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DESIGN AND ENGINEERING OF ECO-FRIENDLY BIOCOMPOSITES FROM HEMP FIBER AND LOW COST NOVEL SOY PROTEIN BASED BIOPLASTICS

presented by

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has been accepted towards fulfillment
of the requirements for

M.S. degree in Materials Science

Lawrence T. Drzal
Major professor

Date 10/31/02

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution

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By

David D. Hokens

A THESIS

Submitted to
Michigan State University
In partial fulfillment of the requirements
For the degree of

MASTER OF SCIENCE

Department of Material Science Engineering

2002

ABSTRACT

DESIGN AND ENGINEERING OF ECO-FRIENDLY BIOCOMPOSITES FROM HEMP FIBER AND LOW COST NOVEL SOY PROTEIN BASED BIOPLASTICS

By

David D. Hokens

The study of developing new structural materials from non-petroleum based materials is investigated with a focus on developing materials from soy protein. A biocomposite material is formed through reinforcement with hemp fiber. This investigation explores processing effects, effect of surface treatment of reinforcing fibers, and environmental effects on the composite material. The development of a biobased material is presented as well as the effects of processing and optimization of the process parameters.

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Chapter 1

Introduction

1.1) Research Goal/Problem Statement

Develop a biobased composite material for structural applications.

1.2) Motivation for research

The increase in the world's population as well as the development of a global community have attributed to an increase in CO_2 emissions. As new technologies are developed to answer the demands from consumers for more products that are less expensive, the ecological impact of this increased consumption of durable goods is beginning to be felt and are requiring solutions to mitigate these potential problems.

Consumption of energy and generation of disposable goods based on fossil fuels have raised concerns over their ecological impact. Fossil fuel based materials also have associated issues; first there is the problem of having a large amount of non-biodegradable plastic waste. Second incineration of these materials leads to a large release of CO_2. With the world's oil reserves decreasing, the rising dependence on fossil fuels raises concerns. What will happen when the reserves run dry? Steps need to be taken to reduce the ramifications of fossil fuel dependence to minimize societal impacts when the reserves run low. The flow of disposable goods will decrease with increasing price until the use of petroleum-based materials is not economical. The same increase in prices of energy and fuel will take place unless there is an alternative technology to replace the dependence on fossil fuel.

The awareness of decreasing oil reserves has raised the questions: What are the potential alternatives? Where and what are the potential new sources for durable goods materials? Universities and government research labs are now beginning to explore replacement materials for the manufacture of durable goods.

1.3) Soy background

This study is focused on finding sustainable, inexpensive materials that will be useful for structural applications. One possible solution is composite materials derived from biobased resources. This study investigates combining a soy plastic as a polymer matrix with a bio-fiber for reinforcement to produce a structural biocomposite. There are a number of synthetic biodegradable polymers that are derived from fossil fuels, although they tend to be high priced and of limited usefulness as a structural material. Soy protein has been shown to be processable into a biobased plastic. Soy protein comes from the soybean, which is made up of about 38% protein. The abundance of soybeans in the U.S. allows for an ample opportunity to process soy protein into useful materials and find a suitable replacement to fossil fuel derived products.

Protein types	Cost ($/lb.)	Percentage protein
Soy flour	0.15	52
Soy concentrate	0.77	65
Soy isolate	1.50	90

Table 1.1 Price and percentage of soy protein sources.

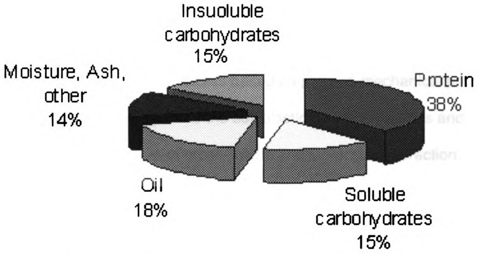


Figure 1.1 Constituents of soybean on a percent basis.

Soy plastic is based on polymerizing soy proteins, which are readily available in nature. Proteins are large macromolecules that are composed of amino acids. Soybean protein is composed primarily of two different proteins: glycinin, with a molecular weight in the range of 330,000 to 360,000 D and conglycinin, which have a molecular weight of 180,000 to 200,000 D. The glycinin protein is composed of 12 primary subunits each with a molecular weight in the range of 20,000 to 37,000 D. The conglycinin protein is composed of three primary subunits with molecular weights in the ranges of 57,000 to 83,000 D. These proteins are polymers of amino acids, pre-polymers of the large polymer chain that they will form. This limits the number of molecular structures, which can be formed from this source, and consequently the mechanical properties of the soy plastic.

The presence of these large, naturally occurring protein molecules gives rise to a unique opportunity to engineer these molecules and create new materials. The prospect of crosslinking protein is a complex task. The task of modeling the molecular interactions, and verifying what occurs during crosslinking is difficult at the molecular level. An alternative process is to conduct structure-processing-property studies based on physico-mechanical property measurements to gain insight into the soy plastic. Higher modulus and strength can be related to the degree of cross-linking and molecular interaction.

There is published information on the properties of soy protein, such as the degradation temperature of each protein, or the percentage of each protein that makes up the total soy concentration of the soybean. However much of this research has been focused on determining how the protein works as a nutrient and has been studied for food science purposes.

Soy protein is readily available from a number of grain processing companies in various forms: soy isolate, soy concentrate, and soy flour. The difference between these soy variations is the percentage of protein. The isolated protein is approximately 90% pure, the concentrate is about 65% and the flour is about 50% soy protein. The isolate and concentrate are processed using an acid-base extraction to remove the protein from the carbohydrate fraction as well as the soybean oil. The soy flour however, is soybean that is de-hulled, ground, and the oil is removed to produce the defatted soy flour. From these raw materials the processing of the proteins begins in order to produce a soy protein polymer. However, there is a large difference in price between the three different materials, largely due to the difference in processing.

There are also differences in the soy product. Soy protein is capable of reacting with itself and crosslinking, however it is very stiff and very brittle, and has little strength. Addition of plasticizers to the soy protein allows it to become more flexible and have increased strength. However the increased strength comes as a trade off, a reduction in modulus. Commonly used plasticizers for modification of the soy protein are glycerol, ethylene glycol and water.

The products in this niche market that these materials will compete with are on the order of twenty or thirty cents a pound. The raw soy protein is not this inexpensive by itself. The addition of wheat starch, as an inexpensive filler aids in plasticizing the proteins, and reduces the cost of the end product. Soy polymers have been used for applications such as biodegradable soy adhesives for making particleboard. Moisture absorption of the soy protein plays a role in potential applications as well. When exposed to moisture the adhesive properties are lost.

The focus of developing a biocomposite is to develop a material that is composed of soy plastic and a natural fiber reinforcement.

1.4) Fiber

A composite is a complex material, in which two or more distinct structurally complementary substances are combined to produce a composite material with structural or functional properties not present in any individual component. Examples of composites are wood or fiberglass. Composite materials have been in existence since biblical times. However, the use of synthetic reinforcing fibers such as glass or carbon with petroleum-based plastics is a relatively new development. Fiber reinforcement of plastics has created high strength, low weight materials that have been used in many different industries. Aerospace industries have used composites for creating lighter aircraft. The automotive industry has used composites in applications from exterior body parts to under the hood applications. The lightweight and corrosion resistance of polymer-reinforced materials has been beneficial for these applications.

There are many different types of reinforcements to add to polymer matrixes that improve the performance of the polymer. For different applications different fillers or reinforcements can be very beneficial. They can decrease the cost of the material and potentially increase the performance of the composite. In an effort to decrease material sensitivity to temperature, it may be appropriate to blend a material with a ceramic filler, such as alumina to calcium carbonate.

Carbon and glass fibers are very common synthetic fibers. Carbon fibers are very good for high stiffness, high strength, low density, high temperature applications, where performance is the overlying goal and cost is not. Glass fiber is very commonly used in a whole host of applications from car bodies to shower paneling. Glass is probably one of the most widely used fibers for reinforcement, with strength between 2 and 3.5 GPa and a modulus of 70 GPa.

For the sake of improving the properties of the soy polymer that is being focused on in this study and keeping in line with the focus of making a material that is agro-based the choice for a reinforcement was to choose a natural fiber, hemp in this case, which has a modulus of 55GPa and a strength of 0.6GPa.

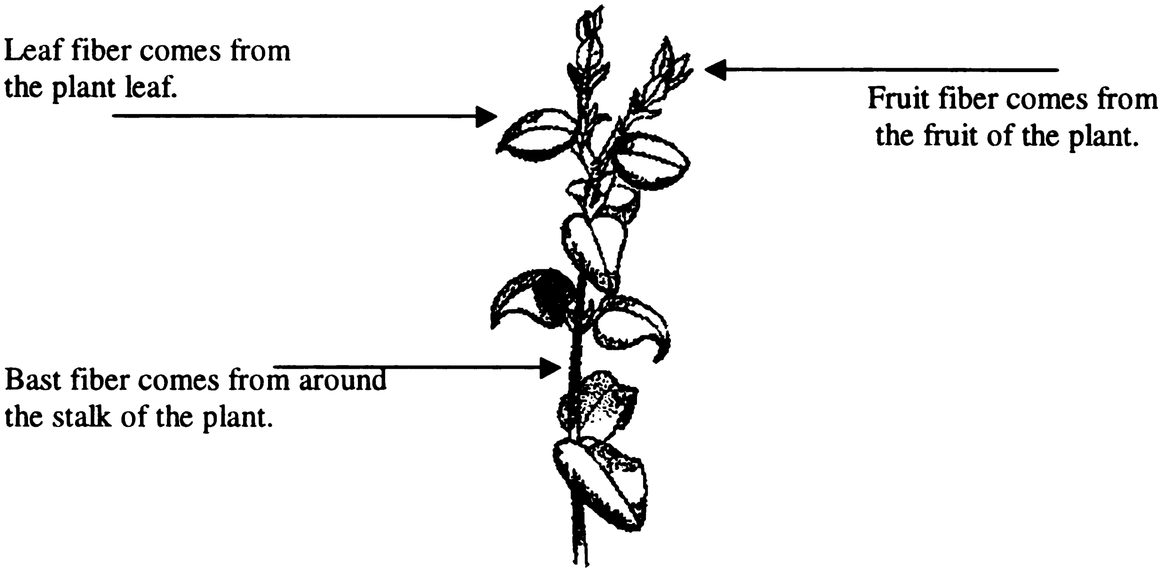


Figure 1.2 Description of natural fiber source.

Figure 1.1 illustrates a typical plant structure and the location of each type of fiber. One of the most common natural fibers is cotton, a fruit fiber. Leaf fibers that are considered possible reinforcements include henequen (sisal) and pineapple leaf fiber. The third type of natural fiber is the bast fibers, which come from around the stem of the plant. Common bast fibers are hemp, flax, kenaf, wheat straw, and corn.

Natural fibers have been used in different applications from clothing to adobe. Research has recently pushed the envelope into finding materials that are less disruptive to the environment. Natural fiber composites first came of-age when lumber manufacturers starting looking for applications of sawdust and discarded wood chips. The invention of Orientated Stand Board (OSB) was basically an application of waste wood fiber. When wood chips were held together with an adhesive the end product became a viable source of building materials and brought about the introduction of biocomposties. Wood fiber paved the way as the first cellulose fiber to be incorporated into a polymer matrix. Cellulose fiber as a reinforcement from trees is a by-product of the lumber industry and secondly the growth cycle of a tree is on the order of 30 years. The use of trees as a source for fibers is not practical since there are more valuable uses for trees.

Natural fibers from non-woody plants are very attractive as alternative sources for cellulose fibers. Agriculture refuse such as corn stubble and wheat straw are attractive commodities in that the wood fiber is attractive; it is currently a waste product in the effort to produce corn and wheat. Research is under way to attempt to use these waste materials as fiber reinforcements in polymers. Although the potential for these fibers is high there is still a great deal of work to do before they are proven.

Research efforts are also being placed into developing natural grasses as a fiber source. All of the above mentioned sources are perennial crops that have 90 to 120 day growth cycles that improve their availability.

Hemp, Kenaf, Flax, Henequen, and Cotton are established fibers that have an active crop base for production that are grown solely as a source for fiber and oil. Cotton fiber has been investigated for reinforcement, as there is a lot of waste fabric that could be used as an acceptable source of reinforcement in composites. Flax fiber has been produced for years as the source of linseed oil, which is used for many applications. Hemp, Kenaf and Henequen fibers each also have traditional applications as well but new interest has been found of late in these fibers for composite applications.

Bast fibers such as the hemp and kenaf are very stiff fibers and when incorporated into the polymer matrix improve the strength and stiffness of the material. The weakness of bast fibers is their lack of impact strength. Leaf fibers on the other hand perform very differently when incorporated into a polymer matrix. Leaf fibers offer very good improvement in impact strength but do not offer the improvement in strength and modulus that bast fibers provide.

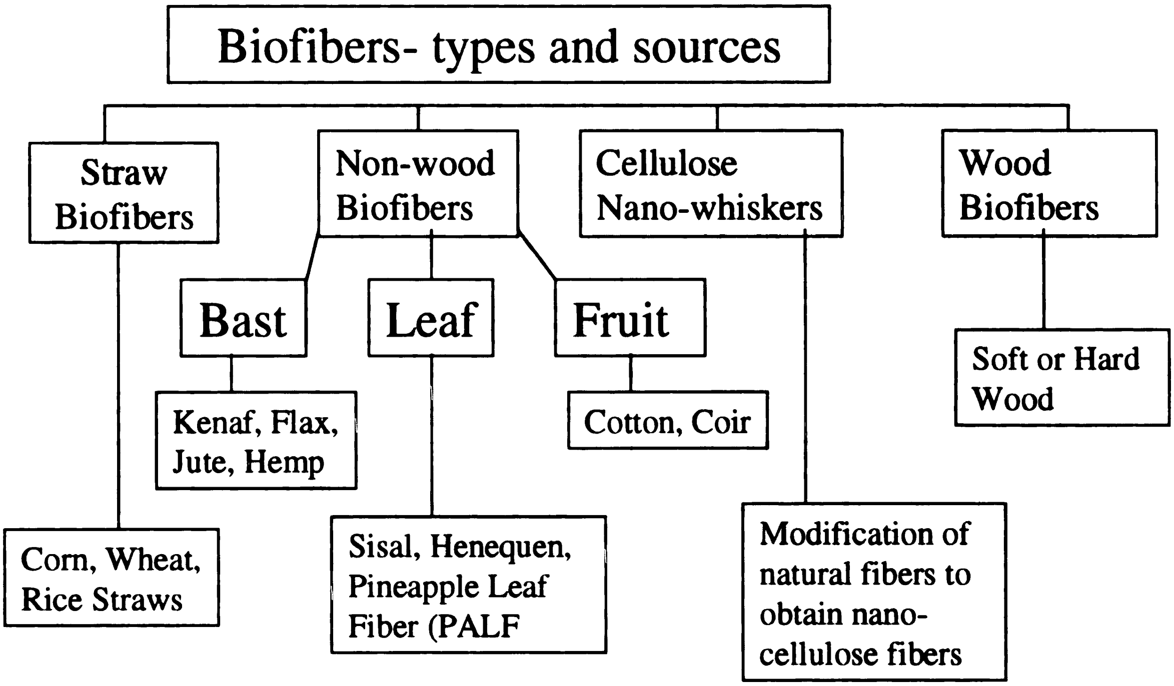


Figure 1.3 Classification of natural fibers.

Of course the standard for performance of the natural fibers is whether they improve the performance of the material as much as their synthetic counter-part would. Glass fiber offers a very good improvement in strength and modulus and impact strength when added to polymers and is reasonable in cost as well. Hybridization of the natural fibers offers the potential for achieving similar levels of performance as glass fiber. Glass fibers do have disadvantages over that of the natural fiber, namely it's density. The density of glass fiber is roughly twice that of natural fiber. The weight savings is an important issue for industries such as automotive where biocomposites could be used to produce structural car parts of lower weight for improved fuel efficiency. Glass fiber although recyclable, is less energy efficient than natural fiber to produce. It has a higher density and is more expensive. Natural fiber when incorporated in a weight percentage shows comparable reinforcing properties as glass. Natural fibers can be surface treated or sized just as glass.

The focus of this study is for a soy plastic based matrix material to be reinforced by hemp fibers. Hemp fiber has the best reinforcing properties of the other natural fibers and therefore the best upside for the material performance

Fiber	**Density (g/cm3)**	**Diameter (mm)**	**Modulus (GPa)**	**Strength (GPa)**
Glass	2.5	20	70	2 - 3.5
Flax	1.4	25	30-50	0.35 - 1
Hemp	1.48	13-30	55	0.6
Jute	1.46	25-200	10-30	0.4 - 0.7
Sisal	1.33	50-200	38	0.5 - 0.6

Table 1.2 Properties of various fibers.

Chapter 2

Literature Review

2.1) Soy plastics

There has been a substantial amount of research done on soybeans. Research examining the nutritional benefits of soy meal has gained knowledge of the thermal and chemical behavior of soy proteins. Of late work has focused on the ability to polymerize soy proteins in an effort to develop plastic.

Soybeans consist of proteins, fat, ash and carbohydrate fractions in a distribution as shown in Figure 1.1. The protein constituent consists of three different fractions, 7S, 11S and 15S. The 7S fraction comprises about 35% of the soluble protein. The 11S fraction also referred to as glycinin comprises from 31 to 52 percent of the soluble soy protein. The final fraction of extractable soy protein is the 15S fraction, which accounts for about 5% of the extractable protein.

The 7S globulin, conglycinin makes up about 85% of the 7S fraction and consists of 4 to 6 different components. The molecular weights of the various 7S fractions range from 140,000 to 170,000 Daltons. At low ionic strengths, the 7S globulins form dimers with molecular weight of 280,000 to 350,000 Daltons.

The 11S globulin, glycinin has a molecular weight of 320,000 to 360,000 Daltons. Glycinin is separated by cryoprecipation. When the 11S globulin is completely dissociated, fractions having molecular weights of 34,800 and 19,600 Daltons are recovered. The larger species have isoelectric points of 4.75 to 5.4 and are called the acidic subunits. The three acidic subunits have isoelectric points of 4.75, 5.15 and 5.40. The basic subunits were also separated into three groups having isoelectric points of 8.0, 8.25 and 8.5. The isoelectric point is the pH value where the protonation and deprotonation rates are equal to one another. Essentially the system is stabilized. The acidic subunits have been shown to contain three proteins with differing N-terminal amino acids, eg., Leucine, Isoleucine and Phenylalanine. The basic subunits all contain a terminal glycine.

Intact 11S globulins are dodecimer compounds of six basic and six acidic subunits. Under proper conditions, 11S can be fractionated into units of 7S. These 7S units appear to be composed of three acidic and three basic subunits. The 11S protein can also be broken to yield 3S subunits which appear to be dimers consisting of one acidic and one basic subunit each. The bond between the acidic and basic subunits might be a disulfide linkage. Reduction of this bond yields individual subunits of about 2S which are individual acidic and basic subunits.

The soy proteins of glycinin and conglycinin are very inter-related structures. Both proteins are quaternary structures with four base subunits on each protein. The 11S protein is the largest and most prevalent of the three and can be broken down into sub-components that are equivalent of the small proteins

When isolated 11S proteins are heated to 80°C, a portion of the protein precipitates. The precipitate consists almost exclusively of basic subunits. The acidic subunits remain soluble after this heat treatment. When the whole soybean protein is given a similar heat treatment, no precipitation occurs. Recent work has shown that the addition of isolated 7S globulin to the 11S fraction will prevent the precipitation of the basic subunits.

The final fraction of extractable soy protein is the 15S fraction. This material comprises about 5% of the total extractable protein. It is poorly characterized, and little is know about the thermal and chemical stability of the 15S protein[4].

The basis of polymerizing proteins is reacting functional groups on the protein. Proteins are large oligimers composed of amino acids. There are twenty amino acids as shown in Figure 2.1. The crosslinking process of the soy protein occurs primarily between carboxyl and hydroxyl groups. When the soy protein unfolds more functional groups are exposed. This increases interaction of functional groups.

The study and development of new materials has many facets, (J.U. Otaigbe, H. Goel, T. Babcock, J Jane)[12] investigated the processing effects on soy protein-starch plastics. There have been many problems associated with protein-based polymers; one of the primary issues is the effect of moisture. The authors suggest that this problem could possibly be addressed by compounding the soy polymer with the addition of polyphosphate fillers.

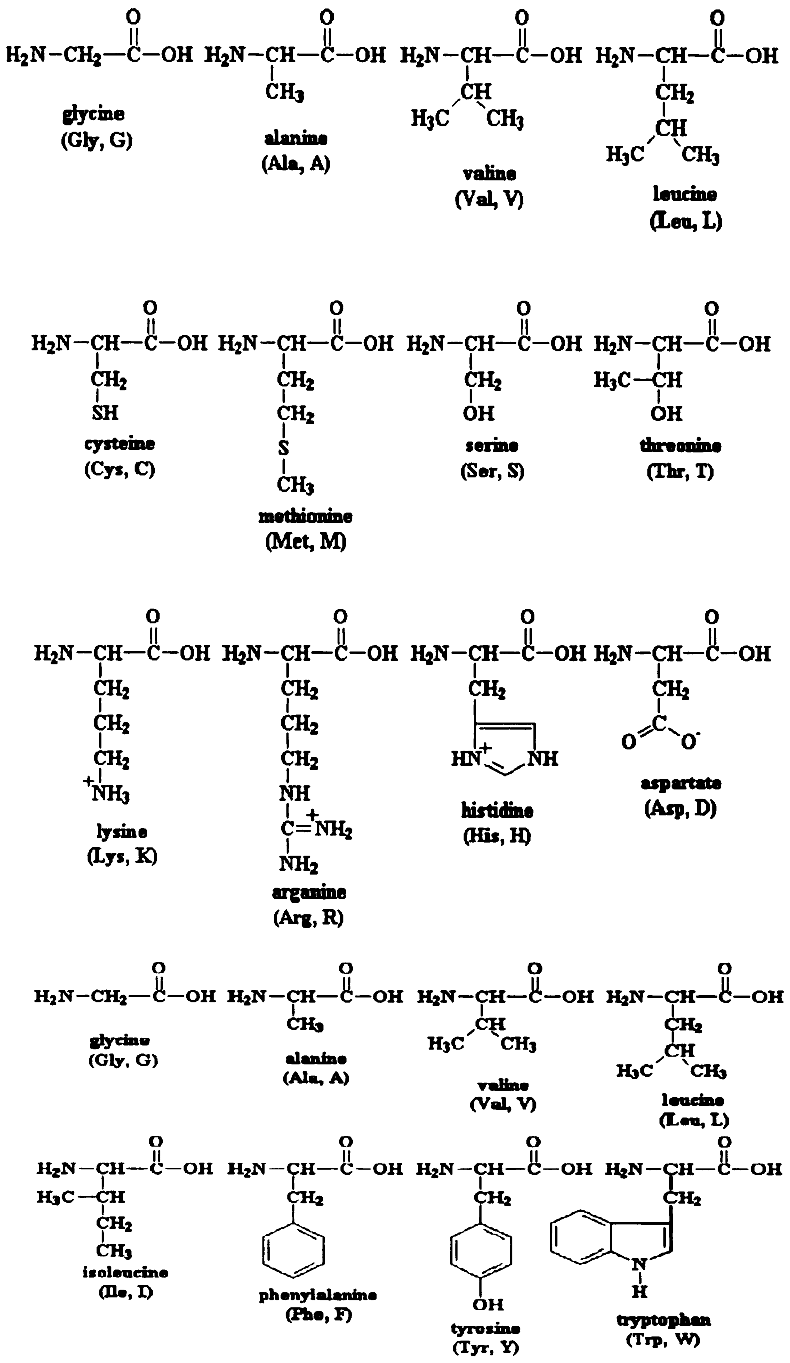


Figure 2.1 The twenty amino acids.

The focus of this study is processing between extrusion and injection molding. Soy isolate mixed with cornstarch, glycerol, water, sodium sulfite, and soybean oil was extruded between 100°C and 125°C, the material was then conditioned to 10wt% moisture and injection molded. The moisture acts as a plasticizer and aids processing of the material. When injection molded the temperatures did not exceed 120°C. The authors cite thermal degradation of the material if the temperatures during compounding and molding are higher than the afore mentioned values. However materials that were processed at higher temperatures manifested changes in properties that could be attributed to higher crosslinking density. The paper does not comment on possible reasons for this change.

Samples were tensile tested and the fracture surfaces were investigated through SEM. DMA testing was run after the samples had been conditioned to 3.5wt% moisture. TGA and DSC studies were run to investigate thermal degradation temperatures of the soy protein – cornstarch plastic and the material seemed stable up to 200°C. More extensive Pressure Volume Temperature (PVT) studies were run on the material to further the investigation into the thermal properties. Through PVT measurements and the use of the Tait equations a glass transition temperature was found at 80°C. The Tait equation allow the T_g to be found through a change in specific volume as a function of change in temperature. The DSC showed a T_g at 60°C, the difference is attributed to moisture content and the effect of heat treatment on crystallinity of the soy isolate.

SEM micrographs of the failure surface reveal a slow crack growth followed by increase in crack growth where the material fails catastrophically. The failure surface is dual phase with a ductile rough surface and a smooth glassy brittle surface. The rough surface results from tearing of the material where the crack growth is slow. The smooth surface is the result of the crack speed increasing to a point where the material behaves as if it were at low temperatures.

The paper reported a modulus of 0.104GPa and strength of 3.45MPa, both properties decreased drastically when moisture or heat were applied during testing.

(Sue HJ, Wang S, Jane JL)[13] focus on soy isolate films, in three conditions; dry, moist and plasticized with glycerol. The materials were molded at 150°C and 19.6 MPa for six minutes. Plaques of both 0.25 and 0.125 inches thick were molded. Samples were machined into specimens for tensile testing and four point bending testing

The soy isolate film becomes thermally unstable at 165°C. Fracture energy of the soy plastic drastically drops off once plasticizers or moisture is introduced into the material.

Dry soy polymer has a reported modulus of 4.4 GPa and a T_g of 150°C. With the incorporation of glycerol as a plasticizer the modulus drops to 0.52 GPa and the T_g drops to -50°C. The virgin soy polymer has a modulus and T_g that would compete with fossil fuel based materials very well. Polycarbonate has a modulus of 2.10 GPa and a T_g of 150°C.

The authors concluded that the potential for the application of soy plastics is high, however the obstacle of moisture absorption, and the correct amount of plasticizer needs to be identified for the material to be an effective engineering polymer.

(Qiagxian Wu and Lina Zhang)[14] also found that the soy polymer has low resistance to water. The soy protein plastics absorb moisture, which causes the material to lose structural integrity through swelling of the polymer. Although the moisture is only physically absorbed into the material the damage that occurs through swelling of the polymer is permanent. The authors have decided to focus their energy on structure, morphology, mechanical properties and water resistance of the soy plastics.

Soy protein isolate was mixed with ethylene glycol and specimens were compression molded at 150°C. Thin sheets were made for FTIR and X-ray diffraction study while large specimens were molded for mechanical testing.

The soy isolate plastic showed a very sensitive relationship to the amount of plasicizer incorporated in the sample. The Modulus drastically decreased with addition of ethylene glycol and the break elongation greatly increased, as shown below in figure 2.2.

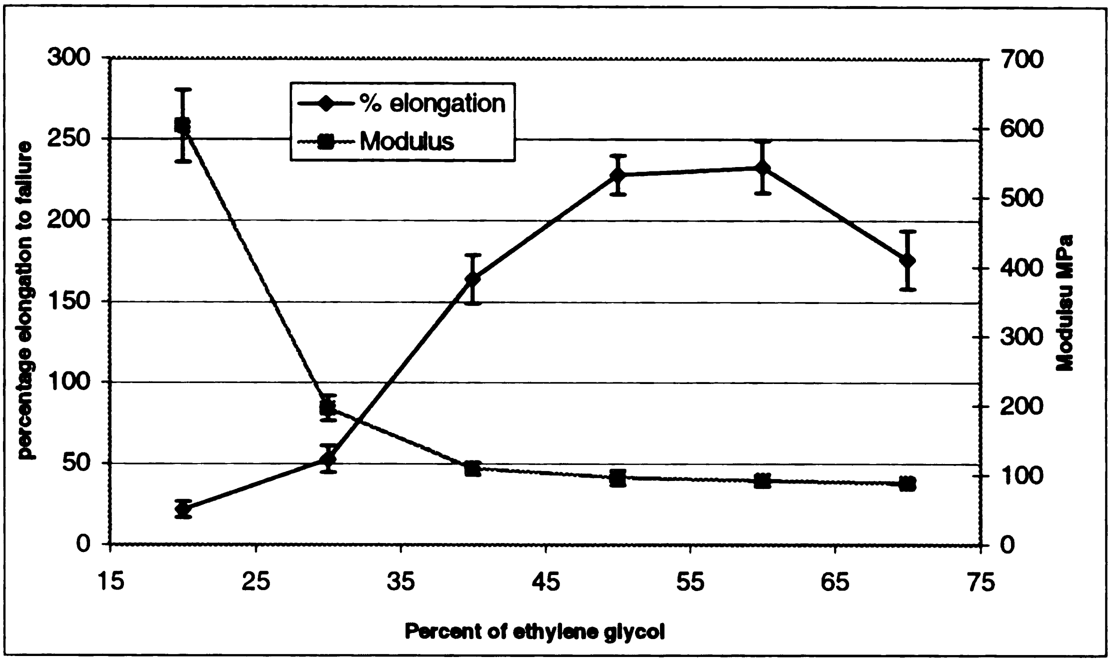


Figure 2.2 Effect of plasticizer on modulus and elongation to failure of the soy polymer[14].

The ethylene glycol content decreased tensile strength and modulus. Percentage of elongation is greatly increased with incorporation of large amounts of plasticizer.

The authors surmised that materials with good material properties could be made from soy protein isolate and ethylene glycol. Soy isolate with 50% ethylene glycol had a tensile strength of 4.23 MPa and a break elongation of 220%.

Other work has been done with soy protein isolate, however most work has been with the use of glycerin as the plasticizer. C. H. Schilling *et al.*[16] discusses the use of soy protein isolate and glycerin to develop soy plastics. The major focus of their study was to examine the mechanical properties and water resistance of the material. The material was compression molded at 140°C for six minutes loaded with eight to ten tons of force. The samples were then tensile tested to determine mechanical properties.

Soy protein plastic without glycerin showed linear elastic deformation. The modulus of the pure protein plastic was measured to be 4.6 GPa. With incorporation of glycerin the modulus drops off and the deformation becomes less and less linear as the content of plasticizer increases. Schilling et al. reported values of 3.5 GPa and 1.8 GPa at 10 and 20% glycerin content.

One unique facet of Shilling et *al.* was their investigation of particle size. The raw materials were sieved before processing. This processing step was found to have a significant effect on the properties of the soy plastic because the soy plastic material is a brittle material and corresponds well with Griffith's brittle crack propagation model. The critical variable in this model is the initial size of the initial imperfection in the material, therefore sieving out the larger particles in the soy powder allows there to be more uniform sized particles. The underlying goal is to improve load-bearing ability of the material by removing large particles that would be stress concentrations and sites to initiate croid development.

The authors also concluded that adding glycerin in the polymer increased strain to failure. Glycerin content also decreased modulus and strength. Hardness of the materials decreased rapidly when immersed in water.

One topic not discussed thoroughly is the concept of blending the soy polymer with synthetic polymers to improve processing and material performance. This is counter-intuitive to the development of a fully agro-based material system, but it could improve material properties and eliminate the need for the use of plasticizers

(Bhattacharya and John)[17] found that blending of plant-based material with synthetic materials could drastically improve properties and applications of the biobased polymer. However the materials usually do not mix well unless the synthetic polymer has a reactive group that would interact with the natural polymer. The authors reference Otaigbe *et al*[21] in their findings of using anhydride groups in the backbone of the synthetic polymer to aid in blending with the plant-based polymer.

In this study, anhydride groups were attached to the polyester chain to improve interaction with the soy protein polymer. The polyester used was polycaprolactone, which is a synthetic biodegradable polyester. The main goal of the research is to investigate the potential of making biodegradable polymeric articles from soy protein.

Polycaprolactone, Eastar polyester and Bionelle were blended with soy protein on a twin-screw extruder. These polymers are all biodegradable synthetic polymers. Easter is Eastman Aliphatic -Aromatic Copolyester. Bionelle is the tread name from Showa Highpolymer, Japan. Chemically it is poly(butylene succinate-co-butylene adipate) or in short PBSA. The extrudate was pelletized, injection molded and tested to obtain mechanical data from the material. DSC, DMA, X-ray diffraction as well as optical microscopy were used to evaluate the materials.

The soy component was not dried before processing, allowing the reported 5 to 7 percent moisture to act as a processing aid (or plasticizer) in the extrusion and injection molding steps. The study found that it was harder to injection mold samples that were extruded at higher temperature. The authors comment that this could be due to protein degradation.

Increasing protein content increased strength and modulus with a decrease in percent elongation to failure of the sample. Samples were compounded with varying degrees of protein with the maximum amount being 65% soy isolate, materials with more than 65% soy isolate were difficult to process. X-Ray diffraction was also used to examine crystallinity of the material. It found that the crystalline nature of the polyester as well as the soy protein did not change through processing, and that the final material was partially crystalline.

Bhattacharya and John conclude that anhydride groups were found to be effective in blending the two non-miscible materials, the protein and polyester. The anhydride was found to decrease the size of aggregates of the individual phases allowing for better phase interaction and ultimately increased material properties.

Mungara et *al.*[18] blend soy protein polymers with synthetic polyesters in an effort to overcome the issue of water absorption of the plant-derived polymer. The authors hypothesized that the hydrophilic polyester would help in repelling moisture from the soy protein.

Soy protein isolate, soy concentrate and soy flour were used and mixed with Biomax as well as glycerol and some compatiblizing reagent salts. A twin-screw extruder was used to compound the materials, and the compounded materials were injection molded to make materials for testing. Polyvinylactams were used as a compatiblizer to improve interaction of the protein and the Biomax. Glycerol was added to the Biomax to decrease the processing conditions so that it could be blended with the soy protein.

The authors found material properties to have tensile strengths between 16 and 22 MPa and a modulus between 1.1 and 1.8 GPa. Water absorption was found to decrease with the incorporation of higher content of synthetic polymer.

Thermal stability and characterization of the soy proteins themselves can also give some insight into the potential for a fully protein based material.

Ogale et *al.*[19] conducted a large amount of research into the thermal stability of soy isolate proteins. Samples were freeze-dried before processing for 24 hours to reduce moisture content to 5-7%. Through the use of TGA Ogale et *al.* were able to find some trends in the soy protein and the plasticized protein plastics. Weight loss is small below 150°C, intermediate between 150°C and 180°C, and significant above 180°C for soy protein isolate with glycerol. For pure soy protein isolate, the ranges move to 180°, 200°, and above 200°. The optimum process temperature is stipulated at 150°C due to the vapor point of glycerol; this is verified from previous studies.

Microstructural analysis of the samples that were compounded for the study suggests that there is a critical amount of plasticizer needed for the protein matrix to develop. Samples were prepared with 0, 20, 30 and 40 percent plasticizer based on weight. The critical value of plasticizer appeared to be around 30% as the material failure surface changed from brittle to ductile at this value. Cross-section SEM micrographs of the films containing 30 and 40 percent glycerol show existence of ductile rupture in the samples as evidenced by the rough appearance of the fracture surface topography in the material.

An issue of interest with the soy polymer is how the plasticizers work within the crosslinking process. (Sun and Mo) discuss how the plasticizers work in the polymer. There are three mechanisms plasticizers use to facilitate polymerization. 1) They can lubricate or facilitate the movement of macromolecules over one another. 2) They can gel or disrupt the polymer-polymer interactions of hydrogen bonds and van der Waals or ionic forces. 3) They can decrease the polymer free volume. Soybean proteins are large oligomers that are mostly stabilized by hydrogen bonds, electrostatic forces and hydrophobic interactions and therefore would be affected by the addition of the proper plasticizer .

This paper focuses on four plasticizers; glycerol, propylene glycol, 1,2-butanediol and 1,3butanediol. Glycerol was the most effective plasticizer as it improved the strain to break more than the other plasticizers.

A larger decrease in T_g of the material would indicate a more favorable or effective interaction of the plasticizer with the soy protein, which occurs with the glycerol. One of the primary jobs of a plasticizer is to improve strain to failure as well as toughness; this is accomplished with a decrease of modulus.

The study also discusses how the protein is structured having amino acid groups arranged with hydrophobic groups folded onto the inside and hydrophilic groups on the outside. Heating of the soybean protein converts the protein from its normal state to a denatured state with unfolding and disruption of the intramolecular bonding. The denaturization process aids in the polymerization of the proteins. This is verified with DSC curves in the study, which shows two endothermic peaks that are present from the soy protein. The peaks correspond with the two different proteins, the glycinin and conglycinin.

Summarizing the above information, soy proteins are complex molecules which makes it hard to predict individual reactions when the proteins are polymerized. The proteins are structured marco-molecules with defined structures that can be manipulated through chemical and thermal treatments. The manipulation of the protein allows the proteins to be polymerized. Polymerizing the virgin soy protein results in a very stiff, brittle material with low strength. The addition of plasticizers to the process reduces the modulus but results in a stronger material.

Moisture has a negative influence on the material properties of the soy polymer. Moisture in the soy protein can act as a plasticizer during processing, however absorption of moisture after process leads to material degradation. Processing conditions from study to study vary, and so do explanation of thermal stability. This leads to some non-conformity from study to study.

2.2) Natural Fibers

The state of natural fiber production, availability, awareness of their potential application, and cost are all issues that effect their current use in industry. Another concern that has been voiced is the potential for the fibers of have varying properties from year to year due to climatic changes. These concerns are all substantial issues that govern the future of biofiber applications. A brief overview of some articles will be given here to allow the reader some explanations as to how biofibers will overcome these obstacles.

Mohanty et *al.*[3] investigated biofibers and their make-up. Biofibers are lignocellulosic materials. Lignocellulose is composed of cellulose, hemicellulose and lignin. The amount of each constituent varies from plant to plant as well as with age. The base constituents are the same from plant to plant but the degree of polymerization in the cellulosic materials varies from one to another. The degree of polymerization is important as it is directly related to the properties of the fiber.

A negative issue of working with bio-fibers is that of dealing with their low degradation temperature. The biofibers begin to degrade at 180°C to 200°C. Incorporation of natural fiber into polymer matrices is governed by this temperature limitation. Another concern with bio-fibers is their affinity to water.

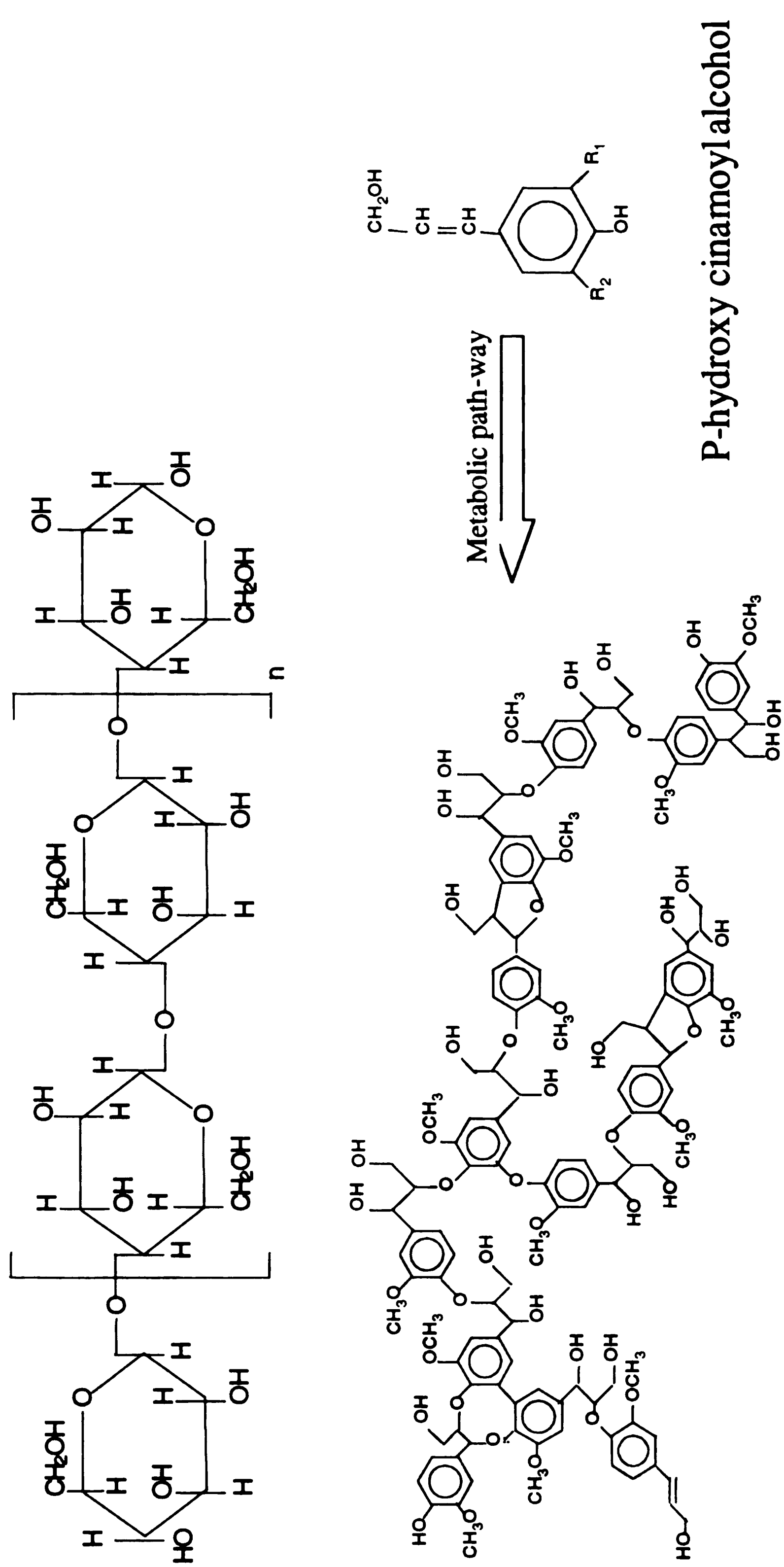


Figure 2.3 Structure of lignin and cellulose, base materials of natural fibers.

There are a lot of different biofibers available in different parts of the world. The cost versus performance relationship of a fiber is fairly dependent on what geographic locale and the availability of the said fiber. Each geographic location tends to produce a dominant biofiber in the region. In temperate areas hemp or flax fiber are the most readily available materials. In tropical regions, jute, pineapple leaf fiber or coconut fruit fiber are abundant and have a cost advantage.

One constant in the synthetic fiber industry is the use of sizing to improve the interaction of the reinforcing fiber and the polymer matrix. This is one technique that will have a lot of effect on natural fibers as well. Sizing natural fibers can be a different endeavor than the sizing of synthetic fibers. When sizing synthetic fibers there is the addition of functional groups. The sizing of biofiber can have a lot to do with the removal of naturally existing compounds that interfere with the bonding of the fiber and matrix.

Ray et *al.*[1] investigated the effects of surface treatment on the performance of natural fiber. Using a 5% NaOH solution to soak the fibers for four and eight hours respectively for different treatments, the researchers attempted to modify the surface of the jute fibers. The fibers were then incorporated into a vinylester thermoset matrix.

The cured samples were tested and the data was analyzed to evaluate the effectiveness of the modification of the fiber. Three-point bending was done on the samples to evaluate flex strength and flexural modulus. Mechanical properties improved with larger percentages of fiber in the material, as expected. Composites with untreated fibers exhibited debonding and some fiber pull-out on the fracture surface. A four hour alkali surface treatment produced fibers with better fiber wet-out and better mechanical bonding between fiber and matrix.

Hodzic *et al*[2] investigated the potential of flax fiber composites with polypropylene. Investigation of the use of silane coupling agents on the biofibers as well as the use of other compatibilizers was explored. The goal of this exploration was to size the fiber for better adhesion to the polymer matrix. There is generally a larger variance within the properties of the natural fibers than synthetic fiber and this increases the difficulty to get standardized material properties of natural fibers.

The authors most specifically investigated flax fiber composites and used flax as an exemplar for other fibers. The study concluded that the flax fiber was useful to reinforce polymers. Silane treated fibers showed the most promise of the natural fiber with better wet-out than untreated fibers.

Natural fibers are a good reinforcement selection and can be modified to achieve similar reinforcing properties, compared to their synthetic counter parts. Fiber treatments are just as easily administered to natural fibers as to conventional fibers and greatly improve the performance of the fiber. Natural fibers are a cost effective, lightweight option for reinforcing polymers. The added environmental benefits are a secondary reason to use them.

2.3) Biocomposites

Biocomposites with soy protein have been around for a while, and soy has also been used as a source for making adhesives. The manufacturing of the adhesives is dependent upon using sodium hydroxide and the like to denature and unfold the protein. The adhesive is primarily used for soft fiber board applications where a strong adhesive bond strength is not needed.

Mo, Sun and Ratto[6] use soy protein and wheat straw in an effort to make biocomposites where soy protein is used as an adhesive to create particleboard. Protein adhesion is related to dispersion and unfolding of the protein molecule much like the crosslinking process. The incorporation of chemical and heat treatments to encourage the unfolding or denaturing of the protein can greatly effect the interaction of the protein to the wheat straw.

Soy protein isolate was used as the base for the adhesive; the isolate was modified with sodium hydroxide, urea, and dodecylbenzene sulfonic acid. The dodecylbenzene sulfonic was used as a promoter to react the urea with the soy protein. The chemically modified protein was stirred for two hours at room temp before being mixed with the wheat straw to make the particleboard. The control adhesive was soy protein isolate and water. The soy adhesives were compared with conventional synthetic adhesive versions of urea-formaldehyde and phenol formaldehyde (no values provided).

In an effort to change the surface of the wheat straw, the straw was soaked in a dilute solution of sodium hydroxide, a dilute solution of hydrogen peroxide and a bleach solution.

The various types of treated straw and chemically altered adhesives were mixed one to one and then pressed at 140°C. The samples were also investigated as a function of moisture content; samples were made with 10, 20, 30, and 40 percent moisture to quantify bonding between the adhesive and the biofiber.

The major bonding interaction between the protein and fiber takes place between polar groups; on the protein these include the amide, hydroxyl, and carboxyl. The sodium hydroxide breaks the internal hydrogen bonds of the protein molecules; thus unfolding the protein molecule and exposing the polar groups results in an improvement in adhesion. Soy protein was also partly unfolded by urea and dodecylbenzene sulfonic acid, however the large molecular size of the protein could have prohibited the protein from interacting with the straw surface. Stearic hindrance is a concern with large molecules like the proteins and interferes with potential reactions.

Soy protein molecules are very large structures, and although there is a lot known about how they react to heat and chemical modification, there is still a lot of supposition as to how they interact with one another and substrates. Specifically, why is it that the mechanical strength is better with increased moisture content as a result of one chemical modification but lower with the same moisture content and another chemical treatment. It would seem that the moisture would interfere with the protein straw interaction and the end result would be poor material procurement.

Mo, Sun and Ratto make several conclusions. The adhesive bonds better with the wheat straw after bleaching; the bleaching removed wax and oils on the surface of the fiber. The best tensile and compression strength values were obtained with 40% moisture and soy adhesive and with 10% moisture using a methylene diphenyl diisocyanate adhesive. Moisture and an isocyanate react to form CO_2, which basically decomposes the isocyanate, making moisture an adversary to processing. Particleboard tensile or compressive strength data reported in this study does not exceed 3000kPa for any material.

Kuo et *al.*[5] outline some previous work done in an attempt to create fiberboard with non-wood agricultural reinforcements and focus on the use of corn stalk for reinforcement. It has received some attention in the past but also has been abandoned due to the high cost of processing compared to that of wood fiber. With the decrease in supply of wood fiber alternative reinforcements are being sought out from agricultural residue.

This study compares various reinforcements bonded with soy adhesive and a synthetic adhesive. Reinforcements that are investigated are switch grass, cornstalk and wood fiber. The study also investigated the feasibility of using a soy-based adhesive versus the use of a synthetic adhesive.

The evaluation of the reinforcement led to the finding that wood fiber produced the best overall material, cornstalk was better than switch grass but not as good as the wood fiber for overall material performance.

The adhesives that were examined were a phenol-formaldehyde, a urea-formaldehyde and a soy protein based adhesive. The phenol and urea formaldehydes performed better than the soy adhesive, material properties as well as manufacturing of the fiberboards were both issues where the soy adhesive was inferior. Another issue of the soy adhesives was that the end product was subject to moisture absorption. However a blend of the synthetic adhesive and the soy adhesive was able to produce a suitable binder with intermediate properties in processing and material performance.

From the information gathered in these articles there are several points to be commented on. Soy protein is temperature sensitive and cannot be processed at high temperatures. 150°C is a high-end limit on process temperatures. The proteins have and can be polymerized but the use of a plasticizer is needed to get a material that is useable. Natural fiber is an effective reinforcement but the use of surface treatment improves the interaction between the fiber and the polymer matrix.

Moisture is the Achilles heal of the soy plastic. Exposure to moisture leads to material property degradation. Biocomposites suffer the same fate as the moisture destroys the fiber matrix interface and the material properties decrease drastically.

Chapter 3

Experimental procedure

3.1) Extrusion of soy concentrate plastics

Materials used to compound the original soy polymer were obtained from different sources. The soy concentrate was obtained from Archer Daniels Midland (ADM), Decatur Illinois. Midwest grain products, Atchison, Kansas, supplied the wheat starch, Midsole 50. Glycerol supplied by J.T. Baker Phillipsburg, New Jersey. Sigma-aldrich chemicals of St. Louis, Missouri supplied maleic anhydride, the compatiblizer and Bis(tert-butyl peroxy)-2,5-dimethyl hexane, the peroxide initiator. Lastly Bayer Corp supplied the polyester-amide synthetic biodegradable polymer, Bak4™.

Soy concentrate, wheat starch and the polyester-amide were dried at 80°C under vacuum for 24 hours before processing. After drying of the materials the soy concentrate, wheat starch, and glycerol along with maleic anhydride and initiator were mixed in a kinetic mixer. Dry powder components were added and mixed for 5 minutes, as the dry powders mixed the liquid components were added, the glycerol and peroxide initiator. The total batch was then mixed for 30 minutes.

5% maleic anhydride	75 grams
1% luprosal (initiator)	15 grams
47% soy concentrate	705 grams
18.8% wheat starch	282 grams
28.2% glycerol	423 grams
Total	1500 grams

Table 3.1 Breakdown of soy polymer components.

After mixing, the batch of 1500 grams was hand fed into the extruder, a ZSK-30 Werner and Pflieder twin-screw extruder. The original soy based polymer, SCP5 was then pelletized and re-extruded with polyester-amide. After blending with polyester amide the polymer was deemed SCP6. SCP is an acronym for Soy Concentrate Plastic. The six indicates which level of revision in order of experimentation the material was.

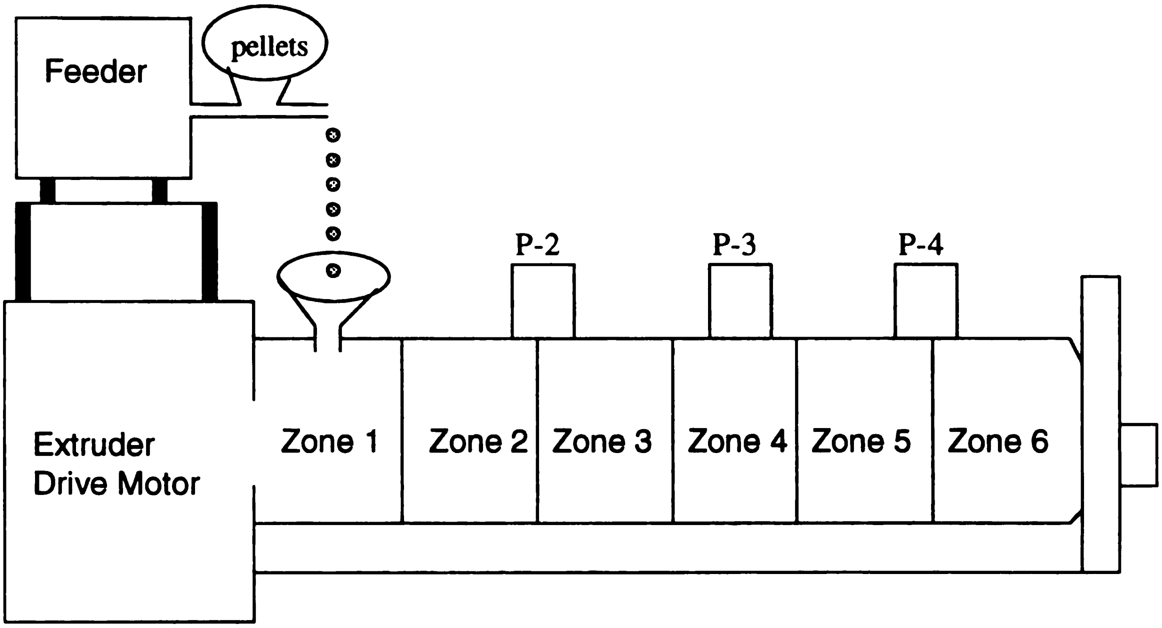


Figure 3.1 Schematic of W&P ZSK twin-screw extruder.

Rpm was a variable in the experiments ran on the soy plastic. Temperature profiles were held constant. Process temperature profiles are shown below in table 3.2.

Zone	Extrusion 1	Extrusion 2
1	110	130
2	120	130
3	130	130
4	140	130
5	150	130
6	150	130
Die	150	130

Table 3.2 Temperature profiles of extrusion runs.

The process to achieve a final material for injection molding took two extrusion runs. The ZSK-30 has six different temperature zones shown in figure 3.1 that are controlled through digital program logic controllers. Zones one through five all are water-cooled. Zone six is not equipped for cooling and the die does not have a temperature controller.

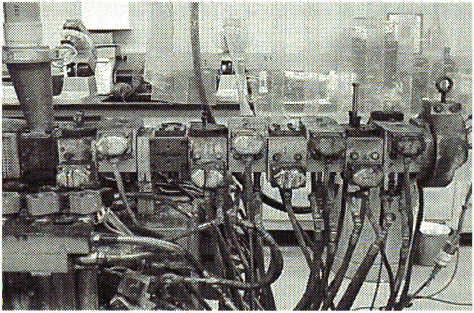


Figure 3.2 Barrel of W&P ZSK-30 twin-screw extruder.

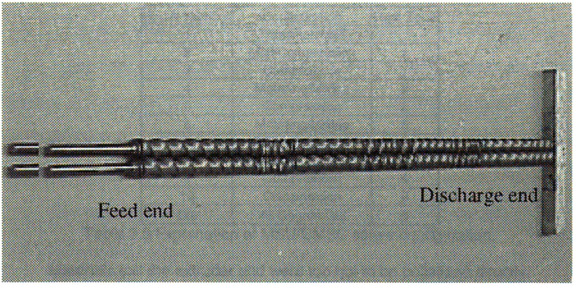


Figure 3.3 MSU/CMSC extrusion screw configuration.

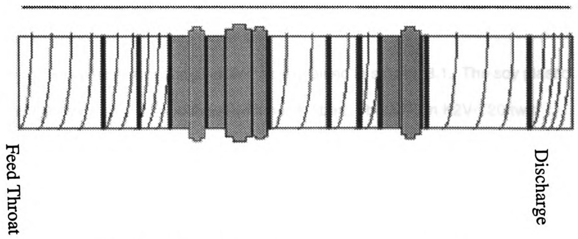


Figure 3.4 MSU/CMSC diagram of screw configuration.

The screw configuration has two kneading zones where the majority of the mixing occurred for the extrudate. Table 3.3 explains how the screw configuration relates to the extruder barrel and where the majority of mixing occurred.

Barrel Number	Configuration	Heat Zone
1	Transition/Melt	
2	Melt/Compression	1
3	Compression	1
4	Metering/Mixing	2
5	Compression	2
6	Metering/Mixing	3
7	Mixing/Metering	3
8	Metering/Compression	4
9	Compression	4
10	Compression	5
Die	45-Degree Die	6

Table 3.3 Explanation of MSU/CMSC screw configuration.

Materials exit the extruder and were too hot to be pelletized directly. Because of this the compounded material was allowed to air cool for three to five minutes before pelletization. After the material cooled sufficiently it was then pelletized and injection molded which is explained in section 3.4.

3.2) Extrusion of composite materials

Soy plastic was compounded as explained in section 3.1. The soy plastic was then extrusion compounded with hemp fiber. The K-Tron K2V-T20 twin auger feeder was calibrated to 85grams/min. 15grams/min of hemp fiber was added by hand onto the screws, the fiber was made into 7.5gram fiber balls that were added to the extruder over a 30 second time period.

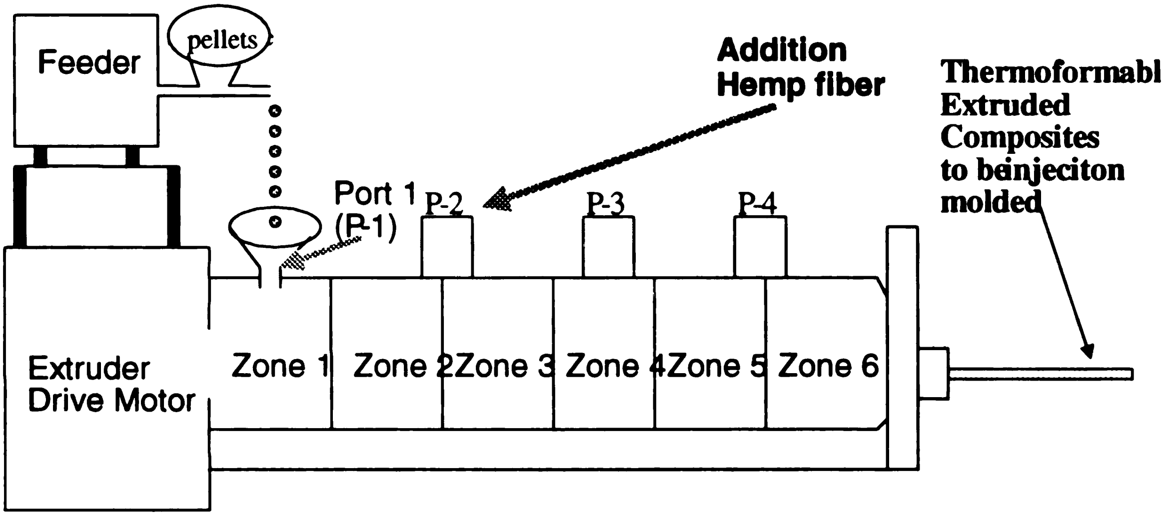


Figure 3.5 extruder schematic for addition of fiber to soy plastic.

Hemp fiber was added into port 2, which is a conveying zone of the screw. Addition of fiber at this point in the extruder allow the fiber and matrix polymer to be passed through a mixing zone of the screw which provides good mixing of the fiber and matrix.

The composite extrudate is then pelletized and injection molded.

3.3) Fiber treatment and preparation

Hempline Corporation supplied hemp fiber. Hemp fiber used in this study was raw and surface treated. Raw fiber was used as received; no treatment was done to the fiber before it was compounded into the plastic. The second form was alkali treated hemp fiber.

The raw fiber from hemp line was two to four inches in length and 50 to 100 microns in diameter. Before addition to the extruder the fiber was dried under vacuum at 80°C for at least 12 hours. The natural fibers absorb moisture and this step ensured removal of all moisture in the fibers before they were added to the soy plastic.

Alkali treated fiber was soaked in a bath of five weight percent sodium hydroxide and water for one hour. Sodium hydroxide was dissolved in distilled water and the hemp fiber was added to the water, in a weight ration of 1:20, i.e. 100grams of fiber for 2000grams or 2000mL of water and sodium hydroxide solution.

After immersion for one hour the fiber was removed and rinsed with water several times to remove excess solution. The fiber was checked for Ph and acetic acid was used as needed to bring the Ph to seven.

At this point the fiber was treated, and neutralized but still saturated with water. The fiber was placed under a hood for 24hours to dry. After this step the fiber was placed in a vacuum oven at 80°C for at least 12 hours before addition to the melt flow in the extruder.

3.4) Injection molding

A Cincinnati Milacron Injection Molder was used to injection mold the soy plastic and the soy plastic composites. The soy polymer and soy polymer composites are new, novel materials. The parameters for injection molding these materials were not established prior to molding these materials.

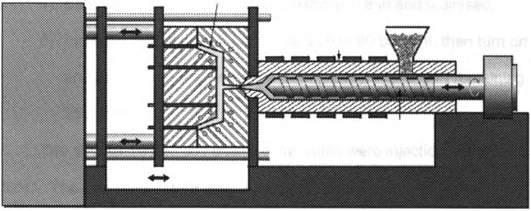


Figure 3.6 Schematic of Cincinnati Milacron Injection Molder.

Process development for the new materials was accomplished using several guidelines. These guidelines were put into place to ensure good part processing parameters and to protect the injection molder from misuse. The parameters used to establish the part processes for the soy plastic and the soy composite materials are outlined below.

An injection molding process has three basic steps to filling the part, fill, pack and hold.

1) Set transfer point to 0.50 inch and ensure that the transfer from fill to pack steps occurs due to position, not from time or pressure.
2) Set the shot cushion to 0.25 inch.

3) Turn off pack and hold pressures to ensure that the filling of the part occurs during the fill process of the cycle and not the pack or hold portions of the cycle. Set the shot size so that during the fill process the part is filled 75 to 90 percent.
4) Begin with low shot size and fill velocity, 0.8 in and 0.3in/sec.
5) Increase shot size until part is filled 75 to 90 percent, then turn on pack and hold pressures. Increase pack pressure to fill part remaining 10 to 25 percent.

The soy plastic and soy plastic composites were injection molded at 132°C. The dye temperature was set at 20°C.

3.5) Material property measurement

Material properties were measured through tensile and impact testing. Fracture surfaces were analyzed with an Environmental Electron Scanning Spectroscopy referred to as ESEM, and morphology was investigated with optical microscopy.

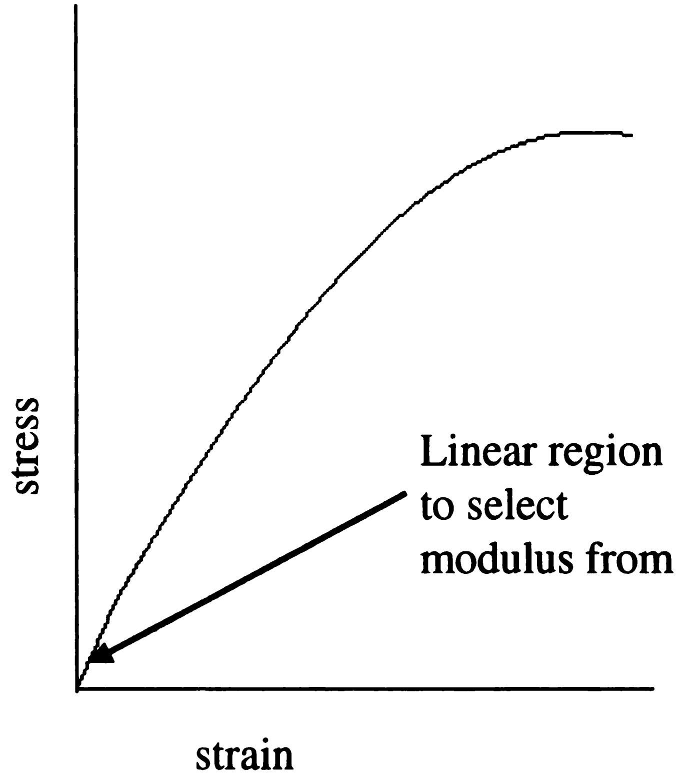


Figure 3.7 Schematic stress strain curve.

The injection molded tensile coupons were tested to determine the tensile strength and tensile modulus as per the ASTM D638 standard. The testing system used was a United Testing System SFM-20 loadframe. System control and data analysis were performed using Datum software. Load was measured using a 1000 lbs. load cell and the strain was measured using a model EXT62LOE laser extensometer with a 2-inch gage length. Crosshead speeds of 0.2 and 0.05 inches per minute were used for testing the plastics and the composites respectively. A preload of 2 lbs was used. Tensile strength was measured form the peak load and tensile modulus was measured from the slope of the tangent line to the initial part of the load-displacement curve.

For impact testing the injection molded tensile coupons are cut so that the samples are 2.5"x0.5"x0.125". 0.1" deep notches were cut into the sample beams using a TMI notch cutter. Notched Izod impact testing was performed on a Testing Machines Inc. 43-02-01 Monitor/Impact machine as per the ASTM D256 standard. A 5 ft-lb pendulum was used to impact the samples

The ESEM used for this work was manufactured by Electroscan Corporation (model number – 2020). It is equipped with a Lanthium Hexaboride filament. Water vapor is used as the imaging gas. The samples to be examined are placed on the sample holder located in the sample chamber. The imaging pressure (chamber pressure) is set between 2 and 3 Torr. The working distance between the detector and the sample is set between 8 and 10 mm. The accelerating voltage is set at 20 kV. The sample is focused at different points on its area and micrograph pictures were taken.

3.6) Data evaluation

Evaluation of the experimental data and comparison to the rule of mixtures was used to evaluate the effectiveness of the composite. The volume fraction of fiber content within the composite had to be measured for rule of mixtures computations. To change the weight fraction to volume fraction the density of hemp fiber needed to be found.

The density of hemp fiber was obtained using Archimedes method. Archimedes method uses buoyancy forces of a liquid medium to measure the volume of an immersed solid. Due to the nature of the hemp fiber, it is hard to measure its volume in other ways. The fiber was dried under vacuum for 24 hours and then small bundles of the fiber were made. The bundles of fiber were weighed dry, and then weighed when they were immersed in ethanol.

The wet weight was then subtracted from the dry weight, which gave the weight or mass of the ethanol displaced. This values was then divided by the density of ethanol, 0.815g/cm^3, which gave the volume of the fiber bundle. The volume of the fiber was then divided the dry weight of the fiber and the density was obtained.

(dry weight) – (wet weight) = weight of displace ethanol

(weight of displace ethanol) ÷ (density of ethanol) = volume of fiber

(dry weight) ÷ (volume of fiber) = density of fiber

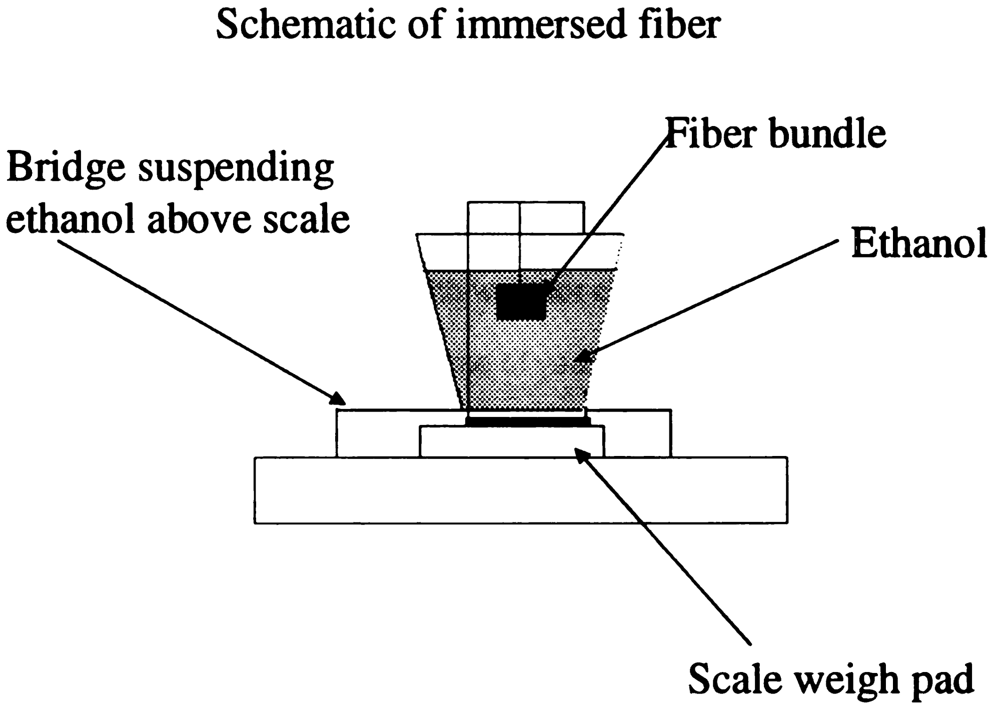


Figure 3.8 Schematic of apparatus used to weigh immersed hemp fiber.

Figure 3.8 gives a schematic of how the weight of the fiber was obtained when immersed in ethanol.

Chapter 4

Results and Discussion

4.1) Soy concentrate plastics/composites

The previously published extrusion of soy protein was summarized in chapter 2. In most instances, researchers were either doing small quantities or examining the physical properties of the specimen. The majority of research done on polymerizing soy polymers has utilized plasticizers in order to aid in the processing of the soy polymer. Scientists have approached the issue in different ways, in some instances the plasticizers are added to the raw materials; in other instances moisture is used as the plasticizer. The presence of moisture poses a problem for processing.

Water acts like a plasticizer, and fortunately or unfortunately there is a certain degree of moisture in the soy protein and wheat starch when received. Moisture levels in the raw materials are affected by the level of humidity in the environment, which changes with weather conditions and the laboratory environment depending on the time of year. Some published reports have conditioned the raw materials to adjust the level of moisture in the soy protein so it is constant, while other groups have attempted to dry or remove all the moisture from the raw materials.

In this project, the latter approach was taken. Experiments were run to evaluate the effect of initial moisture on material properties of the soy plastic. Figures 4.1 and 4.2 show the effect of different moisture content on material behavior and properties. Here there is no baseline data, as the initial moisture content of the samples was not quantifiable. The moisture content increases in the data from left to right. The important conclusion from this data is that with an increase in moisture, which acts like a plasticizer, the material properties (both strength and modulus) decrease, as shown.

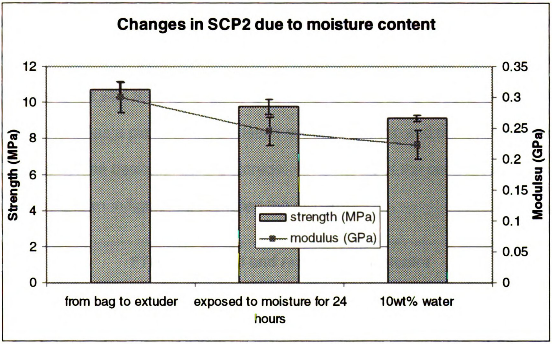


Figure 4.1 Effect of initial moisture content on final material properties.

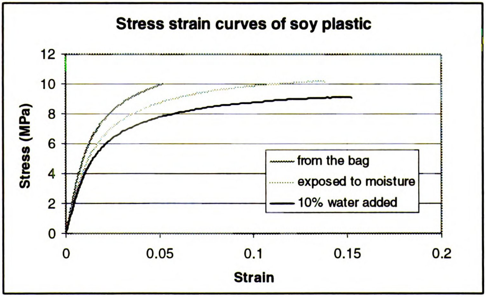


Figure 4.2 Change in stress-stain behavior as a function of moisture content.

The importance of and the sensitivity to moisture were not realized until many experiments were conducted which did not produce reproducible results. Drying of the materials before extrusion, followed by overnight equilibration in the laboratory before being injection molded did not reduce the variability. Drying the material before injection molding the material in a forced air desicator also was not effective. During the course of this study, other interesting phenomena were observed. It was found that glycerol that was added to the soy protein and wheat starch as a plasitizer would leach out of the plastic and then condense on the sides of the desicator during storage. An analysis of the condensate with FTIR as shown in figure 4.2 identified the glycerol.

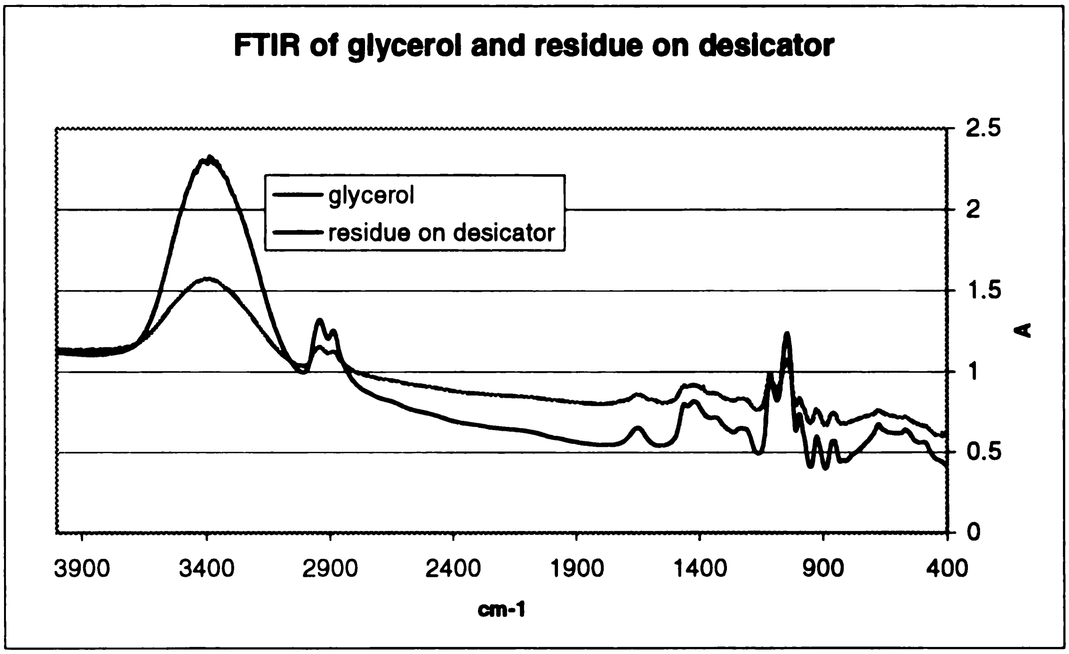


Figure 4.3 FTIR of glycerol and residue on desicator.

As a result several changes were made in the processing. The material could not be easily and reproducibly dried, nor could it be exposed to moisture. Water quenching of the polymer melt out of the extruder was not allowed. Drying of any of the extruded materials was discontinued. The extrudate was immediately injection molded and tested after extrusion to eliminate moisture absorption into the soy plastic.

Moisture content had to be stabilized. Drying the material before processing accomplished this goal. The soy concentrate and wheat starch was dried at 80°C for 24 hours under vacuum to remove all the moisture in the raw materials. The risk of exposing the proteins to temp of 80°C or higher is that they begin to denature at temperatures on this order. The denaturing of the proteins enhances the ability to polymerize the proteins by unfolding of the protein to expose more functional groups. However, to establish a baseline of processing and material properties exposure to heat for removal of moisture is also affecting the structure and property of the protein. Therefore the materials were always given a 24-hour drying cycle to establish a baseline set of process parameters. It is important to point out that this step could not only be removing moisture, but also denaturing the protein, which would improve physio-mechanical properties.

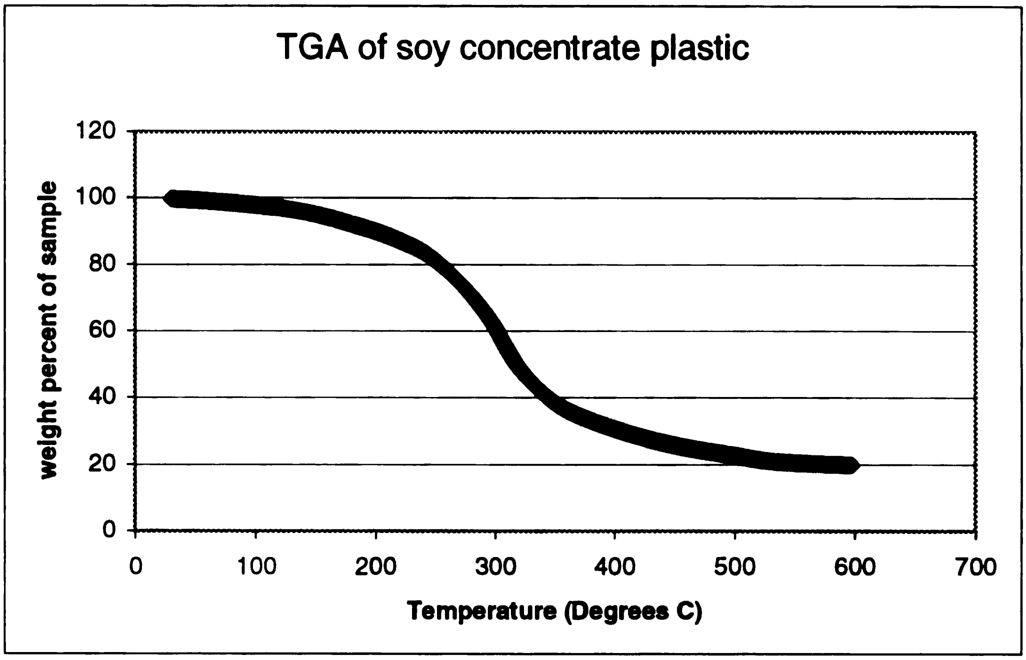


Figure 4.4 TGA of soy concentrate plastic

Drying of the soy concentrate and wheat starch before processing removed the moisture and provided a stable baseline material but it also removed some plasticizing agent in the soy polymer, the water. The removal of the moisture increased the stiffness of the soy concentrate polymer to a point that it could not be processed at the previous temperature profiles. A TGA (Thermal Gravimetric Analysis) was conducted on the soy polymer to determine the onset of degradation. The TGA measures weight as a function of temperature, as the temperature increases, eventually the components begin to volatilize, decreasing the original weight of the sample.

The original TGA temperature-processing profile suggested a maximum processing temperature of 130°C but the TGA profile shown in figure 4.4 demonstrated thermal stability to approximately 180°C. This allowed the extrusion temperature profile to be increased. The profile shown in table 3.1 was necessary in order to reduce the viscosity to improve the processability.

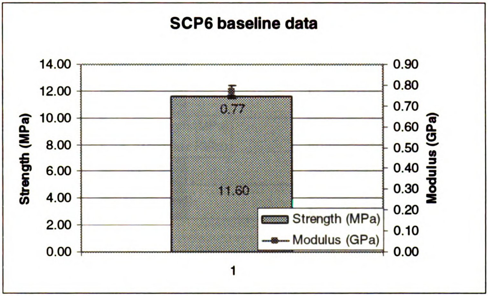


Figure 4.5 baseline material properties of the soy concentrate plastic.

Once the baseline set of extrusion parameters was established, a set of baseline injection molding parameters was also required to be set. All samples were molded with a melt temperature of 132°C. The injection molder has three heating zones and a nozzle temperature control. All temperature controls were set to 132°C. The material was injected into a dogbone cavity mold held at 20°C. The fill pack and hold pressures for the soy plastic were 1100, 1300, and 900 psi respectively. Timers for fill, pack, hold and cooling were set for 10, 3, 3, and 55 seconds. Shot size was found to work best at 1.1inches, and the injection speed was set at 0.3in/sec. This process worked consistently to produce a part without flash and fully filled. Most importantly the material processed in this manner had reproducible properties.

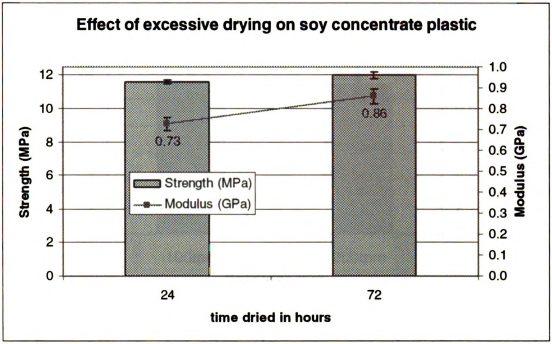


Figure 4.6 effect of extended drying on soy plastic material properties.

The denaturing effect of extended time at temperature that would occur to the soy proteins if they were held at temperature for extended times was investigated as shown in Figure 4.6. The experiment was to investigate if there was a need to consistently dry the materials for 24 hours or if it the material was stable and could be exposed to temperature for indefinite times.

The conclusion from this part of the research was that the soy protein and wheat starch are not stable at 80°C under vacuum for an extended period of time. There is a clear change in material properties with changes in processing. It was also found that the denaturing of the soy protein aids in the polymerization as shown by an increase in modulus and strength of the soy plastic.

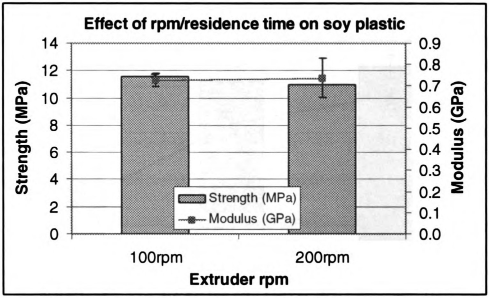


Figure 4.7 effect of change in rpm

Process changes and stability of the soy protein polymer is one area of high interest. Extrusion processing of large quantities of material can lead to small changes from lot to lot. Stability of the soy polymer is of interest in respect of finding a window of operating parameters where the material properties of the soy polymer remain constant. Figure 4.7 illustrates what occurs when residence time is reduced. The soy concentrate plastic was processed at 100 rpm and 200 rpm and each set of processing parameters allowed for the same material properties. The observation being that the soy plastic could be processed at 100 or 200 rpm and it would not affect the properties of the final material.

After standardized material properties were established the next step was to experiment with the addition of the natural fiber to the matrix and to determine the resulting composite material properties.

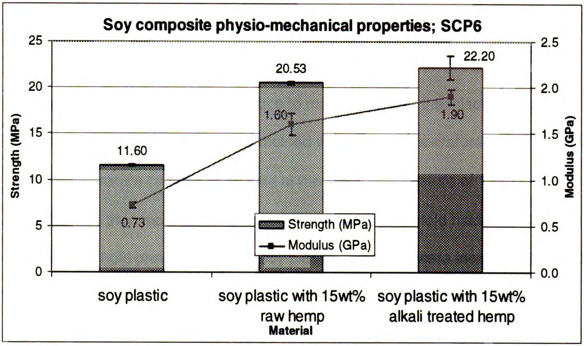


Figure 4.8 Effect addition of fiber on soy plastic.

Figure 4.8 illustrates the effect of addition of hemp fiber on the modulus and strength of the soy plastic. With the addition of 15wt% raw fiber into the soy plastic, modulus is more than doubled and the strength is almost doubled.

The natural fiber is an effective reinforcement for the soy plastic but alkali treatment of the fiber improves the strength and modulus over the raw or untreated fiber. This improvement in modulus with surface modification would seem to imply that the raw fibers were not distributed well within the soy polymer matrix and or they were not fully wet-out. The alkali treatment of the hemp fiber is believed to roughen the surface, remove oils and waxes on the surface allowing for better interaction of the matrix and reinforcement, improving strength. The modulus values of a filled polymer system should be constant with constant filler content. The positive influence of surface treatment on the effecting modulus values would imply poor dispersion of untreated fibers within the matrix.

Addition of the hemp fiber to the soy plastic lead to an increase in the viscosity of the melt flow which require to modifications of the injection molding parameters. All samples were still molded with a melt temperature of 132°C. All of the temperature controls were held at the same temperature of 132°C. The material was then molded into a dogbone shaped with a mold held at 20°C. The fill pack and hold pressures for the soy plastic composite were increased to 2000, 2200, and 1200 psi respectively. Timers for fill, pack, hold and cooling were set for 10, 3, 3, and 45 seconds. The cooling time could be reduced with the addition of the fiber. Shot size was still held at 1.1 inches, and the injection speed was set at 0.3in/sec. The modification of the process allowed composite parts with 15wt% fiber to be molded effectively. This process was used for both raw and alkali fiber reinforced composites.

Notched IZOD impact testing was done on the plastic and composite samples. Figure 4.9 displays the results of the effect of the hemp fiber on the impact properties of the soy plastic composite There was a slight increase in impact energy when the hemp fiber was surface treated, however, without a surface treatment, the impact energy of the composite was the same as the soy plastic.

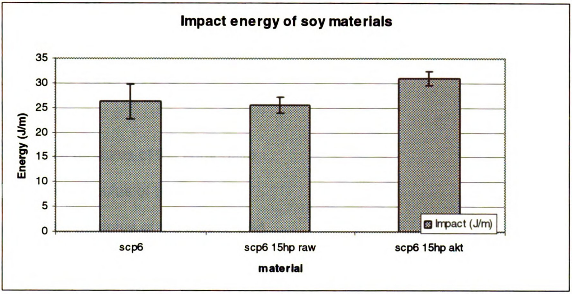


Figure 4.9 Impact energy of soy plastic and composites.

The experimental data was compared to theoretical data. One of the methods was to compare the tensile modulus of the composite data with the values calculated using the rule of mixtures. The rule of mixtures uses volume fractions to calculate the amount of material interacting within the composite. The composite manufacturing process outlined in the experimental section was set up on a weight fraction basis. The conversion of weight fraction to volume fraction was necessary to obtain the density of the hemp fiber. The density of hemp was obtained using Archimedes method as described Chapter 3.

The density of hemp was found to be 1.29g/cm^3. This value was then used to convert the weight fraction values into volume fraction values. The 15wt% values became twelve volume percent.

The rule of mixtures implies that the composite stiffness is a simple weighted mean dependent on the volume fraction of the fiber and matrix. So the modulus of the composite is equal to the modulus of the fiber multiplied by fiber volume fraction plus the modulus of the matrix times the matrix volume fraction.

$$E_c = V_f E_f + V_m E_m$$

Where:

E_c is the modulus of the composite

E_f is the modulus of the fiber

E_m is the modulus of the matrix, and

V_f is the volume fraction of the fiber, and

V_m is the volume fraction of the polymer matrix.

However, this model is designed for 100% aligned fibers. Extrusion and injection molding does not allow the fibers to be fully aligned. Some orientation occurs due to flow of the melt into the part. Because of this, an orientation factor is added to the rule of mixtures as a correction factor for the alignment of the fibers. The equation below is what was used for the prediction of the composite properties.

$$E_c = \sigma V_f E_f + V_m E_m$$

σ is the orientation factor. The data in figure 4.10 was compiled with an orientation of 0.25. The experimental data falls short of the predicted data from the rule of mixtures. The predicted modulus value is 2.3 GPa, the experimental data that collected as shown in figure 4.8 shows a modulus value of 1.6 and 1.9 for the different types of hemp fiber.

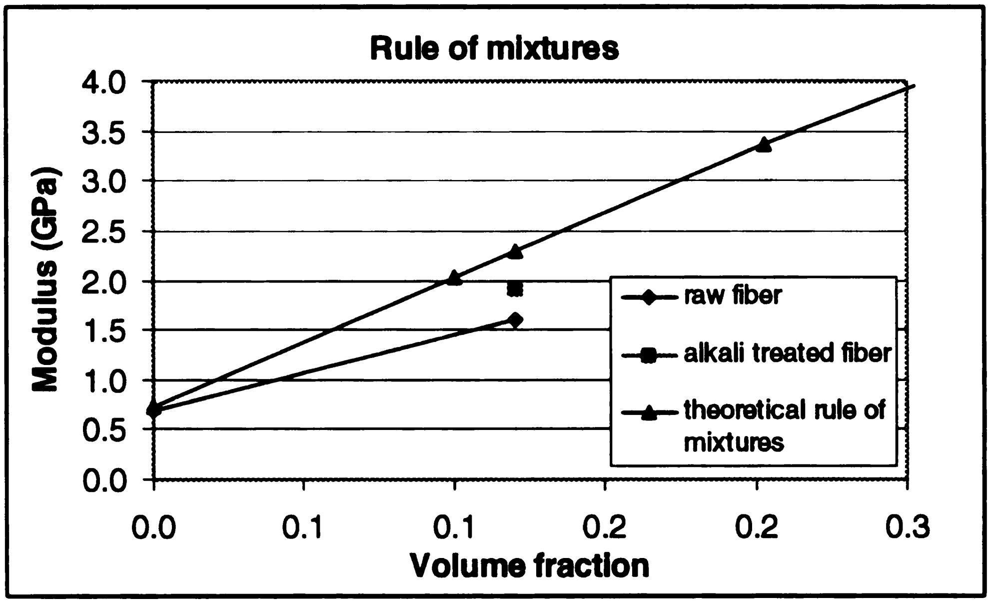


Figure 4.10 Rule of mixtures for composite properties.

Discrepancies between data and predicted values can be explained from microscopy images of fracture surfaces and internal morphology of the composite samples. Lack of good adhesion or poor fiber orientation also could change the predicted values of the composite.

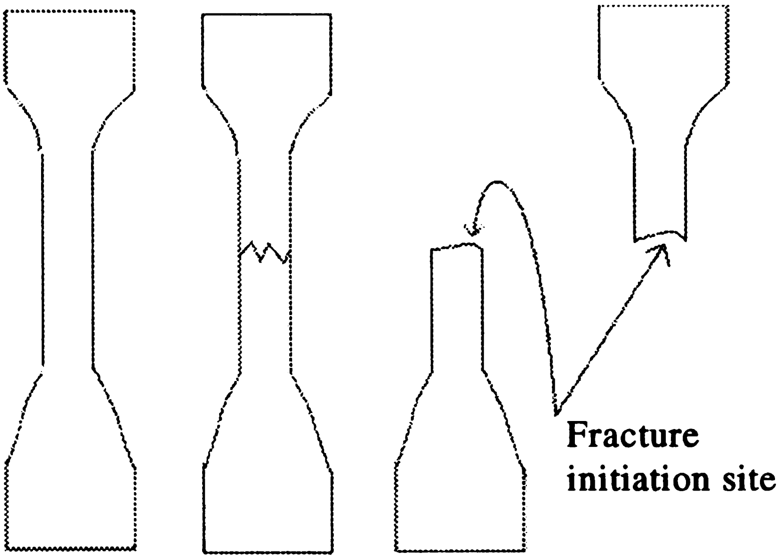


Figure 4.11 Illustration of fracture of soy plastic tensile coupon.

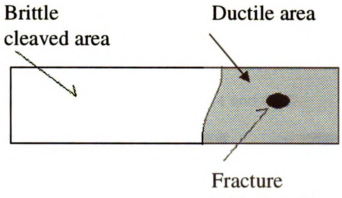


Figure 4.12 End view, schematic of fractured tensile coupon.

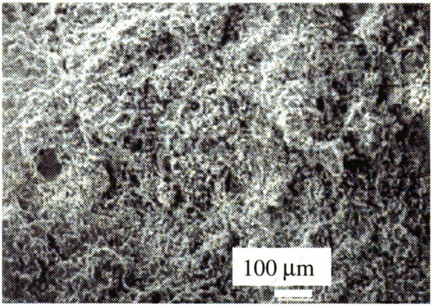


Figure 4.13 SEM of ductile fracture initiation site of soy plastic; 100x.

Fracture surfaces of the plastic or composite can explain a lot about a material. The soy plastic for instance, has a fairly unique fracture mechanism. The soy matrix has a ductile initiation site as illustrated in figures 4.11 and 4.12. Micrographs of this fracture area are shown in figures 4.13 and 4.15. The soy plastic fracture initiation is a slow ductile tearing of the material, however as the crack progress, the load bearing cross-section of the material decreases and the velocity of the crack propagation increases. The increase in crack speed leads to a change in mode of failure. The failure surface changes from a ductile failure to a brittle cleaved fracture surface; this is illustrated schematically in figure 4.12. The actual failure surface is shown in figures 4.14 and 4.16.

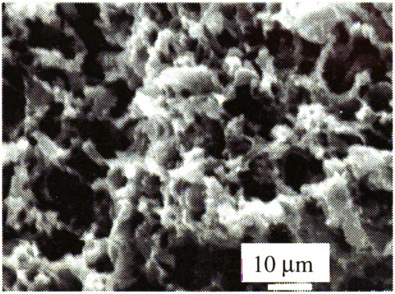


Figure 4.14 100x brittle fracture area of tensile failed specimen.

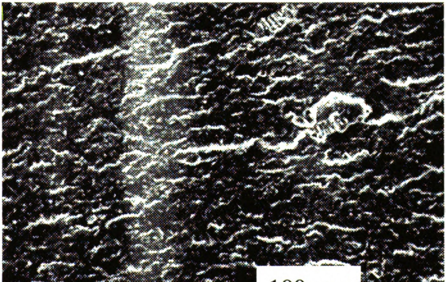


Figure 4.15 1000x ductile initiation fracture area of tensile failed specimen.

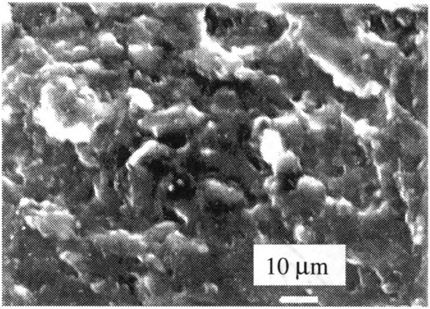


Figure 4.16 1000x brittle fracture area of tensile failed specimen.

With addition of fiber to the soy plastic, elongation to failure drastically decreases. In the soy plastic matrix, elongation to failure was in the five to ten percent range. This is limited in composite materials by the elongation of the fiber. In general the natural fibers will not elongate more than a percent or two. If the sample is elongated further than a percent or two the fiber begins to debond from the matrix. When this occurs it leads to void creation and catastrophic failure of the composite.

Composite fracture surface gives information about the adhesion between the matrix and the fiber, as well as information about fiber dispersion within the matrix. If there is poor wet-out of the fiber or clumping of fibers so that they are not fully distributed within the matrix there is usually evidence of this in the fracture surfaces of the composites. Fiber length in the fracture surface is also a useful piece of information taken from fracture surfaces. Long fiber pull-out indicates poor adhesion between the fiber and matrix and can explain poor material performance of the material. The micrographs of the composite failure surfaces in figures 4.17 – 4.20 focus on the fibers. From these micrographs one can see shorter fiber pull-out in the alkali treated fibers vs. the raw fiber composite samples.

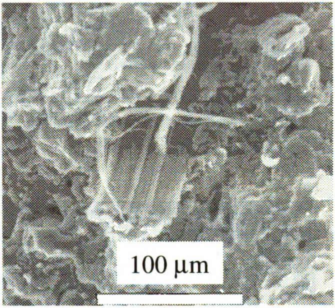


Figure 4.17 15wt% Alkali treated hemp in SCP6, tensile failure surface, 400x

The shorter fiber lengths in the fracture surfaces are indicative of better adhesion and hence the better strength values for the alkali treated fiber composites.

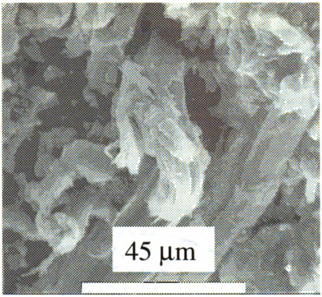
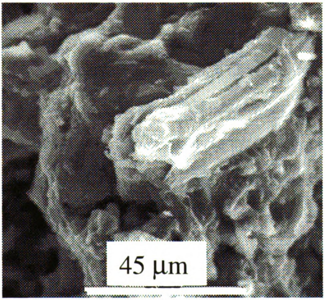
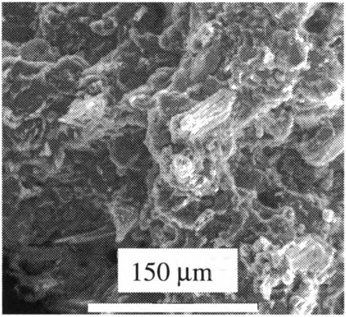


Figure 4.18 15wt% Alkali treated hemp in SCP6, tensile failure surface, 1000x.



4.19 15wt% raw hemp in SCP6, tensile failure surface, 1000x.



4.20 15wt% raw hemp in SCP6, tensile failure surface, 300x.

From the material properties of the alkali treated samples and the fracture surfaces of the failed composites it is clear that the alkali treatment of the fiber improves the properties of the composite. What exactly happens in the alkali treatment process to the fiber? There are a couple things that happen to the fiber. As illustrated in figure 4.21, the surface oils and waxes are washed away from the surface of the fiber. The long cellulose chains within the fiber are also broken up. These two processes allow for the fiber to have more bonding sites available to the polymer, for chemical interaction. The washing away of the oils and waxes also roughens up the surface, which allows for better mechanical interlocking of the fiber and matrix. The alkali treatment enhances the chemical and physical interactions.

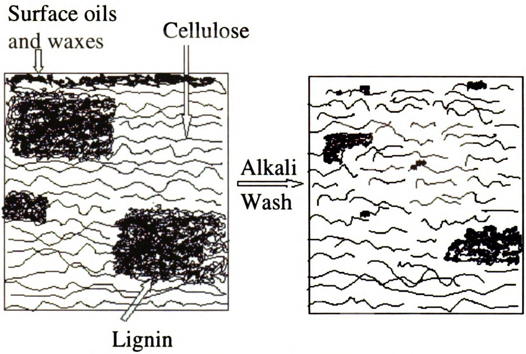


Figure 4.21 Schematic of alkali treatment of natural fiber.

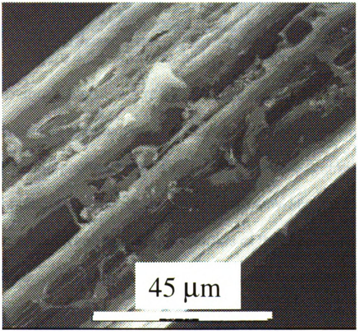


Figure 4.22 1000x raw hemp fiber.

Figure 4.22 shows a raw hemp fiber. In comparison to figure 4.23 in which the fiber has been alkali treated. The physical changes are not overtly significant, yet still effective for improvement in performances. One can see the more exposed fibrils in the alkali treated fiber. In comparison to the alkali fiber, the raw hemp fiber shows a smoother surface.

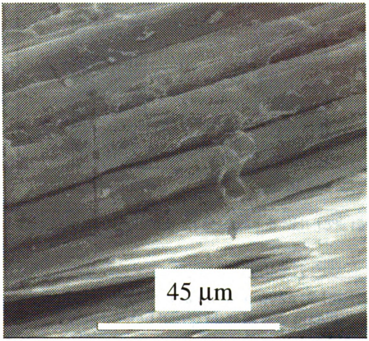


Figure 4.23 1000x alkali treated hemp fiber.

One major unresolved issue of plant-based materials is their affinity to moisture and the drastic effects moisture has on material properties of the plastic or composite. The composite samples were compounded and were placed on a desk in an air-conditioned office for 30 days, approximately one month, then re-tested. Comparison between material properties of the aged samples and the samples tested after compounding is shown in figures 4.24 through 4.27. After exposure to an office environment for thirty days the modulus of the raw fiber composite dropped by thirty one percent, the alkali treated fiber composite modulus dropped by twenty two percent. These are drastic reductions in the material properties that would effect applications of the material.

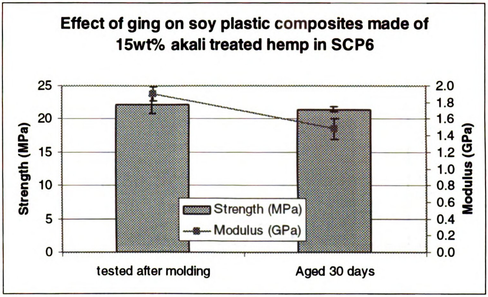


Figure 4.24 Effect of moisture on soy plastic with 15% raw hemp.

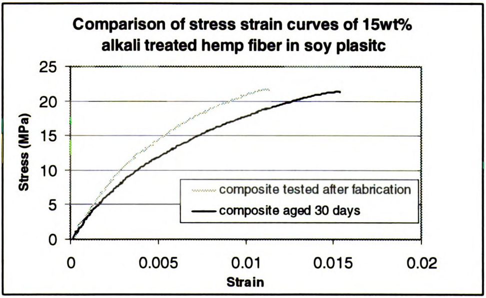


Figure 4.25 Change in stress-strain behavior of alkali fiber composite with aging

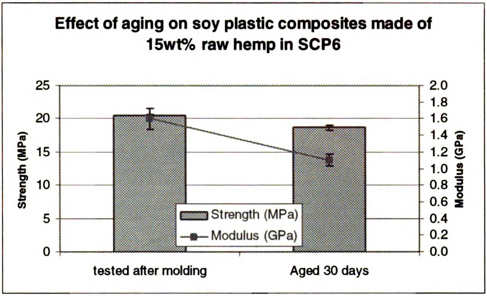


Figure 4.26 Effect of moisture on soy plastic with 15% raw hemp.

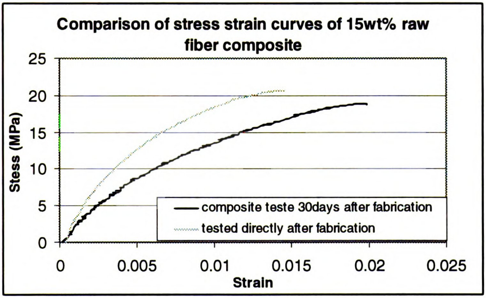


Figure 4.27 Change in stress-strain behavior of raw fiber composite with aging.

What occurs within the material is shown in the below micrographs of the composite sample tensile fracture surfaces in figures 4.28 – 4.31.

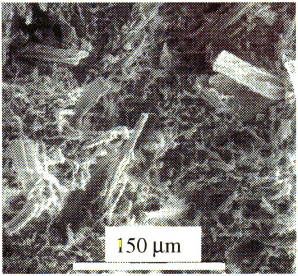


Figure 4.28 Tensile fracture surface of 15wt% raw fiber in soy plastic, tested 30 days after composition, 300x.

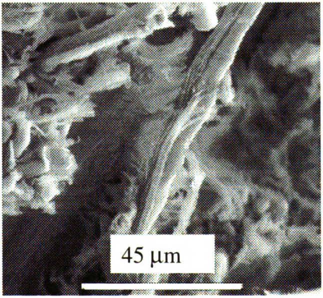


Figure 4.29 Tensile fracture surface of 15wt% raw fiber in soy plastic, tested 30 days after composition, 1000x.

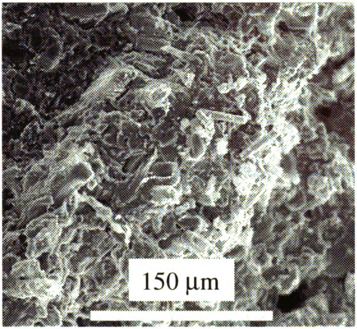


Figure 4.30 Tensile fracture surface of 15wt% alkali treated fiber in soy plastic, tested 30 days after composition, 300x.

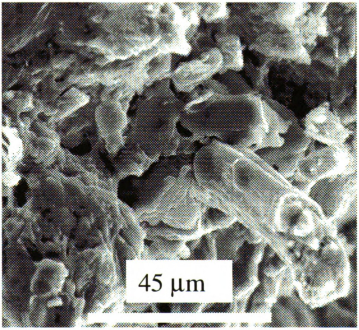


Figure 4.31 Tensile fracture surface of 15wt% alkali treated fiber in soy plastic, tested 30 days after composition, 1000x.

Fiber pull-out lengths in figures 4.28 – 4.31 are much larger than pull-out lengths in figures 4.17 – 4.20. Fiber pullout length is related to the adhesion of the fiber to the matrix. Longer fibers in the fracture surface, relates to a poorer bond between the fiber and matrix. With exposure to moisture of the soy plastic, the soy plastic and fiber debond. This leads to the fiber and matrix, not working as a one material but two separate materials. When the sample is then tested the modulus decreases because of slippage between the fiber and matrix. This is evident in figures 4.24 - 4.26 and the micrographs relate well with this trend in properties.

These micrographs show how the material internal morphology relates to its material properties, the fracture surfaces of the composites tested after fabrication indicate that there is good wet-out of the fiber, within the polymer matrix.

The predicted material properties from the rule of mixtures does not compare well with the actual data collected from the samples. This has to come down to fiber orientation within the matrix.

Figure 4.32 is a schematic of how the composite melt flow fills the mold during the injection molding of the dog-bone samples. The melt flow advances and fills the cavity; as this happens the layer near the surface begins solidify. This forms a skin layer of the sample where the fiber is highly ordered in the flow direction, and in the case of the dog-bone, in the direction of applied load. However further into the bulk of the material the fiber is less aligned and more random, this is illustrated in figures 4.33 and 4.34.

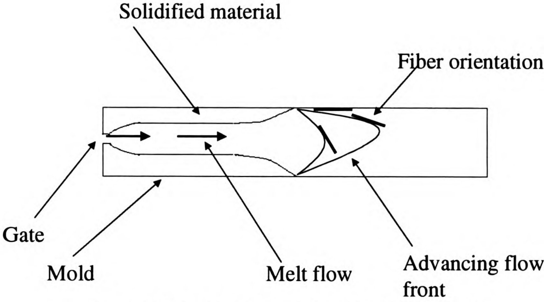


Figure 4.32 Schematic of melt flow filling part cavity.[20]

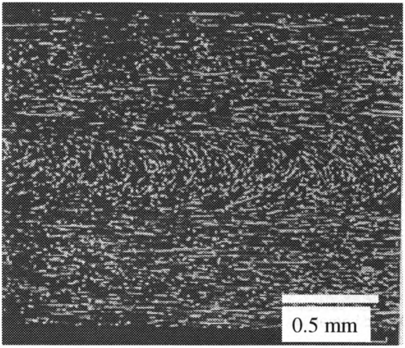


Figure 4.33 An example of a glass filled polypropylene injection-molded part, longitudinal cross-section[20].

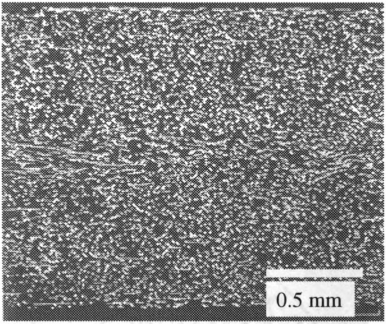
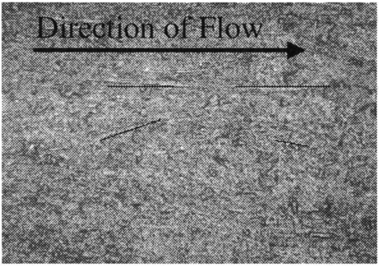


Figure 4.34 An example of a glass filled polypropylene injection-molded part, transverse cross-section.[20]



4.35 Surface of dog bone sample scp6 with 15wt% raw hemp fiber 100x, some fibers highlighted in black.

Figures 4.32 – 4.34 show how the fiber is orientated during the injection molding process, this is evident in the soy composites as well, shown in figure 4.35 the fiber aligned in the direction of the flow. This occurs on the surface; in the bulk the fibers become less orientated as shown in figure 4.36.

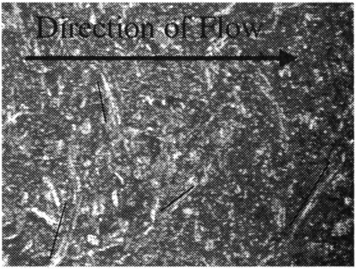


Figure 4.36 Optical micrograph of fibers in bulk of a injection molded dog bone 15wt% raw hemp fiber 100x, some fibers highlighted in black, longitudinal cross-section.

Figures 4.35 and 4.36 illustrate what is shown schematically in 4.32. Fibers within the bulk of the sample are not orientated with the direction of flow and hence not the direction of loading when the sample tested under tensile loading. This is primary reason that the material properties do not come close to the predicted rule of mixture values. Rule of mixture values were computed with an orientation factor of 0.25, implying that 25% of the fibers are aligned in the direction of load.

Break down of soy plastic and soy plastic composites, on weight basis (grams)		
	scp6	scp6 with 15% fiber
maleic anhydride	50	42.5
luprosal (initiator)	10	8.5
soy concentrate	470	399.5
wheat starch	188	159.8
glycerol	282	239.7
BAk4	500	425
Fiber		225
Total weight per batch	1500	1500
Percentage ag-based	43.8% ag-based	52.2% ag-based

Table 4.1 Breakdown of plastic and composite components.

The final comment on the soy plastic hemp fiber composite is to outline the percentage of the plant-based products that are in the final products. In the samples compounded and tested the bio-based components were; soy concentrate, wheat starch and hemp fiber. The break down of the materials that compose the soy plastic and the composite is outlined in Table 4.1. The plastic itself is 43.8wt% bio-based and the composite is 52.2wt% bio-based.

Chapter 5

Conclusions

5.1) Conclusions

From the data presented there are several points and conclusions that can be made:

- Moisture acts like a plasticizer in the raw materials and softens the material.

One of the major issues in establishing baseline material parameters of the plastic was removal of moisture. Due to the varying degree of moisture in the environment there was a varying degree of moisture in the raw materials and hence a varying amount of plasticizer in the final product. This lead to material property values that were inconsistent.

- Drying the material under vacuum and heat removes moisture but also denatures the protein, which increases the modulus.

The soy protein is not thermally stable at 80°C. To ensure removal of all moisture within the raw materials the soy concentrate has to be held at temperature for an extended period, which leads to the proteins denaturing. The final material properties are enhanced due to the protein unfolding that takes place as a result of the denatuization process. Resulting in exposing more reaction sites on the protein and therefore improved cross-link density.

- Removal of moisture increases difficulty of processing.

Removal of excess moisture has the same effect of adding less plasticizer and increases the viscosity of the melt flow. This leads to a need for higher processing temperatures.

- Addition of biofiber improves strength and modulus

The hemp fiber has a modulus of 55GPa. The incorporation of this into a low modulus matrix leads to an overall improvement in modulus. The hemp fiber also has a higher tensile strength than the soy plastic, which leads to an improvement in tensile strength as well.

- Surface treatment of the natural fiber improves fiber matrix bonding and overall strength of the composite, tensile and impact.

The alkali treatment of the hemp fiber improves fiber surface roughness as well as removes oils and waxes that interfere with bonding of the matrix and reinforcement. The rougher surface and better bonding sites allows the polymer and fiber to have a stronger bond and improved material properties.

- The soy plastic failure in tensile loading is a dual mechanism; a ductile initiation site and brittle crack propagation.

The soy plastic elongates slowly and eventually a site of crack initiation is formed. When this occurs the crack slowly begins to grow until it reaches a critical size. When this occurs the material fails catastrophically and the crack growth velocity increases and the material changes failure modes to a brittle or cleavage failure.

- The alkali treated fiber performs better than the raw fiber.

From the data it is observed that the alkali treatment not only improves the strength and modulus but also has shorter fiber pullout lengths, which would imply better adhesion. The alkali fiber composite materials also perform better after aging and exposure to moisture. The samples retain more of their strength and stiffness.

- Fiber orientation in the injection-molded samples is not homogenous through the thickness of the coupon and not aligned with the axis of loading.

The injection molding process allows fibers to randomly orientate themselves with in the bulk of the material. As shown in the micrographs the fiber with in the bulk is not orientated to the axis of loading.

- The bio-based composites achieve the properties of polyethylene.

Table 4.1 shows the breakdown of the martial components that make up the soy plastic and composites and shown the overall composite is more than 50% ag-based. The strength and modulus of PE was achieved. PE has modulus values in the range of 0.7 – 1.4 GPa, and strength values of 18 – 35 MPa.

- Material properties of the biocomposites are comparable to glass reinforced petroleum based polymers.

Chapter 6

Research Recommendations

6.1) Recommendations

As a result of this study, it has been shown that soy protein based plastics reinforced with biofibers can possess significant structural properties, i.e. modulus, strength and strain, to be considered for structural applications and as an alternative to petroleum based materials. However there are significant challenges that remain to be addressed before these biocomposites can be used in a real-world application.

The largest challenge is to improve the hydrothermal stability of the soy plastic. Moisture absorption in unmodified soy plastic is large and has a serious effect on mechanical properties. Long-term applications will depend on the ability to produce a material that is not easily affected by exposure to moisture and temperature extremes.

Another challenge is to improve the properties of the soy matrix to produce a polymer with a higher degree of cross-linking and hence higher stiffness. Reacting more functional groups on the protein could do this, specifically hydroxyl groups. Reaction of these groups could also lessen the effect of moisture absorption. This might be accomplished with additional denaturing of the protein over what was done in the current process before or during extrusion with the addition of sodium hydroxide or urea, either as an additive to the extruder or used as a chemical treatment before processing.

Alternatively, this could be accomplished with a more aggressive heat treatment while drying the material.

The blending of the soy protein polymer with the polyester-amide has been shown to improve the processing and mechanical properties of the end material. Another avenue of interest would be to blend the soy protein and starch directly with the polyester-amide and maleic anhydride. This could eliminate the usage of glycerol, and eliminate the problem of the leaching of the glycerol. This change in processing could also increase the percentage of biobased components in the end product. As a result, the final product could have improved material properties, reduced moisture absorption, and a larger fraction of biobased materials. This could improve material performance to have an extended life expectancy and open the door to applications that require a more durable material that is environmentally stable such as structural materials for housing or transportation applications.

BIBLIOGRAPHY

1) Dipa Ray, B.K. Sarkar, S. Das, A.K. Rana (2002). Dynamic mechanical and thermal analysis of vinylester-resin-matrix composites reinforced with untreated and alkali-treated jute fibers. Composites science and technology: 62, 911- 917

2) A. Hodzic, R. A. Shanks and M. Leorke (2002). Polypropylene and aliphatic polyester flax fibre composites. Polymers & Polymer composites: 10(4), 281 – 290 (2002)

3) A.K. Mohanty, M. Misra, G. Hinrichsen (2000). Biofibres, biodegradable polymers and biocompposties: An overview Macromolecular Materials & Engineering 276/277, 1-24

4) http://class.fst.ohio-state.edu/FST822/lectures/Soy.htm (2001)

5) Monlin Kuo, Daniel Adams, Deland Myers, Daniel Curry, Howard Heemstra, John L. Smith, Yilin Bian (1998), Properties of wood/agricultural fiberboard bonded with soybean-based adhesive Forest products journal: 48(2), 71 – 75

6) Xiaoqun Mo, Jie Hu, X Susan Sun, Jo A. Ratto (2001) Compression and tensile strength of low-density straw-protein particleboard, Kansas State University, Industrial Crops and Products: 14(1), 1-9

7) H.C. Huang, E.G. Hammond, C.A. Reitmeier, and D.J. Meyers (1995) Properties of fibers produced from soy protein isolate by extrusion and wet-spinning Journal of American oil and chemists society: 72(12), 1452 - 1460

8) Delia A. Sorgentini, Jorge R. Wagner, And Maria Cristina Anon (1995) Effects of thermal treatment of soy protein isolate on the characteristics and structure – function relationship of soluble and insoluble fractions Journal of Agricultural food chemicals

9) P. Cunningham, A.A. Ogale, P.L. Dawson, and J.D. Acton (2000) Tensile Properties of Soy Protein Isolate Films produced by a thermal compaction technique. Journal of Food Science: 65 (4)

10) Q. Lei and W.L. Boatright (2001). Compounds Contributing to the odor of aqueous slurries of soy protein concentrate. Journal of Food Science: 66(9), 1306 - 1310

11) C. M. Vax, j.F. Mano, M. Fossen, R. F. van Tuil, L. A. de Graaf, R. L. Reis, and A. M. Cunha (2002) Mechanical, dynamic-mechanical, and thermal properties of soy protein-based thermoplastics with potential biomedical applications Journal of macromolecular science: 41(1), 33-46

12) J.U. Otaigbe, H. Goel, T. Babcock, J Jane (1999) Processability and properties of biodegradable plastics made from agricultural biopolymers Journal of Elastomers and Plastics. 31, 56-71

13) Sue HJ, Wang S, Jane JL (1997) Morphology and mechanical behavior of engineering soy plastics. Polymer: 38(20), 5035 – 5040

14) Qiagxian Wu and Lina Zhang (2000) Properties and structure of soy protein isolate – ethylene glycol sheets obtained by compression molding. Industrual engineering chemical res.: 40, 1879 –1883

15) Xiaoqun Mo, Xiuzhi Sun (2002) Plasticization of soy protein polymer by polyol-based plasticizers. Journal of the American Oil Chemists' Society: 79(2)

16) C.H. Schiling, T. Babcock, S. Wang, and J. Jane, (1995) Mechanical properties of biodegradable soy-protein plastics. Journal of Material Research: 10(9), 2197 – 2202

17) Jacob John and Mrinal Bhattacharya (1999) Properties of reactively blended soy protein and modified polyesters. Polymer International: 48, 1165-1172

18) Perminus M. Mungara, Tao Chang, Jie Zhu and Jay-lin Jane (2000) Processing and physical properties of soy protein/biodegradable synthetic polymer blends Polymeric Materials: Science& Engineering: 86,364-365

19) A.A. Ogale, P. Cunningham, P.L. Dawson and J.C. Acton (2000) Viscoelastic, thermal, and microstructural characterization of Soy Protein Isolate Films. Journal of food science: 65(4), 2000

20) D. Hull and T. W. Clyne second edition; An introduction to composite materials, pages 279-280

21) Otaigbe JU and JaneJ, (1997) Environmental Polymer Degradation: 5(75)