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Improvement of mechanical properties and water stability of vegetable protein based plastics

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**Improvement of mechanical properties and water stability of vegetable protein
based plastics**

by

Gowrishankar Srinivasan

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Industrial & Agricultural Technology

Masters Examination Committee
David Grewell, Major Professor
Michael Kessler
Carl .J. Bern

Iowa State University

Ames, Iowa

2007

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DEDICATION

This work is dedicated to my family, my friends and my year old “nephew”

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ABSTRACT

Bio-renewable bio-degradable plastics are a potential solution to the growing problems of pollution caused by petroleum plastics and dependency on foreign nations for petroleum resources. One possible feed stock for these materials are vegetable proteins, especially from soy bean and corn. These proteins have relatively high molecular weights and have the potential of being processed with standard polymer processing technologies. But some issues that need to be addressed are their water instability (soy protein) and inferior mechanical properties as compared to petroleum derived plastics. In this study, soy protein isolates (SPI) and zein protein was processed with various additives and different process variables to improve their mechanical and water absorption properties.

SPI a food grade protein isolate extracted (90% protein) from soybeans was mixed with solvents such as water and glycerol and preservative salts to form the base resin. The resin was extruded in its control composition as well as with additives such as zinc stearate, zinc sulfite and blended with poly- ϵ caprolactone (PCL) to obtain pellets of five different compositions. The extrudate was pelletized and injection molded into ASTM dog-bone samples, which were used for characterization. The results indicated that the blends with PCL were relatively water stable. Thermocycling of control composition at 100°C improved the tensile strength significantly.

Zein an alcohol soluble protein from corn endosperm was casted into films after dissolution in solvents (ethanol) and addition of additives and/or plasticizers. The control formulation based on screening experiments was varied with the addition of different

percentages of nanoclay. The effect of nanoclay exfoliation by ultrasonics on zein cast sheets was investigated. The results indicated that the control formulation had better mechanical properties but addition of nanoclays improved the water absorption properties in the films.

CHAPTER 1: INTRODUCTION

Plastics have become an integral part of our daily life, from footwear to structural components such as doors and construction components. Further, the use of advanced plastic composites has replaced many conventional metals applications such as aluminum and other alloys in industries like aircraft manufacturing. The plastics industry in the U.S. is the 3rd largest manufacturing industry that employed more than 1.1 million people and shipped a total of \$341 billion of goods in 2005 [1]. Current statistics indicate that the highest consumptions of plastics in the U.S is for packaging followed by consumer plastics which is a broad category that constitutes, bottles, bags and utility supplies. The third largest sector of plastics consumption is domestic structural components [2] as detailed in Figure1.

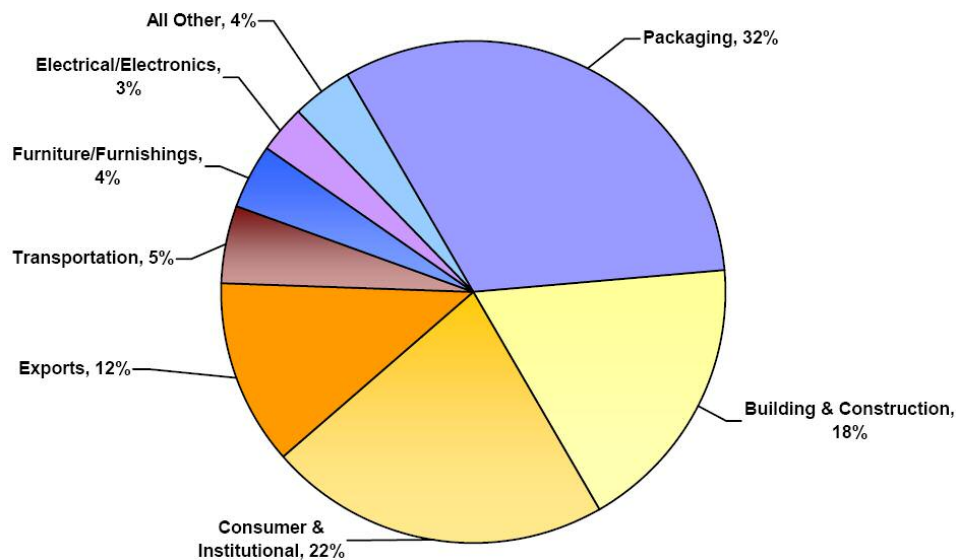


Figure 1 2006 Percentage Distribution of Resin Sales & Captive Use by Major Market [2]

The major resins used in the various markets are:

- Low Density Polyethylene (LDPE)
- Linear Low Density Polyethylene (LLDPE)
- High Density Polyethylene (HDPE)
- Polypropylene (PP)
- Acrylonitrile-Butadiene-Styrene (ABS)
- Styrene-Acrylonitrile (SAN)
- Polystyrene
- Epoxy
- Styrene Butadiene Latexes (SBL)
- Thermoplastic Polyester
- Nylon
- Polyvinyl Chloride (PVC)
- Polyurethanes

All of the above listed resins are petroleum based plastics and represent 95% of the total petroleum plastics consumed and are neither renewable nor bio-degradable. Dwindling reserves of crude oil coupled with regional political tensions and elevated demand has increased oil prices as high as \$70 per barrel. This has ultimately promoted many to ask the question “can we depend on the supply of oil as a source of energy and plastics?” Further, the increasing dependence on foreign nations for oil and hostile international politics has forced the U.S. to consider domestic alternative sustainable resources. In addition, ecologists have raised concerns with the exponential rate of pollution production caused by both the use of petroleum as an energy source and petroleum as a feed stock for plastics. This has promoted investigations to further understand global warming and how future environmental issues can be avoided. Many of these studies have developed fundamental concepts on ecology, climatology and

consumption of fossil fuels that can predict future global weather patterns. A proposed alternative to petrochemicals is to utilize bio-renewable resources. Bio-renewable resources are abundant domestically and give the U.S. an added advantage of reduced emission of various pollutants, which would lower green house gas emissions by circulating the carbon in a closed loop fashion as shown in Figure 2.

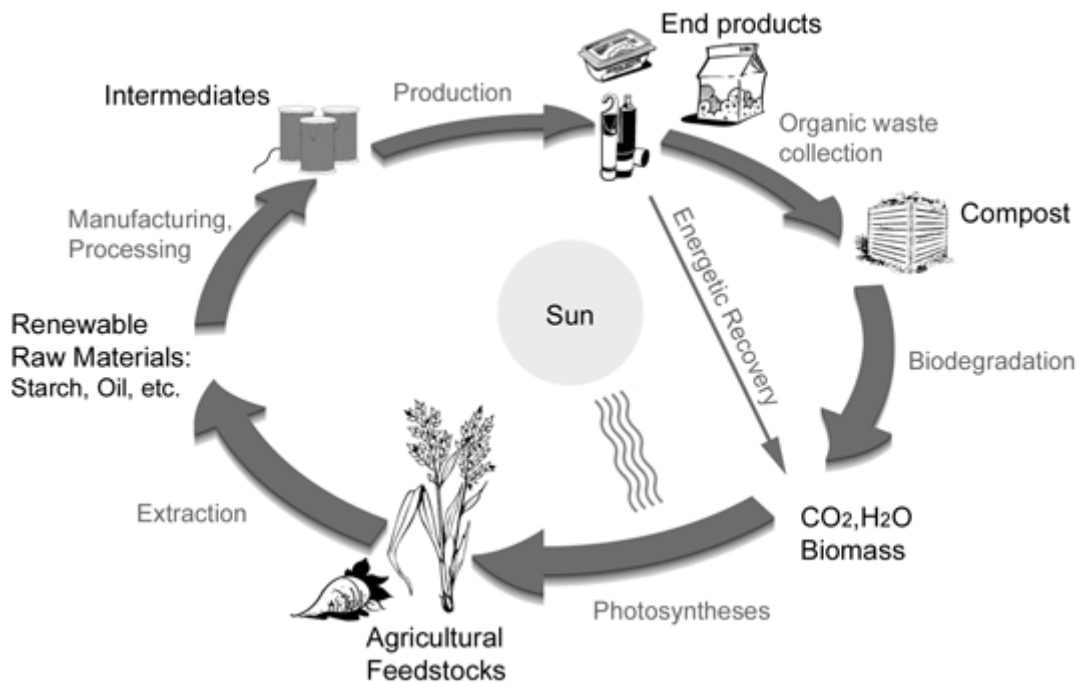


Figure 2 closed cycle of bi-plastics form European bio-plastics [3]

The system modeled in the figure is idealistic and results in no release of additional carbon in the environment. That is to say no fossil fuel resources are utilized. In addition, an added advantage to this model is the strengthening of the nation's economy by promoting agriculture and other supporting industries. This scenario will

ultimately lead to self-sufficiency and will create new employment opportunities by utilizing nationally available bio-renewable resources.

1.1 Environmental Impact and Requirement of Bio-renewable Polymers

As previously detailed, one of the major disadvantages of petroleum plastics is the generation of pollution. This has promoted many to consider other feed stocks for plastics. As mentioned earlier bio-renewable resources are a potential solution. To support this point of view it is necessary to understand the scale of this issue. Data from Environmental Protection Agency (EPA) indicate that plastics contribute up to 11.8% (28.9 Million Ton) of the total Municipal Solid Waste (MSW) generated in the U.S. for 2005, of which only roughly 5.4% of the total generation is recovered [4] as detailed in Table 1. In addition, only 34% of the total soft drink bottles generated are recycled. The overall balance of the material not recovered or recycled are land-filled, incinerated or dumped in the ocean causing pollution. Combustion of petroleum plastics not only produces green house gases but also release harmful emissions such as dioxins. Ocean dumps disturb the aquatic life and release harmful chemicals into the environment through leaching of plastizers and chemical decomposition. Also fish and birds often consume this debris, leading to deaths by choking or digestion problems. While recycling has increased over the last number of years as seen in Figure 3, it is does not offset the additional generation of plastic waste.

Table 1 Generation and recovery of materials in MSW2005 (in millions of tons and percent of generation) [4]

| Material | Weight Generated | Weight Recovered | Recovery As a Percent of Generation |
|------------------------------------|------------------|------------------|-------------------------------------|
| Paper and paperboard | 84.0 | 42.0 | 50.0% |
| Glass | 12.8 | 2.76 | 21.6% |
| Metals | | | |
| Steel | 13.8 | 4.93 | 35.8% |
| Aluminum | 3.21 | 0.69 | 21.5% |
| Other nonferrous metals* | 1.74 | 1.26 | 72.4% |
| <i>Total metals</i> | 18.7 | 6.88 | 36.8% |
| Plastics | 28.9 | 1.65 | 5.7% |
| Rubber and leather | 6.70 | 0.96 | 14.3% |
| Textiles | 11.1 | 1.70 | 15.3% |
| Wood | 13.9 | 1.31 | 9.4% |
| Other materials | 4.57 | 1.17 | 25.6% |
| <i>Total Materials in Products</i> | 180.7 | 58.4 | 32.3% |
| Other wastes | | | |
| Food, other** | 29.2 | 0.69 | 2.4% |
| Yard trimmings | 32.1 | 19.9 | 61.9% |
| Miscellaneous inorganic wastes | 3.69 | Neg. | Neg. |
| <i>Total Other Wastes</i> | 65.0 | 20.6 | 31.6% |
| TOTAL MUNICIPAL SOLID WASTE | 245.7 | 79.0 | 32.1% |

Includes waste from residential, commercial, and institutional sources.

* Includes lead from lead-acid batteries.

** Includes recovery of other MSW organics for composting.

Details may not add to totals due to rounding.

Neg. = Less than 5,000 tons or 0.05 percent.

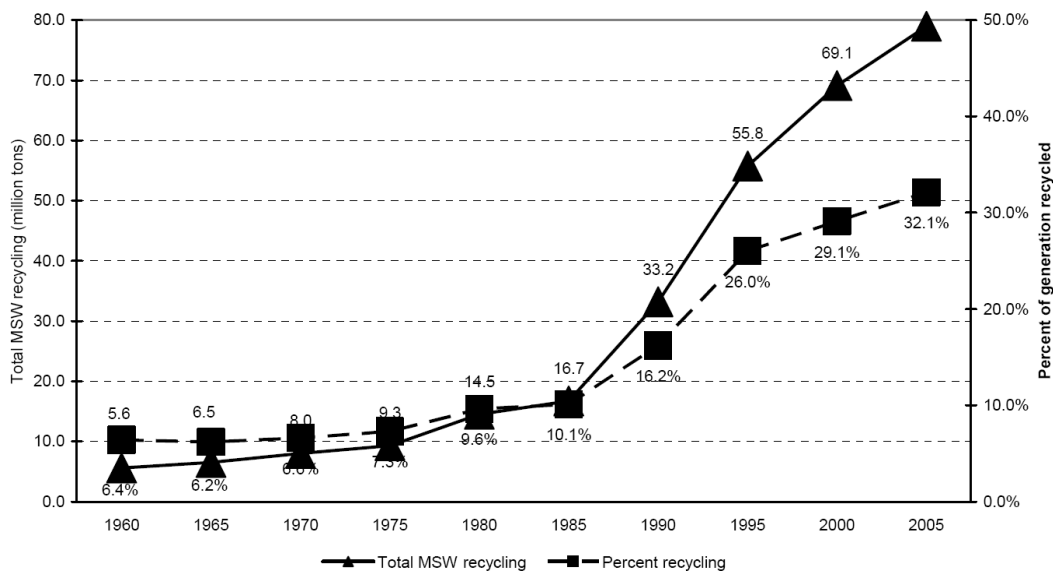


Figure 3 MSW recovery rates 1960-2005 [4]

Such rising trends in solid waste generation, especially the contribution by petroleum plastics, has caused concerns as most of these plastics do not degrade, rather stay intact in their dumpsites for many decades. This creates a reserve of uncirculated carbon. While this effectively removes the carbon from the ecological cycle, it is stored in a form that biological mechanisms can not utilize it as an energy source. Switching to bio-renewable resources for plastics could potentially reduce this effect because many bio-renewable plastics are rich in carbon and nitrogen and act as a energy source for bacteria.

1.2 Bio-renewable resources

Bio-renewable resources by definition are “organic materials of recent biological origin” also defined as “sustainable natural resources” [5]. From these definitions it can be generally stated that bio-renewable resources are from agriculture. Agriculture, one of the strengths of the U.S, suggests opportunities for the use of bio-renewable as a feed stock for plastics. This is especially true with abundance of soy beans and corn crops are two of the major “cash” crops of the nation.

The drive to use bio-renewable fuels such as ethanol and bio-diesel manufactured from corn and soy beans respectively is gaining momentum with the awareness of global warming. The co-products of these processes are typically rich in proteins, which are a vast source of natural polymers derived from amino-acids as a result of plant metabolic activities. To make opportunities more economically attractive these proteinaceous co-

products are also very inexpensive. Hence soy protein and corn proteins are perfect alternative feed stocks for plastics.

1.2.1 Soy Protein Isolate

Soybeans, one of the major agricultural crops in the U.S. with annual productions of up to 3.19 billion bushels [6], are primarily used in a wide variety of food products either in its native form (dried soy bean snacks) or as a processed product, such a soy-milk (SILK ®). Often the food industry uses soy-protein isolate (SPI) as an initial ingredient for many food products. SPI contains at least 90% protein [7]. The protein is extracted from crushed or defatted soy meat free of fats that are removed by dissolving in hexane, following dissolution in caustic at pH 9; precipitation of the protein is promoted by acidifying the extract to pH 4-5 modification.

Soy proteins are primarily composed of two protein structures; 7S and 11S also known as β -conglycinin and glycinin globulins. These are main storage proteins in soy beans and have been reported to be key components in determining functional properties of soy products and are distinctly different in their functional properties. The globulin 7S is a trimer (an oligomer with three monomers) formed by any combination of the α , α' and β , subunits which are helix confirmations of polymerized amino acids as shown in Figure 4, which are non-covalently linked [8]. Each subunit has one or two *N*-linked (nitrogen) glycosyl groups. The globulin 11S subunits consist of the combination of two polypeptides, *A* and *B*, with acidic and basic isoelectric points, respectively, linked by a

disulfide bond. The molecule is formed by six subunits. The molecular weights of 7S and 11S globulins have been reported to be 150–200 and 300–400 KDa, respectively [9].

The presence of high proportions of glutamic and aspartic acid compared to other proteins make both soy globulins more hydrophilic than globular proteins found in wheat gluten. The sulfhydryl groups and disulfide bonds of 7S globulin are zero and two per molecule, respectively. In contrast, 11S globulin has two sulfhydryl groups and 20 disulfide bonds per molecule.

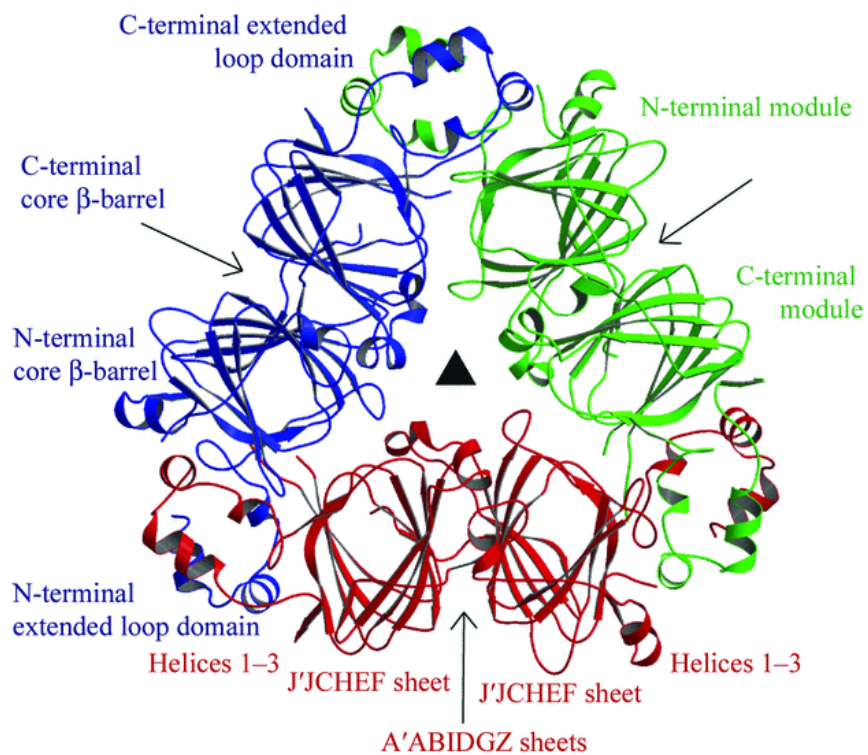


Figure 4 Ribbon diagram of the $\alpha_7\beta_3$ trimer as seen along a molecular threefold axis (black triangle) [10].

1.2.2 Zein Protein

Zein is the alcohol-soluble protein from corn which is another important annual crop for the U.S. with productions of up 10.5 billion bushels a year; also zein is classified as a prolamin protein (rich in proline, an amino acid). It is important to note that there are differences between prolamin zein and commercial zein. Zein is the principal storage protein of corn and 44–79% of the endosperm protein consists of zein, depending on the corn variety and separation method used. In the kernel, zein is located in bodies $\approx 1\mu$ in size. Biologically, zein is a mixture of proteins varying in molecular weight and solubility. These proteins can be separated by differential solubilities and their related structures into four distinct types: α , β , δ and γ [11].

α -Zein is the most abundant protein component in the corn kernel, accounting for $\approx 70\%$ of the total protein content. The next most abundant zein is γ -zein, contributing $\approx 20\%$ to the total protein content of corn. Alpha (α)-Zein can be extracted using aqueous alcohol, whereas the other zeins need a reducing agent in the solvent to be extracted. Zein that is extracted without the use of reducing agents is known as native form of zein. α -Zein that is extracted with a reducing agent has two bands that represent different levels of protein by molecular weight with apparent migration rates (M_r) of 19 and 22 kDa on SDS-PAGE (sodium dodecyl sulfate polyacrylamide gel electrophoresis). Only α -zein is found in commercial zein in large amount. This is both beneficial and understandable. The other types of zeins β , δ and γ are thought to contribute to gelling, which is a shortcoming of commercial zein as they hinder formation of film coatings by α -zein and are also hydrophilic. Early literature divides zein into two classes: α -zein and β -zein. α -

Zein is soluble in 95% aqueous alcohol or 85% aqueous iso-propanol, whereas β -zein was soluble in 60% aqueous ethanol. Only α -zein is suitable for commercial use as β -zein is prone to gelation which is not advantageous and disrupts continuous film formation. α -Zein in today's classification scheme contains the two polypeptides: 19 kDa and 22 kDa as mentioned earlier. Commercial zein primarily consists of α -Zein because of the solvent used and the material from which zein is extracted.

It is important to note that commercial zein is only from corn gluten meal. Corn gluten meal is a co-product of corn wet-milling. Corn wet-milling uses SO_2 to promote softening of the kernels and facilitate removal of starch. SO_2 weakens the matrix structure by breaking disulfide cross-links. The SO_2 also reduces the disulfide bonds found in β , γ , and δ -zein. Once the disulfide bonds are reduced, γ -zein is water-soluble and would be eliminated with water steeping which would dissolve the water soluble protein components and aid the fractionation of α -zein. The extraction solvents used for recovering commercial zein (86% aqueous iso-propanol) also decreases the amounts of β , γ , and δ -zeins being solublized. In more detail, Esen (1986) showed that β and γ -zein were not soluble in solvents containing 90% iso-propanol alcohol. Some of the other characteristics of zeins are they have excellent gas barrier properties, they are insoluble in water and are brittle in the pure state [12].

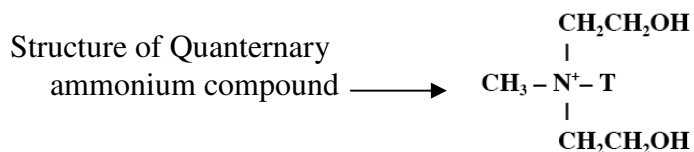
1.3 Additives- Nanoclay (Closite 30 B)

Nanoclays are naturally occurring montmorillonites which naturally occur in the form of sheets or platelets that are stacked together from multilayered tactoids that resemble a deck of cards [13] or multistoried buildings. Historically, utilizing nanoclays for improving mechanical properties of plastics has proven to be beneficial not only in terms of mechanical properties but other functional properties such as gas barrier properties.

Table 2 Details of a typically used nanoclay product (Closite 30B) [14]

Typical Properties:

| <u>Treatment/Properties:</u> | Organic Modifier (1) | Modifier Concentration | % Moisture | % Weight Loss on Ignition |
|------------------------------|----------------------|------------------------|------------|---------------------------|
| Cloisite® 30B | MT2EtOH | 90 meq/100g clay | < 2% | 30% |



Where T is Tallow (~65% C18; ~30% C16; ~5% C14)

Anion: Chloride

(1) MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

In order to improve the interaction between the platelets surface and the polymeric matrix, manufacturers pre-treat the platelet with certain coupling agents or salts such as the quaternary ammonium compound shown above.

Table 3 & Table 4 Details of a typically used nanoclay product (Closite 30B)

Typical Dry Particle Sizes: (microns, by volume)

| | | |
|----------------|----------------|----------------|
| 10% less than: | 50% less than: | 90% less than: |
| 2 μ m | 6 μ m | 13 μ m |

Color: Off White

Density:

| | | |
|---------------------------------|----------------------------------|---------------|
| Loose Bulk, lbs/ft ³ | Packed Bulk, lbs/ft ³ | Density, g/cc |
| 14.25 | 22.71 | 1.98 |

X Ray Results: $d_{001} = 18.5\text{\AA}$

A common issue with nanoclay products is that the agglomeration behavior is similar to tactoids and platelets due to surface interactive forces, namely static charges. In order to attain excellent mechanical properties it is required that maximum surface area of the nanoclay platelets interact with the polymer matrix. For better results an exfoliated distribution of single nanoclay platelets is desired.

1.4 Shape forming of plastics

The most common component or systems in the plastics processing industry are extrusion and injection molding respectively. Primarily utilized for processing thermoplastics, extrusion and injection molding are an integral part of the plastics industry, especially in segments such as bottle manufacturing. They are also used for manufacturing of composite components and in processing of thermoset plastics (reactive extrusion, RTM etc). Both extrusion and injection molding are based on an ancient principle of conveying matter which is the Archimedes screw (circa 287–212 B.C.) [15]. It was invented as a pump to convey water for irrigation and later employed in ships to

pump water fast and efficiently. The simple design has been adopted by the plastics industry for plasticizing, pumping and mixing during polymer processing.

1.4.1 Extrusion

Extrusion can be described as a process where plastics (resins), usually in the form of beads or pellets, are continuously fed to a heated chamber and conveyed by a feed screw. The feed screw is driven via drive/motor and tight speed and torque control for quality control reasons. As the plastic is conveyed it is sheared, melted, compressed and forced through a die that has a predefined profile. The cooling of the melt results in hardening of that plastic into a continually drawn piece whose cross section matches the die pattern [16]. A point to be noted is the phenomenon of “die swell” which occurs due to relaxation of stresses in the sheared molten material, immediately after exiting the die. As a result the extrudate has larger dimensions than the profile on the die. Die swell also depends on other factors such as speed of the screw, drawing rate and most of all the material properties. In an extruder most of the heating is caused by friction between the inner barrel wall, the material and the screw surface. Thus as the screw rotates it both shears and keeps the material at high temperatures inside the barrel. A simple schematic of an extrusion process is shown in Figure 5. In some cases the die at the end/exit can be designed such that the extruded shape of the material is a tube, a film and as complex as a reinforced window treatment frame.

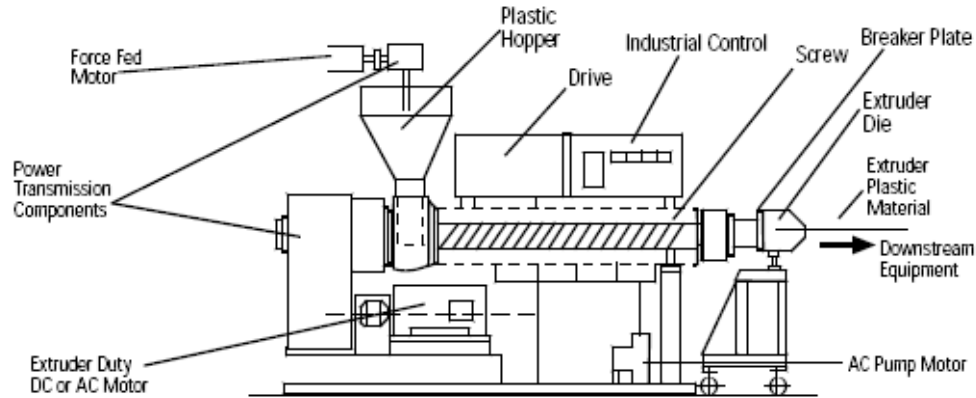


Figure 5 Drawing of extrusion process [14]

1.4.2 Injection molding

Injection molding, which uses extrusion to melt and pressurize plastics, in contrast is a batch process. That is to say, multiple or single components are manufactured in repetitive steps. In this case a plunger or reciprocating screw, injects the molten material into a mold cavity. A clamp force keeps the mold closed so as not to leak and because of the pressure on injection molding (35-70 MPa) the clamp force is typically high. Once filled with a preset amount of material, also called as the shot size, the screw translates forward creating injection pressures between 0.03-140 MPa and displaces the material from the barrel into the mold. The material is rapidly cooled to solidify the melt inside the mold. Once the solid part is formed it is ejected and the process is typically repeated.

Figure 6

shows a schematic of a typical injection molding machine and cycle.

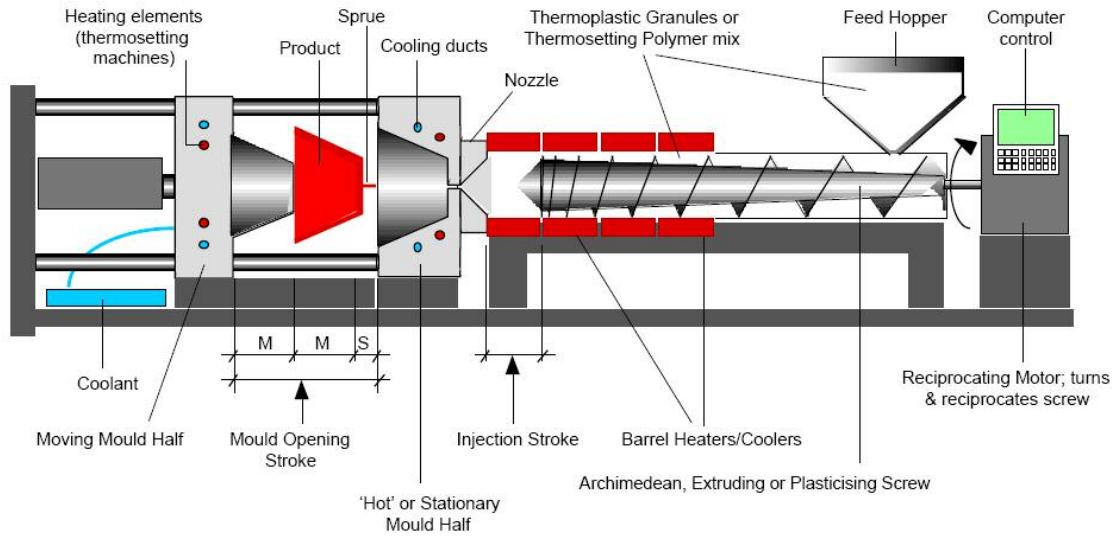


Figure 6 Drawing of injection molding process [17]

1.4.3 Film casting

Film casting is a relatively simple technique to make coatings or sheets with polymers that can be made into solutions. The oldest technology in plastic films manufacturing, the continuous solvent cast process, was developed more than one hundred years ago driven by the needs of the emerging photographic industry. In the years after 1950, new film extrusion techniques of thermoplastic polymers became the dominant production method for plastic films leading to the decline in importance of solvent cast technology. Recently, the solvent cast technology is becoming increasingly attractive for the production of very thin ($<50\ \mu\text{m}$) films as well as difficult to process plastics. The advantages of this technology include uniform thickness distribution, maximum optical purity and extremely low haze [18]. The optical orientation is virtually isotropic and the films have excellent flatness and dimensional stability.

1.5 Objective

The objective of this work was to improve the water stability and the mechanical properties of protein polymer plastics. The focus of this work was the development of water-resistant soy protein plastics prepared from renewable resources via a fast, convenient, and economical polymer processing techniques. Additionally the focus was to explore the feasibility of processing protein polymers such as zein with inherent qualities such as water resistance, film formability to replace petroleum plastics in applications such as packaging.

1.6 Literature review

1.6.1 Disulfide linkages in proteins (sulfite)

In order to facilitate the use of soy protein isolates for manufacturing of plastics, the globular protein structures need to be uncoiled and linearized, to promote order and alignment along the molecular back bone. This alters the flow behavior of SPI resin during processing so as to mechanically and chemically behave similar to synthetic polymers (plastics). The major linkages responsible for holding the globular molecule together are disulfide bonds between the different coil confirmations. Studies by Myers 1996 et.al on alkali modification of SPI for adhesives applications indicate that the use of sodium sulfite Na_2SO_3 (a disulfide bond-cleaving agent) at a pH of 10.0 and a temperature of 50°C promoted breaking of the disulfide bonds. The Na_2SO_3 treatment yielded an SPI adhesive with a relatively low viscosity (110 cP) which retained adhesive

and water-resistive properties. The water resistance of modified soy proteins with and without 0.1 M Na₂SO₃ treatment was not significantly different with 3.3 and 6.6% cumulative delaminations occurring after four water soaking cycles which followed ASTM standard test for water absorption. Treatment with 0.1 M Na₂SO₃ resulted in an isolate with a 28% decrease in disulfide linkages [19]. Thus it was decided to employ Na₂SO₃ as the disulfide bond cleavage agent for linearizing the protein globules.

1.6.2 Processing

1.6.2.1 SPI injection molding

Based on the review of articles on SPI, processing injection molding was selected as the process to be studied and characterized. It was because the usage of solvents such as water or glycerol (plasticizer) the soy protein macromolecules swell. It was theorized that under the high pressures and shearing, the protein globular structure may linearize in to linear macromolecule (Mw 160kDa- 360 kDa) [20]. Other process, such as compression molding where the shear rates are lower, this alignment may not be promoted. In addition, SPI can process similar to a thermoplastic. Lastly injection molding is used for mass production and higher productivity as compared to compression molded.

1.6.2.2 Zein for film casting

Zein primarily composed of α -zein, the alcohol soluble protein that constitutes 70% of the total protein content in the corn kernel, has a lower molecular weight of 19-

22kDa relative to soy protein molecules. Because lower molecular weight plastics are relatively easier to process, requiring lesser energy for processing, more over indistinct melting temperature for zein make it difficult to control it during thermal processing. One of the advantages of zein in comparison with other vegetable proteins like soy protein, casein, is that zein has good barrier properties along with excellent film forming ability [21]. Thus, zein film and casted zein film can be used for packaging applications.

1.6.3 Methods to improve water stability

Water stability of soy protein plastics has been an issue due to the abundance of hydrophilic side groups in the principal storage proteins 11s that has not yet been resolved. In order to replace petroleum based plastics, it is necessary that this water stability issue be resolved. Some of the proposed solution include addition of reagents and processing some of which are reviewed in the following sections.

1.6.3.1 Heat treatment

It is believed that the two main protein components of SPI, 7S and 11S crosslink with prolonged exposure to heat. Extensive studies have carried out on the level of cross-linking in soy protein by Clau'dia et.al 2003. These studies confirm that heat treatment at 80°C for 24 hours reduces the number of free amines and carboxyl groups which were measured in an untreated and heat treated soy protein samples respectively. It was also observed that other than improved water stability the mechanical properties were superior

in comparison with a glyoxyl cross-linked sample group which exhibited lower count of free amine and carboxyl reactive side group than the heat treated specimens [22]. These advantages suggest heat treatment as an attractive possibility to be explored further for improving the water stability of SPI. The previous work referred above has restricted its scope to lower temperatures of thermocycling i.e.80°C. Thus higher temperatures were utilized and its effect on water stability was studied (100 & 120°C).

1.6.3.2 PCL blends

Poly-caprolactone is a petroleum based biodegradable polymer, that is relatively resistant to water was used by Rui et.al (2006) to make water-resistant composite plastics. In this case samples were prepared from soy protein isolate (SPI) or soy dreg (SD), poly(ϵ -caprolactone) (PCL) and toluene- 2,4-diisocyanate (TDI) as the compatibilizer by blending and one-step reactive extrusion (REX) followed by compression-molding. The structure and properties of the materials (SPI series and SD series) were investigated by various characterization methods like DSC, tensile strength and other characterization. The results indicated that SPI and SD series exhibited high water resistance and good tensile strength (14.8 MPa for SPI35 and 16.3 MPa for SD35).This paper provides a convenient way to prepare new soy protein plastics with good biodegradability and water resistivity [23]. Once again like other options the PCL blends were prospective but a different compatibilizer had to be used, as the compatibilizer used in the latter reference was a di-Isocyanate compound. This makes it questionable to be used for biodegradable and non-toxic application applications as di-Isocyanates are toxic.

1.6.3.3 Zinc stearate

Zinc stearate is a salt of a stearic acid $Zn(C_{18}H_{35}O_2)_2$, a zinc soap that repels water and is insoluble in polar solvents such as alcohol and ether but soluble in aromatic hydrocarbons e.g. benzene and chlorinated hydrocarbons when heated. It is the most powerful mold release agent among all metal soaps. It contains no electrolyte and has a hydrophobic effect [24]. Its main application areas of application are in the plastics and rubber industry where it is used as a releasing agent and lubricant which can be easily incorporated.

1.6.4 Methods of improving strength

1.6.4.1 Nano-composites of protein plastics

Nanoclays are special type of additives for many substrates that have high dimensional aspect ratios. If properly mixed (exfoliated) and have the proper surface interactions, they can increase strength of the base material/composite. The results of Chen and Zhangs (2006) work on exfoliated nanoclay composites with soy-proteins indicate that nanoclay percentages below 12 % of the total protein mass give the best results in terms of having a exfoliated distribution of platelets amongst the matrix. Such results of exfoliation were achieved when the clay was mixed in neutral media such as distilled water and the degree of exfoliation was determined by relative comparison of nanographs obtained with TEM. With the optimum level of nanoclay established from literature mentioned above, the effect of nanoclay addition combined with different heat

treated and PCL blends of soy protein isolate and casted zein sheets, on their water absorption as well as tensile strength was studied.

1.6.4.2 Ultrasonics on NC

Ultrasound sound energy is used in the exfoliation of nanoclay platelets. But reports of achieving and maintaining 100% exfoliation are limited. Regions of intercalated nanoclay platelets can be easily formed and agglomerate as tiny clusters [25]. The effects of ultrasound sonication in these intercalated nanoclay clusters have been discussed by Chun et.al (2005). The results show that there exists an optimum ultrasound sonication time where the mechanical properties such as hardness of the composites are mostly enhanced. The cluster sizes of nanoclay change with different sonicating time, without the disturbance to the interplanar distance. This particular technique of nanoclay exfoliation has been utilized for thermo-sets and different fiber-matrix composites. In this study the technique was adopted to improve the strength of protein plastics made from zein in the solution form by improving dispersion and exfoliation of nanoclay platelets in the latter.

CHAPTER 2: INVESTIGATION OF SOY PROTEIN ISOLATE PLASTICS FOR MECHANICAL AND WATER ABSORPTION PROPERTIES

2.1 Abstract

Biodegradable plastics based on soy protein isolate were prepared with glycerol as a plasticizer and compounded with different additives such as: polycaprolactone and zinc stearate as well as heat treated at various temperatures after the injection molding process in order to characterize base material strength and the effect of water absorption. The results indicated that polycaprolactone blends and high heat treatment at 100°C and 120°C enhanced the tensile strength and decreased the water absorption significantly.

2.2 Introduction

SPI is a very attractive source of bio-renewable polymer at our disposal, yet some of its shortcomings have prevented it from being utilized on a mass scale. Two of the main shortcomings are poor water stability and mechanical properties. This chapter is an reviews work to address the issues related to water stability.

2.3 Materials

2.3.1 Formulation constituents

A food grade soy protein isolate (90% protein by weight) was obtained from Solae Company, St. Louis, MO. The primary plasticizers, glycerol and water were obtained from Fisher scientific Pittsburgh, PA and ISU water supply respectively (TDS

and chlorine level of water was unknown). A preservative, sorbic acid potassium salt-99% from SIGMA- Aldrich Inc, St.Louis MO and disulfide bond cleavage agent, sodium sulfite from Fischer scientific, Fair Lawn NJ respectively were used as received. Nanoclay, Cloisite® 30B a natural montmorillonite modified with a quaternary ammonium salt was used as received from Southern Clay Products .Inc, Gonzales, TX. Zinc Stearate was acquired from CG 221, Chemical Group Inc .Poly- ϵ caprolactone (P767) was used as received from, Dow Chemical Co. Poly vinyl-pyrrolidone (PVP 360) the compatibilizer used for stabilizing SPI and PCL phases was obtained from, Sigma Aldrich Inc.

2.4 Procedure/ Protocol

2.4.1 Resin Preparation

2.4.1.1 Control recipe and heat treated sample recipe

All formulations were based on relative amounts of SPI by weight fractions as detailed in Table 5. The preparation of the resin consisted of mixing two material phases, solids and liquid which were mixed separately prior to final mixing.

Table 5 Recipe of all formulations in parts

| Sample | SPI | Water | Glycerol | NC+Salts | Zinc stearate | Compatibilizer | PCL |
|---------------|------------|--------------|-----------------|-----------------|----------------------|-----------------------|------------|
| Control | 100 | 80 | 30 | 11 | - | - | - |
| Heat treated | 100 | 80 | 30 | 11 | - | - | - |
| Zinc stearate | 100 | 80 | 30 | 11 | 3 | - | - |
| PCL | 100 | 80 | 30 | 11 | - | 2 | 100 |

In the solid phase, 100 parts of SPI, 10 parts of nanoclay were mixed together in the dry state. A liquid mixture was prepared separately, with 80 parts of water, 30 parts of glycerol and 0.5 parts of sorbic acid and sodium sulfite each respectively. The solid and liquid mixtures were then mixed together in a high-speed mixer at 2000 rpm (Henschel Mixers American, Inc., Houston, TX) with slow and intermittent introduction of the solution in-order to avoid lump formation in the solids. Once properly mixed, the final product was a moist powdery dough which was further used for extrusion.

2.4.1.2 Zinc stearate recipe

The formulation and the method of mixing was same as the control recipe; except that 2 parts of zinc stearate was added and mixed with the solids per every 100 parts of SPI in the dry state. The zinc stearate was added to the dry mixture because of its water insolubility.

2.4.1.3 PCL blend

Initially the SPI resin was prepared with the same methodology as described for control recipe except that an addition of 3 parts of crushed PVP crystals to 100 parts of SPI was added as a compatibilizer between the SPI and PCL. The PVP was added in the dry state to form the final mixture that was extruded and the PCL beads were compounded in a second stage extrusion.

2.4.2 Extrusion

2.4.2.1 Control

The moist powdery dough obtained from resin preparation was extruded in a twin-screw, co-rotating extruder equipped with an autofeeder (Leistritz Micro 18, L/D ratio 30, American Leistritz Corp., Sommerville, NJ) to produce a continuous length extrudate through a circular die with a cross-sectional diameter of approximately 3mm. The temperature zones were set to: 92, 100, 105, 105, 100, and 85°C from the die to the hopper respectively and at a screw speed of 100 rpm. The extrudate was pelletized with a Brabender pelletizer (Lab. Pelletizer model, C.W. Brabender Instruments, Inc., Hackensack, NJ) into cylindrical pellets which were further air dried to an optimum moisture level of 10 % for good working at the injection molding. The moisture level was selected based on observation made at the screening experiments.

2.4.2.2 Zinc stearate

Zinc stearate resin was processed following the same methodology as described in processing of control pellets and the pellets obtained were air dried to 10% moisture content.

2.4.2.3 PCL

The processing of SPI-PCL blend involved a two-stage extrusion process where the SPI resin with the compatibilizer (as described in resin formulation) was extruded following the methodology of control pellets processing. The pellets (dried to 10% moisture content) were then mixed in a 50:50 ratio with the PCL beads as received to form a heterogeneous mixture of pellets. This mixture was compounded/ extruded with the same parameters used for control. The blend extrudate thus obtained was pelletized and dried to a moisture content of 5 % for ease of working at injection molding.

2.4.3 Injection molding

The pellets were molded into ASTM dog-bone shaped tensile bars using a m/c(Boy 22S, Boy Machine Inc., Berwyn, IL) injection molding machine. The barrel temperatures ranged from 125°C to 150°C from the feeder to the nozzle respectively. In order to assist demolding of tensile bars, “fancy tallow” was utilized as a lubricant and pre-applied in the runner path to ensure even surface smearing between the mold and the sample.

2.4.4 Heat treatment

ASTM dog-bone samples were thermally cured at different temperatures, 80°C, 100°C and 120°C in an oven for 24 hours respectively, forming three populations of samples. Immediately after the curing process, the samples were cooled to room temperature in anhydrous desiccators to avoid potential moisture interactions with the surroundings due to the material's higher temperature prior to cooling.

2.5 Characterization

2.5.1 Water Absorption

Water absorption tests were conducted utilizing the tensile bar samples from the different formulations and treatments following a modified procedure of ASTM 570-81. In the studies with the heat-treated samples, the control, PCL and zinc stearate samples were dried at 50 °C for 24 hours and similar to the heat treated samples these were cooled in an anhydrous dessicator. The conditioned samples were weighed in the dry state and immersed in distilled water for time periods raging from 30 minutes to 24 hours. The samples were removed from the water bath at discrete time intervals and wiped to remove excessive surface water with napkins and weighed. The change in weight was assumed to correlate to water absorption. The recorded difference in weight was converted to a relative percentage change in weight of the sample as a function of time.

2.5.2 Tensile strength

Tensile strength for all samples was determined in the wet state using an Instron Universal Testing Machine (Model 4502, Instron Corporation, Canton, MA) with a cross-head speed of 5 mm/min. The strength values were tested at various time intervals as described in measurement of water absorption. The control specimens were tested in a dry state following the ASTM D638-86 standard procedure.

2.6 Results and discussion

Table 6 details the tensile strength values in the wet state for all the processed samples at different stages of the water submersion for the various compositions and thermal treatments.

Table 6 Tensile strength of all samples

| Treatment | | Tensile Strength (MPa) | | | | | | |
|------------------|--------------------|------------------------|------|------|------|------|------|------|
| | | 0.5h | 1.5h | 2h | 4h | 6h | 8h | 24h |
| Heat treatment | 80 ⁰ C | 1.78 | 0.65 | 0.69 | 0.17 | 0.16 | 0.14 | 0.06 |
| | 100 ⁰ C | 6.38 | 4.31 | 3.66 | 0.64 | 0.39 | 0.18 | 0.21 |
| | 120 ⁰ C | 0.96 | 1.56 | 0.72 | 0.66 | 0.76 | 0.25 | 0.18 |
| Polycaprolactone | | 6.14 | 5.87 | 5.87 | 5.16 | 5.08 | 5.00 | 5.11 |
| Zinc stearate | | 3.7 | 1.07 | 0.55 | - | - | - | - |

Note: The zinc stearate samples were extremely fragile after 4h of immersion in water

As seen in Figure 7 the tensile strength (recorded based on one sample per time interval) is inversely proportional to the submersion time. The trend lines in the graph are added for visualization and are not statistically determined. In more detail, as the submersion time increases from 30 minutes to 24 hours, the tensile strength decreases from 6.3 MPa to 0.2 MPa for the heat-treated samples at 100°C for 24h. It is believed that the loss of strength is the result of the water molecules penetrating between the intermolecular bonds of the soy protein plastics, acting as a solvent.

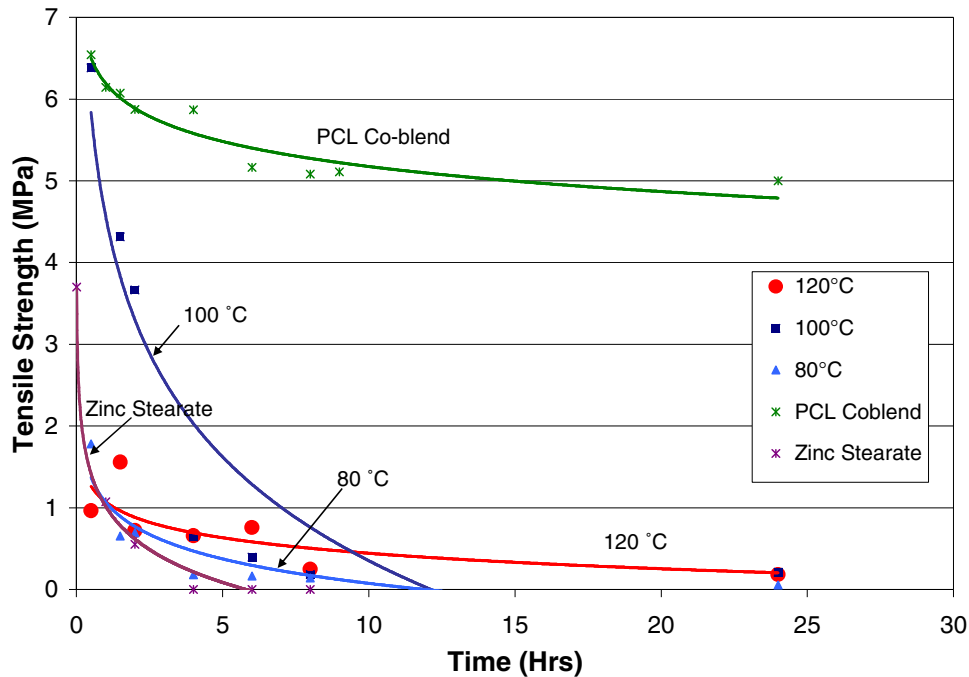


Figure 7 Tensile strength in the wet state at various time intervals for all samples

It was also seen, that with excessive treatment temperatures and times, such as 120°C for 24 hours, the tensile strength decreases from 0.9 MPa to 0.1 MPa for

submersion times from 30 minutes to 24 hours. It is believed that this is due to thermal degradation at high temperature and long time exposures. It is important to note that the strength of the control group in the dry state was approximately 3 MPa and dropped to nearly zero within 60 minutes of exposure to water and thus this data is not included in the graph.

The samples prepared with zinc stearate followed a similar trend. That is to say, base material strength decreased with increased exposure time to water. However, they had a relatively low average tensile strength compared to the heat treated samples (6.3 MPa to 0.2 MPa). It is important to note that it was not possible to measure the tensile strength after 4 hours of immersion because the samples were extremely fragile and soft. It was believed that the zinc stearate would promote water repellency at the intermolecular level after the mixing action by the extrusion and injection molding processes in order to prevent water migration in the samples due to its hydrophobic nature, but such a phenomenon did not appear to occur.

The PCL samples showed a higher and stable value of tensile strength (~5.5 MPa average) compared to the all other samples. As seen in Figure 7 there is a slight decreasing trend with increasing immersion time, but in general, the tensile strength value remained relatively constant. Based on the observation that relatively high base material strengths and enhanced water stability were seen with PCL and SPI blends, it maybe possible to conclude that there is a good compatibility between the PCL and the soy protein isolate. Table 7 details the percentage of water absorption for all the samples studied. It was observed that for the heat treated samples, the water absorption decreases

from 120% to 43% when the temperature was increased from 80°C to 120°C for 24 hours immersion time.

Table 7 Water absorption of SPI variant samples

| Treatment | | Water absorption (%) | | | | | | |
|------------------|--------------------|----------------------|------|------|------|-------|-------|-------|
| | | 0.5h | 1.5h | 2h | 4h | 6h | 8h | 24h |
| Heat treatment | 80 ⁰ C | 20.6 | 37.3 | 39.4 | 52.0 | 67.1 | 80.1 | 120.6 |
| | 100 ⁰ C | 9.7 | 22.8 | 27.2 | 39.6 | 49.9 | 53.0 | 86.8 |
| | 120 ⁰ C | 6.9 | 13.0 | 14.7 | 23.5 | 27.7 | 33.3 | 43.0 |
| Polycaprolactone | | 2.8 | 3.8 | 5.3 | 6.4 | 8.4 | 9.2 | 16.8 |
| Zinc stearate | | - | 38.2 | 54.8 | 91.3 | 112.5 | 120.9 | - |

This may be due to a higher level of denaturization of the soy protein with respect to increased temperatures and heating times. While there is no conclusive evidence, it is theorized that the higher temperatures promote formation of the bonds in the protein molecule. This in affect increased the degree of cross linking between the 7S and 11S protein, making the base material less solvent sensitive to such solvents as water. It is further theorized, that the first affected are the long range interactions that are necessary for the presence of tertiary structure. As these bonds are first weakened and are broken, the protein chains obtain a more flexible structure and the groups are easily exposed to solvent. If heating ceases at this stage the protein should be able to readily refold to the native structure. As heating continues, some of the cooperative hydrogen bonds that

stabilize helical structure begin to break. As these bonds are broken, water can interact with and form new hydrogen bonds with the amide nitrogen and carbonyl oxygen of the peptide bonds. The presence of water further weakens nearby hydrogen bonds by causing an increase in the effective dielectric constant near them. As the helical structure is broken, hydrophobic groups are exposed to the solvent.

Figure 8 shows a significant increase of the water absorption with the submersion times, for all the sample groups.

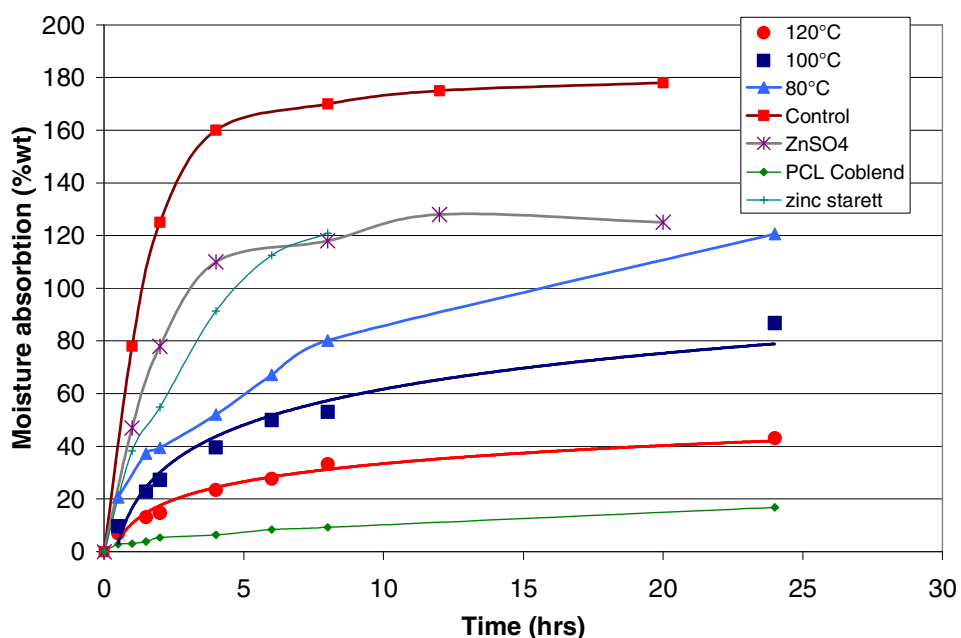


Figure 8 Moisture absorption at various time intervals for all variants

The PCL/SPI samples followed a similar trend in reference to water absorption. An increase with the immersion time corresponds to a decrease in strength and gain moisture. However, as previously mentioned, the amount of absorption is insignificant compared to the previously detailed samples. In the case of the PCL/SPI sample the

moisture only increase by 2.8% for 30 minutes immersion time to only 16% for 24 hour submersion time. It is believed that the water insoluble PCL formed a continuums phase within the blend and shrouded the soy plastic from the water. Figure 9 and Figure 10 show optical microscopy images of microtome samples from the PCL/protein blends. The magnification was arbitrary but higher in Figure 9. In these figures the light colored regions are the continuous phase and correspond to PCL and the darker regions (discontinues phase) correspond to the soy plastics.

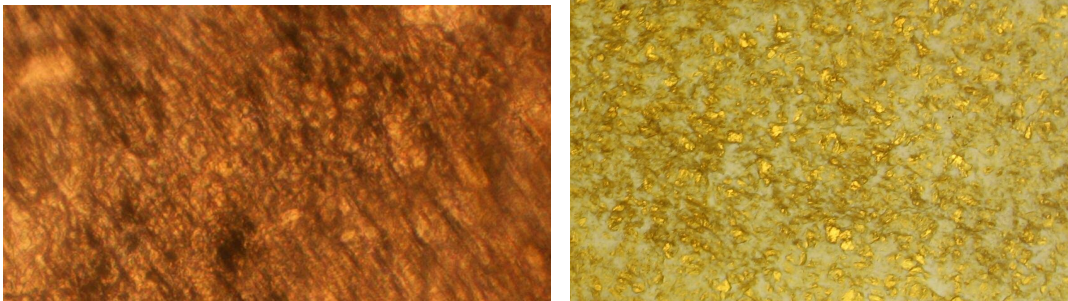


Figure 9 Optical micrograph PCL/Soy blend. Figure 10 Optical macrograph PCL/Soy blend

2.7 Conclusion

Plasticizers such as water, and glycerol enhanced the processability of soy protein isolate. Various additives such as: zinc stearate and PCL, and heat treatments improved the mechanical properties where tensile strengths of up to 6.3 MPa were observed. Heat treatment of SPI plastics increased the tensile strength of the base material and lowered the water absorption. However, the PCL/SPI alloy had the highest tensile strength and the lowest water absorption compared to the balance of the samples studied.

CHAPTER 3: INVESTIGATION OF ZEIN PROTEIN SHEETS FOR FILM FORMATION AND EVALUATION OF MECHANICAL AND WATER ABSORPTION PROPERTIES

3.1 Abstract

This chapter reviews an investigation of the processability and properties of commercially available corn protein polymers for cast film products. Different formulations of zein protein substrates were cast and characterized for their mechanical and water absorption properties along with some characterization of thermal properties. In this study it was seen that zein plastic sheets could be cast with tensile strengths as high as 6 MPa with a strain to failure of 6%. In addition, ultrasonic treatment of the solution prior to casting reduced the tensile strengths. However, the treatment did enhance the strain to failure to as high as 200%. Lastly, the addition of nanoclays also reduced the tensile strength of the cast films but did increase water stability. Thermal characterization runs revealed a T_g of 168°C

3.2 Introduction

The growing corn to ethanol industry has increased the production of proteinaceous co-products making them inexpensive feed stock of protein polymers. In particular, zein an alcohol soluble protein from corn, due to its uniqueness of film forming [26] ability has the potential to replace the petroleum plastics in the packing industry. This chapter concentrates on improving the properties so zein based plastics have sufficient strength that would meet the requirements of many product applications.

For example, polyethylene is one of the most common plastics used in industry and it has a base material strength of 8-23 MPa and thus this would be considered a minimum base material strength goal.

3.3 Materials

Commercial zein, mostly composed of alcohol soluble corn protein (90% by weight) was procured from Zein Protein Corp, Marina, CA, and used as received. Both solvent and plasticizer, ethanol (denatured) and glycerol respectively, were obtained from Fischer scientific, Pittsburgh, PA and silicone mold release was used from spray canisters as received from SLIDE Products USA, Nanoclay, Cloisite® 30B a natural montmorillonite modified with a quaternary ammonium salt was used as received from Southern Clay Products .Inc, Gonzales, TX.

3.4 Procedures and Protocols

3.4.1 Control

Formulations were based on dry zein mass where 10 g of zein and 40g of ethyl alcohol (denatured) was mixed with 4g of glycerol with a magnetic stirrer to avoid phase separations due to difference in densities. The zein mass was gradually added to the solvent mixtures to avoid lumps, bubbles and to achieve even dispersion. The mixture was “pour casted” on to a smooth glass surface pre-coated with silicone mold release to assist release of the dried sheets. Casting was completed in a confined area of 127 mm x 203 mm on the glass surface as shown in Figure11. After pouring, the mixture was

allowed to air dry for a period of 48 hours. The dried sheets were peeled from the glass surface and utilized for characterization after being cut out into ASTM dog-bone shaped samples. Both in the flow direction and the transverse direction were studied.

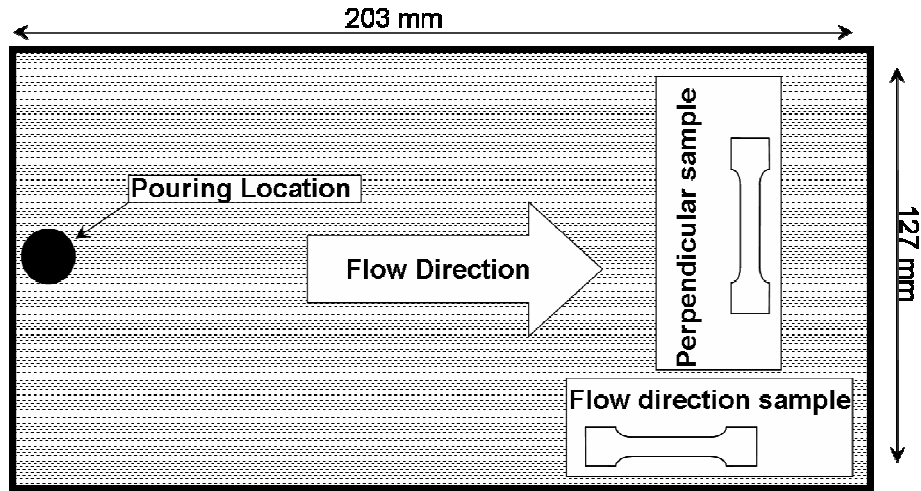


Figure 11 Details of casting and sample preparation

3.4.2 Nanoclay sheets

In order to study the effect of nanoclays, solutions were prepared as detailed in the control sample preparation, and nanoclays were added. The nanoclay was added to the solution and stirred to form a disperse suspension free of bubbles. This suspension was casted and solvent evaporated on a glass surface as described earlier. To study the effect of nanoclay filler levels on the mechanical properties, two levels of nanoclay, 5 and 10 % were added to the reference zein mass respectively.

3.4.3 Exfoliated nanoclay sheets utilizing ultrasonics:

In order to promote exfoliation, mixing the nanoclays in the solution was completed in two steps. In the first step the nanoclay was mixed in the solution and the dispersion was promoted by use of ultrasonic energy. During this step, the amount of zein added was limited in order to keep the viscosity of the solution to a minimum and allow proper ultrasonic treatment. Once treated the balance of the zein was added and mixed with a magnetic stirrer. In more detail, 20 g of ethyl alcohol along with 4 g of glycerol and the nanoclay was exposed to a pulse of ultrasonics for a time period of 45 seconds at a fixed amplitude level to exfoliate the nanoclay platelets. To promote interaction between the nanoclay and zein protein, 20% of the total zein mass fraction (2 g) was added to the exfoliated nanoclay suspension and treated with a second pulse of ultrasonics for 45 seconds at the same amplitude level. In the second stage of mixing, the exfoliated nanoclay colloidal suspension was mixed with the remainder 8 g of the zein mass and 20 g of ethyl alcohol (denatured) to form a uniform colloidal suspension/solution on a magnetic stirrer. The suspensions were casted as previously detailed.

The above procedure with two concentrations of nanoclay (5 and 10 % of the zein mass) was ultrasonically treated with two different ultrasonic probes differing in geometry and ultimately the amplitude of the ultrasonics applied. A flat tip horn and a micro probe horn, shown in Figure 12, with amplitude values of 30 μm_{pp} and 90 μm_{pp} respectively on a Branson “Digital Sonifier 450”, were utilized for the purpose and a summary of all the recipes so far are given in Table 8.



Figure 12 Picture of Microprobe and flat tip horn

Figure 13 Branson Digital Sonifier.

Table 8 Recipes of all formulations in parts(except ultrasonics)

| <u>Sample</u> | <u>Zein</u> | <u>Solvent</u> | <u>Glycerol</u> | <u>NC</u> | <u>Ultrasonics</u> | |
|-----------------|-------------|----------------|-----------------|-----------|--------------------|-----------------|
| | | | | | <u>MP(μmpp)</u> | <u>FT(μmpp)</u> |
| Control | 100 | 400 | 40 | - | - | - |
| Zein+ 5% NC | 100 | 400 | 40 | 5 | - | - |
| Zein+10% NC | 100 | 400 | 40 | 10 | - | - |
| Zein+5% NC+MP | 100 | 400 | 40 | 5 | 30 | - |
| Zein+ 10% NC+FT | 100 | 400 | 40 | 10 | - | 90 |

3.5 Characterization

3.5.1 Tensile strength

The cast sheets were cut out into modified ASTM dog-bone samples with a template as detailed in Figure 14. The thickness of the sheets ranged from 0.3 to 0.5 mm, depending on the sample preparation.

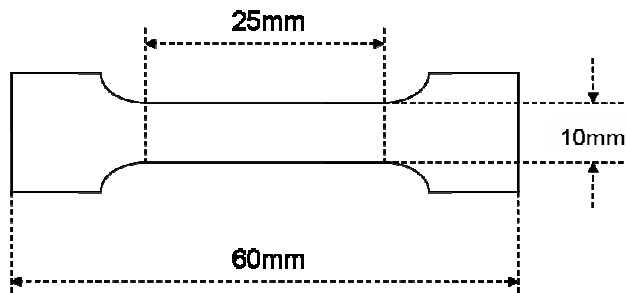


Figure 14 ASTM prescribed dog-bone for thin sheets

In all cases, the thickness and width of the dog-bone sample were measured to allow the cross sectional area to be calculated. Seven samples were cut from the sheets in the flow direction for tensile testing and three were cut from the sheets in the direction perpendicular to the flow (see Figure 11). It is important to note that the number of samples were limited to the numbers specified above due to the area of sheet casted. Care was taken to assure the samples were cut far from the pour location and edges to prevent edge effects. The above samples were tested for their tensile strength on an Instron Universal Testing Machine (Model 4502, Instron Corporation, Canton, MA) with a cross-head speed of 10 mm/min as prescribed by ASTM D-882. Tests were also completed on wet conditioned samples.

3.5.2 Water absorption

The samples were weighed for initial weight and immersed in a tank of distilled water. The samples were retrieved after pre-determined time intervals and weighed after wiping the excess water from the sample surface. The change in weight was used to calculate the percentage change in weight. This procedure was repeated over different times periods of immersion ranging from 30 minutes to 24 hours and 3 samples i.e. data points were collected for each immersion time period and the average was calculated.

3.5.3 Thermal properties with TGA and DSC

In order to gain insight into the thermal behavior of zein, several screening experiments were carried out on a thermo gravimetric analyzer (TGA) from TA Instruments, New Castle, Delaware. The objective of the TGA run was to determine the temperature window within which the sample could be characterized with a DSC (differential scanning calorimetry) without degrading the sample. A heating rate of 20°C/min was used. Based on the temperature values obtained from TGA, a known quantity of dry zein powder (as received from the supplier) was characterized on the differential scanning calorimetry to analyze the thermal properties of zein in the powder form. Both normal and modulated modes of DSC tests were used. The modulated run was conducted at a heating rate of 5 °C/min and a modulation of ± 0.8 °C every 60 seconds. The normal mode runs were completed at a heating rate of 10 °C/min

3.6 Results and discussion

3.6.1 Tensile strength

The resulting films were relatively smooth and uniform as seen in the photograph of the sheet (Figure 15.) The sample appeared homogeneous and there was no evidence of agglomerates of nano-clays. In addition, the samples typically had a slippery surface shortly after curing which was the result glycerin leaching out of the base material. After several days, the samples typically became relative brittle with the excessive loss of the plasticizer.



Figure 15 Photograph of cast film

Figure 16 shows tensile strength of the composite films prepared with various conditions and a nanoclay level of 5%.

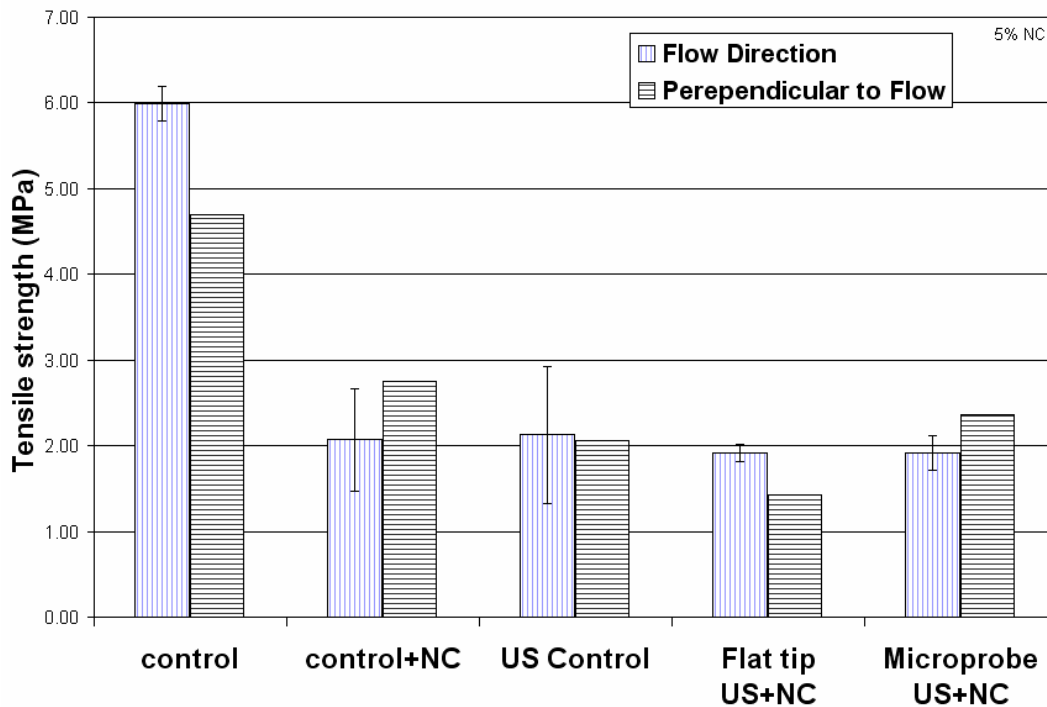


Figure 16 Tensile strength for 5% nanoclay composite with various treatments

It is seen that the tensile strength of the un-filled samples (0% nano-clay “Control”) had the highest strength, independent of the test direction; 6.0 and 4.6 MPa for the flow direction and perpendicular directions, respectively. It is believed that the clay particles were not properly exfoliated even with ultrasonic treatment. Thus, the clays particles acted as stress concentration points rather than reinforcement additives. It is also observed that ultrasonic treatment of the solution had an adverse affect on the tensile strength. That is to say, the strength dropped from 6 and 4.6 MPa to 3.1 and 4.2 MPa for the flow direction and the perpendicular test direction, respectively. It is believed that the ultrasonic energy promoted thermal and/or chemical degradation of the protein molecules. This hypothesis was based on the observation that the temperature of

sonicated solution raised to approximately 50-60°C. It is also seen in the graph that the ultrasonically treated samples with 5% nanoclay had the lowest tensile strengths. It is proposed that this is due to the thermal and/or chemical degradation of the protein caused by ultrasonic treatment coupled with the lack of exfoliation of the nanoclay particles. These two adverse effects acted synergistically and thus resulted in low tensile strengths. It should be noted that the strain to failure of ultrasonically treated samples were dramatically higher compared to the untreated samples. For example, the strain to failure of the treated samples was as high as 200% of the non-filled samples, while with the untreated samples it was only 6%. In addition, the ultrasonic treated samples with 5% nanoclay had approximately 28% strain to failure. It is theorized that the degradation caused by ultrasonic treatment reduced the molecular weight of the proteins, reducing molecular entanglement.

Despite the fact that the samples were cast, even though there was an induced flow direction, with a nanoclay concentration of 5% there is little difference in the tensile strength with respect to the flow direction. This suggests that there is limited linearization of the protein molecules and they were not denatured and remained relatively globular in shape.

It was observed that there is no significant difference in tensile strength between the samples treated with the two different ultrasonic horns, flat and micro-tip except for the directional strength values which reverse in their values in case of 10% nanoclay concentration. The standard deviation is not reported for the perpendicular flow samples

because of the limited population size. Figure 17 shows the tensile strength for the composites made with a 10% nanoclay filling level.

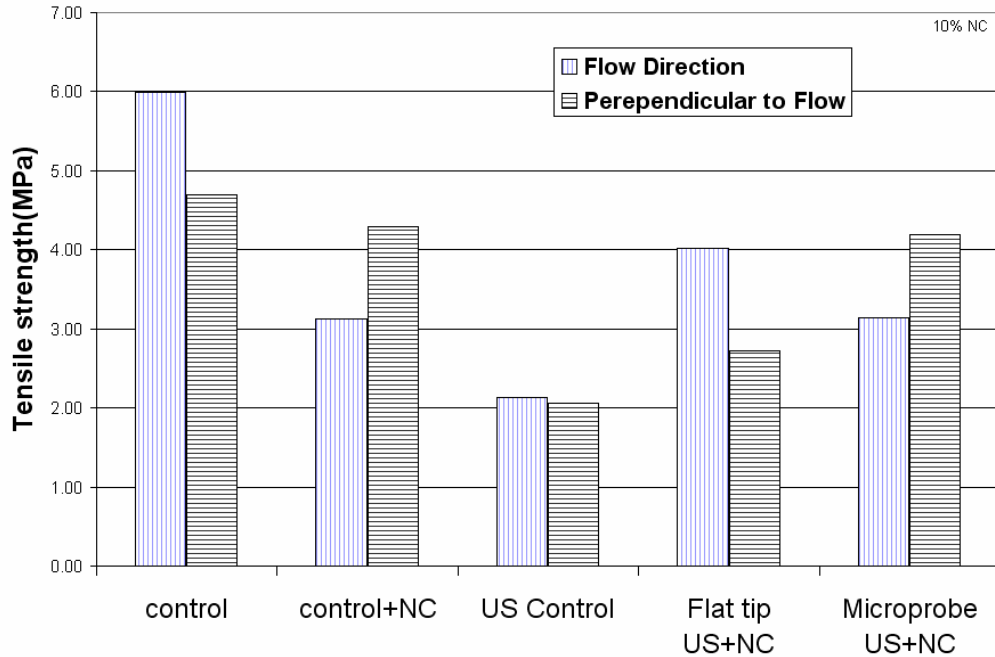


Figure 17 Tensile strength for 10% nanoclay composite with various treatments

The results are very similar to the previously detailed results. That is to say, the ultrasonic treatment and addition of nanoclay particles degraded the mechanical properties of the composites in comparison with values obtained for control samples. But 10% addition of nanoclay had better tensile strength in comparison with 5% nanoclay formulation. This might be due to higher availability of nanoclay particles to interact with the protein molecules and thus increasing the strength as a composite.

3.6.2 Water absorption

It was observed that moisture absorption increased with immersion time. However, an unexpected phenomenon of fluctuation in water uptake was observed with both concentrations of nanoclay formulation. It was observed that initially water absorption was negative and generally remained relatively low and in some cases remained negative. To confirm this observation, the test was duplicated. The same fluctuation was observed in both tests (see Figure 18 and Figure 19). A possible hypothesis for this observation was that the exfoliation nanoclay distribution acted as a diffusion barrier preventing water from diffusing into the samples.

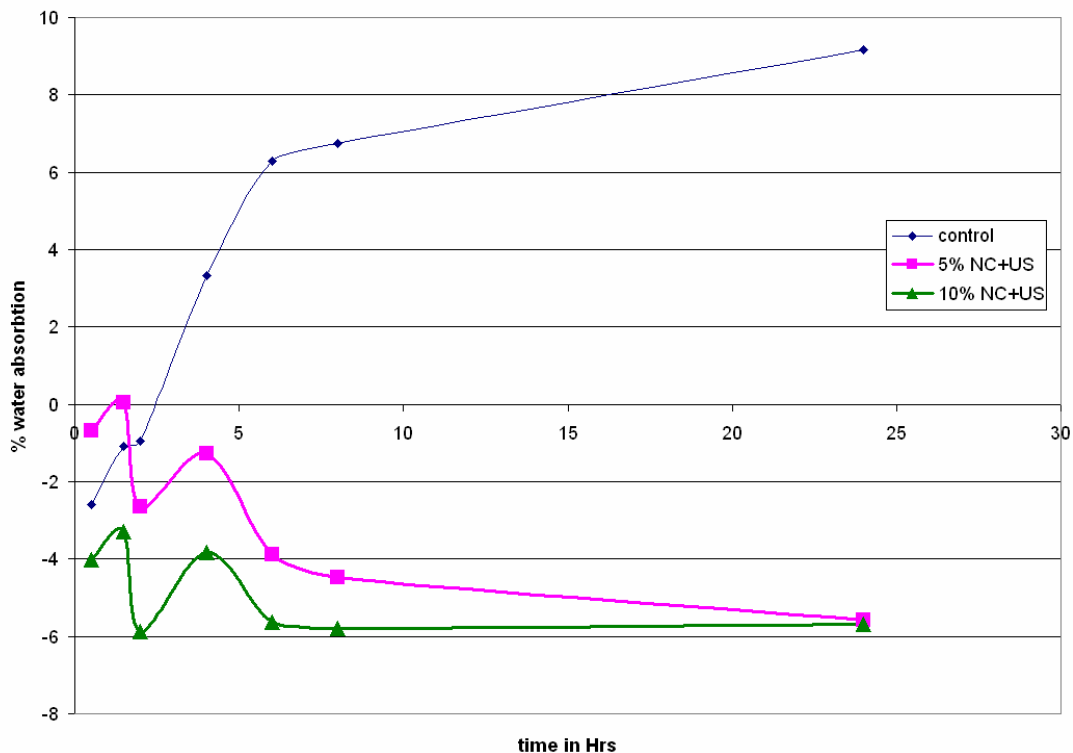


Figure 18 Water absorption by zein sheets (control and nanoclay sheets).

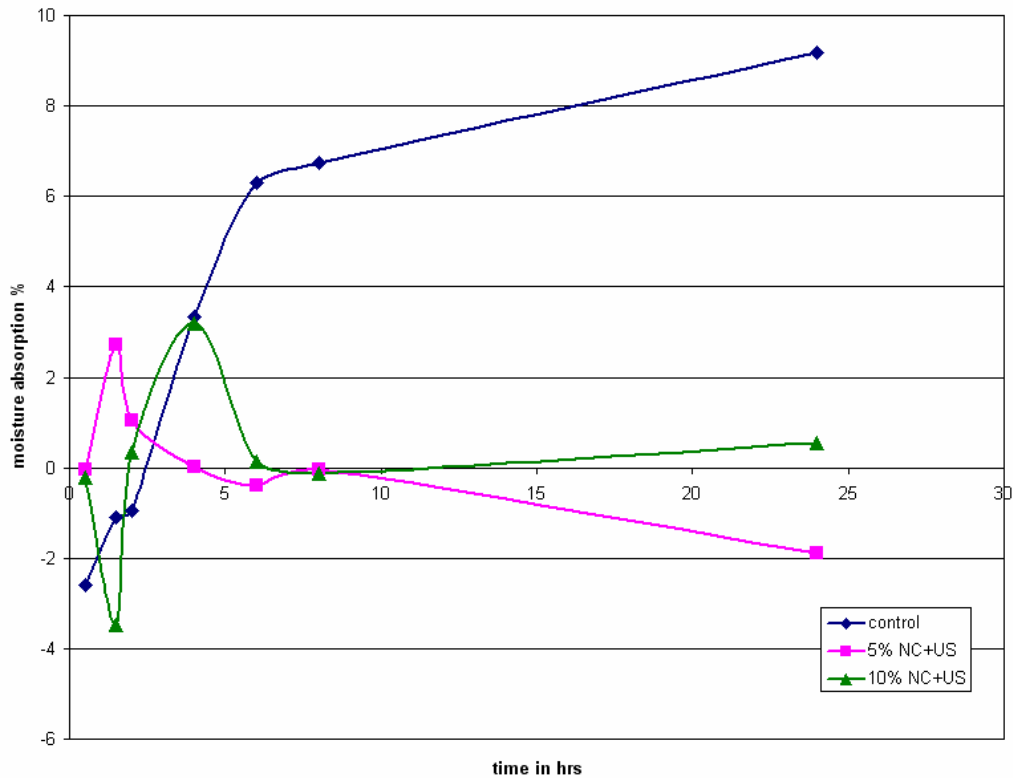


Figure 19 Water absorption by zein control and nanoclay sheets (duplicate test)

It is further theorized that un-mixed glycerin and ethanol near the surface of the sample dissolved in the water accounting for the loss in mass. This was based on the observation that the distilled water used for steeping, when evaporated resulted in Langmuir monolayer diffraction patterns on the vessel wall which were believed to be produced by the residuals.

3.6.3 Thermal analysis results

From the results of TGA it was observed that there was a drop in the mass of the zein sample at a temperature of 310 °C shown in Figure 20. This suggested that the

degradation temperature of zein was approximately 300 °C. Based on this value the samples were analyzed on the DSC, in both modulated and normal modes below this temperature.

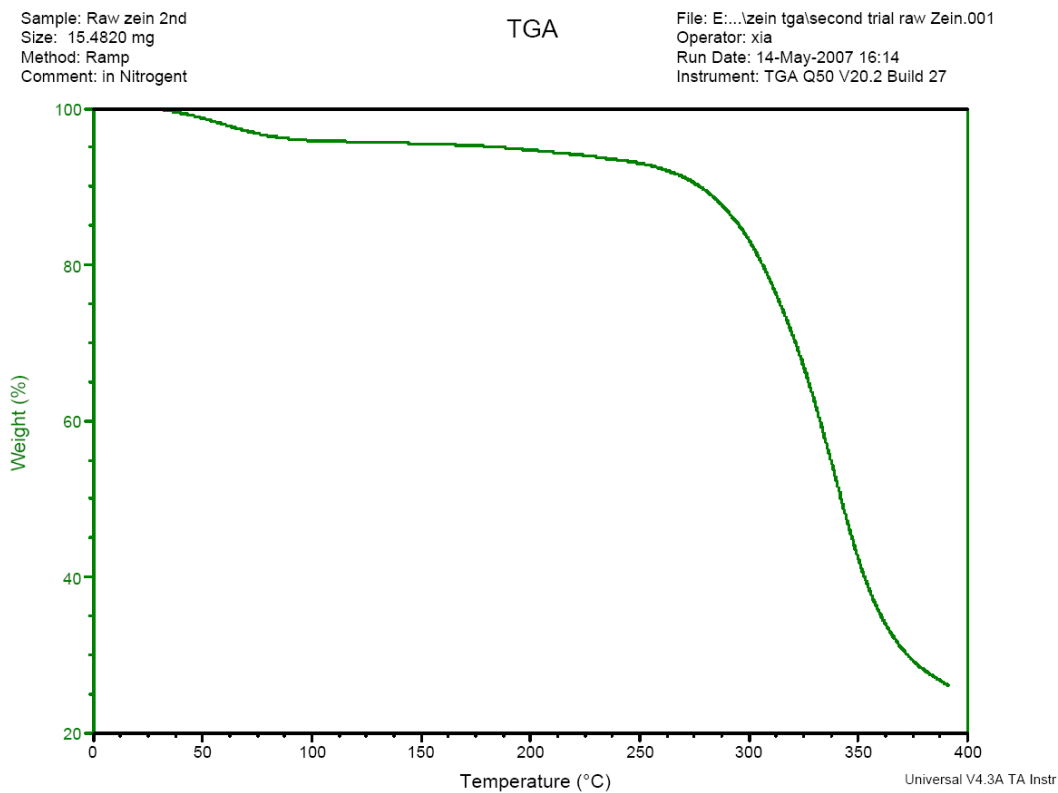


Figure 20 TGA curve for dry zein powder

The heat flow result from the modulated experiment is seen in Figure 21 and an inflection point is seen at 168°C and was confirmed by the reverse heat flow plot.

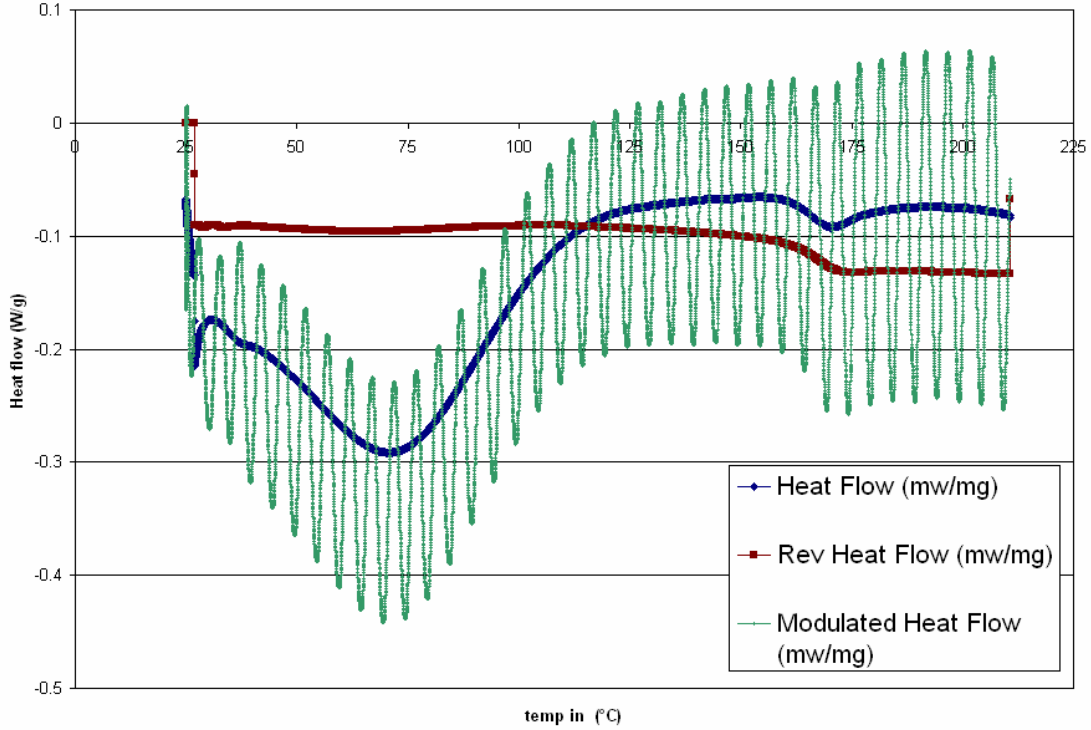


Figure 21 Modulated DSC run on dry zein powder

To confirm the results, consecutive normal mode DSC runs were conducted on the same sample from a lower initial temperature of -25 °C and again an inflection at 168 °C was observed in both the experiments as shown in Figure 22. Further tests on zein films were not carried out due to foaming of casted samples, but remedial steps would be identified and the tests will be conducted as apart of future work.

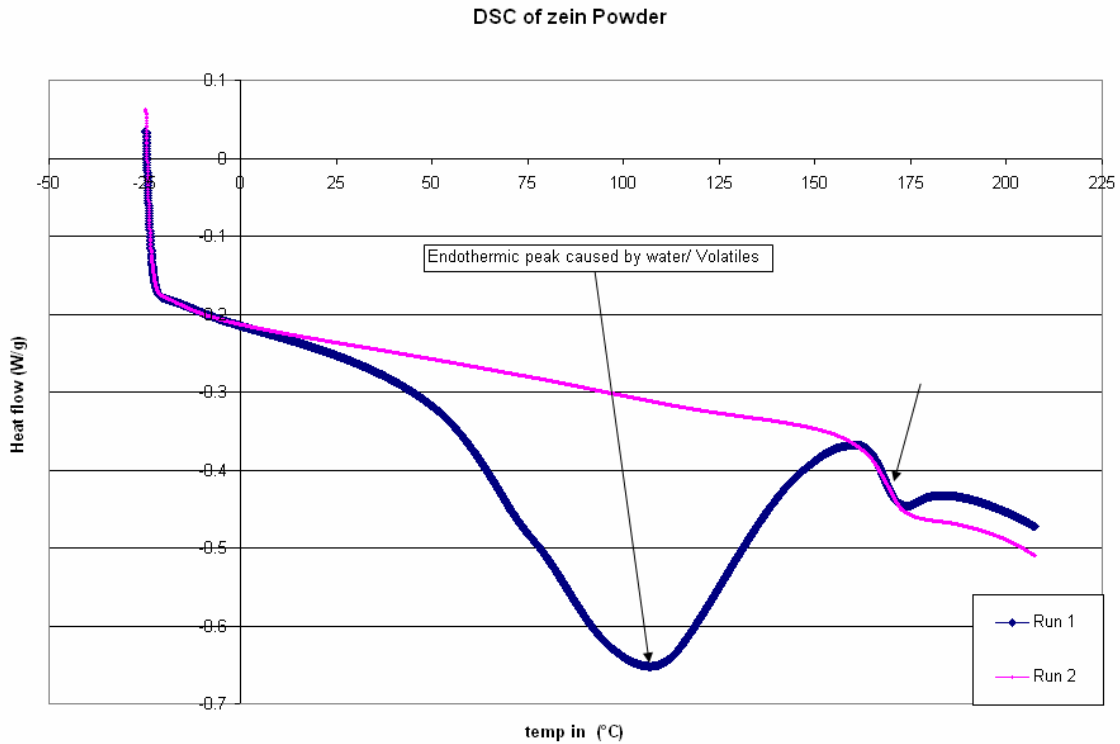


Figure 22 Consecutive DSC runs on the same samples dry zein powder

3.7 Conclusion

In this study it was observed that zein plastic sheets can be casted. Tensile strengths for these sheets were as high as 6.3 MPa with no additives such as nanoclays. The strain to failure was 6% with addition of nanoclays while without nanoclays the strain was only 0.8%. Ultrasonic treatment of the solution prior to casting reduced the tensile strength but reduced water absorption. In addition the ultrasonic treatment did increase the strain to failure. It is believed that the protein molecules were shortened by the mechanical energy leading increasing molecular freedom due to reduction in

molecular size. The addition of nanoclay also reduced the tensile strength of the cast films with increase in extension as mentioned previously. It is theorized this was due to low interaction between the clay platelets, which were coated with a quaternary ammonium compound which is hydrophilic in nature whereas zein protein as a whole is hydrophobic in nature. Thermal characterization of dry powder zein indicated the degradation temperature to be 310 °C. DSC results revealed a T_g of 168 °C.

CHAPTER 4: FINAL CONCLUSION

SPI and Zein protein prove to be potential candidates as biodegradable alternatives over petroleum as a feed stock for plastics. Differing in their interaction with water they can be used for different end-uses where hydrophobic and hydrophilic properties are desired. SPI had better water resistance and mechanical properties when blended with polymers such as PCL or after heat treatment. The tensile strength of SPI based plastics increased with the addition of zinc stearate. In addition, a heat treatment cycle of 100°C increased the tensile strength. When comparing the various formulation and treatment methods, it was seen that SPI/PCL blends provided the highest water stability (16.8% water absorption after 24 hour of water steeping) and tensile strength (6.3 MPa).

Net polymer Zein samples exhibited highest properties without additives. Additives such as nano-clays degraded the mechanical properties of zein polymers however it was observed they decreased the material's water absorption. In reference to the two levels of nanoclay (5 and 10%) studied, it was seen that a higher level of filler increased the tensile strength. It was also seen that the flow direction had little effect on the tensile strength.

Future work should include the study of alternative fillers, a wider range of filler level, alternative processing techniques and more detailed material characterization.

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