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BIOCOMPOSITES FROM ENGINEERED NATURAL FIBERS AND UNSATURATED POLYESTER RESIN FOR HOUSING PANEL APPLICATIONS

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BIOCOMPOSITES FROM ENGINEERED NATURAL FIBERS AND UNSATURATED POLYESTER RESIN FOR HOUSING PANEL APPLICATIONS

By

Geeta Mehta

A THESIS

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ABSTRACT

BIOCOMPOSITES FROM ENGINEERED NATURAL FIBERS AND UNSATURATED POLYESTER RESIN FOR HOUSING PANEL APPLICATIONS

By

Geeta Mehta

The aim of this project is to make low cost 'green materials' (biocomposites) for use in various housing panel applications, for example, wall panels, roofs, doors, floors, etc, to compete with and substitute for glass-polyester panel systems used presently. The starting materials for these products are natural fibers as reinforcements, and unsaturated polyester resin as polymer matrix. The project consists of three interconnected parts: modification and engineering of natural fibers to make them suitable as reinforcements in polymer composites, alteration of the polymer composite matrix to make it more 'green' while maintaining its properties and performance, and the development of a sheet molding compounding panel process (SMC) as a new way for continuous production of biocomposites. The research on 'designed' fiber reinforcement sought to synergistically combine up to four different fibers, which have been effectively surface treated, physically or chemically, to improve the fiber matrix adhesion in the resulting biocomposite. Research was also being conducted to modify the polyester polymer matrix through the addition of modified vegetable oils while maintaining properties and processability. The functionalization of vegetable oils is done in a manner that it is compatible with polyester resin. We have also been successful in developing a SMC process for the continuous manufacturing of bio-composites using chopped natural fibers.

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DEDICATION

And Life, a little bald and gray, Languid, fastidious, and bland, Waits, hat and gloves in hand, Punctilious of tie and suit (Somewhat impatient of delay) On the doorstep of the Absolute.

T. S. Eliot January 1910

This work is dedicated to my father, mother, sisters, and niece, who have given me the wings to fly, strength to persist, inspiration to move forward, faith to be brave in desperate situations, and love to conquer it all. A special dedication to my best friend, philosopher and guide, who has always been there for me through all thick and thin. I thank all of you, I'm so lucky to have you all. Words can not express the warmth of love that I feel all around me because of you all.

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Images in this thesis are presented in color

CHAPTER ONE: INTRODUCTION

1. INTRODUCTION

Fiber-reinforced plastic composite materials were first produced by combining cellulose fibers with phenolic resin in 1908. Since that time, composite materials have advanced to applications ranging from packaging materials to aerospace components and structure, largely based on the utilization of petroleum based constituents, i.e., glass, carbon or aramid fibers reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics. Because of growing environmental consciousness, traditional composite structures are now becoming the subject of legislative initiatives governing their manufacture, use and removal. The most difficult aspect of the problem is the removal at the end of lifetime, as the components are closely interconnected, relatively stable, and therefore difficult to separate and recycle [1]. There is a new and growing requirement for composite materials which are recyclable and/or degradable.

Natural Fibers

By combining natural reinforcing fibers with biopolymer matrices, new fiber reinforced materials called 'biocomposites' are being developed [2-10]. These biocomposites consist of biofiber as the reinforcing element and usually a biodegradable polymer as the matrix material. Since both components are biodegradable, the composite is also expected to be biodegradable. Biopolymers are generally biodegradable, but they do not possess the necessary thermal and mechanical properties useful for engineering applications. On the other hand, common engineering plastics are obtained from synthetic polymers, but are non-biodegradable. Although much research has been carried out on biofiber reinforced

synthetic polymers, they are not completely biodegradable. However, biofibers derived from annually renewable resources, used as reinforcing fibers in both thermoplastic and thermoset matrix composites, provide environmental benefits with respect to ultimate disposability and raw material utilization [1, 5, 7].

In biocomposites, the biofibers serve as reinforcement by enhancing the strength and stiffness of the resulting composite structures. The conventional fibers like glass, carbon, aramid, etc., are produced with very specific properties having little variability, whereas the properties of natural fibers vary considerably. Biofiber properties depend on whether the fibers are taken from plant stem or leaf, the quality of the plants as a function of agricultural practices, the age of the plant, the preconditioning of fibers, and the processing methods adopted for extraction of fibers [5, 6]. Properties such as density, ultimate tensile strength, initial modulus, and toughness are related to the internal structure and chemical composition of fibers [5]. However, pristine natural fibers have the mechanical properties that would allow them to be used as glass fiber replacements in certain composite applications.

In addition to constituent selection, to obtain a good reinforcing effect for plastics composites, it is necessary to increase the adhesion between fibers and resins by using surface treatments [3, 9]. Surface chemical modifications of natural fibers, including dewaxing, alkali treatment, cyanoethylation, vinyl grafting, and treatment with various coupling agents, have been shown to improve fiber matrix adhesion in biocomposites [9]. Thermoset composites are more desirable than thermoplastics because of their superior mechanical properties. Petroleum based matrix resins in thermoset biocomposites are in general, non-biodegradable. Compared to thermoplastics, thermoset polymers have a

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lower viscosity, complex formulations, better damage tolerance, easier fiber impregnation, longer processing cycles, and higher fabrication costs. Thermoplastics are also recyclable, easy to handle, and have unlimited shelf life. However, they are prone to creep, while thermoset are not.

Unsaturated polyester resin

Among various thermoset resins, unsaturated polyesters (UPEs) are the most widely used matrix materials in polymeric composites [11, 12]. They are processed over a wide temperature range involving hand lay-up at low temperatures, resin-transfer molding at medium temperatures, and sheet-molding compound (SMC) compression molding, bulk-molding compound (BMC) injection molding, and pultrusion at high temperatures [19]. UPE resins have many applications in automotive, aircraft, electrical, and appliance components [11-20].

Unsaturated polyester resins (UPE) refer to a large class of polymers containing reactive double bonds in the polymeric chain. The reaction of a UPE resin is a free-radical chaingrowth crosslinking copolymerization between the styrene monomer (25-45 wt %) and the UPE molecules. A source of free radicals, usually organic peroxides, is needed to initiate the reaction. The initiator is disassociated with help of a promoter. Optimum performance can be achieved by controlling the type and concentration of peroxide and promoter. Typical initiator concentrations run from 1 to 3% by weight based on clear resin and, for accelerators, (mostly cobalt) from 0.25 to 4% based on 1% metal content solution [11-14]. Under or overdosing can result in deterioration of cure and mechanical properties.

Project Motivation

The ambitious goals set by the U.S. government for the creation of a biobased economy as an alternative to the existing petroleum-based products are challenging the industry, academia, and agriculture [21]. This project seeks to replace conventional glass fiberpolyester composites by a novel low-cost natural/biofiber composite for housing panel applications. Through use of biofibers, our goal is to make composites, which can outperform current housing panels, while maintaining competitive economic structure.

Objective

The overall objective of this project is to develop environmentally friendly biocomposites as alternatives to the present glass based composites. Although polyester resin is a petroleum based product and not eco-friendly, we have chosen it as the matrix resin as it is required to produce a material which can be integrated easily into the current housing material industries. In the future, replacement or modification of the petroleum based resin by a suitable biobased resin is a logical and desirable direction for this research.

In order to achieve the above objective, several interrelated components are required: *i*) development of a Biocomposite Sheet Molding Compound Panel (BCSMCP) high volume manufacturing process; *ii*) fundamental studies for determining the relationship between structures and properties of the materials;, and *iii*) utilization of 'engineered' natural fibers having good fiber-matrix adhesion, a balance of mechanical properties and processability.

Design of Fibers

'Engineered' biofibers are defined as the suitable blends of surface treated bast, leaf and fruit fibers, which provide an optimum balance in mechanical properties of the final composite. The blending of differently modified fibers is based on the principle that the individual fiber properties vary with their location in the plant and the level of adhesion will determine their contribution to the composite stiffness and toughness. Previous research has shown that fibers originating from the leaf have very high toughness while those originating from bast have very high modulus [1]. Thus, by combining different fibers in optimum weight ratios, it is possible to have very tough and stiff biofibers. The bast fibers used in this research are kenaf, hemp, jute, flax, while the leaf fibers are sisal, henequen, and pineapple leaf fiber.

An optimum fiber matrix interface bond is critical for performance of composite materials. Surface chemical modifications of biofibers have been successful in improving the fiber-matrix adhesion of biocomposites. Surface treatments also improve compatibility between fiber and matrix, dimensional stability and resistance to biodeterioration. The use of low cost, water based surface treatment and sizing for biofibers, for example, low concentrations of alkali treatment, and silane treatment is mandatory if the balance between performance and economic viability is to be maintained. The reinforcing effect of the fiber is also dependent on other parameters, such as, fiber diameter, fiber length, chemical constituents of the fiber, fiber orientation in the composite, number of individual fibers in a fiber bundle, and the fiber volume fraction used in the composite. All of these variables and their effect on the final biocomposite properties will be factored into the experimental plan.



Figure 1.1: Schematic representation of the research plan for this project [22]

Curing of polymer matrix

Temperature and time are the most important parameters in a cure cycle. Curing of thermosets requires an intimate knowledge of the chemical kinetics of the polymerization and crosslinking reactions. The parameters that must be determined in a cure cycle are the number of stages in the cure, the rate of temperature increase, the hold temperature at each stage, the pressure at which the cure takes place, and the time allotted for the cure cycle [23]. Once the kinetics are understood and the actual chemistry behind the curing is established, the cure cycle parameters can be chosen based on the desired polymer properties.

The physical nature of chemical crosslinking is quantified and represented by crosslink density and degree of cure. The crosslink density is a quantitative measure of the number of crosslinks that exist in a given volume in the thermosetting polymer. The degree of cure represents the chemical conversion of the curing reaction [24]. The crosslinking density is determined from Dynamic Mechanical Analysis (DMA), and degree of cure is evaluated from Diffrential Scanning Calorimerty (DSC), and Fourier Transform Infra Red Spectroscopy (FTIR). In addition, the kinetics of curing reaction, including, rate of reaction, order of reaction, etc. can be estimated from DSC and FTIR experiments. It should be noted that the optimum curing conditions will have to re-established after the addition of any fillers, fibers, additives to the polymer matrix.

Matrix modification

Unsaturated polyester resins (UPE) are brittle, undergoing a 7-10% volume shrinkage after curing, and are not very resistant to alkali exposure. Traditionally, these properties are improved by blending with various additives; for example, fracture properties of a cured resin improve after blending with reactive liquid rubber and the shrinkage of UPE is prevented by introduction of a polar low-shrinkage thermoplastic.

Bioresins, or thermoset resins derived from vegetable oils like, soybean, castor, corn, peanut, cottonseed, etc, also increase toughness and reduce volume shrinkage, with the added advantage of lower cost, abundant availability, and lower environmental impact [25]. Adding bioresins to the matrix will reduce the amount of fossil fuel based products in the final composite. It is planned to eventually phase out polyester resin from the formulation of biocomposites, to produce a completely 'green' product.

Processing

Using thermoset resins, biocomposites can be fabricated by compression molding, resin transfer molding and hand lay-up. One goal of this project is to develop a continuous process for making biocomposites, which will be similar to the existing Sheet Molding Compound (SMC) process, and thus could be adopted in the industries without any major change in infrastructure. This new high volume processing technique will be named 'biocomposite stampable sheet molding compound panel' (BCSMCP) manufacturing process. SMC is a continuous sheet containing chopped fibers and mineral fillers embedded in a highly viscous thermoset resin [26]. In the commercial SMC process, continuous glass fibers rovings are fed to a chopper, cut to 6 mm in length, and then distributed onto a carrier film, forming a uniform layer of chopped glass fibers. Since natural fibers cannot be obtained in a continuous from, and making a continuous yarn or roving with these fibers would be difficult and expensive, chopped natural fibers can only be utilized if a new process is developed. Achieving a uniform and continuous dispersion

of a controlled amount of fibers with little variability on the SMC line will be an important goal of this work.

Testing

Mechanical properties of the composites need to be determined in order to insure that the resulting biocomposite has structural parity with the conventional composite. After the composite has been fabricated and conditioned, it is subjected to various tests, in accordance with ASTM standards to evaluate its properties. Properties of interest are tensile strength and modulus, bending strength and modulus of elasticity, impact strength, storage modulus, loss modulus, tangent delta, coefficient of thermal expansion, compressive strength, creep, shear stress and stiffness. The experimental properties are compared with theoretical values obtained from micro-mechanical models such as the Halpin-Tsai, Halpin and Pagano and Piggott models [27]. Morphology and fiber distribution are ascertained by electron microscopy on tensile fractures samples of composites. The durability of biocomposites is tested by moisture absorption test, accelerated weathering test, and fire test.

The untreated and surface treated biofibers and hybrid biofibers are characterized by DSC, Thermal Gravimetric Analysis (TGA), Fourier Transform Infra-Red Spectroscopy (FTIR), Environmental Scanning Electron Microscopy (ESEM), and X-Ray Photoelectron Spectroscopy (XPS) to evaluate degree of crystallinity, maximum degradation temperature, chemical reactions as a result of treatment, topology, and morphology, and surface atomic concentrations, respectively.

Summary

The desire for renewable materials from sustainable sources is increasing for a variety of applications. Polymer matrix composites reinforced with natural plant fibers are one such example. Combining natural fibers with an unsaturated polyester resin matrix, novel low-cost biocomposites with desired properties can be made. Such biocomposites can provide many beneficial additions to the American Advanced Housing program. Fundamental and applied research into the materials, their surface treatments and fabrication processes is necessary to transfer this technology to industry.

The objective of this research is to investigate the properties and processing of biofiber reinforced Unsaturated Polyester Resin (UPE) composites. The biggest advantage of panels made from this type of biocomposite is their low cost, combined with their ecological and technological advantages. If composite panels with acceptable properties can be developed, along with a viable manufacturing method for their continuous processing, housing panels for the future can be produced.

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CHAPTER TWO: LITERATURE REVIEW

2.0 Literature Review

In this chapter, some of the basic definitions and concepts related to natural fiber composites will be introduced, followed by summaries of past research related to natural fiber modification, polyester resin, bioresins, composite fabrication techniques, and applications of natural fiber composites.

2.1 Natural Fibers

The idea of using cellulose fibers as reinforcement in composite materials is not a new or recent one. Ever since the beginning of human civilization, natural fibers like grass and straw were used to reinforce mud bricks. However, with the advent of high performance man made materials, the use of natural fibers diminished. Until recently, the natural fibers were mainly used in the production of rope, string, clothing, carpets and other decorative products. Interest in the use of natural fibers has grown during the last decade due to their various advantages.

Increasing environmental consciousness and demands of legislative authorities are leading to the scrutiny of manufacture, use, and removal of traditional composite structures, usually made of glass, carbon or aramid fibers reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics. The disadvantages of such composite materials is the use of organic materials during their manufacture, high processing temperature and energy use, and disposal and recycling at the end of their

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lifetime. The composite constituents are closely interconnected, relatively stable, and



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Figure 2.1.1: Examples of natural fibers [1] therefore difficult to separate and recycle [1].

Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes. Biodegradable plastics and biobased polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock [2]. To be sustainable, a biobased product derived from renewable resources has to be recyclable, triggered biodegradable, commercially viable and environmentally acceptable.

The Technology Road Map for Plant/Crop based Renewable Resources 2020, sponsored by the U.S. Department of Energy (DOE), has targeted to achieve 10 % of basic chemical building blocks arising from plant derived renewable sources by 2020, with development concepts in place by then to achieve a further increase to 50 % by 2050. The U.S. agricultural, forestry, life sciences, and chemical communities have developed a strategic vision [3] for using crops, trees, and agricultural 2100 residues to manufacture industrial products, and have identified major barriers [4] to its implementation.

2.1.2 Structure of biofibers

Biofibers are generally lignocellulosic consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicellulose [1, 2, 5]. A single fiber of all plant based natural fibers consists of several cells. These cells are formed out of crystalline microfibrils based on cellulose, which are connected to a complete layer, by amorphouse lignin and hemicellulose. Multiple of such cellulose-lignin/hemicellulose layers stick together to a multilayer composite, the cell wall [9]. These cell walls differ in their composition and in the orientation of the cellulose microfibrils. These fibers consist of several fibrils that run along the length of the fiber. The potential fibers are separated from the original plant in several ways like retting, scrapping, decorticating and pulping. Cellulose is the main component of almost all natural fibers. The elementary unit of a cellulose macromolecule is anhydro-D-glucose, which contain three hydroxyl (OH) groups (Figure 2.4). These hydroxyl groups form hydrogen bonds inside the macromolecules itself (intramolecular) and between other cellulose molecules (intermolecular). Therefore all natural fibers are hydrophilic in nature.



Figure 1.1.2: Chemical structure of cellulose molecules: Poly- $\beta(1,4)$ -D-Glucose

2.1.3 Advantages of natural fibers

Natural fibers offer various advantages over other kinds of reinforcements. Biofibers come from annually renewable resources, and are biodegradable. They are much less expensive and less dense as compared to man made fibers like E-glass fibers and carbon fibers [1]. Environmental gains can be made through use of renewable biofibers instead of synthetic fibers. Insulation and sound absorption properties of natural fibers are much better than those of fiberglass.



Figure 2.1.3: Comparison of cost and density between glass fibers and biofibers Natural fibers provide a net energy savings over man-made fibers. Biofibers are produced by solar energy while production of synthetic fiber needs large amounts of petroleum based energy. The processing temperature to make glass fiber exceeds 1200^oC [1, 7, 8]. It

takes 6,500 BTUs of energy to produce one pound of kenaf (not including the energy to produce fertilizer, collect and process the fibers) while it takes almost four times that much energy (23,500 BTUs) to produce one pound of glass fiber [7].

2.1.4 Properties of Natural Fibers

Physical properties of natural fibers are strongly influenced by their chemical structure such as cellulose content, degree of polymerization, orientation and crystallinity, which are affected by the plant genetic makeup, conditions during growth of plants as well as extraction methods used. As a result, there is an enormous variability in fiber properties depending upon which part of the plant the fibers came from, the quality of the plant and its location [1, 5]. The properties of these fibers are very difficult to measure, because a considerable number of fibers need to be tested to obtain statistically significant mean values.

The mechanical properties of biofibers depend greatly on the scale and structure. Smaller structures usually lead to more regular composition and less defects and hence a better mechanical properties. However, with the existing technologies the smallest fiber obtained is in a form of single fiber or microfibril. Research is going on the extraction of nano scale cellulose whiskers from biofibers [10].

2.1.5 Comparison between biofibers and other fibers

The properties of biofibers are comparable to those of some artificial fibers (Table 2.1). Although biofibers have moduli comparable to glass fibers, they are lower in strengths and toughness. They also have a higher hydrophilicity because of the presence of OH groups on their backbones. Thermal degradation in biofibers begins approximately around 200 °C, therefore they must be processed below this temperature.

The specific tensile modulus (modulus of fiber divided by its density) and specific modulus of elasticity of biofibers are higher than those of glass fibers (Figure 2.5). This is because of the low densities of biofibers.

	Fibers			- .		
Properties	E-Glass	Flax	Hemp	Jute	Ramie	Sisal
Density	2 55	1 40	1 48	1 46	1 50	1 33
(g/cm^3)	2.33	1.40	1.40	1.40	1.50	1.55
Tensile		800				
Strength	2400	1500	⁻ 550 - 900	400 - 800	500	600 - 700
(MPa)		1500				
E-Modulus	72	60 80	70	10 20	11	29
(Gpa)	13	00 - 80	/0	10 - 30	44	20
Specific						
Modulus	29	26 - 46	47	7 - 21	29	29
(E/density)						
Elongation at	2	12 16	1.(1.0	2	2.2
Failure (%)	3	1.2 - 1.0	1.0	1.0	Z	2-3
Moisture		7	0	10	10 17	11
Absorption (%)		1	ð	12	12 - 17	11

 Table 2.1.1: Typical properties of glass fiber and natural fibers [11]



Figure 2.1.4: Comparison of moduli of glass fibers and biofibers

2.1.6 Types of natural fibers

There is a wide variety of natural fibers. These include wood fibers, and a variety of agrobased fibers such as stems, stalks, bast, leaves and seed hairs. These fibers are abundantly available throughout the world and they come from renewable resources [1]. Fibers are also obtained from recycled agro fiber-based products such as paper, waste wood, and point source agricultural residues such as rice hulls from a rice processing plant [2]. Depending on their origin, natural fibers may be grouped into: grasses and straw fibers,

non wood fibers, wood fibers, and cellulose nano-whiskers.

1. Straws, grasses and reeds

These fibers come from the stems of monocotyledonous plants such as bamboo and sugar cane, big blue stem grass, switch grass, corn [1, 2, 5]. Most grasses produce biofibers that can be used to reinforce plastics. Higher cellulose content leads to higher mechanical properties in the biofibers, so does a lower microfibrillar angle. The mechanical properties of fibers decrease as the diameter increases.

2. Leaf fibers

Leaf fibers are fibers that run lengthwise through the leaves of most monocotyledonous plants such as henequen, banana, pineapple, sisal, screw pine, and palm [1, 2, 5]. These fibers are also referred to as 'hard fibers'. Leaf fibers generally have a higher microfibrillar angle, leading to lower values of tensile modulus compared to bast fibers.

3. Bast fibers

These fibers (bundles) come from the inner bark (phloem or bast) of the stems of dicotyledonous plants. Common examples are jute, flax, hemp, mesta, and kenaf [1, 2, 3].

Bast fibers generally have a lower microfibrillar angle, and higher cellulose content leading to higher values of tensile modulus compared to bast fibers.

4. Seed and fruit hairs

These are fibers that come from seed-hairs and flosses, which are primarily represented by cotton, coir, kapok, and oil palm [1, 2, 5].

5. Wood fibers

These fibers come from the xylem of angiosperm (hardwood) and gymnosperm (softwood) trees. Examples include maple, yellow poplar and spruce [6].



Figure 2.1.5: Classification of biofibers [2]

2.1.6 Biocomposites

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Biocomposites, in general are materials made naturally or produced synthetically that include some type of natural material in their structure. In our research, biocomposites are also known as natural fiber composites. Biocomposites are formed through the combination of natural cellulose fibers with other resources such as biopolymers or resins or binders based on renewable raw materials or synthetic polymers. The objective is to combine two or more materials in such a way that a synergism between the components results in a new material that is much better than the individual components. Some of the plant fibers with suitable properties for making biocomposites are: industrial hemp, kenaf, henequen, jute, flax, sisal, banana, kapok, etc. [1]. The most commonly used polymer matrices include thermoset polymers such as polyesters, epoxies and phenolics, and thermoplastics like polyethylene (PE), polystyrene (PS), and polypropylene (PP). Since the polymer matrix is soft, flexible and light weight in comparison to fibers, their combination provides a high strength-to-weight ratio for the resulting composite [1, 2, 11].

The properties of composites also depend on those of the individual components and on their interfacial compatibility. The interface between the fiber and the matrix gives the composite its structural integrity. The interface consists of the bond between fiber and matrix and the immediate region adjacent to this bond. At least three types of bonding are thought to exist at the interface: chemical, electrical, and mechanical. A composite with weak fiber matrix interface will not be able to transfer the load from the matrix to the reinforcing fiber and usually leads to poor composite strength [12]. The stress transfer at the interface between two different phases is determined by the degree of adhesion. Strong adhesion at the interface is needed for effective transfer of stress and load

distribution throughout the composite. In the case of short-fiber composites, various factors influencing the properties are: (i) the fiber dispersion, (ii) the orientation and geometry (aspect ratio) of the fibers within the composites, (iii) the fiber volume fraction, and (iv) the quality of the interface between the reinforcing fiber and polymeric matrix phase.

2.1.7 Applications of biocomposites

The applications for which biocomposites have been studied include interior and exterior paneling of automobiles, interior paneling in rail vehicles, furniture, and replacement of wood products in housing applications. Daimler Chrysler has used biocomposites of green flax and hemp fiber mats with polyester for under body panels of the EvoBus (a touring coach) [13]. They found replacing the under body panel, previously a glass fiber composite, with biocomposites required 83 percent less energy to manufacture, and the resulting part was 40 percent cheaper. In addition, the same tools and machine used to manufacture the part with glass-fiber composites were used for manufacturing with biocomposites.

Biocomposite materials have also been used for interior paneling applications in automobiles, including door paneling and rear shelf paneling [14]. The interior paneling of rail vehicles in Germany has also been manufactured using biocomposites, mainly for weight savings over glass-fiber composites [15]. In this application the standards for fire protection are very high in Germany. Thus, the biocomposites were treated with flame retardants to attain the high levels of fire-protection required by the standards.



Figure 2.1.6: Comparison of natural fiber (NF) and glass fiber (GF)-unsaturated polyester (UPE) composites [13]

Phenix Biocomposites of Mankato, Minnesota have developed biocomposite materials with decorative surfaces for furniture, table tops, wall panels, and other home and office finished surface applications [16]. These applications show that biocomposites can be manufactured and used in products where attractive surface finishing is required. Jute and coir based biocomposites have been developed in India as substitutes for plywood and medium density fiber boards for low-cost housing needs [17]. The engine and transmission covers of Mercedes-Benz transit buses now contain biocomposites of polyester resin and natural fibers [18].

Other products under development include the use of sisal-based biocomposites as panels and roofing sheets, which could also be used as false ceilings and partition boards. The current market uses of bio-based composites in North America are shown in Figure 2.7 [19].



Figure 2.1.7: North American major end markets of natural fiber composites, year 2000 [19]

2.1.8 Modification of Natural Fiber

A major disadvantage of biofibers is their highly polar nature, which makes them incompatible with non-polar polymers. This incompatibility usually leads to poor dispersion of the fibers in the matrix material, poor interfacial strength and lower mechanical performance. In addition, the poor resistance to moisture absorption makes the use of natural fibers less attractive for exterior applications or applications where they are exposed to a moist environment. In order to improve compatibility with polymer matrices and to minimize water absorption, the natural fibers need to be modified.

This situation calls for the development of strategies for the modification of the cellulose fiber surface, thereby gaining control over the fiber-polymer interface.

Fiber surface can be modified by either physical or chemical treatments. Physical treatments include fibrillation, plasma treatment, and corona treatment [20]. Physical treatments change the chemical, structural and surface properties of the fiber surface and thereby influence the mechanical bonding with the matrix polymer.

Chemical treatments introduce chemical bonds between the fiber and matrix, and include dewaxing, alkali treatment, cyanoethylation, vinyl grafting, and treatment with various coupling agents (silane, isocyanate, titanate, maleic anhydride etc.) [21]. Pretreatment of fibers by encapsulated coating with coupling agents also provides better dispersion by reducing the fiber-fiber interaction with the formation of coating on the fiber surface.

2.1.9 Past Research on biofibers and biocomposites

2.1.9.1 Studies on biofibers

Han [22] reviewed the characteristics of the non wood fibers, and suggested their use in pulping. The important properties of the fibers are fiber length, lignin content, and cellulose content. Rowell [23] reviewed the various applications possible for the agrobased fiber reinforced composites, ranging from geotextiles to filers to sorbents to structural and nonstructural composites, to packaging and molded products.

Peijs [24] reviewed the developments in the field of biocomposites and their applications. From wood fiber composites, to natural fiber reinforced composites to all green biocomposites, biocomposites have come a long way in the recent years. These fibers have found their own special place in the automotive, sports and transportation sectors, using conventional processing techniques including sheet molding compound (SMC), bulk molding compound (BMC), laminating and resin infusion (RTM and VARTM), etc [11]. Riedel and Nickel [25] advocated the use of natural fibers reinforced with biopoylmers as construction materials in their 1999 article. They discovered a new application of biocomposites, in covering structural elements in automobiles, railway, furniture, and leisure industry.

2.1.9.2 Studies on surface treatments

Mishra *et al.* [26] surface treated pineapple and sisal fiber (alkali treatment, cyanoethylation, and acetylation) to make composites with polyester resin. They also made hybrid composites reinforced with a combination of glass fibers and sisal, as well as glass and pineapple fibers. The water absorption tendency of the biocomposites decreased after surface treatments, and also after glass fibers were introduced in the system.

Mwaikambo and Ansell [27] studied the effect of mercerization and acetylation on the properties of hemp, sisal, jute and kapok by XRD, DSC, FT-IR, and SEM. After the chemical treatments, the surface of the fibers became rough and clean. From XRD they observed that at low alkali concentrations, there was a slight increase in the crystallinity of the fibers, but at higher alkali concentrations, the fiber crystallinity index decreases. Thermal analysis pointed at the optimization of acetyl groups at elevated temperatures. They concluded that the structure of the fibers was altered by alkalization and acetylation. Bisanda [28] studied the effect of alkali treatment on the adhesion characteristics of sisal fiber reinforced epoxy composites. He observed that the alkali treatment of sisal fiber improves the wetting ability of the fiber with the resin, reduces the voids, and improves strength and water resistance.

Rout *et al.* [29] studied the graft copolymerization of acrylonitrile onto coir fibers using $CuSo_4$ and $NaIO_4$, as well as inorganic salts and organic solvents as the initiators. Morphological studies showed the evidence of grafting taking place on the fibers and even penetrating onto the fiber matrix. Grafting resulted in higher maximum stress at break, and increased hydrophobicity of the coir fibers.

Stamboulis *et al.* [30] studied the effect of environmental conditions on mechanical and physical properties of flax fibers. They treated the flax fibers with Duralin treatment, which consists of heating the fibers in steam or water at $160 \, {}^{0}\text{C}$ for 30 min in an autoclave, followed by drying at 250 ${}^{0}\text{C}$ for 2 hours. It was found that Duralin treated fibers absorbed less moisture than untreated green flax fibers. Treated fibers were smooth and well separated, and have uniform higher strength. Zeta potential measurements confirmed higher hydrophilicity of green flax, and hydrophobicity of Duralin treated fibers.

Silva *et al.* [31] performed mechanical and thermal characterization of alkali treated native Brazilian coir fiber. Mechanical and morphological results pointed at higher ultimate tensile strength and modulus of coir fibers after treatment. Thermal stability of fibers increased up to 48 hours of mercerization.

Gassan and Bledzki [32] determined the relationship between the structure and mechanical properties of alkali treated jute fibers. Due to alkali treatment, there is shrinkage of the jute fibers which influences fiber structure, crystallinity ratio, degree of polymerization and Hermans factor, as well as mechanical properties.

Bismarck *et al.* [33] studied the effect of fiber surface treatments on the thermal and electrokinetic properties of coir and sisal fibers. The fibers were dewaxed, alkali treated and grafted with methylmethacrylate (MMA). It was seen from SEM micrographs that coir fibers were larger in diameter than sisal. After dewaxing and alkali treatment, the fibers became rougher, while, after MMA grafting they became very smooth. The maximum degradation temperature of the fibers increased after alkali treatment and MMA grafting. All treatments led to an increase in the water absorbed by the fibers.

Higher accessibility of the surface functional groups resulted in lower zeta potential, improving the interaction between the fibers and the matrix.

Mohanty *et al.* [34] alkali treated and exploded the corn stalks with ammonia and carbon dioxide and studied their morphology and thermal properties of the fibers. As a result of these treatments, some fibrils got separated from the fiber bundle, and the thermal stability increased.

Samal and Ray [35] studied FTIR spectra of chemically modified pineapple leaf fibers. The treatments done on the fibers were: alkali, dinitrophenylation, benzoylation, and benzoylation-acetylation.

Pavithran *et al.* [36] evaluated the impact performance of unidirectional sisal-polyester composites. Owing to the optimum microfibrillar angle of sisal fibers, they exhibit a very impact amongst lignocellulosic materials. Energy absorption in the sisal biocomposites occurred by fiber failure and fiber pull outs. The same authors also examined the impact performance of pineapple, banana, coir and sisal fibers in an unsaturated polyester resin matrix [37].

Oksman *et al.* [38] evaluated the mechanical and morphological properties of unidirectional sisal-epoxy composites made using resin transfer molding (RTM). The sisal fibers were non-uniformly distributed in the polymer matrix, and the adhesion between fibers and matrix was weak.

Belcher *et al.* [39] studied the fiber matrix adhesion of the silane treated aligned henequen fiber reinforced epoxy composites. Coupling with γ -glycidoxypropy ltrimethoxy silane (GPS) led to compatibilization between henequen fibers and epoxy matrix, thereby improving the thermal and mechanical properties of the biocomposites.

Belcher *et al.* [40] also studied the effects of epoxy modifications and surface modifications on the aligned henequen fiber reinforced epoxy composites. They introduced various amounts of epoxidized soybean oil and epoxidized linseed oil into the matrix, and also modified the fibers by using alkali treatment, plasma treatments, silane treatment and ultraviolet treatment.

Varma *et al.* [41] made hybrid composites with glass fibers and jute fibers in a polyester resin matrix. The jute fibers were modified with γ -aminopropyl trimethoxy silane, isopropyl triisostearoyl titanate, and tolylene diisocyanate (TDI). Although titanate treatment resulted in the properties of hybrid composites, Silane and TDI treated jute fibers were not compatible with the polyester resin.

Mishra *et al.* [42] studied the tensile, flexural, impact and hardness properties of the unidirectional untreated and bleached jute-epoxy composites. Bleaching the fibers caused delignification which led to improvement in toughness, hardness, interlaminar shear strength and flexural properties of the composite.

Rout *et al.* [43] studied the influence of surface modifications of coir fibers on the coirpolyester resin composites. The fibers were either alkali treated, bleached or grafted with acrylonitrile. The authors observed that adhesion between the coir fibers and the matrix improved after all surface treatments. The water absorption tendencies of the composites also decreased after the treatments.

Zimmerman and Losure [44] reported the use of non-woven kenaf fiber mats as reinforcements for epoxy matrix. Although they found voids in the samples led to lower properties, they recommended pursuing this research.

Rong *et al.* [45] studied the interfacial interaction in sisal-epoxy composites and its effect on impact properties. The fibers were subjected to alkali treatment, acetylation, cyanoethylation, γ -aminopropyl triethoxy silane, heat treatment, and mixed treatments. The modifications led to increased surface energy of sisal fibers after treatments, and chemical bonding between the fiber and the matrix. The microfailure mechanism of the composites was a function of interfacial adhesion and the fiber length continuity. For chopped fiber reinforced composites, the interfacial strength should be tailored to enhance the energy dissipation through debonding and pull out of the fiber bundles.

Mishra et al. [46] analyzed the effectiveness of various types and degrees of surface modifications of sisal fibers in improving mechanical properties of sisal-polyester composites. 5% alkali treatment, 10% acrylonitrile grafting and cyanoethylation at 60 $^{\circ}$ C were the optimum modification conditions with respect to mechanical properties.

Sydenstricker *et al.* [47] performed thermal, morphological and pull out analysis on siaslpolyester composites. The Brazilian sisal fibers were treated with alkali and N-isopropylacrylamide. The fibers treated with acrylamide solution performed better in tensile properties, moisture content and pull out lengths as compared to untreated and alkali treated fiber based composites.

Hill and Khalil [48] studied the effect of treatments on mechanical properties of composites made with polyester resin and coir or oil palm as reinforcements. The fibers were treated with acetylation, γ -methacrylopropyltrimethoxy silane, and nepentyl(diallyl)oxytri(dioctyl)pyrophosphate titanate.

Khalil *et al.* [49] observed the effect of various anhydride treatments on the mechanical properties and water absorption tendency of oil palm empty fruit bunches in a polyester

matrix. The fibers were reacted with acetic, succinic, or propionic anhydride without any catalysts at 100 0C for 1 hour. Modifications resulted in hydrophobic fibers and improved fiber-matrix bonding. Acetylated fibers had better properties compared to propionylated or succinylated fibers.

Mohanty *et al.* [21] reviewed the surface modifications of natural fibers and the properties of resulting biocomposites. They highlighted recent studies and developments in the area of improvement of the fiber-matrix adhesion for thermoplastic as well as thermoset matrices reinforced with natural fibers.

Mohanty *et al.* [50] also reported surface treatments of natural fibers in a polyester resin matrix which improved the interface. The modifications included: alkali treatment, acrylonitrile grafting, methyl methacrylate grafting, and cyanoethylation.

Ray *et al.* [51, 52] studied the effect of alkali treatments on the flexural and tensile properties of jute-vinyl ester composites. The improvements in mechanical properties were highest for a composite made with 4 hours alkali treated jute fibers with 35% fiber weight.

Ray *et al.* [53] analyzed the dynamic mechanical properties of alkali treated jute-vinyl ester composites. For alkali treated fiber based composites, the rate of all of storage modulus with temperature was inversely proportional to the defect concentration in the composites.

Gassan and Bledzki [54] evaluated the effect of cyclic moisture absorption-desorption on the mechanical properties of silane treated jute-epoxy composites. The absorptiondesorption cycle led to debonding of the resin from the fibers, and introduced craks in the

matrix. It also changed the fracture mechanism of the composite, but did not alter the tensile strength.

Depworth *et al.* [55] produced high volume fraction of hemp and flax fiber composites using low viscosity epoxy and phenolic resins. The fibers used were untreated, retted, mechanically decorticated or soaked in urea.

Rout *et al.* [56] studied the effect of fiber surface treatments on the mechanical properties of coir-polyester composites. The surfaces of coir fibers were changed by use of dewaxing, alkali treatment, and graft copolymerization with methyl methacrylate onto alkali treated fibers.

Joseph *et al.* [57] studied the effect of hybridization in jute/cotton fabric reinforced polyester resin composites. Giacomini et al. [58] manufactured composites containing curaua fiber and unsaturated polyester resin. Pothan et al. [59] studied the vicsoelastic properties of banana fiber reinforced polyester composites. Oksman et al. [60] analyzed the morphology and mechanical properties of sisal-epoxy composites made using resin transfer molding (RTM).

2.1.9.3 Studies on biofiber reinforced thermoplastics

As mentioned before, one of the major drawbacks of using cellulose fibers as reinforcement is because of their poor dispersion characteristics in many thermoplastic melts, such as polypropylene and polystyrene, due to their hydrophilic nature. Several methods have been suggested and described in the literature to overcome this problem. Among them are fiber surface modification, use of dispersing agents such as stearic acid, and fiber pre-treatments such as acetylation. Fiber dispersion can also be improved with

increased shear force and mixing time [61]. A careful selection of initial fiber lengths, processing aids, processing techniques as well as processing conditions then is necessary in order to produce high performance composites.

Raj and Kokta [62] investigated the influence of using various dispersing aids (stearic acid and mineral oil) and a coupling agent (maleated ethylene) in cellulose fiber reinforced polypropylene composites.

Good fiber dispersion is generally the ultimate objective of any mixing process [61]. Various mixers are available to mix short fibers in thermoplastics such as extruders, plasticorder, injection molding machines and kneaders. Different mixing techniques, however, do not produce composites with the same degree of fiber dispersion. Thermokinetic mixers have also been used to mix cellulose fibers with thermoplastics to effectively disperse the cellulose fibers within thermoplastic matrices [63, 64]. Pereira *et al.* [65] investigated the effect of several processing techniques on the properties of polypropylene composites reinforced with short sisal fibers. The best processing method involved a twin-screw extruder.

Childress and Selke [66] investigated the effectiveness of several additives in enhancing mechanical properties of wood fiber/high-density polyethylene composites. The additives used were ionomer-modified polyethylene (ION), maleic anhydride modified polypropylene (MAPP), and two low molecular weight polypropylenes [67]. The mechanical properties of the composites studied increased with increasing additive concentration. The most effective additive was MAPP, followed with ION.

Thomas *et al.* [68] reinforced polystyrene with benzoylated sisal fibers. The results revealed better compatibility between treated cellulose fibers and the polystyrene matrix,

and this resulted in enhanced tensile properties of the resulting composite. These improvements were attributed to the similarity between the phenyl-structure present in both benzoylated sisal fibers and polystyrene, which makes them thermodynamically compatible with each other.

Ali *et al.* [69] studied the effects of processing conditions on the viscoelastic and mechanical properties of biodegradable composites made with extrusion of sisal fibers and mater Bi-Y and mater Bi-Z. Tensile and creep behavior of composites was affected by type of polymer matrix and processing conditions such as: speed of mixing, time of mixing and temperature.

Alvarez *et al.* [70] evaluated the mechanical properties and water uptake of the compression molded composites made of alkali treated sisal fibers and MaterBi-Y, which is a biodegradable polymer. They found that the fiber treatment produced an increase in the equilibrium moisture content and a decrease in the diffusion coefficient.

2.2 Unsaturated polyester resin

The majority of resins used in the composite industry are thermosets (see Figure 2.2.1) [71]. About 65 % of all composites produced currently for various applications, use glass fiber and polyester or vinyl ester resins. Unsaturated polyester resins (UPE) are widely used in the composite industry because of their relatively low price, low density, ease of handling, thermal and dimensional stability, good chemical and weather resistance, and excellent mechanical, chemical and electrical properties. Furthermore, compared to other thermosets, unsaturated polyester resins over can be pigmented, and can be easily filled and fiber reinforced in a liquid form. The use of reinforced thermoset composites by

automakers has nearly doubled in the last decade, and is expected to increase 47 percent during the next five years through 2004 [50, 72].



Figure 2.2.1: Matrix pattern of polymer composites [71]

The polyester resins, because of their versatility and low cost, are widely used throughout the world. Polyester resins are classified as: (1) ortho resins, (2) isoresins, (3) bisphenol-A-fumarates, (4) chlorendics, and (5) vinvl ester [73]. Ortho resins, known as general-

Polyester Resins	Cost (Cents/lb)		
Ortho resin	60-68		
Iso-resin	73-83		
Bisphenol-A	123-153		
Vinyl ester	147-161		

Table 2.2.1: Cost of various polyester resins

purpose polyester resin, are based on phthalic anhydride, maleic anhydride and glycols (Figure 2.2.2). Ortho-resin is the least expensive among all the polyester resins (Table 2.2.1). The solutions of unsaturated polyesters and styrene vinyl monomers (reactive diluent) are known as UPE resins.

2.2.1 Making UPEs:

The first unsaturated polyester resins of similar type as used today were synthesized in the 1930s. Polyesters are subdivided into three classes: aliphatic, aromatic, crosslinked. The third category is thermosetting polymers. Polyester resins are manufactured by a step growth polymerization reaction of unsaturated acids (or anhydrides), saturated aromatic acids, and difunctional alcohols glycols [73].





The basic chemistry of linear unsaturated polyesters is rather simple. A mixture of unsaturated and saturated dicarboxylic acids is reacted with diols in a melt polycondensation. Monofunctional alcohols and acids are also used in some formulations to tailor the properties. The most traditional composition is maleic anhydride, *o*-phthalic anhydride and 1.2-propanediol, which are cheap raw materials. Other common raw materials are fumaric acid, isophthalic anhydride, terephthalic acid, adipic acid, ethylene glycol, diethylene glycol, dipropylene glycol, neopentyl glycol and bisphenol A [74]. The properties of the final product can be varied almost endlessly by changing the composition of the unsaturated polyester using these raw materials. Generally aromatic groups improve the hardness and the stiffness while aliphatic chain components increase the flexibility.

The unsaturated polyester has typically a molecular mass between 1000 and 5000. The molecular mass is regulated by the diol/dicarboxylic acid ratio [75]. Usually the diol is in

excess, as the used diols are liquids, while the dicarboxylic acids and anhydrides are solids. An excess of solid reactants can cause a problem in the form of sublimation of the reactants during polycondensation. A high molecular mass will give a higher hardness, tensile and flexural strength of the final cured material. If the molecular mass is too low, the mechanical properties of the cured resin will be poor. A too high molecular mass increases the viscosity of the resin solution, which will cause problems with the processing of the resin. Air entrapment in the laminate, poor wetting of the reinforcement, long mould filling times and processing times are typical practical problems due to the resin viscosity.

Almost all commercial production of unsaturated polyesters is done by the melt polycondensation of unsaturated and saturated acids or anhydrides with glycols. No solvents are used, and the formed water is continuously removed, in order to force the esterification reaction towards completion. The condensation temperature is typically between 170 and 230 °C. At the end of the condensation, vacuum is often applied in order to remove remaining water from the viscous melt. The total reaction time can be from 8 h up to 25 h, and the reaction is followed by acid number titrations and viscosity measurements [76]. Azeotropic polycondensation in the presence of organic solvents such as xylene or toluene can also be used. The reaction takes place at lower temperatures and it is possible to avoid losses of volatile reactants. The drawbacks are longer reaction times and environmental problems with solvent removing and recycling.

The most common glycol used is propylene glycol. It is low cost and has good balance of properties. A combination of bisphenol A and propylene glycol provides good chemical resistance and high HDT to the oligomer. The most common anhydride used is

maleic anhydride, it provides cure sites. Fumaric acid is the best unsaturated acid used. Amongst saturated acids/anhydrides, phthalic anhydride is low cost and hard, isophthalic acid improves strength and chemical resistance, and adipic acid imparts flexibility and toughness. The UPE provides polymer properties, including modulus, toughness, glass transition temperature, and durability to the resin formulation [77].



Figure 2.2.3: Preparation of polyester resin [74]

2.2.2 Diluent (Monomer)

The polyester resins are usually diluted by adding a low molecular weight comonomer to adjust the viscosity of the mixture. Reactive diluent or monomer is added to the oligomer in the weight range of 0-60 %, typically 35-45 %. It helps to control the viscosity of the UPE, acts as a crosslinker, and improves wetting behavior [78]. Because of its lower cost, the most common monomer used for UPE is styrene, but other monomers can also be used. The examples of monomers used for UPE system cross linking are shown in table 2.2.2

Methylmethacrylate	Mainly used for translucent parts. Always used in combination with styrene (50:50). Excellent weathering.				
Alphamethyl styrene	Used for some special applications where a good control of the reactivity and good control of shrinkage is needed. Unpleasant odor.				
Divinyl benzene	High reactivity. Provide high chemical resistance. Lower impact resistance.				
Diallyl phthalate	Low volatility. Used in molded parts with good electrical performances.				
Vinyl acetate	Used in special applications like stratification of PS foam. Low hydrolysis resistance.				

Table 2.2.2: Examples of monomers used for UPE system cross linking

2.2.3 Curing of UPE

The curing of polyester resin occurs by free-radical chain-growth crosslinking. In addition to the monomer and oligomer, curing agents need to be added for the reaction to proceed. Curing agents include initiator, promoter, accelerator and inhibitor.

Initiator

To initiate the reaction a source of free radicals is needed. Organic peroxides are used as the source of free radicals [74]. They refer to a family of molecules containing at least two oxygen atoms, single-bonded together. The general structure is:

 $R^{1} - O - O - R^{2}$ $R^{1} - O - O - R^{3} - O - O - R^{2}$ $R^{1} - O - O - H$

The O-O bond can be easily broken to generate very reactive species called free radicals. The free radicals can be generated either by the action of heat (homolitic scission), or at room temperature in presence of an activator like metallic salts compounds or an amine. The first step of initiation is the decomposition of the peroxide. The second step is chain propagation reaction via styryl radical formation capable of reacting with a double bond.



Figure 2.2.4: Chemical structure of methyl ethyl ketone peroxide (MEKP)

The main families of organic peroxides used for curing unsaturated polyester are: ketone peroxides, diacylperoxides, peresters, hydroperoxides, and perketals. Ketone peroxides are generally used at room or mid temperature in combination with Cobalt salts. Diacylperoxides like Benzoyl peroxide can be used at room temperature, activated by tertiary aromatic amines, or without promoter at higher temperature (100°C). Peresters and perketals are used at higher temperatures and are preferred in injection and compression molding processes. Hydroperoxides are used at higher temperatures in injection and compression molding processes [79].

Ketone peroxides are the most commonly used for curing UPE systems. They have 8-10 % active oxygen. For room temperature curing as in the case of hand-lay-up structures, methyl ethyl ketone peroxide (MEKP) is used; for moderate temperature curing benzoyl peroxide is used. For hot press di-t-butyl peroxide or t-butyl perbenzoate is used. A mixture of initiators is used when a large temperature increase is expected.

Figure 2.2.5: Chemical structure of benzoyl peroxides (BPO)

The selection of the peroxide determines the kinetics of reaction and is also an important parameter for the "pot life". Final part quality is also linked to the peroxide used (aspect, curing efficiency). The selection of the right peroxide system involves several parameters including: part produced, associated process, processing temperature, timing of the process, nature of the pure resin used, and formulation. Optimum performance can be achieved by controlling the type and concentration of peroxide and promoter [80].

Promoters and accelerators

Promoters and accelerators are used to help initiate cure at room temperature by accelerate the decomposition of peroxides. Commom accelerators include metallic salts, amines, or mercaptants. Cobalt naphthenate (CoNap) and cobalt octanoate (CoOc) are the most widely used accelerators.

Cobalt naphthenate (CoNap) is usually added to systems containing MEKP, in weight range of 0-0.3%. Dimethyl aniline (DMA) is usually added in the weight range of 0-0.3% to systems containing BPO and MEKP. Gel time for a given resin depends on initiator level, promoter level, second promoter level, and temperature.

 $ROOH + Co^{3+} \longrightarrow ROO^{*} + H^{+} + Co^{2+}$ $ROOH + Co^{2+} \longrightarrow RO^{*} + OH^{*-} + Co^{3+}$

Figure 2.2.6: Reaction mechanism of polyester resin with cobalt activator

Inhibitors

In order to prevent premature curing and to extend pot-life, inhibitors are also introduced into the curing system, typically in concentrations less than 100 ppm. Inhibitors are free radical scavengers like Hydroquinone derivatives, terbutylcatechol, cresol derivatives. Some examples of inhibitors used for UPE system are shown in Table 2.2.3

Hydroquinone	Excellent for stabilization during storage No color issues		
Tertiobutylhydroquinone	Can be used in a wide range of temperatures. Very efficient with systems initiated by Dibenzoylperoxide		
Ditertiobutylhydroquinone	Provides very good stability to the resin until 60°C. Used when short gelling time is needed (cold and hot process)		
Toluhydroquinone	Can be used in a wide range of temperature. Very efficient with systems initiated by Dibenzoylperoxide. Provides excellent thermal resistance		
Benzoquinone	Excellent performances. Provides yellow color to the system		
Tertiobutylcatechol	Active until 40°C. Rapidly absorbed by the resin. Excellent adjustment of pot-life		

I ADIC 2.2.3. Examples of minutions used for OFE system	Tab	le	2.2.3	: Examples	of inhibitors	used for UPI	E system
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Crosslinking

Polymerization may occur by any of three mechanisms: free radical, cationic, anionic. Chain polymerization is characterized by the presence of a few active sites which react and propagate through a sea of monomers. It may be formed via a two step process, where a polymer with unsaturations is first formed (a thermoplastic formed via step polymerization), and then these unsaturated sites are reacted with a crosslinking agent in a second step to produce the final structure. The reaction of a UPE resin is a free-radical chain-growth crosslinking copolymerization between the styrene monomer and the UPE molecules.

The curing reaction involves a sequence of steps: initiation, inhibition and/or retardation, propagation, and termination. Polyester molecules are the crosslinkers while styrene serves as the agent to link adjacent polyester molecules. The polymer chains grow and become crosslinked in three possible reactive processes: styrene–polyester co-polymerization, styrene homopolymerization, and polyester homopolymerization [81].

The curing behavior is complex due to the interaction between the resin chemistry and the variation of the physical properties. There are four stages in the crosslinking of UPE: *Gelation*: incipient formation of an infinite molecular network

Vitrification: glass transition temperature of the forming polymer rises above the temperature of cure

Full cure: highest attainable degree of cure

Devitrification: degradation

Before the free-radical polymerization proceeds, the resin is a viscous liquid. During the curing reaction, the chain length of the resin molecules grows through the crosslinking reaction of functional groups and the resin becomes more viscous. As the curing advances further, the reacting system forms a highly crosslinked network, which results in a rapid increase in the resin viscosity [73].

Gelation corresponds to the formation of the first insoluble fraction of the polymer with an infinite molecular weight. The onset of gelation is of critical importance to processing thermoset systems. The general crosslinking mechanism is shown in Figure 2.2.7.



Figure 2.2.7: Crosslinking mechanism of UPE resins

The reactivity, the viscosity and the final properties of UP resins can be adjusted by changing either the nature of the UPE chain, chemical composition (aliphatic, aromatic, number of double bonds), resin molecular weight, nature and concentration of the crosslinking monomer (containing at least one double bond or ratio of the styrene/polyester content. [76-81].

Autoacceleration

Autoacceleration effect can occur when the increasing viscosity limits the rate of termination because of diffusional limitations. The free radicals can't terminate with as easily as they can find other monomers to propagate with. Rate decrease occurs because of further diffusional limitations caused by vitrification [].

Effect of Additives on Cure

Surfaces, sizings, and surface treatments on fibers and fillers can significantly alter not only the final properties of a composite, but also resin cure kinetics. Polyester resins are generally associated with fillers (silica, CaCO₃, MgO, clay), and fibers (glass fibers, glass fibers mats or fabrics) acting mainly as a binder.

2.2.3.1 Curing performance measurement

Lots of methods are used for determination of curing kinetics. As an example, the curing kinetic and performance in a cold cure system can be measured by the viscosity increase over time and/or the temperature increase over time. The crosslinking reaction between the unsaturated polyester and styrene is exothermic. The exothermic heat generated is proportional to the level of unsaturation of the chain and the amount of styrene. The heat

generated can auto accelerate the hardening reaction but some processes cannot sustain high temperatures. In molding processes, high temperatures can lead to excessive shrinkage, warpage and cracking for high thicknesses. Figure 2.2.8 below shows the principle of one possible measurement and the typical curves obtained.



Figure 2.2.8: Curing reaction rate of UPE

2.2.4 Studies on UPE

Considerable work has been reported on the synthesis, characterization, curing behavior of UP resins [82-155].

2.2.4.1 Studies on curing of UPE

Kamal and Sourour [82] modeled of the DSC cure reaction with empirical equation $dx/dt=kx^{m}(1-x)^{n}$ by assuming the total reaction order m+n=2 and a zero initial cure rate [82]. Salla and Martin [83] observed the dynamic, isothermal and residual heats of curing UPE at different scanning rates, temperatures and setting times by use of DSC. At room temperature, UPE curing follows an autocatalytic reaction system. It was difficult to find extent of reaction for such a system because at lower temperatures, the instrument was not sensitive enough, and at higher temperatures, some heat was lost even before the instrument could detect it. Residual heat can help to determine the ultimate extent of curing of any system.

Salla *et al.* [84] used DSC to study the thermo-dependence and thermodynamics of the curing of UPE with different catalyst systems. For curing the UPE, they used BPO (0.03-3.0 % wt), DMA, MEKP (1 wt %) and CoOc (0.2-10 wt %). In dynamic DSC experiments, more than one exothermic peak was seen. In the absence of a promoter, only one peak was observed. When the amount of initiator is varied, the exothermic peak gets shifted. Without post curing, all the formulations are only partially cured.

Paci *et al.* [85] used pulsed nuclear magnetic resonance (NMR) at 20 MHz to monitor the middle to end stage of curing of UPE. The gelling and network formation process was followed by measuring spin lattice relaxation time of the system. A semi-empirical kinetic equation was used to evaluate degree of cure as a function of time, kinetic constants, and activation energy.

Ramis and Salla [86] investigated the theoretical and experimental curing reaction of UPE system with different polyester/styrene ratios by means of DSC and gel permeation chromatography (GPC). The theoretical heat of reaction corresponding to complete conversion was extrapolated from DSC curves. Experimentally, complete conversion was not seen in nay of the resin systems. From the molecular weight distribution obtained

from GPC, it was seen that part of styrene and polyester, as well as low molecular weight oligomer s of styrene and branch styrene on polyester molecules, do not form the polyester network.

Rouison *et al.* [87] used an autocatalytic model to study the curing kinetics of a polyester resin containing various promoters and an inhibitor. They used an isothermal DSC method to obtain curing rate, rate constants, enthalpy of reaction, and order of equation. The experimental plots fitted well with the model and were temperature dependent.

Nzihou *et al.* [88] utilized DSC for studying the polymerization kinetics of a thermoset resin under isothermal and dynamic conditions. They proposed a phenomenological kinetic model, which took into account diffusion effects, for curing reaction. They found that under isothermal conditions conversion was less than 100 % because of presence of unreacted monomer in the system. Dynamic studies in DSC revealed higher conversion at higher temperatures.

Vilas *et al.* [89] studied the curing kinetics of UPE using DSC and thermal scanning rheometry (TSR). When the concentration of initiator (MEKP), or the cure temperature is increased, the gel time decreases, and the reaction rate increases.

Huang and Leu [90] studied the effects of temperature, initiator and promoter on low temperature curing $(30-50 \ ^{0}C)$ of UPE. In the early stages of reaction, the copolymerization is azeotropic. During diffusion controlled propagation stage, the conversion of styrene is greater than that of vinylene groups. The cross link lengths of styrene decrease with increasing temperature. At moderate reaction rates, the intermicrogel crosslinking reaction is more dominant than intramicrogel crosslinking
reaction. At later stage of reaction, intramicrogel crosslinking is more favorable than intermicrogel crosslinking.

Yang and Lee [91] quantified the effects of resin type, temperature, curing agents, on the reaction kinetics of UPE and vinyl ester cured at low temperatures by DSC and rheometry. When MEKP is used as the initiator, inhibitor benzoquinone provides a longer induction period and higher final conversion for UPE compared to vinyl ester resin. Pentanedione is a good retarder for vinyl ester but acts as an accelerator for UPE. They also developed a gel time model to quantify the effects of temperature, inhibitor, retarder, on both polyester and vinyl ester resin. UPE is more sensitive to temperature changes than vinyl ester resin.

Yang and Lee [92] studied the reaction kinetics of three UPE resins having different C=C bonds per molecule, by using a differential scanning calorimeter (DSC) Fourier transform infrared (FTIR), and electron spin resonance (ESR) spectroscopy. They also developed a diffusion-controlled model to simulate the reaction rates and conversion profiles of polyester vinylene and styrene vinyl groups, as well as the total reaction rate and conversion. The results from DSC and FTIR match well. The reaction rate increases with increase in the degree of C=C unsaturation per molecule.

The diffusion-limitation effect is more significant for the polyester resin with a higher degree of unsaturation, leaving more unreacted C=C bonds trapped inside the matrix after vitrification, resulting in lower final conversions of polyester and styrene C=C bonds. The glass transition temperature measured by the DSC is a linear function of the final conversion within the temperature range studied, and it is used to monitor the change of the final conversion.

ł, 0 z Ċ 20 Ũ Ċ . 12 4 Ľ K 15 Ä 3 ł 2) Ċ, . 21 According to ESR measurements, for the polyester resin with a higher degree of unsaturation, the polymer formed is more compacted due to more intramolecular reaction, and more radicals are trapped in the cured resin without termination. The mechanistic kinetic model was capable of reasonably predicting the reaction rate and conversion profiles of polyester vinylene and styrene vinyl groups, as well as the total reaction rate and conversion at different temperatures and at nonisothermal conditions.

Chen and Yu [93] studied the microgelation phenomenon of UPE curing by static and dynamic light scattering as well as DSC. The formation of microgels due to intramolecular crosslinking reaction inside the UPE coils, was observed by studying the variation between UPE particle size and the depolarization ratio. There is a decrease in the compatibility between partially cured UPE and styrene monomer as the intermolecular crosslinking reactions amongst the microgel particles proceeds further.

Kosar and Gomzi [94] evaluated the thermal effects of curing reaction of UPE by isothermal and dynamic DSC experiments. They also developed a numerical model which took into account the heat transferred by conduction through the resin, as well as the kinetics of heat, generated by cure reaction. There was good agreement between the predicted model and the experimental data.

Yun *et al.* [95] examined the curing kinetics of unsaturated polyester resin system exhibiting apparent induction periods by modeling free radical initiation and propagation processes. After making a master curve of the reaction exotherms, a single activation energy of the reacting system was determined for both induction time (ti) and the maximum reaction-rate time (tm). Using the power-law equation for the initiation efficiency function, two elementary model equations were proposed for the radical and

monomer reaction rates. The developed model equations predicted isothermal as well as dynamic heating curing reactions very well with only five model parameters without any modification in different thermal conditions.

Ziaee and Palmese [96] evaluated the effects of cure temperature on proprieties of vinyl ester resin system using NMR, FTIR, AFM and tensile properties. Post curing the samples after isothermal curing showed the same conversion of styrene and vinyl ester bonds regardless of the initial cure temperature. The glass transition temperature was observed between 118-122 ^oC, irrespective of curing temperatures. The fracture toughness of samples cured at lower temperature (30 ^oC) was three times higher than those cured at higher temperature (90 ^oC). AFM revealed nodular morphology which could be microgels.

Brill and Palmese [97] used FTIR spectroscopy to investigate vinyl ester-styrene bulk copolymerization curing kinetics. The depletion of vinyl ester and styrene double bonds was monitored separately. Styrene monomer continues to react even after vinyl ester has completely reacted. Overall conversion increases with increase in isothermal cure temperature.

Near IR and mid IR spectroscopic techniques were used for cure characterization of UPE by Grunden and Sung [98]. In addition to NIR analysis, they calculated the extent of reaction of styrene and vinylene C=C, in comparison to extent of reaction values from conventional mid–IR. The differences between the conversion of styrene and vinylene C=C is due to reduced diffusion of styrene into tightly crosslinked microgels.

Lin and Hsu [99] studied the cure reactions of aromatic dicyanate, diepoxide, diamaine system using in situ FTIR and DSC. They proposed six reaction paths for dicyanate

/diepoxide system, four reaction paths for diepoxide /diamine system, and four reaction paths for dicyanate /diepoxide /diamine system.

2.2.4.2 Studies on properties of UPE

Shan *et al.* [100] studied the effect of vinyl ester-styrene network structure on the thermal and mechanical properties by using DSC and DMA. The crosslink density of the vinyl ester resin was changes by two methods: by changing molecular weight of oligomer and by changing amount of styrene added to the curing system. Vinyl ester /styrene systems have secondary relaxations, which are indistinguishable from each other, though the physical network and the composition of network chains are different. Tg of the systems increases with decrease in cross link density.

Han and Lem [101] studied the curing kinetics and the rheological properties of unsaturated polyester resins. They found that as cure progressed, the steady shear viscosity increased very rapidly with cure time at all shear rates investigated. The normal forces showed negative values at low shear rates and positive values at high shear rates. The negative normal forces may be due to material shrinkage during cure, and positive normal forces due to deformation of large molecules, formed by crosslinking reactions during cure. They explained the increase of viscosity with the degree of cure, at various values of isothermal curing temperature by combining the rheological and DSC measurements.

Han and Lem [102] investigated the effect of particulates on both the rheological properties and the curing kinetics of unsaturated resin. In the formulation, calcium

carbonate and clay were used as inorganic particulates and high-density polyethylene powder as organic particulates. They authors found that as the particulate content increased, the resin formulation gave rise to shear-thinning behavior and the rate of cure increased. The observed shear-thinning behavior is attributable to breakage of the particle agglomerates as the shear rate is increased, behavior which is typical of concentrated suspensions. The CaC03 particles also helped to control shrinkage during cure when the material was subjected to steady shear deformation. The gel time was shorter for mixtures of resin and particulates than for the neat resin alone. A UPE system with particulates showed negative normal stress effects at rest, which originated from polymerization shrinkage. However, when the fluid is subjected to steady shearing deformation, the normal stress response was found to vary greatly among the various particulates investigated.

Han and Lem [103] explored the effect of low-profile thermoplastic additives on rheology and curing kinetics of unsaturated polyester resin. The authors used UPE with two different types of LPAs: poly(viny1 acetate) (PVAc) and poly(methy1 methacrylate) (PMMA). They observed that during cure the UPE/PMMA system exhibits shear thinning behavior even before the cure time reaches the critical value whereas the UPE/PVAc system does not. Both PVAc and PMMA helped to reduce the shrinkage of the resin during cure. The rate of cure and the final degree of cure are decreased when the amount of low-profile additive is increased. The shrinkage control becomes effective only when the shear rate is greater than a certain critical value. The shrinkage of the resin during cure, judged by the normal stress response is decreased by the addition of thermoplastic additive. The shrinkage control is found to be more effective when the

mixture of UPE/LPA is subjected to intensive shearing deformation than when the material is at rest. An optimum amount of low-profile additive must be used in order to minimize the sacrifice of the rate of cure and yet maximize the shrinkage control.

Serre *et al.* [104] examined the morphology of the outermost layer of a compression molded samples made of UPE, glass fibers, calcium carbonate, low profile additives and release agents by using atomic force microscopy (AFM), dispersive x-ray spectrometry (EDX), scanning electron microscopy SEM, and XPS. The positions of fibers, filler, and mold release, were observed.

Serre *et al.* [105] used atomic force microscopy (AFM) in the tapping mode to investigate the morphology of cured four blends based on miscible UPE/LPA (low profile additive)/ST (styrene) systems. AFM identified particles, nanoparticles and nanogels (with sizes varying from 20 to 57 nm), besides aggregates and microgels previously observed by scanning electron microscopy (SEM). All samples were miscible with each other, and indicated that miscibility was an important parameter in the morphology of the whole network. Higher miscibility resulted in more numerous nanogels, and smaller microgels. They also developed a relation between the microgels sizes and the void volumes.

Marieta *et al.* [106] utilized AFM for studying the morphology of thermoset resins toughened by incorporation of core shell particles and thermoplastics. They used AFM in tapping and contact modes to look at the topographical, force and phase images of these systems.

2.2.4.3 Studies on flammability of UPE

Mazrouh [107] analyzed the fire retardant characteristics of polyvinyl chloride (PVC) and antimony trioxide (Sb2O3) in a UPE-fiberglass formulation. Addition of PVC (1-6%) and Sb2O3 (4-9%) enhanced the fire retardancy of the composites, with very little effect on the mechanical properties of the composites.

Hangzhou JLS Flame Retardants Chemical Co. [108] developed a flame retardants for thermosets or for intumescent coatings. These retardants are based on ammonium polyphosphate, which is a non halogen, environmentally friendly product. When combined with the standard flame retardant filler, aluminum trihydrate (ATH), it lowers the levels of ATH needed to reach the required fire retardation regulations.

M. Chaote [109] described some of the chemical approaches for halogen free flame retardants in circuit boards industry. He recommended the use of phosphate esters, melamine cyanurate, and phosphorous compounds as fire retardants. However, in these compounds, nitrogen and phosphorus have an intrinsic affinity towards moisture. They are also greatly susceptible to oxidative attack, and are readily thermally degraded. Another approach is to reduce the amount of resinous fuel, and increase the amount of hydrated filler content (aluminum trihydrate).

Avtec Industries has developed a polymeric additive, TSWB[™], for fire retardancy and smoke suppressing, which is free from bromine, antimony, and magnesium. It is designed and engineered to be incorporated within composite laminate structures (UPE based) to provide fire protection and thermal insulation properties and smoke suppression [110].

2.2.4.4 Studies on toughening of UPE

Rosa and Felisberti [111] modified the UPE with poly(organosiloxanes) to improve its impact resistance. Glycidyl methacrylate, 1,3-aminopropyltriethoxy silane(ATPS), and 1,1,3,3-tetramethyl-1,3-diehtoxysiloxane were used as modifiers for UPE resin. From dynamic mechanical analysis, it was observed that APTS was incorporated into the resin by reaction of its amino group with GMA. In systems with lower weight fraction of additives (7.23%), there was improvement in impact strength, however due to phase separation; there was no improvement in systems with higher amounts of additives (14.5%).

Rosa *et al.* also studied the adhesion between siloxane modified UPE and glass fiber by acoustic emissions of composites [112].

Rajulu, *et al.* [113] blended epoxy and unsaturated polyester resin in chloroform and studied the viscosity, ultrasonic velocity, and refractive indices of the blends.

Gawdzik *et al.* [114] evaluated the effect of concentrations of toluene diisocyanate (TDI) on the thermo-mechanical properties of unsaturated polyester resins. 1-3 % by weight of TDI was added to the UPE, and the samples were subjected to FTIR, thermo-gravimetric analysis, Charpy impact test, and rheometry. TDI should not be added to UPE resins in amounts exceeding 1 wt %. At higher concentrations if TDI, there is a huge increase in the viscosity of the materials, and thixotropy is observed in samples containing 3 % TDI. Min et al. [115] used polyurethane (PU) was used as a modifier for UPE to improve the toughness of the resin. They studied the effect of the polyol molecular weight as a polyurethane (PU) soft segment and the PU contents on the toughness of PU-modified UPE resins. The PU was prepared by reaction between polymeric methyl diisocyanate

(MDI), a difunctional poly(ether polyol), a trifunctional poly(ether polyol) and dibutyltin dilaurate as the catalyst. The maximum toughness was observed in the case of 2 wt % of PU in the curing system, due to the network formation of UPE with PU. Above 2 wt %, the toughness value deteriorated because of the presence of unreacted polyol in the system. In the case of difunctional polyol, polyol cannot participate in the network reaction effectively as the molecular weight increases, so the toughness decreased because the chain mobility decreased. But in the case of trifunctional polyol, that toughness was not affected considerably by the molecular weight.

Cherian and Thacil [116] performed the toughening studies of UPE by introducing maleated elastomers using physical or chemical methods. The elastomers are either dissolved in styrene and then blended with UPE, or elastomers are modified by grafting with maleic anhydride.

Cherian and Thacil [117] prepared blends of UPE with functional rubbers, and studied their mechanical properties. As the compatibility of the UPE with unmodified elastomers is poor, and a suitably distributed rubber phase of optimum size is not formed, they used elastomers bearing functional groups. The elastomers used were epoxidized natural rubber, hydroxyl terminated natural rubber, hydroxyl terminated natural rubber, hydroxyl terminated polybutadiene, and maleated nitrile rubber. Toughness and tensile properties were maximum at 2.5 wt % of rubber in the system (studied range: 0-5 wt % rubber). Maleated nitrile rubber had the best performance compared to all other elastomers.

Thouless *et al.* [118] discussed the mechanics of toughening of brittle polymers. There are tow principles for toughening of brittle polymers. The first is by manipulating the cohesive processes acting across a crack tip, to increase the intrinsic toughness of the

materials. The second is by manipulation of the microstructure of the polymer, to make it easier to trigger non-linear dissipative processes around the crack tip.

Huang *et al.* [119] reviewed the developments in toughening mechanisms of thermoset polymers. A toughened thermoset usually contains elastic or thermoplastic domains dispersed in discrete for throughout the matrix resin to increase the resistance to crack growth initiation. The phenomenon of viscoelasticity, shear yielding, and dilatational deformation involving cavitations govern the fracture behavior of thermosets.

McGarry and Subramaniam [120] prepared a toughened cross linked molecular network system with unsaturated polyester, styrene, diglycidyl ether of bisphenol A, and a reactive liquid runner, namely, amino terminated butadiene-acrylonitrile. The network is a two phase system, which has one phase containing no rubber, and the second phase with uniform distribution of rubber.

2.2.4.5 Studies on modification of UPE

Synthetic modifications of unsaturated polyester resins have been done in order to achieve lower styrene emission, better styrene solubility and lower processing viscosity. Two concepts were used; introduction of liquid crystalline segments into the unsaturated polyester and end-capping the unsaturated polyester with poly(ethylene glycol)s of various molar mass[121].

Hegemann [122] developed a comonomer free low viscosity unsaturated polyester resin for electrical industry. Two C=C bonds were found in a system by combining standard UPE resin (has a C=C from maleic/fumaric unsaturation), and the adduct of cyclopentadiene with a functional group, which allows for a condensation reaction. These

unsaturations were incorporated in one resin, without copolymerization during the polycondensation of the polyester. Crosslinking was studied by using DSC.

Douglas and Pritchard [123] studied the effect of substituents in the styrene ring, on the water absorption characteristic and thermal stability of UPE. They used styrene, 4-mehtyl styrene, 4-ehtyl styrene, 4-n-butyl styrene, 4-isoproyl styrene, tertiary butyl styrene, 4- chlorostyrene, and 3, 4,-dichlorostyrene to crosslink a maleic/phthalic anhydride based unsaturated polyester. Loss of water resistance was seen in systems with chloro substituents and most systems with alkyl groups. System with tertiary butyl group leads to a decrease in water absorption. Thermal stability is decreased by chloro substituents and increased by n-alkyl groups.

Guo and Zheng [124] studied the miscibility and crystallization of thermosetting polymer blends of unsaturated polyester resin and poly(ε -caprolactone) (PCL). Before curing, only one glass transition temperature (Tg) is present in (PCL) UPE blends, showing miscibility. But after crosslinking, the blend was partially miscible. FTIR studies revealed that intermolecular hydrogen bonding interaction between the components is an important driving force to the miscibility of PCL/UPE blends and the partial miscibility of crosslinked PCL/UPE blends. The spherulitic morphology of the blends was remarkably affected by crosslinking.

Guo and Zheng [125] also studied the crystallization kinetics of thermosetting polymer blends of poly(ε -caprolactone) and unsaturated polyester resin. The overall crystallization rate of PCL decreases with the addition of amorphous component, UPE. The kinetic rate constant decreases rapidly for both the PCL/UPE blends and the crosslinked PCL/UPE

blends with decreasing PCL concentration. However, neither of these papers presented a study on effect of PCL addition on volume shrinkage of the unsaturated polyester resin.

2.2.4.6 Studies on low profile additives for UPE

In low temperature molding processes, control of resin shrinkage and residual monomer is an important concern. The presence of low profile additives (LPAs) can reduce the shrinkage of unsaturated polyester (UPE)/styrene resins under proper processing conditions but may increase the residual styrene content. It is believed that the reactioninduced phase separation and the polymerization shrinkage in both the LPA-rich and UPrich phases result in the formation of microvoids, which partially compensates the resin shrinkage. The relative reaction rate in the two phases plays an important role in shrinkage control.

Han and Lem [126] measured the bulk rheological properties of polyester resin formulation containing UPE/fillers and UPE/fillers/LPAs using cone-and-plate rheometer. The fillers used were clay, calcium carbonate, and milled glass fiber. The low-profile additives, poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA), were dissolved in styrene. The bulk viscosities of all blends of polyester resin and PVAc lie between those of the individual components, whereas the bulk viscosities of some blends of polyester resin and PMMA go through a minimum and a maximum, depending on the composition of the mixture. On adding both the filler and low-profile additive together in polyester resin, the rheological behavior became quite complex, indicating presence of interactions between the filler and the low-profile additive. Han and Lem [127] investigation was made of the rheological behavior of unsaturated polyester resin during thickening in the presence of filler or low-profile additive alone and, also, in the presence of both filler and low-profile additive. They used CaC03 and clay as fillers and poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) as the low-profile additives. The viscosity behavior of the resin/filler/LPA system was similar to that of the resin/ LPA. From the rheological standpoint, the different types of low-profile additive had little influence on the thickening behavior of the respective filled systems.

Ruffler *et al.* [128] characterized the fissures occurring during curing of blends of UPE with PVAc using fractal analysis. The LPA effect arises by fissuring with fractal geometry. The fractal dimensions of fissures depend on the PVAc concentration and the cure temperature.

Huang and Su [129] studied the effects of two LPAs, PVAc and PMMA on the curing kinetics during the cure of UPE resins by use of DSC and FTIR. There is a kinetically controlled plateau (small shoulder) in the initial portion of the DSC rate profile depending on the molar ratio of styrene to polyester C=C bonds, in the sample containing LPA. Adding LPA enhanced the relative conversion of polyester C=C bonds to styrene throughout the reaction, as shown by FTIR results. A microgel-based kinetic model was developed to explain the effects of LPAs on reaction kinetics (intramicrogel and intermicrogel crosslinking reactions), relative conversion of styrene and polyester C=C bonds, and the final conversion. The LPAs induced a globule microstructure during the curing, which enhanced the final conversion of polyester, but would result in an increase

or a decrease of the final conversion of styrene, depending on the initial molar ratio of styrene to polyester C=C bonds.

Huang and Su [130] investigated the effects of two LPAs, PVAc and PMMA, on the morphological changes during the cure of UPE resins by using DSC, SEM, optical microscopy, and low-angle laser light-scattering (LALLS). Under SEM, the microvoids and microcracks which are responsible for the volume shrinkage control were observed at the later stage of reaction. The morphological changes during curing varied considerably, depending on the types of LPA and the initial molar ratios of styrene to polyester C=C bonds. Adding LPA in the neat UP resin reaction system enhanced the clear identification of microgel particles, because a layer of LPA could cover the surface of microgel particles when the microgel particle phase separates from the matrix of unreacted resin containing LPA. The segregating effect of LPA led to reduced merging of microgel particles and helped to retain the identity of the individual microgel particle.

Sun and Yu [131] used gel permeation chromatography (GPC) and DSC to study the effect of LPAs, PVAc and PMMA, on the curing reaction of UPE resins. According to DSC results the curing reaction rate decreased as the concentration of LPA increased. The concentration of LPA and the compatibility of LPA with UPE resins had a strong influence on the polyester microgel formation and the curing behavior. There was evidence of the shrinkage of UPE microgels at the early stage of curing reaction witnessed from GPC results. The formation of microgel particles has been found to be the key feature of the UPE-styrene copolymerization. For UPE resins mixed with LPA, the curing reaction rate of UPE with styrene decreased as the concentration of LPA increased. Increase of the LPA concentration facilitates the UPEs to form coils in the styrene

monomer and to undergo an intramolecular crosslinking reaction, which causes a delay of gelation.

Huang and Liang [132] compared the volume shrinkage abatement caused by four LPAs, including PVAc, PMMA, thermoplastic polyurethane (PU), and polystyrene (PS), in polyester resin. The effectiveness of volume shrinkage agent decreased in the following manner: PVAc > PMMA > PS. The shrinkage effect with PU depended on its concentration. In case of relatively polar LPAs like PVAc and PMMA, the fractional volume change after curing is controlled by microvoid formation. For nonpolar LPAs like PS, it is controlled by intrinsic polymerization shrinkage. For polar LPAs which can react with UPE, both factors play a role.

Siato *et al.* [133] studied the rheological and morphological changes in polyester resin after incorporation of methyl diphenyl isocyanate (MDI) and magnesium oxide (MgO) as thickeners into a UPE-LPA system. The MDI based system exhibited rapid viscosity build up and followed by stable viscosity for long storage times, and the shrinkage control by this system of poor due to lack of phase separation. For MgO based systems, the viscosity increased slowly and it changed during the long storage time. There was phase separation during curing which led to a better shrinkage control in MgO based system.

Li and Lee [134] found out the shrinkage mechanism of UPE/LPA systems at low temperature cure using rheometry, kinetics, morphology and dilatometry study. The competition of the shrinkage induced by resin polymerization and the expansion induced by microvoid formation, strongly determine the shrinkage behavior of the UPE resin. At

low temperature cure, the systems with higher molecular weight and lower LPA content are more effective shrinkage controllers.

Huang and Jiang [135] explored the effects of chemical structure and composition of UPE on the miscibility of UPE/styrene/LPA system having PU, PVAc, PMMA as LPAs. The dipole moments of UPE and LPAs were calculated, and it was found that the increasing order of polarity in terms of dipole moment per unit volume was PMMA<PVAc<UPE<PU. If the molecular weight of UPE is increased, the phase separation rate for systems with PVAc and PMMA would decrease. The miscibility of UPE/styrene/LPA systems and samples morphologies were correlated with polarity differences per unit volume between UPEs and LPAs.

Huang and Chen [136] investigated the effects of three different UPE resins with different chemicals composition on the mechanical properties of the UPE/LPA systems with PU, PVAc, and PMMA. The UPE resin series were made of different anhydrides, acids, alcohols in different molar ratios. The authors discussed the effects of glycol ratios, modification of dibasic acids, C=C unsaturation, and molecular weight on the mechanical properties of the polymers formed.

Hsieh and Yu [137] explored the phase separation occurring during curing of UPE resin with PVAc by low-angle laser light scattering (LALS) and scanning electron microscopy (SEM). It was seen that the PVAc rich phase was regularly dispersed in the UPE matrix. But as the PVAc content was increased (greater than10 wt %), a co-continuous morphology of PVAc and UPE was seen. According to LALS data indicated a regularly discrete phase dispersed in a continuous matrix phase, as observed from scattering intensity profiles with maximum peak intensities. Huang *et al.* [138] studied the effects of chemical structure and molecular weight of three series of thermoplastic polyurethane (PU) based LPA on the miscibility of UPE resin/styrene/LPA ternary systems prior to reaction by using the DSC, SEM, and correlated them with Flory-Huggins theory and group contribution methods. From morphological data and DSC reaction rate profile, the phase-separation characteristics of UPE resin/styrene/LPA systems during the cure could be predicted by the calculated upper critical solution temperature for the uncured UPE/styrene/LPA systems. Moderate phase separation between the LPA and crosslinked UPE phases during the cure would be indispensable for the microcrack and microvoid formation, while either too little or too much phase separation would be unfavorable.

Zhang and Zhu [139] investigated the characteristics and mechanisms involved in the microvoid formation of a low shrinkage UPE resin with PVAc. PVAc and styrene were found to play vital roles in controlling the microvoid formation. The voids changed from isolated type to interconnected type by increasing PVAc content, and their sizes were significantly enlarged by increasing styrene content. The microvoid formation was also affected by the curing conditions and compositions. It was enhanced by high curing temperature, but substantially restrained by an applied external pressure. When a filler (CaCO3) was introduced to the PVAc-containing resin or when the resin was cured with *t*-butyl perbenzoate (TBPB), the number of voids increased. They suggested that the microvoid formation did not arise from the strain-relief cracking but from the nucleation and expansion of surplus styrene in the PVAc rich phase.

Cao and Lee [140] examined the effect of secondary monomers, divinylbenzene (DVB) and trimethylopropane trimethacrylate (TMPTMA), and a co-promoter, 2,4-pentandione

(2,4-P), on the shrinkage control of UPE/styrene/ LPA cured at low temperatures. Addition of both TMPTMA and 2,4-P results in an earlier formation of microvoids, earlier volume expansion and better shrinkage control. a better shrinkage control can be obtained when the volume expansion occurs at a lower conversion. There is no further improvement final volume shrinkage after introduction of TMPTMA and 2,4-P into UPE formulation. The morphology of the samples with TMPTMA is quite different from that without TMPTMA, therefore, TMPTMA affects both crosslinking and phase-separation processes in the curing system. The samples with 2,4-P had no morphology changes.

Cao and Lee [141] carried out a systematic study to investigate the effect of the initiator system and reaction temperature on sample morphology, final resin conversion, and resin shrinkage of UPE resins with LPA. It was found that the final conversion of the resin system could be improved by using dual initiators. The effect is more obvious at low temperatures. Volume shrinkage measurements of the resin system initiated with dual initiators revealed that good LPA performance was achieved at low (35 0 C) and high (100 0 C) temperatures but not at intermediate ones.

Cao and Lee [142] investigated the effect of a comonomer, methyl methacrylate (MMA), on volume shrinkage and residual styrene content of UPE resin with low profile additives cured at low temperature by an integrated reaction kinetics-morphology property analysis. MMA affects the volume shrinkage and residual styrene content differently depending on MMA to styrene C=C bond molar ratio. At low MMA/styrene ratio, residual styrene decreases and the volume shrinkage of the resin system remains unchanged, while at high MMA/styrene ratio, residual styrene can be substantially reduced, but the resin system suffers poor volume shrinkage control. MMA has a negative effect on shrinkage control of UEP/styrene/LPA system because the system becomes more compatible with the addition of MMA. Therefore, phase separation becomes more difficult, leading to poor shrinkage control. The surface quality and the flexural properties of UPE depend strongly on the volume shrinkage and final conversion of the resin system.

Boyard *et al.* [143] studied the dynamic curing of a polymer blend containing unsaturated polyester, styrene, and a saturated polyester based on adipic acid and propylene glycol as a LPA using a homemade dilatometer that simultaneously determined conversion degree, volume, pressure, and temperature. They also developed a model based on physical considerations which fitted well with the experimental results.

Huang *et al.* [144] investigated the effect of three series of LPAs on the volume shrinkage and internal pigmentability of the unsaturated polyester resin. Differential scanning calorimetry, scanning electron microscopy, optical microscopy, and image analysis were used to measure static phase characteristics of the UPE/styrene/LPA system, including the reaction kinetics, sample morphology, and microvoid formation. Volume shrinkage control and the internal pigmentability are influenced by microvoid formation during the cure of UPE/ styrene/ LPA system. A higher volume fraction of microvoids can generally lead to better volume shrinkage control but more haziness of pigment color. A cocontinuous globule cured sample morphology leads to the generation of sufficient interfacial area between the densely crosslinked polyester phase and the LPA-rich phase during the cure, lower stiffness of the UP resin, and lower Tg for the LPA in reference to the cure temperature, which results in a higher volume fraction of microvoids and microcracks generated during curing. Huang *et al.* [145] examined the effect of three series of LPAs on the Tg and mechanical properties of the crosslinked polyester resin. The LPAs were synthesized by the authors, and included poly(vinyl acetate) (PVAc), poly(vinyl chloride-*co*-vinyl acetate), and poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride), with different chemical structures and molecular weights. The mechanical properties depended on the interfacial adhesion between the LPA-rich and major St-crosslinked polyester phases, molar ratio of styrene/polyester C=C bonds, sample morphology, and the volume fraction in the major continuous phase of styrene-crosslinked polyester as a result of phase separation during cure. The Tg in the major continuous styrene-crosslinked polyester phase depends on the relative importance of the two opposing effects, namely, the plasticization effect of the LPA phase on the continuous phase and the crosslinking effect of the continuous phase itself in terms of the molar ratio of styrene/polyester C=C bonds.

Wang *et al.* [146] examined the effect of low profile additives (LPA) on the shrinkage behavior of UPE during curing at low to medium temperatures. The shrinkage of UPE is related not only to the temperature, but also LPA type, molecular weight of LPA, concentration of LPA, and also the competition between the shrinkage induced by resin polymerization and the volume compensation by LPA. Poly(vinyl acetate) (PVAc), polystyrene and poly(methyl methacrylate) (PMMA) were used as the LPA. Volume shrinkage was measured in an in-house dilatometer. Low concentrations of PVAc with high molecular weight or high concentrations of PVAc at low molecular weight provide good shrinkage control.

Xue *et al.* [147] developed a simulation for shrinkage mechanism in UPE-PVAc system after characterizing the system using DSC and SEM. There are five steps in the curing of UPE-PVAc system. Firstly, a homogeneous mixture of UPE, styrene and PVAc is formed at room temperature. In the second step, reaction starts near the initiator to form microgels. The segments of PVAc drift from microgel core to the surface because of the decrease in the compatibility between the components. In the thirds step, microgelation takes place. In the fourth and most important step, microvoids are formed in the LPA phase to compensate for the shrinkage stresses. Finally, on cooling the system down, many more microvoids appear in the LPA phase and in the interfaces between UPE and LPA. After all these steps, the low profile phase separation structure of the PVAc systems is formed.

2.2.4.7 Studies on interpenetrating networks with UPE

An interpenetrating networks (IPN) material is a polymer network intermeshed with another polymer network. An IPN is any material containing two polymers, each in network form. Most of the IPNs do not form a network at molecular scale, but may form finely divided phases of sizes in nanometers. In most IPNs polymers form phases that are continuous on macroscopic scale. The networks either have to be made at the same time or the second component must be polymerized inside of the first component after its crosslinked [148, 149]. In Figure 2.2.9, one network is represented by solid lines, while the other network is shown by dotted lines. The circles represent points at which the chains are connected (crosslinked)



Figure 2.2.9: A depiction of a simple IPN material.

IPNs are composite materials in a special way. A very general, simplistic definition of an IPN is a material with two co-continuous phases or a material with 2 parts intertwined throughout. The main goal of an IPN is to trap 2 polymer phases in each other thus causing a possible synergistic behavior or an addition of properties as opposed to a compromise of properties is the scenario which typically results in most composites [150]. Thus, there are two networks co-existing within one another.

Gunanathan *et al.* [151] formulated a tri-component interpenetrating network containing castor oil, toulenediisocyanate, acrylonitrile, ethylene glycol diacrylate, and UPE with different compositions for the toughening of UPE. The polyurethane (PU)/polyacrylonitrile (PAN)/UPE network undergoes single decomposition showing ideal compatibility at the composition of 10:90 (PU/PAN: UPE). The impact strengths of the IPNS were higher than control UPE.

Chou and Lee [152] studied the IPNs based on polyurethanes and three different polyester resins. The interaction between the two phases was studied by reaction kinetics and rheological changes. The reaction between the end groups of UPE molecules and isocyanate led to more reactive vinyl polymers. The presence of carboxylic groups on the

UPE chain increased the rate of formation of the polyurethane network. The extent of chemical grafting governed the morphologies of the IPNs formed.

Sperling [153] reviewed the different IPNs, methods of their synthesis, applications to the plastics and the industry, and history of IPNs.

Frischinger and Dirlikov [154] formed two phase interpenetrating epoxy networks with homogeneous formulations of diglycidyl ether of bisphenol-A, epoxidized soybean oil, and vernonia oil. At low oil contents, the DGEBA matrix is rigid and rubbery particles of oils are randomly distributed, and at higher oil contents, the rubbery phase is continuous and the DGEBA is rigid small particles. Phase inversion and particle size depends on the miscibility of the two phases.

Frischinger *et al.* [155] discussed the commercial applications of interpenetrating epoxy networks made with DGEBA and epoxidized vegetable oils. These IPNs can be used for toughening of epoxy resin and also for preparation of crack resistant coatings. The systems with a continuous vegetable oil rubbery phase and small DGEBA rigid particles are especially suited for stress-resistant and crack-resistant coatings.

2.3 Bioresins

There is a growing urgency to develop novel bio-based products (based on renewable resources) and associated technologies that reduce widespread dependence on fossil fuels. Bio-based products can form the basis for an assortment of green materials that can compete with and take over markets currently dominated by products exclusively from petroleum feed stocks. Interest in the use of green materials has also grown due to their various advantages, like ready availability and low cost. Currently, various renewable

resources are being used to prepare products like starches, proteins, fats, and oils for a range of applications in building materials, structural and automotive parts, absorbents, coatings, inks, plasticizers, lubricants, adhesives, bonding agents and agrochemicals [156-161].

Vegetable oils such as soybean, cottonseed, linseed, castor, are available on a global basis in large quantities at affordable costs and are possibly biodegradable. These naturally hydrophobic plant oils are used as starting materials for a range of resin products for example, resin precursors, produced by the transformation of vegetable oils that will polymerize when heated in the presence of catalysts. This technology uses the reactivity of the monomers to attack the double bonds present in the oil, forming linkages that can subsequently be reacted into crosslinkable units. Other reactive chemicals can also be incorporated into the formulation to facilitate curing [156].

Because of different kinds of fatty acids present in oils, on a molecular level they are composed of many different types of triglycerides with varying levels of unsaturation [157]. Recently, genetic engineering techniques have helped to regulate the variation of unsaturation in plant oils such as soybean, flax, and corn [158]. These oils have also been used as toughening agents [156, 159, 160]. There also has been an extensive amount of work in their use to produce interpenetrating networks (IPNs) [161].

Vegetable oils are an abundant natural resource that has yet to be fully exploited as a source for polymers and composites. This area of research sets a foundation from which completely new materials can be produced with novel properties. Research continues to try and optimize the properties of these materials and understand the fundamental issues

that affect them. In this manner, more renewable resources can be utilized to meet the material demands of many industries.

2.3.1 Soybean oil

Soybean oil is a complex mixture of five fatty acids (palmitic, stearic, oleic, linoleic, and linolenic acids) that have vastly differing melting points, oxidative stabilities, and chemical functionalities [157]. Soybean oil is the world's most widely used edible oil. In the US, more than 13 billion pounds of soybean oil are used annually in foods and food





processing. Also, more than 600 million pounds of the soybean oil produced annually in the US is used for non-edible applications, including the production of industrial materials [162]. More than half of this soybean oil use falls in the category of fatty acids, soaps, and feed. The remainder of the non-edible soybean market is in the manufacturing of inks, paints, varnishes, resins, adhesives, coating, lubricants, plasticizers, plastics, biodiesel, and specialty products. There are five primary target areas that hold great potential for soy-based products: adhesives, coatings and printing inks, lubricants, plastics, and specialty products.

2.3.2 Linseed oil (from Flax seeds)

Linseed oil is obtained from seed of the flax plant. It is primarily used in industry; but



Figure 2.2.10: Flax plant and flower

some is also used for edible purposes. Flax seed is grown for oil in the U.S. with production of 200 million pounds, in 2002 [163]. The global production of flaxseed is about 2750 million pounds per year; of which over 40 percent is grown in Canada. Britain and France are the other major producers of linseed. In the US, North Dakota is the biggest producer of linseed. Linseed oil has long been used in making linoleum, oilcloth, certain inks, varnishes, paints, drying oils, printing inks, soaps and for some finishing processes in the manufacturing of leather [164]. The crude linseed oil is an organic mixture of linolenic acid, linoleic acid and oleic acid.

2.3.3 Modifications of vegetable oils

In recent times, there have been a lot of research and publication on the use of soybean oils as epoxy, polyol, polyurethane, and polyester resins. The triglyceride molecules contain active sites, which are prone to chemical reaction; these sites are the double bond, the allylic carbons, the ester group, and the carbons alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride using synthetic techniques that have been applied for the petroleum-based polymers. A higher molecular weight, increased crosslink density, and incorporation of chemical functionalities that impart stiffness, can be accomplished by several synthetic pathways [165-174].

In recent years, extensive work has been done to develop polymers for engineering applications using vegetable oils as the main component. The following is the description of the most notable work that has been done in this area:

Mulhaupt and coworkers [165-166] developed polyester networks based upon epoxidized and maleinated natural oils.

Wool *et al.* have synthesized liquid thermosetting bioresins from soybean oil which can be reinforced with glass, carbon or kevlar fibers, and can be processed by methods such as hand lay-up, resin transfer, spray-up, filament winding, and pultrusion. These resins have the same mechanical properties as unsaturated polyester or vinyl ester resins. They have also synthesized and polymerized maleate half esters of fatty acid monoglycerides derived from soybean oil. [167].

Can *et al.* [168-169] prepared rigid thermoset polymers from the radical copolymerization of the soybean oil monoglyceride maleates (SOMG) with styrene. SOMG were produced from the reaction of soybean oil with glycerol with an optimization of the reaction to maximize the monoglyceride yield, following by reaction with maleic anhydride to produce the SOMG maleate half esters. In another study, the same authors reacted the copolymers of the SOMG maleates with styrene to produce rigid thermosetting polymers. They used mixtures of SOMG with neopentyl glycol (NPG) and SOMG with bisphenol A (BPA), and maleinized them under the same reaction conditions, and copolymerized the resulting maleates with styrene.

Li and Larock [170-173] were successful in direct cationic polymerization and copolymerization of the C=C bonds of various soybean oils and several other biological oils. They used regular soybean oil, low-saturation soybean oil (LSS) and conjugated LSS (CLS), to develop a series of polymers ranging from rubbery to rigid by cationic polymerization with styrene and divinyl benzene. The thermophysical and mechanical properties of the resulting materials were also determined. The biological oils that they studied were tung oil, Norway fish oil ethyl esters, conjugated Norway fish oil, and triglyceride fish oil.

Dweib *et al.* [174] manufactured structural panels and unit beams from soybean oil based resin and natural fibers (flax, cellulose, pulp, recycled paper, chicken feathers) using vacuum assisted resin transfer molding (VARTM) technology.

Soucek *et al.* [175] synthesized norbornyl epoxidized linseed oil via Diels-Alder reaction of cyclopentadiene with linseed oil at high pressure and high temperature, followed by an epoxidation using hydrogen peroxide with a quaternary ammonium catalyst. In another study, Soucek *et al.* [176] prepared epoxy norbornane linseed oils (ENLOs) as a function of the norbornene content, and carried out cationic photopolymerization of ENLOs.

Latere *et al.* [177-180] made polyurethanes from soybean oil derived polyols and synthetic isocyanate, and made composites with glass fibers, hemp fibers and kenaf fibers. Petrovic and coworkers [181-186] have developed various polyols from different vegetable oils. They were also successful in making polyurethanes from soybean derived polyols. Uyama *et al.* [187] synthesized green nanocomposites consisting of epoxidized soybean oil and nano clay (Figure 2.2.11).

The manufacturing and characterization of pultruded composites from glass fibers and epoxidized allyl soyate and epoxidized soybean oil was done by researchers from the University of Missouri–Rolla [188].

Eren and Kusefoglu [189] have simultaneously added bromine and acrylate groups to the double bonds of fatty acids in triglycerides soybean oil, sunflower oil and methyl oleate. Eren *et al.* [190] also reacted soybean oil triglycerides with maleic anhydride to introduce more than two maleate residues per triglycerides. The maleinized soybean oil (SOMA) was then polymerized with diols to half-esters.

Neckers *et al.* have researched UV curing of soybean oil or epoxy soybean oil for use in coatings. With their experiments, they developed a new series of photoinitiators that allow the curing of epoxy soybean oil as a coating [191].

Miyagawa *et al.* [192-199] have developed bio-based epoxy materials containing functionalized vegetable oils (FVO), such as epoxidized linseed oil (ELO), epoxidized soybean oil (ESO), acrylated epoxidized soybean oil (AESO), and, octyl epoxy linseedate (OEL) by processing with an anhydride or amine curing agent. They have also used bio-epoxies to make nanocomposites with nano fillers including clay, silica, alumina, vapor grown carbon fibers, and carbon nanotubes.

In another study, people at composite materials and structures center (CMSC) of Michigan State University designed and engineered biocomposites from plant biofibers and a blend of unsaturated polyester resin and derivitized vegetable oil to replace existing glass fiber-polyester composites for use in housing applications [156, 200].



Figure 2.2.11: Photograph of ESO-clay nanocomposite showing high flexibility [187]

2.3.4 Modified matrix

In this study, we propose to make bio-based resins by the modification of vegetable oils, such as soybean oil, linseed oil, etc., and polymerize them with UPE. The development of such bioresins would ensure reduced dependence on petroleum products for a variety of industrial applications.

The vegetable oils will be modified according to the functionality desired. New methods for adding one or more functional groups like acrylates, epoxies, ethers, hydroxyl and esters to the natural oils will be developed. The modified vegetable oils (bioresins) will then be crosslinked by the free radical polymerization with UPE. The amount of initiator will be optimized by the evaluation of mechanical and thermal properties of the resulting polymerized bioresin. A unique initiator system will be designed for each type of modified oil.

The bioresins hence developed, will also be used for the fabrication of composites using an optimum amount of reinforcement. The fibers can be. The resulting composite will thus be more than 50 % bio-based.

2.4 Processing of biocomposites

The goal of modern composite material processing is to obtain high-quality structural components at lower cost. To this end, biocomposites are processed by injection molding, extrusion, compression molding (CM), pultrusion, resin transfer molding (RTM), resin injection molding (RIM), vacuum assisted resin transfer molding (VARTM), bulk molding compound (BMC), hand lay-up, and (now) sheet molding compounding (SMC). Discussed below are some of the processing techniques pertinent to thermoset composites.

Compression molding

Compression molding (CM) is a high-volume, high-pressure method suitable for molding complex, high-strength fiberglass reinforcements. Compression molding is a processing technique in which the molding material, generally preheated, is first placed in an open, heated mold cavity. The mold is closed with a top force or plug member, pressure is applied to force the material into contact with all mold areas, and heat and pressure are maintained until the molding material has cured. Compression molding was specifically developed for replacement of metal components with composite parts.

The molding process can be carried out with either thermosets or thermoplastics. Compression molding is the most common method of processing thermosets. Composite can also be compression molded with unidirectional tapes, woven fabrics, randomly orientated fiber mat or chopped fibers. The advantages of compression molding are the ability to mold large, fairly intricate parts, short cycle time (typically 1-6 minutes), high volume production, high quality surfaces [201]. Compression molding produces fewer knit lines and less fiber-length degradation than injection molding. However, it involves high initial capital investment, is labor intensive, and sometimes requires secondary operations. It is very popular with automotive industry, and products like front and rear end automobile panels, hoods, roofs, scoops, fenders, spoilers, air deflectors, and lift gates are made using CM.

Resin Transfer Molding (RTM)

Resin Transfer Molding or RTM literally means the transfer of the resin mix from one system (the RTM machine) to another system (the closed mold containing the reinforcement) while molding a product. It bridges the gap between labor intensive hand lay-up process and capital intensive compression molding process.

In a traditional RTM process; a dry, fibrous preform is loaded into a matched-metal mold. The mold is then closed, which compacts the preform, and a thermosetting resin is injected into the preform. The resin and fiber remain in the mold until crosslinking occurs, after which the composite can be removed. The material can be cured at room temperature or in heated mold by proper choice of initiator.

There are several advantages in using RTM over more traditional composite processing techniques. Some of these advantages are: very large and complex shapes can be made efficiently and inexpensively, elimination of the labor and skill required in hand lay-ups, better reproducibility of parts due to the high dimensional accuracy of the mold, reduction in the exposure to volatile organic compounds (VOC). Along with the advantages, there are the inevitable disadvantages: the mold design is critical, and it can

become quite expensive, resin rich areas often form in the edges and radii, reinforcements that move during injection can alter the quality of the finished part.

Applications of RTM are in consumer goods such as helmet, bathroom fixtures, boats, car body panels, instrument panels, truck caps, building panels etc. Factors affecting RTM processing are: resin characteristics, reinforcement characteristics, resin injection pressure, design of the mold, mold temperature, vacuum state of the system, flow rate of resin mix, and mold filling time [202].

Some of the advantages of RTM process include: relatively low tooling cost, design flexibility, faster productivity, labor savings, energy savings, lower emissions of volatiles, no air entrapment, smooth surface finishing on both sides, both sides can be gel-coated, close dimensional tolerances maintained, a more consistent product, thus reducing bad product thrown away, and more parts for the money.

O'Dell [203] made composite of jute mats and unsaturated polyester resin through resin transfer molding (RTM). The author also evaluated the mechanical properties and resistance of the composites to wood-degrading fungi and simulated weathering. The suitability of resin transfer molding equipment with regard to resin flow, air entrainment, and surface properties for jute-UPE composites were determined. There were no problems in processing, thus, jute fibers could be processed just as well as glass fibers in resin transfer molding. The samples exposed in a accelerated weatherometer for 1,200 hours showed minimal surface erosion or color change, the samples also showed negligible weight loss when exposed to wood degrading fungi.

Rowell *et al.* [204] manufactured composite samples with jute and UPE by RTM, jute and epoxy resin by RTM, and jute-polyurethane by structural reaction injection molding

(SRIM). The samples were subjected to mechanical testing as well as weather resistance analysis. The jute fiber mats used in the RTM as well as SRIM system wetted well with the respective resins. On comparing glass fiber and jute fiber based composites, the surface finish of both composites were nearly equal. The samples exposed to accelerated weathering for 600 hours showed surface whitening and nearly identical fiber exposure.

VARTM

The VARTM process has its roots in early composite manufacturing. However, modern VARTM is traced to the patenting of SCRIMP – Seemann's Composite Resin Infusion Molding Process. This method employed the use of a vacuum bag, resin supply tubing, a resin conduit and a distribution medium. RTM has lead to the evolution of Vacuum-Assisted Resin Transfer Molding (VARTM) in order to overcome some of its inherent flaws. In the VARTM process, a vacuum bag is used as one of the tool surfaces. This eliminates the need for precise matched-metal mold making that is crucial in conventional RTM. The exact fit of the vacuum bag to the preform drastically reduces resin rich areas, and it also allows for a more efficient way of trapping and controlling VOC emissions that are being more strictly regulated. A final advantage of VARTM lies in the low injection pressures (~1 atm). These low pressures allow for little movement of the reinforcement during processing, which produces a better quality part [205].

This lay-up begins with a dry, fibrous preform laid onto an open-faced tool plate. Then, a porous peel-ply is placed on top of the preform, but underneath a resin distribution tube. Next, comes the resin distribution medium. This material, which is also known as the

high-permeable distribution medium, covers a large portion of the preform and peel-ply. Even though VARTM processes do not technically require these high-permeable distribution media, they can be helpful in significantly reducing processing times by providing a low resistance resin pathway. The final step in the lay-up is the placement of a vacuum bag over the entire assembly.

Once the lay-up is complete, the processing can be carried out. First, a vacuum pump is turned on to expel any air from the preform assembly. After the system has equilibrated, the resin is allowed to flow through the resin distribution tube and across the highpermeable distribution medium. The resin then fills the preform in the transverse, or through the thickness, direction by leaking downward from the high-permeable distribution medium. The vacuum source is left on until the resin system begins to gel. Once the vacuum is turned off, the part may either cure at room temperature, or it can be placed in an oven to assist the curing process.

The VARTM process is currently implemented in the manufacturing of Naval structural components (masts, hulls, and bridge decks), automobile chassis and body components, transportation infrastructure, railroad cars, and turbine blades A great deal of work still needs to be done on efforts to reduce the costly trial-and error methods of VARTM processing that are currently in practice today. An understanding of the flow behavior of the system prior to production is crucial. For rigid monolithic structures this provides several advantages: reduced labor, good surface mold side, and improved fiber volume fraction.
Shenton *et al.* [206] discussed a collaborative effort to manufacture a roof made from completely natural composite material for residential construction. The raw materials used for the composite were soy bean based resins and natural fibers.

Dweib *et al.* [207-209] manufactured structural panels and unit beams from soybean oil based resin (Acrylated, Epoxidized Soybean Oil, (AESO)), natural fibers (flax, cellulose, pulp, hemp, old newspaper, recycled paper, chicken feathers), and woven glass fiber and closed cell structural foam, using vacuum assisted resin transfer molding (VARTM) technology. Structural parts incorporating a foam core were also manufactured and tested to give the required strength for roof applications. Stay-in-place bridge decking form was successfully manufactured and tested to replace the current in use metal form. Same material can be used as a good insulation material in housing and refrigerating trucks for transportation.

Hong and Wool [210] have developed a low dielectric constant material from chicken feathers and acrylated epoxidized soybean oils by a vacuum assisted resin transfer molding (VARTM) process. A natural, bio-based and environmentally friendly material from hollow keratin fibers and chemically modified soybean oil was thus obtained. The dielectric constant values were lower than that of a conventional semiconductor insulator material such as silicon dioxide, epoxies, polyimides and other dielectric materials.

Quagliata *et al.* [211] improved the material stiffness shortcomings of biocomposites through efficient structural configurations. They used the popular designs for advanced composites based on this idea, namely cellular and sandwich structures which respectively maximize material and structural performance. They investigated the feasibility of using biocomposite materials for primary load-bearing components in civil

structures by utilizing high-performance structural forms. Their research work focused on the investigation of this concept through the development, manufacturing, and characterization, both experimental and analytical, of laboratory-scale cellular beams and plates. These studies were used to analytically investigate the feasibility of using biocomposite materials for full-size structural components for civil structures, and assess the future research needs for the development of load-bearing biocomposite structures.

SMC

Biocomposites have been traditionally manufactured with techniques like extrusion, injection molding, compression molding, resin transfer molding, and pultrusion, etc. But they have never been produced using an SMC line. SMC is a very useful processing technique usually used for fabricating glass-polyester resin composites. Today more and more parts and products from cars to skis, hockey sticks to microwaves are being molded from SMC. This is not too surprising since thermoset composite plastics have been used for more than sixty years around the world. A recent U.S. report states that the demand for thermoset composites in the automotive industry will rise by 68 per cent to 467 million pounds by the middle of this decade. The reason is easy. SMC combines high strength and light weight. Other advantages of thermoset composites are durability and resistance to corrosion in a wide range of temperature environments. The application of a priming and topcoat will allow SMC components to meet automotive 'class A' surface finish requirements.

Ever since 1960's there have been numerous patents on SMCs. US 3615979 granted in 1971 was a patent for glass fiber-reinforced sheet molding compound, by Owens-Corning

Fiberglas Corp [212]. US 3713927 granted in 1973, thermosetting sheet molding compounds [213]. US 3835212 granted in 1974 was a patent for resinous sheet like products [214]. DE 2357000 granted in 1974 was a patent for sheet molding compounds [215]. JP 49076988 granted in 1974 was a patent for unsaturated polyester compositions for moldings [216]. JP 49107086 granted in 1974 was a patent for unsaturated polyester compositions [217]. JP 50005463 granted in 1975 was a patent for molding resin compositions [219]. JP 50014792 granted in 1975 was a patent for sheet molding compositions [220]. JP 50036588 granted in 1975 was a patent for sheet molding compositions [221]. US 3931095 granted in 1976 was a patent for fire retardant thermosetting resin composition [222].

The traditional SMC (Sheet Molding Compound) is a combination of chopped glass strands and filled polyester resin, in the form of a sheet. SMC is a fully formulated system (fiber, resin, and additives), which can be molded without additional preparation. Sheet molding compound can be made with random chopped fiber reinforcement, with continuous fibers, or with a mixture of the two. The variety of fiber architectures available for sheet molding compound means a variety of properties can be achieved in compression molded parts. SMC prepreg is made from chopped glass strands, sandwiched between two layers of film, onto which the resin paste has already been applied. The prepreg passes through a compaction system that ensures complete strand impregnation before being wound into rolls. These are stored for a few days before molding to allow the prepreg to thicken to a moldable viscosity.

SMC is aged to a state near gelation. The manufacturer allows the SMC to reach an extent of reaction close to gelation because it stabilizes the polymer. This light crosslinking increases viscosity and improves processability of the SMC. This ready-to-mold glass fiber reinforced polyester material primarily used in compression molding. SMC is not just fiber mixed with resin. The other fillers have an important role. SMC is made by dispensing mixed resin, fillers, maturation agent, catalyst and mold release agent onto two moving sheets of carrier film. SMC can be molded into complex shapes with little scrap. It is also called the "raw material" for compression molding. It is suitable for production runs in excess of 10,000 parts per year.

Processing of SMC by compression molding enables the production of bodywork or structural automotive components and electrical or electronic machine housings in large industrial volumes or body panels (hoods and deck lids). The process also penetrates sectors such as sanitary ware (baths) and urban furniture (stadium and cinema seating), etc. Its characteristics allow it to fill a mold under the effects of the molding temperature and pressure.

Sheet Molding Compound (SMC) produces highly cross-linked and highly filled systems, in which polymer component is polyester. The molded product combined high modulus with high strength. This is more expensive than metal, but has lower tooling cost.

There have been many improvements in the SMC processing since 1970s, and hence many more patents. But none of these cater to SMCs with natural fibers and resins. However, there is one patent and two papers which talk about SMC processing for biocomposites. These include, US 2003088007 granted in 2003 to Wool et al, which is a patent for sheet molding compound resins from plant oils [223].

van Voorn *et al.* [224] discussed a non automated SMC process for making flax fiber reinforced unsaturated polyester resin composites using sheet molding compounding in 2001. A homogeneous product was obtained after development of fiber distributor, use of compaction rollers, and drying of fibers before compounding. The natural fibers in their process are not continuously fed to the SMC line. They do so by a batch process. Thus, their process is not fully automated, and hence cannot be used in an industrial setting. Goswami *et al.* [225] made jute (cloth) reinforced sheets with the help of polyester resin in "Jute reinforced sheets based on shellac filled SMC", in 2003.

So far, no industrial process exists for using sheet molding compound panel processing to fabricate bio-composites. No other process has been reported in literature for fabrication of bio-composites via SMC. Our sheet molding process is different from all the above mentioned ones, because of its uniqueness of fiber dispersion, ability to run the process for any kind of natural fiber, automated fiber feeding to the production line, and flexibility with resin formulations.

Kawamura *et al.* [226] described warpage prediction method for compression molded SMC products. Warpage relates to material anisotropy caused by fiber orientation distribution. Charge pattern, which is one of molding conditions, has a significant effect on fiber orientation distribution. So, mechanical properties such as bending modulus and the coefficient of thermal expansion were evaluated in two different charge patterns in order to examine the relationship with warpage. Temperature distribution of each layer (surface layer, middle layer) in the thickness direction was also measured during curing.

The temperature difference between the top and bottom mold causes different heat generation in each layer. It was found that anisotropy of the coefficient of thermal expansion caused by fiber orientation distribution and the inversion phenomenon of temperature gradient in the thickness direction during the curing process were dominated in inducing warpage. Warpage prediction method utilizing finite element method has been developed based on these causes of warpage. Predicted warpage coincides well with warpage of molded products quantitatively. This warpage prediction method is able to reduce warpage of compression molded SMC products.

Odenberger *et al.* [227] focused on experimental visualization of the flow during mold closure in compression molding of sheet molding compound (SMC). Special attention was given to the advancing flow front, for which the full complexity is captured by means of continuous high resolution close-up monitoring. From the experimental visualisation of the flow front, three phases were defined, namely pitch, floating, and boiling. A qualitative investigation of the surface quality of the molded plates was also carried out. It was observed that the surface void is reduced with an increased mold temperature and that the mould closing speed does not seem to have any influence on the surface quality at lower mold temperatures while at higher mold temperatures, an increased mold closing speed clearly gives a reduction of surface void.

Feuillade *et al.* [228] studied the influence of chemical structure of two glass fiber sizings on the impregnation of the fibers by an unsaturated polyester matrix before the curing reaction. The fibers were chosen to provide a low and a high surface quality respectively for two fiber types for the final SMC part. Individual characteristics of each component and their interactions play important roles on the processing of SMC paste and on final

product properties, such as surface aspect and uniformity. Two of these characteristics are fiber wetting by the resin and fiber/matrix adhesion. Results give evidence of the various mechanisms occurring at the surface. The main parameters which should influence fiber impregnation are: the film former quantity, the antistatic agent type, the deposition method and the nature of the film former.

Massardier-Nageotte *et al.* [229] developed a methodology based on visible light transmission and x-ray imaging, for the characterization of glass fiber orientation and distribution in large components molded using sheet molding compounds. They observed that for planar components, the fibers were uniformly distributed and orientation was in the flow direction.

2.5 Weathering

Biocomposites have always been looked at suspicion with regards to their durability. It is known that the thermal as well as mechanical properties of the wood composites and natural fiber based composites fade with time. Numerous studies in the literature have talked about the moisture absorption or water uptake of the biocomposites. Furthermore, even though durability of wood composites has been studied in detail [230-238], not many people have studied the weathering of biocomposites. To counter questions about the durability of biocomposites, it is necessary to evaluate the effect of long-term weathering on biocomposites.

The weathering of biocomposites can be done in an accelerated weathering chamber, where the samples can be exposed to harsh weather conditions including harmful ultra

violet rays, condensation, humidity, elevated temperatures, and rain simulating water spray. At regular intervals of time, the samples can be evaluated for physical properties like color, surface roughness, weight change, and mechanical and thermal properties like, tensile and flexural strength, modulus of elasticity, impact strength, storage modulus, coefficient of thermal expansion etc.

It is expected that with the increment in the exposure time of the samples to accelerated weathering conditions, the surface roughness should increase, while color should turn lighter, and thermal as well as mechanical properties should decrease, compared to their properties at the beginning of the test. Such weathering experiments can give an insight about the amount of damage the samples can undergo in accelerated weathering conditions, and can also help to set guidelines about the life time of the products performing at the acceptable levels. However, such tests cannot be compared to real time, and no correlation exists to convert the test time in the chamber to actual time in the real world

Ever since 1990s many researchers have actively examined the durability of woodfiber/plastic composites. Fungal attacks on wood composites have been studied by different lab and field tests.

Matuana *et al.* [230] investigated the durability of polyvinyl chloride (PVC)/ woof fiber composite samples subjected to a cyclic UV light/spray weathering tests for a duration of 1200 hours. The samples were analyzed by FTIR, colorimeter, contact angle, and surface roughness. They observed that the wood fibers are sensitizers and their reinforcement in a PVC matrix accelerated the photo-degradation of the polymer matrix. There was greater discoloration in the composite samples compared to neat plastic.

Kalnins and Feist [231] exposed the western redcedar panels to outdoor weathering. They measured the wettability of the panels with water using contact angle analysis. They found that the contact angle decreased as the exposure time increased, leading to greater wettability. Increased wettability might be a factor contributing to the degradation of wood structures and articles.

Feist [232] performed outdoor study of various finish systems on aspen siding. He found that acrylic latex paints are best protection for weathering.

Ultraviolet weathering performance of rigid PVC filled with different concentrations of wood flour was studied by Matuana and Kamdem [233]. The extruded and compression molded samples were subjected to a cyclic UV lamps, condensation, and exposed for 300 hours. The samples were regularly assessed over a wide range to time during exposure. The samples were analyzed by FTIR, colorimeter, contact angle, tensile test and notched Izod test. It was found that incorporation of wood fibers in the PVC matrix led to a increased degradation of the matrix material. The exposed PVC plastic samples also had lower impact strength and lower elongation at break compared to original plastics. However, all of the composites retained their impact strength, tensile strength, tensile modulus as well as elongation at break.

Podgorski *et al.* [234] developed an artificial weathering method to assess the durability of exterior wood coatings and wood in a short period of time. The optimized cycle they developed contained a condensation period of 24 hours, UVA at 340 nm for 2.5 hours and water spray for 0.5 hours. The total duration of exposure was 2016 hours. This

optimized cycle was tested on different wood substrates, wood coatings, and also checked for reproducibility.

P. Chow and D. S. Bajwa studied the weathering effects on the decay resistance of creosote treated oak [235]. They used a standard soil block culture method to test decay resistance of naturally and artificially aged oaks infected with brown and white rot fungi. They found that naturally aged samples were more vulnerable to fungal attack as compared to artificially aged ones.

Nzokou and Kamdem studied the weathering of African paduak and red maple, both of which are hardwoods. The wood samples were artificially weathered for 1000 hours, and changes in color, roughness and contact angle were measured at regular intervals of exposure [236]. They observed that the color change for both species was very fast during the first 24 hours of exposure. With increment in exposure time, the roughness of both wood types increased, and the contact angle decreased due to a decrease in lignin and extractive content of the wood surface.

Feist [237] and team evaluated the long term effect of solvent borne and waterborne water repellent preservative treatments on the performance of various paint systems applied to different wood substrates. Six substrates were subjected to nine years of outdoor exposure and evaluated for degradation, finish and decay. They found that the performance of substrates treated with waterborne preservatives was slightly better than those treated with solvent-borne preservatives.

Stark and Matuana [238] studied the performance of photostabilized HDPE/wood flour composites after accelerated weathering exposure of 2000 hours. They found that both colorants and UVA are better photostabilizers than hindered amine light stabilizers for

HDPE/wood composites. The flexural properties of neat HDPE dropped significantly after weathering, but those of photostabilized HDPE/wood composites remained same until 2000 hours of exposure.

Gassan and Bledzki [239] determined the thermal degradation of untreated and alkalitreated jute and flax fibers. The fibers were exposed to temperatures between 170 and 210 ^oC for a maximum of 120 min. The exposed fibers were mechanically tested in a yarn tensile test to measure the influence on tenacity. In all cases both fibers showed none or only a slight decrease in tenacity and degree of polymerization at temperatures below to 170°C. For temperatures above 170°C the tenacity as well as the degree of polymerization decrease rapidly, and depended on both exposure time and temperature. In general, a higher temperature or longer time of exposure led to an increase in level of depolymerization and to a drop in tenacity. Because of chain scission due to this thermal treatment, an increase in degree of crystallinity with a maximum of 20% was found.

Degradation consists of loss of strength and/or stiffness. The relationship between the decay during accelerated experimental testing and long-term testing is expressed through an *acceleration factor* k. The acceleration factor is the ratio between time exposures after natural aging and after accelerated aging to obtain a similar decay. For instance, an acceleration factor k = 400 means that every hour under accelerated laboratory aging testing corresponds to 400 hours of aging under normal conditions.

Flammability

Schartel *et al.* [240] studied thermal and fire behavior of flax-PP composites containing ammonium polyphosphate and expandable graphite as fire retardants. The biocomposites

were analyzed using TGA, FTIR, cone calorimeter, limiting oxygen index, and glow wire test. As expected fire retardancy was better for samples containing ammonium polyphosphate and expandable graphite, compared to neat biocomposite. Comparing same amounts of both fire retardants, graphite was better than ammonium polyphosphate.

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CHAPTER THREE: EXPERIMENTAL METHODS

3. EXPERIMENTAL METHODS

3.1 Materials

The raw materials used for the fabrication of biocomposites were natural fibers (from plants) and matrix materials (Table 3.1.1 and 3.1.2). Non woven mats of industrial hemp fibers, chopped industrial hemp fibers (green and retted), chopped flax fibers, kenaf fibers, chopped big blue stem grass, green flax core, chopped henequen, chopped coir, chopped pineapple leaf fiber, woven jute mats, chopped E- glass fibers and non woven glass mat were used as reinforcements for different composites. Two kinds of non-woven hemp fiber mats, one containing 90% randomly oriented hemp fibers and 10% poly ethylene terephthalate (PET) as binder (see Figure 3.1.1.), and a second containing 100% hemp fibers was kindly provided by FlaxCraft Inc. Kenaf fibers were procured from Texas Kenaf Industries, USA. Another kind of kenaf was obtained from China. Chopped hemp, chopped green hemp and chopped green flax core fibers were kindly provided by FlaxCraft Inc. Cresskill, USA. Jute mats were obtained from IJIRA, India. Henequen fibers were provided by Dr. Pedro Herrera-Franco of Mexico. Chopped E- glass fibers and non woven glass mat were supplied by Kemlite Inc. Joliet, USA. Rovings of E-glass for SMC line were purchased from Owens Corning.

The natural fibers were surface treated with various chemicals such as alkali, acrylonitrile, silanes etc. Sodium hydroxide, gamma methacryloxy propyl trimethoxy silane, amino propyl trimethoxy silane, ethanol, methanol, chloroform and acetone were purchased from J. T. Baker. Acrylonitrile, maleic anhydride, methyl methacrylate, and glycidyl mehtacrylate were obtained from Aldrich.

The polymer matrix used in this project is a combination of ortho unsaturated polyester resin (UPE) and styrene, which was obtained from Kemlite Inc. The initiator used for curing the resin was methyl ethyl ketone peroxide (MEKP), and the promoter used was cobalt naphthenate (CoNap). Both MEKP and CoNap were obtained from Aldrich.

Pure double refined soybean oil, castor oil and acrylated epoxidized soybean oil (AESO) were procured from Aldrich. Methyl ester of soybean oil (MESO) was kindly provided by AG Environmental Products. Epoxidized methyl linseedate (EML), soybean oil phosphate ester polyol (SOPEP), methyl ester of epoxidized soybean oil (MEESO) and epoxidized linseed oil (ELO) were obtained from Atofina Chemicals.

All materials were used as such without further purification.

Name of fibers	Composition	Length of Density of		Source of
		fibers (mm)	fibers	fibers
Non-woven	90% hemp 10%	45-50	$274 (gm/m^2)$	Flaxcraft Inc.
hemp mat-1	PET			
Non-woven	100% hemp	45-50	$600 (gm/m^2)$	Flaxcraft Inc.
hemp mat-2				
Green hemp	100% hemp	6	$1.2 (gm/m^3)$	Flaxcraft Inc.
Retted hemp	100% hemp	6	$1.2 (gm/m^3)$	Flaxcraft Inc.
Big blue stem	100% BBSG	4	$1.2 (gm/m^3)$	Michigan,
grass (BBSG)				USA
Green flax core	50% flax bast	1-2	$1.2 (gm/m^3)$	Flaxcraft Inc.
	50% flax core			
Kenaf	100% kenaf	6-8	1.2 (gm/m ³)	Flaxcraft Inc.
Henequen	100% henequen	6-8	1.2 (gm/m ³)	Mexico
Coir	100% coir	6-8	1.2 (gm/m ³)	India
Jute mats	100% jute	continuous	$1.2 (gm/m^3)$	India
Pineapple leaf fiber (PALF)	100% PALF	6-8	$1.2 (gm/m^3)$	India

Table 3.1.1: Reinforcements for composites made in this project

Table 3.1.1 (continued)

E-glass chopped	100% UPE sized glass	55-60	2.6 (gm/m ³)	Kemlite Company Inc.
E-glass chopped	100% UPE compatible glass	55-60	2.6 (gm/m ³)	Owens Corning
E-glass mat	100% UPE sized glass	6-8	2.6 (gm/m ³)	Kemlite Company Inc.
E-glass roving	100% UPE compatible glass	continuous	2.6 (gm/m ³)	Owens Corning



Figure 3.1.1: Hemp mat with filler (Bastmat 115) obtained from FlaxCraft Inc.

Table	312.	Materiale	and	sumpliere
I able	3.1.2:	waterials	anu	suppliers

Material	Supplier		
Unsaturated polyester resin (UPE)	Kemlite Company Inc.		
Methyl ethyl ketone peroxide (MEKP)	Sigma Aldrich		
Cobalt naphthenate (CoNap)	Sigma Aldrich		
Pure double refined soybean oil	Sigma Aldrich		
Castor oil	Sigma Aldrich		
Acrylated epoxidized soybean oil (AESO)	Sigma Aldrich		
Methyl ester of soybean oil (MESO)	Atofina Chemicals		
Epoxidized methyl linseedate (EML)	Atofina Chemicals		
Soybean oil phosphate ester polyol (SOPEP)	Atofina Chemicals		
Methyl ester of epoxidized soybean oil (MEESO)	AG Environmental Products		
Epoxidized linseed oil (ELO)	Atofina Chemicals		

Table 3.1.2 (Continued)

Poly(butadienemaleic anhydride) (PBMA)	Sartomer Chemcial Company
Epoxy resin (Epon 828)	Shell Chemical Company
Sodium hydroxide	J. T. Baker
γ-methacryloxypropyl trimethoxy silane (MPS)	Gelest Inc.
aminopropyltrimethoxy silane (APS)	Gelest Inc.
Ethanol	J.T. Baker
Methanol	J.T. Baker
Chloroform	Sigma Aldrich
Acetone	J.T. Baker
Acrylonitrile (AN)	Sigma Aldrich
Maleic anhydride (MA)	Sigma Aldrich
Glycidyl mehtacrylate (GMA)	Sigma Aldrich
Methyl methacrylate (MMA)	Sigma Aldrich
Glacial acetic acid	Sigma Aldrich
Dicumyl peroxide (DCP)	Sigma Aldrich
Dueterated chloroform	Sigma Aldrich
Polycaprolactone (PCL)	Union Carbide
Polyoxypropylene triamine (Jeffamine-T403)	Hunstman
meta-phenylene diamine (MPDA)	Aldrich

3.2 Surface Modification of natural fibers

Prior to any treatment, non woven hemp mats and jute fabrics were cut into small uniform rectangles of desires sizes. These mats and other chopped fibers were dried in the vacuum oven at the temperature of 80 °C and vacuum pressure of -30 in Hg (-102 kPa) for five hours before any treatment (see Figure 3.2.1). The pre treatment and post treatment steps of these surface treatments are tabulated in Table 3.2.1. All surface treated biofibers were characterized and used for composite fabrication.



Figure 3.2.1: Vacuum oven for drying biofibers

3.2.1 Alkali treatment

A 5% solution of Sodium Hydroxide (NaOH) was made using pellets of NaOH in deionised water (DI) water using a magnetic stirrer. The fibers were placed in this solution for 1 hour at room temperature. Then the fibers were washed with tap water until all alkali was removed from their surface. The fibers were then neutralized in tap water with 2 % glacial acetic acid, and tested for neutralization using pH paper to maintain a pH of 6. This solution was then drained and the fibers were washed with DI water and then stored overnight under the hood followed by vacuum drying.

3.2.2 Acrylonitrile treatment

With DCP as initiator: The required amount of fibers was vacuum dried prior to sizing. The dried fibers were soaked in a solution containing 3.0% acrylonitrile (AN), 0.5% dicumyl peroxide and 96.5 % ethanol for 15 minutes. *With MEKP as initiator:* The fibers were soaked in a premixed solution containing 3.0% acrylonitrile, 0.5% methyl ethyl ketone peroxide and 96.5% ethanol for 15 minutes.

3.2.3 Silane treatment

A 1 % gamma methacryloxy propyl trimethoxy silane (γ -MPS) solution was made in 99% DI water and ethanol (1:1), maintaining the pH of the solution by using 2 % glacial acetic acid .The solution was continuously stirred for two hours in a closed lid plastic container and kept under the hood. The vacuum dried fiber was soaked in this solution, under the hood, for 1 hour. The solution was then drained from the fibers, and kept for curing in an air oven for 5 hours. Fresh solution was made each time this surface treatment was used.

3.2.4 Steam treatment

Fibers were placed in a pressure explosion vessel (PARR) containing hot water, and pressure (90-120 psi) was applied. The fibers were thus steam treated (160-170 0 C, 90-120 psi) for 15 min.

3.2.5 Unsaturated polyester resin treatment

For unsaturated polyester resin (UPE) treatment, fibers were soaked in a premixed solution containing 5% of UPE and MEKP in acetone (UPE: MEKP = 99:1) for 30 minutes.

3.2.6 Maleic anhydride treatment

The fibers were soaked in a premixed solution containing 3.0% maleic anhydride, 0.5% dicumyl peroxide and 96.5% ethanol for 15 minutes.

3.2.7 Methyl methacrylate treatment

Natural fibers were then soaked in a premixed solution containing 3.0% methyl methacrylate, 0.5% dicumyl peroxide and 96.5% ethanol for 15 minutes.

3.2.8 Epoxy treatment

With Jeffamine: A 5% solution of epoxy resin and polyoxypropylene triamine (stoichiometric amounts of epoxy resin and jeffamine were used) was made in acetone with constant stirring using a magnetic stirrer. The fiber mats were placed in this solution at room temperature for 1 hour.

With MPDA: A 5% solution of epoxy resin and meta- phenylene diamine was made (stoichiometric amounts of epoxy resin and MPDA were used) in acetone with constant stirring using a magnetic stirrer. The fiber mats were placed in this solution at room temperature for 1 hour.

3.2.9 Glycidyl methacrylate treatment

The fibers were soaked in a premixed solution containing 3.0% glycidyl methacrylate, 0.5% dicumyl peroxide and 96.5% ethanol for 60 minutes.

Hemp mats 1, and 2, and kenaf fibers were treated with three different concentrations of silane solution to find an optimum silane treatment. In the case of all fibers, 1% solution

of silane (1 % vol silane in 99 % vol solution of ethanol and DI water (50:50)) resulted in highest mechanical properties compared to the other concentrations of silane solutions (0.5 %, 1 %, and 2 %).

Fiber	Surface Treatment			
	Name	Preparation	After treatment- Step1	Post treatment- Step 2
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf,	Alkali (NaOH)	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood.	Vacuum dry at ~80 °C, and -102 kPa for 5 hours
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf,	Acrylonitrile (AN)-DCP	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood.	Vacuum dry at ~80 °C, and -102 kPa for 5 hours
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf,	Acrylonitrile (AN)-MEKP	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood.	Vacuum dry
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf, BBSG, green flax core	Silane(MPS)	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood, followed by curing in air oven.	Vacuum dry
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf,	Silane(APS)	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood, followed by curing in air oven.	Vacuum dry
Non-woven hemp mat-1, kenaf,	Steam	Dry the fibers in vacuum oven for 5 hours	Drain and dry for a day under hood.	Vacuum dry
Non-woven hemp mat-1, non-woven hemp mat-2, kenaf.	UPE-MEKP	Dry the fibers in vacuum oven	Drain and dry for a day under hood.	Vacuum dry

Table 3.2.1: Pre-treatment and post treatment for surface treatments of the natural fibers

Non-woven	hemp	Maleic	Dry the fibers in	Drain and dry	Vacuum dry
mat-1		anhydride	vacuum oven for	for a day	
			5 hours	under hood.	
Non-woven	hemp	Methyl	Dry the fibers in	Drain and dry	Vacuum dry
mat-1		methacrylate	vacuum oven for	for a day	
			5 hours	under hood.	
Non-woven	hemp	Ероху-	Dry the fibers in	Drain and dry	Vacuum dry
mat-1		Jeffamine	vacuum oven for	for a day	
			5 hours	under hood.	
Non-woven	hemp	Epoxy-	Dry the fibers in	Drain and dry	Vacuum dry
mat-1		MPDA	vacuum oven for	for a day	
			5 hours	under hood.	
Non-woven	hemp	Glycidyl	Dry the fibers in	Drain and dry	Vacuum dry
mat-1	-	methacrylate	vacuum oven for	for a day	
			5 hours	under hood	

3.3 Bioresin

Two approached were used for modifying vegetable oils to introduce reactive functional groups in the unsaturated inert backbones of oils like soybean oil, castor oil. In the first approach, a reactive monomer (here acrylonitrile) was grafted on to the oils by using a catalyst. In the second method, soybean polyols were reacted with a reactive monomer, (maleic anhydride), to produce a UPE compatible resin.

3.3.1 Grafting Of MSO, Refined Soybean Oil and Castor Oil

The vegetable oils were grafted with a reactive monomer in an effort to introduce polymerizable groups on the backbone of natural oils. Acrylonitrile was selected as the monomer, and benzoyl peroxide was selected as the initiator. The grafting was done in the following manner:

A three-necked round-bottomed 500 ml flask was kept in the silicone oil bath. The oil bath was placed on a hot plate/stirrer (Corning), and heated by an electric temperature
controller (Corning). The temperature was first set at 100 0 C, and required amount of benzyl peroxide (BPO) with adequate vegetable oil was added to the flask. This solution was continuously mixed with the help of a magnetic stir bar. The mixture was heated for 15 minutes at 100 0 C. It is believed that BPO degrades into free radicals around this temperature. The set point was then changed to 70 0 C (the boiling point of acrylonitrile is 77 0 C). The flask was taken out of the oil bath. When the oil bath reached the desired temperature, required amount of acrylonitrile was added to it. The flask was then lowered into the oil bath. This mixture was heated for 4 hours at 70 0 C. At the end of four hours, the solution was removed from the flask, weighed and stored in a container. The grafting reaction was quantified by using FTIR. The various compositions, parameters, and results of the grafted samples are tabulated in Table 3.3.1.

	BPO content	AN content	Oil content	Oil		Time
Sample	(wt %)	(wt %)	(wt %)	type	Viscosity	(hrs)
ANMSOBP1	0.1	5	94.9	MSO	no change	2
					little	
ANMSOBP2	0.5	10	89.5	MSO	increase	2
ANMSOBP3	0.5	10	89.5	MSO	viscous	3
ANMSOBP4	0.1	5	94.9	MSO	no change	4
ANMSOBP5	0.2	5	94.8	MSO	increased	4
ANMSOBPW1	1	20	79	MSO	solidified	1
					very	
ANMSOBPW2	0.5	10	89.5	MSO	viscous	1
ANCASBP1	0.2	5	94.8	CAS	no change	4
ANSOYBP1	0.5	5	94.5	SOY	no change	4
ANSOYBP2	0.2	5	94.8	SOY	no change	4

Table 3.3.1: Bioresins from grafting of vegetable oils

*MSO=Methyl ester of soybean oil, CAS= Castor Oil, SOY=Refined soybean oil

Development of Bioplastics

Bioplastics are plastic samples made from a bioresin, with or without a synthetic resin, without any reinforcement. The following plastics were made with grafted oils, UPE, MEKP, CoNap, and polybutadiene adducted maleic anhydride (PBMA). PBMA is a liquid rubber, and was added to the bioresin to bring about an ease in phase separation during curing.

Plastic	Grafted oil content	Grafted oil	UPE	РВМА	МЕКР	CoNap
name	(wt %)	used	(wt %)	(wt %)	(wt %)	(wt %)
GFT1	30	ANMSOBP1	70	0	1	0.03
GFT2A	30	ANMSOBP2	70	0	1	0.03
GFT 2B	20	ANMSOBP2	80	0	1	0.03
GFT 2C	20	ANMSOBP2	78	2	1.5	0.03
GFT 4A	20	ANMSOBP4	80	0	1	0.03
GFT 4B	20	ANMSOBP4	78	2	1.5	0.03
GFT 1B	20	ANSOYBP1	80	0	1	0.03
GFT 1A	20	ANSOYBP2	78	2	1.5	0.03
GFT 5B	20	ANMSOBP5	80	0	1	0.03
GFT 5A	20	ANMSOBP5	75	5	1.5	0.03
MSO-		None (pure				
UPE	20	MSO)	75	5	1.5	0.03

Table 3.3.2: Bioplastics obtained from grafted oils

Bioplastic samples were also made with MSO, MEESO, ESO, EML, and ELO. Bioplastics were made by blending the UPE and the functionalized oils and curing them in silicone molds or compression molding. Biocomposites were also made with biofibers and blends of UPE and functionalized oils as matrix by compression molding. The bioplastic samples were characterized by FTIR, DSC, TGA, mechanical and morphological analyses.

3.3.2 Grafting Soybean Oil Phosphate Ester Polyol (SOPEP) with maleic anhydride

The soybean oil phosphate ester polyol (SOPEP) was used as the starting material. The OH content of this polyol is 122 mg of KOH. The polyol was reacted with maleic anhydride in presence of a catalyst, N, N-Dimethylbenzylamine. The solution containing polyol, maleic anhydride and catalyst were heated for some time.

It is expected that during this reaction maleic anhydride will react with OH groups of the polyol, and will result in double bonds in the backbone of the oil. These double bonds can easily be polymerized during curing of the resin.

Three different bioresin products were obtained by the following reactions:

a) *GFTSOPEP1*: 1 mole of pure SOPEP, 0.9 moles of pure maleic anhydride powder and N,N-Dimethylbenzylamine as catalyst (5% of total weight) were reacted together in a round bottomed three necked flask at 80 ^oC for 4 hours. The resulting modified polyol was brown in color and very viscous. The starting material was orange in color and less viscous.

b) *GFTSOPEP2*: 1.0 mole soy polyol + 1.0 mole maleic anhydride + 5.0% by weight catalyst

c) *GFTSOPEP3*: 1.0 mole soy polyol + 0.5 mole maleic anhydride + 5.0% by weight catalyst

As a result of these experiments, the grafted polyol was optimized. The grafted polyols were kept in a vacuum oven for 24 hours at a pressure of -103 kPa to get rid of any unreacted maleic anhydride. There was no change in the FTIR spectra of the grated polyol before and after being exposed to vacuum for 24 hours. This indicated that all maleic anhydride in the reaction vessel had been used.

Development of Bioplastics

Bioplastics comprising of different weight fraction of the grafted soy polyols and UPE resin were made. All plastics were made in small DMA coupons using conventional oven curing. All the samples were cured at standard curing conditions. The samples having grafted oil 30% or greater had to be post cured at $150 \, {}^{0}$ C for 2 hours.

Compositions made were:

a) 50% Grafted Soy Polyol (GFTSOPEP1, GFTSOPEP2, or GFTSOPEP3) + 50% UPE

+ 3.0% MEKP + 0.03% CoNp

b) 40% Grafted Soy Polyol (GFTSOPEP1, GFTSOPEP2, or GFTSOPEP3) + 60% UPE
+ 3.0% MEKP + 0.03% CoNp

c) 30% Grafted Soy Polyol(GFTSOPEP1, GFTSOPEP2, or GFTSOPEP3) + 70% UPE
+ 3.0% MEKP + 0.03% CoN

d) 20% Grafted Soy Polyol(GFTSOPEP1, GFTSOPEP2, or GFTSOPEP3) + 80% UPE
+ 3.0% MEKP + 0.03% CoNp

e) 10% Grafted Soy Polyol (GFTSOPEP1, GFTSOPEP2, or GFTSOPEP3) + 90% UPE
+ 3.0% MEKP + 0.03% CoNp

The samples made with 30%, 40% and 50% of GFTSOPEP2 had inferior properties. Biocomposites were also made with biofibers and blends of UPE and functionalized oils as matrix by compression molding. The pure polyol was characterized using DSC, TGA and FTIR. The pure maleic anhydride and modified polyol were also scanned under FTIR. The bioplastic samples were characterized by FTIR, DSC, TGA, mechanical and morphological analyses.

3.4 Fabrication of composites

Composites and plastics were made by either conventional curing in an oven, compression molding, sheet molding compounding, or vacuum assisted resin transfer molding.

3.4.1 Silicone Molds

Aligned Fibers: For aligned fiber composites, combed unidirectional kenaf fibers were used. The biocomposites were made in coupons. In this study, composites with 30 vol. % fibers content were used for making the biocomposites. The fabrication of the composite was done in the following way. The UPE was mixed well with the initiator MEKP and the promoter CoNap in required amounts and then degassed at room temperature for 2 minutes. The fibers were laid out on silicone molds after weighing. The resin was poured under and over them; another mold was kept over this mold leaving enough space for air bubbles to move out. Some heavy weights (3-5 lbs) were put over it, and it was oven cured at 100 0 C for 2hours, followed by 150 0 C for 2 hours.

UPE Control: For making the control panel from neat resin, degassed UPE solution was poured over degassed silicone molds and cured in a conventional oven using the same temperature profile.

Bioplastics: Derivitized vegetable oils were mechanically blended with UPE in the ratio of 10%, 20%, 30%, 40%, or 50% functionalized oil, and 90%, 80%, 70%, 60%, or 50% UPE, respectively by weight. Bioplastics were made by blending the UPE, the functionalized oils and the curing agents (MEKP and CoNap), followed by curing them in silicone molds in a conventional oven with the standard curing conditions. Five percent by weight of PBMA was added to one of the blends of MESO and UPE. The resulting plastics were cut into required shapes for various tests. Table 3.4.1 shows different plastics and composites made using silicone molds.



Figure 3.4.1: Conventional oven for curing silicone molds

Table 3.4.1: Samples made using s	ilicone molds
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Sample			Composition	1	
	Fiber	UPE	Vegetable Oil	Initiator	Promoter
UPE Control	0	99.7 % wt	0	1.0 % wt	0.03% wt
Aligned fiber					
Water washed kenaf- UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
Alkali treated kenaf- UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
AN-DCP treated kenaf- UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
UPE-MEKP treated kenaf-UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
Silane treated kenaf- UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
Untreated kenaf- Bioresin-UPE	30 % vol	50 % vol	20 % vol	1.5 % wt	0.03% wt
E-glass-UPE	30 % vol	70 % vol	0	1.0 % wt	0.03% wt
Bioplastics*					

Table 3.4.1 (continued)

UPE-MSO	90, 80	10, 20	1.5 %	0.03% wt
			wt	
UPE-MSO-MA	90, 80	10,20	1.5 %	0.03% wt
			wt	
	80	20 (5%	1.5 %	0.03% wt
MEESO-PBMA		PBMA)	wt	
	80	20	1.5 %	0.03% wt
ESO-UPE			wt	
	80	20	1.5 %	0.03% wt
EML-UPE			wt	

*Grafted bioresins-UPE have already been discussed in section 3.3.

3.4.2 Compression Molding

For Mats: The required amounts of fiber mats were vacuum dried for 5 hours. The polyester resin (UPE) was mixed well with MEKP and CoNap, in required amounts and then degassed under vacuum at room temperature for 2 minutes. The fiber mats were individually coated with the degassed resin. They were then placed between two aluminum plates covered with teflon release sheets. The plates were placed in a compression molding press (Carver \circledast Laboratory Press) and the composites were cured at 80 psi for 2 hours at 100° C followed by 2 hours at 150° C.

For chopped fibers: The polyester resin (UPE) was mixed well with the initiator, methyl ethyl ketone peroxide (MEKP) and the accelerator, cobalt naphthenate (CoNp), in required amounts and then degassed under vacuum at room temperature for 2 minutes. The fibers were mixed nicely with the degassed resin by hand. Uniform resin distribution in the entire fiber mass was ensured. This fiber-resin mixture was then placed in a picture frame mold which was kept between two aluminum plates covered with teflon release sheets. The plates were placed in a compression molding press (Carver ® Laboratory

Press) and composites were cured at 80 psi for 2 hours at 100° C followed by 2 hours at 150° C. The biocomposite using untreated fiber mats was made in same way. The resulting composite plaques were cut into required shapes for various tests. *Bioplastics:* Derivitized vegetable oils were mechanically blended with UPE in the ratio of 10%, 20%, 30%, 40%, or 50% functionalized oil, and 90%, 80%, 70%, 60%, or 50% UPE, respectively by weight. Bioplastics were made by blending the UPE, the functionalized oils and the curing agents (MEKP and CoNap), followed by curing them in silicone molds in a conventional oven with the standard curing conditions. The resulting plastics were cut into required shapes for various tests. Figure 3.4.2 shows a four platen Carver lab press. The samples made with compression molding are described in Table 3.4.2 and some are shown in Figure 3.4.3.



Figure 3.4.2: Carver compression Press

Sample		Co	mpositio	n	
_	Fiber	UPE	Natural	Initiator	Promoter
			Oil	(wt %)	(wt %)
Non woven mats					
Untreated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Alkali treated hempmat1- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
AN-DCP treated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
UPE-MEKP treated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Silane treated hempmat1- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Untreated hempmat1- Acrylonitrile(5%) in UPE	30 % vol	65 % vol 5% AN	0	1.0 %	0.03%
MA treated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
MMA treated hempmat1- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
EPON-MPDA treated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
EPON-T403 treated hempmat1-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
GMA treated hempmat1- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Steam treated hempmat1- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Untreated hempmat1- Bioresin-UPE	30 % vol	50 % vol	20 %	2.0 %	0.03%
Untreated hempmat1- Bioresin-UPE	30 % vol	40 % vol	30 %	2.0 %	0.03%
Untreated hempmat1-E- glass mat-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Pure hemp mat-(hempma	t2)				
Untreated pure hempmat2- UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Alkali treated pure hempmat2-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
AN-DCP treated pure hempmat2-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
UPE-MEKP treated pure hempmat2-UPE	30 % vol	70 % vol	0	1.0 %	0.03%
Silane treated pure hempmat2-UPE	30 % vol	70 % vol	0	1.0 %	0.03%

Table 3.4.2: Samples made using compression molding

Untreated hempmat2-	30 % vol	50 % vol	20 %	2.0%	0.03%
Bioresin-LIPE	50 /0 /01	30 /0 /01	20 /0	2.0 /0	0.05/0
Bioresin-OTE	20.0/ 1	40.04	20.0/	2 0 0 (0.000/
Untreated hempmat2-	30 % vol	40 % vol	30 %	2.0 %	0.03%
Bioresin-UPE					
Untreated hempmat1-E-	30 % vol	70 % vol	0	1.0 %	0.03%
glass mat-UPE					
E-glass mat-UPE	30 % wt	70 % wt	0	1.0 %	0.03%
E-glass mat-Bioresin-UPE	30 % wt	50 % wt	20 %	2.0 %	0.03%
E-glass mat-Bioresin-UPE	30 % wt	40 % wt	30 %	2.0 %	0.03%
Chopped fibers					
Hemp-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
Kenaf-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
Henequen-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
BBSG-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
Green flax core-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
Coir-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
Indian grass-UPE	35 % wt	65 % wt	0	1.0 %	0.03%
E-glass-UPE	30 % wt	70 % wt	0	1.0 %	0.03%

Table 3.4.2 (continued)

*Bioplastics have already been discussed in section 3.3



Figure 3.4.3: Picture of bioplastic samples made using compression molding

(a)= Henequen-UPE, (b)=Kenaf-UPE, (c)=Green hemp-UPE, (d)=Coir-UPE, (e)=E-Glass-Bioresin-UPE, (f)=E-Glass-UPE-CaCO3, (g)= Hempmat1 (Bastmat 115)-E-Glass-UPE, (h)= Hempmat1(pure hemp mat)-E-Glass-UPE

3.4.3 Sheet molding compound panel processing

A new process for large-scale production of biocomposites containing thermoset resins and natural fibers was designed. The equipment used for this processing is the common industrial SMC line. Currently, natural fibers reinforced thermoset composites are not prepared using SMC. We aim to use SMC process to fabricate these natural fiberthermoset composites. In commercial SMC set-up, continuous glass fibers rovings are fed to a chopper, which cuts them to a 6 mm size, and they fall on the carrier film, forming a uniform layer of chopped glass fibers. Since, natural fibers cannot be obtained in a continuous from, and making a continuous yarn or roving with these fibers would be a difficult and expensive, chopped natural fibers were used in this new process. The chopped natural fibers are dried for 3-4 hours to remove any ambient moisture, and then fed to a calibrated vibratory feeder. The fibers are first fed into a screw feeder, which delivers these fibers to the vibratory feeder; from which they fall onto the carrier film at a constant flow rate.

The resin formulation was prepared in a Ross mixture. The Ross mixer was connected to cooling water. The polyester and calcium carbonate were combined and mixed for 10 minutes. The Cobalt Naphthanate was added and mixed for 5 minutes. Finally the MEKP was added and mixed for 5 minutes. The Ross mixing pot-cooling water was shut off and disconnected. Resin was transferred into a 3.5 gal epoxy coated steel storage container. The Ross mixer was then cleaned several times with acetone.

The twin-screw feeder and vibratory feeder were turned on. The SMC line was turned on shortly before the upper and lower resin pots were filled and was run at an optimum speed. The process was allowed to run to see what the product looked like after the compaction rollers. The product appears uniform in thickness and the fiber distribution in the product appears even. Several feet of product are produced at these settings.

The finished product was cut into 1 ft long segments and was placed flat in sealed polyethylene container. This container was labeled with the date and time and is immediately put into a freezer for storage. Gel time of the resin formulation was observed to be approximately 2 hr 30 min.

Various process parameters, for example, line speed, cutter pressure, idler roll pressure, wipe blade gap height upper, wipe blade gap height lower, compaction roller pressure, compaction roller gap, grip assembly, twin screw feeder, etc. were adjusted and optimized for natural fibers. The prepregs from SMC line were matured for desired time and then compression molded. The molded samples were tested for various mechanical, and thermal properties, in accordance with ASTM procedures.

Batch to batch repeatability was established after running numerous experiments with glass fibers and base resin, and adjusting all of the parameters.

The new SMC processing for natural fibers can be done on normal commercial SMC equipment with a minor change on the way fibers are fed to the line. In industrial SMC set-ups, the glass fibers rovings are fed to a chopper, and chopped fibers fall onto the carrier film. But the natural fibers are not supplied as continous rovings or yarns, and must be fed to the film in a chopped form. Therefore, in the new set –up, the chopped fibers fall from a calibrated vibratory feeder onto the carrier film, and get drenched in

resin flowing from two resin pots, and advance to the compression rollers, and finished product is obtained at the end of the line. The prepreg from SMC line is refrigerated for certain time to reach desirable gelation. The gelled product is then compression molded in variety of molds to get the desired shape.

SMC Line description

Figure 3.4.4 shows the schematic of the proposed invention. The process begins with an upper and lower supply roll of carrier film material. The upper and lower carrier film is



Figure 3.4.4: Scheme of BCSMCP process

fed beneath the upper and lower resin pots respectively, which deposits a pre-determined thickness of resin onto the carrier film by means of adjustable height wipe blades. The lower carrier sheet then passes beneath the bio-fiber vibratory feeder, which deposits a calibrated weight % of bio-fiber uniformly onto the surface of the resin. The upper and lower carrier sheets are then brought together creating a sandwiched SMC sheet material. The sheet material is then fed through compaction rollers to help provide a uniform sheet cross section and to also to provide some mixing forces to ensure the even distribution of fiber in the resin. Grip wheels near the end of the line provide the necessary mechanical force to pull the sheet material through the system at a controlled rate. The sheet material is then cut to the desired length.

Feeder Description

The biofiber feeder system consists of four main components (see Figure 3.4.5):

- 1.) The material feed hopper
- 2.) The twin screw feeder
- 3.) The fiber distribution feed chute
- 4.) The vibratory feeder

Biofiber is put in the hopper for feeding. The fiber is then fed onto the fiber distribution feed chute by the twin-screw feeder, which is calibrated to output the required fiber weight/minute. The fiber distribution chute spreads the fiber out uniformly from the width of the twin feeding screws to the width of the vibratory feeder. The vibratory feeder then conveys the fiber to the opening at the end of the feeder tray providing the uniform distribution of fiber onto the SMC sheet.

This new processing has been used to make various biocomposite samples with different composition and weight fraction of natural fibers and polyester resin. The process has been optimized for natural fibers after many experimentations and repetitions. We have already established this process with glass fibers, polyester sized glass fibers, big blue stem grass fibers, silane sized big bluestem grass fibers and hemp fibers. So far, we have used unsaturated polyester resin, calcium carbonate, methyl ethyl ketone peroxide and cobalt naphthenate in the matrix for these composites. We have achieved very promising results from these experiments.



Figure 3.4.5: Scheme of vibratory feeder and screw feeder

Experiments with Glass fibers:

Experiments were done with glass fibers to ensure that the composites developed using SMC process had consistent properties. An unsaturated polyester resin compatible glass roving, called Owens Corning 985, was used for making composites. Other glass fibers like Owens Corning 485, and other sized glass fibers were not compatible with polyester resin. The major goal of the run was to produce .188 thick SMC using Owens Corning 985 E-glass and then to compression mold the resultant sheet material. The resulting

glass composites were of the following composition: glass fibers 30 wt %, CaCO₃ 42 wt

%, and UPE 28 wt %

The runs were conducted using the following parameters:

Line speed - Dial setting of 1.5/.3 in/sec

Glass cutter - Dial setting of 3.2/approx. 223 g/min (31% by weight)

Four tows were fed into the glass cutter to improve glass distribution

Cutter Pressure – 40 psi

Idler roll pressure - 56 psi

Wipe blade gap height upper - .060"

Wipe blade gap height lower - .060"

Compaction roller pressure – 30 psi

Compaction rollers shimmed to ensure a minimum .250 gap

Upper carrier sheet roller shimmed to a gap of .265

Upper resin tray assembly shimmed up .500

Grip assembly used with slight preload on roller for friction

Procedure

A total of 8971.3 g of resin was mixed shortly before the SMC run using the following formulation:

40% Unsaturated Polyester Resin- 3580.92 g60% Calcium Carbonate Filler- 5371.38 g.03% Cobalt Naphthanate Promoter- 1.074 g.5% MEKP- 17.90 g

The Ross mixer speed dial was set to 5.0. Cooling water to the mixing pot was connected and turned on. The polyester and calcium carbonate were combined and mixed for 10 minutes. The Cobalt Naphthanate was added and mixed for 5 minutes. Finally the MEKP was added and mixed for 5 minutes.

The Ross mixing pot cooling water was shut off and disconnected. Resin was transferred into a 3.5 gal epoxy coated steel storage container. The Ross mixer was then cleaned several times with acetone using blue WypAll Plus all-purpose wipes.

The SMC line was turned on shortly before the upper and lower resin pots were filled and was run at a speed of .3 in/sec. The glass cutter was then turned on. The process was allowed to run to see what the product looked like after the compaction rollers. The product appeared uniform in thickness and the glass distribution in the product appeared even. Several feet of product were produced at these settings.

From the point where the MEKP was introduced into the resin, a total time of approximately 45 minutes elapsed including cleanup time. The finished product was cut into 1 ft long segments and was placed flat in sealed polyethylene container. This container was labeled with the date and time and was immediately put into a freezer for storage. Gel time of the resin formulation was observed to be approximately 2 hr 30 min. After the prepreg was properly frozen, it was compression molded in the Carver Press. The prepregs was placed in a picture frame mold, and placed between two aluminum plates, lined with Teflon sheets. This sample was cured at around 80 psi for 2 hours at 100° C followed by 2 hours at 150° C. The resulting composite is cut into desired shapes for various tests.

For making the control sample, a degassed UPE solution is poured into degassed silicone molds and cured in a conventional oven at the same curing conditions.

Glass fiber composites were fabricated using SMC until consistent materials with same mechanical properties were obtained. The parameters mentioned for this particular run were obtained after optimization. Data from two SMC runs with glass fibers, after all optimizations are discussed in the upcoming section. Biocomposites with natural fibers were fabricated after success with glass composites.

Experiments with natural fibers:

Experiments were done to produce biocomposites using the SMC line. The major goal of these runs was to produce sheet material using natural fibers as the reinforcement.

The natural fibers were vacuum dried overnight at 80 ^o C and -102 kPa, before being used in the biocomposite fabrication. Some composites were made with untreated fibers as such, and some were made with chemically treated fibers. In particular, silane treatment was used on big blue stem grass and green flax core. The silane treatment of these fibers was done in the following way:

A 1 % methacryloxypropyltrimethoxy silane (γ -MPS) solution was made in 99% DI water and Ethanol (1:1), maintaining the pH of the solution at 4.0 by using 2 % Glacial Acetic Acid .The silane solution was hydrolyzed for 2 hours by continuously stirring using a magnetic stir bar. The fibers were soaked in this solution for 1 hour .The solution was then drained from the fibers, and theyr were dried under the hood for at least one day. They were then cured in an air oven for 5 hours at 80 $^{\circ}$ C. The fibers were then dried in a vacuum oven at 80 $^{\circ}$ C and - 30 in Hg.

When two fibers were used for making hybrid biocomposites, the fibers were mixed well by continuous agitation, and the resulting uniform mixture was vacuum dried before using to make biocomposites.

The natural fibers also had to be introduced in to the SMC line in a different way as compared to glass fibers. They were fed by a combination of twin screw feeder and vibratory feeder. This way of fiber introduction was optimized after various attempts with vibratory feeding.

The resulting biocomposites contained 20 wt % fiber, 30 wt % CaCO₃, and 60 wt % UPE. This composition is different from that of glass composites discussed earlier, because, natural fibers have a tendency to soak up resin. As the natural fibers are hollow, when they are mixed with resin, they absorb resin in their interstitial paces. An experiment was done to measure the amount of resin absorbed by big blue stem fiber. It was found that 1 gram of fiber absorbed 1.85 grams of resin (average of three readings). The experimental runs were conducted using the following parameters:

- Line speed Dial setting of 1.5 (.3 in/sec)=(18 in/min)
- K-tron twin screw feeder Hi gear with a digital readout setting of 550 RPM
- Vibratory feeder dial setting 100%
- Feeders calibrated to approximately 101g/min. (20% fiber content) over the 12" wide resin coverage area
- A modified fiber spreading dispersion tray was used to spread fibers to the vibratory feeder 18" width
- Wipe blade gap height upper .050"
- Wipe blade gap height lower .050"

- Compaction roller pressure/Open Position 30 psi
- Compaction rollers shimmed to ensure a minimum .250 gap
- Upper carrier sheet roller shimmed to a gap of .265
- Upper resin tray assembly shimmed up .500
- Grip assembly used with slight preload on roller for friction
- Big Blue Stem Grass fiber and Flax fiber was dried for approximately 16 hrs in a vacuum oven at approximately 80 °C before run.

Procedure

A total of 6560g of resin was mixed shortly before the SMC run using the following formulation:

60% Unsaturated Polyester Resin	- 5182.76 g
30% Calcium Carbonate Filler	- 1350.00 g
.03% Cobalt Naphthanate Promoter	- 1.56 g
.5% MEKP	- 26.06 g

The Ross mixer speed dial was set to 5.0. Cooling water to the mixing pot was connected and turned on. The polyester and calcium carbonate were combined and mixed for 10 minutes. The Cobalt Naphthanate was added and mixed for 5 minutes. Finally the MEKP was added and mixed for 5 minutes.

The Ross mixing pot cooling water was shut off and disconnected. Resin was transferred into a 3.5 gal epoxy coated steel storage container. The Ross mixer was then cleaned several times with acetone using blue WypAll Plus all-purpose wipes.

The SMC line was turned on shortly before the upper and lower resin pots were filled and was run at a speed of .3 in/sec. Resin was then transferred to the resin pots. The K-tron

twin screw feeder and vibratory feeder were then turned on. The process was allowed to run to see what the product looked like after the compaction rollers. The sheet material looked very good. The modified feeder setup distributed fiber evenly and consistently. Several feet of product was produced at these settings.

The resultant sheet material looked very good. Fiber dispersion uniformity from the modified dispersion tray setup was good, but could be better if the house air pressure could steadily supply more air pressure. The pneumatic rotary vibratory feeder on the dispersion tray was set to 75 psi, but the house air supply had trouble keeping up pressure after a period of time. A drop in pressure was not observed until the run was complete. 90 psi provided the best fiber distribution but was not sustainable for than a minute or so.

The finished product was cut into 1 ft long segments and was placed flat in a sealed polyethylene container. This container was labeled with the date and time and was immediately put into a freezer for storage. After cooling in the freezer for several hours, the sheet material was compression molded in the Carver press for mechanical testing.

Figures 3.4.6, 3.4.7 and 3.4.8 show the various aspects of BCSMCP processing technique. In Figure 3.4.6, the mixing of resin components can be seen. In Figure 3.4.7, the entire SMC processing of biocomposites is highlighted. In Figure 3.4.8, the method for natural fiber feeding to the SMC line is shown.

Figures 3.4.9, 3.4.10, 3.4.11 and 3.4.12 showcase different composite samples made using SMC line.



a) Weighing CaCO3 and UPE



b) CaCO3 and UPE mixed in Ross mixer





c) After mixing initiator and promoter d) All resin components mixed in the Ross mixer **Figure 3.4.6:** Mixing of resin components in the Ross mixer

The different biocomposites made using BCSMCP processing were of the following compositions:

line
SMC
using
made
Samples
3.4.3:
Table.

Sample	Fiber 1	Fiber 2	Fiber 1 wt%	Fiber 2 wt %	CaCO3 wt %	UPE wt%	Bioresin wt%	TOTAL %
A	Untreated BBSG		20		20	60	0	100
В	Silane treated BBSG		20		20	60	0	100
с С	Untreated BBSG	Untreated green flax core	8	12	20	60	0	100
٥	Silane treated BBSG	Silane treated green flax core	8	12	20	09	0	100
ш	Untreated green flax core		20		20	60	0	100
ш	Untreated hemp	Untreated jute mat	18	2	20	55	0	100
თ	Untreated hemp	Untreated jute mat	13	2	20	60	0	100
н	Untreated hemp	E-glass mat	12	8	20	60	0	100
	E-glass		20		20	60	0	100
ſ	E-glass mat		30		0	50	20	100
X	Untreated hemp		35		0	65	0	100
	Untreated henequen		35		0	65	0	100
Μ	Untreated kenaf		35		0	65	0	100
Z	Untreated hemp	Untreated henequen	25	10	0	65	0	100
0	Untreated kenaf	Untreated henequen	25	10	0	65	0	100
Р	Untreated hemp	Untreated henequen	20	10	0	50	20	100

*BBSG = Big blue stem grass



a) Resin poured in resin pot 1

b) Resin pot1 and vibratory feeder



c) Fibers falling from feeder

d) Uniform sheet of fibers



- e) Resin flowing down from pot 2
- f) Fibers being sandwiched between resin



g) Pre-preg moving towards rollers

h) Sheet of pre-preg coming out



i) Sheet coming from last of compaction rollers j) Sheet falling down the floor



k) Pre-preg after the SMC line

l) sheet being cut to 1 ft long pieces



m) Rectangular pieces of pre-preg

n) pre-preg ready to be stored in freezer





Figure 3.4.8: Feeding natural fibers though a vibratory feeder

The chopped natural fibers were dried for 3-4 hours to remove any ambient moisture, and then fed to a calibrated vibratory feeder. The fibers were first fed into a screw feeder, which delivers these fibers to the vibratory feeder; from which they fell onto the carrier film at a constant flow rate.

The resin formulation was prepared in a Ross mixture. The Ross mixer was connected to cooling water. The polyester and calcium carbonate were combined and mixed for 10 minutes. The Cobalt Naphthanate was added and mixed for 5 minutes. Finally the MEKP was added and mixed for 5 minutes. The Ross mixing pot-cooling water was shut off and disconnected. Resin was transferred into a 3.5 gallon epoxy coated steel storage container. The Ross mixer was then cleaned several times with acetone.

The twin-screw feeder and vibratory feeder were turned on. The SMC line was turned on shortly before the upper and lower resin pots were filled and was run at an optimum speed. The process was allowed to run to see what the product looked like after the compaction rollers. The product appeared uniform in thickness and the fiber distribution in the product appeared even. Several feet of product were produced at these settings.

The finished product was cut into 1 feet long segments and was placed flat in sealed polyethylene container. This container was labeled with the date and time and was immediately put into a freezer for storage. Gel time of the resin formulation was observed to be approximately 2 hours and 30 minutes.

Various process parameters, for example, line speed, cutter pressure, idler roll pressure, wipe blade gap height upper, wipe blade gap height lower, compaction roller pressure, compaction roller gap, grip assembly, twin screw feeder, etc. were adjusted and optimized for natural fibers. The prepregs from SMC line were matured for desired time

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and then compression molded. The molded samples were tested for various mechanical and thermal properties, in accordance with ASTM procedures. Batch to batch repeatability was established after running numerous experiments with glass fibers and base resin, and adjusting all of the parameters.



Figure 3.4.9: An E-Glass-CaCO₃-UPE composite



Untreated big blue stem grass (BBSG) - UPE bio-composite



Untreated green flax core-UPE biocomposite



30 weight % % calcium carbonate (CaCO₃)-70 wt% UPE

Untreated BBSG -Flax-CaCO₃-UPE Bio-composite

Figure 3.4.10: Composite samples made using SMC line



18 % Hemp 7% Jute mats 20%CaCO3 55%UPE

20% Hemp 10% Henequen 20% Bioresin 50%UPE

Figure 3.4.11: Composite samples made using SMC line



30 volume % hempmat1-20 volume % bioresin (from modified polyol)-50 volum % UPE



30 volume % hempmat1-30 volume % bioresin (from modified polyol)-40 volume % UPE



Untreated BBSG -Flax-UPE composite



Untreated BBSG -CaCO3-UPE biocomposite



Hybrid biocomposite of 25% Kenaf and 10% Henequen



Hybrid biocomposite of 25% Hemp and 10% Henequen

Figure 3.4.12: Composite samples made using SMC line

The biocomposite and composites samples made suing SMC were characterized by mechanical, thermal, and morphological tests.

3.4.4 Biobeams and bioplates

The work on bioplates and biobeams was done in collaboration with Mario Quagliata, and Dr. Rigoberto Burgueño of the Department of Civil and Environmental Engineering. More details on this part of the work can be obtained from Mario's M.S. thesis, "Development and Characterization of Biocomposite Cellular Beams and Plates for Load-Bearing Components", Masters Thesis, Michigan State University, East Lansing, MI; 2003. A brief description of this work is presented in the literature review.

3.5 Testing

To evaluate thermal, mechanical, morphological, physical and chemical nature of the systems under study, various kinds of tests are carried on. Some tests are specifically done on fibers, and some on composites and plastics. All tests methods comply with relevant standards such as ASTM (American Society of Testing Methods) standards.

3.5.1 Natural fiber

The fibers were characterized using Fourier Transform Infra Red Spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Environmental Scanning Electron Microscopy (ESEM) and X-Ray Photo Spectroscopy (XPS).

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3.5.1.1 Thermogravimetric analysis (TGA)

The thermal behavior of the surface modified fibers was measured using thermogravimetric analyzer (Hi-Res TGA 2950, TA instruments, USA). TGA measures the mass change of a sample as a function of temperature. The TGA measuring cell may be used for making content determinations, or to characterize phenomena such as evaporation and drying, decomposition, oxidation, and oxidative stability.



Figure 3.5.1: Hi-Res TGA 2950 (TA instruments) in CMSC lab

The data from TGA in is the form of plots showing variation of sample weight and derivative weight with temperature. The fibers to be analyzed were finely chopped fibers and then kept in an Aluminum pan which goes inside the furnace. It was programmed to go from room temperature to 600 ⁰C at the rate of 20 ⁰C per minute. The weight of the fibers used for analysis ranged from 7-19 mg. Dry nitrogen gas was circulated within the test cell at a flow rate of 60 cc/min.

3.5.1.2 Fourier Transform Infra Red Spectroscopy (FTIR)

Fourier transform infra red spectroscopy (FTIR) was used for characterizing the constituent functional groups in the fiber. The fibers were finely chopped into small particles. These chopped fibers and potassium bromide (KBr) were placed in a mortar in

the ration of 1:5. The solids were ground to make a homogeneous mixture using a pestle. Approximately 200 mg of mixture was equally distributed in a pellet press. A pressure of 8000 psi was applied to the press for 5 minutes. The pellet of KBr and fiber was removed from the press and scanned in a Perkin Elmer spectrum 2000 FT-IR.



Figure 3.5.2: Perkin Elmer spectrum 2000 FT-IR in CMSC lab

3.5.1.3 X-Ray Photo Spectroscopy (XPS)

In X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), X-rays excite photoelectrons, and the emitted electron signal is plotted as a spectrum of binding energies. Differing chemical states resulting from compound formation are reflected in the photoelectron peak positions and shapes. Spectral information is collected from a depth of 2-20 atomic layers, depending on the material studied. The XPS technique involves the bombardment of a sample surface with X-rays and the measurement of the concomitant photoemitted electrons. The photoemitted electrons have discrete kinetic energies that are characteristic of the emitting atoms and their bonding states. XPS goes beyond elemental analysis to provide chemical information. It can distinguish chemical arrangements such as silicon-to-silicon bonds from silicon-to-oxygen bonds. The strength of XPS is its ability to identify different chemical states. This ability is useful in a range of physical studies, for example, oxidation/corrosion products, adsorbed species, and thin-film growth processes. Applications of XPS include:

1) Chemical-state analysis: Evaluates valence states, bonding environments, and the molecular composition of surface layers.

2) Elemental analysis: Identifies elements from lithium to uranium, with detection levels down to 0.5 at. %.

3) Imaging: Uses raster scanning to produce images with a spatial resolution of 26 μm.
4) Depth profiling: By sputtering material from a surface, generates compositional depth profiles for materials up to 1 μm thick

5) Thin-films: Frequently used for the analysis of surfaces of thin-film materials.
6) Polymers: Especially valuable for analyzing functional groups in polymers and other organic materials. (Particularly useful in this regard when used as a complementary tool with static SIMS analysis)

7) Catalysts: Evaluates the surface of catalysts to determine reactive species.8) Other materials: Valuable for chemical-state analysis of materials ranging from metals to insulators to semiconductors


Figure 3.5.3: PHI 5400 ESCA (XPS) system in CMSC lab

The X-ray photoelectron spectra (XPS) of the untreated and surface treated fibers were determined by Per Askeland (PHI 5400 ESCA system). A non-monochromatic Mg source was used with a take-off angle of 45 degrees. Fiber samples were carefully cut and affixed to a stainless steel sample holder by a molybdenum mask. Relative atomic concentrations were determined by measuring the area under an element's spectral envelope and applying the appropriate correction factor.

XPS is an information rich method. The surface to be analyzed is first placed in a vacuum environment and then irradiated with photons. For XPS, the photon source is in the X-ray energy range. The atoms comprising surface emit electrons (photoelectrons) after direct transfer of energy from the photon to the core-level electron.

These emitted electrons are subsequently separated according to energy and counted. The energy of the photoelectron is related to the atomic and molecular environment from which they originated. The number of the electrons emitted is related to the concentration of the emitting atom in the sample. The most basic XPS analysis of a surface will provide qualitative information on all the elements present (except H and He). More sophisticated application of the method such as curve fitting can yield much detailed information about the chemistry, organization, and morphology of a surface. The probe depth is less than 10nm so this method is very surface sensitive and is a great tool to characterize the functional groups on the cellulose fiber surface.

Chemical information indicating changes in the treated fiber surface was elucidated by curve fitting the carbon 1s (C1s) and oxygen 1s (O1s) spectra. The C1s and O1s curves were fitted with a Lorentzian-Gaussian mix Voigt profile using a nonlinear least-squares curve-fitting program. The resulting curve fit has a level of experimental error around 5-10%. All peaks are referenced to adventitious carbon at 284.6 eV.

3.5.1.4 Differential Scanning Calorimetry (DSC)

Thermal scans of untreated and surface treated fiber samples were done using Differential Scanning Calorimetry (TA 2920 Modulated DSC, TA instruments, USA). DSC is used for finding the variation of heat with temperature, which helps to get glass transition temperature (T_g), degradation temperature, crystallization temperature, melting temperature, heat of reaction etc. Differential scanning calorimetry is a technique used to study the thermal transitions of a polymer. Thermal transitions are the changes that take place in a polymer when it is heated. The fibers were finely chopped and then placed in an aluminum pan and weighed. The sample pan along with a reference aluminum pan was kept inside the furnace. The DSC furnace was programmed to go from -60 $^{\circ}C$ to 300

 ${}^{0}C$ at 10 ${}^{0}C$ per minute. The data from DSC is in the form of plots of heat flow with respect to temperature.



Figure 3.5.4: TA 2920 Modulated DSC (TA instruments) in CMSC lab

3.5.1.5 Environmental Scanning Electron Microscopy (ESEM)

The morphology of the untreated and surface treated fibers was investigated using Environmental Scanning Electron Microscopy (ESEM). The ESEM used for this work was manufactured by Electroscan Corporation (ESEM Model no. 2020). It is equipped with a Lanthium Hexaboride filament. Water vapor acts as the imaging gas. The fiber samples to be examined were mounted on an aluminum stub using an adhesive, and placed in the sample chamber. The imaging pressure (Chamber pressure) was set between 2-3 Torr. The working distance between the detector and the sample was set between 8– 10 mm. The accelerating voltage was set to 20 kV. The scan time was 2.1 seconds, the condenser was set to 40% and the filament was heated to 1.86 A. The sample was focused at different points in its area, and micrograph pictures were taken at different magnifications.



Figure 3.5.5: Sputter coater (left) and ESEM (right) Model no. 2020 at CMSC lab

3.5.2 Bioplastics and biocomposites

The plastics and composites are characterized using Fourier Transform Infra Red Spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), thermo-mechanical analysis (TMA), Environmental Scanning Electron Microscopy (ESEM), impact, flexural, tensile, moisture absorption, weatherability, and flammability tests.

3.5.2.1 Thermogravimetric analysis (TGA)

The thermal behavior of the polyester resin and modified resin was measured using thermogravimetric analyzer (Hi-Res TGA 2950, TA instruments, USA). The samples to be analyzed were either liquid or solid. A drop of liquid sample or a small piese of solid samole were placed on tared aluminum pan. The sample went inside the TGA furnace. It was programmed to go from room temperature to 600 °C at the rate of 20 °C per minute. The weight of the samples used for analysis ranged from 10-30 mg. Dry nitrogen gas was circulated within the test cell at a flow rate of 60 cc/min.

3.5.2.2 Differential Scanning Calorimetry (DSC)

To study the curing characteristics of the thermoset polyester resin, blends of polyester with initiator methyl ethyl ketone peroxide and promoter cobalt naphthenate were scanned in DSC (TA 2920 Modulated DSC).

In order to obtain heat flow curves for curing characterization, all experiments must be done under isothermal conditions. The DSC cell should be allowed to stabilize at each isothermal condition before introduction of the sample. Once an isothermal experiment is over, the DSC must be cooled quickly to room temperature, and when stabilized, the residual heat of reaction of the sample is measured with a constant heating rate until no exotherm is observed. When using DSC for isothermal curing of thermoset resins, it is assumed that the amount of heat generated is proportional to degree of cure, α (or the extent of reaction) of the sample at that time. So, the rate of curing, d α /dt, may be related to rate at which heat is evolved, dQ/dt, by:

$$d\alpha/dt = (1/Q_{tot})(dQ/dt)$$
 -(1)

Therefore the relative degree of cure is determined by integrating equation (1) from 0 to t:

$$\alpha = (1/Q_{\text{tot}})_0 \int^t (dQ/dt)_T dt \qquad -(2)$$

The total heat for curing reaction (Q_{tot}) is given by:

$$Q_{tot} = Q_{iso} + Q_r$$

Where Q_{iso} is the heat generated during isothermal DSC runs at each temperature, and Q_r is the residual heat released when the sample is heated up to a high temperature (200^oC) at a constant heating rate. But, it is also important to run one sample from room temperature to a high temperature (200^oC) to see where the exotherm peak appears on the heat flow curve. This curve will also give Qr.

A reference Aluminum pan and a weighed sample pan were kept inside the furnace, which was programmed specifically according to the nature of the experiment. Heat flow was kept constant at 5 $^{\circ}$ C / min in all runs.

3.5.2.3 Dynamical Mechanical Analysis (DMA)

Dynamical Mechanical Analyzer measured the storage modulus, loss modulus and tan Delta. The DMA apparatus is a TA DMA 2890 model, and the measurement was done at the frequency of 1 Hz with a heating constant rate of 4 °C /min (cpm). Rectangular bars, 50mm X 12 mm X 3 mm were placed on the 3 point bending fixture in the furnace and heated from room temperature to 150 °C. A minimum of three specimens of each composition were tested.

The heat deflection temperature (HDT) of the samples was determined using the same machine at a heating rate of 2 °C /min. HDT is widely used in automotive applications and represents the temperature at which the material deflects by 0.25 mm at an applied force (three point bending arrangement) of 66 psi (ASTM D 648). A modified ASTM D 648 in a single cantilever mode was used for HDT measurement since the DMA could only handle a smaller size of specimen as compared to that of ASTM D 648.



Figure 3.5.6: TA DMA 2890 in CMSC lab

3.5.2.4 Flexural testing

The biocomposites, bioplastics and control samples are used for flexural tests complying with ASTM D790 standards. A United Calibration Corp. SFM – 20 machine was used for tensile and flexural testing. System control and data analysis were performed using Datum software.



Figure 3.5.7: UTS in flexural testing mode at CMSC lab

3.5.2.5 Impact testing

The biocomposites, bioplastics and control samples are used for notched Izod impact tests complying with ASTM D 256 standards. The impact test was carried out using an impact tester from Testing Machines Inc. 43-OA-01. Izod impact specimens with the same dimension as indicated in ASTM D256 were tested with a 5.0 lb pendulum. The dimension of the notched Izod impact specimens was 12.7 mm (length) \times 12.7 mm (width) \times 10 mm (thickness), and a notch of 1.5 mm length and 0.25 mm radius was marked along the thickness direction. The specimen was held as a vertical cantilever beam and was impacted on the notched face by a single swing of the pendulum. Therefore, the crack propagated from the tip of the notch. A minimum of three specimens for each composition were tested.



Figure 3.5.8: Impact testing machine (left) and notching machine (right) at CMSC lab

3.5.2.6 Tensile testing

The biocomposites, bioplastics and control samples are used for tensile tests complying with ASTM D638 standards. A United Calibration Corp. SFM – 20 machine was used for

tensile and flexural testing. System control and data analysis were performed using Datum software.



Figure 3.5.9: United Corporation "SFM-20" Test System

3.5.2.7 Thermo-mechanical Analysis (TMA)

The thermal mechanical analysis was done on a TMA 2980 (TA instruments) to determine the coefficient of thermal expansion (CTE) of each material type. The samples were heated to 140 $^{\circ}$ C at a rate of 4 $^{\circ}$ C per minute. A plot of the change in length of the sample versus the temperature was tracked by the software and used to compute the CTE of the material.



Figure 3.5.10: TMA 2980 (TA instruments) in CMSC lab

3.5.2.8 Environmental Scanning Electron Microscopy (ESEM)

The impact-fractured surfaces of composites and plastics were investigated using Environmental Scanning Electron Microscopy (ESEM). The ESEM used for this work was manufactured by Electroscan Corporation (Model no. 2020). It is equipped with a Lanthium Hexaboride filament. Water vapor acts as the imaging gas. The samples to be examined were placed in a sample holder located in the sample chamber. The imaging pressure (Chamber pressure) was set between 2-3 Torr. The working distance between the detector and the sample was set between 8 –10 mm. The accelerating voltage was set to 20 kV. The sample was focused at different points in its area, and micrograph pictures were taken at different magnifications. The fractured specimens were gold sputtered before taking the images.

3.5.2.9 AFM

The atomic force microscope (AFM) is one of about many types of scanned-proximity probe microscopes. All of these microscopes work by measuring a local property - such as height, optical absorption, or magnetism - with a probe or "tip" placed very close to the sample. The AFM works by scanning a fine ceramic or semiconductor tip over a surface much the same way as a phonograph needle scans a record. The tip is positioned at the end of a cantilever beam shaped much like a diving board. As the tip is repelled by or attracted to the surface, the cantilever beam deflects. The magnitude of the deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever (See Figure 3.5.11). A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface. The AFM can work with the tip touching the sample (contact mode), or the tip can tap across the surface (tapping mode).



Figure 3.5.11: (a) Working of a contact mode AFM. (b) MultiMode Scanning Probe Microscope (SPM) from Digital Instrument.

In this research, the bioplastic samples were evaluated using a multimode Scanning Probe Microscope (SPM) (Figure 3.5.11). AFM imaging was conducted using a Nanoscope IV atomic force microscope from Digital Instruments (Santa Barbara, CA) equipped with an E scanner. Samples were mounted onto a stainless steel disk using a sticky tab (Latham, NY). The microscope was allowed to thermally equilibrate for thirty minutes before imaging. Scanning rates less than 1 Hz were used. Room temperature was maintained at 22 ± 1 °C. Images were recorded in tapping mode using etched silicon probes (Digital Instruments). The parameters, especially the set point and the gain, were adjusted to obtain the best image resolution. For every sample, images were collected at different locations to obtain reproducible and reliable images. The images are presented in top view and the surface topography is expressed by different colors. Most images are presented without treatment unless specified. Injection molded samples were used for AFM imaging. The samples are cross, plane, and 45° titled cross-sectioned with a diamond knife at room temperature. The cross section surface was polished with 4000# grit from until a smooth surface was obtained.

3.5.2.10 FTIR

FTIR was used for studying the constituent functional groups in the various chemicals used in the matrix and also to study the kinetics of curing. For finding the constituent functional groups in a chemical, scans were made at room temperature with a drop of liquid between two sodium chloride plates (NaCl). For studying the kinetics, isothermal experiments were run at one specific temperature for 4 hours. The scans were taken every 5-10 minutes. One drop of the reaction mixture was placed between two undrilled NaCl IR crystal windows, 2mm thick. The NaCl plates were then placed inside the IR heated cell. The temperatures were: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150 and 160 °C. This kinetic study was done to determine the curing of the system at these conditions.

3.5.2.11 Moisture Absorption Test

Moisture absorption test was carried out to find out the moisture uptake by the composites and control. Moisture absorption tests determine the rate of absorption of materials and also showcase the equilibrium moisture content of the samples. The samples were dried until their weight stabilized, their weight was recorded, and then they were placed in a relative chamber operating at 30 ^oC and 90% relative humidity. At regular intervals, they were taken out of the chamber, wiped properly with dry paper towels, and weighed again. After weighing the samples, they were reinserted in the humidity chamber. Measurements were taken once a week until the material reached a steady state (no longer absorbing moisture).



Figure 3.5.12: Humidity chamber in CMSC lab

3.5.2.12 Weatherability Test

Biocomposite samples were placed in an accelerated weatherometer (QUV, Dr. Pascal Kamdem's laboratory, Department of Forestry, MSU) for weathering tests. The accelerated weatherometer was set to the following cycle to expose the samples to UV, condensation, and water spray: UV (340 nm) at 60°C for 2:30 hrs followed by water spray for 0:30 hrs, repetition of preceding steps, 48 times, and finally condensation at 45°C for 24:00 hrs. Twelve cycles were repeated in the test, and the total duration for the whole test was 2016 hours. The measurements for color, surface roughness test weight change, and dynamical mechanical analysis were taken at regular intervals of time.

Sample preparation

Samples of biocomposites were cut into the dimensions of 76.2mm X 31.75 inch X 4 mm. The samples were conditioned at 65% RH and 25 ^oC after machining and polishing. Thirteen specimen of each sample were used for these experiments.

Weatherometer (QUV)

The samples were subjected to weathering in a QUV accelerated weathering tester Model QUV/Spray (Accelerated Weathering Tester, Q-Panel, Cleveland, OH, USA), which allowed for water spray as well as condensation. The samples were subjected to accelerated weathering by exposure to fluorescent ultraviolet light radiation at a wavelength of 340 nm and temperature of 60 ^oC for two and a half hours, followed by a spray of water for half an hour, followed by condensation at 45 ^oC for twenty four hours. The average irradiance was set to 0.85 W/m² at a wavelength of 310 nm. The temperature of the spray was set to 25 ^oC. The exposure times for the samples in this study were 0, 500, 1000, 1500, and 2000 hours approximately. The measurements for

color, surface roughness test weight change, and dynamical mechanical analysis were taken at regular intervals of time.



Figure 3.5.13: QUV weatherometer in Dr. Kamdem's lab



Figure 3.5.14: Open panel of QUV weatherometer

Color measurements

The color of the biocomposite samples was determined in accordance with the ISO-2470 standard, using a reflectometer (Datacolor international, Lawrenceville, NJ, USA) with CIELAB system. The CIELAB system is characterized by three parameters, L*, a*, b*. The L* axis represents the lightness, whereas, a* and b* axes are the chromaticity co-

ordinates. In the CIELAB co-ordinates, +a* is for the red, -a* for green, +b* for yellow, b* for blue and L* varies from 100 (white) to zero (black). L*, a*, and b* color coordinates of each specimen were measured before and after the exposure to weathering conditions. These values were then used to calculate the color change, ΔE^* and the color saturation, C* as a function of the weathering exposure duration.



Figure 3.5.15: CIELAB system for color measurement

Surface roughness measurement

A surface profilometer system (HommelWerke, Germany) was used to evaluate modifications on the biocomposites' surface before and after weathering. The system was equipped with a 25 mm long stylus, which traverses the surface and its vertical displacement is converted into an electrical signal. The signal is amplified before it is converted into a set of digital information. The digital information is transmitted to the computer and the surface roughness parameters calculated from this information. The stylus travel speed was set at 0.5 mm⁻¹ across the biocomposites sample with a span of 25.6 mm. The maximum range was set at 800 µm and an average of five measurements

was taken from each sample. Each sample was evaluated before and after the exposure to weathering.

Several surface-texture parameters were obtained from this method: R_a , R_z , R_{max} , R_k , R_{pk} , and R_{vk} . R_a is the average surface roughness and it represents the deviation from the mean peak. R_a is often used to define surface roughness, but it does not differentiate between the peaks and the valleys of a surface profile. R_z is the mean of the peak-tovalley height. R_{max} is the maximum of the peak-to-valley height. R_a , R_z , and R_{max} were measured to characterize the physical changes of the biocomposite sample surfaces.





Figure 3.5.16: Surface profilometer for roughness measurement

Weight change

The weights of the samples were measured before and after the weathering exposure. The samples were dried until their weight stabilized, and then their weight was recorded to four significant figures.



Figure 3.5.17: Weathered samples, on left, a hempmat-UPE biocomposite, on right, a BBSG-GFC-UPE biocomposite

3.5.2.13 Flammability Test

Fire test of biocomposite samples was carried out in accordance with ASTM protocol. The dimensions of the samples for the fire test were: 0.5 inch X 0.125 inch X 2.5 inch. Two to four samples were tested for each composite/plastic.

The samples tested were: UPE Control, untreated hemp mat (90 hemp+10 PET)-UPE, acrylonitrile treated hemp mat (90 hemp+10 PET)-UPE, untreated hemp mat (pure)– UPE +Styrene, UPE treated hemp mat (pure)–UPE +Styrene, untreated hemp mat(pure)-Glass mat-UPE, untreated hemp mat(BM115)-Glass mat-UPE, untreated BBSG-CaCO3-UPE, silane treated BBSG-CaCO3-UPE, silane treated green flax core-CaCO3-UPE, untreated BBSG& GFC-CaCO3-UPE, silane treated BBSG& GFC-CaCO3-UPE, jute-Hemp-CaCO3(20)-UPE(55), E-glass mat-CaCO3(30)-UPE(50), CaCO3(30)-UPE, untreated hemp mat(BM115)-bioresin 30-UPE 70, E-glass mat-Bioresin-UPE, E-glass mat-UPE, Particle board, dry wall, and wood (douglas fir).

CHAPTER FOUR: RESULTS ON ENGINEERED FIBERS

4.0 RESULTS ON ENGINEERED FIBERS

This chapter describes the results of the studies done to make an engineered biofiber by surface modifications and hybridization.

4.1 Effect of surface modification on hemp mat with filler

The following surface treatments were done on hempmat fibers: alkali treatment, γ methacryloxypropyltrimethoxy silane (γ -MPS) treatment, acrylonitrile treatment, and UPE-MEKP treatment. The composites were made by compression molding (process depicted in Figure 4.1.1).



Figure 4.1.1: Schematic representation of the compression molding process

Analysis of surface treated hemp fibers

The surface treated fibers were characterized with TGA, DSC, and XPS.

Thermogravimetric analysis (TGA)

Thermogravimetric curves for untreated and surface treated hemp fibers are shown in Figure 4.1.2 and 4.1.3. Table 4.1.1 summarizes the maximum decomposition temperatures for untreated and surface treated hemp fibers. Up to 200 $^{\circ}$ C, there was less than 5 % loss in weight of untreated as well as surface treated hemp fibers. After the alkali treatment, the temperature at the maximum rate of decomposition of hemp fiber increased, indicating that the alkali treatment lead to an enhancement in the thermal stability of the hemp fiber, as has been noted by other authors [1, 2]. Weight loss of 10% occurred between 288-332 $^{\circ}$ C for the untreated and surface treated fibers, while a weight loss of 20% occurred in the range of 329-366 $^{\circ}$ C, and weight loss of 30% was observed in range of 346-378 $^{\circ}$ C for untreated and surface treated hemp fibers.



Figure 4.1.2: TGA of surface treated hemp fibers



Figure 4.1.3: Derivative thermo-gravimetric analysis (DTGA) of surface treated hemp fibers

	10% Weight loss (⁰ C)	20% Weight loss (⁰ C)	30% Weight loss (⁰ C)	Max. degradation temperature (°C)
Α	311	348	363	381
B	332	366	378	395
C	295	339	357	383
D	288	329	346	369

Table 4.1.1: Thermogravimetric results for surface treated hemp fibers

Legend:

A= Untreated hemp fiber, B= Alkali treated hemp fiber, C= UPE-MEKP treated hemp fiber, D= Acrylonitrile treated hemp fiber

Differential scanning calorimetry (DSC)

The DSC curves for untreated and surface treated fibers expressed in terms of heat flow are shown in Figure 4.1.4. The melting point of cellulose has been reported to be near $300 \, {}^{0}$ C [3]. However, a controversy surrounds the glass transition temperature (Tg) of

cellulose, which has been reported between -30 to 160 0 C [4]. The Tg for lignin has been reported between 135- 172 0 C [5, 6].



Figure 4.1.4: DSC of surface treated hemp fibers

It is observed from Figure 4.1.4 that the crest associated with weight loss due to evaporation of water was found in all fiber samples, and ranged from 10-130 °C in hemp fibers, depending upon the degree of hydrogen bonding interaction [7]. Furthermore, this transition shifted towards the right after surface treatment of the hemp fiber. It was also observed that fibers had less amount of moisture percentage because they had been predried before any kind of treatment. This ensured that the inherent moisture of the fibers, which is 12-14% of the total fiber weight, was not able to interact with the surface treatments in any way. Therefore, the chemicals of the surface treatments had an opportunity to react with the actual fiber surface and fiber constituents. This would lead to a direct link between the chemicals used and the fiber constituents such as cellulose and hemicelluse. The T_g for lignin and cellulose were not observed by this particular method in DSC. Two exothermic peaks were observed by some researchers from 300 $^{\circ}$ C to 500 $^{\circ}$ C for untreated and surface treated natural fibers, indicating the thermal stability of the fibers as a function of the treatment [8]. However, we were not able to see such peaks in out DSC thermograms as our experiments were conducted only up to 300 $^{\circ}$ C.

X-ray photon spectroscopy (XPS)

XPS survey scans were taken for untreated as well as surface treated hemp fibers. These scans revealed the presence of carbon, oxygen, nitrogen, calcium, and silicon in the hemp fibers. Table 4.1.2 and 4.1.3 show the elemental composition and elemental ratios of the hemp fibers, respectively. Following an hour long treatment with alkali solution it is observed that the carbon content increases, while oxygen and nitrogen content decrease. After silane treatment, there is a marked increase in silicon as well as carbon content, and a decrease in oxygen and nitrogen content. Again, after treatment with the matrix, there is an increase in carbon content, while a decrease in oxygen and nitrogen content. However, with acrylonitrile treatment, there is a decrease in carbon content and an increase in ratio.

It is well known that natural fibers consist of cellulose, hemi-cellulose and lignin [9]. Hemicellulose consists of a mixture of different sugars and other subsituents which are soluble in water or bases. Lignin is similar to a highly unsaturated or aromatic polymer in structure and has low oxygen to carbon ratio, and is partially soluble in water [9, 10]. Due to the alkali treatment, a part of hemicellulose and lignin might have dissolved, and washed away, leading to a decrease in oxygen content. The increase in carbon and silicon content after silane treatment might be due to the attachment of bulky alkyl group and silicon to the hemp fiber as a result of this treatment. The large increase in carbon content of UPE treated hemp fiber can again be due to the large oligomer molecule of UPE reacting with hydroxyl groups of fiber. Meanwhile, the increase in nitrogen content after treatment with acrylonitrile might be due to grafting of acrylonitrile monomer to the fiber surface.

	C1s[.314]	N1s[.499]	O1s[.733]	Si2p[.368]	Ca2p[1.927]
Α	71.64	2.63	24.39	0.75	0.52
В	73.74	2.23	21.21	0.36	0.56
C	79.44	0.77	16.09	3.12	0.59
D	80.17	0.98	18.85		
E	69.91	2.92	26.79		0.38

Table 4.1.2: Elemental composition of surface treated hemp fibers (from XPS analysis)

Legend:

A= Untreated hemp fiber, B= Alkali treated hemp fiber, C= Silane treated hemp fiber, D= UPE-MEKP treated hemp fiber, E= Acrylonitrile treated hemp fiber

Table 4.1.3: Elemental ratios of surface treated hemp fibers (from XPS analysis)

	C/O	C/N	C/Si	C/Ca
Α	2.94	27.24	95.52	137.77
В	3.48	33.07	-	131.68
C	4.94	103.17	25.46	134.64
D	4.25	81.81	-	-
E	2.61	23.94	-	183.97

Legend:

A= Untreated hemp fiber, B= Alkali treated hemp fiber, C= Silane treated hemp fiber, D= UPE-MEKP treated hemp fiber, E= Acrylonitrile treated hemp fiber

Reaction schemes

The schematic diagram of reactions that might result due to surface treatment of fibers is

shown in Figure 4.1.5. Figure 4.1.6 and 4.1.7 show the reactions that might take place

after the surface treated fibers react with UPE matrix, during curing, and produce three dimensional networked structures. Conclusive proofs for these reactions will be discussed in future work.



Figure 4.1.5: Proposed reaction for surface treatment of hemp fibers



Figure 4.1.6: Proposed reaction for curing of surface treated hemp fibers and UPE



Figure 4.1.7: Proposed reaction for curing of surface treated hemp fibers and UPE

Optimization of fiber volume fraction

The fiber volume fraction was optimized by making bio-composites with non woven hemp mat fiber volume fractions of 20 %, 30 % and 40 %, and testing the mechanical properties of the resulting biocomposites. It should be noted that with 40 % volume fraction of hemp fibers, a consolidated biocomposite with a complete wet out could not be manufactured. Figure 4.1.8 shows the result from flexural test of fiber volume fraction optimization study. The biocomposite with 30 volume (vol) % hemp fibers had higher bending strength and modulus of elasticity as compared to composite with 20 vol % hemp fibers as well as UPE control. The bending strength of 30 vol % hemp fiber composite was 16 % higher than that of UPE control, and 9 % higher than 20 vol % hemp fiber composite. Its modulus of elasticity was 150 % higher than the neat resin, and 45 % higher than 20 vol % hemp fiber composite. Similar results were obtained from tensile strength, tensile modulus and impact strength (data not shown). Therefore, it was decided that 30 volume % of hemp fibers were optimum for a biocomposite made of hemp mats and UPE resin.



Figure 4.1.8: Optimization of fiber volume fraction by evaluation of mechanical properties

Legend: A= UPE control, B= Untreated hemp mat (20 % vol)–UPE, C= Untreated hemp mat (30 % vol)–UPE

Tensile Properties

Figure 4.1.9 shows the comparison of tensile properties of various composites. The tensile properties of biocomposites with surface treated hemp fibers were higher than that of untreated hemp mat composite as well as that of neat resin. The tensile strength and modulus of untreated hemp fibers based biocomposite was 45 % and 325 % higher than that of neat resin, respectively. Comparing surface treated fiber based composites, the tensile strength of alkali treated fiber based biocomposite was 34 % higher than that of untreated hemp fiber based composite, while that of silane treated fiber based biocomposite was 48 % higher than that of untreated hemp composite. UPE-MEKP treated hemp fiber based biocomposite has tensile strength of 57 % higher than that of untreated hemp fiber based composite. In terms of tensile modulus, silane treated fiber had enhancement of 6 % as compared to that of untreated hemp, while UPE-MEKP treated fibers had an enhancement of 4 %, and acrylonitrile treated fibers had a 25 % enhancement compared to that of untreated hemp.

The tensile strength of E-glass-UPE composite was 130 % higher, and the tensile modulus was 70 % higher as compared to that of untreated hemp mat biocomposite at same volume %. The hybrid E-glass-hemp mat-UPE composite had an increment of 76 % in tensile strength, and 34 % in tensile modulus compared to that of untreated hemp mat based biocomposite. The E-glass-UPE composite had 23 % higher tensile strength as compared to that of hybrid composite of E-glass and hemp mats. On comparing specific tensile strength (tensile strength divided by density of composite) and specific tensile

modulus (tensile modulus divided by density of composite) of all composites, it was found that the biocomposites and glass composites were in the same range.

This increase in tensile strength and modulus of the chemically treated hemp fibers based biocomposites may be an outcome of the improved adhesion between the fiber and the matrix. This improved adhesion might have enhanced the interfacial bonding and thus, made it easier for the stress to be effectively transferred from the matrix to the fiber (as depicted in reaction schemes 3, 4, and 5) [11-13].



Figure 4.1.9: Comparison of tensile properties of surface treated composites *Legend:* A= UPE control, B= Untreated hemp mat (30 % vol)–UPE, C= Alkali treated hemp mat (30 % vol)–UPE, D=Silane treated hemp mat (30 % vol)–UPE, E= UPE-MEKP treated hemp mat (30 % vol)–UPE, F=Acrylonitrile treated hemp mat (30 % vol)-UPE, G=E-glass mat-UPE, H=E-glass mat-hemp mat-UPE

Flexural Properties

Flexural strength is a combination of the tensile and compressive strengths which directly varies with the interlaminar shear strength. In flexural testing various mechanisms such

as tension, compression, shearing etc. take place simultaneously. In a three point flexural test, the failure occurs due to bending and shear failure. The bending strength and modulus of elasticity of different composites are compared in Figure 4.1.10.

The flexural properties of biocomposites with surface treated hemp fibers were higher than that of untreated hemp mat composite; also, the flexural properties of all composites were higher than that of neat resin. Comparing surface treated fiber based composites, the modulus of elasticity as well as bending strength of alkali treated, silane treated and UPE-MEKP treated hemp fiber based biocomposites lie in the same range. However as discussed earlier [14], the modulus of elasticity and bending strength of acrylonitrile treated fibers based composites were 7%, and 35% higher than those of untreated hemp fiber biocomposite respectively. As compared to UPE control, the surface treated fiber based biocomposites had a 10-16% enhancement in bending strength, and 140-225% increment in modulus of elasticity.

The bending strength of E-glass-UPE composite was 144 % higher, and the modulus of elasticity was 56 % higher as compared to that of untreated hemp mat biocomposite. The hybrid E-glass-hemp mat-UPE composite had a bending strength 83 % higher, and modulus of elasticity 66 % higher than that of untreated hemp mat based biocomposite. The E-glass-UPE composite had 25 % higher bending strength as compared to that of hybrid composite of E-glass and hemp mats, but its modulus was 7 % lower than that of hybrid composite.

On comparing specific bending strength and specific modulus of elasticity of all composites, it was found that the biocomposites and glass composites were in the same range.

The increment in the flexural properties of biocomposites after surface treatment of the hemp fibers can be attributed to the modifications in the molecular level of the fibers due to chemical bonding between fiber components and the treatment reagents. Such linkage might have lead to better interfacial bondage, better adhesion, and effective stress transfer (as depicted in reaction schemes shown in Figure 4.1.5, 4.1.6, and 4.1.7) [11-13].



Figure 4.1.10: Comparison of flexural properties of surface treated composites *Legend:* A= UPE control, B= Untreated hemp mat (30 % vol)–UPE, C= Alkali treated hemp mat (30 % vol)–UPE, D=Silane treated hemp mat (30 % vol)–UPE, E= UPE-MEKP treated hemp mat (30 % vol)–UPE, F=Acrylonitrile treated hemp mat (30 % vol)-UPE, G=E-glass mat-UPE, H=E-glass mat-hemp mat-UPE

Impact Strength

Impact strength is the ability of a material to resist the fracture under stress applied at high speed. The impact properties of the composite are directly related to its overall toughness. The fibers play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. It is a common observation that with any surface treatment, the flexural and tensile properties of the composite increase, but the impact strength (shown in Figure 4.1.11) will decrease.

The impact strength of all composites were higher than that of neat resin. The impact strength of biocomposites with surface treated hemp fibers was higher than that of untreated hemp mat composite. As compared to neat resin, there was an increment of 82 % in impact strength of untreated hemp fiber based composites, 49 % for alkali treated fibers, 94 % for silane treated fibers, 120 % for UPE-MEKP treated fibers, and 180 % for acrylonitrile treated hemp fiber based biocomposites. On comparing the impact strength of untreated biocomposites, it was found that the impact strength of silane treated fibers was 7 % more than that of untreated fibers, and that of uPE-MEKP treated fibers was 54 % more than that of untreated fibers.

The impact strength of E-glass-UPE composite was 16.3 times higher than that of neat resin and 8.5 times higher than that of untreated hemp fiber based biocomposite. The hybrid E-glass-hemp mat-UPE composite had impact strength 16.5 times higher than that of neat resin and 8.6 times higher than that of untreated hemp fiber based biocomposite. The impact strength of hybrid composite of E-glass mats and hemp mats was almost same as that of E-glass-UPE composite (within error bars).



Figure 4.1.11: Impact strength of surface treated composites *Legend:* A= UPE control, B= Untreated hemp mat (30 % vol)–UPE, C= Alkali treated hemp mat (30 % vol)–UPE, D=Silane treated hemp mat (30 % vol)–UPE, E= UPE-MEKP treated hemp mat (30 % vol)–UPE, F=Acrylonitrile treated hemp mat (30 % vol)– UPE, G=E-glass mat-UPE, H=E-glass mat-hemp mat-UPE

Dynamic Mechanical Analysis

Dynamic mechanical methods expose the specimen to periodic stresses. The polymer is subjected continuously to forced oscillations, and the applied stress is sinusoidal with a frequency. The deformation of ideal-elastic bodies follows the stress instantaneously but that of viscoelastic polymer experiences a delay. The stress vector is assumed to be a sum of two components: one component is in phase with the deformation; the other is not. Each of these two components possesses a modulus. The real modulus (shear storage modulus) G' measures the stiffness and shape stability of the specimen, whereas the imaginary modulus (shear loss modulus) G" describes the loss of usable mechanical

energy by dissipation into heat. The maximum of tan δ as a function of temperature is generally identified as the glass transition temperature T_g , which is dependent on the deformation rate. The damping properties of the material are related to energy absorption. The area below tan delta is function of the absorption of the energy necessary to pass from glassy state to rubbery state.



Figure 4.1.12: Typical storage modulus curves of surface treated composites The typical curves of storage modulus and tan delta for neat resin and composites can be seen in Figures 4.1.12 and 4.1.13 respectively. The storage modulus decreased as a function of temperature, as is commonly observed for composites. At higher temperatures, all biocomposites plateau to the same value of modulus. The storage moduli of surface treated hemp fibers based biocomposites were higher than that of untreated hemp fiber based biocomposite. A comparison of storage moduli of composites at 40 ^oC was made in Figure 4.1.14. The storage modulus of biocomposites at 40 ^oC was enhanced by 110-

190 % compared to neat resin. Glass mat based composite had a storage modulus 307 % higher than that of neat resin, 68 % higher than that of untreated hemp fiber based composite, and 26% higher than that of hemp mat-glass hybrid composite at 40 $^{\circ}$ C.



Figure 4.1.13: Typical tan delta curves of surface treated composites

The loss modulus of composites was higher than that of the neat resin. This follows the trend found previously for natural fiber-thermoset composites, where the loss modulus increased after addition of fibers to the plastic [15].

Over the entire range of temperature, tan δ was highest for the neat resin due to huge reduction in the storage modulus values at higher temperatures. The lower values of tan δ for the biocomposite made with surface treated hemp fibers suggest that there is less damping in the chemically treated hemp fiber based composites. The tan δ vs.
temperature plot for biocomposites as well as E-glass composite is similar. The tan δ curve of all composites shifted towards right as compared to neat resin, but this shift was significant in case of glass based composite. The T_g of the neat resin was 95 °C. For biocomposites, the T_g increased about 2-5 °C as compared to neat resin.



Figure 4.1.14: Storage modulus of surface treated composites at 40 0 C Legend: A= UPE control, B= Untreated hemp mat (30 % vol)-UPE, C= Alkali treated hemp mat (30 % vol)-UPE, D=Silane treated hemp mat (30 % vol)-UPE, E= UPE-MEKP treated hemp mat (30 % vol)-UPE, F=Acrylonitrile treated hemp mat (30 % vol)-UPE, G=E-glass mat-UPE

Morphology of fiber surface

The micrographs of untreated and surface treated hemp fibers are shown in Figure 10. The distribution of the fibers in the hemp mat was random, and uneven. The micrographs in Figure 4.1.15 focus on single fiber surface. Fibrillation was observed in fibers after surface treatment.



Figure 4.1.15: ESEM micrographs of surface treated hemp mat fibers

- a) Untreated hemp mat, magnification 1200 X, scale bar 45 µm
- b) Alkali treated hemp mat, magnification 900 X, scale bar 50 µm
- c) Silane treated hemp mat, magnification 900 X, scale bar 50 µm
- d) Acrylonitrile treated hemp mat, magnification 1000 X, scale bar 45 µm

This could provide more anchorage for the matrix, and hence improve the strength of the composite. In general, the surface of chemically treated fibers looked different from that of the untreated hemp fiber.

In the biocomposites, the fiber pull out was clearly observed (pictures not shown). Biocomposite with untreated hemp fibers showed poor interfacial bonding between the fiber and matrix, which resulted in relatively clean surface over the pulled out fibers due to greater extent of delamination. In case of untreated fiber based biocomposites, shear failure results in high degree of pull out. The adhesion between the fiber and the matrix was enhanced in biocomposites with surface treated fibers. The fibers were covered with matrix, and the fiber pull out was relatively smaller.



Figure 4.1.16: Schematic representation of the fiber matrix interface and various factors affecting the fiber-matrix adhesion

Although there have been many studied on natural fiber thermoset composites, only a few mention the use of non woven fiber mats as reinforcement in biocomposites [16-19]. For useful composites, fiber-matrix adhesion has to be optimized for ensuring good mechanical properties. The surface chemical modifications of natural fibers like dewaxing, alkali treatment, cyanoethylation, vinyl grafting and treatment with various coupling agents, are some means to improve fiber matrix adhesion of the resulting biocomposites (as shown in Figure 4.1.16) [11-12, 20-26]. Surface modification also results in enhancement of the aspect ratio, improves the wettability of the fibers, and forms a strong interface between polar natural fiber and non polar matrix.

The adhesion between hemp fibers and UPE matrix was increased by treatment of hemp fiber surface with alkali, silane, UPE (matrix), and acrylonitrile. The surface treatment of hemp mats also resulted in higher mechanical and thermal properties. Other modifications which could bring about the same effects are acetylation, bleaching, UV/plasma, microwave, and steam explosion. It is our future plan to optimize these treatments for natural fibers. The gap between performance of glass based composites and biocomposites was bridged by fabricating a hybrid composite comprising of glass and hemp fibers. In terms of specific modulus and strength, glass composites and biocomposites were in the same range.

4.1 Effect of surface modification on pure hemp mat

The results of the following surface treatments done on pure hemp mat are discussed in this section: alkali treatment, γ -methacryloxypropyltrimethoxy silane (γ -MPS) treatment, and UPE-MEKP treatment.

Analysis of surface treated hemp fibers

The surface treated fibers were characterized with TGA, DSC, and XPS.

Thermogravimetric analysis (TGA)

Thermogravimetric curves for untreated and surface treated hemp fibers are shown in Figure 4.2.1 and 4.2.2. Table 4.2.1 summarizes the maximum decomposition temperatures for untreated and surface treated pure hemp fibers. Up to 200 ^oC, there was less than 8 % loss in weight of untreated as well as surface treated hemp fibers. After the alkali treatment, the temperature at the maximum rate of decomposition of hemp fiber





increased, indicating that the alkali treatment lead to an enhancement in the thermal stability of the hemp fiber, as has been noted by other authors [1, 2]. Weight loss of 10% occurred between 278-308 $^{\circ}$ C for the untreated and surface treated fibers, while a weight loss of 20% occurred in the range of 323-359 $^{\circ}$ C, and weight loss of 30% was observed in range of 342-373 $^{\circ}$ C for untreated and surface treated hemp fibers. The maximum

decomposition temperature ranged from 362-392 ⁰C.These results are comparable to those of hemp mat with filler, discussed in Section 4.1.



Figure 4.2.2: Derivative thermo-gravimetric analysis (DTGA) of surface treated pure hemp fibers

Table 4.2.1: Thermogravimetric results for surface treated pure hemp fib

	10% Weight loss (°C)	20% Weight loss (⁰ C)	30% Weight loss (⁰ C)	Max. degradation temperature (⁰ C)
Α	296	339	360	390
В	308	359	373	391.7
С	278	323	342	384.1
D	292	329	349	367.5

(Table 4.2.1 continued)

Legend: A= Untreated pure hemp fiber, B= Alkali treated pure hemp fiber, C= UPE-MEKP treated pure hemp fiber, D= Silane treated pure hemp fiber

Differential scanning calorimetry (DSC)

The DSC curves for untreated and surface treated fibers expressed in terms of heat flow are shown in Figure 4.2.3. It is observed from Figure 4.2.3 that the crest associated with weight loss due to evaporation of water was found in all fiber samples, and ranged from 7-150 6 C in pure hemp fibers, depending upon the degree of hydrogen bonding interaction [7]. Furthermore, this transition shifted towards the right after surface treatment of the hemp fiber. It was also observed that fibers had less amount of moisture percentage because they had been pre-dried before any kind of treatment. This ensured that the inherent moisture of the fibers, which is 12-14% of the total fiber weight, was not able to interact with the surface treatments in any way. Therefore, the chemicals of the



Figure 4.2.3: DSC of surface treated pure hemp fibers

surface treatments had an opportunity to react with the actual fiber surface and fiber constituents. This would lead to a direct link between the chemicals used and the fiber constituents such as cellulose and hemicelluse. The T_g for lignin and cellulose were not observed by this particular method in DSC. Exothermic peaks were not observed between 300 $^{\circ}$ C to 500 $^{\circ}$ C in our DSC thermograms as our experiments were conducted only up to 300 $^{\circ}$ C.

X-ray photon spectroscopy (XPS)

XPS survey scans were taken for untreated as well as surface treated pure hemp fibers. These scans revealed the presence of carbon, oxygen, nitrogen, calcium, and silicon in the hemp fibers. Table 4.2.2 and 4.2.3 show the elemental composition and elemental ratios of the pure hemp fibers, respectively. Following an hour long treatment with alkali solution it is observed that the carbon content increases, while oxygen and nitrogen content decrease. After silane treatment, there is a marked increase in silicon as well as carbon content, and a decrease in oxygen and nitrogen content. However, after treatment with the matrix, there is an increase in carbon content, while a decrease in oxygen and nitrogen content.

Due to the alkali treatment, a part of hemicellulose and lignin might have dissolved, and washed away, leading to a decrease in oxygen content. The increase in carbon and silicon content after silane treatment might be due to the attachment of bulky alkyl group and silicon to the hemp fiber as a result of this treatment. The large increase in carbon content of UPE treated hemp fiber can again be due to the large oligomer molecule of UPE reacting with hydroxyl groups of fiber.

	C1s[.314]	N1s[.499]	O1s[.733]	Si2p[.368]	Ca2p[1.927]
Α	74.48	2	22.52	0.75	0.47
В	76.38	1.95	19.9		1.19
C	79.44	0.77	16.09	3.12	0.59
D	81.46	1.47	15.52	1.14	0.41

Table 4.2.2: Elemental composition of surface treated pure hemp fibers (from XPS analysis)

Legend:

A= Untreated hemp fiber, B= Alkali treated hemp fiber, C= Silane treated hemp fiber, D= UPE-MEKP treated hemp fiber

Table 4.2.3: Elemental ratios of surface treated p	pure hemp fibers ((from XPS analysis)
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	C/O	C/N	C/Si	C/Ca
Α	3.3	37.24	99.31	158.47
В	3.84	39.17	-	64.18
С	4.94	103.17	25.46	134.64
D	5.25	55.42	71.46	198.68

Legend:

A= Untreated hemp fiber, B= Alkali treated hemp fiber, C= Silane treated hemp fiber, D= UPE-MEKP treated hemp fiber

Reaction schemes

The schematic diagram of reactions that might result due to surface treatment of fibers is shown in Figure 4.1.5. Figure 4.1.6 and 4.1.7 show the reactions that might take place after the surface treated fibers react with UPE matrix, during curing, and produce three dimensional networked structures. Conclusive proofs for these reactions will be discussed in future publications.

Optimization of styrene content

The high density of the hemp fiber mats led to a resin impregnation problem, due to which it was not possible to obtain fully consolidated biocomposites. This problem was solved by adding extra styrene to the UPE resin to reduce the viscosity of the polymer matrix. The styrene content was optimized by making biocomposites with non woven pure hemp mat fiber, UPE, and styrene, with extra styrene weight percentage of 10%, 20 %, 30 % and 40 %, and testing the mechanical properties of the resulting biocomposites. All of the biocomposites had 30 % volume of hemp fibers; the change was only done to the matrix which comprised 70% volume of the composites. Figure 4.2.4 shows the result from flexural test of styrene optimization study. The biocomposite with 20 wt % extra styrene had higher bending strength and modulus of elasticity as compared to composite



Figure 4.2.4: Optimization of styrene content by evaluation of flexural properties Legend: A=30% untreated pure hemp mat-10% styrene, B= 30% untreated pure hemp mat-20% styrene, C= 30% untreated pure hemp mat-30% styrene, D=30% untreated pure hemp mat-40% styrene

with 10 wt % extra styrene as well as UPE control. The bending strength of 20 wt % extra styrene-hemp fiber composite was 12 % higher than that of 10 wt % extra styrene biocomposite, and its modulus of elasticity was 142 % higher than that of 10 wt % extra styrene biocomposite. In the case of 30 wt % extra styrene-hemp fiber composite, the bending strength was 36 % higher than that of 10 wt % extra styrene biocomposite, and

its modulus of elasticity was 115 % higher than that of 10 wt % extra styrene biocomposite. Whereas, for the 40 wt % extra styrene-hemp fiber composite, the bending strength was 36 % higher than that of 10 wt % extra styrene biocomposite, and its modulus of elasticity was 112 % higher than that of 10 wt % extra styrene biocomposite. Similar results were obtained from tensile strength, tensile modulus and impact strength. The tensile strength of 20 wt % extra styrene-hemp fiber composite was 31 % higher than that of 10 wt % extra styrene biocomposite, and its tensile modulus was 40 % higher than that of 10 wt % extra styrene biocomposite (Figure 4.2.5). In the case of 30 wt % extra styrene-hemp fiber composite, the tensile strength was 67 % higher than that of 10 wt % extra styrene biocomposite, and its tensile modulus was 25 % higher than that of 10 wt % extra styrene biocomposite. Whereas, for the 40 wt % extra styrene-hemp fiber



Figure 4.2.5: Optimization of styrene content by evaluation of mechanical properties Legend: A=30% untreated pure hemp mat-10% styrene, B= 30% untreated pure hemp mat-20% styrene, C= 30% untreated pure hemp mat-30% styrene, D=30% untreated pure hemp mat-40% styrene

composite, the tensile strength was 20 % higher than that of 10 wt % extra styrene

biocomposite, and its tensile modulus was 22 % higher than that of 10 wt % extra styrene biocomposite.

The impact strength of 20 wt % extra styrene-hemp fiber composite was 23 % higher than that of 10 wt % extra styrene biocomposite (Figure 4.2.6). In the case of 30 wt % extra styrene-hemp fiber composite, the impact strength was 58 % higher than that of 10 wt % extra styrene biocomposite. Whereas, for the 40 wt % extra styrene-hemp fiber composite, the impact strength was almost same as that of 10 wt % extra styrene biocomposite within error bars.



Figure 4.2.6: Optimization of styrene content by evaluation of mechanical properties *Legend:* A=30% untreated pure hemp mat-10% styrene, B= 30% untreated pure hemp mat-20% styrene, C= 30% untreated pure hemp mat-30% styrene, D=30% untreated pure hemp mat-40% styrene

Therefore, it was decided that 30 wt % extra styrene was optimum for biocomposites made of pure hemp mats and UPE resin. For all biocomposites made henceforth with pure hemp mat, 30 wt % extra styrene was added to the matrix.

Tensile Properties

Figure 4.2.7 shows the comparison of tensile properties of various composites. The tensile properties of biocomposites with surface treated hemp fibers were higher than that of untreated hemp mat composite as well as that of neat resin. The tensile strength and modulus of untreated pure hemp fibers based biocomposite was 45 % and 222 % higher



Figure 4.2.7: Comparison of tensile properties of surface treated pure hemp mat based composites

Legend: A= UPE control, B= Untreated pure hemp mat (30 % vol)–UPE, C= Alkali treated pure hemp mat (30 % vol)–UPE, D= UPE-MEKP treated pure hemp mat (30 % vol)–UPE, E= Silane treated pure hemp mat (30 % vol)–UPE, F=E-glass mat-UPE, G=E-glass mat-pure hemp mat-UPE

than that of neat resin, respectively. For alkali treated hemp fibers based biocomposite,

the tensile strength and modulus was 81 % and 293 % higher than that of neat resin, respectively. For UPE-MEKP treated hemp fibers based biocomposite, the tensile strength and modulus was 70 % and 284 % higher than that of neat resin, respectively. For silane treated hemp fibers based biocomposite, the tensile strength and modulus was 62 % and 287 % higher than that of neat resin, respectively.

Comparing surface treated fiber based composites, the tensile strength of alkali treated fiber based biocomposite was 25 % higher than untreated hemp fiber based composite, while that of silane treated fiber based biocomposite was 12 % higher than untreated hemp, whereas for UPE-MEKP treated hemp fiber based biocomposite it was 18 % higher than untreated hemp fibers. In terms of tensile modulus, alkali treated fiber had an enhancement of 22 % as compared to untreated hemp, while silane treated and UPE-MEKP treated fibers had an enhancement of 20 % each compared to untreated hemp.

The tensile strength and modulus of E-glass-UPE composite was 232 % and 620 % higher than that of neat resin, respectively. The tensile strength and modulus of hemp mat-E-glass-UPE hybrid composite was 112 % and 471 % higher than that of neat resin, respectively. The tensile strength of E-glass-UPE composite was 129 % higher, and the tensile modulus was 124 % higher as compared to untreated hemp mat biocomposite. The hybrid E-glass-hemp mat-UPE composite had an increment of 47 % in tensile strength, and 78 % in tensile modulus compared to untreated hemp mat based biocomposite. The E-glass-UPE composite had 56 % higher tensile strength and 26 % higher tensile modulus as compared to hybrid composite of E-glass and hemp mats. On comparing specific tensile strength (tensile strength divided by density of composite) and specific tensile modulus (tensile modulus divided by density of composite) of all composites, it was found that the biocomposites and glass composites were in the same range.

As discussed in Section 4.1, the increase in tensile strength and modulus may be attributed to the fact that due to chemical treatment of hemp fiber, the adhesion between the fiber and the matrix is improved and the interfacial bonding is adequate making it easier for the stress to be effectively transferred from the matrix to the fiber.

Flexural Properties

Flexural strength is a combination of the tensile and compressive strengths which directly varies with the interlaminar shear strength. In flexural testing various mechanisms such as tension, compression, shearing etc. take place simultaneously. In a three point flexural test, the failure occurs due to bending and shear failure. The bending strength and modulus of elasticity of different composites are compared in Figure 4.2.8.



Figure 4.2.8: Comparison of flexural properties of surface treated composites Legend: A= UPE control, B= Untreated pure hemp mat (30 % vol)–UPE, C= Alkali treated pure hemp mat (30 % vol)–UPE, D= UPE-MEKP treated pure hemp mat (30 % vol)–UPE, E= Silane treated pure hemp mat (30 % vol)–UPE, F=E-glass mat-UPE, G=E-glass mat-pure hemp mat-UPE

The flexural properties of biocomposites with surface treated hemp fibers were higher than that of untreated hemp mat composite; also, the flexural properties of all composites were higher than that of neat resin. Comparing surface treated fiber based composites, the modulus of elasticity as well as bending strength of alkali treated, silane treated and UPE-MEKP treated hemp fiber based biocomposites lie in the same range.

As compared to UPE control, the surface treated fiber based biocomposites had a 10-24% enhancement in bending strength, and 140-172% increment in modulus of elasticity. The bending strength of E-glass-UPE composite was 165 % higher, and the modulus of elasticity was 273 % higher as compared to UPE control. The bending strength of Eglass-UPE composite was 139 % higher, and the modulus of elasticity was 54 % higher as compared to untreated hemp mat biocomposite. The hybrid E-glass-hemp mat-UPE composite had a bending strength 70 % higher, and modulus of elasticity 280 % higher than the UPE control. The hybrid E-glass-hemp mat-UPE composite had a bending strength 53 % higher, and modulus of elasticity 57 % higher than the untreated hemp mat based biocomposite. The E-glass-UPE composite had 56 % higher bending strength as compared to hybrid composite of E-glass and hemp mats, but its modulus was same as the hybrid composite within error bars. On comparing specific bending strength and specific modulus of elasticity of all composites, it was found that the biocomposites and glass composites were in the same range. As can be observed from Figures 4.2.7 and 4.2.8, the trends in flexural and tensile properties were similar.

Again, the increment in the flexural properties of biocomposites after surface treatment of the hemp fibers can be attributed to the modifications in the molecular level of the fiber which lead to better interfacial bondage, better adhesion, and effective stress transfer.

Impact Strength

The fibers play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. It is a common observation that with any surface treatment, the flexural and tensile properties of the composite increase, but the impact strength (shown in Figure 4.2.9) will decrease.



Figure 4.2.9: Impact strength of surface treated composites *Legend:* A= UPE control, B= Untreated pure hemp mat (30 % vol)–UPE, C= Alkali treated pure hemp mat (30 % vol)–UPE, D= UPE-MEKP treated pure hemp mat (30 % vol)–UPE, E= Silane treated pure hemp mat (30 % vol)–UPE, F=E-glass mat-UPE, G=E-glass mat-pure hemp mat-UPE

The impact strength of biocomposites with surface treated hemp fibers was higher than that of untreated hemp mat composite; also, the impact strength of all composites were higher than that of neat resin. As compared to neat resin, there was an increment of 8 % in impact strength of untreated hemp fiber based composites, 36 % for alkali treated fibers, 30 % for silane treated fibers, and 21 % for UPE-MEKP treated fibers based biocomposites. On comparing the impact strength of untreated and surface treated biocomposites, it was found that the impact strength of alkali treated fibers was 26 % more than untreated fibers, while that of UPE-MEKP treated fibers was 21 % more than untreated fibers, and that of silane treated fibers was 12 % more than untreated fibers. The impact strength of E-glass-UPE composite was 16.3 times higher than neat resin and 15 times higher than untreated hemp fiber based biocomposite. The hybrid E-glass-hemp mat-UPE composite had impact strength nine times higher than neat resin and 8.27 times higher than untreated hemp fiber based biocomposite. The impact strength of E-glass-UPE composite was 73 % higher than that of hybrid composite of E-glass mats and hemp mats.

Dynamic Mechanical Analysis

Dynamic mechanical methods expose the specimen to periodic stresses. The polymer is



Figure 4.2.10: Typical storage modulus curves of surface treated composites

subjected continuously to forced oscillations, and the applied stress is sinusoidal with a frequency. The deformation of ideal-elastic bodies follows the stress instantaneously but that of viscoelastic polymer experiences a delay. The stress vector is assumed to be a sum of two components: one component is in phase with the deformation; the other is not. Each of these two components possesses a modulus. The real modulus (shear storage modulus) G' measures the stiffness and shape stability of the specimen, whereas the imaginary modulus (shear loss modulus) G' describes the loss of usable mechanical energy by dissipation into heat. The maximum of tan δ as a function of temperature is generally identified as the glass transition temperature T_g , which is dependent on the deformation rate. The damping properties of the material are related to energy absorption. The area below tan delta is function of the absorption of the energy necessary to pass from glassy state to rubbery state.

The typical curves of storage modulus and tan delta for neat resin and composites can be seen in Figures 4.2.10 and 4.2.11 respectively. The storage modulus decreased as a function of temperature, as is commonly observed for composites. At higher temperatures, all biocomposites plateau to the same value of modulus. The storage moduli of surface treated hemp fibers based biocomposites were higher than that of untreated hemp fiber based biocomposite. A comparison of storage moduli of composites at 40 °C was made in Figure 4.2.12. The storage modulus of biocomposites at 40 °C was enhanced by 135-225 % compared to neat resin. As compared to neat resin at 40 °C, there was an increment of 135 % in storage modulus of untreated hemp fiber based composites, 177 % for alkali treated fibers, 190 % for silane treated fibers, and 169 % for UPE-MEKP treated fibers based biocomposites. On comparing the storage modulus of

untreated and surface treated biocomposites at 40 6 C, it was found that the storage modulus of alkali treated fibers was 18 % more than untreated fibers, while that of UPE-MEKP treated fibers was 15 % more than untreated fibers, and that of silane treated fibers was 24 % more than untreated fibers.

The storage modulus of E-glass-UPE composite at 40 $^{\circ}$ C was 307 % higher than neat resin and 74 % higher than untreated hemp fiber based biocomposite. The hybrid E-glasshemp mat-UPE composite at 40 $^{\circ}$ C had storage modulus 225 % higher than neat resin and 39 % higher than untreated hemp fiber based biocomposite. Glass mat based composite had a storage modulus 25 % higher than hybrid hemp fiber-glass based composite at 40 $^{\circ}$ C.



Figure 4.2.11: Typical tan delta curves of surface treated composites

The loss modulus of composites was higher than that of the neat resin. This follows the trend found previously for natural fiber-thermoset composites, where the loss modulus increased after addition of fibers to the plastic.



Figure 4.2.12: Storage modulus of surface treated composites at 40 $^{\circ}$ C *Legend:* A= UPE control, B= Untreated pure hemp mat (30 % vol)–UPE, C= Alkali treated pure hemp mat (30 % vol)–UPE, D= UPE-MEKP treated pure hemp mat (30 % vol)–UPE, E= Silane treated pure hemp mat (30 % vol)–UPE, F=E-glass mat-UPE, G=E-glass mat-pure hemp mat-UPE

Over the entire range of temperature, tan δ was highest for the neat resin due to huge reduction in the storage modulus values at higher temperatures. The lower values of tan δ for the biocomposite made with surface treated hemp fibers suggest that there is less damping in the chemically treated hemp fiber based composites. The tan δ vs. temperature plot for biocomposites as well as E-glass composite is similar. The tan delta curve of all composites shifted towards right as compared to neat resin, but this shift was very big in case of glass based composite. The T_g of the neat resin was 95 0 C. For biocomposites, the T_g increased about 2-5 0 C as compared to neat resin.

Morphology of fiber surface

The micrographs of untreated and surface treated pure hemp fibers are shown in Figure





- a) Untreated pure hemp mat, magnification 1000 X, scale bar 45 µm
- b) Alkali treated pure hemp mat, magnification 1000 X, scale bar 45 µm
- c) Silane treated pure hemp mat, magnification 1000 X, scale bar 45 µm
- d) Unsaturated polyester treated pure hemp mat, magnification 1000 X, scale bar 45 µm

4.2.13. The distribution of the fibers in the hemp mat was random, and uneven. The

micrographs in Figure 4.2.13 focus on single fiber surface. Fibrillation was observed in fibers after surface treatment. This could provide more anchorage for the matrix, and hence improve the strength of the composite. In general, the surface of chemically treated fibers looked different from that of the untreated hemp fiber.

In the biocomposites, the fiber pull out was clearly observed (Figure 4.2.14). Biocomposite with untreated hemp fibers showed poor interfacial bonding between the fiber and matrix, which resulted in relatively clean surface over the pulled out fibers due to greater extent of delamination. In case of untreated fiber based biocomposites, shear failure results in high degree of pull out. The adhesion between the fiber and the matrix was enhanced in biocomposites with surface treated fibers. The fibers were covered with matrix, and the fiber pull out was relatively smaller.



Figure 4.2.14: ESEM micrographs of tensile fractured surfaces of biocomposites from pure hemp mat fibers

- a) Untreated pure hemp mat, magnification 100 X, scale bar 450 µm
- b) Alkali treated pure hemp mat, magnification 100 X, scale bar 450 µm
- c) Silane treated pure hemp mat, magnification 100 X, scale bar 450 µm
- d) Unsaturated polyester treated pure hemp mat, magnification 100 X, scale bar 450 μm

4.2 Effect of surface modification on aligned kenaf fibers

The effects of the following surface treatments on the thermal, mechanical and physical porpoerties of the kenaf-UPE composites are discussed in this section: alkali treatment, γ methacryloxypropyltrimethoxy silane (γ -MPS) treatment, acrylonitrile treatment, and UPE-MEKP treatment.

Analysis of surface treated hemp fibers

The surface treated fibers were characterized with TGA, DSC, and XPS.

Thermogravimetric analysis (TGA)

Thermogravimetric curves for untreated and surface treated hemp fibers are shown in



Figure 4.3.1 and 4.3.2. Table 4.3.1 summarizes the maximum decomposition temperatures for untreated and surface treated kenaf fibers. Up to 200 ⁰C, there was less

than 7 % loss in weight of untreated as well as surface treated kenaf fibers. After the alkali treatment, the temperature at the maximum rate of decomposition of kenaf fiber increased, indicating that the alkali treatment lead to an enhancement in the thermal stability of the hemp fiber. Weight loss of 10% occurred between 272-310 0 C for the untreated and surface treated fibers, while a weight loss of 20% occurred in the range of 313-353 0 C, and weight loss of 30% was observed in range of 340-373 0 C for untreated and surface treated kenaf fibers.



Figure 4.3.2: Derivative thermo-gravimetric analysis (DTGA) of surface treated kenaf fibers

The maximum decomposition temperatures ranged from 364-395 0C for untreated and

surface treated kenaf fibers.

	10% Weight loss (⁰ C)	20% Weight loss (⁰ C)	30% Weight loss (⁰ C)	Max. degradation temperature (⁰ C)
Α	275	323	353	389
В	310	353	373	395
C	294	330	353	379
D	272	313	340	364
E	299	343	371	392

Table 4.3.1: Thermogravimetric results for surface treated kenaf fibers

Legend: A= Water washed kenaf fibers, B= Alkali treated kenaf fibers, C= Acrylonitrile treated kenaf fibers, D= UPE-MEKP treated kenaf fibers, E= Silane treated kenaf fibers

Differential scanning calorimetry (DSC)

The DSC curves for untreated and surface treated fibers expressed in terms of heat flow are shown in Figure 4.3.3. It is observed from Figure 4.3.3 that the crest associated with weight loss due to evaporation of water was found in all fiber samples, and ranged from 6-140 $^{\circ}$ C in kenaf fibers, depending upon the degree of hydrogen bonding interaction. Furthermore, this transition shifted towards the right after surface treatment of the kenaf fiber. It was also observed that fibers had less amount of moisture percentage because they had been pre-dried before any kind of treatment. This ensured that the inherent moisture of the fibers, which is 12-14% of the total fiber weight, was not able to interact with the surface treatments in any way. Therefore, the chemicals of the surface treatments had an opportunity to react with the actual fiber surface and fiber constituents. This would lead to a direct link between the chemicals used and the fiber constituents such as cellulose and hemicelluse. The T_g for lignin and cellulose were not observed by this particular method in DSC. No exothermic peaks were observed from 300 $^{\circ}$ C to 500 $^{\circ}$ C, which are indicative of the thermal stability of the fibers as a function of the treatment.



Figure 4.3.3: DSC of surface treated kenaf fibers

X-ray photon spectroscopy (XPS)

XPS survey scans were taken for untreated as well as surface treated kenaf fibers. These scans revealed the presence of carbon, oxygen, nitrogen, calcium, and silicon in the kenaf fibers. Table 4.3.2 and 4.3.3 show the elemental composition and elemental ratios of the hemp fibers, respectively. Following an hour long treatment with alkali solution it is observed that the carbon content increases, while oxygen and nitrogen content decrease. After silane treatment, there is a marked increase in silicon as well as carbon content, and a decrease in oxygen and nitrogen content. Again, after treatment with the matrix, there is an increase in carbon content, while a decrease in oxygen and nitrogen content. However,

with acrylonitrile treatment, there is a decrease in carbon content and an increase in nitrogen and oxygen content.

Due to the alkali treatment, a part of hemicellulose and lignin might have dissolved, and washed away, leading to a decrease in oxygen content. The increase in carbon and silicon content after silane treatment might be due to the attachment of bulky alkyl group and silicon to the hemp fiber as a result of this treatment. The large increase in carbon content of UPE treated hemp fiber can again be due to the large oligomer molecule of UPE reacting with hydroxyl groups of fiber. Meanwhile, the increase in nitrogen content after treatment with acrylonitrile might be due to grafting of acrylonitrile monomer to the fiber surface.

 Table 4.3.2: Elemental composition of surface treated hemp fibers (from XPS analysis)

	C1s[.314]	N1s[.499]	O1s[.733]	Si2p[.368]	Ca2p[1.927]
Α	73.8	1.55	23.4	0.75	0.5
В	75.9	1.6	21.7	0.3	0.5
С	71.01	2.94	25.32	0.32	0.46
D	80.41	1.48	17.28	0.35	0.48
Е	78.19	1.52	16.63	3.42	0.24

Legend: A= Water washed kenaf fibers, B= Alkali treated kenaf fibers, C= Acrylonitrile treated kenaf fibers, D= UPE-MEKP treated kenaf fibers, E= Silane treated kenaf fibers

Table 4.3.3: Elemental ratios of surface treated hemp fibers (from XPS analysis)

	C/0	C/N	C/Si	C/Ca
Α	3.15	47.61	98.4	147.6
В	3.5	47.44	253	151.8
С	2.8	24.15	221.9	154.37
D	4.65	54.33	229.74	167.52
E	4.7	51.44	22.86	325.79

Legend: A= Water washed kenaf fibers, B= Alkali treated kenaf fibers, C= Acrylonitrile treated kenaf fibers, D= UPE-MEKP treated kenaf fibers, E= Silane treated kenaf fibers

Flexural Properties

The effect of various surface treatments on performance of biocomposites is illustrated in Figure 4.3.4.The bending strength and modulus of elasticity all increase with use of surface treated fibers as compared to raw kenaf fibers; also, the flexural properties of all composites were higher than that of neat resin. The highest values for strength and modulus of the biocomposites are obtained for acrylonitrile treated kenaf fiber based composite.



Figure 4.3.4: Comparison of flexural properties of surface treated kenaf based composites *Legend:* A= UPE control, B= Water washed kenaf (30 % vol)–UPE, C= Alkali treated kenaf (30 % vol)–UPE, D= Acrylonitrile treated kenaf (30 % vol)–UPE, E= UPE-MEKP treated kenaf (30 % vol)–UPE, F= Silane treated kenaf (30 % vol)-UPE, G=Aligned E-glass-UPE

Comparing surface treated fiber based composites, the bending strength of alkali treated, silane treated and UPE-MEKP treated kenaf fiber based biocomposites lie in the same range. However, the modulus of elasticity and bending strength of acrylonitrile treated fibers based composites were 20 %, and 15 % higher than untreated kenaf fiber

biocomposite respectively. As compared to UPE control, the biocomposites had 12-28 % enhancement in bending strength, and 125-175 % increment in modulus of elasticity. The bending strength of water washed kenaf based biocomposite was 12 % higher, and the modulus of elasticity was 128 % higher as compared to UPE control. The bending strength of alkali treated kenaf-UPE biocomposite was 17 % higher, and the modulus of elasticity was 146 % higher as compared to UPE control. The UPE-MEKP treated kenaf-UPE biocomposite had the bending strength 21 % higher, and the modulus of elasticity 176 % higher as compared to UPE control. The silane treated kenaf-UPE biocomposite had the bending strength 21 % higher, and the modulus of elasticity 176 % higher as compared to UPE control. Whereas, the bending strength of acrylonitrile treated kenaf based biocomposite was 28 % higher, and the modulus of elasticity was 172 % higher as compared to UPE control.

The bending strength of alkali treated kenaf-UPE biocomposite was 5 % higher, and the modulus of elasticity was 8 % higher as compared to water washed kenaf based biocomposite. The UPE-MEKP treated kenaf-UPE biocomposite had the bending strength 8 % higher, and the modulus of elasticity 20 % higher as compared water washed kenaf based biocomposite. The silane treated kenaf-UPE biocomposite had the bending strength 11 % higher, and the modulus of elasticity 15 % higher as compared to water washed kenaf based biocomposite.

The bending strength of E-glass-UPE composite was 313 % higher, and the modulus of elasticity was 5.7 times higher as compared to UPE control. The bending strength of E-glass-UPE composite was 270 % higher, and the modulus of elasticity was 194 % higher as compared to water washed kenaf based biocomposite. The E-glass-hemp mat-UPE

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composite had a bending strength 222 % higher, and modulus of elasticity 147 % higher than the acrylonitrile treated kenaf-UPE biocomposite.

On comparing specific modulus of elasticity (modulus divided by the density of composite) of all composites, it was found that the biocomposites and glass composites were in the same range (Figure 4.3.4). Whereas, the specific bending strength of all biocomposites were in the same range, while that of aligned E-glass composites was higher than that of biocomposites.



Figure 4.3.6: Specific Flexural Properties of Kenaf-UPE composites, Legend: A= Water washed kenaf (30 % vol)-UPE, B= Alkali treated kenaf (30 % vol)-UPE, C= Acrylonitrile treated kenaf (30 % vol)-UPE, D= UPE-MEKP treated kenaf (30 % vol)-UPE, E= Silane treated kenaf (30 % vol)-UPE, F-Aligned E-glass-UPE

The increment in the flexural properties of biocomposites after surface treatment of the hemp fibers is again attributed to the modifications in the molecular level of the fiber which led to better interfacial bondage, better adhesion, and effective stress transfer.

Impact Strength

Acrylonitrile treated kenaf fibers based biocomposites also show the highest impact strength compared to other biocomposites (shown in Figure 4.3.5). The impact strength of all composites was higher than that of neat resin. The notched Izod impact strength of biocomposites was enhanced by 330-420 % compared to neat resin. As compared to UPE control, there was an increment of 385 % in impact strength of water washed kenaf fiber based composites, 331 % for alkali treated fibers, 352 % for silane treated fibers, 375 % for UPE-MEKP treated fibers based biocomposites, and 420 % for acrylonitrile treated fibers based biocomposites, it was found that the impact strength of alkali treated fibers was 11% less than untreated fibers, while that of UPE-MEKP treated fibers was 2 % less than untreated fibers, and that of silane treated fibers was 7 % less than untreated fibers. On the other hand, the impact strength of acrylonitrile treated kenaf fiber based biocomposite was 7 % higher than water washes kenaf composite.

The impact strength of E-glass-UPE composite was 57.7 times higher than neat resin and 11.1 times higher than water washed kenaf fiber based biocomposite. The acrylonitrile treated kenaf fiber based biocomposite had impact strength 10.3 times lower than the aligned E-glass based composite.



Figure 4.3.5: Notched Izod Impact strengths of kenaf-UPE composites Legend: A= UPE control, B= Water washed kenaf (30 % vol)-UPE, C= Alkali treated kenaf (30 % vol)-UPE, D= Acrylonitrile treated kenaf (30 % vol)-UPE, E= UPE-MEKP treated kenaf (30 % vol)-UPE, F= Silane treated kenaf (30 % vol)-UPE, G=Aligned Eglass-UPE

Dynamic Mechanical Analysis (DMA)

The typical curves of storage modulus and tan delta for neat resin and composites can be seen in Figures 4.3.6 and 4.3.7 respectively. The storage modulus decreased as a function of temperature, as is commonly observed for composites. At higher temperatures, all biocomposites plateau to the same value of modulus. The storage moduli of surface treated kenaf fibers based biocomposites were higher than that of untreated kenaf fiber based biocomposite.

The acrylonitrile treated kenaf fiber based biocomposite has the highest storage modulus. At 40 0 C, the storage modulus of all composites and biocomposites is greater than that of UPE control (see Figure 4.3.8). The storage modulus of biocomposites at 40 0 C was



Figure 4.3.6: Typical storage modulus curves of surface treated kenaf composites enhanced by 170-270 % compared to neat resin. As compared to neat resin at 40 6 C, there was an increment of 204 % in storage modulus of water washed kenaf fiber based composites, 175 % for alkali treated fibers as well as UPE-MEKP treated fibers based biocomposites, 192 % for silane treated fibers, and 270 % for acrylonitrile treated kenaf fiber based biocomposites. On comparing the storage modulus of untreated and surface treated biocomposites at 40 6 C, it was found that the storage modulus of acrylonitrile treated kenaf fiber was 21 % more than untreated fibers.

The storage modulus of E-glass-UPE composite at 40 $^{\circ}$ C was 6.7 times higher than neat resin and 152 % higher than untreated hemp fiber based biocomposite. Glass fiber based composite had a storage modulus 109 % higher than acrylonitrile treated kenaf fiber based biocomposite at 40 $^{\circ}$ C. The storage modulus of the UPE control and the UPE resin reinforced with kenaf fibers at 40 ^oC follow the same trend as the flexural modulus. At higher temperatures, the storage modulus values of the composites and plastic decreased. Treating the surface kenaf fiber with alkali, silane, acrylonitrile and UPE led to an improvement in the mechanical and thermal properties of the biocomposite.



Figure 4.3.7: Typical tan delta curves of surface treated kenaf composites The loss modulus of composites was higher than that of the neat resin. This follows the trend found previously for natural fiber-thermoset composites, where the loss modulus increased after addition of fibers to the plastic.

The maximum of tan δ as a function of temperature is generally identified as the glass transition temperature T_g, which is dependent on the deformation rate. The damping properties of the material are related to energy absorption.
The area below tan delta is function of the absorption of the energy necessary to pass from glassy state to rubbery state. Over the entire range of temperature, tan δ was highest for the neat resin due to huge reduction in the storage modulus values at higher temperatures. The lower values of tan δ for the biocomposite made with surface treated kenaf fibers suggest that there is less damping in the chemically treated hemp fiber based composites. The tan δ vs. temperature plot for biocomposites as well as E-glass composite is similar. The tan δ curve of all composites shifted towards right as compared



Figure 4.3.8: Storage modulus of Kenaf-UPE composites at 40 ^oC Legend: A= UPE control, B= Water washed kenaf (30 % vol)–UPE, C= Alkali treated kenaf (30 % vol)–UPE, D= Acrylonitrile treated kenaf (30 % vol)–UPE, E= UPE-MEKP treated kenaf (30 % vol)–UPE, F= Silane treated kenaf (30 % vol)-UPE, G=Aligned Eglass-UPE

to neat resin, but this shift was significant in case of glass based composite. The T_g of the

neat resin was 95 0 C. For biocomposites, the T_g increased about 2-5 0 C as compared to

neat resin.

The improvement in properties after surface treatment can be explained by the fact that UPE resin sizing creates a coating on the uneven fiber surface thereby enhancing the scope for improved fiber-matrix adhesion. The resin moves to all the free spaces available in the fiber. When the composite is made, these chemically modified fibers have a better chance to adhere to the matrix. Therefore, the adhesion between fiber and matrix is improved because resin can penetrate well through these fibers, and the wet out is better.

Morphology of fiber surface

The micrographs of untreated and surface treated kenaf fibers are shown in Figure 4.3.9 and 4.3.10. The ESEM micrographs of impact fractured surface of UPE treated kenaf-UPE composite shows smaller fiber pull out and good adhesion between fiber and matrix as compared to water washed kenaf-UPE based biocomposite (Figure 4.3.10). Unmodified composite shows poor interfacial bonding between the fiber and matrix. In case of untreated fiber-polyester composites, shear failure results in high degree of pull out. The ESEM micrographs quantify the claims that adhesion and interface bond between fiber and matrix is improved by surface modifications.



Figure 4.8.9: SEM micrographs of surface treated kenaf fibers

- a) Water washed kenaf fiber, scale bar 20 µm
- b) Silane treated kenaf fiber, scale bar 20 µm
- c) Alkali treated kenaf fiber, scale bar 20 µm
- d) Acrylonitrile treated kenaf fiber, scale bar 20 µm



Figure 4.3.10: SEM micrographs of surface treated kenaf fibers based composites

- a) Untreated kenaf-UPE, scale bar 200 µm
- b) Alkali treated kenaf-UPE, scale bar 200 µm
- c) Water washed kenaf-UPE scale bar 200 µm
- d) Silane treated kenaf-UPE, scale bar 200 µm
- e) Acrylonitrile treated kenaf-UPE, scale bar 200 µm
- f) UPE-MEKP treated kenaf-UPE, scale bar 200 µm

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CHAPTER FIVE: RESULTS ON MATRIX MODIFICATION 5.0 RESULTS ON MATRIX MODIFICATION

5.1 Curing Kinetics

The curing kinetics of the cross linking reaction of polyester resin and styrene were studied by DSC and FTIR. Following are the results obtained from these experiments.

5.1.1 DSC

Dynamic and isothermal experiments were carried out in DSC to study the curing characteristics of the thermoset polyester resin, blends of polyester with initiator methyl ethyl ketone peroxide and promoter cobalt naphthenate.

In order to obtain heat flow curves for curing characterization, some experiments were done under isothermal conditions. The DSC cell was allowed to stabilize at each isothermal condition before introduction of the sample. Once an isothermal experiment was over, the DSC was cooled quickly to room temperature, and when stabilized, the residual heat of reaction of the sample was measured with a constant heating rate until no exotherm is observed. During isothermal curing of thermoset resins, it was assumed that the amount of heat generated is proportional to degree of cure, α (or the extent of reaction) of the sample at that time.

So, the rate of curing, $d\alpha/dt$, was related to rate at which heat is evolved, dQ/dt, by:

$$d\alpha/dt = (1/Q_{tot})(dQ/dt) - (1)$$

Therefore the relative degree of cure was determined by integrating equation (1) from 0 to t:

$$\alpha = (1/Q_{\text{tot}})_0 \int^t (dQ/dt)_T dt \qquad -(2)$$

The total heat for curing reaction (Q_{tot}) was given by:

$$Q_{tot} = Q_{iso} + Q_r \qquad -(3)$$

Where Q_{iso} was the heat generated during isothermal DSC runs at each temperature, and Q_r was the residual heat released when the sample is heated up to a high temperature (200⁰C) at a constant heating rate.

Some samples were also tested in dynamic DSC where, the sample was subjected to a program which went from room temperature to a high temperature (200-350 $^{\circ}$ C) to see the appearance of the exotherm peak on the heat flow curve. This curve also gives Qr.

The plots from two different kinds of DSC experimental runs: isothermal runs, and temperature sweeps, are showcased in Figures 5.5.1 to Figure 5.1.6. The first two figures are curing curves of temperature sweep for UPE control. The temperature sweeps were done at heating rates of 5 $^{\circ}$ C/min and 10 $^{\circ}$ C/min. The rest three figures are isothermal runs for UPE control at 50-160 $^{\circ}$ C. For isothermal runs, the experiment was carried out for at least 2 hours. The data from isothermal runs can also be plotted as dQ/dt versus time. The last figure (Figure 5.1.6) shows the residual plots of the isothermal experiments.

It can be observed from Figure 5.1.1 and 5.1.2 that the exothermic peak for curing of UPE lies between 35 $^{\circ}$ C and 150 $^{\circ}$ C. Therefore, the curing cycle of UPE needs to be

set up in this temperature range. This particular range of temperature has also been used by several authors for the curing of systems containing UPE [1-19].



Figure 5.1.1: Temperature sweep for curing UPE from 25 °C to 160 °C



Figure 5.1.2: Temperature sweep for curing UPE from 35 ^oC to 300 ^oC

Figure 5.1.3, 5.1.4, and 5.1.5 show the isothermal cure plots of UPE at 50 $^{\circ}$ C, 60 $^{\circ}$ C, 70 $^{\circ}$ C, 80 $^{\circ}$ C, 90 $^{\circ}$ C, 100 $^{\circ}$ C, 110 $^{\circ}$ C, 120 $^{\circ}$ C, 130 $^{\circ}$ C, 140 $^{\circ}$ C, 150 $^{\circ}$ C and 160 $^{\circ}$ C. On comparing these curves is observed that the heat flow curve for curing UPE at 50 $^{\circ}$ C has the lowest height. On increasing the temperature, the peak becomes narrower, and increases in height. This indicates that the conversion of the UPE curing reaction is increasing with temperature because the heat flow curves are directly proportional to dQ/dt, which in turn is directly proportional to fractional conversion. The same trend was observed in Figures 5.1.4 and 5.1.5. An interesting point to note from all these figures was that the curves for 80 $^{\circ}$ C and higher, have a very steep initial slope. This behavior again points out that the UPE systems at such temperatures were getting cured very quickly.



Figure 5.1.3: Isothermal DSC cure of UPE at 50, 60, 70, 80 °C



Figure 5.1.4: Isothermal DSC cure of UPE at 90, 100, 110, 120 °C



Figure 5.1.5: Isothermal DSC cure of UPE at 130, 140, 150, 160 °C

Figure 5.1.6 shows the residual heat curves for UPE systems at 50 $^{\circ}$ C, 130 $^{\circ}$ C, 140 $^{\circ}$ C, 150 $^{\circ}$ C, and 160 $^{\circ}$ C. Residual runs were done in order to find out the heat of reaction of any unreacted monomer that might not have consumed during the isothermal run at

a particular temperature. From the Figure 5.1.6, it can be observed that there was no visible exothermic peak in the heat flow curves at all temperatures. The residual temperature sweeps at other temperatures have not been shown. In fact, the residual heat flow curve in most cases was a flat line. Therefore, the residual heat of reaction, if any, was very small. Also, there was very little unreacted monomer present after the isothermal curing had been performed for two hours.



Figure 5.1.6: Residual heat flow (temperature sweep) DSC UPE curing

Figures 5.1.7 and 5.1.8 show the comparison of isothermal heat of reaction and fractional conversion at all temperatures studied in DSC. The curves in these two plots were fitted to obtain some kinetic constants.



Figure 5.1.7: Comparison of isothermal heat of reaction at different temperatures



Figure 5.1.8: Comparison of maximum conversions at different temperatures

The isothermal heat of reaction and the conversion are related to temperature by the following equations:

- $Q_{iso} = \mathbf{a} + \mathbf{b} \mathbf{T} \qquad -(4)$
- $\alpha = c + d T \qquad -(5)$

The value of constants a, b, c and d was found out by plotting Q_{iso} versus temperature, and α versus temperature. Therefore, a = 523.49, b =1.233, c = 0.8222, and d = 0.0012. Thus, from our DSC data,

$$Q_{iso} = 523.49 + 1.233 \text{ T}$$
 -(4)
 $\alpha = 0.8222 + 0.0012 \text{ T}$ -(5)

For an autocatalytic reaction, Kamal and Sourour approximated the DSC cure reaction with the following empirical equation [1].

$$\frac{d\alpha}{dt} = \left(k_1 + k_2 \alpha^m\right) \left(\alpha_u - \alpha\right)^n$$
 -(6)

where m, n are the order of the reaction, k_1 and k_2 are rate constants, and α_u is the maximum conversion.

And
$$k = k_0 \exp(E_a/RT)$$
 -(7)

where E_a is activation energy, R is universal gas constant and T is the absolute temperature. In order to find the values of k_1 , k_2 , k_0 , Ea, m and n, a numerical method has to be used.

From the isothermal plots, it is seen that conversion is directly dependent on temperature. The higher the temperature, the better the conversion. The highest conversion is seen at 160 ^oC. Similar results and conclusions were arrived at by several authors [1-19].

DSC only gives an overall conversion of the UPE curing reaction. But, the UPE system is very complex and the double bonds of UPE and styrene are consumed in

separate events in the curing reaction. Thus, to find out the individual conversions of the UPE and styrene, the curing reaction was studied by the use of FTIR.

5.1.2 FTIR

Isothermal experiments were carried out in FTIR to study the curing characteristics of the UPE system which consisted of 99.7% of unsaturated polyester resin, 1.0% of methyl ethyl ketone peroxide (MEKP) and 0.03% of cobalt naphthenate (CoNap). The isothermal experiments were run at each temperature for four hours. The scans were taken every 5-10 minutes. One drop of reaction mixture was placed between two undrilled NaCl IR crystal windows, 2mm thick. The NaCl plates were then placed inside the IR heated cell.

The major peaks to look forwarding the FTIR were: at 980 CH=CH2 of UPE (due to =CH out of plane deformation), at 910 CH=CH- of styrene (due to =CH out of plane deformation), at 842 C-H of UPE (due to CH_2 out of plane wag), and at 700 C-H of styrene (due to CH out of plane deformation) [20]. The peaks at 980 and 910 are changing due to reaction, but the peaks at 842 and 700 remain constant through out the experiment. Thus, normalized conversion of UPE and styrene can be found by the formulae below:

$$\alpha_{\text{UPE}}(t) = 1 - (Abs(t)_{980} / Abs(t=0)_{980}) (Abs(t=0)_{842} / Abs(t)_{842}) - (8)$$

$$\alpha_{\text{sty}}(t) = 1 - (Abs(t)_{910} / Abs(t=0)_{910}) (Abs(t=0)_{700} / Abs(t)_{700}) - (9)$$

Figures 5.1.9 and 5.1.10 show the FTIR spectra of unreacted UPE and styrene respectively, at room temperature. The peaks mentioned in the above paragraphs can be clearly noted in these two figures.









Figure 5.1.11: FTIR spectra of UPE system at 150 °C at t=0 minutes and t= 250 minutes.

Figure 5.1.11 shows the FTIR spectra of UPE system at $150 \,^{0}$ C at t=0 minutes and t= 250 minutes. At t=0 minutes, when the reaction has not yet started, the peaks of UPE system at 980 and 910 cm⁻¹ look very distinct. However, after t=250 minutes, when the reaction has been completed, the peaks at 980 and 910 cm⁻¹ are no longer visible. The FTIR spectra of UPE system at other temperatures, at the beginning and end of the reaction look similar to Figure 5.1.11, and thus have not been shown.

Figures 5.1.12 through 5.1.23 show the fractional conversion of C=C bonds of UPE as well as styrene at 50 $^{\circ}$ C, 60 $^{\circ}$ C, 70 $^{\circ}$ C, 80 $^{\circ}$ C, 90 $^{\circ}$ C, 100 $^{\circ}$ C, 110 $^{\circ}$ C, 120 $^{\circ}$ C, 130 $^{\circ}$ C, 140 $^{\circ}$ C, 150 $^{\circ}$ C and 160 $^{\circ}$ C respectively. The peak heights were normalized and calculated by using the PerkinElmer Spectrum 2000 software. The values of fractional conversion were calculated using equations 7 and 8 on peak heights of all FTIR spectra taken for four hours.



Figure 5.1.12: Fractional conversion at 50 °C from in situ FTIR study



Figure 5.1.13: Fractional conversion at 60 °C from in situ FTIR study

In Figure 5.1.12, fractional conversions of double bonds of UPE and styrene at different times are shown for an isothermal experiment at 50 $^{\circ}$ C. The conversion curves were very

smooth, and the initial slopes of both curves were very gradual. At the beginning of the reaction, the conversion of UPE was higher than that of styrene, but after 50 minutes, the conversion of double bonds of styrene was more than those of UPE.

In Figure 5.1.13, fractional conversions of double bonds of UPE and styrene at different times are shown for an isothermal experiment at 60 $^{\circ}$ C. Again the curves were smooth, and the initial slope was gradual. As seen in figure 5.1.12, initially the conversion of UPE double bonds were higher, however after 50 minutes, the conversion of double bonds of styrene was more than those of UPE.



Figure 5.1.14: Fractional conversion at 70 ^oC from in situ FTIR study

Figure 5.1.14 shows fractional conversions of double bonds of UPE and styrene at 70 $^{\circ}$ C. It can be seen that the initial slope became less gradual and more steep, compared to Figures 5.1.12 and 5.1.13. Also, the initial conversion of UPE double bonds was higher, however after about 20 minutes; the conversion of double bonds of styrene was more than those of UPE.



Figure 5.1.15: Fractional conversion at 80 ⁰C from in situ FTIR study



Figure 5.1.16: Fractional conversion at 90 °C from in situ FTIR study

Figure 5.1.15 shows fractional conversions of double bonds of UPE and styrene at 80 $^{\circ}$ C. The initial slope of both curves became very steep, compared to Figures 5.1.12, 5.1.13 and 5.1.14. The initial conversion of UPE and styrene double bonds was almost the same. The maximum conversion of styrene was higher than that of UPE, as already discussed by many authors [15-18].

The fractional conversion of UPE and styrene double bonds at 90 0 C is shown in Figure 5.1.16. The initial slope of both curves became very steep, compared to Figures 5.1.12, 5.1.13 and 5.1.14. The initial conversion of UPE and styrene double bonds was almost the same.



Figure 5.1.17: Fractional conversion at 100 ^oC from in situ FTIR study



Figure 5.1.18: Fractional conversion at 110 °C from in situ FTIR study

Figure 5.1.17 shows fractional conversions of double bonds of UPE and styrene at 100 0 C. The initial slope of both curves was very steep, similar to Figures 5.1.15, and 5.1.16. The initial conversion of UPE and styrene double bonds was almost the same. The maximum conversion of styrene was higher than that of UPE.

The fractional conversion of UPE and styrene double bonds at 110 ^oC is shown in Figure 5.1.18. The initial slope of both curves, again, became very steep. The initial conversion of UPE and styrene double bonds was almost the same.



Figure 5.1.19: Fractional conversion at 120 ⁰C from in situ FTIR study

Figure 5.1.19 shows fractional conversions of double bonds of UPE and styrene at 120 0 C. The initial slope of both curves was very steep, similar to Figures 5.1.16, 5.1.17, and 5.1.18. The initial conversion of UPE and styrene double bonds was almost the same. The maximum conversion of styrene was higher than that of UPE.



Figure 5.1.20: Fractional conversion at 130 ^oC from in situ FTIR study



Figure 5.1.21: Fractional conversion at 140 °C from in situ FTIR study

In Figure 5.1.20, fractional conversions of double bonds of UPE and styrene at $130 \,^{\circ}$ C are shown. The conversion of double bonds of styrene was more than those of UPE. At this

temperature, the conversion rates were much higher than at 50 or 60 °C. The curves reached their maxima very quickly, in a matter of minutes.

Figure 5.1.21 shows fractional conversions of double bonds of UPE and styrene at 140 ^oC. The initial slope of both curves was, again, very steep. The initial conversion of UPE and styrene double bonds was almost the same. The maximum conversion of styrene was higher than that of UPE.



Figure 5.1.22: Fractional conversion at 150 ^oC from in situ FTIR study



Figure 5.1.23: Fractional conversion at 160 °C from in situ FTIR study

In Figure 5.1.22, fractional conversions of double bonds of UPE and styrene at different times are shown for an isothermal experiment at 150 °C. The initial slopes of the curves are again, very sharp. The conversion of double bonds of styrene was more than those of UPE. This temperature was 90 °C higher than the one shown in Figure 5.1.12; therefore the conversion rates are much higher. The curve reaches its maxima very quickly.

In Figure 5.1.23, fractional conversions of double bonds of UPE and styrene at different temperatures are shown for an isothermal experiment at 160 °C. The conversion of double bonds of styrene was more than those of UPE. Here again, the temperature was 110 °C higher than the one shown in Figure 5.1.12; therefore the conversion rates were much higher. The maximum of the curves was reached in a few minutes.

Table 5.1.1: Comparison of maximum conversion at different temperatures from FTIR experiments

Temperature (C)	Time (min)	α max UPE	α max STY
50	220	0.87	0.89
60	220	0.88	0.90
70	261	0.89	0.91
80	240	0.90	0.92
90	253	0.90	0.93
100	271	0.90	0.93
110	280	0.91	0.94
120	300	0.91	0.94
130	240	0.91	0.95
140	285	0.91	0.97
150	240	0.92	0.97
160	242	0.92	0.99

In Table 5.1.1, a comparison is made of the maximum fractional conversions of double bonds of UPE and styrene at different temperatures measured at the end of experiment. As expected, conversions are directly depending on temperature, and they increase with increment in temperature. The conversion of double bonds of styrene is more than those of UPE. This has been already reported in the literature [1-19].

5.2 Bioresins and bioplastics

The results of matrix modification experiments by introducing a derivatized vegetable oil in the UPE curing system are described in this section. The first part deals with the results from bioplastic obtained by grafting of acrylonitrile on vegetable oil like soybean, castor, and MSO. The second part discusses the results of bioplastics obtained after grafting soybean polyol with maleic anhydride.

5.2.1 Bioplastics made by grafting of vegetable oils with acrylonitrile

The bioresins formed were characterized by FTIR, TGA, DSC, and the bioplastics developed from the bioresins were analyzed by mechanical, thermal and morphological tests.

FTIR

The bioresin obtained after reacting acrylonitrile with natural oils, were characterized by FTIR to validate the proof of reaction. FTIR scans of pure acrylonitrile, pure vegetable oils, and, modified vegetable oils were taken and compared. Figure 5.2.1 through 5.1.7 show the above mentioned FTIR spectra of acrylonitrile, pure natural oils, as well as grafted oils. In Figure 5.2.1, the spectrum of pure acrylonitrile is seen. The main peaks to be observed are: $C\equiv N$ stretch from 2260-2200 cm⁻¹, C=C stretch of vinyldene from 1665-1620 cm⁻¹, and C-C-C=N bend from 580-530 cm⁻¹. On comparing all of the spectra, it was seen that while the peak at 2200 cm⁻¹ was not found in pure castor oil, pure soybean oil and pure MSO, it could be easily spotted on grafted castor oil, grafted soybean oil and grafted MSO. Also, the peaks at 1620 cm⁻¹ and 530 cm⁻¹ increased in height in grafted MSO, and grafted castor oil, compared to pure MSO and pure castor oil (Figure 5.2.2, 5.2.4, 5.2.5, and 5.2.7).



Figure 5.2.1: FTIR spectra of pure acrylonitrile



Figure 5.2.2: FTIR spectra of pure castor oil



Figure 5.2.3: FTIR spectra of pure soybean oil



Figure 5.2.4: FTIR spectra of pure methyl ester of soybean oil



Figure 5.2.5: FTIR spectra of grafted castor oil



Figure 5.2.6: FTIR spectra of grafted soybean oil



Figure 5.2.7: FTIR spectra of grafted methyl ester of soybean oil

Reaction scheme

Figure 5.2.8 shows the probable reaction scheme of the grafting process of vegetable oil with acrylonitrile. This reaction mechanism has not been confirmed yet, but it might be the way acrylonitrile grafted to the unsaturated backbone of natural oils.



Figure 5.2.8: Scheme showing probable reaction between vegetable oil and reactive monomer, resulting in modified vegetable oil

Notched Izod impact strength

Figure 5.2.9 shows the notched Izod impact strength of the bioplastics. Impact energy is the energy absorbed into the specimen during the impact event divided by its crosssectional area. For the bioplastics, the impact strength increased after addition of biobased oil into the matrix (Figure 5.2.9). The impact strength of plastic containing MSO was 25 % higher than that of neat UPE resin, and impact strength of plastic containing EML is 96 % higher than neat UPE resin.



Figure 5.2.9: Impact strength of the bioplastics

Legend: A= UPE control, B= MSO-UPE, C= GFT 2C-UPE, D= GFT 2B-UPE, E= GFT 2A-UPE, F= GFT 4A-UPE, G= GFT 4B-UPE, H= GFT 5A-UPE, I= GFT 5B-UPE, J= MSO-PBMA-UPE, K= EML-UPE

Flexural properties

Figure 5.2.10 shows the bending strength and the elastic modulus of the bioplastics. The trend in flexural properties was opposite to that of impact strength. All bioplastics had lower bending strength and elastic modulus as compared to neat UPE resin (Figure 5.2.10). The bending strength of plastic containing modified MSO was 20% lower than strength of neat resin, and its modulus was 30% lower than that of neat resin. In the case of biocomposites made with blends of oils and resin, the impact strength increased, but the flexural properties decreased.



Figure 5.2.10: Flexural properties of the bioplastics

Legend: A= UPE control, B= MSO-UPE, C= GFT 2C-UPE, D= GFT 2B-UPE, E= GFT 2A-UPE, F= GFT 4A-UPE, G= GFT 4B-UPE, H= GFT 5A-UPE, I= GFT 5B-UPE, J= MSO-PBMA-UPE, K= EML-UPE, L=AESO-UPE

Biocomposites made with bioresins

Biocomposites were also made by impregnating hemp mat1 and kenaf fibers with blends

of natural oils and UPE.

Impact strength of biocomposites

The impact strength of biocomposite containing hemp fibers in a matrix of bioresin, was 96 % more than that of biocomposite made with hemp fibers and UPE resin (Figure 5.2.11). Similarly, the kenaf based biocomposites gained about 95% strength compared to a biocomposite containing kenaf fibers in UPE matrix.

Flexural properties of biocomposites

However, the bending strength of the hempmat1 biocomposite with bioresin was 20% lower than that of biocomposite with neat resin and the modulus of elasticity for this

biocomposite was 7 % higher than that of biocomposite with neat UPE resin (Figure 5.2.12). In case of kenaf composite too, the bending strength decreased (20%) but the elastic modulus was higher (9%) on introduction of bioresin in the polymer matrix.



Figure 5.2.11: Impact strength of biocomposites containing bioresins Legend: A= UPE control, B= EML-UPE, C= Untreated hempmal1-UPE, D= Untreated hempmal1-EML-UPE, E= Untreated kenaf-UPE, F= Untreated kenaf-EML-UPE



Figure 5.2.12: Flexural properties of biocomposites containing bioresins Legend: A= UPE control, B= EML-UPE, C= Untreated hempmat1-UPE, D= Untreated hempmat1-EML-UPE, E= Untreated kenaf-UPE, F= Untreated kenaf-EML-UPE
Dynamic mechanical analysis of bioplastics

Following the trend of flexural properties, the storage modulus for bioplastics decreased in the same manner as the neat resin. As seen with bending strength and modulus of elasticity, there was a 20–30% reduction in the storage modulus of the bioplastic (figure not shown). This result was expected because vegetable oils are intrinsically low modulus materials because of their molecular structure, and when they are added to the polyester matrix, they lower the stiffness of the resulting material. The glass transition temperature of neat UPE resin, obtained from a tan delta plot was 95 $^{\circ}$ C (figure not shown). For all bioplastics, the *T*g decreased by 10–12 $^{\circ}$ C as compared to neat UPE resin. The glass transition temperatures of plastics based on vegetable oils have been reported from 240 to 80 $^{\circ}$ C in the literature [21-23].

Morphology of bioplastics



Figure 5.2.13: ESEM micrographs of impact fractures surface of bioplastic containing MSO-PBMA-UPE, a) Magnification 2000X, Scale 25 μ m, b) 250 X, Scale 200 μ m

ESEM micrographs of the impact fractured surfaces of the bioplastics show phase



Figure 5.2.14: ESEM micrographs of impact fractures surface of bioplastic containing MSO-UPE, a) Magnification 300 X, Scale 150 µm b) Magnification 2000X, Scale 25 µm

separation (Figures 5.2.13 and 5.2.14). These pictures showed discrete microstructures of the dispersed phase which are scattered throughout the entire surface. SEM images (Figure 5.2.15) of the impact fractured surfaces of plastic samples showed contrast between the neat UPE resin and bioresin (MSO-PBMA-UPE). Phase separation was observed in the bioplastics samples.

From ESEM and SEM images, it was observed that addition of small amount of liquid rubber, PBMA, improved the distribution of the second phase in the bioplastics, by making it more uniformly spread out over the entire surface.



Figure 5.2.15 a): Impact fractured surface of neat polyester resin, scale 20 µm



Figure 5.2.15 b): Impact fractured surface of bioplastic (MSO-UPE-PBMA), scale 20 µm



Figure 5.2.15 c): Impact Fractured surface of bioplastic (MSO-UPE-PBMA), scale 2 µm



Figure 5.2.16: AFM picture of neat unsaturated polyester resin (deflection image, scan size: 5 µm X 5 µm)

AFM images (Figures 5.2.16-18) also validated the existence of two phases in bioplastic samples, and a single phase in neat polyester resin. As can be seen in Fig. 5.2.17, there was uniformity in the distribution of hemispherical shaped craters of the second phase. According to all ESEM, SEM and AFM images, the second phase seemed to be present in craters or holes, which contain crosslinked molecules of the MESO, UPE and polystyrene. They appeared in different sizes, but had the same content. In Figure 5.2.17, the circular parts contain the second phase, which is the methyl ester of soybean oil. This picture specially looked at the smaller circular particles, and represented different sized domains distributed uniformly across the entire matrix. Figure 5.2.18 shows the inside view of one such crater of the second phase. It was different in structure compared to the neighboring UPE resin.



Figure 5.2.17: AFM picture of bioplastic (MSO-UPE-PBMA) (deflection image, scan size: 60 μm X 60 μm)

A lamellar structure was observed inside the circular crater, validating the difference in mechanical properties of the UPE and MESO. The granular looking objects in Figure 5.2.16 (neat UPE), were probably micro gels formed during curing. It can be inferred that the lamellar structured second phase particles, absorbed the impact energy, and thus improved the impact strength of brittle neat polyester resin.



Figure 5.2.18: AFM picture of bioplastic (MSO-UPE-PBMA) (deflection image, 9 µm X 9 µm)

Most unmodified thermosets are brittle materials at ambient temperature. Consequently, most polymers have to be impact modified in order to satisfy end-use requirements for rigid applications. In most cases, the problem can be solved by incorporating rubber domains into the polymer matrix. However, the nature and the size of the elastomeric phase have to be adapted to each polymer matrix [24]. In most cases, it is also desirable to use the minimum amount of rubber modifier, in order not to affect other physical properties such as modulus. The most important characteristics of an impact modifier are: rubber glass transition temperature, rubber domain particle size in the matrix, quality of dispersion, and adhesion to the polymer matrix. Historically, several technical approaches for toughening have been developed, which can be divided into three categories all based on the incorporation of an elastomeric damping phase: elastomer introduction during polymerization, dispersion of a thermoplastic elastomer phase during compounding (uncrosslinked), and incorporation of elastomeric core-shell particles.

Traditionally, elastomeric additives have been used for toughening in the free radical cross-linking of unsaturated polyester resin [25, 26]. But polyester blends with vegetable based oils can also achieve the same purpose. The blends of oils and polyester resin form semi immiscible systems. Here, the oil phase provided the rubbery structures after curing. The oil phase was acting as an impact modifier; hence, it absorbed impact energy and delayed catastrophic failure.

The main toughening mechanisms which have been identified for thermoplastics as well as thermosets are namely: crazing of the polymer matrix, shear yielding of this matrix, and cavitation of the rubber phase. Depending on the polymer system, either a single mechanism or a combination of different mechanisms will be activated [27].

The oil phase of the system consisted of small discrete rubbery particles, with an average size of 5–15 mm. They were randomly distributed in the glassy brittle polyester resin matrix. As reported in the literature about rubber toughened thermosets, these oil phase particles relieved the constraints in the matrix through principal mechanisms of cavitation and forming shear bands [28]. This phase separation phenomenon is similar to that in the low profile mechanism of unsaturated polyester resins.

The miscibility and interfacial properties of additive and resin blends play a major role in the toughening process. Improvements in the fracture impact of thermoset polyester resin can be obtained by dispersing elastomer particles with diameters from 0.5 to 5 mm in the blends. The smaller particles produce more microcracks in the matrix and enhance the fracture-impact energy. The additive is immiscible with the resin and gets phase

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separated from the matrix during curing. Unsaturated polyester resins systems are very reactive materials, which are initially in a liquid state, and become solid after curing. The morphology of the polyester resin systems is decided by thermodynamics and polymerization kinetics. Phase separation brings about a change in polydispersity. Usually, the size of additive particles in the matrix is 1–40 microns. A way to reduce this size is to decrease interfacial tension between two phases. Adding a small percentage of coupling agent like maleic anhydride solves this problem. In this system, poly-(butadiene-maleic anhydride) brought about uniformity in the dispersion, as well as uniformity in sizes of the second phase. Therefore, smaller microcracks were formed in the matrix leading to an increase in impact strength. These microcracks were produced during the large volumetric shrinkage which takes place during polymerization. Microvoids also occurred around the fibers in the composite.

Microvoid formation is an important phenomenon for systems consisting of blends of bioresin and UPE. It compensates for resin shrinkage, but induces intrinsic brittleness. Increased additive content in the UP resin should produce higher impact strength, but if the microvoid content is also enhanced, impact strength is reduced. But in this system, the reverse effect was observed. Even after addition of 20% bioresin into the polyester matrix, the impact strength was improved, with a little sacrifice of modulus of elasticity. Well-dispersed particles in the resin matrix induced homogeneous distribution of internal stresses due to network formation. Thus, low energy impact fractures in the unsaturated polyester resin composites were eliminated by the use of this additive in the system. The addition of the blends of derivatized oils and UPE in the matrix of the natural fibre biocomposites lead to an increase in the impact strength of the composites.

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Thus, using bioresins as polymer matrices provides a two fold benefit over thermoset resins in biocomposites. Their presence can improve the impact strength of the resulting bioplastic, as well as produce a material with higher biobased content.

5.2.2 Bioplastics made by reaction of vegetable oils with maleic anhydride

Bioresins were also made by chemical modification of the vegetable oil (SOPEP) with a functional reactive monomer (MA). The OH content of this polyol is 122 mg of KOH. The pure polyol was characterized using mass spectroscopy (MS), nuclear magnetic resonance (NMR), DSC, TGA and FTIR. The pure maleic anhydride and modified polyol were also scanned under FTIR. The bioplastics developed from the bioresins were analyzed by mechanical, thermal and morphological tests. These results are discussed in this section.

TGA



Figure 5.2.19: TGA of pure soybean oil phosphate ester polyol (SOPEP)

Figure 5.2.19 shows the curves from thermo gravimetric analysis of pure SOPEP. As can be seen from the graph, pure polyol is stable until 200 0 C. The maximum decomposition temperature of pure SOPEP is 400 0 C.

DSC

Figure 5.2.20 shows the curves from differential scanning calorimetry of pure SOPEP. The DSC plot shows no crystallization peaks.



Figure 5.2.20: DSC of pure soybean oil phosphate ester polyol (SOPEP)

FTIR

The modified polyol obtained after reacting maleic anhydride with soybean oil polyol, were characterized by FTIR to validate the proof of reaction. FTIR scans of pure maleic anhydride, pure soybean oil, pure soybean polyol, and, modified polyol were taken and compared. Figure 5.2.21 through 5.2.24 show the FTIR spectra of MA, pure soybean oil,

pure SOPEP, and grafted SOPEP respectively. In Figure 5.2.21, the spectrum of pure MA is seen. The main peaks to be observed are: C=O symmetric stretch from 1765-1725 cm⁻¹ (1772), C=C stretch from 1680-1630 cm⁻¹ (1631), CH out of plane deformation from 730-665 cm⁻¹, C-O-C anti-symmetric stretch from 1280-1070 cm⁻¹, COO- at 1567 cm⁻¹ and OH at 3600 cm⁻¹.

In pure SOPEP (Figure 5.2.23), a high peak of OH is seen at 3467 cm⁻¹ which is not seen in pure soybean oil (Figure 5.2.22). In modified SOPEP (Figure 5.2.24), the OH peak at 3460 cm⁻¹ is small compared to that in pure SOPEP. Other significant peaks seen in modified SOPEP are: C=O at 1725 cm⁻¹, C=C at 1643 cm⁻¹, and COO- at 1547 cm⁻¹.



Figure 5.2.21: FTIR spectra of pure maleic anhydride (MA)



Figure 5.2.22: FTIR spectra of pure soybean oil



Figure 5.2.23: FTIR spectra of pure SOPEP



Figure 5.2.24: FTIR spectra of modified SOPEP

Reaction mechanism

Figure 5.2.25 shows the probable reaction scheme of the grafting reaction of soybean oil phosphate ester polyol with maleic anhydride. This reaction mechanism has not been confirmed yet, but it might be the way maleic anhydride attacks the OH groups of SOPEP, and gets grafted.

DMA of bioplastics

Dynamic mechanical analysis was done on bioplastics with modified polyols GFTSOPEP1, GFTSOPEP2, and GFTSOPEP3. Storage Modulus, tan delta and crosslinking density of the bioplastics were found out. Figures 5.2.26, 5.2.27, and 5.2.28 show the typical storage modulus curves of bioplastics made using GFTSOPEP1, GFTSOPEP2, and GFTSOPEP3. Typical tan delta curves of bioplastics made using GFTSOPEP1, GFTSOPEP2, and GFTSOPEP3 are shown in Figures 5.2.29, 5.2.30, and 5.2.31.



Figure 5.2.25: Proposed reaction mechanism for grafting of SOPEP with MA The bioplastics samples with 30%, 40% and 50% GFTYSOPEP 2 had physical problems and couldn't be tested. The bioplastic samples with 30%, 40% and 50% GFTSOPEP 3 were post-cured. For finding out the T_g of the bioplastic samples with GFTSOPEP2 and GFTSOPSP3, the DMA was carried out from -20 °C to 160 °C. In Figure 5.2.26, the storage modulus of bioplastics samples containing 40% and 50% of GFTSOPEP1, dramatically decreases as compared to samples with 10%, 20% and 30% GFTSOPEP1. The storage modulus of samples with containing 40% and 50% of

GFTSOPEP1 is very low as compared to neat UPE, while the bioplastics containing 10%, 20%, and 30% GFTSOPEP1 (8.5-11.5 GPa at room temperature) have very higher storage modulus compared to UPE control (2.3 GPa at room temperature). Similarly, in the case of GFTSOPEP3 bioplastics, the 10%, 20%, and 30% GFTSOPEP3 samples have very higher storage modulus compared to UPE control (Figure 5.2.27). And, for bioplastics containing GFTSOPEP2, the samples with 10% and 20% GFTSOPEP2 samples have very high storage modulus compared to UPE control (Figure 5.2.28).

Since flexural and tensile moduli follow the same trend as storage modulus, it can be argued that the bioplastics containing 10, 20, and 30% of GFTSOPEP1, 2, and 3 have very high elastic moduli and tensile moduli compared to UPE control.

The glass transition temperatures (T_g) of the bioplastics samples were evaluated from the maxima of the tan delta plots (Figures 5.2.29, 5.2.30, and 5.2.31).



Figure 5.2.26: Storage modulus of bioplastics made with GFTSOPEP1



Figure 5.2.27: Storage modulus of bioplastics made with GFTSOPEP2



Figure 5.2.28: Storage modulus of bioplastics made with GFTSOPEP3



Figure 5.2.29: Tan delta of bioplastics made with GFTSOPEP1



Figure 5.2.31: Tan delta of bioplastics made with GFTSOPEP3

Figures 5.2.32, 5.2.33, and 5.2.34 show the T_g of the bioplastic samples made from all the grafted polyols. From Figure 5.2.32 it was seen that the glass transition temperature increases after addition of grafted soy polyol for 10, 20 and 30% GFTSOPEP1, but for samples with 40% and 50% GFTSOPEP1 was not determined from this experiment. The highest T_g was observed for samples with 20% GFTSOPEP1. In the case of bioplastics with GFTSOPEP2 too, the sample with 20% GFTSOPEP2 registered the highest T_g (Figure 5.2.33). The highest T_g in case of bioplastics containing GFTSOPEP3 was demonstrated by the sample with 20% GFTSOPEP3 (Figure 5.2.34). The T_g of samples with 40% and 50% GFTSOPEP was below the T_g of neat UPE. The low T_g of the samples with 40 and 50% grafted polyol hits at higher flexibility and higher mobility of these samples, which was also physically evidenced.



Figure 5.2.32: Glass transition temperature of bioplastics made with GFTSOPEP1 *Legend:* A=UPE control, B=10% GFTSOPEP1-UPE, C=20% GFTSOPEP1-UPE, D=30% GFTSOPEP1-UPE



Figure 5.2.33: Glass transition temperature of bioplastics made with GFTSOPEP2 Legend: A=UPE control, B= 10% GFTSOPEP2-UPE, C= 20% GFTSOPEP2-UPE, D= 30% GFTSOPEP2-UPE



Figure 5.2.34: Glass transition temperature of bioplastics made with GFTSOPEP3 Legend: A=UPE control, B=10% GFTSOPEP3-UPE, C= 20% GFTSOPEP3-UPE, D= 30% GFTSOPEP3-UPE, E= 40% GFTSOPEP3-UPE, F= 50% GFTSOPEP3-UPE

Figures 5.2.35, 5.2.36, 5.2.37 show the cross link density of the bioplastic samples. An important property from a characterization standpoint of crosslinked networks is the number of crosslinked sites and the molecular weight or length of chain between sites. The crosslink density of bioplastics samples were measured in the rubbery region, 40 0 C above the T_g of the material, by the following formula:

$$v_c = E_i / (3 R^*T) - (10)$$

where, υ_c =crosslink density, R=universal gas constant, T=T_g+40 0 C, and E_i= storage modulus at temperature T.

The change in glass transition temperature is directly proportional to crosslink density. As compared to neat polyester resin, 10, 20 and 30% GFTSOPEP1 samples show a large increment in the cross linking density. With 40 and 50% GFTSOPEP1, cross link density couldn't be found out because their T_g was not in the range on the temperature profile of the DMA test (room temperature to $160^{\circ}C$ @ 4 °C/min). For finding out T_g of these samples, the DMA will have to carried out from a much lower temperature, like -20°C to $160^{\circ}C$. Similarly, in the case of GFTSOPEP2 bioplastics, the 10%, 20%, and 30% GFTSOPEP2 samples have very higher cross linking density compared to UPE control (Figure 5.2.36). And, for bioplastics containing GFTSOPEP3, the samples with 10%, 20%, and 30% GFTSOPEP3 samples have very high cross linking density compared to UPE control (Figure 5.2.37). These results are in coherence with the storage modulus results. The high values of cross link density of the bioplastic samples demonstrate a tightly wound rigid network of the polymer formed by blending bioresins with UPE.

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Figure 5.2.35: Crosslinking density of bioplastics with GFTSOPEP1 Legend: A=UPE control, B=10% GFTSOPEP1-UPE, C= 20% GFTSOPEP1-UPE, D= 30% GFTSOPEP1-UPE



Figure 5.2.36: Crosslink density of bioplastics made with GFTSOPEP2 Legend: A=UPE control, B=10% GFTSOPEP2-UPE, C= 20% GFTSOPEP2-UPE, D= 30% GFTSOPEP2-UPE



Figure 5.2.37: Crosslink density of bioplastics made with GFTSOPEP3 Legend: A=UPE control, B=10% GFTSOPEP3-UPE, C= 20% GFTSOPEP3-UPE, D= 30% GFTSOPEP3-UPE, E= 40% GFTSOPEP3-UPE, F= 50% GFTSOPEP3-UPE

Impact strength of bioplastics

The notched Izod impact strength of the bioplastic samples made from all the grafted

polyols are shown in Figures 5.2.38, 5.2.39, and 5.2.40.







Figure 5.3.39: Impact strength of bioplastics made with GFTSOPEP2 *Legend:* A=UPE control, B=10% GFTSOPEP2-UPE, C= 20% GFTSOPEP2-UPE



Figure 5.2.40: Impact Strength of bioplastics made with GFTSOPEP3 *Legend:* A=UPE control, B=10% GFTSOPEP3-UPE, C= 20% GFTSOPEP3-UPE, D= 30% GFTSOPEP3-UPE, E= 40% GFTSOPEP3-UPE, F= 50% GFTSOPEP3-UPE It is well known that impact strength and storage modulus (DMA) track trends opposite to each other. It was earlier seen that storage modulus of 10%, 20% and 30%

GFTSOPEP1 bioplastic samples was much higher than UPE control, while that of 40% and 50% GFTSOPEP1 samples was much lower than the storage modulus of neat resin (Figure 5.2.26). From Figure 5.2.37 it was observed that impact strengths of 10%, 20%, and 30% GFTSOPEP1 is much lower than neat UPE, while that of 40% and 50% GFTSOPEP1 is higher than that of neat UPE. This trend was also seen in impact strength of bioplastics samples of GFTSOPEP2 and GFTSOPEP3. Thus, the flexible samples containing 40% and 50% grafted polyols were much higher in toughness, and low in stiffness.

Morphology of bioplastics samples



Figure 5.2.41: ESEM micrographs of impact fractures surface of bioplastic containing a) 10%GFTSOPEP1-UPE, Magnification 3000 X, Scale bar 15 μm b) 20% GFTSOPEP1-UPE, Magnification 300 X, Scale bar 150 μm c) 30% GFTSOPEP1-UPE, Magnification 800 X, Scale bar 150 μm d) 40% GFTSOPEP1-UPE, Magnification 285 X, Scale bar 150 μm Figures 5.2.41 and 5.2.42 show the ESEM micrographs of impact fractures surfaces

of bioplastics made from grafted polyols. In all of the bioplastics examined under

ESEM, phase separation was observed between grafted soy polyol rich phase and

UPE rich phase. But the surface features changed with different compositions.



Figure 5.2.42: ESEM micrographs of impact fractures surface of bioplastic containing

- a) 10%GFTSOPEP3-UPE, Magnification 400 X, Scale bar 100 µm
- b) 20% GFTSOPEP3-UPE, Magnification 400 X, Scale bar 100 μm
- c) 30% GFTSOPEP3-UPE, Magnification 600 X, Scale bar 200 μm
- d) 40% GFTSOPEP3-UPE, Magnification 300 X, Scale bar 150 µm

In all of the bioplastics, circular or spherical shapes are observed on the surface. In bioplastics with 10 and 20% modified polyol, there were only circular trenches, where the dispersed phase might be present. The diameter of these circular objects varied greatly, but these were present all over the entire fractured surface. In bioplastics with 30 % modified polyol, circular as well as spherical objects were seen on the surface. In bioplastics with 40 and 50% modified polyol, there are more spherical objects and lesser circular objects. The size of the spherical looking balls also varied over the entire surface, but the distribution was very uniform.

Figures 5.2.43 through 5.2.46 show the AFM images of a sample containing 20% GFTSOPEP3 in a UPE matrix. The images for the GFTSOPEP3 samples show phase separation. The height features are indicators of the second phase in these pictures. The picture focuses on a relatively empty portion of the matrix, where small particles of second phase, which is modified polyol, can be seen, strewn about in the entire area. The morphology of this sample can be clearly observed from TV images of this sample shown below in Figures 5.2.47.

Flatten -25.0

Figure 5.2.43: AFM picture of 20% GFTSOPEP3-UPE (deflection image, 50 µm X 50 µm)



Figure 5.2.44: AFM picture of 20% GFTSOPEP3-UPE (deflection image, 50 µm X 50 µm)



Figure 5.2.45: AFM picture of 20% GFTSOPEP3-UPE (Z scale: 1000 nm, scan size, 16 μ m X 16 μ m)



Figure 5.2.46: AFM picture of 20% GFTSOPEP3-UPE (deflection image, 16 μ m X 16 μ m)



Figure 5.2.47: Picture of 20% GFTSOPEP3-UPE on TV screen

Figure 5.2.44 focused on an area devoid of circular geometries, and looks at second phase particles distributed on the UPE matrix. Figure 5.2.45 showed the top view of a spherical object on the matrix. This object looks like a mercury drop on a solid surface, but is composed of both modified polyol and UPE resin. The concave shape of the spherical object can be easily seen. This is a height image, while Figure 5.2.46 is the deflection image of the same object. The composition of the spherical object was clearly observed here.

Thus phase separated bioplastic samples resulted in changes in mechanical, thermal and morphological characteristics of the polymers formed.

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CHAPTER SIX: RESULTS ON NEW PROCESSING

6.0 RESULTS ON NEW PROCESSING

The results obtained from testing biocomposites manufactured with a new SMC technique are described in this chapter.

6.1 **Biocomposites from SMC**

The new SMC processing for natural fibers can be done on normal commercial SMC equipment with a minor change on the way fibers are fed to the line. In industrial SMC set-ups, the glass fibers rovings are fed to a chopper, and chopped fibers fall onto the carrier film [1-11]. But the natural fibers are not supplied as continuous rovings or yarns, and must be fed to the film in a chopped form. Therefore, in the new set –up, the chopped fibers fall from a calibrated vibratory feeder onto the carrier film, and get drenched in resin flowing from two resin pots, and advance to the compression rollers, and finished product is obtained at the end of the line. The prepreg from SMC line is refrigerated for certain time to reach desirable gelation. The gelled product is then compression molded in variety of molds to get the desired shape.

For glass composites:

The glass fiber polyester resin composites from SMC line were tested for mechanical and thermal properties including, bending strength, modulus of elasticity, storage modulus and tan delta.

The flexural properties of glass composites are shown in Figure 6.1. There was consistency in the data for samples B and C, which represented glass composites made using SMC processing. This was a verification of the fact that SMC process had been optimized for Glass-UPE-CaCO3 system. The bending strength and modulus of elasticity

for samples B and C are almost same at 125 MPa, and 12.5 GPa respectively. The bending strength of glass composites was 32 % more than that of UPE control, while their modulus of elasticity was 370 % more than neat polyester resin.



Figure 6.1: Flexural properties of glass composites Legend: A= UPE control, B= SMC Composite 1, C= SMC Composite 2

The storage modulus of glass fiber–UPE composites at 40 ⁰C is shown in Figure 6.2. Again, both B and C have almost the same values of storage modulus. As compared to UPE control, glass composites had very high storage modulus, (1600 % more than that of neat polyester) which reflected high stiffness of glass fibers.

Figure 6.3 shows a typical dynamical mechanical analysis plot for glass fiber composites. As is common in all thermoset systems, the storage modulus decreased with increasing temperature. The glass transition temperature of this composite was 110 ^oC. As compared to storage modulus, loss modulus was very low over the entire range of test temperature.







Figure 6.3: DMA plot for glass composites

The data for glass fiber composites confirmed that consistent materials had indeed been produced, meaning thereby, that the process parameters also had been optimized. Thus, the next step was development of SMC processed natural fiber composites.
For natural fibers:

The thermal properties of natural fibers used for making biocomposites are shown in Figures 6.4, 6.5 and Table 6.1. Figure 6.4 shows the plots from DSC for five fiber samples. All the fibers showed same transition from -60 °C to 300 °C. A trough was observed in all of the five samples. This ranged from 74 °C for untreated BBSG, 94 °C for untreated green flax core, 106 °C for untreated hemp, 83 °C for silane treated BBSG, to 99 °C for silane treated green flax core. This was because of evaporation of water from natural fibers. This phenomenon is very common for natural fibers. From this data, it was interpreted that after silane treatment of fibers, the water evaporation occurs at a higher temperature as compared to that for untreated fibers.

Figure 6.5 shows TGA plots for the same five fiber samples which were analyzed in DSC. Here too, all fibers showed same kind of transition. The maximum degradation temperatures were found out from the TGA plots and are listed in Table 6.1. The maximum degradation temperature for BBSG and green flax core increased after silane treatment. The percentage weight at 600 ^oC ranged from 18 % for untreated BBSG to 22.5 % for silane treated BBSG and silane treated green flax core. At higher temperatures, big blue stem grass was more stable than flax, as can be seen from the weight % curves.



Figure 6.4: DSC plots of natural fibers used for SMC line Legend: A= Untreated big blue stem grass, B= Untreated green flax core, C=Untreated hemp, D= Silane treated big blue stem grass, E= Silane treated green flax core



Figure 6.5: TGA plots of natural fibers used for SMC line

Legend: A= Untreated big blue stem grass, B= Untreated green flax core, C=Untreated hemp, D= Silane treated big blue stem grass, E= Silane treated green flax core

Samples	Td,max (C)
Α	305.47
В	305.79
С	307.96
D	326.54
E	307.21

Table 6.1: Maximum degradation temperatures for natural fibers

Table 6.2 and 6.3 show the results from XPS of natural fiber samples. These results also depict changes occurring in the fibers after surface treatment. According to Table 6.2, untreated BBSG and green flax core, contain no silicon, while the presence of silicon was found in silane treated BBSG and green flax core. As compared to untreated BBSG and green flax core, silane treated BBSG and green flax core had a decreased concentration level of carbon, and an increased concentration of oxygen.

Table 6.3 shows the ratio of atomic concentrations of C/O, C/Si and C/N in all four samples. The C/O ratio decreased while moving from untreated BBSG to silane treated BBSG, and from untreated flax core to silane treated flax core. Between silane treated BBSG and silane treated flax core, C/Si ratio was higher for silane treated flax core.

	C1s[.314]	N1s[.499]	O1s[.733]	Si2p[.368]
Α	85.77	2.55	11.68	0
В	84.55	1.46	13.99	0
C	84.26	1.24	12.3	2.2
D	81.66	1.51	15.57	1.25

Table 6.2: Atomic concentrations on the surfaces of fibers used for SMC line

Legend: A= Untreated big blue stem grass, B= Untreated green flax core, C=Silane treated big blue stem grass, D= Silane treated green flax core

Legend: A= Untreated big blue stem grass, B= Untreated green flax core, C=Untreated hemp, D= Silane treated big blue stem grass, E= Silane treated green flax core

C/Si	C/O	C/N
	7.34332	33.6353
	6.0436	57.911
38.3	6.85041	67.9516
65.328	5.2447	54.0795
	C/Si 38.3 65.328	C/Si C/O 7.34332 6.0436 38.3 6.85041 65.328 5.2447

Table 6.3: Ratio of atomic concentrations of fibers

Legend: A= Untreated big blue stem grass, B= Untreated green flax core, C=Silane treated big blue stem grass, D= Silane treated green flax core

Due to the large number of composites, the mechanical and thermal properties of these composites have been divided into two groups, and each group is individually discussed. The groups are: composites containing 20% calcium carbonate, and the composites containing no calcium carbonate at all. The properties of the group with CaCO₃ are first discussed.

The tensile strengths and moduli of SMC produced biocomposites containing calcium carbonate, are shown in Figure 6.6. The bars represent tensile strength and the points denote tensile modulus.

The tensile strength of silane treated big blue stem biocomposite is 29% more than strength of untreated big blue stem (BBSG) biocomposite. While, the tensile strength of silane treated big blue stem & green flax core biocomposite, is 25% more than strength of untreated big blue stem & green flax core biocomposite. And, the tensile strength of untreated treated big blue stem biocomposite is 12% more than strength of untreated big blue stem & flax biocomposite. The strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 70% higher than that of untreated BBSG biocomposite. The strength of untreated green flax core biocomposite is 40% lower than that of untreated BBSG biocomposite. The strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 20% higher than that of untreated jute-hemp (20 wt %) hybrid biocomposite. The strength of chopped E-glass composite is 20% higher than that of hybrid of E-glass mat-Hemp composite. The strength of chopped E-glass composite is 170% higher than that of untreated BBSG biocomposite. The strength of E-glass mat (30wt%)-Bioresin (20wt %)- is 40% higher than that of chopped E-glass composite.

In case of tensile modulus, silane treated big blue stem biocomposite, has a modulus value 11.5% more than strength of untreated big blue stem biocomposite. The tensile modulus of silane treated big blue stem & green flax core biocomposite, is 12% more than that of untreated big blue stem & green flax core-UPE-CaCO3. And, the tensile modulus of untreated treated big blue stem biocomposite is 22% more than modulus of untreated big blue stem & green flax core biocomposite is 22% more than modulus of untreated big blue stem & green flax core biocomposite. The tensile modulus of untreated big blue stem & green flax core biocomposite. The tensile modulus of untreated big blue stem & green flax core biocomposite. The tensile modulus of untreated BBSG biocomposite is 65 % higher than that of untreated BBSG biocomposite. The modulus of untreated green flax core biocomposite is 27 % lower than that of untreated BBSG biocomposite. The modulus of untreated jute-hemp (25 wt %) hybrid biocomposite. The modulus of untreated jute-hemp (25 wt %) hybrid biocomposite is 28 % higher than that of untreated jute-hemp (20 wt %) hybrid biocomposite. The modulus of chopped E-glass composite is 18 % higher than that of hybrid of E-glass mat-Hemp composite. The modulus of chopped E-glass composite is 100% higher than that of untreated BBSG biocomposite. The modulus of E-glass mat (30wt%)-Bioresin (20wt %)-is 60% lower than that of chopped E-glass composite.

The highest tensile strength was of the samples containing E-glass mat (30wt%)-Bioresin (20wt %). The chopped E-glass composite and E-glass mat-hemp hybrid biocomposite had second and third highest tensile strengths, respectively. The highest tensile modulus was of the samples containing chopped E-glass. The E-glass mat-hemp hybrid biocomposite and untreated jute-hemp (25 wt %) biocomposite had second and third

highest tensile moduli, respectively. The low values of tensile strengths and moduli of composites containing big blue stem grass and grass flax core were because of short length of these fibers.



Figure 6.6: Tensile properties of biocomposites

Legend: A=UPE Control, B= Untreated BBSG-Caco3-UPE, C= Silane treated BBSG-CaCO3-UPE, D= Untreated flax&BBSG-CaCO3-UPE, E=Silane treated Flax &BBSG-CaCO3-UPE, F= Jute-Hemp(25%wt)-CaCO3-UPE (SMC), G= Untreated core flax-CaCO3-UPE (SMC), H= Jute-hemp(20 wt %)- CaCO3-UPE (SMC), I= E-glassmat-Hemp(20 wt%)- CaCO3-UPE (SMC), J= Chopped glass(20 wt%)-CaCO3-UPE (SMC), K= E-glass mat(30wt%)-Bioresin(20wt %)-UPE

The bending strengths and moduli of elasticity of SMC produced biocomposites containing calcium carbonate, are shown in Figure 6.7. The bars represent bending strength and the points denote modulus of elasticity.

The bending strength of silane treated big blue stem-UPE-CaCO₃, is 15% more than strength of untreated big blue stem-UPE-CaCO₃. While, the bending strength of silane treated big blue stem & flax -UPE-CaCO₃, is 10% more than strength of untreated big blue stem & flax-UPE-CaCO₃. And, the bending strength of untreated treated big blue

stem-UPE-CaCO₃, is 6% more than strength of untreated big blue stem & flax-UPE-CaCO₃. The strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 165% higher than that of untreated BBSG biocomposite. The strength of untreated green flax core biocomposite is 7% lower than that of untreated BBSG biocomposite. The strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 40% higher than that of untreated jute-hemp (20 wt %) hybrid biocomposite. The strength of chopped E-glass composite is 215% higher than that of untreated BBSG biocomposite. The strength of the strength of E-glass mat (30wt%)-Bioresin (20wt %)-is 40% lower than that of chopped E-glass composite.

In case of modulus of elasticity, silane treated big blue stem-UPE-CaCO₃, has a modulus value 21% more than strength of untreated big blue stem-UPE-CaCO₃. The modulus of elasticity of silane treated big blue stem & flax -UPE-CaCO₃, is 17% more than that of untreated big blue stem & flax-UPE-CaCO₃. And, the modulus of elasticity of untreated treated big blue stem-UPE-CaCO₃, is 5% more than modulus of untreated big blue stem & flax-UPE-CaCO₃. The modulus of elasticity of untreated big blue stem UPE-CaCO₃, is 5% more than modulus of untreated big blue stem & flax-UPE-CaCO₃. The modulus of elasticity of untreated jute-hemp (25 wt %) hybrid biocomposite is 102 % higher than that of untreated BBSG biocomposite. The modulus of elasticity of untreated jute-hemp (25 wt %) hybrid biocomposite is 25 % higher than that of untreated jute-hemp (20 wt %) hybrid biocomposite. The modulus of elasticity of chopped E-glass composite is 5 % higher than that of untreated big blue stem (20 wt %) hybrid biocomposite is 126% higher than that of untreated BBSG biocomposite. The modulus of elasticity of chopped E-glass composite. The modulus of elasticity of chopped E-glass composite is 126% higher than that of untreated BBSG biocomposite. The modulus of elasticity of chopped E-glass composite. The modulus of elasticity of chopped E-glass composite is 126% higher than that of untreated BBSG biocomposite. The modulus of elasticity of chopped E-glass composite. The modulus of elasticity of chopped E-glass composite is 126% higher than that of untreated BBSG biocomposite. The modulus of elasticity of chopped E-glass composite is 126% higher than that of untreated BBSG biocomposite. The modulus of elasticity of chopped E-glass composite is 126% higher than that of untreated BBSG biocomposite. The modulus

of elasticity of E-glass mat (30wt%)-Bioresin (20wt %)-is 55% lower than that of chopped E-glass composite composite.

The highest bending strength was of the samples containing E-glass mat-hemp hybrid. The chopped E-glass composite and untreated jute-hemp (25 wt %) hybrid biocomposite had second and third highest bending strengths, respectively. The highest modulus of elasticity was of the samples containing chopped E-glass. The E-glass mat-hemp hybrid biocomposite and untreated jute-hemp (25 wt %) hybrid biocomposite had second and third highest moduli of elasticity, respectively. The bending strengths and moduli of elasticity followed the same trend as tensile strengths and moduli.



☑ BS (MPa) ● MOE(GPa)



Legend: A=UPE Control, B= Untreated BBSG-Caco3-UPE, C= Silane treated BBSG-CaCO3-UPE, D= Untreated flax&BBSG-CaCO3-UPE, E=Silane treated Flax &BBSG-CaCO3-UPE, F= Jute-Hemp(25%wt)-CaCO3-UPE (SMC), G= Untreated core flax-CaCO3-UPE (SMC), H= Jute-hemp(20 wt %)- CaCO3-UPE (SMC), I= E-glassmat-Hemp (20 wt%)- CaCO3-UPE (SMC), J= Chopped glass(20 wt%)-CaCO3-UPE (SMC), K= E-glass mat(30wt%)-Bioresin(20wt %)-UPE

Figure 6.8 shows the impact strength of composites of SMC produced biocomposites containing calcium carbonate. The impact strength of silane treated big blue stem-UPE-

CaCO₃, is 65% less than strength of untreated big blue stem-UPE-CaCO₃. While, the impact strength of silane treated big blue stem & flax -UPE-CaCO₃, is 20% less than strength of untreated big blue stem & flax-UPE-CaCO₃. And, the impact strength of untreated big blue stem-UPE-CaCO₃, is 66% less than strength of untreated big blue stem & flax-UPE-CaCO₃. The strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 86% higher than that of untreated BBSG biocomposite. The impact strength of untreated green flax core biocomposite is 20% lower than that of untreated BBSG biocomposite. The impact strength of untreated jute-hemp (25 wt %) hybrid biocomposite is 20% higher than that of untreated jute-hemp (25 wt %) hybrid biocomposite is 20% higher than that of untreated jute-hemp (20 wt %) hybrid biocomposite. The impact strength of chopped E-glass composite is 83% higher than that of untreated BBSG biocomposite. The impact strength of E-glass mat-Hemp composite. The impact strength of chopped E-glass composite is 1330% higher than that of untreated BBSG biocomposite. The impact strength of the impact strength of chopped E-glass composite. The impact strength of untreated BBSG biocomposite. The impact strength of chopped E-glass composite is 1330% higher than that of untreated BBSG biocomposite. The impact strength of chopped E-glass mat-Hemp composite. The impact strength of chopped E-glass composite is 1330% higher than that of untreated BBSG biocomposite. The impact strength of chopped E-glass composite. The impact strength composite. The impact strength composite. The impact strength composite. The impact strength of chopped E-glass composite is 1330% higher than that of untreated BBSG biocomposite. The impact strength composite. The impact strength com

The impact strengths of composites followed a pattern completely opposite to that of bending and tensile strengths. This is a common behavior for fiber reinforced plastics. The highest impact strength was of the samples containing of E-glass mat (30wt%)-Bioresin (20wt %). The chopped E-glass composite, and E-glass mat-Hemp hybrid composite had second and third highest impact strength, respectively. The impact strengths of composites containing big blue stem grass and grass flax core were very small, because, these fibers very small in length. In particular, the length of BBSG fibers was about 4 mm, and that of green flax core was 1mm.





Legend: A=UPE Control, B= Untreated BBSG-Caco3-UPE, C= Silane treated BBSG-CaCO3-UPE, D= Untreated flax&BBSG-CaCO3-UPE, E=Silane treated Flax &BBSG-CaCO3-UPE, F= Jute-Hemp(25%wt)-CaCO3-UPE (SMC), G= Untreated core flax-CaCO3-UPE (SMC), H= Jute-hemp (20 wt %)- CaCO3-UPE (SMC), I= E-glassmat-Hemp(20 wt%)-CaCO3-UPE (SMC), J= Chopped glass(20 wt%)-CaCO3-UPE (SMC), K= E-glass mat(30wt%)-Bioresin(20wt %)-UPE

The storage modulus of composites of SMC produced biocomposites containing calcium carbonate, are shown in Figure 6.9. The storage modulus of silane treated big blue stem-UPE-CaCO₃, at 40 $^{\circ}$ C, is 17.5% more than that of untreated big blue stem-UPE-CaCO₃. The modulus of silane treated big blue stem & flax -UPE-CaCO₃ is 13 % more than modulus of untreated big blue stem & flax-UPE-CaCO₃. The modulus of untreated big blue stem & flax-UPE-CaCO₃.

treated big blue stem -UPE-CaCO₃ is 26 % more than modulus of untreated big blue stem & flax-UPE-CaCO₃. The modulus of silane treated big blue stem -UPE-CaCO₃ is 32 % more than modulus of silane treated big blue stem & flax-UPE-CaCO₃. The modulus of untreated jute-hemp (25 wt %) hybrid biocomposite is 45 % higher than that of untreated BBSG biocomposite. The modulus of chopped E-glass composite is 105% higher than that of untreated BBSG biocomposite. The modulus of E-glass mat (30wt%)-Bioresin (20wt %) is 55 % lower than that of chopped E-glass composite.

The data for storage modulus followed the same trend as tensile modulus and modulus of elasticity.



Storage Modulus at 40 ⁰C



Legend: A=UPE Control, B= Untreated BBSG-CaCO3-UPE, C= Silane treated BBSG-CaCO3-UPE, D= Untreated flax&BBSG-CaCO3-UPE, E=Silane treated Flax &BBSG-CaCO3-UPE, F= Jute-Hemp(25%wt)-CaCO3-UPE (SMC), G= Untreated core flax-CaCO3-UPE (SMC), H= Jute-hemp(20 wt %)- CaCO3-UPE (SMC), I= E-glassmat-Hemp(20 wt%)- CaCO3-UPE (SMC), J= Chopped glass(20 wt%)-CaCO3-UPE (SMC), K= E-glass mat(30wt%)-Bioresin(20wt %)-UPE

The tensile strengths and moduli of SMC produced biocomposites containing no calcium carbonate, are shown in Figure 6.10. The bars represent tensile strength and the points denote tensile modulus.

The tensile strength of untreated hemp (25 vol %)-UPE biocomposite is 145 % more than strength of untreated henequen (25 vol %)-UPE biocomposite. The tensile strength of untreated kenaf (25vol %)-UPE biocomposite, is 138 % more than strength of untreated henequen-UPE biocomposite. And, the tensile strength of untreated hemp-henequen -UPE biocomposite is 107 % more than strength of untreated henequen (25 vol %)-UPE biocomposite. The strength of untreated kenaf-henequen-UPE hybrid biocomposite is 13 % lower than that of untreated kenaf-UPE biocomposite. The strength of untreated hemphenequen (30 wt %)- bioresin (20 wt%) hybrid biocomposite is 10% lower than that of untreated hemp biocomposite. The strength of untreated henequen biocomposite is 38 % lower than that of neat polyester resin. The strength of untreated hemp biocomposite is 51 % higher than that of neat polyester resin. The strength of untreated kenaf biocomposite is 47 % higher than that of neat polyester resin. The strength of untreated hemp-henequen hybrid biocomposite is 27 % higher than that of neat polyester resin. The strength of untreated kenaf-henequen hybrid biocomposite is 27% higher than that of neat polyester resin. The strength of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 35 % higher than that of neat polyester resin.

In case of tensile modulus, the modulus of untreated hemp (25 vol %)-UPE biocomposite is 104 % more than modulus of untreated henequen (25 vol %)-UPE biocomposite. The tensile modulus of untreated kenaf (25vol %)-UPE biocomposite, is 125 % more than modulus of untreated henequen-UPE biocomposite. And, the tensile modulus of untreated

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hemp-henequen -UPE biocomposite is 120 % more than modulus of untreated henequen (25 vol %)-UPE biocomposite. The modulus of untreated kenaf-henequen-UPE hybrid biocomposite is 24 % lower than that of untreated kenaf-UPE biocomposite. The modulus of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 14 % lower than that of untreated hemp biocomposite. The modulus of untreated henequen biocomposite is 195 % higher than that of neat polyester resin. The modulus of untreated kenaf biocomposite is 500 % higher than that of neat polyester resin. The modulus of untreated hemp-henequen hybrid biocomposite is 550 % higher than that of neat polyester resin. The modulus of untreated hemp-henequen hybrid biocomposite is 550 % higher than that of neat polyester resin. The modulus of untreated hemp-henequen hybrid biocomposite is 402 % higher than that of neat polyester resin. The modulus of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 415% higher than that of neat polyester resin.

The highest tensile strength was of the samples containing untreated hemp fibers. The untreated kenaf biocomposite and untreated hemp-henequen hybrid biocomposite had second and third highest tensile strengths, respectively. The highest tensile modulus was of the samples containing untreated kenaf fibers. The untreated hemp-henequen hybrid biocomposite and untreated hemp biocomposite had second and third highest tensile moduli, respectively. The low values of tensile strengths and moduli of composites containing big blue stem grass and grass flax core were because of short length of these fibers.





Legend: A=UPE Control, B= Untreated henequen (25 vol %)-UPE, C= Untreated hemp (25 vol %)-UPE, D=Untreated kenaf (25vol %)-UPE, E= Untreated hemp-henequen (25 vol %)-UPE, F= Untreated kenaf- henequen (25 vol %), G= Untreated hemphenequen(30 wt %)- Bioresin (20 wt %)-UPE

The bending strengths and moduli of elasticity of SMC produced biocomposites containing no calcium carbonate are shown in Figure 6.11. The bars represent bending strength and the points denote modulus of elasticity.

The bending strength of untreated hemp (25 vol %)-UPE biocomposite is 28 % more than strength of untreated henequen (25 vol %)-UPE biocomposite. The bending strength of untreated kenaf (25vol %)-UPE biocomposite, is 12 % more than strength of untreated henequen-UPE biocomposite. And, the bending strength of untreated hemp-henequen -UPE biocomposite is 7 % less than strength of untreated henequen (25 vol %)-UPE biocomposite. The bending strength of untreated henequen-UPE hybrid biocomposite is 11 % lower than that of untreated kenaf-henequen-UPE biocomposite. The bending strength of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 20 % lower than that of untreated hemp biocomposite. The bending strength of untreated henequen biocomposite is 18 % lower than that of neat polyester resin. The bending strength of untreated hemp biocomposite is 4 % higher than that of neat polyester resin. The bending strength of untreated kenaf biocomposite is 8 % lower than that of neat polyester resin. The bending strength of untreated hemp-henequen hybrid biocomposite is 23 % lower than that of neat polyester resin. The bending strength of untreated hemp-henequen hybrid biocomposite is 23 % lower than that of neat polyester resin. The bending strength of untreated hemp-henequen hybrid biocomposite is 27% lower than that of neat polyester resin. The bending strength of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 17 % lower than that of neat polyester resin.

In case of modulus of elasticity, the modulus of untreated hemp (25 vol %)-UPE biocomposite is 66 % more than modulus of untreated henequen (25 vol %)-UPE biocomposite. The modulus of elasticity of untreated kenaf (25vol %)-UPE biocomposite, is 70 % more than modulus of untreated henequen-UPE biocomposite. And, the modulus of elasticity of untreated hemp-henequen -UPE biocomposite is 16 % more than modulus of untreated henequen (25 vol %)-UPE biocomposite. The modulus of untreated henequen (25 vol %)-UPE biocomposite is 16 % more than modulus of untreated henequen (25 vol %)-UPE biocomposite. The modulus of untreated kenaf-henequen-UPE hybrid biocomposite is 38 % higher than that of untreated kenaf-UPE biocomposite. The modulus of untreated hemp-henequen (30 wt %)- bioresin (20 wt%) hybrid biocomposite is 24 % lower than that of untreated hemp biocomposite. The modulus of untreated hemp biocomposite is 222 % higher than that of neat polyester resin. The modulus of untreated kenaf biocomposite is 230 % higher than that of neat polyester resin. The strength of untreated hemp-henequen hybrid biocomposite is 125 % higher than that of neat polyester resin. The modulus of untreated kenaf-henequen

hybrid biocomposite is 170 % higher than that of neat polyester resin. The modulus of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 145 % higher than that of neat polyester resin.

The highest bending strength was of the samples containing untreated hemp fibers. The untreated kenaf biocomposite and untread hemp-hennequen hybrid biocomposite had second and third highest bending strengths, respectively. The highest modulus of elasticity was of the samples containing untreated kenaf fibers. The untreated hemp biocomposite and untreated kenaf-henquen hybrid biocomposite had second and third highest moduli of elasticity, respectively. The bending strengths and moduli of elasticity followed the same trend as tensile strengths and moduli.







Legend: A=UPE Control, B= Untreated henequen (25 vol %)-UPE, C= Untreated hemp (25 vol %)-UPE, D=Untreated kenaf (25vol %)-UPE, E= Untreated hemp-henequen (25 vol %)-UPE, F= Untreated kenaf- henequen (25 vol %), G= Untreated hemphenequen(30 wt %)- Bioresin (20 wt %)-UPE Figure 6.12 shows the impact strength of composites of SMC produced biocomposites containing no calcium carbonate. The impact strength of untreated hemp (25 vol %)-UPE biocomposite is 50 % less than strength of untreated henequen (25 vol %)-UPE biocomposite. The impact strength of untreated kenaf (25vol %)-UPE biocomposite, is 60 % less than strength of untreated henequen-UPE biocomposite. And, the impact strength of untreated hemp-henequen -UPE biocomposite is 30 % less than strength of untreated henequen (25 vol %)-UPE biocomposite. The impact strength of untreated kenafhenequen-UPE hybrid biocomposite is 9 % higher than that of untreated kenaf-UPE biocomposite. The impact strength of untreated hemp-henequen (30 wt %)-bioresin (20 wt %) hybrid biocomposite is 16 % lower than that of untreated hemp biocomposite. The impact strength of untreated henequen biocomposite is 430 % higher than that of neat polyester resin. The impact strength of untreated hemp biocomposite is 170 % higher than that of neat polyester resin. The impact strength of untreated kenaf biocomposite is 115 % higher than that of neat polyester resin. The impact strength of untreated hemphenequen hybrid biocomposite is 270 % higher than that of neat polyester resin. The impact strength of untreated kenaf-henequen hybrid biocomposite is 135 % higher than that of neat polyester resin. The impact strength of untreated hemp-henequen (30 wt %)bioresin (20 wt %) hybrid biocomposite is 82 % higher than that of neat polyester resin. The impact strengths of composites followed a pattern completely opposite to that of bending and tensile strengths. This is a common behavior for fiber reinforced plastics. The highest impact strength was of the samples containing untreated henequen fibers. This result is not surprising because, it is known that leaf fibers have high toughness and low stiffness, while, bast fibers have low toughness and high stiffness. A hybrid biocomposite of 25 wt % untreated hemp and 10 wt % untreated henequen had second highest impact strength.



Figure 6.12: Impact properties of biocomposites Legend: A=UPE Control, B= Untreated henequen (25 vol %)-UPE, C= Untreated hemp (25 vol %)-UPE, D=Untreated kenaf (25vol %)-UPE, E= Untreated hemp-henequen (25 vol %)-UPE, F= Untreated kenaf- henequen (25 vol %), G= Untreated hemphenequen(30 wt %)- Bioresin (20 wt %)-UPE

The storage modulus of composites of SMC produced biocomposites containing no calcium carbonate, are shown in Figure 6.13.

The storage modulus of untreated hemp (25 vol %)-UPE biocomposite is 22 % more than storage modulus of untreated henequen (25 vol %)-UPE biocomposite. The storage modulus of untreated kenaf (25vol %)-UPE biocomposite, is 30 % more than storage modulus of untreated henequen-UPE biocomposite. The storage modulus of untreated henequen biocomposite is 50 % more than that of neat polyester resin. The storage modulus of untreated hemp biocomposite is 83 % higher than that of neat polyester resin. The storage modulus of untreated kenaf biocomposite is 93 % higher than that of neat polyester resin.

The data for storage modulus followed the same trend as tensile modulus and modulus of elasticity.



Figure 6.13: Storage modulus of biocomposites at 40 ^oC Legend: A= Unsaturated polyester resin, B= Untreated henequen (25vol%)-UPE, C= Untreated hemp (25%vol)-UPE, D= Untreated kenaf (25%vol)-UPE

Figure 6.14 shows the ESEM micrographs of four biocomposite samples made using SMC line. They are: untreated BBSG-UPE-CaCO₃, silane treated BBSG- UPE-CaCO₃, untreated BBSG-green flax-UPE-CaCO₃, silane treated BBSG-green flax-UPE-CaCO₃. All the micrographs are at the magnification of 100 X and scale bar of 450 μ m. The ESEM pictures were taken from the tensile fractured surfaces of these composites. In all the pictures, fiber pull out was observed. The length of the fiber pulled out became shorter after the chemical treatment, as is seen in b) and d).



a) Untreated BBSG-UPE-CaCO3

b) Silane treated BBSG- UPE-CaCO3



c) Untreated BBSG-GFC-UPE-CaCO3

d) Silane treated BBSG-GFC-UPE-CaCO3

Figure 6.14: ESEM micrographs of SMC biocomposites, at magnification of 100 X and scale bar of 450 μm

CONCLUSIONS

Biocomposites have been successfully made using natural fibers, unsaturated polyester resin, and bioresin by sheet molding compound panel processing. These biocomposites were made in the same SMC equipment, which is used to fabricate glass-polyester composites. As a comparison, we also fabricated glass-polyester composites on this equipment. The biocomposites were made on this SMC line after a few minor adjustments. Instead of using the traditional fiber feeding system, we used a screw feeder and a vibratory feeder to supply natural fibers to the set-up. Consistent and repeatable results were obtained showing that this process is consistent and can be used for fabrication of bio-composites.

We have also found that glass-UPE composites have almost same specific strength and modulus as natural fiber-UPE composites. But, with optimization of the entire BCSMC process, use of engineered natural fibers, and inclusion of desirable additives, we seek to achieve best mechanical, thermal and physical properties as comparable as to glass based SMC, and thus replace/substitute glass-UPE composites with natural fiber biocomposites. We aim to use biocomposites sheet molding compound panel processing (BCSMC) for fabrication of biocomposites composed of natural fibers and unsaturated polyester resin. Chopped natural fibers like, hemp, kenaf, pineapple leaf fiber, glass fibers, hybrid fibers, will be used to reinforce unsaturated polyester resin and bioresins in high speed sheet molding compound panel processing. This process would result in continuous and high volume manufacture of biocomposites. As a result, the industrial scale production of biocomposites would be possible. This will lead to accessibility of environmental goods for multiple uses in automotives, buildings as well as in furniture industries.

The newly developed process focuses on large-scale production of biocomposites containing thermoset resins and natural fibers. The equipment used for this processing is the common industrial SMC line. Currently, natural fibers reinforced thermoset composites are not prepared using SMC [12-14]. Our processing aims to use SMC

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process to fabricate these natural fiber-thermoset composites. In commercial SMC set-up, continuous glass fibers rovings are fed to a chopper, which cuts them to a 6 mm size, and they fall on the carrier film, forming a uniform layer of chopped glass fibers. Since, natural fibers cannot be obtained in a continuous from, and making a continuous yarn or roving with these fibers would be a difficult and expensive, we make use of chopped natural fibers in this new process.

Biocomposites have been successfully made using natural fibers, unsaturated polyester resin, and bioresin by sheet molding compound panel processing. These biocomposites were made in the same SMC equipment, which is used to fabricate glass-polyester composites. As a comparison, we also fabricated glass-polyester composites on this equipment. The biocomposites were made on this SMC line after a few minor adjustments. Instead of using the traditional fiber feeding system, we used a screw feeder and a vibratory feeder to supply natural fibers to the set-up. Consistent and repeatable results were obtained showing that this process is consistent and can be used for fabrication of biocomposites.

We have also found that glass-UPE composites have almost same specific strength and modulus as natural fiber-UPE composites. But, with optimization of the entire BCSMC process, use of engineered natural fibers, and inclusion of desirable additives, we seek to achieve best mechanical, thermal and physical properties as comparable as to glass based SMC, and thus replace/substitute glass-UPE composites with natural fiber biocomposites. A novel high volume processing technique named 'biocomposite stampable sheet molding compound panel' (BCSMCP) manufacturing process was developed so as to mimic the continuous sheet molding compound (SMC) as is currently used in making

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glass fiber-polyester resin composites. Natural fiber-unsaturated polyester resin biocomposites were fabricated using the biocomposite stampable sheet molding compound panel' (BCSMCP) manufacturing process.

The natural fibers used for making the biocomposites using this process were: big blue stem grass, green flax core, hemp, henequen, kenaf, coir, flax and jute. For biocomposite fabrication using SMC line, 20% calcium carbonate by weight was added to the matrix as a filler. The natural fiber content was 20% by weight in biocomposites with big blue stem grass, silane treated big blue stem grass, silane treated big blue stem grass and green flax core, and, hemp and jute. Unsaturated polyester resin content in the formulations was 60% by weight. The highest fiber content for biocomposites, achievable using SMC process with UPE and CaCO3 in the matrix was 25 % by weight, achieved in the case of a hybrid of untreated jute and hemp. Hybrid biocomposites were made by combining, hemp with jute mats, hemp with kenaf, hemp with henequen, big blue stem grass with green flax core, silane treated big blue stem grass with silane treated green flax core, hemp with sisal. A hybrid composite was made by combining E-glass mats with hemp. To reduce the amount of UPE in the matrix, 20% by weight of bioresin was added to a hybrid biocomposite with hemp and henequen. The bioresin was a soybean oil phosphate ester polyol modified with maleic anhydride. The mechanical properties of hybrid biocomposites with BBSG and green flax core increased after chemical treatment with 1% methacryloxypropyltrimethoxy silane (γ -MPS). For the SMC samples containing calcium carbonate, the highest tensile strength was of the samples containing E-glass mat (30wt%)-Bioresin (20wt %). For the SMC samples containing calcium carbonate, the chopped E-glass composite and E-glass mat-hemp hybrid biocomposite had second and third highest tensile strengths, respectively. For the SMC samples containing calcium carbonate, the highest tensile modulus was of the samples containing chopped E-glass. For the SMC samples containing calcium carbonate, the E-glass mat-hemp hybrid biocomposite and untreated jute-hemp (25 wt %) biocomposite had second and third highest tensile moduli, respectively. For the SMC samples containing calcium carbonate, the highest bending strength was of the samples containing untreated hemp fibers. For the SMC samples containing calcium carbonate, the untreated kenaf biocomposite and untreated hemp-henequen hybrid biocomposite had second and third highest bending strengths, respectively. For the SMC samples containing calcium carbonate, the highest modulus of elasticity was of the samples containing untreated kenaf fibers. For the SMC samples containing calcium carbonate, the untreated hemp biocomposite and untreated kenaf-henequen hybrid biocomposite had second and third highest moduli of elasticity, respectively. For the SMC samples containing calcium carbonate, the highest impact strength was of the samples containing of E-glass mat (30wt%)-Bioresin (20wt %). For the SMC samples containing calcium carbonate, the chopped E-glass composite, and Eglass mat-Hemp hybrid composite had second and third highest impact strength, respectively. For the SMC samples containing no calcium carbonate, the highest tensile strength was of the samples containing untreated hemp fibers. For the SMC samples containing no calcium carbonate, the untreated kenaf biocomposite and untreated hemphenequen hybrid biocomposite had second and third highest tensile strengths, respectively. For the SMC samples containing no calcium carbonate, the highest tensile modulus was of the samples containing untreated kenaf fibers. For the SMC samples containing no calcium carbonate, the untreated hemp-henequen hybrid biocomposite and untreated hemp biocomposite had second and third highest tensile moduli, respectively. For the SMC samples containing no calcium carbonate, the highest bending strength was of the samples containing untreated hemp fibers. For the SMC samples containing no calcium carbonate the untreated kenaf biocomposite and untreated hemp-henequen hybrid biocomposite had second and third highest bending strengths, respectively. For the SMC samples containing no calcium carbonate, the highest modulus of elasticity was of the samples containing untreated kenaf fibers. For the SMC samples containing no calcium carbonate, the untreated kenaf fibers. For the SMC samples containing no calcium carbonate, the untreated hemp biocomposite and untreated kenaf-henquen hybrid biocomposite had second and third highest moduli of elasticity, respectively. For the SMC samples containing no calcium carbonate, hybrid biocomposite of 25 wt % untreated hemp and 10 wt % untreated henequen had second highest impact strength. For the SMC samples containing no calcium carbonate, untreated henequen biocomposite had the highest impact strength.

6.2 **Biobeams and bioplates from VARTM**

The work on bioplates and biobeams was done in collaboration with Mario Quagliata, and Dr. Rigoberto Burgueño of the Department of Civil and Environmental Engineering. More details on this part of the work can be obtained from Mario's M.S. thesis, "Development and Characterization of Biocomposite Cellular Beams and Plates for Load-Bearing Components", Masters Thesis, Michigan State University, East Lansing, MI; 2003. A brief description of this work is presented in the literature review.

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CHAPTER SEVEN: RESULTS ON DURABILITY

7.0 Results on weathering, moisture absorption, and flammability

The biocomposites were exposed to moisture absorption tests, accelerated weathering and flammability tests to assess their durability. The results of these tests are illustrated in the following sections.

7.1 Moisture Absorption

The samples of bioplastics and biocomposites were subjected to controlled moisture absorption analysis in a humidity chamber. The percent weight gained by the samples was plotted against square root of time. The test was continued until the curve plateued off, and the equilibrium moisture content was achieved. Figures 7.1.1, 7.1.2, and 7.1.3 show the moisture absorption characteristics of the bioplastic samples made from grafted soybean polyol, compression molded hempmat1 samples, and biocomposites manufactured using SMC, respectively.



Figure 7.1.1: Moisture absorption of bioresins



Figure 7.1.2: Moisture absorption of biocomposites of hemp mat



Figure7.1.3: Moisture absorption of SMC manufactured biocomposites

From Figure 7.1.1, it was seen that the bioplastics samples made using 10%, 20%, and 30% GFTSOPEP3, lost weight in the beginning of the experiment until 100 hours,

and then started gaining weight. The equilibrium moisture content for these samples was about 0.06 % moisture. This shows very high hydrophobicity of the samples made using bioresins, because under the same conditions, UPE control would have the equilibrium moisture content of about 1 %. However, the initial weight loss of these bioplastics samples was not understood. Possible explanations for this cause were either leaching out of bioresin from the plastic samples, or presence of any unreacted bioresin in the plastic. To investigate these claims, thermal analysis of the samples was done after their initial exposure to humidity chamber.

Figure 7.1.2 shows the moisture absorption characteristics of biocomposite samples made with untreated and acrylonitrile treated hempmat1ina UPE matrix. The samples started gaining weight right from the beginning of the experiment, and continued doing so until the equilibrium was reached. This tendency was due to hydrophilic nature of the fibers due to the presence of many OH groups in the cellulosic backbone of biofibers. Water molecules get hydrogen bonded to the hydroxyl groups within the fiber cell wall of the biofibers. The equilibrium moisture content for the samples with untreated hemp mat1 was 0.7 %, while that for the one with acrylonitrile treated hempmat1 was about 0.3 % moisture. Thus, it was observed that in addition to increment in mechanical and thermal properties, acrylonitrile treatment leads to less moisture absorption, giving rise to a more stable composite.

In Figure 7.2.3 the plot of weight gain % versus time is seen for silane treated BBSG-CaCO3-UPE and silane treated BBSG & green flax core-CaCO3-UPE, both of which were processed by BCSMCP. It was seen that these biocomposites too started gaining weight right from the beginning of the experiment, and continued doing so until the

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equilibrium was reached. This weight gain has been observed by many authors, and was due to hydrophilic nature of the fibers due to the presence of many OH groups in the cellulosic backbone of biofibers [1-9]. The equilibrium moisture content for the samples with silane treated BBSG was 0.28 %, while that for the one with silane treated BBSG & green flax core was about 0.55 % moisture. Here, the equilibrium moisture content of silane treated BBSG & green flax core, which constitutes 50 % fiber and 50 % core, is more hydrophilic than grass because of the presence of powdered core. This led to higher weight increase in the hybrid biocomposite containing grass and green flax.

Thermal analysis of bioplastics

The bioplastics which lost weight in the initial period of moisture absorption test were thermally investigated by TGA and DSC. These samples were at room temperature before the test. Figure 7.1.4 and 7.1.5 show the plot from TGA analysis and DSC analysis of the bioplastics. Table 7.1.1 shows the maximum degradation temperature of the bioplastics examined by TGA. It was observed that on increasing the amount of bioresin in the bioplastic, the maximum degradation temperature decreased. For a bioplastic with 10% GFTSOPEP3, the maximum degradation temperature was 346 ^oC; for a bioplastic with 20% GFTSOPEP3, it was 341 ^oC; and for a bioplastic with 30% GFTSOPEP3 it was 333 ^oC. The initial decomposition temperature of the bioplastics was measured from Figure 7.1.4. The initial decomposition temperature clearly became lower with an increase of bioresin concentration. The reduction of the initial decomposition temperature is indicative of the existence of unreacted

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constituents. Generally, thermoset polymers having higher cross-link density show higher maximum decomposition temperature.



Figure 7.1.4: TGA of bioplastics



Figure 7.1.5: DSC of bioplastics

Figure 7.1.5 shows the hest flow curves from -60 to 300 ^oC, obtained from DSC. There were no exothermic peaks in the DSC curves of any of the bioplastic samples. This indicated the absence of any unreacted bioresin in the bioplastic samples.

Table 7.1.1: Maximum degradation temperature of the bioplastic	Table	• 7.1.]	l:	Maximum	degradation	temperature	of	the	biopl	astics
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	Maximum decomposition
Sample	temperature (⁰ C)
Α	346.15
В	341.23
C	332.66

Legend: A= 10% Bioresin, B=20% Bioresin, and C=30% Bioresin

7.2 Accelerated weathering

The accelerated weathering of the biocomposite samples was done to study the effect of harsh weather elements on the properties of biocomposites. The exposed samples were evaluated by color test, surface roughness, weight change, and dynamical mechanical analysis. The results from these analyses are presented below.

Color change



Figure 7.2.1: Change in color parameter 'L' over time for biocomposites

Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.2: Change in color parameter 'a' over time for biocomposites *Legend:* A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.3: Change in color parameter 'b' over time for biocomposites *Legend:* A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.4: Change in color parameter 'E' over time for biocomposites *Legend:* A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE

Figures 7.2.1 to 7.2.4 show the change in various color parameters of the biocomposite samples with exposure to accelerated weathering.

In the CIELAB system, there are three parameters for color, L*, a*, b*. The L* axis represents the lightness, whereas, a* and b* axes are the chromaticity coordinates. While +a* is for the red, -a* is for green, +b* for yellow, -b* for blue, and L* varies from 100 (white) to zero (black). The changes in the values of L, a, b were used to calculate dE*, which is the cumulative color change.

The values of dL increased from 0 at beginning of the experiment to 50 for samples exposed for 85 days. This was because the samples were changing color from greenish brown to white after being exposed to UV, rain, condensation and humidity. The combination of water, oxygen and UV irradiation promotes the change of color of these biocomposite samples. The change in L was less pronounced for samples containing BBSG and green flax core which were processed in SMC. The values of da decreased from 0 for all samples. The values of db changed from 0 to positive in case of hemp mat1 composites, but changed from 0 to negative in case of BBSG and GFC biocomposites. The overall color change of the biocomposites, dE, increased from 0 to 50 for all biocomposites. Here again, the dE values of biocomposites with hemp mat1 were higher than those of samples containing BBSG and green flax core which were processed in SMC. The color change of untreated hemp mat1 based biocomposites was slightly higher than that of the acrylonitrile treated hemp mat1 based biocomposite.

Weight change

Figures 7.2.5 shows the plot of percentage weight gain with exposure time for biocomposite samples. All of the samples were gaining weight in the beginning of the weathering test, until about 30 days into the test. The weight gain was due to hydrophilicity of the biofibers.



Figure 7.2.5: Change in weight over time for biocomposites

Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE After 30 days of exposure, the biocomposite samples started losing weight and continued doing so until the end of the exposure time. This weight loss was due to the biodegradation of the biocomposites, which began after 30 days of exposure to weathering. However this weight loss was less than 2% for samples with untreated hempmat1 and silane treated BBSG. The weight loss was less than 5% for biocomposite sample with silane treated BBSG and GFC, while, it was about 1.25% for the sample with acrylonitrile treated hemp mat1. Therefore, it was established that acrylonitrile treatment of the hemp fibers makes them more stable compared to untreated hemp based ones. This could be due to improved adhesion between fibers and the matrix, and better interfacial bonding in a composite made with surface treated fibers. The values of weight loss was highest for the biocomposite containing silane treated BBSG and GFC was again because of presence of core particles which do not have the characteristics as the fibers.

Surface roughness

Figures 7.2.5, 7.2.6, and 7.2.7 show the comparison of surface roughness parameters of the biocomposite samples as a function of exposure time. In general, the roughness of the composite samples increased with exposure time. Of all surface roughness parameters, the values of R_a were smallest, followed by those of R_z , and finally those of R_{max} . The roughness parameters of the samples with untreated hemp mat1 were the highest, followed by samples with silane treated BBSG and GFC, followed by sample
with acrylonitrile treated hemp mat1. The biocomposite samples with silane treated BBSG had the lowest values of surface roughness parameters.



Figure 7.2.6: Change in roughness parameter R_a over time for biocomposites *Legend:* A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.7: Change in roughness parameter R_z over time for biocomposites

Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.8: Change in roughness parameter R_{max} over time for biocomposites Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE

The samples get washed over by water, irradiated by UV, and react with ambient oxygen while in the accelerated weathering chamber. These conditions lead to breaking of the linkages between the fibers and the matrix, and the biocomposite surface stats crumbling. On increasing the exposure time of weathering, this spreads though the thickness of the composite. The reactions involved in the weather degradation are oxidation, reduction, dehydration, hydrolysis, swelling, shrinking, freezing, and cracking.

The cell wall polymers responsible for the moisture sorption of biofibers are: hemicellulose, accessible cellulose, non-crystalline cellulose, lignin, and crystalline cellulose. The cell wall polymers accountable for the ultraviolet degradation are: lignin, hemicellulose, accessible cellulose non-crystalline cellulose, and crystalline cellulose. While, the cell wall polymers responsible for the thermal degradation properties of biofibers are: hemicellulose, cellulose, and lignin. The strength of the biofibers is controlled by crystalline cellulose, matrix (non-crystalline cellulose + hemicellulose + lignin), and lignin. The biological degradation if cell wall of biofibers is influenced by hemicellulose, accessible cellulose, and non-crystalline cellulose.

Dynamic mechanical analysis

Figures 7.2.9 and 7.2.10 show the storage modules at 40 $^{\circ}$ C and the T_g of the biocomposites as a function of the exposure time of weathering, respectively, analyzed by DMA. With the physical and chemical changes occurring in the samples in the course of artificial weathering, it was no surprise to see that the values of storage modules at 40 $^{\circ}$ C and T_g of the biocomposites decreased as the weathering time increased. However, this decrease in modulus was reasonably small, as was seen by other authors earlier [10-12].



Figure 7.2.9: Change in storage modulus over time for biocomposites

Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE



Figure 7.2.10: Change in T_g over time for biocomposites Legend: A=Untreated hempmat1-UPE, B=Acrylonitrile treated hempmat1-UPE, C=Silane treated BBSG-CaCO3-UPE, D= Silane treated BBSG & Green Flax Core-CaCO3-UPE

The highest storage modulus was of the sample containing acrylonitrile treated hemp mat1based biocomposite, followed by untreated hempmat1, silane treated BBSG, and silane treated BBSG & green flax core. The same trend was observed for glass transition temperatures of biocomposites. The overall decrease in T_g for all samples was less than 3 $^{\circ}$ C for the entire exposure time. The overall decrease in modulus of surface treated hemp fibers based biocomposites was 8.6% over the entire weathering exposure time, 10% for silane treated BBSG-UPE, 10.3 % for untreated hempmat1-UPE, and 11.5% for silane treated BBSG and GFC based biocomposite. The change in storage modulus was related to change in weight of these samples.

The tendency of biofibers to absorb moisture causes off-gassing (void formation) during compounding. This results in a molded article with a microstructure having

variable porosity and resembling that of high-density foam. The pores formed will act as stress concentration points which then lead to an early failure of the composite during loading. Another major drawback of using biofibers as reinforcing agent is the high moisture absorption of the fibers due to hydrogen bonding of water molecules to the hydroxyl groups within the fiber cell wall. This leads to a moisture build-up in the fiber cell wall (fiber swelling) and also reduction in the fiber-matrix interface bonding. This is responsible for changes in the dimensions of biofiber-based composites, particularly in the thickness and the linear expansion due to reversible and irreversible swelling of the composites. As a consequence, the fiber-matrix adhesion is weak and the dimensional stability of biofiber-based composites particularly for outdoor applications will be greatly affected.

Nature builds lignocellulosic resources from carbon dioxide and water, and it has all the tools to recycle them back to the starting chemicals. Possible ways of degradation include biological, thermal, aqueous, photochemical, chemical, and mechanical means of degradation. In order to produce cellulose fiber-based composites with a long service life, the degradation processes caused by nature need to be retarded. One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry of the material which is responsible for many of its properties. This can be accomplished by chemical modification of the fibers.

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CHAPTER EIGHT: CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

Environmental and economic consciousness around the world had led to a revolution in interest in the use of renewable and sustainable materials for a variety of applications. Biocomposites, which comprise of biodegradable or synthetic polymers reinforced with natural fibers, are one example of this new class of sustainable products.

The objective of this research was to develop novel low-cost biocomposite panels with desired properties by incorporation of natural fibers in an unsaturated polyester resin matrix so that these biocomposites could then be used in structural and building applications. Three interconnected parts of this project were completed in order to achieve the research objective and included: i) design of engineered natural fibers, ii) modification of the polymer matrix, and iii) development of a new process for continuous production of biocomposites. In addition, the durability of these biobased materials was investigated as well.

Conclusions: I. Engineered Biofibers

The objective of this part of the work was to design the fibers responsible for the reinforcement of the composite. Engineered biofibers with optimized fiber-matrix adhesion are required for good mechanical, thermal and physical properties. The optimum fiber volume fraction was found to be 30% based on a comparison of the mechanical properties of composites with three different volume fractions of fibers.

The surface chemical modifications of natural fibers like alkali treatment, vinyl grafting and treatment with various coupling agents, were some means we employed to improve

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fiber matrix adhesion of the resulting biocomposites. Surface modification also resulted in enhancement of the aspect ratio, improved the wettability of the fibers, and formed a strong interface between polar natural fiber and non polar matrix. An acrylonitrile treatment for the hempmat1 fibers produced a 80% higher increase in tensile strength over untreated hempmat1 fiber based composites, a 430% increase in tensile modulus over the UPE control, and a 53% increase in impact strength over the untreated hempmat1-UPE composite.

The gap between performance of glass based composites and biocomposites was bridged by fabricating a hybrid composite comprising of glass and biofibers. Hybrid biofibers were also custom made to give maximum stiffness and toughness by blending different weight fractions of different untreated or surface treated biofibers (bast, leaf, seed, fruit, or grasses). In terms of specific modulus and strength, glass composites and biocomposites were in the same range. Hybridization of the composite through combining E-glass mats with hempmat1 led to a 23% decrease in tensile strength, a 25% decrease in bending strength, and a 26% reduction in storage modulus at 40 °C compared to a composite of 100% E-glass fiber mat in the UPE matrix. The specific elastic modulus of a biocomposite containing acrylonitrile treated hempmat1 fibers was 70% greater than that of glass-UPE composite. Hybrid biofibers can be designed to meet the desired requirements of a particular application.

From the various experimental results, it can be concluded that the fiber-matrix adhesion for a natural fiber reinforced composite system can be improved by the introduction of chemical bonding at the interface. The effect of increasing the surface area and hence the interfacial friction was not as significant compared to the effect of increasing chemical bonds across the fiber-matrix interface. It can be inferred that the interfacial adhesion is directly related to the amount of reactive functional groups, in this particular case the hydroxyl content on the biofiber surface. When the possibility of chemical bonding is removed from the fiber matrix interface, the interfacial adhesion no longer relates to the interfacial chemistry and becomes a pure mechanical phenomenon.

It is also important to note that the composite properties can also depend on various other factors such as void content and processing conditions. Good interfacial adhesion between the natural fiber and matrix polymer can only be significant when other major factors are optimized.

In summary, biocomposites were successfully made using various natural fibers with different surface treatments. An increase in mechanical and thermal properties is seen for all surface treated fiber based biocomposites most probably due to the formation of covalent bonds across the fiber-matrix interface. The UPE and alkali treatments are low cost treatments, which increase the performances of the resulting biocomposites. The specific modulus of this type of biocomposite is comparable to that of conventional glass fiber-UPE composites. Therefore, these biocomposites have the potential to replace glass-based composites.

Conclusions: II. Matrix Modification

The second major portion of this project was directed at modification of the petroleumbased polymer matrix by incorporation of substantial concentrations of natural oil based resins to increase its biocontent and to improve the matrix properties. Polymerizable bioresins were developed from natural oils by chemical modification (grafting). Bioresins were prepared from vegetable based oils by two methods: i) grafting vegetable oils with acrylonitrile, and ii) grafting maleic anhydride onto the natural polyols.

Utilization of bioresins as polymer matrices provides a two fold benefit over thermoset resins in biocomposites. Their presence can improve the toughness of brittle unsaturated polyester resin as well as produce a material with higher biobased content. The bioresins produced can be 'tuned' to produce a range of bioplastics which varied from high in stiffness to high in toughness by changing the amount of bioresin introduced into the UPE matrix.

The kinetic parameters of the UPE as well as UPE-bioresin curing reaction were investigated by kinetic studies. The fractional conversion of styrene double bonds was higher than those of UPE. The reaction rate of curing increases with an increase in the temperature. 100% conversion was not observed in any of the curing systems because of the entrapment of monomers in crosslinked segments of the matrix however, fractional conversion of styrene double bonds was 99% at a temperature of 160 $^{\circ}$ C, and for UPE double bonds was 92% at a temperature of 160 $^{\circ}$ C.

In all bioplastics, phase separation was observed between the bioresin component and the UPE component. The impact strength of the bioplastics and biocomposites was increased by 100% by acrylonitrile grafting to the natural oils. At the same time, the bending strength reduced by 20% (by adding 20% bioresin). Alternatively, maleic anhydride was grafted onto soybean polyols. The bioplastic samples containing 40% and 50% grafted polyols had higher toughness, and lower stiffness, while bioplastic samples containing 10%, 20%, and 30% grafted polyols had a very high modulus (from 2.8 GPa for UPE control to 10 GPa for 10%GFTSOPEP1 at 40 $^{\circ}$ C) and very low impact strength.

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Conclusions: III. New Processing

The objective of developing a new continuous biocomposites sheet molding compound panel (BCSMCP) processing was to create a process for making biocomposites that could be scaled up to commercialization levels and at the same time take advantage of the unique properties of these biocomposites. The BCSMCP method is a variation of the traditional SMC processing method and was invented to enable high volume industrial scale continuous production of biocomposites using any type of natural fiber, UPE and even bioresins. After the SMC process was optimized for natural fiber-polyester resin composites, several composites made with various untreated and surface treated chopped hybrid fibers, biofibers, calcium carbonate, UPE, and bioresin were successfully produced.

As part of this research, a new fiber feeder was designed to handle biofibers and produce a uniform distribution of chopped biofibers onto the SMC line. A hybrid composite of Eglassmat-hemp was made in the BCSMCP which had a tensile strength only 20% lower than a chopped E-glass composite, a tensile modulus only 8% lower than, and a bending strength only 4% lower, the tensile modulus only 5 % lower than chopped E-glass composite, also made in the BCSMCP. The chopped E-glass composite had the tensile strength 170% higher than untreated BBSG biocomposite, and had a storage modulus 105% higher than untreated BBSG biocomposite at 40 ^oC (untreated BBSG biocomposite had lowest properties of all SMC composites). The new BCSMCP process can easily be integrated to any existing SMC infrastructure supporting the commercialization of biocomposites by SMC.

Conclusions: Durability

The objective of this part of the project was to evaluate performance and longevity of bioplastic and biocomposite samples after exposure to the weather elements. The durability of bioplastics as well as biocomposites were evaluated by moisture absorption tests, accelerated weathering and flammability tests. Moisture absorption tests indicated that the equilibrium moisture content was 0.06 % for these polyester bioplastics, and was less than 0.7 % for biocomposites.

The environmental exposed biocomposites changed color from brown to white as the exposure time increased. The weight of the samples first increased (up to 1% in 30 days), and then decreased (up to 5% in 90 days). Surface roughness of the samples increased with exposure time, and warpage was also observed. The maximum loss in storage modulus after moisture equilibration and subsequent drying was about 12% for a sample containing silane treated BBSG-green flax core hybrid. Surface treated fiber based composites performed better in terms of these characteristics compared to untreated fiber reinforce composites. These tests suggest that biocomposites can be used for interior applications for prolonged periods of time without excessive degradation due to environmental conditions.

General Conclusions

Biocomposites were made using various types of natural fibers with different surface treatments by use of different processing techniques. Hybrid composites were made by combining different varieties of biofibers in different weight fractions, and also by combining biofibers and E-glass fibers. Biocomposites could be produced within 30-80% of the mechanical and thermal properties of glass composites in most cases. Parity in properties could be achieved by hybridization of the biofiber and glass fibers based composites.

The impact strength and modulus could be improved by adding different types of bioresins into the UPE matrix resulting in a phase separated material. Incorporating certain bioresins in the matrix increased the biomass content of composites up to 60%. Continuous production of biocomposites was demonstrated by utilization of the SMC process. Engineered fibers were designed to compete with glass fiber based SMC composites. The mechanical properties of biocomposites do not change significantly on accelerated weathering.

Through the integration of all parts of this project, we were able to develop new cost effective biocomposites for future applications in structural and building industries. Our ultimate goal of replacing existing glass fiber-polyester composite panels currently used in the housing industry by biocomposites has been demonstrated. Biocomposites have the potential to replace glass fiber-UPE composites.

8.2 FUTURE WORK

We have been successful in making structural biocomposites for future applications, however, some more additional research needs to be completed before this technology is placed in widespread use.

The adhesion between fibers and the matrix must be improved by surface treatment. Alternative surface treatments such as acetylation, bleaching, UV/plasma, and microwave should be investigated and optimized for each type of natural fiber in the future.

Bioresins having different chemistries can be developed from natural oils. These bioresins then must be polymerized by blending with synthetic resins or by themselves to increase the amount of 'green' material in a thermoset composite. Further experiments need to be aimed at studying in detail the behavior of the second phase, the actual mechanism of toughening and control of the dispersed phase in the bioresin-UPE systems. The fracture studies must be performed in further detail to find the critical parameters like fiber-matrix adhesion and fracture dynamics. Alternative strategies to improve the toughness of brittle UPE resins by adding rubbery particulates also should be investigated. The curing times of the UPE or bioresin-UPE systems also must be optimized to get maximum conversion in shortest amounts of time. There should be some solutions to the volume shrinkage problems of the UPE and bioresin-UPE systems. The amount of renewable and biodegradable materials in the biocomposites and bioplastics must be increased to at least about 60% of the entire weight of the product. One option to consider would be the incorporation of a small volume fraction of economic nanoparticles into the biofiber-bioresin-UPE system, to make a bio-nano-composite, with the added advantages of increased stiffness, strength, and heat resistance; and decreased moisture absorption, flammability, and permeability.

An effort must be made to study in detail the various parameters that affect the properties of composites in hybrid fibers systems. A universal model needs to be developed which allows for inclusion of natural fiber properties to estimate the theoretical values of the biocomposite properties.

A cost analysis for the biocomposite sheet molding compound panel processing should be performed, and compared with conventional SMC technique processing glass-UPE composites.

Finally, collaboration with our industrial partners, FlaxCraft Inc. and Kemlite Chemical Company Inc. needs to be enhanced to promote and commercialize this technology in housing panel applications.

