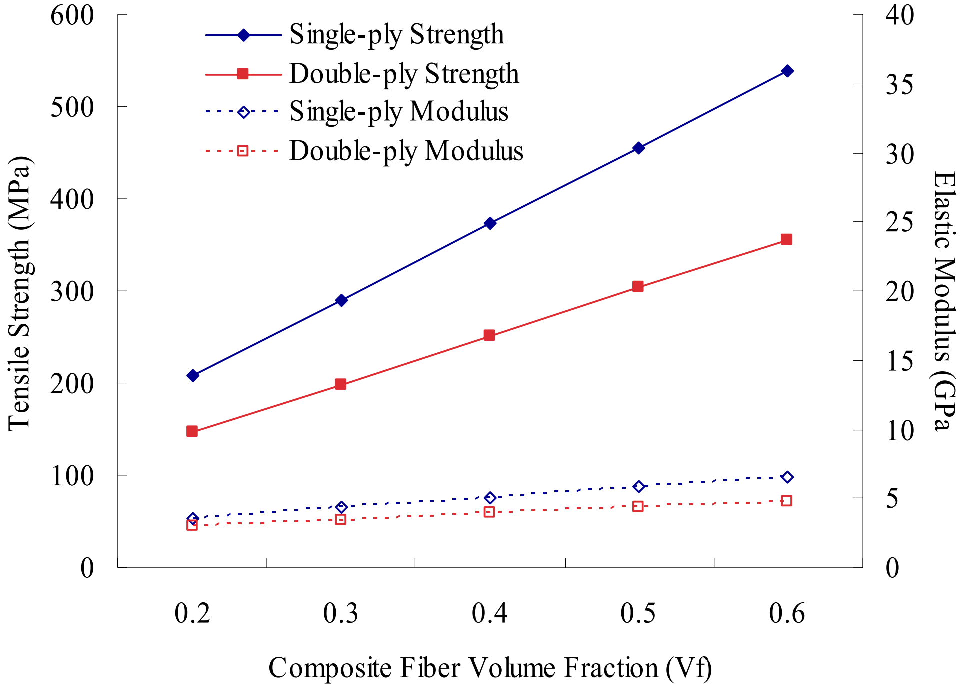

Figure 5.4: Prediction of composite strength and modulus values at varying fiber contents using ROM with experimentally determined hemp fiber properties

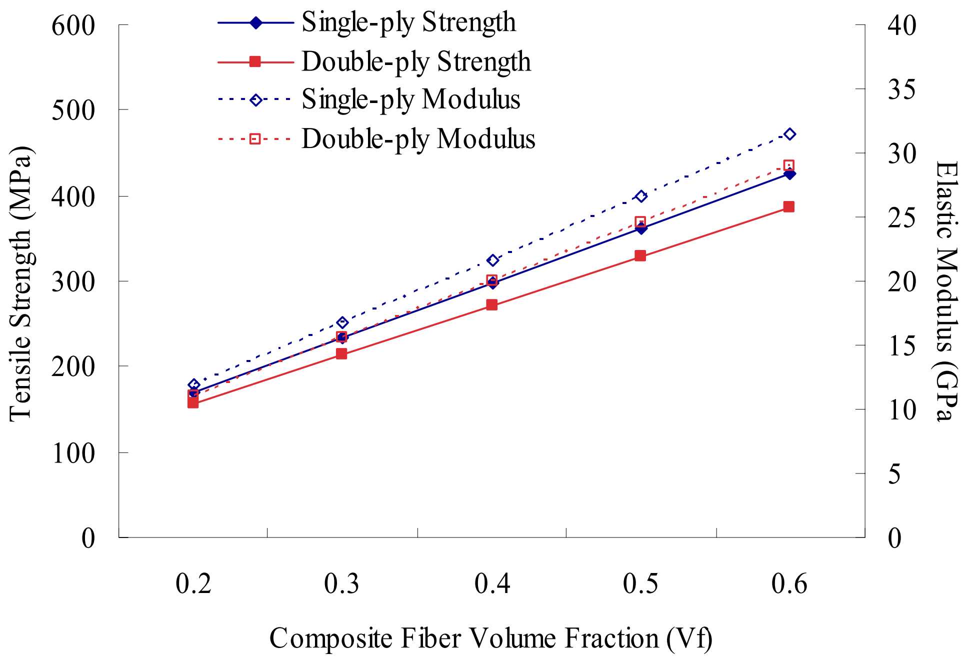

Figure 5.5: Prediction of composite strength and modulus values at varying fiber contents using ROM with hemp fiber properties reported in the literature

Table 5.3: Comparison of predicted longitudinal properties for biocomposites with respect to varied fiber contents, fiber types, and material values used for predictions

Fiber Volume Fraction (V_f)	**SINGLE-PLY COMPOSITES**				**DOUBLE-PLY COMPOSITES**			
	Modulus (GPa)		**Strength (MPa)**		**Modulus (GPa)**		**Strength (MPa)**	
	$\mathbf{E_{cE}}$ *	$\mathbf{E_{cR}}$ **	$\boldsymbol{\sigma_{cE}}$ *	$\boldsymbol{\sigma_{cR}}$ **	$\mathbf{E_{cE}}$ *	$\mathbf{E_{cR}}$ **	$\boldsymbol{\sigma_{cE}}$ *	$\boldsymbol{\sigma_{cR}}$ **
0.2	3.58	11.88	208	170	3.00	11.08	147	157
0.3	4.32	16.77	290	234	3.45	15.57	199	214
0.4	5.06	21.66	373	298	3.90	20.06	251	271
0.5	5.80	26.55	456	362	4.35	24.55	304	328
0.6	6.54	31.44	539	426	4.80	29.04	356	386

* Composite predictions based on experimentally determined fiber properties

** Composite prediction based on fiber properties reported in literature

It can be seen that the ROM approach predicts a direct increase in composite properties with increasing fiber volume fraction. The slope of the model is also proportional to the ratio of fiber properties to matrix properties. Therefore the higher the fiber material values used in the model, the greater the slope of the relationship between composite properties and fiber volume fraction. Based on these predictions it is expected that tensile strength and stiffness values for composites with the single-ply yarn reinforcements will be greater than those reinforced with the double-ply yarns. These predictions are, however, based on material strength properties only and are not able to predict the effect of physical properties and processing characteristics on the final composite properties. For that, we must examine the results from experimental testing.

5.2.2 Predicted Transverse Properties

Predictions for transverse composite tensile strength were done using the strength-of-materials approach as presented in Equation 5.26. Similarly, the predictions for the composite transverse modulus were calculated using the Halpin-Tsai (HT) Equations presented in Equations 5.23. The HT equation was used in replacement of the strength-of-materials approach because it has been shown to be a better approximation of the exact solutions found through more rigorous mathematical predictions [1]. The polymer matrix is an isotropic material; therefore, the modulus and strength values calculated experimentally for the CAB polymer matrix were used in the model predictions for the composite transverse properties. In contrast, the transverse strength and modulus properties of the hemp fibers are not expected to equal the fiber properties in the longitudinal direction. No published mechanical properties for hemp fibers in the transverse direction could be found, therefore, an estimate of these properties was based off of well known ratios of longitudinal to radial properties for wood species. In general, the ratio of radial modulus to longitudinal modulus of wood fibers is between 0.05 and 0.16 [16]. Based off these reported values, transverse hemp fiber strength and modulus values were estimated to be one tenth (0.1) of the properties in the longitudinal direction were used in the composite predictions. An overview of the material properties used for these predictions is outlined in Table 5.4. The transverse mechanical composite predictions using the experimentally determined and the literature reported properties for hemp fibers are depicted in Figure 5.6 and Figure 5.7, respectively.

Table 5.4: Summary of fiber and polymer properties used for transverse composite strength and modulus predictions

Material	**Modulus (GPa)**		**Strength (MPa)**	
	E_E *	**E_R ****	**σ_E ***	**σ_R ****
Single-ply	0.95	5.10	87	68
Double-ply	0.66	4.70	57	61
Resin A	2.1	-	42	-
Resin B	2.1	-	42	-

* Experimentally determined material properties

** Average reported fiber properties with twist angles

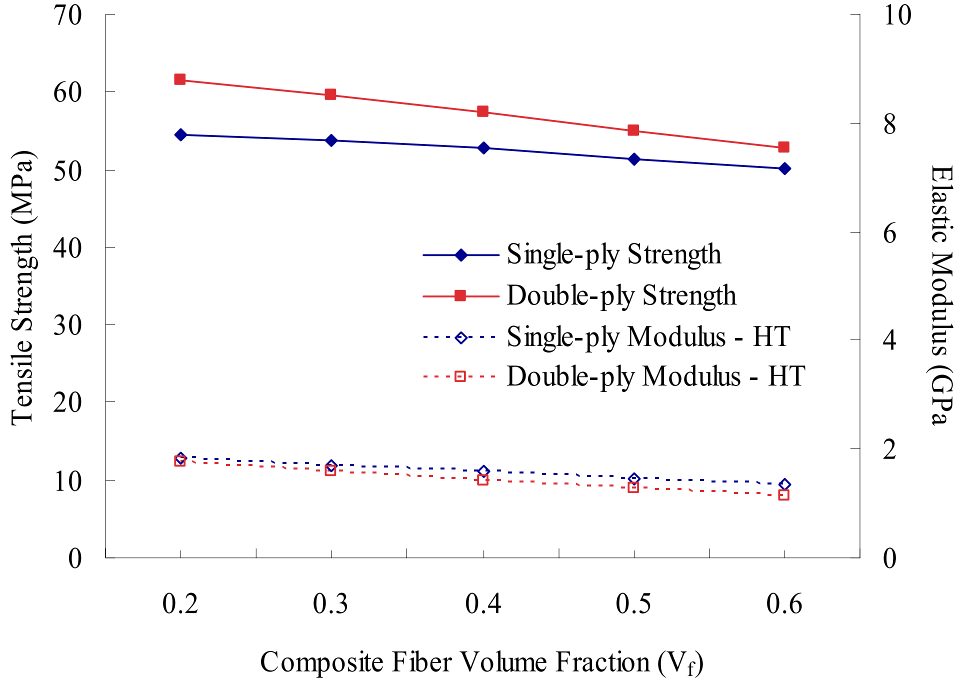

Figure 5.6: Transverse composite strength and modulus predictions using experimentally determined fiber properties versus composite fiber volume fraction

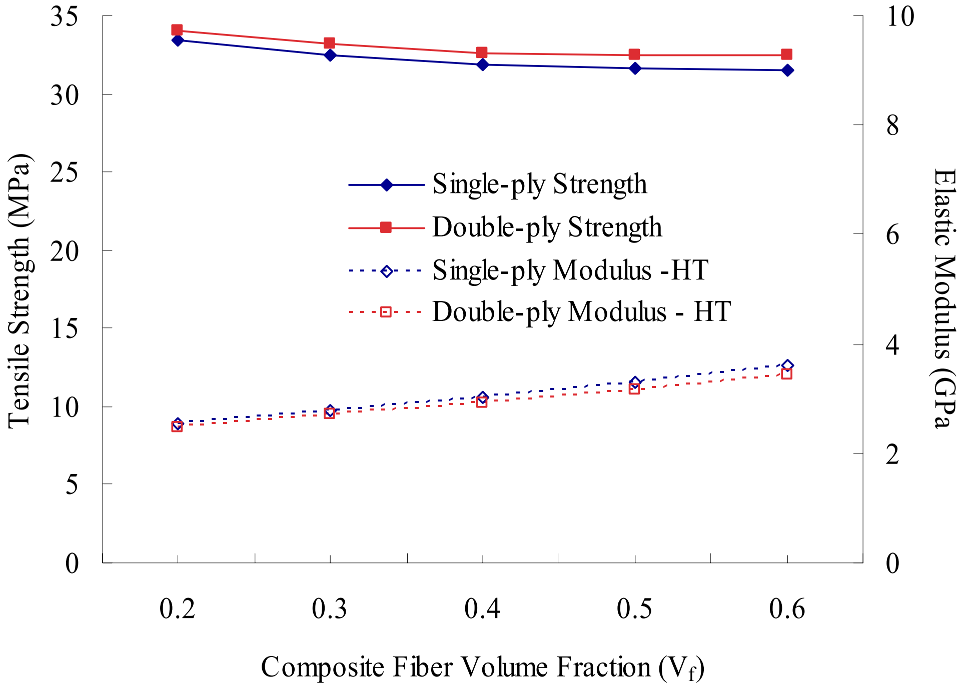

Figure 5.7: Transverse composite strength and modulus predictions using literature reported fiber properties versus composite fiber volume fraction

Firstly, it should be noted that the fiber properties have a less significant effect on transverse properties than was seen in the longitudinal composite predictions. Additionally, the low experimental fiber modulus values are clearly not representative of the idealized composite system, and therefore the modulus predictions based off of literature reported fiber values is expected to better predict the composite transverse modulus. The HT approach predicts an increase in composite transverse modulus with increased fiber volume fraction when the fiber modulus is greater that the matrix modulus, as is the case for the literature reported values. The strength of materials approach used to predict the composite transverse strength shows a decrease in composite properties with increasing fiber content. This negative trend is a result of an increase in the stress-concentration-factor for composites with higher fiber volume fractions. It is therefore important to choose fiber volume fractions that offer a balance of transverse strength and modulus properties if loading in this direction is anticipated.

5.3 Experimental Test Results

The four composite systems, A1, A2, B1, and B2, were produced in this study under a defined manufacturing procedure with a target fiber volume fraction of 0.5. The results of tensile, flexural, impact and thermal testing following the procedures outlined in Section 4.3 of this report are presented below.

5.3.1 Mechanical Characterization

The composites were tested in tension and flexure to quantify the mechanical performance of the various hemp/CAB systems. In Section 4.2.4 of this report, it was shown that the actual fiber volume fraction of the individual composite panels deviated slightly from the target value of 0.5 as a result of manufacturing and high void content. Therefore, the experimentally determined mechanical properties were normalized to a fiber volume fraction of 0.5 for comparison purposes. Both the actual and normalized data is reported.

5.3.1.1 Tension

Tension tests were performed on the four composite material systems following the procedure outlined in Section 4.3.1.1 of this report. Table 5.5 shows a summary of the original and normalized axial tensile properties of the composites calculated according to the specifications of ASTM D3039 [17]. Additionally, a comparison between the mean tensile strengths, stiffness, and elongation at failure of the normalized composite systems are shown in Figures 5.8, 5.9 and 5.10, respectively.

Table 5.5: Summary of actual and normalized ($V_f = 0.5$) tensile properties for unidirectional hemp/CAB composites

Composite Sample	**V_f**	**ACTUAL PROPERTIES**						**NORMALIZED PROPERTIES**			
		Tensile Strength (MPa)		**Tensile Modulus (GPa)**		**Elongation at Break (%)**		**Tensile Strength (MPa)**		**Tensile Modulus (GPa)**	
		Average	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
A1	0.514	224.27	19.37	25.20	1.74	3.30	0.15	218.33	18.42	24.53	1.69
B1	0.509	209.58	10.53	20.32	1.25	3.67	0.21	206.00	10.10	19.98	1.20
A2	0.536	187.62	9.13	18.63	2.06	3.55	0.23	175.00	8.31	17.38	1.88
B2	0.520	186.68	11.13	18.50	0.84	3.64	0.09	179.34	10.45	17.77	0.79

For the four hemp/CAB composite systems with a fiber volume fraction of 0.5, the average longitudinal tensile strength was between 175 and 218.33 MPa, the composite stiffness was between 17.38 and 24.53 GPa and the ultimate elongation ranged from 3.3 to 3.67 percent. It is interesting to compare the properties for the composites in this study with results from other studies on unidirectional-aligned natural fiber composites reported in the literature [5,18-22].

Most recently, Madsen et al. [5], reported ultimate strength values of 280 MPa and stiffness of values of 28 GPa for hemp yarn-reinforced polypropylene (PP) composites with a fiber volume fraction of 0.48 and manufactured through a filament winding and compression molding process. Bledzki [18], however, reported ultimate strengths of only 125 MPa for hemp-reinforced PP composite with a fiber volume fraction of 0.35 manufactured by a similar winding and hot-press procedure. Sanadi [22] reported values of ultimate strengths of 148 MPa and stiffness of 14 GPa for sun hemp-reinforced polyester composites with a fiber volume fraction of 0.4 and manufactured by the hand lay-up process.

Goutianos et al. [19], reported ultimate tensile strengths of 248 MPa and stiffness of 24 GPa for low twist flax yarn-reinforced vinyl ester composites with a fiber volume fraction of 0.37 produced through resin transfer molding (RTM). Similar work by Oksman [21], on flax-reinforced epoxy composites prepared through RTM, reported ultimate strengths of 280 MPa and stiffness of 39 GPa for composites with

0.47 fiber volume fraction. Roe and Ansell, reported ultimate tensile strengths 250 MPa and stiffness of 35 GPa for untwisted jute fiber-reinforced polyester composites with a fiber volume fraction of 0.60 produced through press-molding and cure. Khondker et al. [20], using braided jute/PP yarns, also reported ultimate strengths of 142 MPa and stiffness of 11 GPa for composites with fiber volume fractions of 0.21 manufactured through compression molding. By normalizing the data from these studies to represent composites with equivalent fiber volume fractions, it is seen that the tensile properties for the composites in this study are comparable to a majority of the properties reported for these composite systems (Table 5.6). In addition, the composite in this study have the advantage of being made with polymers derived from cellulose biomass as well as natural fiber reinforcements, making them more environmentally friendly.

Table 5.6: Actual and normalized ($V_f = 0.5$) tensile properties of published values for unidirectional natural fiber-reinforced composites

Composite Materials (fiber/matrix)	**V_f**	**Tensile strength (MPa)**	**Tensile modulus (GPa)**	**Norm. Tensile strength (MPa)**	**Norm. Tensile modulus (GPa)**	**[Ref.]**
Hemp/CAB	0.51	224	25.2	218	25	*
Hemp/PP	0.48	280	28	292	29	[5]
Hemp/PP	0.35	125	-	179	-	[18]
Hemp/Polyester	0.4	148	14	185	18	[22]
Flax/VE	0.37	248	24	335	32	[19]
Flax/Epoxy	0.47	280	39	298	41	[21]
Jute/PLA	0.38	78	8.5	103	11	[20]

*Current Study

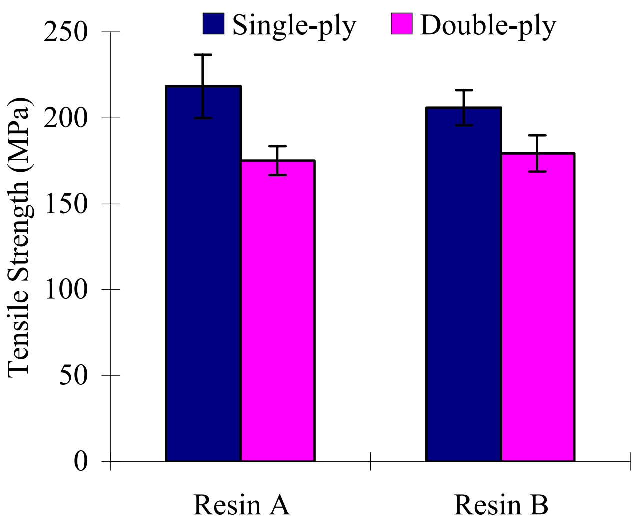

Figure 5.8: Summary of tensile strength properties for hemp/CAB composites

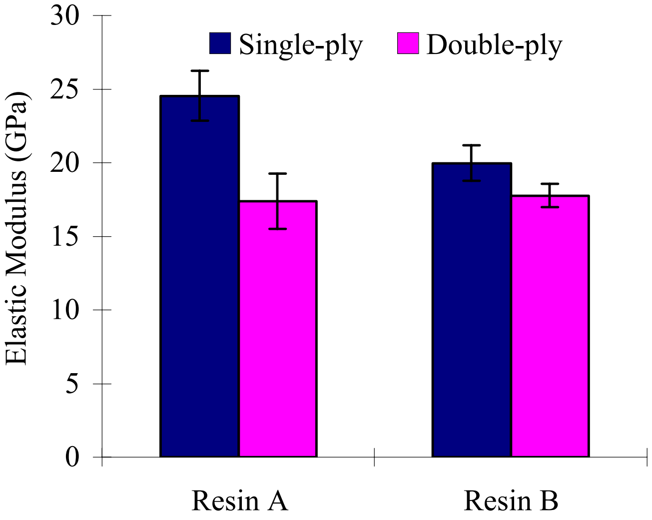

Figure 5.9: Summary of elastic modulus properties for hemp/CAB composites

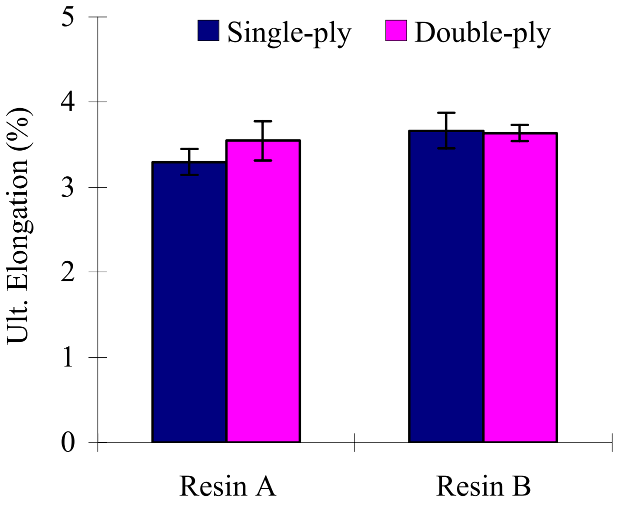

Figure 5.10: Summary of ultimate elongation values for hemp/CAB composites

Figures 5.8-5.9 clearly show that the A1 composite system outperformed the other systems in terms of longitudinal tensile properties. In addition, it can be seen that the composites reinforced with the single-ply yarns outperformed those reinforced with the double-ply yarns. This was somewhat expected as the tensile properties for the single-ply yarns exceeded those of the double-ply yarns during the material characterization tests. In addition the single-ply yarns had smaller diameters, more uniform cross-sections, and lower fiber packing ratios making them advantageous from a yarn packing and impregnation standpoint.

The tensile failure behavior observed for the composite specimens varied depending on the type of fiber reinforcement and degree of adhesion between the fiber and matrix. In both cases, examination of the fracture surfaces showed fiber pull-out suggesting poor adhesion between the fiber and matrix constituents (Figure 5.12a-b).

The composites with single-ply yarns predominately showed tensile failure by fiber pull out and fracture and the composites with the double-ply yarns commonly exhibited failure by fiber pullout and shear failure of the matrix along the yarn length (Figure 5.11a-b). When put in tension, the twist angle in the yarns results in transverse shrinkage of the fiber and simultaneously, disbond between the fiber and matrix constituents. Therefore, the difference in failure behavior between these single- and double-ply composite systems is likely dependent on their respective twist angle, suggesting that yarns with minimal twist should be used.

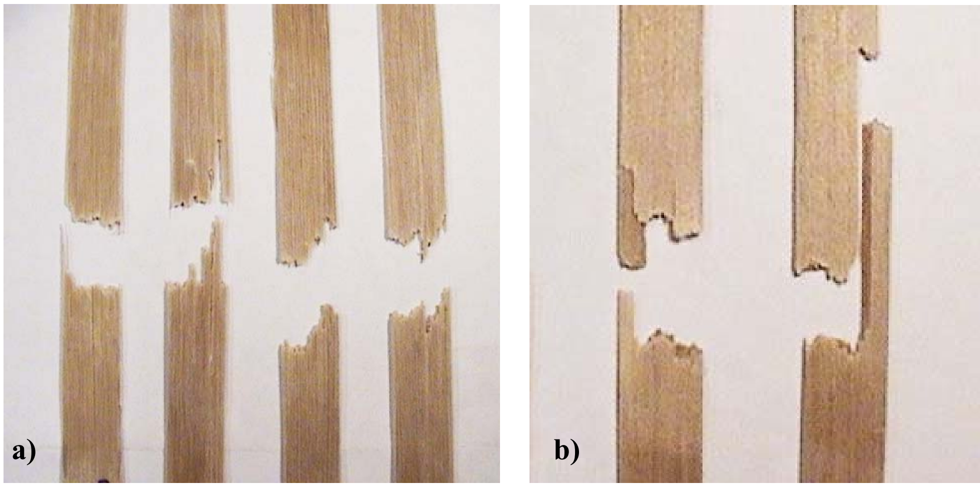

Figure 5.11: Composite specimens subjected to tensile loading a) single-ply yarn and b) double-ply yarn

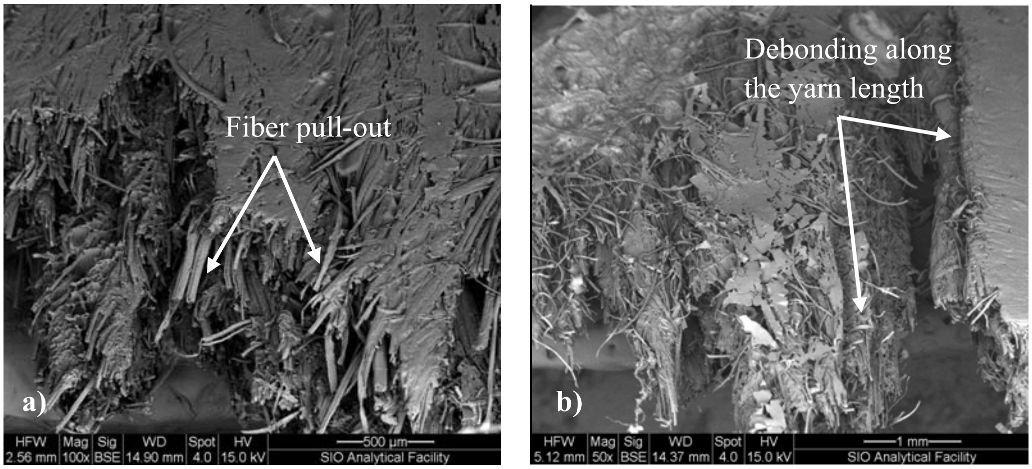

Figure 5.12: SEM images of composite fracture surfaces showing fiber pull-out and shear failure along the length of the yarn a) 100x magnification and b) 50x magnification

5.3.1.2 Flexure

Composite samples were tested in 3-point bending following the procedure outlined in Section 4.3.1.2 of this report. Test results were analyzed according to ASTM D790 [23] to determine the bending strength and stiffness values for each composite system at a fiber volume fraction of 0.5. The actual and normalized ($V_f = 0.5$) flexural properties for the composite in this study are shown in Table 5.7. It can be seen that the experimentally determined composites flexural properties are lower than the tensile properties reported in the previous section of this report. Maximum flexural strength and modulus values of 129 MPa and 21 GPa, respectively, were obtained for the A1 composite samples. Flexural properties of the other three composite systems were significantly lower. It is theorized that the low flexural properties for the composites in this study are a results of high composite void content. Hagstrand et al. [2], studied the effect of void content on the flexural properties of unidirectional-glass fiber reinforced PP composites. The results of this study indicate that composite flexural strength and modulus properties can be reduced by as much as 1.5 percent for every 1 percent void content up to 14 percent. For the composites in this study, average void fractions were found to range from 0.09 to 0.17, or 9 to 17 volume percent, with samples A1 having the lowest void fractions. This could equate to a reduction of flexural properties by as much as 13 to 25 percent as a result of voids. The lower than expected flexural properties for the composite specimens are, therefore, hypothesized to be a result of high void content.

Several studies characterizing the flexural properties of unidirectional natural fiber-reinforced composites have been reported in the literature. Although most of the reported composite systems utilize traditional petroleum based thermosetting or thermoplastic polymers, and several have enhanced properties due to coupling agents or additives, it is still interesting to compare the reported values to those obtained for the hemp/CAB composites in this study.

The flexural strength and stiffness properties for unidirectional natural fiber-reinforced composites with thermoplastic polymers varies greatly depending on the fiber and matrix constituent properties, method of composite manufacture, and resulting fiber volume fraction. Pal et al. [24] reported flexural properties of several unidirectional-aligned polyester composites, including those with jute, sisal, and ramie fiber reinforcements. The ramie, sisal, and jute fiber-reinforced composites had high fiber volume fractions of 0.62, 0.64, and 0.68 and likewise exhibited flexural strength values of 197, 250, and 280 MPa and bending stiffness values of 43, 49, and 41 GPa, respectively. In a study by Bledzki et al. [18], hemp and flax yarn-reinforced PP composites were made by alternating filament wound fiber layers and resin films and then hot pressing; where the resulting hemp/PP and flax/PP composites had fiber volume fractions between 0.3-0.35 and flexural strengths of 125 and 149 MPa, respectively. Khondker et al. [20], reported flexural strength and stiffness values for jute yarn-reinforced composites in a PP and PLA matrix. For composites with the PP matrix and fiber volume fraction of 0.21, reported bending strength and stiffness properties were 122 MPa and 9.1 GPa, respectively. Lower composite flexural strength and stiffness properties of 85 MPa and 7 GPa, respectively, were reported for the jute/PLA composites having a fiber volume fraction of 0.22. Most recently, Angelov et al. [25], have reported results for unidirectional flax yarn-reinforced PP composites produced by pultrusion followed by compression molding with fiber volume fractions of 0.4 and flexural strength and stiffness properties of 135 MPa and 11 GPa, respectively.

Table 5.7: Summary of actual and normalized ($V_f = 0.5$) flexural properties for unidirectional hemp/CAB composites

Composite Sample	Fiber Volume Fraction	ACTUAL PROPERTIES				NORMALIZED PROPERTIES			
		Flexural Strength (MPa)		Bending Modulus (GPa)		Flexural Strength (MPa)		Bending Modulus (GPa)	
		Average	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
A1	0.514	132.83	20.93	21.66	3.10	129.31	20.38	21.09	3.02
B1	0.509	93.36	14.72	14.16	3.80	91.77	14.47	13.91	3.74
A2	0.536	79.48	14.77	12.67	2.14	74.13	13.78	11.82	1.99
B2	0.520	92.89	10.76	11.03	1.37	89.24	10.33	10.60	1.32

More notable flexural properties are reported for studies on natural fiber reinforced composite utilizing thermosetting polymers as the composite matrix. These higher properties seem to suggest that if bending strength and stiffness are of greatest importance, more brittle and highly cross-linked thermosetting polymers should be used in biocomposites. Goutianos et al. [19], conducted several studies on unidirectional flax and jute fiber-reinforced composites. The reported flexural strength and stiffness properties for flax yarn-reinforced composites with unsaturated polyester (UPE) matrix produced by hand lay-up having a fiber volume fractions of 0.28 were 170 MPa and 15 GPa, respectively. Composites with the same materials but a fiber volume fraction of 0.31 were made using the RTM process and yielded slightly higher flexural strength and stiffness properties of 198 MPa and 17 GPa, respectively.

A study by Bledzki et al. [18], reported flexural strength and stiffness values of 228 MPa and 12 GPa, respectively, for filament wound hemp-reinforced epoxy composites with fiber volume fractions of 0.35. Additionally, Netravalli [8] has reported flexural strength and stiffness values of 225 MPa and 12 GPa, respectively, for consolidated unidirectional composites with fiber volume fractions up to 0.65 made from long ramie fiber and a soy based thermosetting polymer. This study suggests that with further development of biobased thermosetting resins, natural fiber composites could achieve much higher performance levels.

Table 5.8: Actual and normalized ($V_f = 0.5$) flexural properties of published values for unidirectional natural fiber-reinforced composites

Composite Materials (fiber/matrix)	V_f	**Flexural strength (MPa)**	**Bending modulus (GPa)**	**Norm. Flexural strength (MPa)**	**Norm. Bending modulus (GPa)**	**[Ref.]**
Hemp/CAB	0.51	133	22	129	21	*
Hemp/PP	0.35	125	-	179	-	[18]
Hemp/Epoxy	0.35	228	12	326	17	[18]
Flax/PP	0.4	135	11	169	14	[25]
Flax/Polyester	0.31	198	17	319	27	[19]
Jute/PP	0.21	122	9.1	290	22	[20]
Jute/PLA	0.21	85	7	202	17	[20]
Jute/Polyester	0.68	280	41	206	30	[24]
Ramie/Soy	0.65	225	12.5	173	10	[8]
Ramie/Polyester	0.62	197	43	159	35	[24]

*Current Study

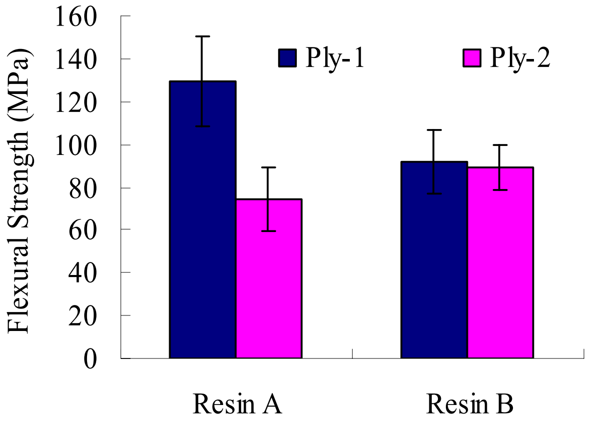

Figure 5.13: Summary of flexural strength properties for hemp/CAB composites

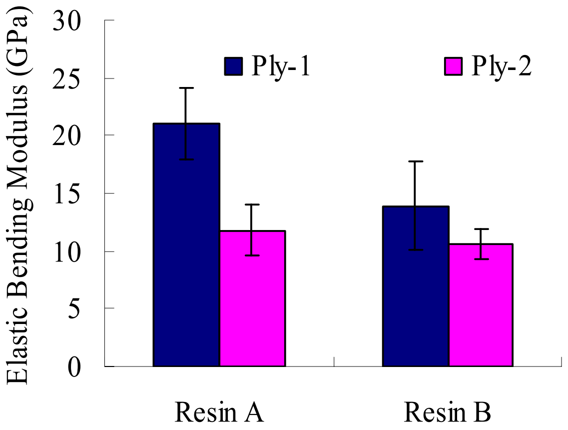

Figure 5.14: Summary of flexural stiffness properties for hemp/CAB composites

5.3.2 Impact

Impact tests were performed on the composite systems in this study to determine the toughness of these materials. Additionally, the failure behavior under sudden loading was of interest. Un-notched Charpy impact tests were performed on unidirectional composite laminates according to standard ISO 179 [26] and the procedures outlined in Section 4.3.2 of this report. The impact energy, impact strength, and elastic bending modulus properties of the four composite systems were calculated and the results are summarized in Table 5.9. All samples exhibited tensile failure modes initiating in the outer fibers as shown in Figure 5.15. Fiber pullout was also seen in all samples further reinforcing the poor interface bond between the fiber and matrix. Some crushing at the point of impact was seen, in particular for the single-ply composite samples with higher impact strengths (Figure 5.16a-b). Additionally, none of the samples exhibited complete break at failure, but instead broke in the form of a partial hinge break as defined by ISO 179. Because all samples exhibited the same failure mode, the results can be used to comparatively examine the toughness and stiffness of the different systems under sudden loading conditions.

Table 5.9: Summary of impact properties for unidirectional hemp/CAB composites

Composite Sample	**Total Energy (J)**		**Impact Strength (kJ/m^2)**		**Bending Modulus (GPa)**	
	Average	**Std. Dev.**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
A1	3.49	0.33	95.40	11.48	13.64	1.51
B1	3.14	0.20	81.35	8.08	10.22	0.93
A2	3.32	0.45	89.75	14.46	12.31	0.98
B2	2.72	0.35	70.13	9.72	9.37	1.03

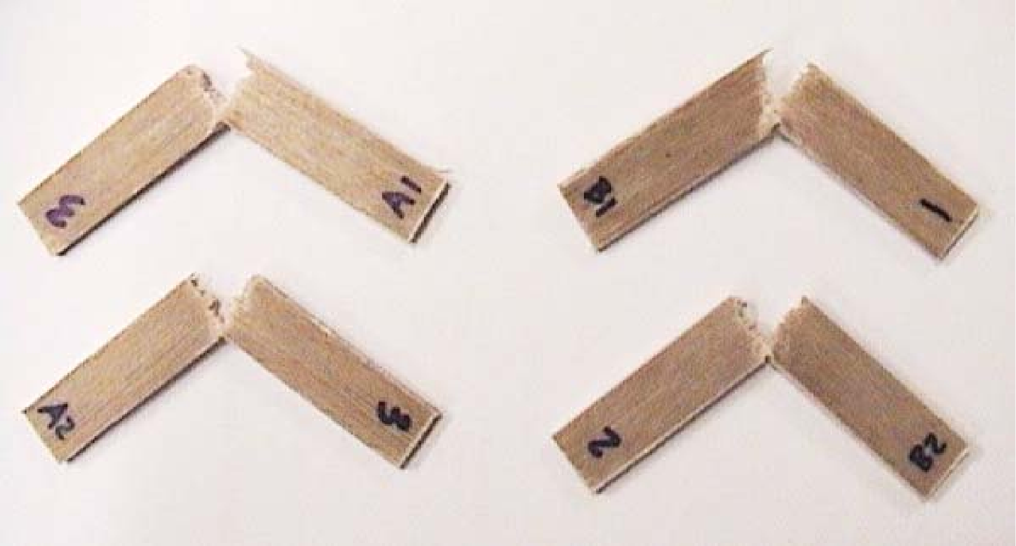

Figure 5.15: Composite specimens subjected to edgewise impact loading (from left to right and top to bottom are samples A1, B1, A2, and B2)

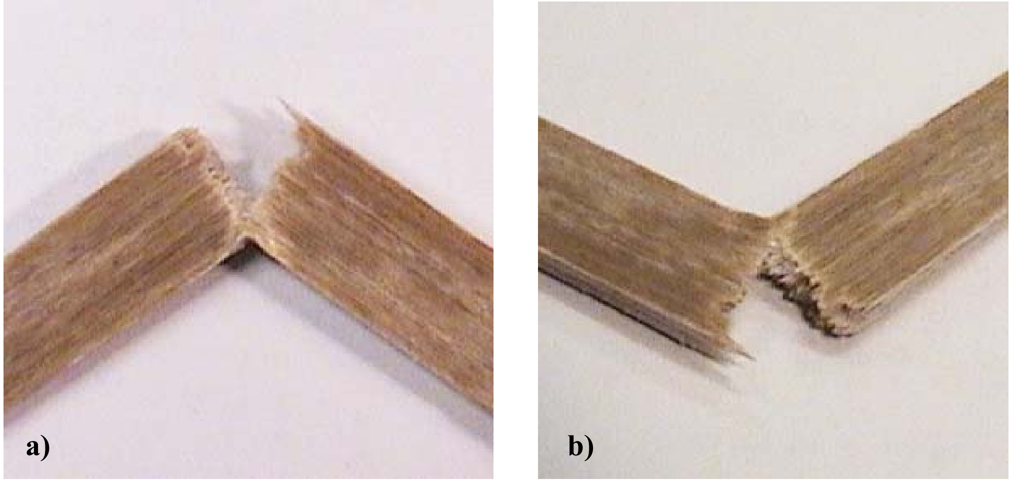

Figure 5.16: Single-ply composite specimens subjected to edgewise impact loading a) failure behavior and b) fracture surface

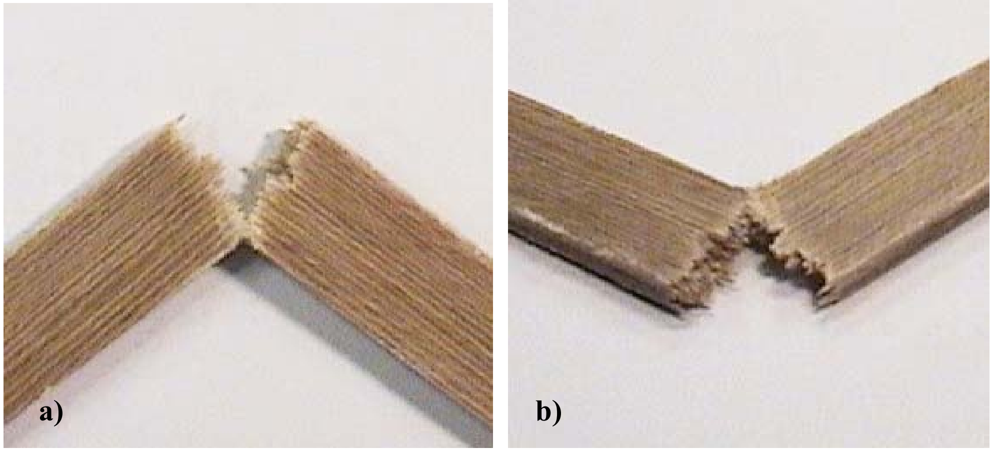

Figure 5.17: Double-ply composite specimens subjected to edgewise impact loading a) failure behavior and b) fracture surface

Although the longitudinal properties of unidirectional composites typically exceed those with randomly oriented fiber reinforcements, the impact properties do not always follow the same trend. A material's impact strength is a result of its toughness or ability to absorb energy during failure. The inclusion of fibers can negatively affect a traditionally tough polymer's impact properties by limiting the elongation to break of the material. In other cases, such as for the unidirectional composites in this study, the fibers can also increase impact properties of a polymer by inhibiting crack growth [27].

It can be clearly seen that the impact performance of the hemp fiber reinforced composites over the neat cellulose resin is significant (Figure 5.18). The averaged impact strength values of the hemp/CAB composites systems range from 70.13 to 95.50 kJ/m^2. The values of the elastic bending stiffness were calculated using the initial slope of the impact load-deflection curve following the same procedure as was done for the flexural tests results in Section 5.3.1.2. The elastic bending modulus of the composites under high velocity (3.4 m/s) loading ranged from 9.37 to 13.64 GPa. Similar for the tension and flexure results, the performance of the A1 composite system exceeds the other three composite systems. The composite with the resin A matrix exhibited higher values of elastic bending modulus and impact strength over those with the resin B matrix. This result correlates well with the slightly higher stiffness properties seen for resin A in the constituent characterization phase of this project (Section 3.3.1.2) both of which can be explained by the slightly higher molecular weight of polymer A over polymer B [28].

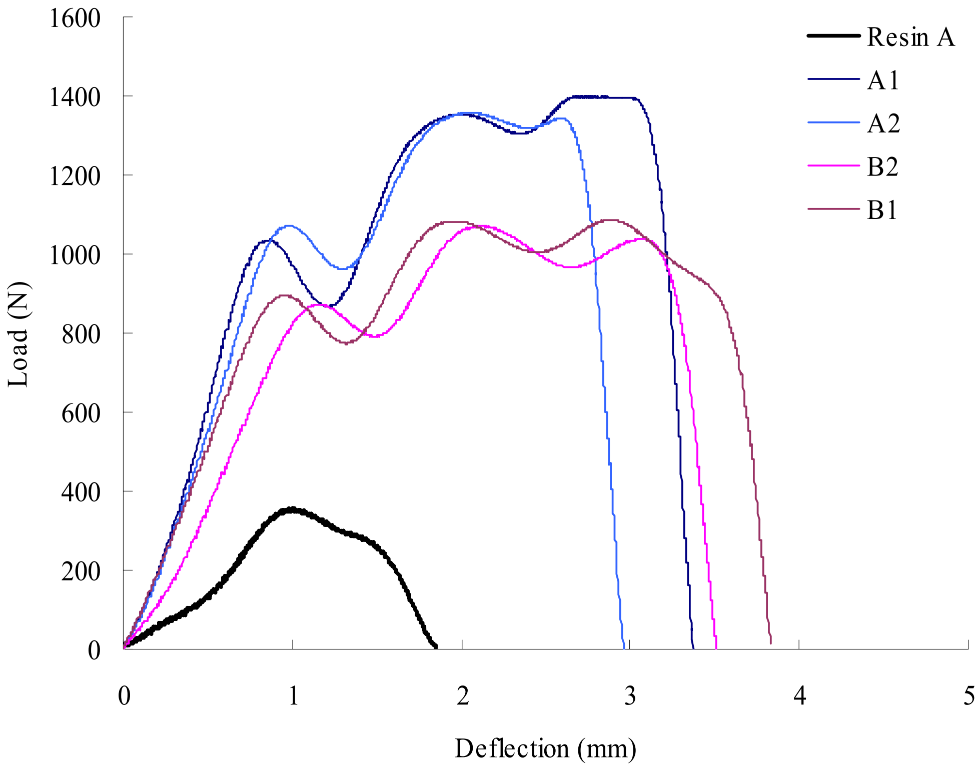

Figure 5.18: Typical load deflection curves for cellulose polymer and biocomposite subjected to impact loading

It is also interesting to examine the typical load deflection curves of the composites during impact testing, shown in Figure 5.18. The area under the load deflection curves is proportional to the impact energy. Additionally, the point of maximum load represents a transition from crack initiation to crack propagation in the samples. Therefore, samples A1 and A2 are shown to be higher strength materials in impact, with most of the materials energy representing crack initiation, compared to the lower strength failure mode of samples B1 and B2. When comparing the effect of reinforcement structure on impact properties of the individual resins it can be seen that the samples with lower twist lower diameter single ply yarns have greater impact strength to failure as compared to the higher twist, higher diameter double-ply yarns.

The meaning of this reinforcement effect is not clearly understood, however, it is thought that this could be a result the greater surface area and fiber pull-out length of the single-ply yarn samples resulting in higher failure energies.

As a result of recent interest in natural fiber reinforced composites for automotive applications, there have been numerous studies on the impact properties of randomly oriented natural fiber-reinforced composites as compared to glass fiber-reinforced composites [29]. In general, the impact performance of the natural fiber reinforced composites has been shown to be good and exhibit less splintering upon fracture. However, there is little reported regarding the impact performance for unidirectionally-aligned natural fiber composites. Additionally, because of the difficulty in correlating properties from the different impact test procedures, even less information is known about the comparison of unidirectional natural fiber composites to traditional composite materials. A few studies have reported impact properties for unidirectional natural fiber composites and are presented here for comparison purposes. Roe et al. [30] reported impact strength values of 20 and 100 kJ/m^2 for unidirectional jute and glass fiber reinforced polyester composites, respectively, with fiber volume fractions of 0.6. Aziz and Ansell [31,32], reported impact strengths ranging from 38 to 75 kJ/m2 in a study on hemp and kenaf reinforced composites with polyester and cashew nut shell based resins. Zhang et al. [33], reported impact strengths of 65 kJ/m^2 for sisal fiber-reinforced benzylated-wood flour composites with a fiber volume fraction of 0.3. Angelov et al. [25], studied several performance characteristics of pultruded flax yarn reinforced PP composites and found maximum impact strengths of these materials to be 98 kJ/m^2 for composite samples with a fiber volume fraction of 0.4.

Table 5.10: Actual and normalized ($V_f = 0.5$) impact strength (work of fracture) of published values for unidirectional natural fiber-reinforced composites

Composite Materials (fiber/matrix)	**V_f**	**Impact strength (kJ/m^2)**	**Norm. Impact strength (kJ/m^2)**	**[Ref.]**
Hemp/CAB	0.51	95	92	*
Jute/Polyester	0.6	20	17	[30]
Glass/Polyester	0.6	100	83	[30]
Kenaf/CNSL	0.66	57	43	[31]
Hemp/CNSL	0.65	38	29	[31]
Kenaf/Polyester	0.64	73	57	[32]
Hemp/Polyester	0.6	75	63	[32]
wood flour	0.3	65	108	[33]
Flax/PP	0.4	98	123	[25]

From examination of these studies, it can be seen that the impact properties for the hemp/CAB composites being studied in this project are within the range of properties reported for other unidirectional natural-fiber reinforced composites. Work by Aziz and Ansell [31,32] suggests that the impact strength of natural fiber reinforced composites can be improved by reducing the friction stress between the fiber and matrix in a controlled manner. Similar findings by van den Oever et al. [34] and Mieck et al. [35], reflect a decrease in composite impact strengths as a result of increased fiber/matrix adhesion and attribute this to the shorter average pull-out lengths during fracture when a good fiber/matrix bond is present. The higher toughness properties of the natural fiber composites in this study compared to values reported in some other studies can therefore be attributed in part to the relatively poor bonding between the fiber and matrix.

5.3.3 Thermal Characterization

5.3.3.1 DSC

Differential scanning calorimetry (DSC) is a common thermal method used to determine temperature related transitions in a polymer. For this study, DSC was used to verify the glass transition temperature (T_g) of the neat polymers as well as determine the effect of adding fiber reinforcements on the materials transitions. In this method, energy is supplied to the sample and changes in heat capacity are reported. An increase in the heat capacity is associated with the increased molecular motion of the polymer; therefore, the glass transition temperature is taken as the temperature at which one half of the increase in heat capacity has occurred.

The heavy weighted curves in Figure 5.19 and 5.20 represent the neat polymer samples, whereas the lighter weight curves represent the polymers reinforced with single- and double-ply yarn reinforcements. The glass transition temperatures were determined from these curves and a summary of the values of the glass transition temperatures for each polymer and composite sample can be seen in Table 5.11. Determination of the T_g for the neat polymer resins was straightforward, however, for the highly reinforced composite materials determination becomes more challenging because the specific heat capacity of the sample is only slightly changed by the polymer glass transition. Determination is further complicated by the poor thermal conductivity introduced by the reinforcing fibers [36]. For the neat polymer samples and those with the single-ply reinforcements a distinct lower temperature transition is seen. The meaning of this transition is not clearly known; however, it is though this could be a result of the branching of the polymer. The reason for a lack of this lower transition in the double-ply samples is also not clear, however, could be due to changes in the polymer molecular structure around the fiber reinforcements.

The glass transition for polymer A is slightly lower than that of polymer B which was unexpected as it is commonly assumed that an increase in molecular weight results in an increase in polymer T_g [37]. A slight reduction in the glass transition temperature is seen with the addition of the hemp fiber reinforcements as has been shown for other biocomposites with significant natural fiber content [38,39]. The decrease in T_g suggests a possible change in the molecular arrangement of the polymer allowing for molecular movement at lower temperatures when the hemp fibers are present [40]. It should be noted, however, that the reductions in T_g for samples A1 and A2 are within the bounds of instrument sensitivity. No defined melt temperature is seen confirming that the cellulose polymers are amorphous as was shown by other researchers [41].

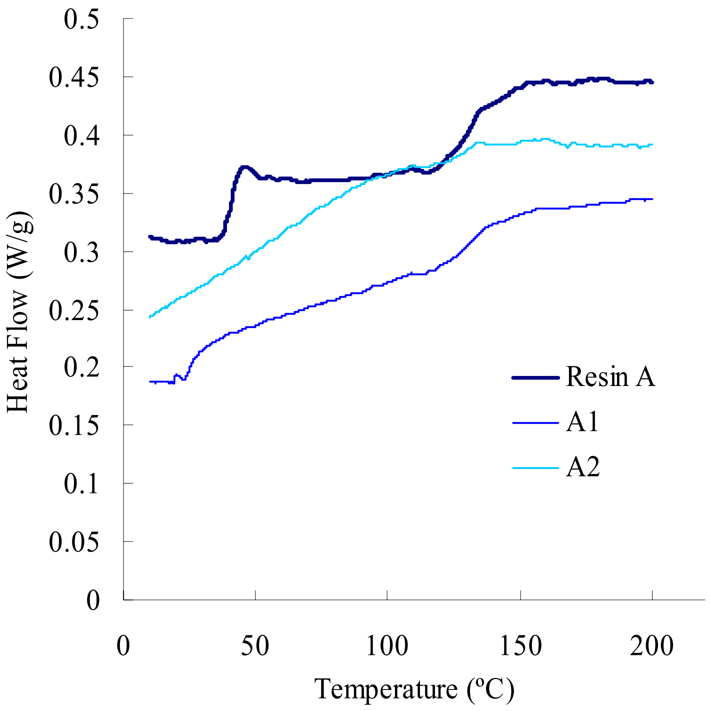

Figure 5.19: DSC curves for neat cellulose polymer A and hemp reinforced composite samples

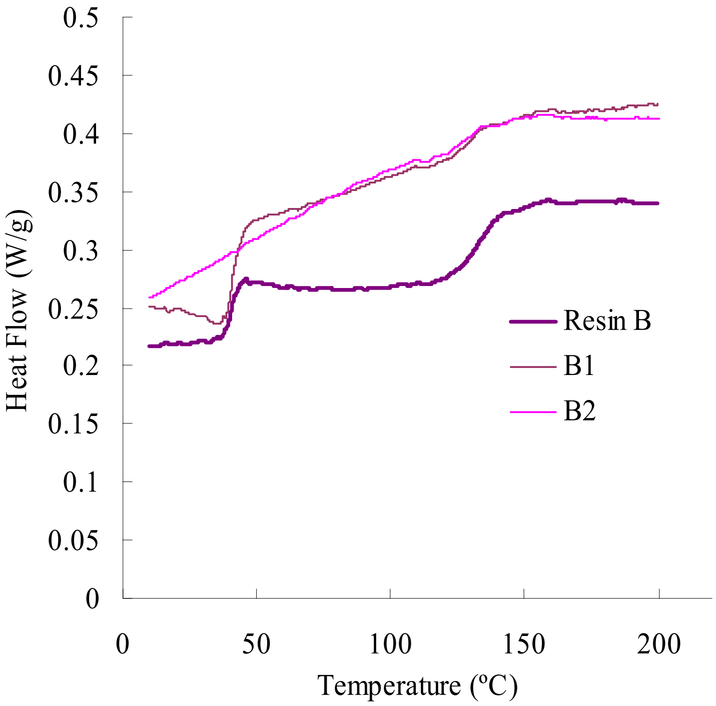

Figure 5.20: DSC curves for neat cellulose polymer B and hemp reinforced composite samples

Table 5.11: Summary of glass transition temperature (T_g) for neat polymer and reinforced composite samples obtained by DSC

	Temperature (°C)		
Sample	**T_g**	**Onset**	**Endset**
Resin A	131.77	123.48	140.06
A1	130.1	127.03	133.17
A2	129.05	127.51	131.78
Resin B	133.14	124.75	141.53
B1	129.39	124.63	134.15
B2	128.71	126.68	130.74

5.3.3.2 TGA

Thermogravametric analysis was performed on the hemp fibers, cellulose polymers, and composites, according to the procedure outlined in Section 4.3.3.2 of this report, to determine their respective degradation temperatures as well water contents. The percent weight loss of the samples plotted with respect to temperature is shown in Figures 5.21 and 5.22. It was expected that the degradation temperature of the constituent samples would be very close as both the fiber and polymers are primarily comprised of cellulose. The degradation temperature of the pure cellulose resin was, however, slightly higher than for the hemp fiber and composites suggesting a more regular molecular structure in the CAB polymers as compared to the fibers. The hydrophilic nature of these fibers is well known and therefore, the presence of moisture in the composites and its effect on composite properties should be investigated. Initial weight loss in the hemp and composite samples, not seen in the neat polymer samples, indicates the presence of water in the hemp fibers (Table 5.12). Furthermore, the residual weight, most likely carbon, seen in the hemp fiber samples shows these materials are lower purity than the cellulose polymer.

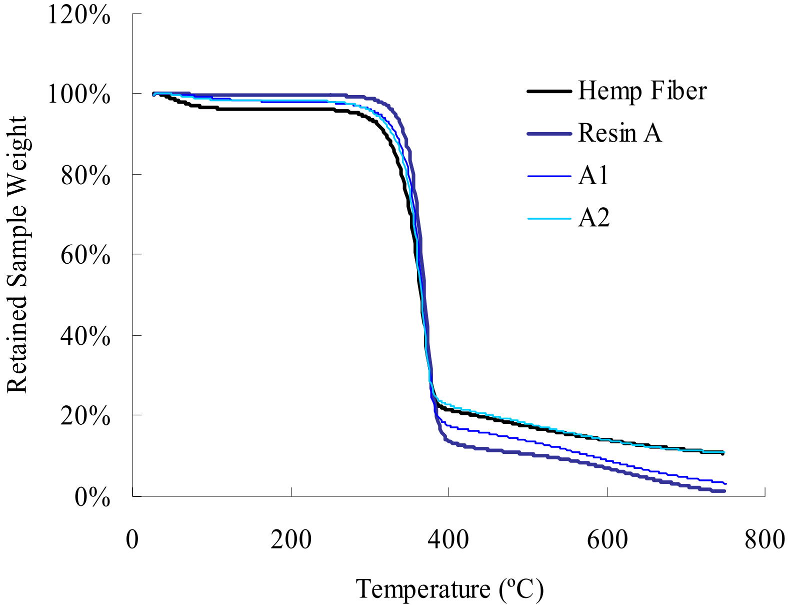

Figure 5.21: TGA weight loss curve showing the temperature dependent degradation profiles for the hemp fiber, neat cellulose polymer A, and reinforced composite samples

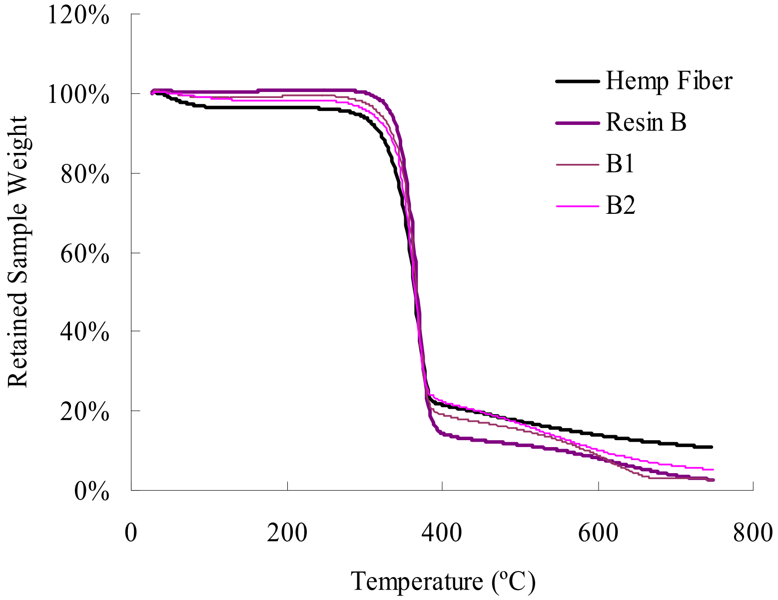

Figure 5.22: TGA weight loss curve showing the temperature dependent degradation profiles for the hemp fiber, neat cellulose polymer B, and reinforced composite samples

The onset and endset degradation temperatures are automatically calculated through the TGA software based off predetermined sample weight loss percentages, equal to 15 percent for this study. A summary of these calculations for the constituent and composite materials is shown in Table 5.12. Although, these properties are a good representation of the temperatures resulting in significant loss of material, it has been shown that the performance properties of materials can begin to degrade at temperatures far below the TGA determined degradation temperature [13,42,43]. The loss of mechanical properties in natural fibers as a result of exposure to elevated temperatures has already been described in this report (Section 4.2.3.1). Additionally, visual degradation and the loss of mechanical properties for the cellulose polymers processed at elevated temperatures was shown during the material characterization portion of this report (Sections 3.3.1). When comparing the degradation curves for these materials to their mechanical performance, it can therefore be seen that the temperature suggesting an onset of degradation from thermal analysis is much higher than what was determined based on mechanical testing. It is therefore important that both mechanical testing as well as thermal testing should be considered when determining the processing parameters for natural fiber composites.

Table 5.12: Summary of TGA data showing degradation temperatures and moisture contents of neat cellulose polymer and hemp reinforced composite samples

	Water	**Residual**	**Degradation Temperature**	
Sample	**(%)**	**(%)**	**Onset (°C)**	**Endset (°C)**
Hemp	3.66	10.82	333.85	385.31
Resin A	0	1.51	348.7	387.5
A1	2.02	3.22	341.68	383.34
A2	1.65	10.91	339.86	381.28
Resin B	0	2.74	345.65	387.45
B1	0.98	2.94	344.07	387.27
B2	1.74	5.45	342.91	383.84

5.3.3.3 DMTA

The determination of a material's performance under short term static or quasi-static loading is important when considering it to be used in a load bearing situation. It has been shown that these material properties, such as the tensile and flexural modulus, can be easily determined by the mechanical testing techniques previously used in Section 5.3.1. A process known as dynamic mechanical thermal analysis (DMTA) is used in which a sample is subjected to vibratory excitations over a defined temperature range. When the molecules of the material are perturbed in this manner, they store a portion of the imparted energy elastically and dissipate a portion, typically in the form of heat. The measure of the energy stored elastically during deformation is known as the Young's storage modulus, *E*', whereas the energy converted to heat is defined as the loss modulus, *E"*. Additionally, the ratio of the loss modulus to storage modulus is known as the loss tangent, *tan δ*, and is commonly used to study the behavior of the T_g as well as a materials damping characteristics.

In this study, multi-frequency and single frequency DMTA was performed on the neat resin and four composite systems in the form of single cantilever beam bending according to the procedure described in Section 4.3.3.1 of this report. The composite samples were tested in the longitudinal, fibers running parallel to the beam length, and transverse, fibers perpendicular to the beam length, directions. The *E'* and *tan δ* values were of interest in this study and an overview of these properties for the, single frequency (1 Hz) specimens are presented in Table 5.13.

It can be seen that the addition of fiber reinforcement to the neat CAB polymer has a significant positive effect on the storage modulus values in the longitudinal direction, thereby increasing the thermal stability of the polymer. At high temperatures, the benefits of fiber reinforcement on longitudinal composite storage modulus increase significantly. As reported by other authors [36], this is likely a result of the reduced mobility of the polymer molecules when reinforcing materials are present. It can also be seen that the addition of reinforcing fibers has in many cases a negative effect on the transverse stiffness of the composite material. This is somewhat expected as the transverse properties of the composite are highly dependent on the matrix properties and the interface between the fiber and matrix materials. For samples A2, B1, and B2 the transverse composite stiffness is below that of the neat resin. This further emphasizes the presences of poor adhesion between the fiber and matrix constituents. Similar to the results for the mechanical testing, the performance of the A1 composite sample exceeds those of the other composites in both the longitudinal and transverse directions further enforcing the effect of void and fiber contents on composite properties.

The position of the maximum in the *tan δ* curve is indicative of the polymer relaxation process typically associated with the T_g of a polymer or composite material. Although the previously reported [39] trend of decreasing T_g is again seen with the addition of fiber reinforcements, it is interesting to note the difference between T_g values obtained for the polymer and composites by DSC (Table 5.11) and DMTA (Table 5.13). Although, the DMTA value of T_g is typically considered less precise than the T_g found though DSC, the magnitude of the *tan δ* curve is a good descriptor for the polymer properties. In general, the greater the height of the *tan δ* peak the greater the portion of the material that is involved in the glass transition. Therefore, it is not surprising that the addition of fiber reinforcements reduces the height of this peak as a result of reduced polymer content. Toriz et al. [39] have reported similar results for flax fiber reinforced CAB composites.

Table 5.13: Summary of DMTA data for neat cellulose based resin and hemp reinforced composites

	E'		tan δ peak			
	Longitudinal	Transverse	Longitudinal		Transverse	
Sample	(Pa)	(Pa)	Temp (°C)	Height	Temp (°C)	Height
Resin A	1.20E+09	1.20E+09	163.65	1.2242	163.65	1.2242
A1	7.02E+09	1.59E+09	153.57	0.427	160.57	0.5146
A2	3.38E+09	1.11E+09	159.06	0.4998	161.48	0.6132
Resin B	1.28E+09	1.28E+09	163.27	0.9691	163.27	0.9691
B1	5.75E+09	5.44E+08	161.41	0.4597	161.72	0.4526
B2	5.78E+09	7.38E+08	160.57	0.4033	161.57	0.5938

E' - storage modulus (dynamic elastic bending modulus)

tan *δ - loss tangent (related to the glass transition of the matrix)*

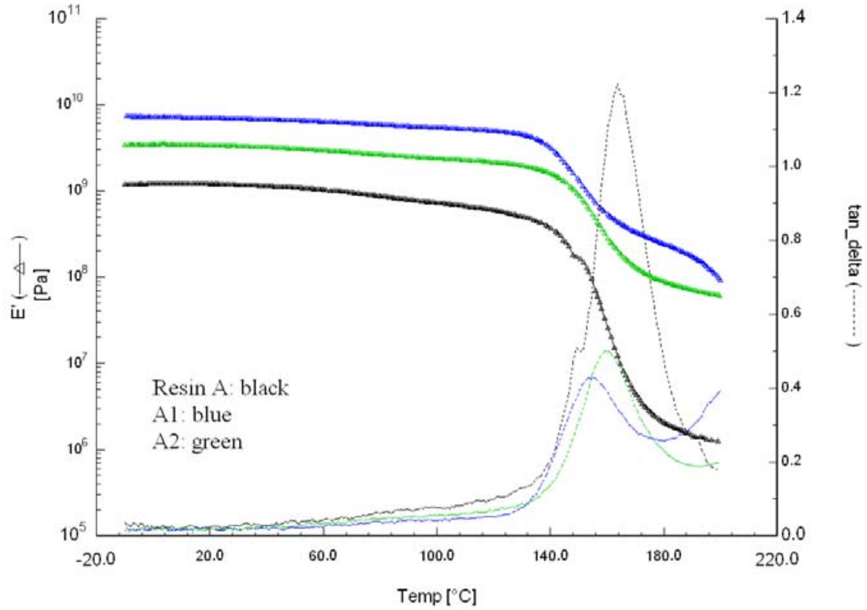

Figure 5.23: Typical storage modulus (E') and tan δ curves for neat cellulose based resin A and composites with longitudinal hemp reinforcement

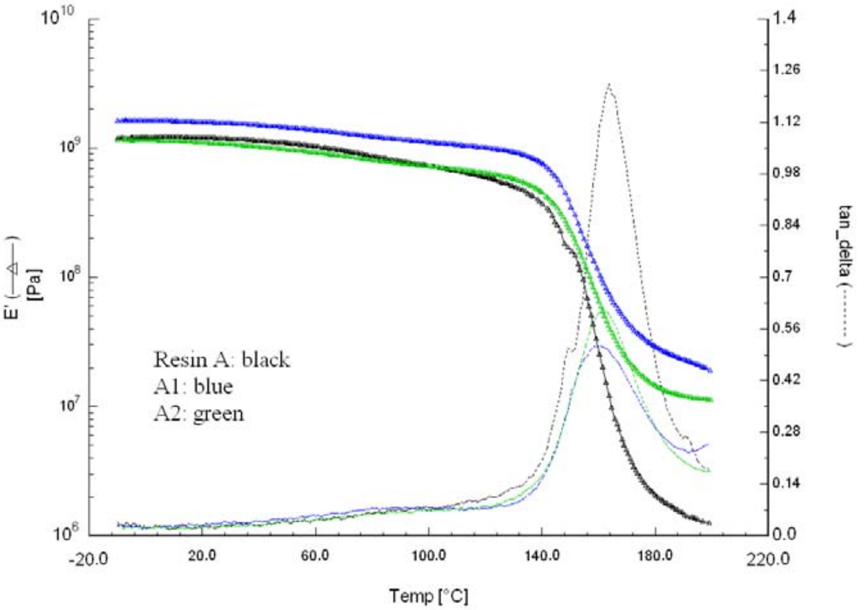

Figure 5.24: Typical storage modulus (E') and tan δ curves for neat cellulose based resin A and composites with transverse hemp reinforcement

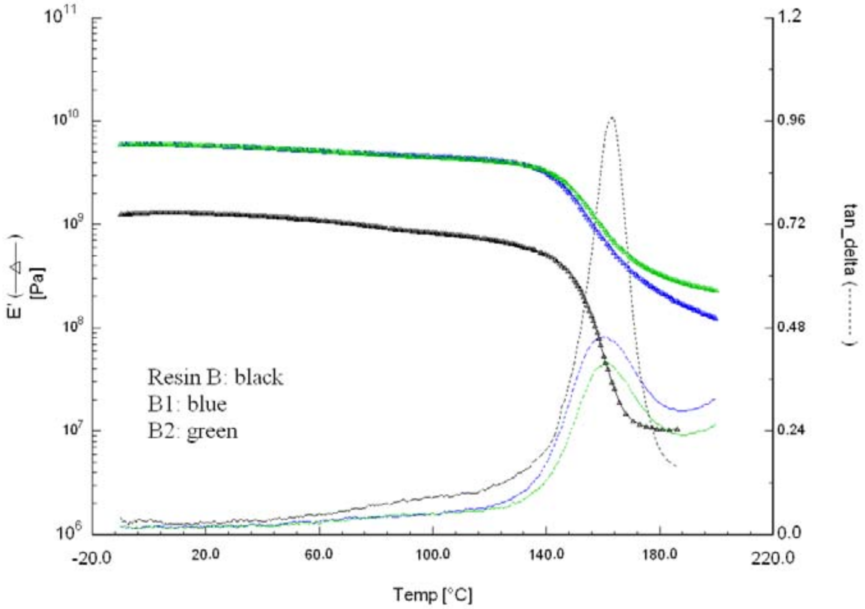

Figure 5.25: Typical storage modulus (E') and tan δ curves for neat cellulose based resin B and composites with longitudinal hemp reinforcement

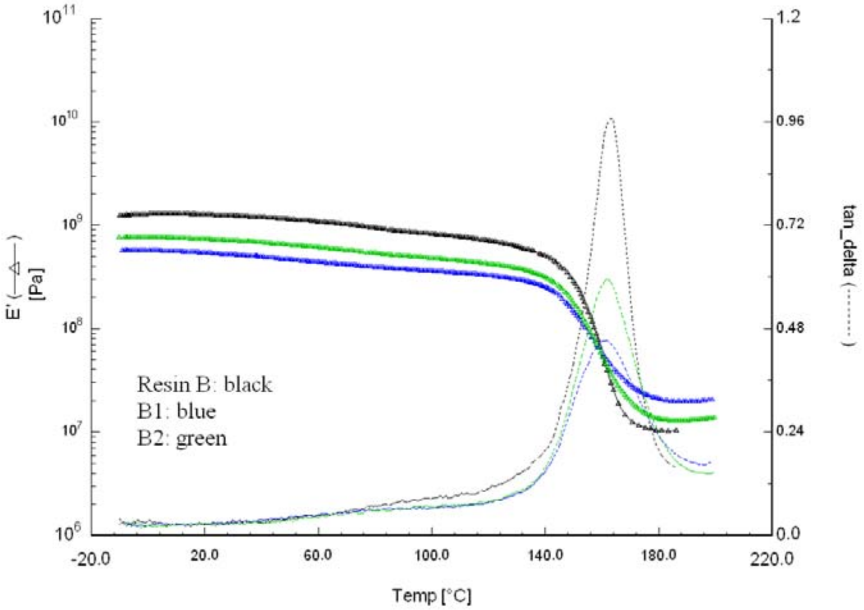

Figure 5.26: Typical storage modulus (E') and tan δ curves for neat cellulose based resin B and composites with transverse hemp reinforcement

5.4 <u>Evaluation of Hemp/CAB Composite Performance</u>

5.4.1 Comparison of Experimental and Predicted Longitudinal Properties

The comparison between experimentally determined and predicted (Section 5.2) tensile properties for the hemp/CAB unidirectional biocomposites yields interesting results. The composite strength properties determined through tensile testing are significantly below the range of predicted values for composites using either the hemp fiber strength values reported in the literature or those determined experimentally in this study. The elastic modulus of the hemp/CAB composites, however, is just slightly below the predicted values for the composites using the literature reported modulus values for hemp fibers, and substantially higher than the values predicted from the experimentally determined hemp yarn modulus.

When the theoretical composites properties in the longitudinal direction were predicted for the composite constituents used in this study, many simplifying assumption regarding the physical variables of the system were made. In reality, however, it is rare that all these assumptions are met through the composite processing procedure. The deviations of the experimental values from predicted values for the properties of the composite systems are likely a result of these assumptions not being met. There are several factors that are known to influence the longitudinal properties such as strength and stiffness of a composite with a defined fiber volume fraction. Primarily, these factors include (1) non-uniform fiber properties, (2) discontinuous fiber structure, (3) misorientation of fibers, (4) interfacial conditions, (5) residual stresses, and (6) void content [1].

Natural fibers are known to have a high variation in mechanical properties as a result of defects, changes in diameter, and growing conditions. The hemp yarns used in this study are no exception and it is expected that the variability in the fiber properties would directly affect the composite properties. Although the yarn structure of the fiber reinforcement allows for effective continuous reinforcement during processing, the yarns are unlike traditional monofilament glass fibers and instead are composed of many shorter discontinuous fibers. The discontinuity of the reinforcing fibers is a possible reason for discrepancy between the experimental and predicted composite properties.

Fiber orientation with respect to the loading axis is an important parameter as the fiber orientation directly affects the ability of the fibers to carry load as well as the transfer of stresses between the fiber and matrix in a composite. Although yarn alignment was highly controlled during composite manufacture, the individual hemp fibers had some degree of misorientation as a result of the twisted structure of the yarns used in this study. If the average degree of fiber misalignment is taken as the mean twist angle of the yarns, the single- and double-ply reinforced unidirectional composites actually have fiber alignments of approximately 9 and 16 degrees, respectively. This misalignment is clear when examining images (Figure 5.27a-b) of the composite failure surfaces and is one possible reason for the lower than predicted composite properties.

Poor fiber/matrix adhesion is another likely reason for reduced composite properties. By examining SEM images of the fracture surface of the fiber reinforced composites significant pullout of the fibers was seen (Figure 5.28a-b). Additionally, protruding fibers did not exhibit any polymer coating or pieces of adhered CAB matrix. This verifies the presence of poor adhesion between the fiber and matrix. Poor fiber/matrix adhesion is known to result in inadequate transfer of stressed between the composite constituents resulting in premature failure by fiber debonding and matrix failure.

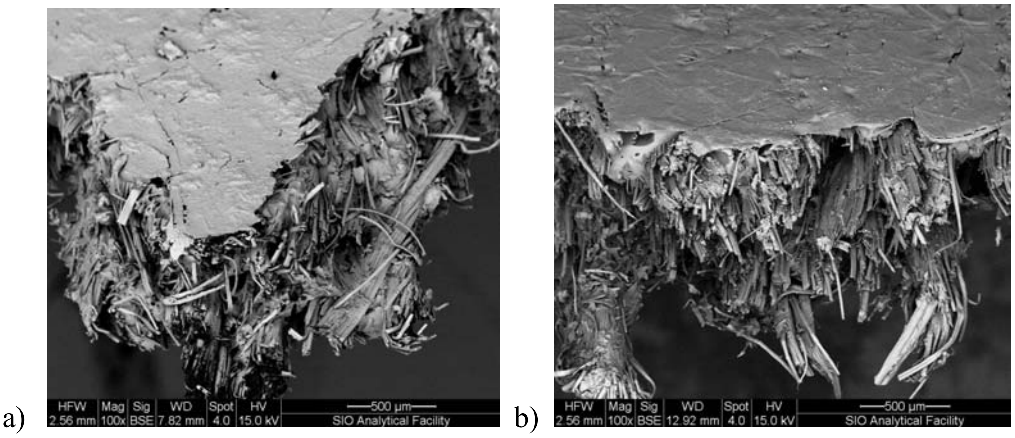

Figure 5.27: SEM images of failure surfaces of hemp-reinforced CAB composites at 100x magnification showing fiber misalignment of a) single-ply yarn and b) double-ply yarn

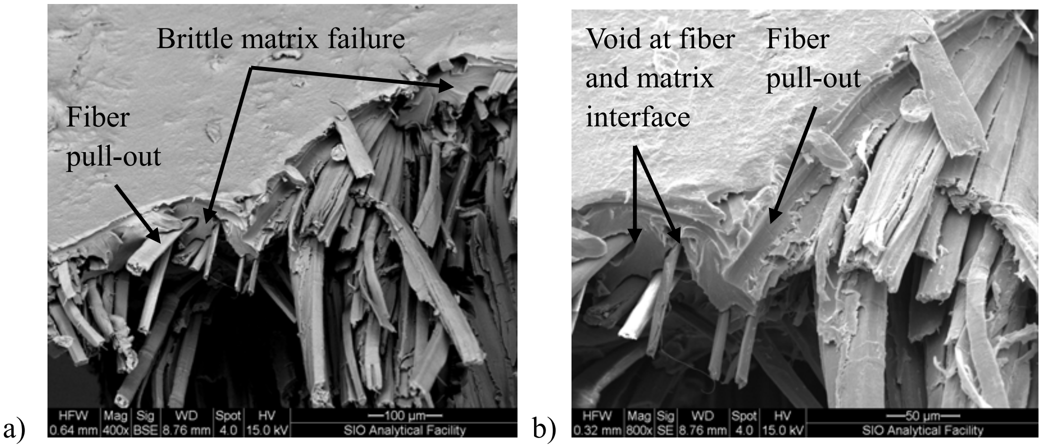

Figure 5.28: SEM images showing failure surfaces of hemp-reinforced CAB composites and poor fiber/matrix adhesion at a) 400x magnification and b) 800x magnification

To further explain the discrepancies between the predicted and experimental composite longitudinal properties the effect of composite void contents, calculated in Section 5.1, was investigated. For this procedure several different models were used to back calculate the effective fiber properties based on composite performance and void contents. In each method, however, the matrix strength, σ_m, was equal to the matrix strength on the neat resin stress-strain curves at the point of ultimate composite elongation to ensure consistency to previous composite predictions. For all the composite systems, the elongation to break was between 3.3 and 3.67 percent (Table 5.5), therefore a generalized value of 3.5 percent elongation, or strain of 0.035 mm/mm, was used to determine an approximated strength value for the matrix at composite failure. These values were calculated from the typical polymer stress-strain curves to be approximately 36 and 37 MPa for polymer A and B, respectively.

First, the traditional ROM equations were used to back-calculate the effective fiber strength and stiffness, Equation 5.27 and 5.28, respectively, using the original fiber and matrix volume fractions derived from the constituent weight percentages and theoretical composite densities in each composite sample. In this case the sum of the fiber and matrix volume fractions, V_f and V_m, equals 1.

$$E_f = \frac{E_c - (1 - V_f)E_m}{V_f} \tag{5.27}$$

$$\sigma_f = \frac{\sigma_c - (1 - V_f)\sigma_m}{V_f} \tag{5.28}$$

Because the ROM approach does not account for void contents, the modified rule of mixtures (MROM) equations are often used to predict composite properties when there are voids present. The equations for the MROM approach are identical in theory as those used for the ROM approach, however the fiber and matrix volume fractions are now experimentally calculated, V_{fe} and V_{me}, and no longer sum to one but are instead are defined by Equations 5.29. Therefore, the *(1-V_f)* term in the ROM approach is replaced by the experimentally determined matrix volume fraction V_{me} as shown in the Equations 5.30-5.31.

$$V_{fe} + V_{me} = \left(\frac{v_f}{v_{ce}}\right) + \left(\frac{v_m}{v_{ce}}\right) = (1 - V_v) \tag{5.29}$$

$$E_f = \frac{E_c - (E_m V_{me})}{V_{fe}} \tag{5.30}$$

$$\sigma_f = \frac{\sigma_c - (\sigma_m V_{me})}{V_{fe}} \tag{5.31}$$

Although the MROM equations are an improvement in composite predictions over the traditional ROM approach, these equations assume that voids only effect the composite by introducing an area of no strength and stiffness, thereby reducing the composites load bearing volume or cross-sectional area. It has been shown, however, that the voids also introduce stress concentrations into the composite material. Madsen and Lilholt [4] have proposed a model based off of the ROM approach incorporating an additional term to account for the reduced material properties from decreased load bearing volume and stress concentrations as a result of voids (Equations 5.32-5.35). The equations can then be solved for E_f and σ_f, as was done with the ROM and MROM equations, to determine the effective fiber properties.

$$E_c = (E_f V_f + E_m (1 - V_f))(1 - V_v)^2 \tag{5.32}$$

$$\sigma_c = (\sigma_f V_f + \sigma_m (1 - V_f))(1 - V_v)^2 \tag{5.33}$$

$$E_f = \frac{\left(E_c\left(1-V_v\right)^{-2} - E_m\left(1-V_f\right)\right)}{V_f} \tag{5.34}$$

$$\sigma_f = \frac{\left(\sigma_c\left(1-V_v\right)^{-2} - \sigma_m\left(1-V_f\right)\right)}{V_f} \tag{5.35}$$

A summary of the back-calculated effective fiber properties, E_f and σ_f, using the three models explained above is shown in Table 5.14. It is interesting to note that the effective fiber properties of the single-ply yarn exceed those of the double-ply yarns in all cases. This trend supports the hypothesis of a reduced translation of fiber properties to composite properties as a result of the additional fiber twist observed in the double-ply yarns. A comparison of the range of effective fiber properties to those reported in the literature is also shown (Table 5.15). For the hemp reinforcing fibers in this study, the back-calculated fiber modulus values using ROM, MROM, and the model developed by Madsen are within the range, but on the low end, of the literature reported values previously determined in Section 3.3.2.2 of this report. In comparison, the back-calculated values of fiber strength were consistently below the range of values reported in the literature for hemp fibers. These low effective strengths calculated for the fibers could suggest several things: (i) the longitudinal strength of the composites is substantially more affected by void content than is predicted by even the Madsen and Lilholt model; (ii) the effect of fiber twist is greater than is predicted by the fiber models; or (iii) poor adhesion between the fiber and matrix layers has a greater effect on the composite strength than modulus. Most likely, the below average strength values are result from a combination of the above mentioned issues.

Table 5.14: Back-calculated effective fiber strength and stiffness from several prediction models for longitudinal composite properties

	Effective fiber Modulus: E_f (GPa)			**Effective fiber Strength: σ_f (MPa)**		
Composite Samples	**ROM**	**MROM**	**Madsen and Lilholt**	**ROM**	**MROM**	**Madsen and Lilholt**
A1	46.39	51.14	56.36	404	446	492
B1	38.17	44.37	51.58	380	444	519
A2	32.66	39.65	48.08	315	384	468
B2	33.43	39.76	47.26	324	387	462

Table 5.15: Comparison between experimentally determined and reported values of strength and stiffness for hemp fiber reinforcement

	Fiber Modulus (GPa)		**Fiber Strength (MPa)**	
Fiber type	**E_{fE}***	**E_{fR} ****	**σ_{fE} ***	**σ_{fR} ****
Single-ply	38.17-56.36	37-65	380-519	518-847
Double-ply	32.66-48.08	34-60	315-468	466-743

* Back-calculated effective fiber properties

** Fiber properties reported in literature with respective twist angles

Using the back-calculated fiber properties from the Madsen and Lilholt model, predictions were made for the A1 composite system to determine its potential to compete with other unidirectional natural fiber composites (Figure 29). These findings suggest that with better processing conditions, reduced void content, and improved fiber/matrix adhesion hemp/CAB composite tensile properties in excess of those found experimentally in this study are possible.

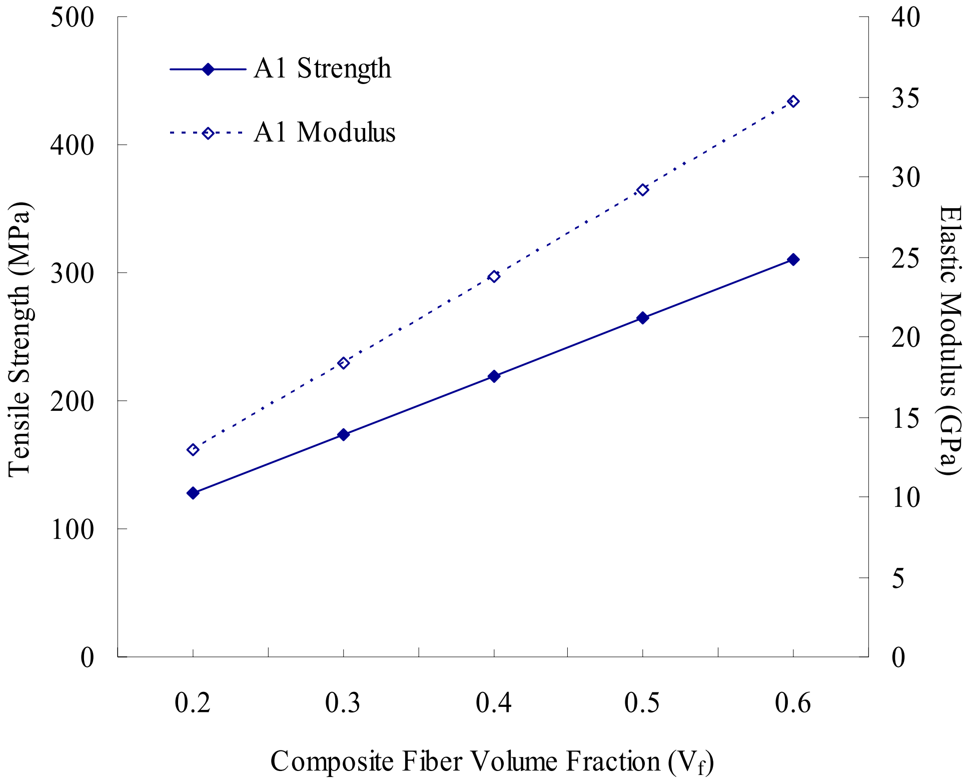

Figure 5.29: Predicted composite strength and stiffness values for biocomposite system A1 at various fiber volume fractions using the back-calculated effective fiber properties from the Madsen and Lilholt model [4]

5.4.2 Comparison of Hemp/CAB Biocomposites with Other Known Materials

It is also of interest to compare the properties of the biocomposite system developed in this study to other unidirectional natural fiber composites as well as traditional building materials such as GFRPs and wood products. The general objective of this study was to develop a biocomposite system that can compete with these traditional building materials, so as to provide a more environmentally friendly choice for building materials. It has already been shown that there are many environmental benefits to using natural fibers and biopolymers over traditional synthetic or petroleum derived composite materials [44,45]. Additionally, the fast growth cycles and high yield of plant crops makes natural fiber composites superior from a sustainability standpoint to wood products.

Although the current applications of randomly aligned natural fiber reinforced polymer composites in the automotive industry have demonstrated the potential for these materials to compete with traditional GFRP composites in certain applications, virtually no application of directionally aligned natural fiber composites has been shown. An overview of the current reported mechanical properties for unidirectional aligned biocomposites is presented in Table 5.16. In addition, this table shows several published values for unidirectional GFRP composites. Although the strength properties of the natural fiber composites are lower that the GFRP composites, the stiffness of the biocomposites is comparable to GFRPs. The density of glass fibers can also be as much as double the density of natural fibers thus making both the specific strength and stiffness of the natural and glass-fiber reinforced composites more comparable. The results of this study have shown that strategic alignment of the reinforcements can be used to dramatically improve the mechanical performance of natural fiber reinforced composites. Additionally, the use of a thermoplastic biopolymer instead of traditional petroleum polymers was successfully demonstrated from a composite manufacturing and performance perspective.

Table 5.16: Summary of some unidirectional composite properties with glass and natural fiber reinforcements

Uni. Composite Materials (fiber/matrix)	V_f	**Tensile strength (MPa)**	**Tensile modulus (GPa)**	**Flexural strength (MPa)**	**Bending modulus (GPa)**	**[Ref.]**
Glass/Epoxy	0.55	1560	56	1145	41	[46]
Glass/PP	0.6	-	-	774	27	[47]
Glass/Polyester	0.52	905	39	450**	20.8**	[19]
Glass/Epoxy	0.48	817	31	-	-	[21]
Glass/PP	0.6	1020	45	-	-	[48]
Hemp/CAB	0.51	224	25.2	133	22	*
M.Hemp/Starch	0.7	365	28	223	25	[42]
Hemp/PP	0.48	280	28	-	-	[5]
Hemp/Epoxy	0.35	-	-	228	12	[18]
S.Hemp/Polyester	0.4	148	14	-	-	[22]
Flax yarn/Soy	0.45	-	-	126	2.24	[6]
Flax yarn/Soy	0.6	-	-	259	3.7	[47]
Flax/Epoxy	0.25	-	-	182	19.5	[19]
Flax/Vinylester	0.37	248	24	-	-	[19]
Flax/Epoxy	0.47	280	39	-	-	[21]
Flax/PP	0.4	-	-	135	11	[25]
Ramie/SPC	0.65	271	4.9	225	12.5	[8]
Ramie/Polyester	0.62	-	-	197	43	[24]
Jute/PP	0.21	142	11	122	9.1	[20]
Jute/PLA	0.38	78	8.5	-	-	[20]
Jute/PLA	0.23	-	-	85	7	[20]
Jute/Polyester	0.6	250	35	-	-	[30]
Jute/Polyester	0.68	-	-	280	41	[24]
Lyocell/CAB	0.65	250	20	-	-	[9]
Curaua/Starch	0.7	327	36	-	-	[7]
Sisal/Polyester	0.64	-	-	250	49	[24]
Sisal/Epoxy	0.58	310	9.8	240	17.8	[49]

*Current Study

**$V_f = 0.25$

Table 5.17: Comparison of properties for several common wood and plant based building materials [16,46,47]

Material	**Density (g/cm^3)**	**Elastic modulus (GPa)**	**Flexural strength (MPa)**
Hemp/CAB Composite**	1.25	22	133
HARDWOOD			
Red Maple Wood	0.6-0.75	11.3	92
White Oak Wood	0.6-0.9	12.3	105
SOFTWOOD			
Douglas Fir	0.53	13.4	85
Pine (ponderosa)	0.35-0.6	8.9	65
Spruce	0.4-0.7	8.9	64
PARTICLEBOARDS			
Flax	0.6	-	16-18
Hemp	0.6	-	15-16
Bagasse	0.6	-	20-21
Jute	0.58	-	15-16
Bamboo	0.625	-	18-19
MEDIUM DENSITY FIBERBOARDS			
Flax	0.785	-	29-35
Hemp	0.88	-	7.8-20.8
Kenaf	0.817	-	19.3
NATURAL FIBER/POLYESTER COMPOSITE LAMINATES			
Sisal ($W_f = 0.5$)	1.05	-	40**
Jute ($W_f = 0.3$)	1.22	-	66**
Coir ($W_f = 0.3$)	1.4	-	20.4**

*Current study

**Value represents tensile strength

A summary of typical reported material properties for some wood and plant based materials currently used in the building industry are shown in Table 5.17. It is clear that the properties of the unidirectional composites in this study exceed those of traditional wood and offer the benefit that their orientation can be highly tailored through stacking of various angle-plies. The high strength and stiffness properties of the unidirectional biocomposites in this study suggests their potential application as face sheets or veneers for particle and fiberboards to improve their tensile and flexural properties. Limitations on these materials still exist, however, as a result of the lack of knowledge on their long term loading behavior as well as moisture resistance and durability. These properties must be further investigated before their use in applications requiring significant long-term load bearing capacity can be warranted.

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6. SUMMARY AND CONCLUSIONS

6.1 Summary

In general, the unidirectional biocomposites manufactured in this study show significant potential for such materials to be used in secondary and possibly even primary load-bearing applications. The experimentally determined and predicted composite properties compare well with other literature reported values for unidirectional aligned natural fiber composites, and in many cases they outperform timber products and traditional glass fiber reinforced composite materials, particularly when compared on the basis of weight. By incorporating the effect of void content on composite properties, back-calculated effective fiber properties compared well with the values reported in the literature for hemp fibers. Predicted composite properties using the ROM approach with the effective fiber properties show even greater promise for these materials to carry high loads. Although the results from experimental testing show promise for these materials, several improvements in reinforcement characteristics, void content, and adhesion between the fiber and matrix are needed to optimize the biocomposite system. Additionally, studies on the durability, biodegradation, and long term behavior of the composites are necessary if they are to be used in load bearing applications.

6.2 Major Conclusions

Unlike the majority of previous biocomposite studies, the composites in this study are made entirely from renewable resources, and therefore are superior from an environmental viewpoint. These could be considered precursors of composites that are made from renewable resources using environmentally benign processes which is the ultimate goal for materials used in structural and construction applications. In the current study, fibers derived from fast growing and environmentally friendly hemp plants were shown to have excellent performance as the reinforcing phase in biocomposites. Several benefits to using these fibers in the form of industrial textile yarns were seen. First, the processing procedure to make the hemp yarns involves isolation of the high strength fibers and simultaneously allows for removal of impurities, degraded portions of the fiber and lower strength constituents such as lignin, pectin, and waxes. Additionally, the continuous structure of the hemp yarns facilitates ease of composite processing and allows for controlled alignment of the reinforcement.

Although the twisted structure of the hemp yarns is necessary to develop a continuous fiber material, high twist angles were seen to have a negative effect on the composite performance. High fiber twist not only led to individual fiber misalignment but also led to tighter fiber packing making resin impregnation of the yarns more difficult. This resulted in the presence of entrapped air, i.e. megavoids, within the composite cross-section observable by optical image analysis as well as SEM imaging. In contrast to the high twist double ply yarns, the smaller diameter and lower twist single-ply yarns showed better impregnation capability and composite consolidation resulting in lower void content. It is therefore recommended that plied yarns be avoided and overall yarn diameters and twist angles be kept to a minimum when used as reinforcements in biocomposites.

The plasticized cellulose resin systems investigated in this study had good mechanical and processing properties and therefore proved adequate as matrix materials for biocomposites. Optimization of the processing window for the polymers suggested that adequate melt flow could be achieved within the temperature range selected in this research (i.e. 185-190°C). In general, composites with polymer A showed superior properties as compared to those with resin B. The benefits of higher molecular weight in these polymers seem to outweigh the processing difficulties associated with a higher polymer melt viscosity. The difficulty in attaining a good bond between the polar natural fibers and non-polar thermoplastic matrix was seen to extend to the biopolymers studied in the current investigation. The use of fiber surface treatments and/or coupling agents is needed to ensure a better bond between the composite constituents resulting in higher mechanical performance and lower susceptibility to moisture and thermal degradation.

The composite manufacturing procedure developed in this study showed promising results for manufacturing of biocomposites with good repeatability and control of fiber and matrix constituent contents. The ability to produce unidirectional composites with high fiber volume fractions was successfully demonstrated through this processing technique. Additionally, control of fiber alignment and dispersion was shown to be good as well. In the current study, the use of chemical solvents was found to be necessary to create a low viscosity resin solution able to achieve good impregnation of the yarns. Although the solution resin had good fiber coating capabilities, evaporation of the solvent is potentially harmful and can result in high a void content in the final composite. However, the void content can easily be reduced through the use of vacuum, and eventually through replacement of current solvents by more environmentally benign and specially designed solvents that are miscible in biopolymers. The investigation also showed that processing methods such as filament winding could be adapted for use with natural fibers and biopolymers. This is important for the implementation of such systems in actual industrial applications needing high performance composites.

6.3 Aspects for Further Research

Although the research completed in the current investigation has successfully demonstrated that unidirectional hemp/CAB biocomposites can be fabricated with high levels of performance characteristics, substantial improvements can still be made such that these materials are not just viewed as being environmentally attractive in secondary structural applications, but also as regular materials selected on the basis of performance alone. True sustainability and greening of construction materials will only be achieved if the environmental aspects are an inherent characteristic of the system rather than the primary one. In order to reach this level there are a few aspects of research that still need to be conducted and these are outlined below:

i. Investigate physical and chemical methods to reduce the hydrophilic nature of fibers and provide better adhesion between fibers and the matrix through:
    - Mercerization or acetylation could be researched as a means of removing impurities and non-structural materials from the fiber and to increase surface roughness leading to better mechanical interlock between the fiber and the biopolymer matrix.
    - Incorporation of chemical coupling agents to provide enhanced mechanisms of chemical bonding between polar and non-polar composite constituents

ii. Develop an automated composite manufacturing system integrating yarn impregnation, solvent evaporation and controlled winding scheme with the aims of:
    - Easy control and adjustment of fiber and matrix contents
    - Reduced composite void content
    - Reduced composite processing time

iii. Investigate durability and long term behavior of biocomposite systems especially when exposed to levels of high humidity, temperature cycling and sustained load.

iv. Investigate mechanisms of obtaining well compacted and structured yarns and fabrics using hemp feedstock with low degrees of misalignment and twist and complete removal of micro-scale voids within the individual fibers.

v. Investigate environmentally friendly disposal and degradation techniques for hemp/CAB composite system to result in systems that are biodegradable on command (i.e. when specially designed triggers are activated) to ensure that the overall product is designed from a “cradle-to-cradle” perspective.

vi. Determine the applicability of composite processing procedures for alternate biocomposite material systems such natural fiber reinforced PLA or soy protein-based polymers thermoplastic polymers or cross-linked plant oil-based polymers.

vii. Manufacture and test structural biocomposites prototypes to replace traditional GFRP composite, wood, or metal members in elements such as beams, ceiling or wall panels, or window or door frames (fenestration products).