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DEVELOPMENT OF BIODEGRADABLE PLASTICS BY BLENDING A BY-PRODUCT OF THE CORN BASED ETHANOL INDUSTRY AND POLY (ϵ-CAPROLACTONE)

presented by

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has been accepted towards fulfillment
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Amar Kumar Mohanty
Major Professor's Signature

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By

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ABSTRACT

DEVELOPMENT OF BIODEGRADABLE PLASTICS BY BLENDING A BY-PRODUCT OF THE CORN BASED ETHANOL INDUSTRY AND POLY (Є-CAPROLACTONE)

By

Dinesh C. Aithani

Development of new value-added green materials from byproducts of corn-based ethanol industries would provide a substantial economic return to the corn growers. Corn gluten meal (CGM), a major byproducts of corn-based wet milling ethanol industries has most of its use as livestock feed. In this research CGM was plasticized using glycerol/ethanol mixture, destructurized by the addition of guanidine hydrochloride (GHCl) and then blended with poly (ε-caprolactone) (PCL). Extrusion followed by injection molding was adopted to fabricate the newly blended bioplastics/green materials. The GHCl modified corn gluten meal was characterized by infra-red (IR) spectroscopy. The effect of processing conditions on properties of blends was investigated. The thermo-mechanical properties of the blends were studied using DMA (Dynamic Mechanical Analyzer), TGA (Thermo-Gravimetric Analyzer) and UTS (Universal Testing System). Significantly higher elongation and an almost equivalent tensile strength was observed for GHCl modified blend in contrast to the non-GHCl modified blend. The blends were also observed to be more thermal stable with addition of GHCl. Scanning electron microscopy (SEM) was used to study the surface morphology of the blends. The SEM analysis revealed better compatibility of PCL with GHCl modified plasticized CGM in contrast to plasticized CGM.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

INTRODUCTION

Biodegradable polymers are getting increasing attention recently due to their possible environmental benefits and societal attractions. Renewable resource-based biodegradable materials can reduce the use of our depleting petroleum reserves as well as can also reduce our dependence on foreign countries for fossil fuels and thus enhancing our national security. A considerable number of biodegradable polymers are available, derived from both natural and synthetic sources. The growing concern regarding environment has driven an urgent need to develop new biodegradable polymers with properties and cost comparable to those of available synthetic polymers. The use of agricultural products in plastic applications is considered an interesting way to utilize surplus farm production and to develop non-food packaging applications[1]. Plastics accounts for 11.3% by weight of the total waste generation in United States[2] and the major portion of this waste comes from packaging. The use of biodegradable polymers can reduce the waste disposal problems associated with traditional petroleum derived plastics[3]. The main interest in the use of biodegradable materials is to develop a solution for growing waste disposal problem due to the shortage of available landfill space and the need for environmentally responsible use of resources[4]. Biodegradable plastic can be a very good choice for packaging of items used for a short period time and disposed as they can be degraded in suitable environment unlike the conventional plastic, which persists for many years after disposal. The use of biodegradable plastic can also avoid the recycling of plastics, which are undesirable due to soiling by food or other biological substances[5]. The life cycle of biodegradable polymers is represented in Figure 1[6].

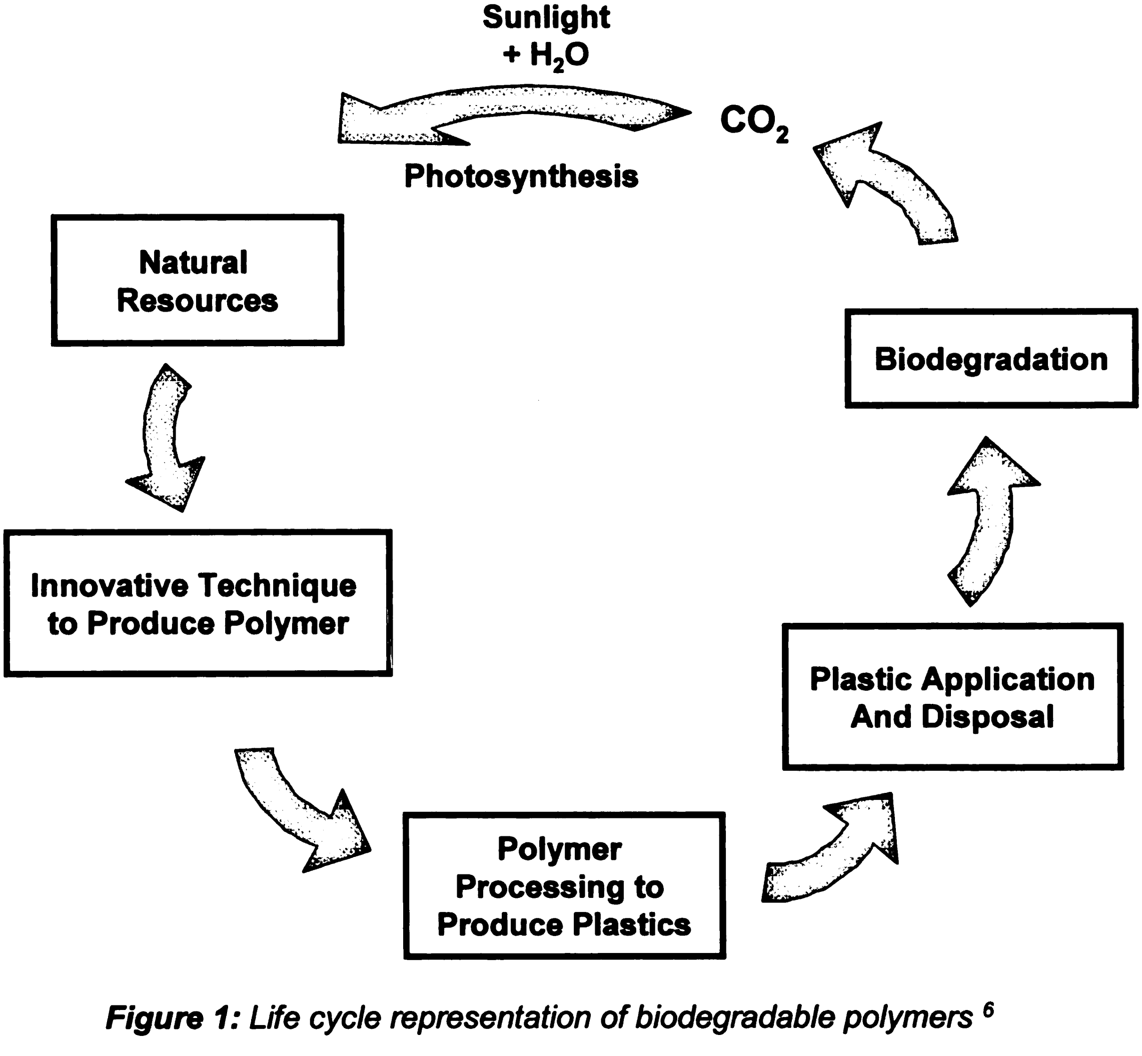


Figure 1: *Life cycle representation of biodegradable polymers* [6]

Albertsson and Karlsson[7] defined biodegradation as a process, which involves an action of enzymes and/or chemical decomposition associated with living organisms (like bacteria and fungi) and their secretion products. There can be other abiotic reactions like photodegradation, oxidation and hydrolysis, which may alter the biodegradation rate.

Biodegradable polymers are classified[3, 8] as: biosynthetic, semi-biosynthetic and chemosynthetic. The biosynthetic polymers obtained from renewable resources are biodegradable but with varying rate and extent while the semi-biosynthetic and chemosynthetic polymers may be biodegradable based on their bonding, chemical structure and the degrading environment.

Biodegradable polymers like poly(lactic acid), polyhydroxybutyrate, etc. are biopolymers made from renewable resources whereas poly(ε-caprolactone), poly(butylene succinate) etc. are biodegradable polymers made from fossil fuel resources. Biodegradable polymers are gaining importance in recent years because of increasing environmental consciousness [9].

An interesting source of producing thermoplastic materials are the ethanol industries, which use corn as a source of raw material and convert the starch present in corn into ethanol and gives corn gluten meal (CGM) and distiller's dried grain (DDG) as by-products. Such by-products contain substantial amount of protein that can be converted into thermoplastic material. The use of corn in ethanol industries has a remarkable trend. It is a good substitute to the ethanol produced from non-renewable sources. The high production of ethanol in U.S. has made ethanol the single most important and fastest growing value added market for farmers, stimulating rural development, creating jobs and increasing farm income. The use of ethanol can not only reduce our dependence on other countries for oil but also can reduce ozone pollution and greenhouse gas-forming emission[10]. The ethanol production from corn is done by two different processes i.e. dry milling and wet milling. The major by-products obtained from wet milling industries are CGM. The major by-products/co-products obtained from dry milling industries are distiller's dried grains with soluble (DDGS). These by-products from corn based ethanol industries are mostly used for animal feeds. But extensive research can find the value-added applications of such by-products in making biodegradable plastics. In US, 26 million metric tons of plastic waste was generated in year 2003[11]. The development of biodegradable plastic from by-products can help to reduce the waste generation. The high production of ethanol and the value-added application from its by-products will benefit the corn growers by providing new markets for corn and rural development opportunities for grower's communities as well as benefit the bio-products industry as a whole.

1.1 Production of Ethanol

The United States currently produces 4.2 billion gallons of ethanol in 94 different facilities with more 85% production based on corn[10, 12]. There are 28 facilities under construction and 7 under expansion, which adds up another billion gallons to the total production capacity[10, 12]. The other sources of ethanol include milo, barley, sorgum, cheese whey, waste beer, wheat, etc.[10]. The use of ethanol in gasoline helps to replace imported methyl tertiary butyl ether (MTBE) used as oxygenate agent. A recent study in 2005 found that ethanol industry is boosting the U.S. economy by creating more than 147,000 jobs, enhancing household income by \$4.4 billion and reducing the trade deficit by \$5.1 billion[13]. In 2004[10], dry mill facilities accounted for 75% of U.S. ethanol production, and wet mills 25%. The ethanol dry mills produced approximately 7.3 million metric tons of distiller grain. Ethanol wet mills produced 426,000 metric tons of corn gluten meal[10].

1.2 Production of corn in USA

The annual production of corn in US in 2004/05 was around 11.8 billion bushels (1 bushel = 56 lbs), which is almost 42 percent of the global corn

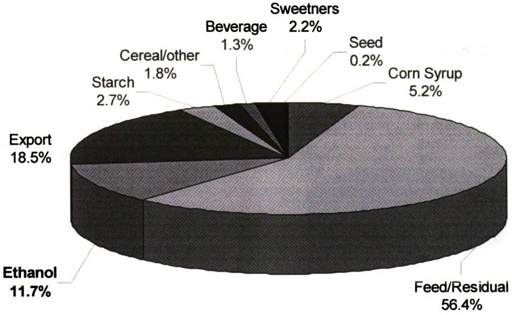


Figure 2: *Representation of corn use in food and Industrial field in 2004*[10]
(Source: USDA, ERS, Feed Outlook, December 2004)

production and 90 percent of US feed grains production[14]. The corn is not only used as a main energy ingredient in livestock feed but is also processed into a number of food and industrial products including starch, sweeteners, corn oil and ethanol. The proportion use of corn in food and industrial use is shown in Figure 2[10]. A record use of 11.8 billion bushels of corn toward the ethanol industry indicates the importance of corn and the new value markets for corn growers[10].

1.3 Constituents of corn

The corn kernel consists of four major components i.e. bran, gluten, starch and germ. The bran is the outer covering of the corn kernel and is mostly the fibrous part, the gluten consists of most of the protein, the starch is found at the top, on the sides and in the middle of the kernel while the germ is at the center of the kernel[15]. The composition of the corn kernel is shown in Figure 3[16].

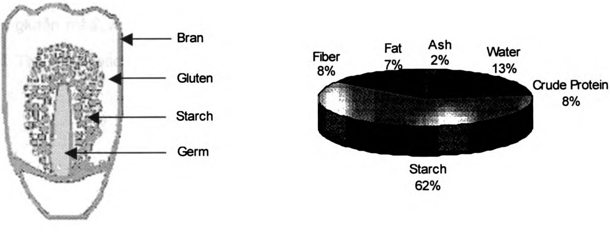


Figure 3: *Structure and composition of corn kernel* [16]

1.4 Ethanol Production Processes

The ethanol can be made from corn by using two different processes. The two different processes are:

1. Wet milling
2. Dry milling

1.4.1 Wet Milling

This process starts with the cleaning of the corn grains and soaking or steeping in dilute sulfur dioxide solution for a sufficient time of 30-50 hours in order to separate the grains into its components. The steeped grains are separated from the water and passes through grinding to separate the germ from the rest of the grain, which is further used for corn oil extraction. The fibers can be separated from the gluten and starch by the filtration and washing. These fibers can be mixed with the steep water to get the gluten feed. The gluten and starch is separated by centrifugation. The wet gluten can be dried to get the gluten meal while starch can be fermented and distilled to get the ethanol[17, 18]. The schematic in Figure 4[17, 18], shows the steps of wet milling process.

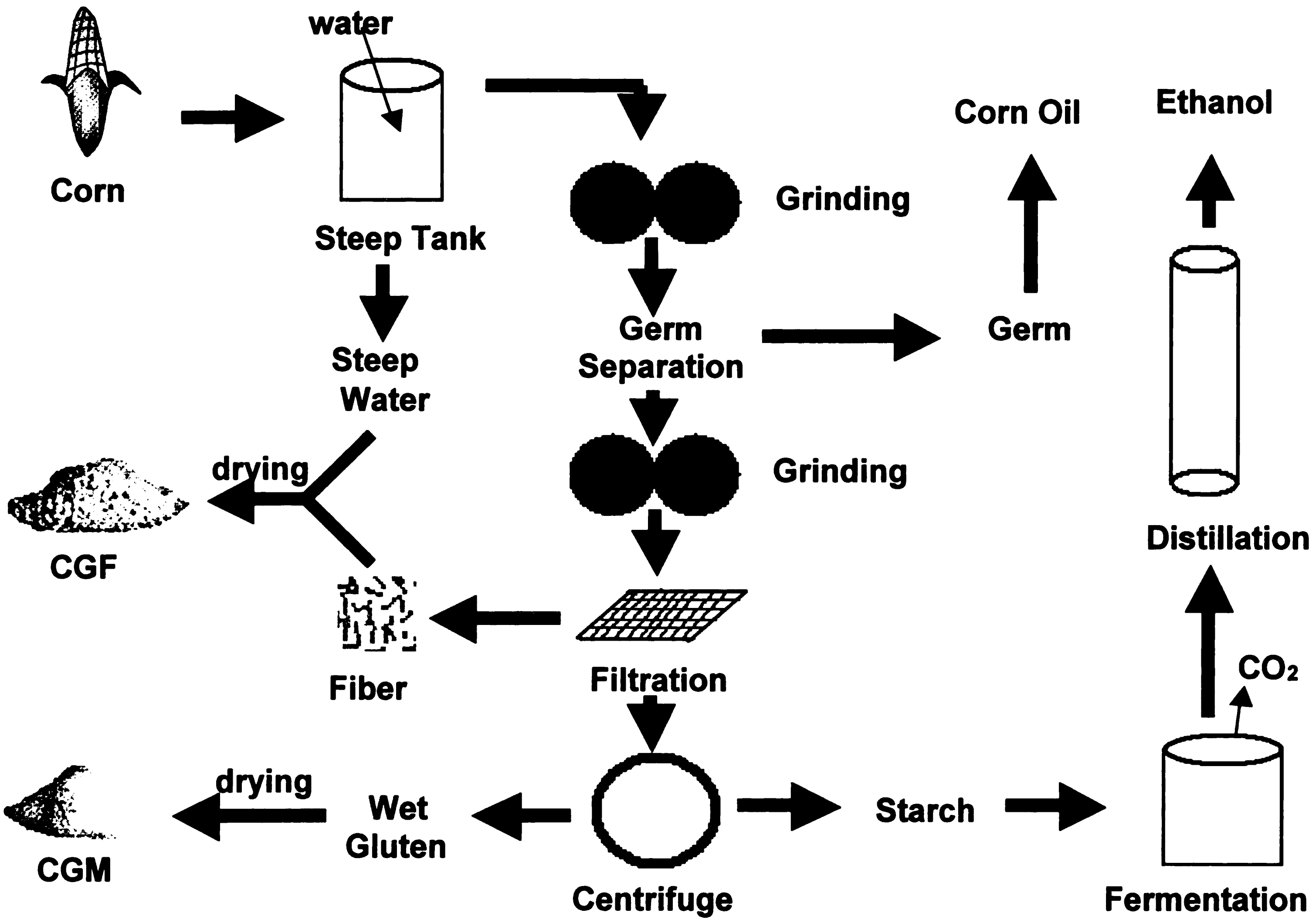


Figure 4: Flow diagram for production of ethanol by wet milling process[17, 18]

1.4.2 Dry Milling

The process initiates with the cleaning and grinding of the corn grains followed by mixing with water and an enzyme and heating to high temperature to liquefy the starch. The mixture is further cooled down and enzymes are added to convert the starch into sugar and the sugar is fermented into ethanol and carbon dioxide by addition of yeast. This process results in alcohol and some non-fermented products, which are separated by distillation. The alcohol can be removed from the top of the distillation column and the residue mash can be received from the bottom of the column and can be centrifuged to obtain dry distiller's dried grain (DDG). The thin stillage is condensed by evaporation of liquid and further mixed with DDG to get distiller's dried grain with soluble (DDGS). The schematic in Figure 5 [17, 18], shows the steps of dry milling process. The dry milling process yields in distiller's dried grain (DDG) as its major by-product/co-products[17, 18] .

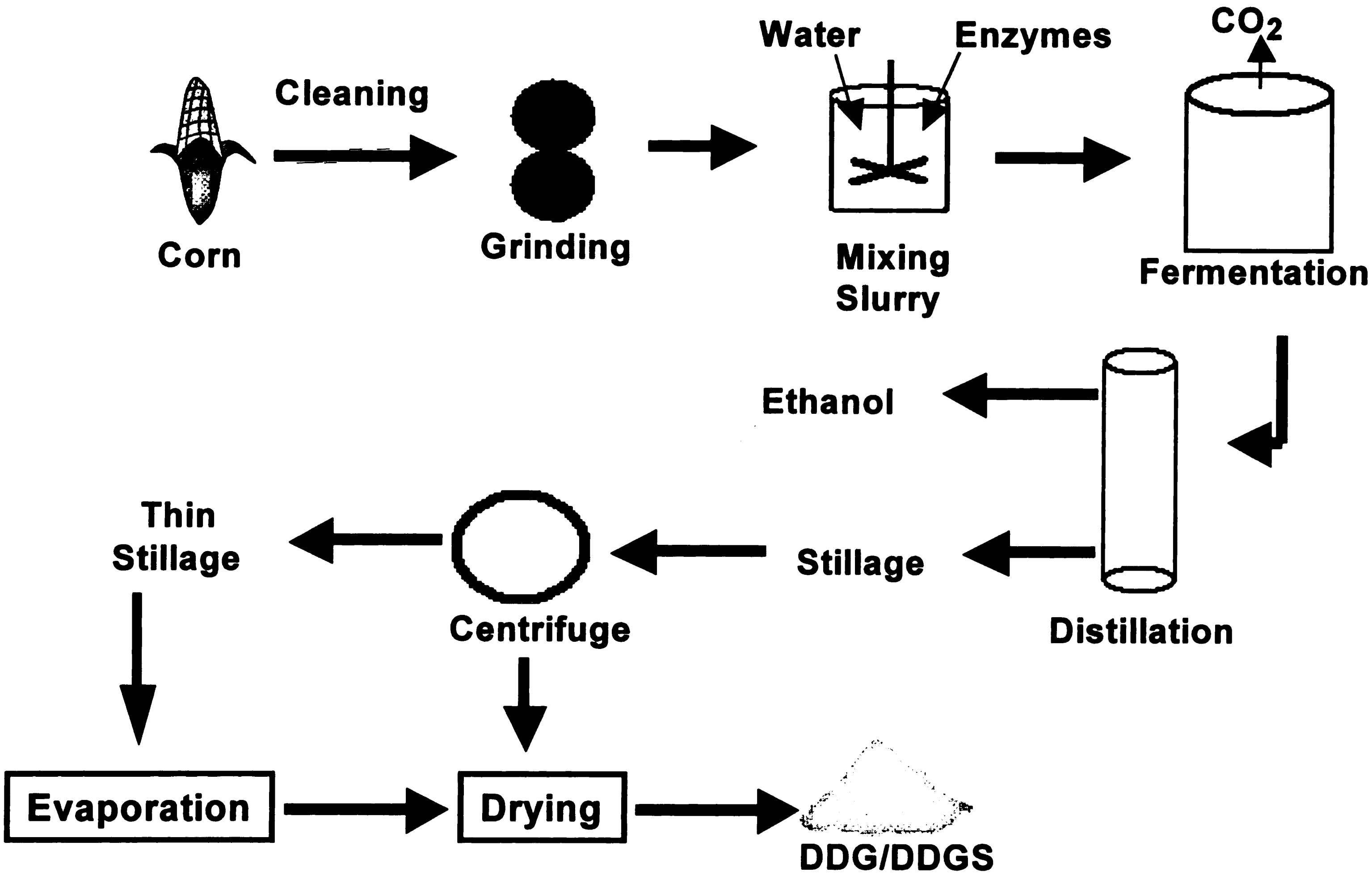


Figure 5: *Flow diagram for production of ethanol by dry milling process*[17, 18]

1.5 By products

The by-product obtained from dry milling process is mainly the distiller's dried grain (DDG) while there is a variety of by-product obtained from the wet milling process. The main by-products obtained from wet milling process are corn gluten meal (CGM), corn gluten feed, corn oil (see Table 1[19, 20]). The by-products like corn gluten meal and distiller's dried grain, which contains considerable percentage of thermoplastic protein, can be potential source of biodegradable plastics. The thermoplastic nature of protein and its origin from renewable and abundant resources has attracted the attention for packaging application due to its biodegradability[21].

Table 1: *Average yield of ethanol and its by-product per bushel of corn*[19, 20]

Products	Wet Milling	Dry Milling
Ethanol	2.5 Gallons	2.7 Gallons
CO_2	18.0 lbs	18.0 lbs
Gluten Feed	13.5 lbs	-
Gluten Meal	2.5 lbs	-
Corn Oil	1.6 lbs	-
DDG	-	18.0 lbs

***Table 2:** The composition of corn gluten meal and distiller's dried grain*[22-25]

Component	CGM	DDG
Starch	20	-
Protein	65	27
Oil	4	13
Ash	1	4
Others*	10	56

*Includes fibers, nonprotein nitrogen, soluble sugar and other by-product of ethanol fermentation

Corn gluten meal (CGM) is a by-product obtained from the corn based ethanol industries using a wet milling process that has been shown to exhibit high thermoplasticity[9]. It mainly consists of proteins (60%) and has a high percentage of hydrophobic amino acids (10% leucine) with the remaining components mainly being moisture, fiber, and lipids[25]. The high demand for the production of bio-ethanol, a better substitute for the ethanol produced from non-renewable sources means increased generation of CGM. The current use of CGM is mainly as animal feed but extensive research is directed towards finding additional value-added applications for CGM. One of the growing avenues is in the design and engineering of CGM-based biodegradable plastics to compete with the petroleum based products on the basis of cost and performance.

Recently, several studies have been made on CGM based biodegradable materials. Wu et al.[26] have successfully extruded and compression molded

CGM/wood fiber composite into sheets and injection molded pots for agriculture. CGM, glycerol, urea and an organic acid were used to prepare compression molded thermoplastic by Nobuhiro et al[27]. Gioia et al.[28] studied the interaction of CGM with polar and amphiphilic plasticizers.

1.6 Poly (ε-caprolactone) (PCL)

PCL, is an aliphatic polyester. It is one of the important biodegradable polymers gaining interest due to its inherent biocompatibility[29-32]. It has application in packaging, plant containers and medical devices[33, 34]. It is semi-crystalline in nature with a melting point of ~60°C[35] and a glass transition temperature (T_g) in the range of -65 to -60°C. PCL can be blended with a variety of other polymers to improve their mechanical properties[36]. Blending a natural polymer with polyester is one way to reduce cost and to improve the biodegradability of the resulting polymeric blend[37]. Therefore, blending of a petroleum-based biodegradable polymer (PCL) with a low cost natural biodegradable material like CGM may provide an eco-friendly alternative packaging material.

The uniqueness of the present investigation includes the plasticization along with the destructurization of CGM that imparted a much improved elongation to the blends. This newly developed green plastic shows certain properties comparable with one specific HDPE grade and an added advantage of biodegradability.

The purpose of this research was to develop a biodegradable plastic by blending a chemically modified and plasticized CGM with PCL. This research is covered under the following guidelines-

- Investigation of processing parameters.
- Investigation of guanidine hydrochloride (GHCl) compatibility with blending partners through characterization by Infra red spectroscopy
- Investigation of thermo-mechanical properties of the blend by DMA (Dynamic Mechanical Analyzer), TGA (Thermo-Gravimetric Analyzer) and UTS (Universal Testing System).
- Comparison of mechanical properties of the blend with a commercial grade high density polyethylene (HDPE).
- Study of blend morphology by SEM (Scanning electron microscopy)
- Investigation of thermo-mechanical properties of blends with higher PCL content

CHAPTER 2

Literature Review

2.1 Biodegradable Plastics

Weber et al.[38] defined biobased food packaging materials as substances derived from renewable sources that have food packaging applications. They divided these biobased polymers into three categories based on their origin and production (Figure 6)[38].

Plastics offer enormous advantage for handling, distribution and storage of food over other packaging materials. The plastics from renewable sources like starch offer an alternative to the plastics from non-renewable sources. Initial hurdles with starch like water resistance, performance and appearance were overcome by reactive blending to give plastics with desired characteristics. The reactive blending technique can help to convert the thermoplastic material into cast film and other packaging containers like trays, yogurt pots, cartons and boxes using the conventional processing methods. These materials are not just biodegradable but totally decompostable[39].

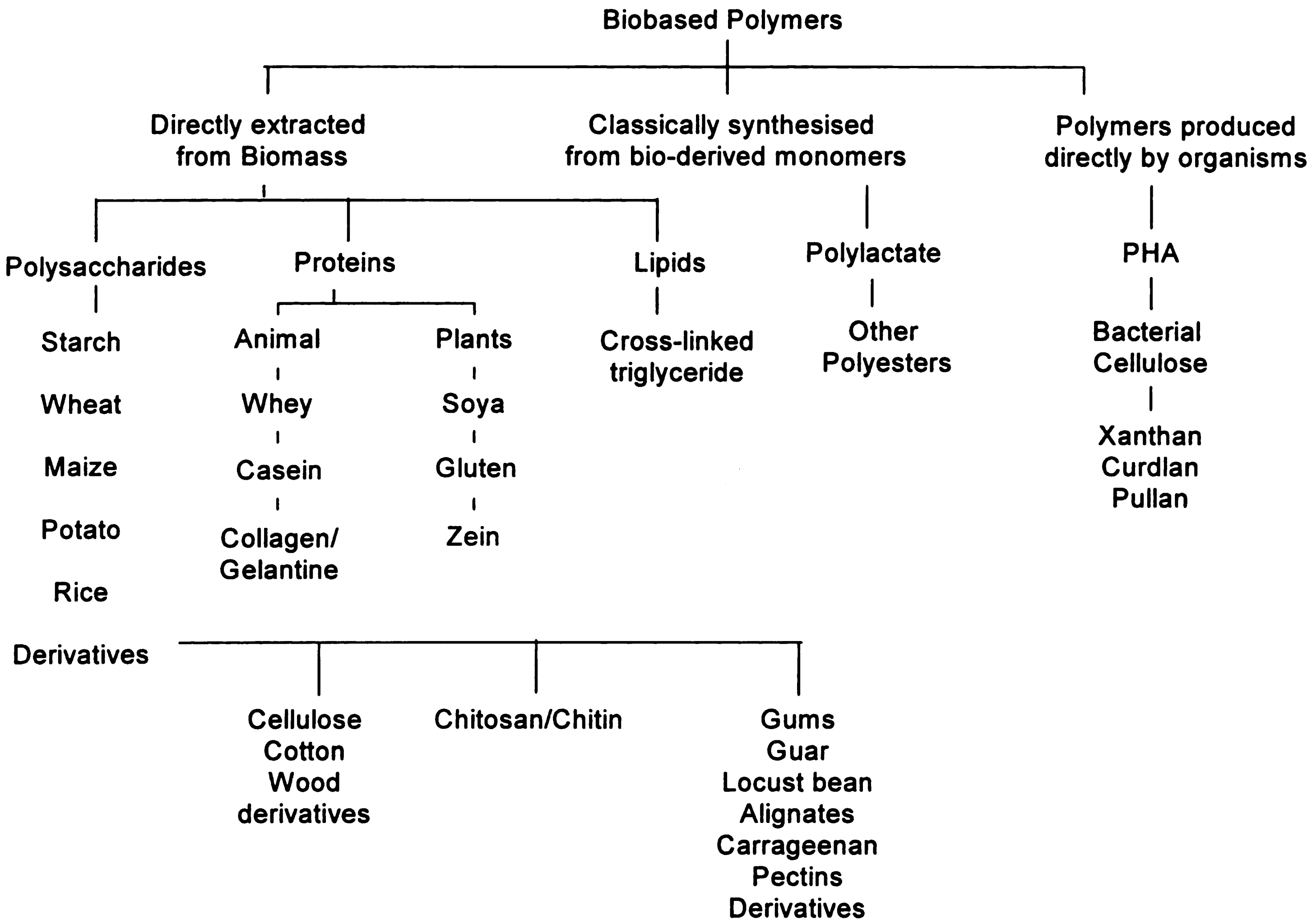


Figure 6: *Schematic representation of biopolymers based on their origin and method of production* [38]
Adapted from Biobased Packaging Materials for food Industry (status and perspectives) by C.J. Weber)

The non-biodegradable plastics are considered to be strong, light weight, inexpensive, easily processable, durable, good barriers and energy efficient in comparable to metal or glass used for packaging but have issues with the ultimate disposability. These plastics have irreversible nature since they cannot be easily broken down by available natural elements such as composting to become a part of the biological carbon cycle of our ecosystem. Therefore, it imay be advantageous to introduce biodegradable plastics wherever possible like single use disposable short-life packaging materials, service ware items (cups, plates, cutlery), coating for paper and paper-board. The biodegradable materials like PCL, Polylactic acid (PLA), poly(hydroxybutyrate-co-hydroxyvalerate), thermoplastic starch, polyvinyl alcohol and protein polymers, already introduced in the market place show tremendous growth opportunity [40].

Karlsson and Albertsson[41] defined biodegradable polymers as polymers which degrade as a result of the microbial and/or enzymatic action. Biodegradable polymers are obtained from both natural and synthetic sources with varying susceptibility to microbial and enzymatic degradation. The biodegradation process may take years like for lignin to hours for proteins. The authors mentioned the influence of structure, hydrophilicity, morphology, surface area and additives used on the rate of biodegradation. They also claimed the design of biodegradable polymers by choosing an appropriate molecular architecture with predetermined degradation rates without losing important polymeric properties. The natural polymers use either oxidation or hydrolysis as a mode of degradation. The polymers that degrade by oxidation have a slower rate than the polymers that degrades by hydrolysis. Some biodegradable polymers have an induction time before degradation process, hence avoiding degradation during process and use.

Polyesters lead the category of biodegradable plastics because of their water induced degradable ester bonds[42]. The polyesters are derived from both renewable and non-renewable sources and are both aromatic and aliphatic in structure. The aromatic polyesters have excellent mechanical properties and are resistant to microbial attack. The aliphatic polyesters are usually biodegradable. The strength and mechanical properties of most aliphatic polyester are inferior to the most aromatic polyesters. Aliphatic polyester can be blended with other biodegradable materials like starch to make the process cost effective. Some of the commercially available biodegradable polymers are[42]:

1) Polyhydroxyalkanoate (PHA) is aliphatic polyester synthesized by microbes and is brittle in nature due to high crystallinity. The packaging application of PHA is for injection molded bottles and plastic films.

2) Polylactic acid (PLA) is aliphatic polyester prepared by condensation of lactic acid or by ring opening polymerization of the lactide group. The applications are thermoformed products like food trays, containers. The material has potential to replace polystyrene and PET in some applications.

3) Polycaprolactone (PCL) is synthetic aliphatic polyester prepared by ring opening polymerization of caprolactone. The applications of PCL includes food trays, loose fill and film bags.

4) Aliphatic-aromatic copolyester (AAC) is combination of aliphatic and aromatic polyester to give good biodegradable and mechanical properties. The mechanical properties of such biodegradable plastics can be compared with the traditional non-biodegradable polymers like low density polyethylene (LDPE). Ecoflex polymer from BASF is an example of aliphatic aromatic copolyester.

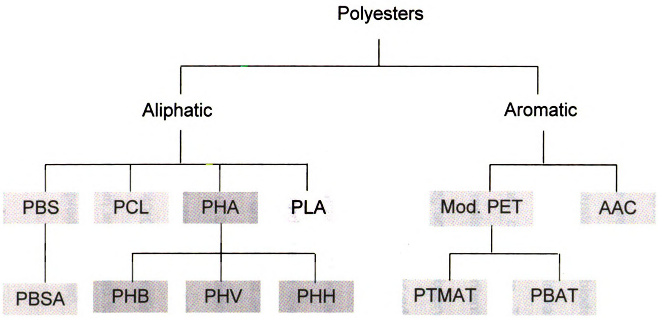


Figure 7: Schematic representing biodegradable polyester family[42]
(adapted from- http://www.deh.gov.au/settlements/publications/waste/degradables/biodegradable/chapter3.html)

PHA- Polyhydroxyalkanoates	PCL- Polycaprolactone	PBS- Polybutyl succinate
PHB- Polyhydroxybutyrate	PLA- Polylactic acid	PBSA- Polybutyl succinate adipate
PHV- Polyhydroxyvalerate	AAC- Aromatic-aliphatic copolyesters	PMAT- Polymethylene adipate/terephthalate
PHH- Polyhydroxyhexanoate	PBAT- Polybutylene adipate/terephthalate	

2.2 Corn gluten meal and its based polymers

The extent and rate of biodegradation of biodegradable materials vary from one material to another. So, the information and studies relating to biodegradable materials are very helpful in designing the biodegradable products. Imam et al.[43] evaluated the biodegradability of corn gluten meal, distiller's grain, corn starch, corn zein and corn fibers under different temperature, pH and moisture conditions. They observed that there was a marked difference when the moisture content was raised from 30% to around 60% and there was 100% degradation observed for CGM and zein at 50-60% moisture content in just 7 days. They observed a typical degradation behavior for these materials under different pH's. The CGM and zein were observed to degrade completely under neutral conditions and the degradation was effectively reduced to 60% under acidic and alkaline conditions while the starch degraded 40% under neutral and 60% under acidic and alkaline conditions in 20 days period. This rate and extent of biodegradation was observed to increase with temperature. They concluded the ideal conditions for composting of corn co-products by degradation as 40°C temperature, 50-60% moisture content and neutral pH. The CGM and zein were tested to have the best rate and extent of degradation among all the co-products tested.

Jane et al.[44] investigated the properties of biodegradable plastics made from starch, protein and mixture of starch and protein. They evaluated these biodegradable plastics based on the starch from different sources, effect of processing conditions, effect of cross-linking agent and the pH. They observed the plastics with different kinds of starch produced plastic with different properties; for example, plastics made from potato starch had significantly higher water absorption in comparison to other starches. This was attributed to the water affinity of the phosphate derivate present in higher percentage in potato starch. They also observed that optimum moisture content is required during the processing of starch-protein mixture to gelatinize starch (melt the starch crystallites) and mold the plastics as the lower moisture content couldn't gelatinize the starch and the higher moisture content affects the physical properties. They found a significant effect of cross-linking on the water absorption and tensile properties. They explained the effect of pH depends on the isoelectric points, which is the point when the protein has net electric zero charge and it accounts to the least water solubility and highest physical strength. This isoelectric point is characteristic to a protein type.

Proteins[38] are random copolymers of amino acids and have numerous and diverse side chains, which offer limitless opportunities to specifically design the final polymer by suitable chemical modification. The origin of protein is from plant and animal. The plant protein includes gluten and soy while the animal protein includes casein, collagen and whey. The thermoplastic nature and excellent gas barrier properties of protein makes it highly suitable as packaging material while its hydrophilic nature requires some modification or protection like lamination from moisture.

The main storage of protein in corn is gluten, which is rich is in disulfide linkages and needs to be broken down for better processing. The gluten is available in abundance at low price and therefore an important area of research for edible films, adhesives and other thermoplastic applications. Zein is another source of thermoplastic polymer obtained from purification of CGM, a by-product from corn based wet-milling industries. It is currently used in food and pharmaceutical coatings. Though the films made from zein are brittle, they can be plasticized to make it flexible. These films have potential for edible and biobased packaging [38].

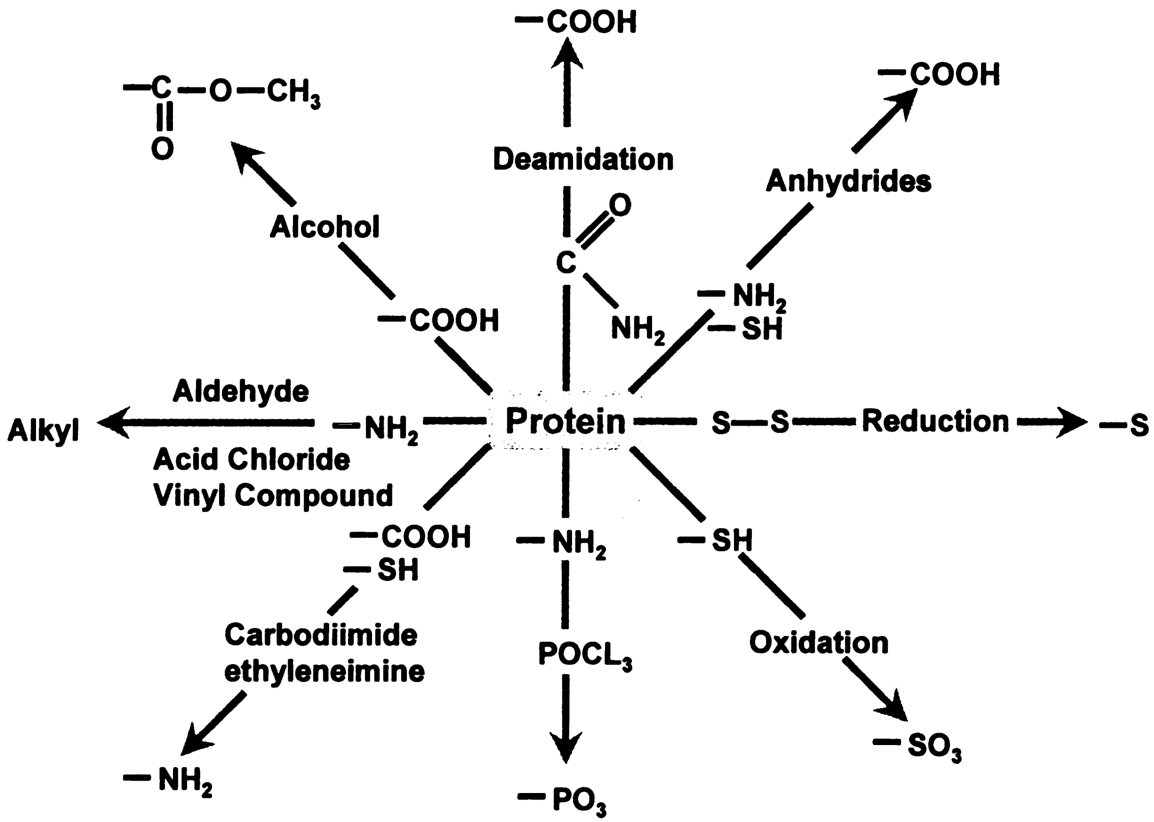


***Figure 8**: Structure of Protein showing various side chains available for Chemical modification*[38]

(Adapted from Biobase Packaging Materials for the Food Industry by C.J.Weber)

CGM is one of the major sources of zein. There are various extraction techniques used to extract zein from CGM based on the required quality and purity of zein (see Table 3[45-65]). The other extraction sources of zein are corn and DDGS. It is a major storage of protein in corn and is insoluble in water except in the presence of alcohol, high concentration of urea, high concentration of alkali (pH ≥11) or anionic detergents. The current zein manufacturing is limited to 500 tons per year from corn gluten meal due to their high cost. The development of low cost manufacturing methods for zein can create new promising opportunities. The zein forms tough, glossy, hydrophobic and grease resistant coating. The zein are resistant to microbial attack. The applications of zein are into adhesives, binders, biodegradable plastics, edible moisture resistant coating for food products, photographic films and printing inks[45].

__Table 3:__ Various extraction techniques and recovery methods used for zein[45-65]

Extraction Techniques	**Recovery Methods**	**Quality/purity of zein**
Wet in 85-95% Ethyl alcohol for several days[46]	Precipitate in 1% NaCl and followed by discolorization in ethylene dichloride/ether or acetone and air dried.	White zein is produced.
Continuously extract with 80% ethyl alcohol, n-butanol or isopropyl alcohol (IPA) at 62°C [47]	Alkali treatment followed by acidification and precipitation in cold water.	Zein purity (>97%) but 100% pure zein can be obtained by extraction with benzol, carbon tetrachloride or ether.
Use 85% IPA at 60°C in the ratio of 4:1[48]	Alkali treatment and hexane clarification	50% yield
Extract with 80% ethyl alcohol [49]	Precipitate by dilution with water. Treat precipitate with 20-25% toluol/benzol.	Ethyl alcohol by distillation. Fine granular zein obtained

Extraction Techniques	Recovery Methods	Quality/purity of zein
Continuously extract with 85% IPA/ 92% ethyl alcohol at 60°C in the ratio of 3.5:1[50]	Alkali treatment followed by filtration, acid treatment, water displacement and spray drying.	50% yield and zein powder may contain some impurities.
Extract with 55-65% IPA followed by 1hr ageing and cooling [51].	Filtration followed by acid treatment and precipitation.	Unstable and poor quality zein obtained.
Extract with a mixture of 5 parts-37% formaldehyde and 20-parts 55% ethyl alcohol/ 80% IPA at 120°C for 15-30 minutes in the ration of 3:1[52]	Cool and filter through diatomaceous earth.	55% protein recovery.
Extract with 91% IPA at 82°C for 30 minutes in the ratio of 4:1[53].	Filtration followed by stabilization with propylene glycol at 121°C.	90% protein extracted but zein solution can be used as coating.

Extraction Techniques	Recovery Methods	Quality/purity of zein
Extract with 80% IPA for 30 minutes at 50-60°C in the ratio of 3:1[54].	Washing followed by precipitation at 4-10°C with oil/pigment removal by petroleum ether.	90% protein extracted.
Extract with 40-60% ethyl alcohol at 75-85°F in the ratio of 3:1, followed by filtration with diatomaceous earth. Halogen treatment and bleaching for pigment removal [55].	Chilling and water precipitation.	Zein produced in 40% concentration and is soluble in ammonia.
Extract with 28-33% IPA with 6% lime at 70°C to boiling for 15-30 minutes in the ratio of 7-8.5:1[56].	By solvent evaporation.	75% yield but higher purity with repeated extraction process.
Extract with 88% IPA and 0.25% NaOH at 55-60°C in the ratio of 4:1[57]	Chill extract to -10 to -20°C to precipitate protein.	20-24% yield. For high purity, repeated extraction with fresh IPA.

Extraction Techniques	Recovery Methods	Quality/purity of zein
Extract with 85% methyl alcohol at 130°C for 2 min. in ratio of 5:1, followed by filtration and NaOH addition at 100°C [58].	Solution is cooled and filtered below -25°C followed by washing precipitate with methanol.	Colorless and pigment-free zein obtained.
Extract with 3%NaCl at 4°C/30min. followed by extraction with 60%ethyl alcohol at 60°C/30 min. in ratio of 10:1[59].	Zein precipitated in equal volume of 1% NaCl and centrifuged.	Good quality zein produced.
Enzymatic starch hydrolysis followed by alkaline treatment and alcohol wash [60, 61].	Zein precipitated in cold water, dried and ground.	>96% purity with defatted and discolored zein.
Extract with 70% acetone at 40°C/4hrs in the ratio of 5:1[62].	Evaporation of solvent followed by concentration and precipitation.	30% recovery in white porous granular form.
Extract with 95% ethyl alcohol at 70°C in the ratio of 8:1[63].	Centrifugation and precipitation at -10°C and zein wash with hexane.	30% recovery
Extract with 88% IPA at 12.5 pH in the ratio of 4:1[64, 65].	Chill to -18°C to precipitate.	21-32% recovery with 80-87% purity.

An investigation on processing and properties of low cost corn gluten meal/ wood fiber composite was made by Wu et al.[26]. They mixed the corn gluten meal and wood fiber in different composition and plasticized with glycerol, distilled water and ethanol and extruded into pellets. They used these pellets to form sheets by compression molding and injection molding to prepare low cost seedling pots. These samples were studied for water resistance, thermal stability and morphology. They reported that the mixture of zein and water was an excellent plasticizer to disrupt the intermolecular interaction in zein and therefore resulted in improvement of melt mobility. The melt viscosity increases with increase in wood fiber and decreased water content, which led to a decrease in melt mobility. The water content should be decreased to increase the processing temperature and should be increased to increase the fiber content for injection molding. Based on the thermal analysis results, they observed the optimum processing temperature of 125-160°C. Based on the morphology results, they reported that with higher content of wood fibers, the breaking occurred at the fiber-matrix interface. They also reported the sheets and agricultural pots showed medium water resistance and concluded that the biodegradable seedling pots could have a good market potential.

Corradini et al.[37] investigated the mechanical, thermal and morphological properties of PCL/zein blends. They prepared blends of the corn derived zein and PCL in different proportions of 100/0, 75/25, 50/50, 25/75, 0/100. They added 5 wt% glycerol as plasticizer and prepared sheets by compression molding. These blends were compared for thermal and mechanical properties using therogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA) and universal testing machine. The blends were reported to have reduced tensile strength and elongation at break but improved Young's modulus compared to pure PCL. The increase in PCL content in the blend resulted in improved thermal stability, while the increase in zein content resulted in improved storage modulus. The morphologies of these blends were also studied using SEM and reported to have two distinct phases for PCL and zein, indicating the immiscibility of polymers while the fractured surface of the blend at 75% zein indicate the weak interfacial adhesion between PCL and zein.

Padua et al.[66] studied the properties of biodegradable plastic derived from corn proteins. They prepared zein based resin by plasticizing zein with palmitic, stearic, oleic and linoleic acids in different weight ratios and melting the mixtures in microwave oven. They rolled the resulted mixtures into sheets and replasticized by soaking in the respective plasticizers. These prepared samples were tested for tensile strength, elongation, Young's modulus and toughness using tensile testing machine and water absorption using standard water immersion test. The saturated fatty acids plasticized sheets produced rigid sheets good enough for food application while the unsaturated fatty acids plasticized sheets resulted into flexible and elastic sheets. They also observed that there was considerable decrease in water absorption after the sheets were coated with linseed oil. The authors proposed the use of these sheets for packaging application

Chemical modification of zein was made by Wu et al.[67] using polycaprolactone (PCL) and hexamethylene diissocyanate (HDI). They first synthesized isocyanate (NCO) terminated PCL prepolymer (PCLH) by reacting hexamethylene diissocyanate (HDI) with PCL diol and than modified the zein by PCL prepolymer. These zein based modified polymers containing different content of PCLH, were converted into sheets by compression molding. These samples were tested for mechanical and thermal properties. They observed the increase in elongation at break by 15 times and reduction in strength at break by 2 times, when modified zein based polymer contained 10% of PCLH in comparison to commercial zein. They also observed the flexibility of modified zein based polymer improved dramatically with negligible reduction in strength on increasing the PCHL content. Therefore, the zein can be modified by PCL to improve its mechanical properties.

Wu et al.[68] investigated the toughness and water resistance of zein based polymers modified by using various content of polycaprolactone (PCL) / hexamethylene diisocyanate (HDI) prepolymer. Dibutyl L-tartrate (DBT) was used as a plasticizer. They prepared the sheet samples by compression molding and studied for mechanical, water resistance, thermal properties and morphology. The toughness of the samples improved significantly in presence of small amount of PCLH due to the existence of micro-phase separation structure. The sheets were reported to exhibit better mechanical properties when modified with 20-50% PCLH followed by immersion in water for 24 hours than when stored in 75% relative humidity, which is an indication for excellent water resistance. DBT had better interaction with zein than PCLH and therefore acted as compatibilizer for the zein matrix and PCLH component.

Lai et al.[69] investigated and compared the properties of the zein films, plasticized by oleic acid. They prepared samples by casting and stretching the zein resin. They observed the films produced by cast process were translucent, had glossy surface on one side and the dull on the other and could be bended but fractured when folded. The films prepared by stretching were translucent to transparent, smooth surface, flexible and creased when folded. They reported that there was phase separation of oleic acid and zein in cast film while the stretched film remained a homogenous mixture when heated. Therefore, films drawn from resin had higher elongation and were tougher and more flexible than cast films. The film morphology studied by SEM revealed that the stretched films formed fibers and ribbon-like structure and hence had better orientation in contrast to deposition of solids without distinguishable pattern in cast films. The low glass transition temperature of – 94°C of stretched films can make them flexible at frozen storage temperature.

Rakotonirainy et al.[70] evaluated corn zein films as modified atmosphere packaging for fresh broccoli. They had plasticized the zein film with oleic acid and coated and/or laminated with tung oil and studied for 6 days for packaging of fresh broccoli. These finished films were reported to have improved water vapor and gas barrier. The tensile properties were reported to increase significantly for the films coated and/or laminated with tung oil. The broccoli florets were reported to maintain their firmness and color after 6 days of study. The zein film coated and laminated was found to perform best for odor control and stability. The uncoated and unlaminated zein films had poor dimensional stability and were found to be soft and soggy after the study due to the low CO_2 permeability, which establish high CO_2 atmosphere and hence retard respiration process.

Wang et al.[71] investigated the water interaction of extruded zein films through moisture sorption isotherm. They used a regular grade zein powder with 90% protein content. They plasticized zein with oleic acid and emulsified with distilled monoglycerides to form a blown film on single screw extruder while zein sheets were prepared by slit die single screw extruder without adding plasticizer. They reported zein powder had high moisture content due to the presence of multiple pores and capillaries that may hold water droplets. The zein powder possess high moisture uptake, which induces protein swelling, exposing previously occluded polar amino acid groups to water. They reported extruded products had less moisture adsorption and moisture content than zein powder, which was caused by modification of zein morphology after compression of zein mass into compact solid, free from pores and capillaries. They observed moisture adsorption of zein films plasticized with oleic acid was lower than zein sheets, indicating that the incorporation of hydrophobic oleic acid prevents moisture sorption.

Thermal behavior of corn zein was investigated by Magoshi et al.[72] using differential scanning calorimetery (DSC), thermogravimetery analysis (TGA), X-ray differaction (XRD) and infrared spectroscopy (IR). They had first produced zein by grounding corn meal followed by using different separation technique based on precipitation and distillation. The zein was dissolved in aqueous ethanol and casted into film on a glass plate. They concluded that casted zein film is amorphous in the random-coil conformation and this amorphous zein crystallizes to β-crystals at about 210°C accompanied by the random coil β-form conformational transition. They found the glass transition temperature at 165°C and thermal degradation of zein occurring at 320°C. The steam treatment of zein film resulted in the conformational change to the α- and β-forms, simultaneously, irrespective of treating temperature.

Lai et al.[73] investigated the structure of granular zein, zein fibers, zein-oleic acid resin and zein-oleic acid film by wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS). They observed WAXS patterns showed the diffused rings, which is an indication of non-crystalline structure. The interhelix spacing in zein-oleic acid resin and films was higher than granular zein and zein fibers, which was due to the presence of oleic acid and was related to the resin preparation process. The SAXS results showed that the periodicity was observed for oleic acid based resin and film while no periodicity was observed for granular zein and zein fibers. The biaxially drawn resin films showed different periodicity than the cast film, which indicate that the film morphology was affected by forming process.

Sessa et al.[74] investigated the enhancement of metal-binding properties of distiller's dried grain (DDG) and corn gluten meal (CGM) by generating acid stable products on reaction with citric acid. Citric acid dehydrated at higher temperature can formed anhydride that can interact with functional groups in the protein of DDG and CGM to form ester and carboxyl linkages, which was confirmed by FTIR studies. The solid state NMR analysis supported the metal binding characteristic of citric acid reaction products and demonstrated that Al^{3+} was bound ionically to carboxyl group. The authors claimed that these biobased products possess cation-exchange capability and potential biodegradability that may be a channel to industrial wastewater treatment.

Tensile properties of the film extruded from blends of corn zein or corn gluten meal with low density polyethylene (LDPE) was investigated by Herald et al.[75] The film samples were prepared by melt extrusion and tested for tensile strength, percentage elongation and modulus at different composition of zein or corn gluten meal with LDPE. The authors reported a decrease in all tensile properties tested. They also added that the film containing zein has better tensile properties than the film containing CGM, which may be contributed due to the better compatibility of zein with PE than CGM.

Parris[76] studied the characteristic properties of zein films extracted from dry milled corn and corn gluten meal. They reported that the insoluble particles, identified as protein aggregates were formed during extraction of zein from dry milled corn while these insoluble aggregates were not observed in the zein extracted from corn gluten meal. On further investigation using polyacrylamide gel electrophoresis, they reported that β- and γ-zeins were detected in dry milled corn while only a trace of β-zein were found in corn gluten meal. They reported when the dry milled corn was pretreated, it resulted into higher solubility due to the cleavage of disulphide linkages of the β- and γ-zeins and hence improvement in tensile properties.

Gioia et al.[77] investigated the effect of some polar and amphiphilic plasticizer on the properties of corn based resins. They selected glycerol and water as polar plasticizers and octanoic and palmitic acids, dibutyl tartrate and phthalate, and diacetyl tartaric acid ester of mono-diglycerides (DATEM) as amphiphilic plasticizers. The blending of corn gluten meal and plasticizers was made by hot mixing process and the samples were prepared by compression molding. They reported that the plasticizing efficiency at equal molar content was proportional to the percent of hydrophilic groups of the plasticizer. They have reported that both the family of plasticizer interact differently to different parts of protein and hence gives different outcomes. They also mentioned that the polar plasticizer interacts well with the accessible polar amino acids whereas amphiphilic plasticizer interacts well with the non-polar zones. The octanoic acid was reported to be a promising plasticizer for corn protein in terms of volatility, water resistance and extrudation. The authors claim that this new low cost biomaterial could be used for applications in the field of agriculture, packaging and compostable short life items.

Tilekeratne et al.[78] had modified corn zein film by incorporating plasticizer of two different molar masses. (i.e. 400 and 1000 g/mole) and investigated the thermal and mechanical properties using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile strength, moisture absorption isotherms and water vapor transmission rate measurements. They had concluded that the polyethylene glycol (PEG) is an effective plasticizer for the corn zein film. The incorporation of PEG up to 30 wt% substantially enhances the tensile strength and its resistance to water vapor transmission into the protein film. The PEG400 had higher hydrophilicity group density than PEG1000, which result in higher rate of water absorption. They concluded that the PEG acts by reducing the intermolecular forces with in the protein chains. The higher molecular mass PEG was found to be a more effective plasticizer than the lower molecular mass PEG.

Effect of gamma-irradiation on the physiochemical properties of zein film was investigated by Lee et al.[79]. In their study they irradiated 10% zein solution in ethanol to gamma radiation and reported the change in the structure of zein molecules and also reported the cross-linking, degradation and aggregation of the polypeptide chains. They also reported that gamma irradiation also causes the increase in solubility of zein and decrease in viscosity of zein solution due to the cleavage of peptide chains. They also observed the decrease in water vapor permeability and increase in elongation.

Ha et al.[80] had proposed the use of zein sheets plasticized by fatty acids for various food industry and food service packaging applications by use of extrusion technology. They had plasticized the zein by fatty acids mixture comprising linoleic, linolenic, streaic, oleic and palmitic acid in aqueous ethanol solution. The solid zein resin was recovered and melt extruded in a twin screw extruder and rolled into sheets. The effect of extrusion temperature and ethanol added during extrusion were studied by evaluating their mechanical and water resistance properties. The high extrusion temperature resulted in the increase in tensile strength and decrease in elongation. The plasticized zein sheets showed good storage stability for 3 months of study.

Takahashi et al.[81] designed a process for preparing zein based water resistant film. They dispersed the zein in 65-70 volume% aqueous solution of acetone and converted them into film by drying at humidity less than 85% and initial drying temperature less than 55°C. The authors reported that these dispersions can also impart water resistance to the articles with poor water resistance by coating them and drying them at humidity less than 85% and initial drying temperature less than 55°C. The authors claimed that these film or coating neither dissolve nor becomes weak when in contact with water.

Trezza et al.[82] studied the water vapor and oxygen barrier properties of corn zein coated paper. They reported the water vapor transmission rates (WVTR) were 70-131 g/100 in^2/day for paper coated with 5-15 lb/ream corn zein but the addition of plasticizer increased the WVTR for a 10 lb/ream paper coating. The oxygen transmission rates for coating levels of 5, 10 and 15 lb/ream were observed to be 95,000, 35,000, and 16,000 cm^3/100 in^2/day respectively. This improved oxygen barrier may be attributed to good film flowing properties of solution into the paper matrix. They claimed this paper has potential to be used in packaging for improved barrier properties.

Lawton [83] investigated different plasticizers for zein and their effects on tensile properties and water absorption. It is reported that cast zein films are brittle at room temperature so the plasticizers are added to make them flexible. The cast films were prepared using various plasticizers as glycerol, triethylene glycol, dibutyl tartarate, levulinic acid, polyethylene glycol and oleic acid. These film samples were prepared and stored for one week at different RH. He observed that the tensile strength and young modulus decreased with increased RH. The films with glycerol and oleic acid as plasticizer did not show any effect on elongation with increase in RH while the other plasticizers showed the increase in elongation with increase in RH. The author added that film with glycerol absorbed the most amount of water while the film with oleic acid absorbed the least therefore the film with hygroscopic plasticizer are weak and the film with hydrophobic plasticizer have good mechanical properties at high RH.

Yoshino et al.[84] investigated the influence of preparation conditions on the physical properties of zein films. They made the zein film under various controlled drying conditions and tested for tensile strength, puncture strength, gas and water vapor permeability. The author reported a variation in the results in the tensile properties and concluded that these properties are very much dependent on the drying conditions of the film during preparation. The water vapor permeability was also reported to be different on both sides of zein film at high humidity.

Dejing et al[85] studied the properties, preparations and applications of zein, a water insoluble protein, obtained from corn. As reported, zein has excellent antioxidant properties for lipids and good film forming properties therefore it is a potential material for biodegradable and edible packaging. The authors reviewed the different characteristics and properties of zein and their possible end uses. They concluded that although zein has unique characteristics but its expensive cost prohibits its viable use in competition with petroleum plastics.

Lawton et al.[86] explained that the corn gluten meal is a co-product of corn wet milling and contains 60-70% protein and the remainder is starch and fibers. The zein is a prolamine protein and had shown the thermoplastic properties under perfect conditions. They concluded that research is being conducted to identify the appropriate conditions, which may result into a thermoplastic melt. They also added that water is an important plasticizer for corn gluten meal when used in combination with other plasticizer.

Effect of UV light on the physical properties of corn zein was investigated by Rhim et al.[87]. They exposed the films to 51.7 J/m^2 UV light for 24 hours and evaluated tensile strength, water vapor permeability, soluble matter and color. They observed that the tensile strength increased on UV exposure due to cross-linking while there was no effect on water vapor permeability. The UV light causes the destruction of zein pigments, resulting in fading out the yellow color of zein film. They concluded that the UV light could be used to modify zein film properties.

Esposito[88] reported that scientists at Illinois University claimed that a by-product from corn based ethanol industry could help to develop environmental friendly plastics, which decays naturally in the soil. They said the zein extracted from corn gluten meal can be plasticized with fatty acid to improve its properties. They observed that these plastics could be further coated with hot flax oil to make strong and waterproof sheets, which can be molded to sandwich boxes, plates and food trays. But to make it commercially viable, cheaper zein extraction techniques need to be developed in order to lower the cost of zein.

Wang et al.[89] investigated the effect of processing methods on the thermal behavior of zein film. They prepared a solution by dissolving the zein in 75% ethanol at 60°C and gradually adding 41% by weight of oleic acid. The resin was prepared by precipitating the zein-oleic solution, which was further extruded in single screw and twin screw to form films. The cast films were prepared by pouring the solution on flat surface and cooling at room temperature. Non-extruded resin films were also prepared by stretching the resin for testing. The DSC thermograms showed large melting peak for cast films while there was no peak for the film samples prepared by extrusion or heat treatment. They concluded an enhanced interaction between oleic acid and zein under heat treatment diminishes the peak. A low glass transition temperature Tg of -80°C was observed for the films due the plasticization effect of oleic acid.

Wang et al.[90] plasticized the zein with oleic acid and studied the tensile properties of extruded zein sheets and blown films. The authors analyzed the effect of hot rolling on the properties of the extrudate. They also studied the influence of moisture content and the barrel temperature on the extruded films. They observed that both single and twin screw extruded sheets showed higher elongation, lower tensile strength and lower modulus than the non-extruded samples. They also observed a difference in the tensile strength and elongation in the samples prepared from single and twin screw extruder, which was attributed to the voids created in the single screw extruded samples as observed by SEM. The blown film was observed to be affected by feed moisture content and the barrel temperatures. The optimum moisture content was determined to be 14-15% while the temperature was 20-25, 20-25 and 35ºC for three extruders zones respectively and the temperature of the blowing head was 45ºC.

2.3 Chemical modification of protein

Kumar et al.[91] studied the effect of guanidine hydrochloride (GHCl) as a denaturant to protein structure. GHCl cross link in different parts of protein due to the noncovalent interaction between protein groups and itself. This results into a stabilized form, which is dynamically constrained and lower in entropy. But if the concentration of GHCl is increased beyond certain limit, it leads to the unfolding of protein structure. The cross-linking is supposed to restrict the freedom of the molecules and hence producing stiffening in the protein structure.

Dunbar et al.[92] studied the effect of denaturant on protein. They claimed all the protein folding reactions are either aided by heat, acid or chemical denaturant. High concentration of denaturants is required in order to alter the protein structure and the surrounding solvent. These changes in the structure can be studied by X-ray crystallography. The denaturants like guanidine hydrochloride and urea form hydrogen bonding with the protein structure therefore they act as non-covalent cross-linking agent. These denaturants interact with both the protein side chain and the backbone. The actual position of these non-covalent cross-linking is not known specifically. Guanidine hydrochloride and urea have similar effects on the native structure of protein.

Stability of protein at different concentration of guanidine hydrochloride and urea was investigated by Bhuyan[93]. They added that the guanidine hydrochloride and urea stabilize the protein at low concentration and this stability increases with the increase in concentration of denaturant to a limit of its subdenaturing effect. The further increase in concentration of denaturant causes the protein unfolding effect. The author explained that the stability at lower concentration of the denaturant is entropic due to the non-covalent interaction between the denaturant molecules and the protein structure.

Monera et al.[94] studied whether guanidine hydrochloride and urea have the same effect on stability of a particular protein. The process of folding and the resulting structure has been long and difficult task due to the complex structure of native protein and its denaturation process. They designed four coiled-coil analogs and studied the intra-chain and inter-chain electrostatic interactions. They concluded that guanidine hydrochloride does not contribute to the electrostatic interaction at low concentration due to its ionic property, which might mask the positively and negatively charged amino acid side chains. But at the higher concentrations, guanidine hydrochloride becomes denaturant irrespective of the types of the electrostatic interactions present in the protein while urea, being an uncharged molecule, has no significant electrostatic effect and the denaturing action of urea is based on the ability to bind the protein. Therefore, guanidine hydrochloride and urea may give totally different estimate of protein stability.

Mayr et al.[95] studied the effect of guanidinium chloride on the stability of protein structure. They have addressed that the guanidinium chloride has a dual effect on the stability and folding of protein structure. At low concentration it acts as stabilizer and stabilizes the protein structure while at high concentration the denaturant character dominates and they unfold the protein structure. This is unlike urea where only unfolding takes place. They suggested this behavior of guanidinium chloride at low concentration being due to the binding of guanidine ions with other cationic sites in the native protein structure.

2.4 Polymer blending

Polymer blending is an economical technique to modify the properties of the polymers. Blending of polymers is very complex and unlike the low molecular liquids where the compatibility is only controlled by cohesive energy density and polarity. Blending of polymer has many other additional factors controlling the nature of compatibility because of the large molecules. Blending has great importance in using the scrap or defective material produced during manufacturing and hence producing new material without adversely affecting the properties of material. Blending resulting in immiscible blends also have great relevance. For example the immiscibility of polybutene with LLDPE or LDPE may help to produce peel heat seal layers[96].

Blending is really useful to incorporate the properties from two different polymers into the resulting polymer. If the polymer blends are miscible than the resulting blend will have the properties somewhere in between the unblended polymers. In miscible blends the properties of resulting blend is generally linear but may be sometimes higher or lower depending on the degree of binding forces between the polymer is higher or lower than the polymer themselves[97] (See Figures 9 and 10)[97].

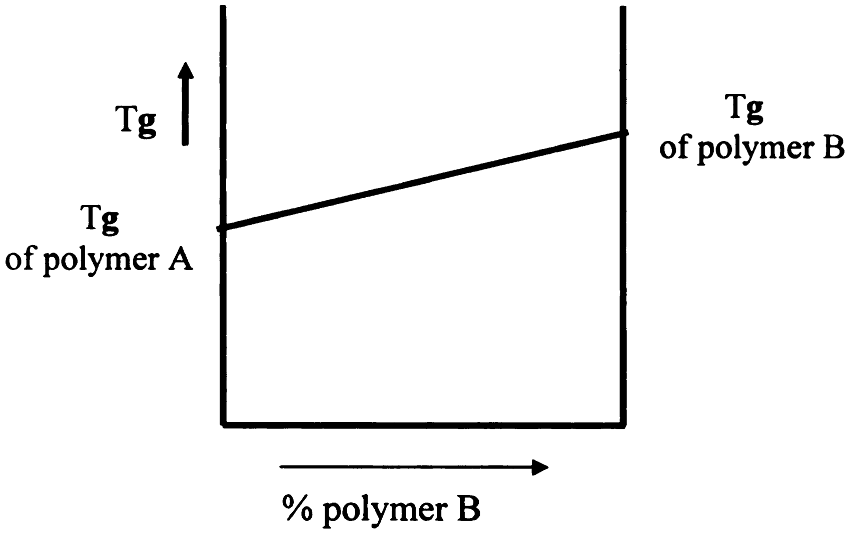


Figure 9: *Perfect linear relationship of Tg with polymer ratio*[97]

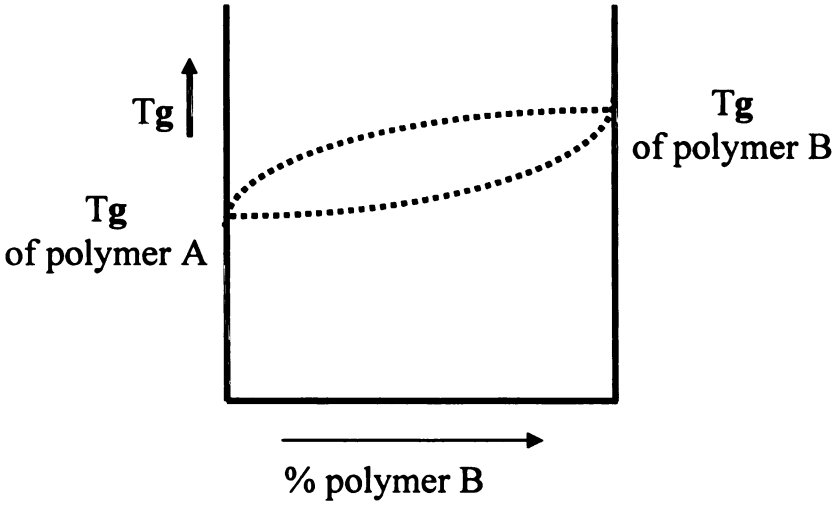


Figure 10: *Non-perfect linear relationship of Tg with polymer ratio*[97]

Some polymers form miscible blends only in certain proportions and immiscible in the other proportions, which is due to the lower free energy in the miscible regions than the immiscible regions (see Figure 11[97]). These miscibility regions may change with temperature. If they disappear at some higher temperature, then the temperature is called as upper critical solution temperature and if disappears at lower temperature then called as lower critical solution temperature[97].

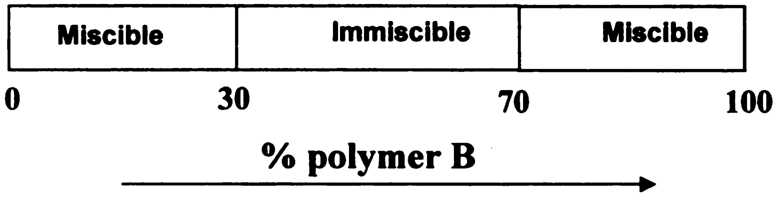


***Figure 11:** Schematic representation of miscible and immiscible* regions in polymer blend in certain proportions[97]

In the immiscible blends the polymers do not have a continuous phase and tend to separate from each other. Immiscible blends sometimes result in enhancement of properties. For example, the immiscible blend of polystyrene and polybutadiene results into HIPS, a tougher and more ductile material. Compatibilizers are sometimes used to enhance the properties of the immiscible blends. They help in binding the two immiscible phases to give a synergistic effect[97].

Poly(ε-caprolactone) (PCL), cellulose acetate (CA) and their blends were analyzed by Braganca et al.[98] for their thermal, mechanical and morphological properties. They studied the compatibility of the blend by using optical microscope, which showed the separate phases indicating the incompatibility of the blend. The characteristic melting temperature peaks for PCL and CA also indicated the incompatibility in the blend. Tensile properties decreased on blending at different composition of PCL and CA except for the blend 20/80 (PCL/CA), where the tensile strength was higher than PCL. This was supported by the prevalent nature of CA at this blending ratio. The authors claimed that the lower cost of this polymer blend than PCL makes it more attractive along with its favorable biodegradation properties due to the weak interactions.

The moisture sensitivity, critical ageing, dimensional stability and resilience of thermoplastic starch can be improved by blending it with PCL maintaining its biodegradable properties. Averous et al.[99] studied the different compositions of PCL and thermoplastic starch with different proportion of glycerol. They extruded the samples by melt blending and injection molding to study the tensile, thermal and thermo-mechanical and hydrophobic properties. Although the phase separation was observed but these blends have improved properties in contrast to thermoplastic starch.

The biodegradability of poly(ε-caprolactone)/starch blends and composites was studied by Singh et al.[100] under composting and culture environment. They prepared four types of PCL-starch compositions as "PCL-granular starch blends", "hydrophobic coating of starch granules and melt blending with PCL", "PCL-grafted dextran copolymer and used as a compatibilizer in PCL-granular starch blends" and "in-situ PCL grafting onto starch granules and melt blending with PCL". They evaluated the samples based on the weight loss on composting and surface morphology by SEM. They concluded that the biodegradability of PCL was increased with addition of the "PCL-grafted dextran copolymer" as compatibilizing agent and further increased with the addition of starch content. They also added that the grafting of PCL onto starch granules affected the degradation process.

Voigt et al.[101] designed a biodegradable thermoplastic material by blending starch esters and polyalkylene glycols with addition of polybasic aliphatic carboxylic acid. Blending with aliphatic polycarbonates modified the mechanical and barrier properties. These thermoplastic materials were processed by premixing and extruding into granules followed by injection molding or extrusion into films as required. These thermoplastic biodegradable materials can be used in packaging of food, cosmetics, detergent, paper tissues and toilet articles. These thermoplastic materials were claimed to feed into special recycling process or may be conventional recycling process without adversely affecting their properties.

Lepoittevin et al.[102] studied the mechanical, thermal and rheological properties of PCL nanocomposites, prepared by melt blending with natural and modified montmorillonite clay. They prepared the blends with varied percentage of clay and tested for tensile, Izod impact and thermal properties. The stiffness and the thermal properties were observed to increase up to 5% clay. The further addition of clay resulted in decrease of these properties.

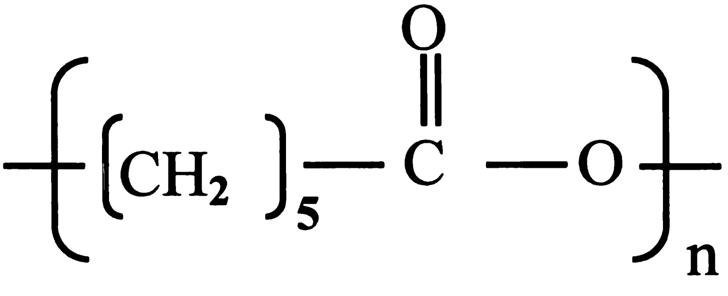
CHAPTER 3

MATERIAL AND METHODS

3.1 Materials

Commercial corn gluten meal (CGM), a by-product from corn based ethanol industries with a protein content of (~60%) was supplied by Cargill Inc., MN. Distiller's dried grain with solubles (DDGS) was supplied by Michigan ethanol, Caro,MI.

A commercial grade PCL (TONE® 787) was obtained from Union Carbide Corporation. The chemical structure of PCL is represented in Figure 12. It is a homopolymer made by ring opening polymerization of ε-Caprolactone, a seven member ring compound. It has density of 1.145 g/cc. It is a semi crystalline polymer with low sharp melting temperature (T_m) of 60°C and has the glass transition temperature (T_g) range of – 65 to – 60°C. It has melt flow index (MFI) of 0.5 – 4 (g/10min). The pellets were sufficiently dried in the vacuum oven prior to process. The important features of this grade are its biodegradability, low and sharp melting point, outstanding adhesion to a broad spectrum of substrates, broad miscibility with many polymers, pigments and fillers, mechanical

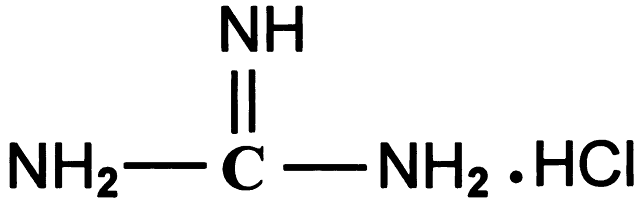


$$\left[\left(CH_2 \right)_5 - \overset{O}{\overset{\|}{C}} - O \right]_n$$

***Figure 12** : Chemical structure of Poly(ε-caprolactone)*

compatibility with many polymers and its non-toxic nature[103].

Glycerol (99.9 % purity) ACS grade from J.T.Baker and ethanol 190 proof ACS grade from Pharmco was used. Guanidine hydrochloride was supplied by Acros Organic, NJ. The chemical structure of guanidine hydrochloride is shown in Figure 13.



$$\mathrm{NH_2}-\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}-\mathrm{NH_2}\cdot\mathrm{HCl}$$

Figure 13: *Chemical structure of Guanidine Hydrochloride*

3.2 Preparation of blends

A micro scale extruder with injection molder (DSM) (DSM Research, Netherlands) was used for blending. The blending was accomplished by plasticizing CGM with glycerol and ethanol (denoted as plasticized CGM or CGMP) followed by chemical modification with guanidine hydrochloride (GHCl). The CGMP was made by weighing the CGM and glycerol/ethanol separately and the adding glycerol/ethanol slowly into the CGM while mixing to ensure a uniform distribution. The specified ratio of CGMP and GHCl were weighed and melt blended using the DSM. This GHCl modified CGMP was dried at 80°C for 3 hrs in a vacuum oven before blending with PCL. Injection molded test samples were prepared for dynamic mechanical analysis (DMA) and tensile testing. The schematic representation for mixing, blending and sample preparation is shown in Figure 14. The different blending compositions were made as shown in Table 4.

***Table 4:** Composition of different blends considered for study.*

Blends	CGMP	GHCl	PCL
1	45	5	50
2	42.5	7.5	50
3	37.5	12.5	50
4	50	0	50
5	34	6	60

Note:

CGMP- Plasticized corn gluten meal
GHCl- Guanidine hydrochloride

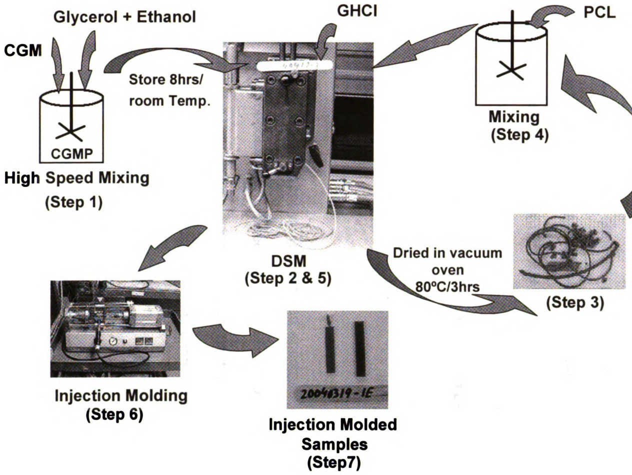


Figure 14: *Schematic representation of sequence for mixing, blending and preparing the samples for testing*

3.2.1 DSM

DSM is a micro compounding instrument consists of twin vertical screws, with a length of 150 mm, L/D of 18 and a maximum capacity of 15 cc. It has co-rotating screws, which blend and circulate the material inside the barrel and then the material is extruded out from the bottom. The extruded material from the blend can be injection molded at a specific temperature and pressure into molds designed to prepare samples for DMA, tensile and izod testing. The samples were sealed in airtight bags to avoid any moisture contact and were stored at room temperature for at least 24 hours for conditioning before testing.

3.3 Characterization

3.3.1 Infrared Spectroscopy: The infrared spectrum was measured using a FT-IR spectrophotometer (Spectrum 2000, PerkinElmer, MA). An ATR attachment was used to measure the IR-spectrum for the CGMP before and after chemical modification in order to observe the chemical changes that occurred in the structure. The samples were analyzed in the range of 4000-650 cm^{-1}. The IR-spectrum of GHCl was also obtained.

3.3.2 Moisture Content : The moisture content of CGM and DDG was measured by using a standard AACC 44-15A, where a 2-3g sample was placed in oven at 103 ± 1 °C for 72 hours. The samples were placed in the desicator to cool down after heating to prevent absorption of any moisture. The difference in weight was calculated for moisture content (wet basis) determination.

3.3.3 Nitrogen Content Analyzer: The nitrogen content was measured by using Nitogen Content Analyzer (Model 428, LECO Corp., MI). This instrument detects the nitrogen percent by measuring the thermal conductivity of the evolved nitrogen gas for a given weight of sample. A blank run was made initially made by purging O_2 (99.9%) in order to remove nitrogen from the furnace space. The schematic representation of operation process of nitrogen content analyzer is in Figure 15. The instrument is than calibrated before starting the actual samples. A standard factor[104] of 5.7 used to convert the percentage of nitrogen into percentage of protein. The picture of the instrument is given in Figure 16.

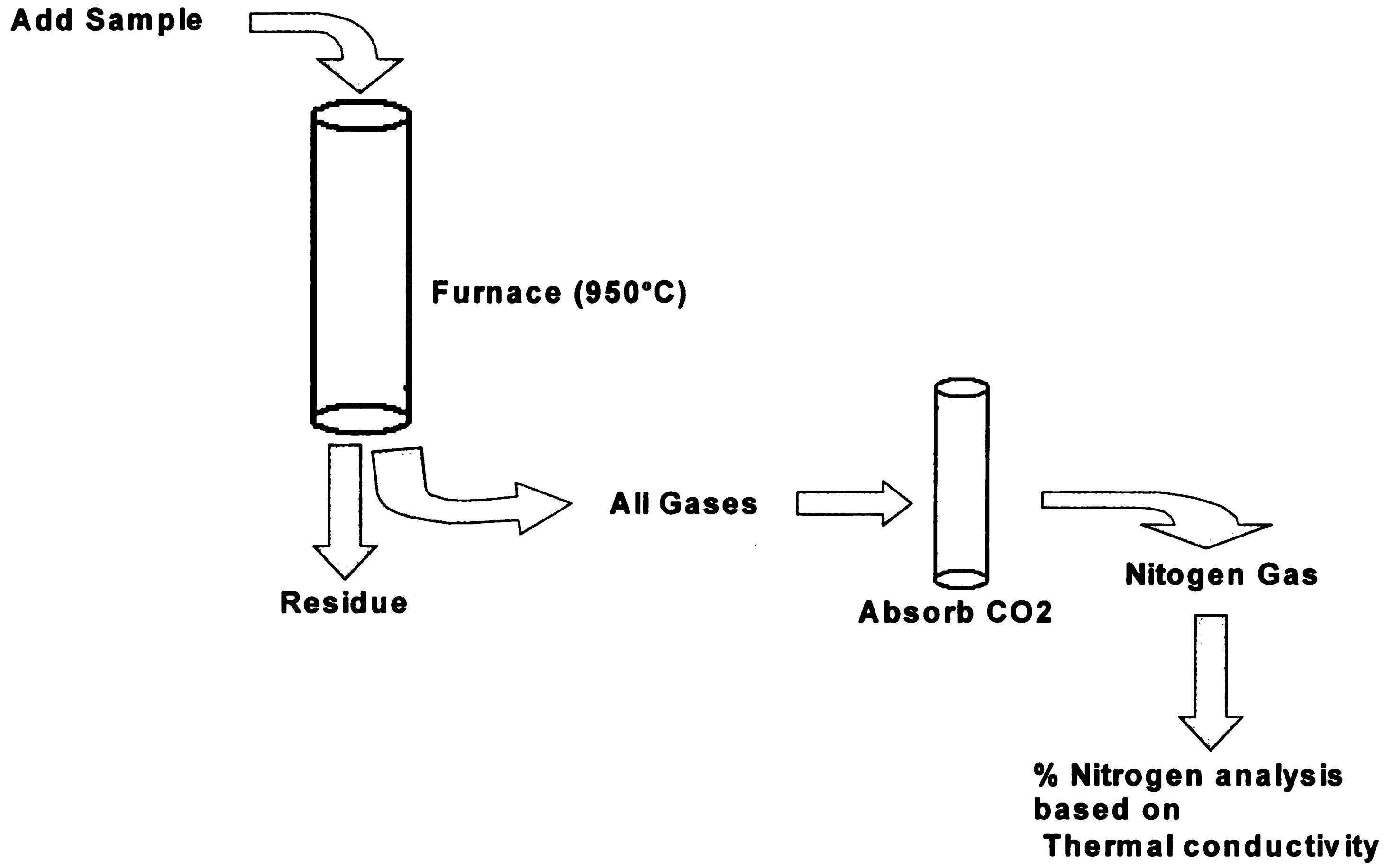


Figure 15: Schematic representation of operation process of Nitrogen Content Analyzer Instrument

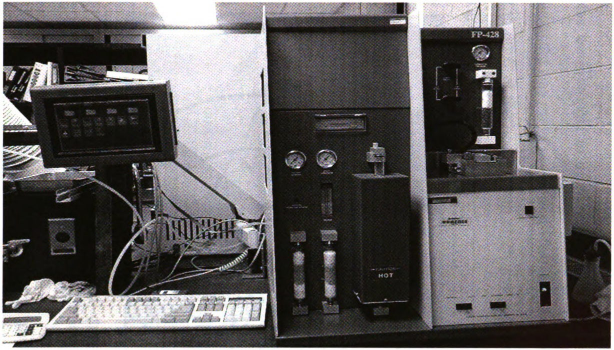


Figure 16: *Nitrogen Content Analyzer (Model FP-428, LECO® Corporation, MI*
(Courtsey - Dr. Ng, FSHN Dept., MSU, East Lansing, MI)

3.3.4 Dynamic Mechanical Analyzer (DMA): The storage modulus of the blend was measured using a Model Q800 DMA from TA Instruments (TA, Wilmington, DE), using a single cantilever clamp and multi frequency strain mode. The samples were brought to equilibrium temperature at 30° for 15 minutes. The measurement was made at 1Hz and 15μm amplitude over the temperature range of 30 to 60°C at the heating rate of 2°C/min. The picture of the instrument is given in Figure 17.

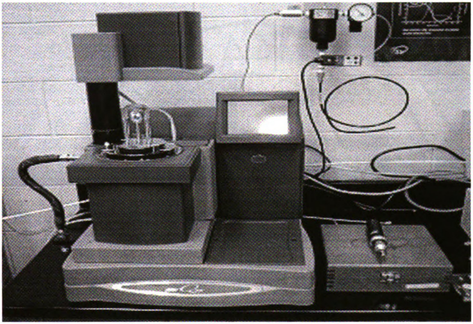


Figure 17: *Dynamic Mechanic Analyzer, Q800, TA Instruments*
(Courtsey: AKM Research Group)

3.3.5 Tensile Testing: The tensile testing was performed at Universal testing machine (UTS, Model SFM-20) according to ASTM D638. The tensile samples were made by injection molding immediately after extrusion from the DSM. A load cell of 1000 lbs capacity was used for the testing, with a cross-head speed of 2 in/min for tensile tests. Five samples were tested for evaluation.

3.3.6 Thermal Gravimetric Analyzer: The thermal stability was measured by using thermal gravimetric analyzer 2950 series from TA Instruments (TA, Wilmington, DE). The measurement was done in nitrogen environment. An auto sampler was used to test a series of samples and an equilibrium temperature was achieved before the test of every sample. The samples were subjected to a temperature ramp of 10ºC/ minutes to 400ºC. The picture of the instrument is given in Figure 18.

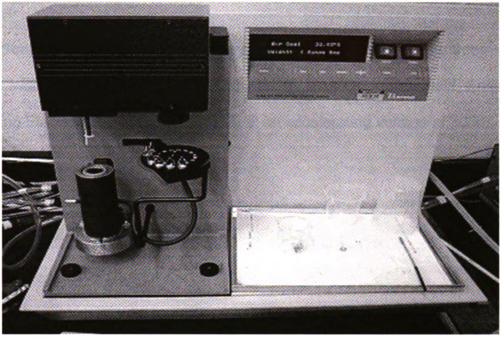


Figure 18: *Thermogravimetric Analyzer 2950, TA Instruments.*
Coursesy: AKM Research Group

3.3.7 IZOD Impact Tester: The samples were notched using a TMI® notching cutter (model TMI 22-05, Testing Machine Inc., Amityville, NY) and the impact strength was measured using a TMI® IZOD impact strength tester (model 43-02).

A 5 lb pendulum was used for impact measurement. ASTM D 256 was followed for this testing. The samples were notched and conditioned for 48 hrs at 23°C and 50% relative humidity. Five samples were tested for evaluation.

3.3.8 Scanning Electron Microscopy (SEM): The fractured surfaces were coated with gold thin films and examined in a JEOL 6300 Field Emission Scanning Electron Microscope (FESEM) at an accelerating voltage of 10 kV.

CHAPTER 4

Results and Discussion

Distiller's dried grain (DDG) and corn gluten meal (CGM) are the by-products obtained from different types of ethanol industries. CGM, which contains a higher percentage of protein than DDG, is an important source for development of biodegradable polymers. Zein, an alcohol soluble protein can be extracted from CGM through solvent extraction. Polymers derived purely from zein are very expensive and have found limited applications[105]. Therefore, this research examined the use of CGM without any purification in order to make a cost effective CGM based plastic.

The brittle nature of the corn protein based materials necessitates the use of plasticizers. Glycerol has been extensively studied as a plasticizer[26, 106]. The plasticization effect of glycerol is attributed to its small size which helps in its insertion and positioning within the protein network[107, 108] and therby reducing the intermolecular forces and increasing the mobility of protein chains [109]. The use of ethanol aids the processing of CGM[26]. The glycerol/ethanol (3:1) mixture was used for better plasticization of CGM system. The GHCl was used to breakdown the protein structure (destructurize) in order to make it more flexible and compatible with the other components of the polymer system.

Various studies have been done on the interaction of GHCl with proteins, which revealed the induction of denaturation and unfolding of the protein structure[110-112]. Denaturation is the alteration of secondary, tertiary or quaternary structures in the protein molecules. The GHCl forms cross-link at different locations in the side chains and on the backbone of the protein molecule, by means of hydrogen bonding[113]. This phenomenon is likely responsible for the improvement of mechanical properties of the protein blends.

The processing conditions, i.e. the temperature and processing speed play an important role in determining the final properties of the plasticized cellulose acetate as explained by Mohanty et al.[114]. To analyze the effect of processing conditions, a blend containing PCL:CGMP:GHCl at the ratio of 50:37.5:12.5 on a weight basis were processed at 120°C and 150°C. The mechanical properties (modulus) of the resulting blends were evaluated using DMA. Although the average modulii of the blends was comparable, the material processed at 120°C had a much larger standard deviations versus the material processed at 150°C (Table 5).

***Table 5:** Modulus of PCL blends with GHCl modified CGMP processed at 150 rpm and temperatures of 120°C and 150°C at the ratio of PCL:CGMP:GHCl = 50:37.5:12.5 (wt%)*

Processing Temperature, °C	**Storage Modulus (MPa) at 30, 40 & 50°C**		
	30°C	**40°C**	**50°C**
120	88 ± 10.77	75 ± 9.43	49 ± 5.52
150	87 ± 3.17	74 ± 2.57	48 ± 1.73

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal

The consistent modulus obtained at the higher processing temperature is based on the fact that a processing temperature allowed better melt mixing of the components. Based on these results, a processing temperature of 150°C was used versus 120°C in the subsequent studies.

In order to study the effect of extruder screw speeds on blend properties, the blends were prepared at 150°C using two different screw speeds. Speeds of 75 and 150 rotations per minute (rpm) were used during processing. The modulus of the blend was reduced by about 50% with an increase in processing speed (Table 6). The material blended at 75 rpm had large standard deviations in its modulus. The material blended at 150 rpm exhibited a much improved percent elongation (Figure 19) in contrast to their counterparts blended at 75 rpm. Based on such results a processing speed of 150 rpm was chosen for further studies. Such observations were attributed to inconsistent mixing at lower screw speeds.

Table 6: *Modulus of PCL blends with GHCl modified CGMP processed at 150°C and different processing speeds of 75 and 150 rpm at the ratio of PCL:CGMP:GHCl = 50:37.5:12.5 (wt%)*

Processing speed, rpm	**Storage Modulus (MPa) at 30, 40 & 50°C**		
	30°C	**40°C**	**50°C**
75	170 ± 31.64	148 ± 29.27	105 ± 22.28
150	87 ± 3.17	74 ± 2.57	48 ± 1.73

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal

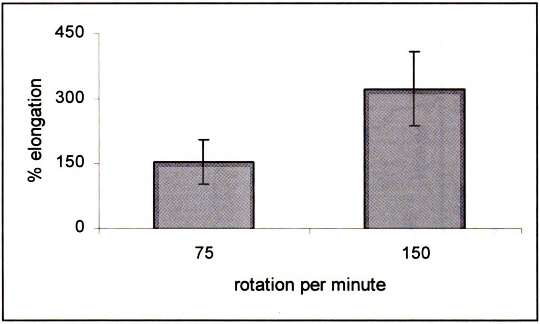


Figure 19: *Percentage elongation of PCL blends with modified CGMP processed at 150ºC and different processing speeds of 75 and 150 rpm.*

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal

Through IR spectra, the GHCl modified corn gluten meal based bioplastics were characterized. A peak shift was observed in GHCl modified CGMP bioplastic at 1651 cm^{-1} (Figure 20) in contrast to CGMP bioplastic (e.g. unmodified CGMP) at 1624 cm^{-1}. This peak shift is attributed to hydrogen bonding[113]. Research by Dunbar et al[112] also supports the formation of hydrogen bonds during the interaction of GHCl with protein.

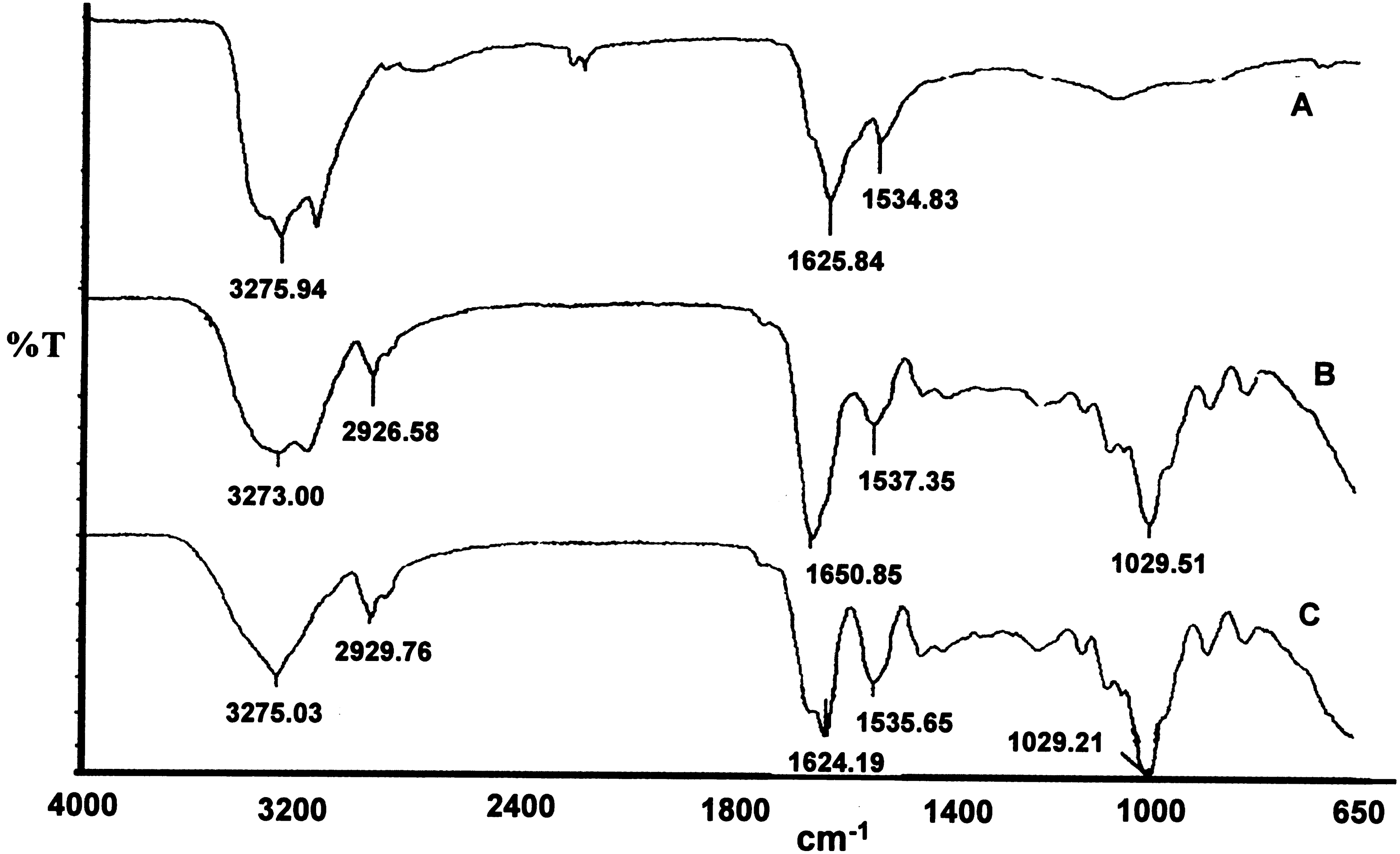


Figure 20: *IR Spectroscopy of CGMP before and after chemical modification with GHCl A=GHCl; B= GHCl:CGMP=25:75 (wt%); C= CGMP*

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal

The protein percentage was determined for CGM and DDG. A standard factor 5.7 was used to convert the nitrogen percentage to protein percentage. The protein percentage in CGM and DDG were 60 and 25.4% respectively (see Table 7)

Table 7: *Protein percentage determined by Nitrogen Content Analyzer Instrument*

Material	% Nitrogen sample# 1	% Nitrogen sample# 2	% Nitrogen (Average)	% Protein
CGM	10.55	10.51	10.53	60.00
DG	4.51	4.40	4.45	25.40

The water also acts as a plasticizer for CGM during the processing[26]. So the presence of moisture will assist in the processing. The moisture content in CGM and DDG measured by AACC 44-15A method was calculated as 7.9 and 11.75% respectively (wet basis).

Blends of PCL and zein have shown poor mechanical properties in previous research[37]. These results were attributed to incompatibility between the components of the system. In this present study, plasticized CGM as well as GHCl modified plasticized CGM were used as the blending partners for PCL. This was done in order to study the effectiveness of GHCl in designing new biodegradable plastics.

The tensile strength of PCL was reduced upon blending with CGMP (see Table 8 & Figure 21) as expected. The percent elongation of PCL decreased when blended with CGMP but showed significant improvement when blended with GHCl modified CGMP. The comparative results with different proportions of GHCl into the blends are shown in Figure 22 (also see Table 9). As apparent from the Figure 22, the percent elongation was not proportional to the percentage of GHCl in the blend. The elongation of the blend first increased with increasing GHCl content from 5 to 7.5% then decreased with further addition of GHCl content to 12.5%.

Table 8: *Effect of GHCl on tensile strength of PCL blends*

PCL:CGMP:GHCl (Blend Composition)	**Tensile Strength (MPa)**	**Std Dev**
100:0:0	37.0	4.4
50:37.5:12.5	8.4	1.5
50:42.5:7.5	10.2	1.6
50:45:05	8.7	0.6
50:50:0	9.5	0.6

Table 9: *Effect of GHCl on percent elongation of PCL blends*

PCL:CGMP:GHCl (Blend Composition)	**% elongation**	**Std Dev**
100:00:00	657	57.9
50:37.5:12.5	323	84.4
50:42.5:7.5	463	33.3
50:45:05	418	19.8
50:50:00	10	2.1

Therefore, 7.5% GHCl was considered as the optimum under the present experimental conditions. The stress-strain curve in Figure 23 shows the effect of GHCl in the blend. The higher area under the curve for the blend that was modified with GHCl indicates higher plastic character as contrast to its counterpart not modified with GHCl.

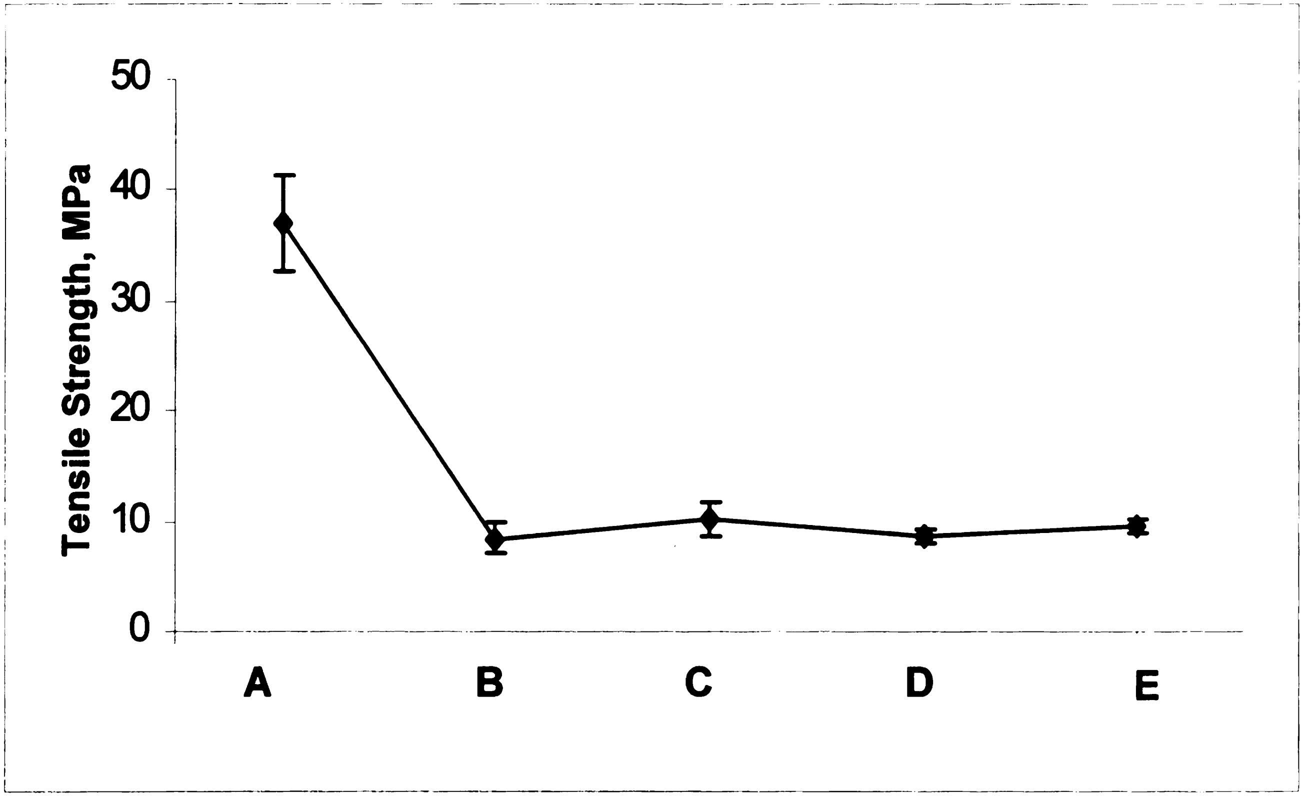


***Figure 21**: Effect of GHCl on tensile strength of PCL blends.*
A= PCL:CGMP:GHCl (100:0:0); B= PCL:CGMP:GHCl (50:37.5:12.5);
C= PCL:CGMP:GHCl (50:42.5:7.5); D= PCL:CGMP:GHCl (50:45:5);
E= PCL:CGMP:GHCl (50:50:0);

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal. All components are in wt%

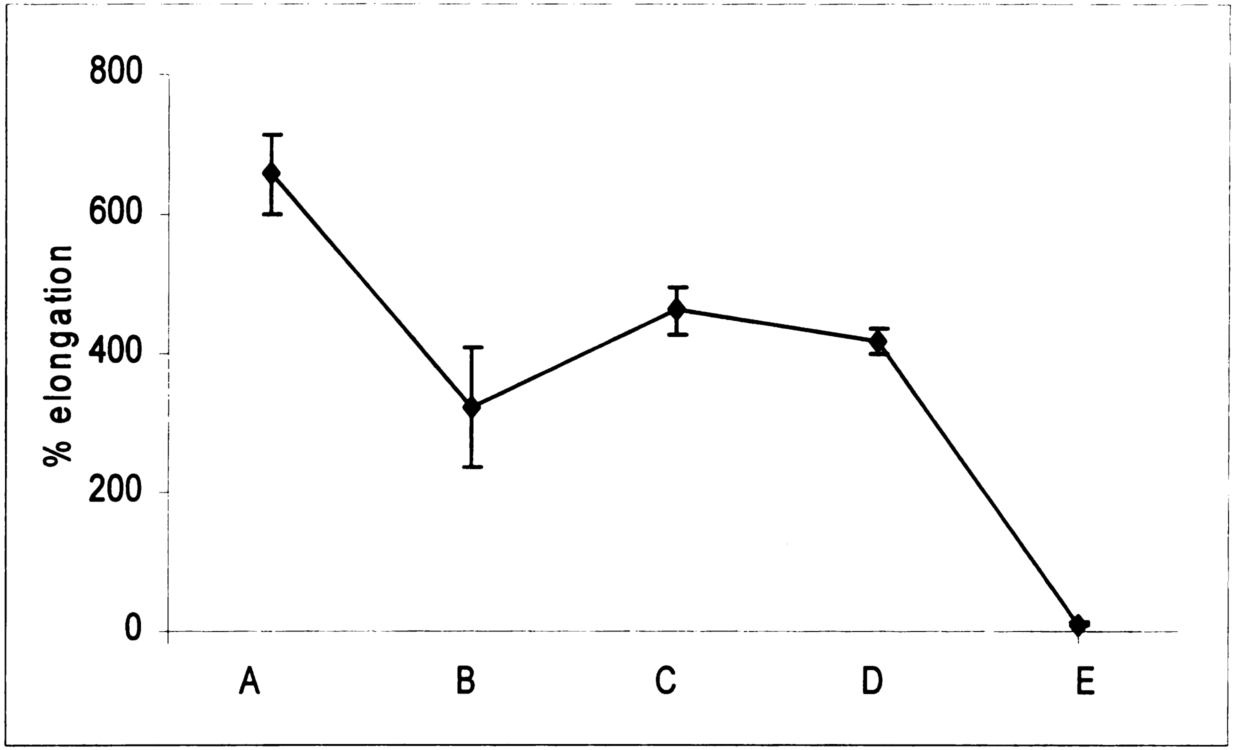


***Figure 22**: Effect of GHCl on percentage elongation of PCL blends*
A= PCL:CGMP:GHCl (100:0:0); B= PCL:CGMP:GHCl (50:37.5:12.5);
C= PCL:CGMP:GHCl (50:42.5:7.5); D= PCL:CGMP:GHCl (50:45:5);
E= PCL:CGMP:GHCl (50:50:0);

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal. All components are in wt%

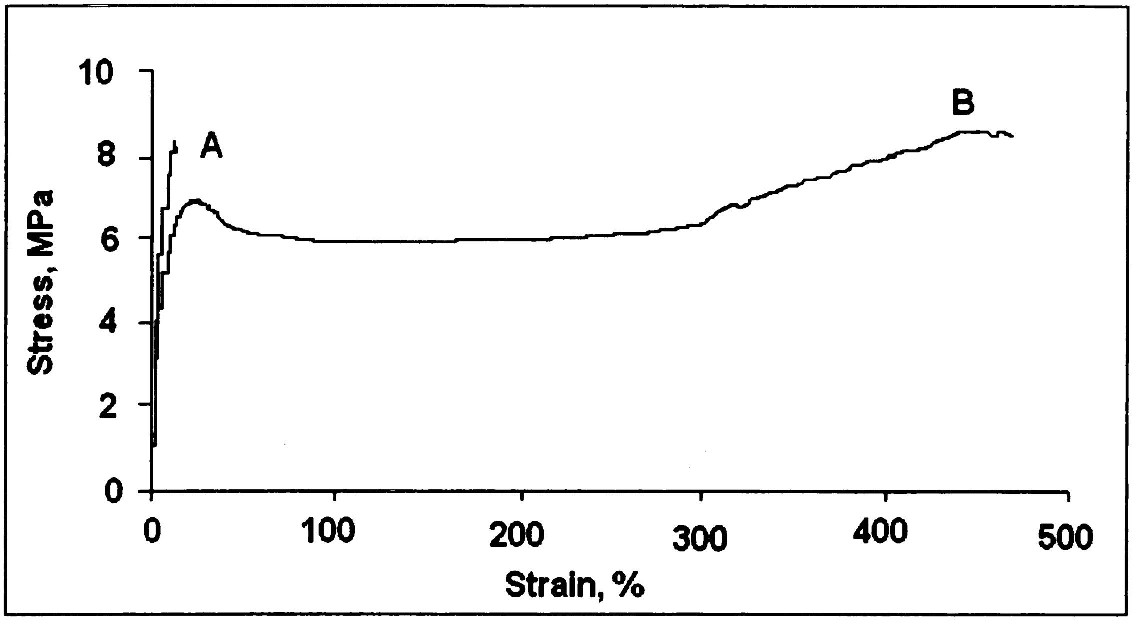


***Figure 23**: Stress-strain curves for PCL blends with and without GHCl.*
A= PCL:CGMP:GHCl- (50:50:0)
B= PCL:CGMP:GHCl- (50:42.5:7.5)

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn All compositions are in wt%.

Table 10: *Comparison of percent elongation and Impact strength of PCL, PCL blend and HDPE*

Sample	Ratio	%elongation	stdev	Impact (J/m)	stdev
A	PCL- 100%	677	51.5	283	12.0
B	PCL:CGMP:GHCl= 50:42.5:7.5	463	33.3	55	3.1
C	HDPE*- 100%	320	NA	47	NA

** The data obtained from Technical Data Sheet of Dow Polyethylene 25455N (Injection molding resin), Dow Plastics, Published 08/01.*

Among the blends prepared and tested, the PCL-CGMP blend with 7.5% GHCl (sample B) was found to be better in comparison to the other composition containing 0, 5 and 12.5% GHCl. This blend composition containing 7.5% GHCl was compared to HDPE[115] (sample C), Figure 24, Table 10). The percent elongation of this blend was 463% while HDPE has a percent elongation of 320%. So, the higher percent elongation of blend can allow the addition of some filler in order to enhance the strength/stiffness. This blend was also found to have higher impact strength versus HDPE[115] (Figure 24). The comparison of 7.5% GHCl containing PCL-CGMP blend and HDPE is presented in Table 10 and Figure 24.

The storage modulii of PCL and its blends with CGMP as well as with GHCl modified (with varying content of GHCl) CGMP were measured using Dynamic Mechanical Analyzer (DMA) at 30, 40 and 50°C. The comparison of storage modulus of PCL-CGMP blend with different percentage of GHCL is presented in Table 11 and Figure 25. The PCL as well as all of the blends

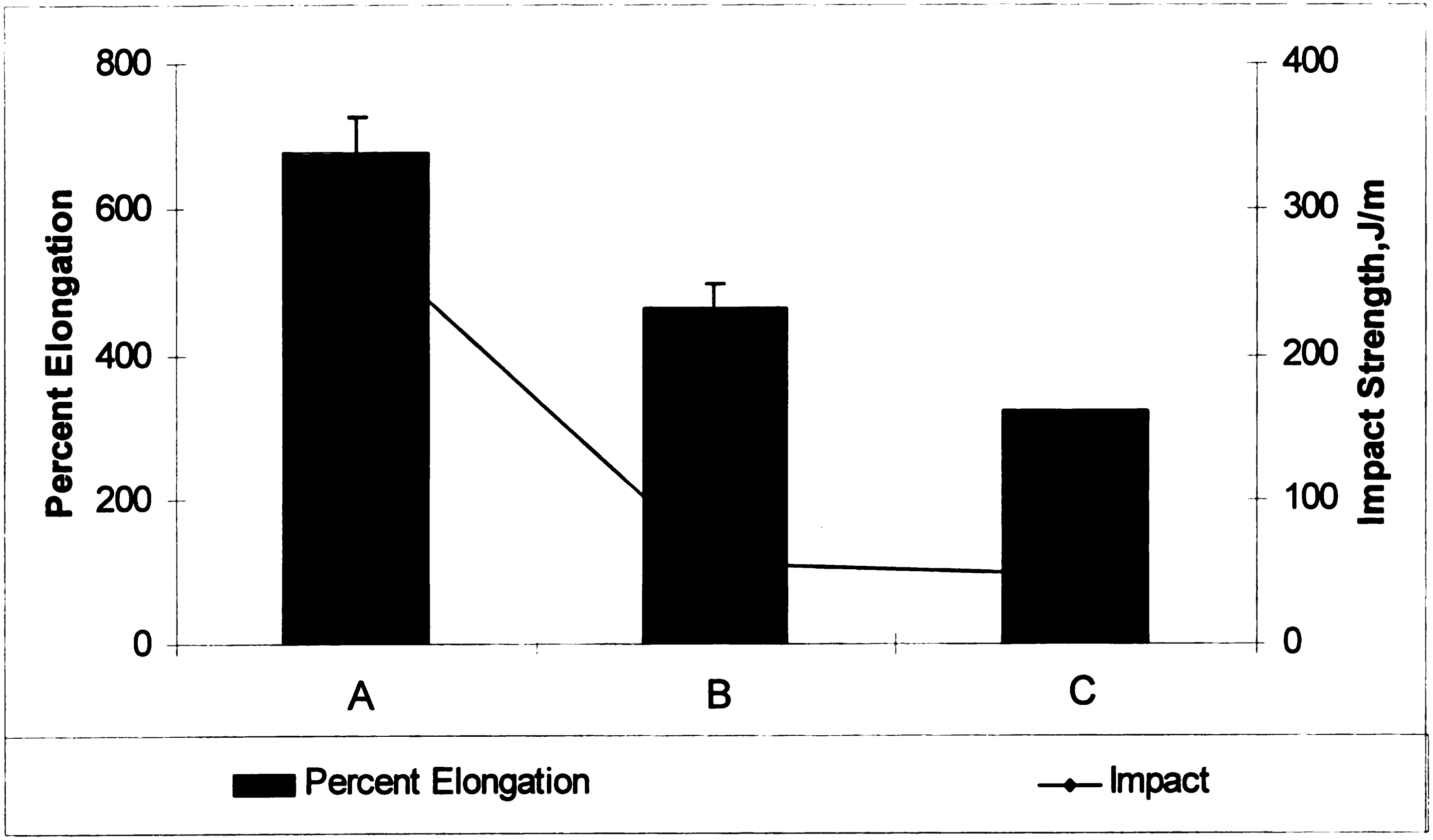


Figure 24: *Comparison of percent elongation and Impact strength of PCL, PCL blend and HDPE*[125]*.*

A= PCL:CGMP:GHCl (100:0:0);

B= PCL:CGMP:GHCl (50:42.5:7.5);

C=HDPE

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn. All components are in wt%
The HDPE data are as per technical data sheet from Dow Plastics

exhibited decreasing modulus values with an increase of temperature from 30 to 50°C. As expected, the modulus of the PCL decreased on blending with CGMP as well as GHCl modified CGMP bioplastics. The main thrust of this investigation is to find green biodegradable plastics for plastic packaging applications where high strength and modulus are not required through blending an inexpensive proteineous by-product, like CGM, with a commercial biodegradable plastic like PCL. While studying the effect of the amount GHCl in the GHCl modified CGMP it was observed that 7.5% of GHCl resulted an optimized modulus and percent elongation values (Figures 21, 22 and 25) of the resulting biodegradable blends.

Table 11: *Comparison of storage modulus of PCL and its blend at 30, 40 and 50°C.*

PCL:CGMP:GHCl (Blend Composition)	**Storage Modulus (MPa) at 30, 40 & 50°C**		
	30	**40**	**50**
100:0:0	459 (25)	427 (28)	339 (31)
50:37.5:12.5	87 (3)	74 (3)	48 (2)
50:42.5:7.5	140 (18)	116 (16)	75 (12)
50:45:05	171 (23)	140 (17)	86 (11)
50:50:0	265 (31)	227 (27)	145 (19)

Note: The values in ( ) represents the standard deviation.

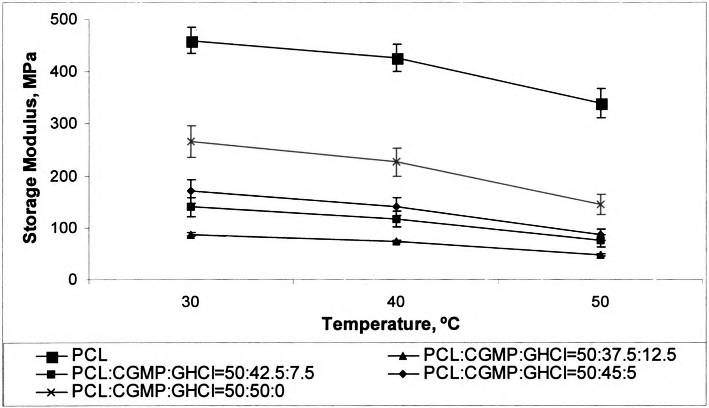


Figure 25: *Storage modulus of PCL and its blends*

Note: GHCl is guanidine hydrochloride and CGMP is plasticized corn gluten meal. All components are in wt%

The thermal stability for CGM and DDGS was analyzed with Thermal Gravimetric Analyzer (TGA) (Figure 26). There was an initial loss in weight in both CGM and DDGS, which represents the loss of the moisture. There were two different weight loss peaks observed for DDGS at 159 and 247°C, which may represent mixture of different material mixtures like hull, fibers, etc. The processing temperature for DDGS should be less than the lower degradation temperature. The CGM was observed to be quite stable until 254°C. Therefore, CGM was found to have higher processing temperature range and was more stable.

PCL and its blends with CGM were also analyzed for thermal stability. The blends considered were PCL: CGMP: GHCL (50: 37.5:12.5), PCL: CGMP: GHCL (50: 42.5: 7.5), PCL: CGMP: GHCL (50: 45: 5), PCL: CGMP (50: 50). It was observed that the blends containing higher percentage of GHCl were found to be more thermal stable than the blends with lower percentage of GHCl. The blend with no GHCL was found to be least stable (See Figure 27)

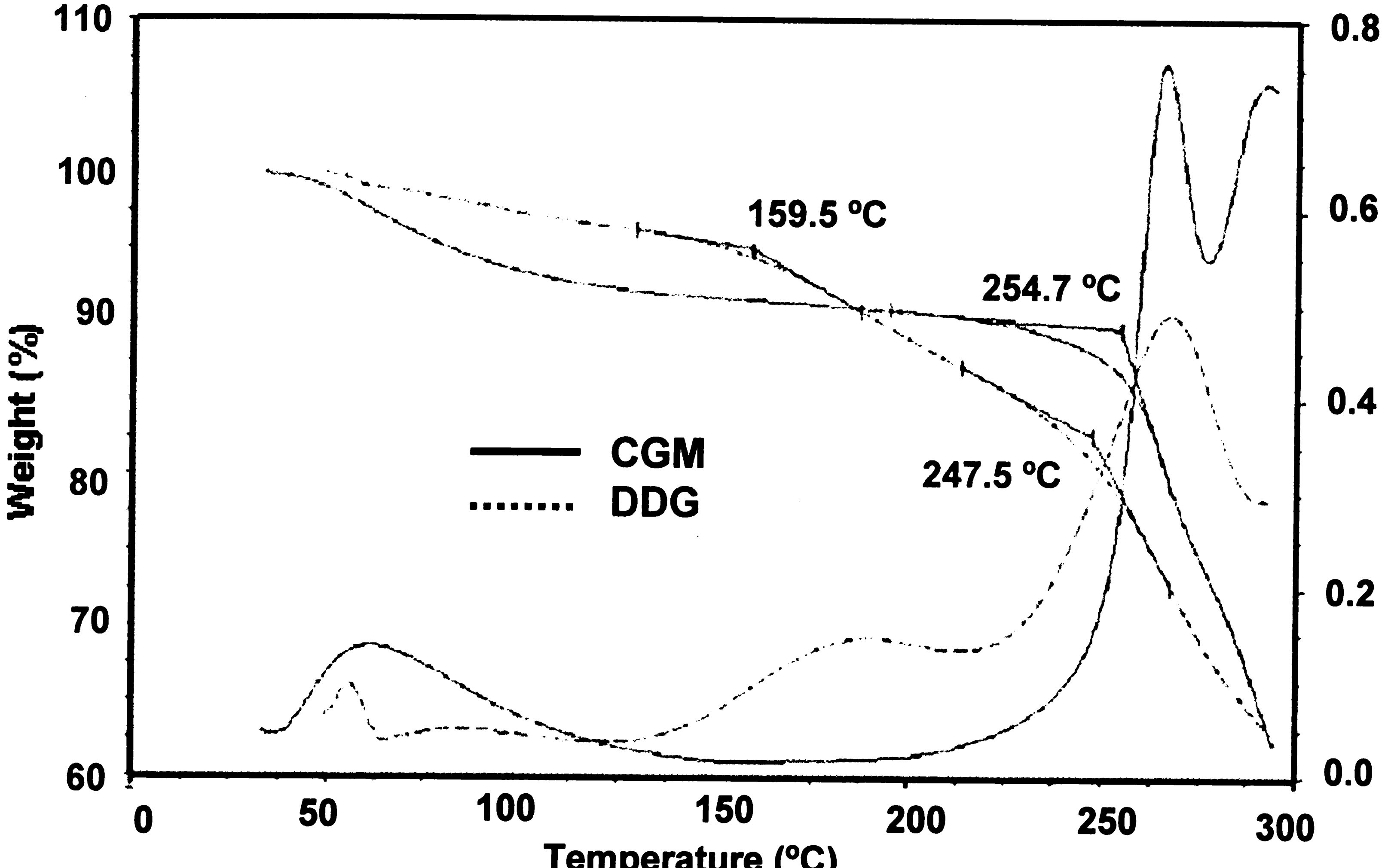


Figure 26: *Thermal analysis of CGM and DDG by TGA*

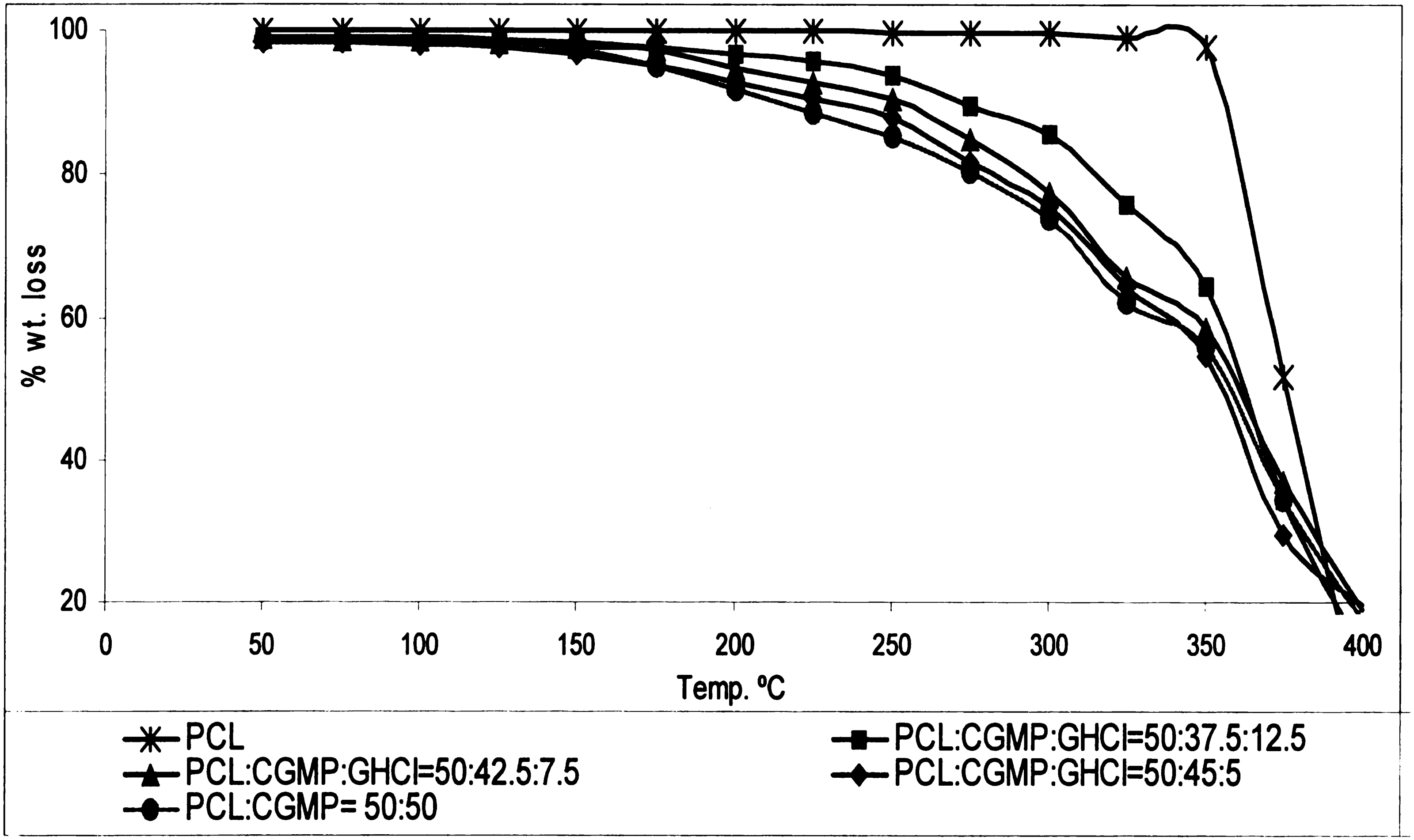


Figure 27: *Thermal analysis of PCL and its blends with different percentage of CGMP and GHCl.*

The blend morphology is closely related to its mechanical properties. In our investigations of blend compositions and their mechanical properties evaluations we found that GHCl modified CGMP was superior to the unmodified counterpart in properties like percent elongation and impact. Blends with PCL:CGMP:GHCl in the ratio of 50:42.5:7.5 and 50:50:0 were selected and the fractured surfaces of these compositions were examined using SEM in order to reveal the morphology of the blend with and without GHCl. The morphological analysis revealed that the blend without GHCl contained cavities, which were likely to be created in the fracture region during the spontaneous separation of the PCL and CGMP regions due to the weak interfacial adhesion between PCL and CGMP. The presence of GHCl in the blend exhibited quite a high degree of homogeneity, which was a sign of increased compatibility between PCL and CGMP phases (Figure 28).

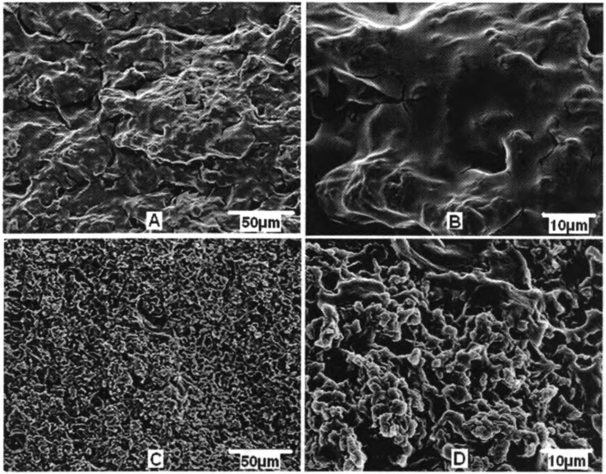


Figure 28: *SEM photomicrograph of the blends*

A & B: PCL:CGMP:GHCl = 50:42.5:7.5 (Scale bar: 50μ and 10μ respectively)

C & D: PCL:CGMP:GHCl = 50:50:0 (Scale bar: 50μ and 10μ respectively)l

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal. All compositions are in wt%.

The main motivation of the present investigations was to design novel biodegradable plastics with the maximum permissible content of CGM, thereby finding value-added application of the by-products of corn-based ethanol industry. The use of unique chemical modification of CGMP with GHCl followed by blending with PCL has resulted in a new biodegradable plastic composition having a tensile strength of ~10 MPa and a percent elongation of 462%. The newly developed biodegradable plastic shows immense potential for plastic film applications. One can manipulate the properties by changing the ratio of the blend's components. In separate investigation, the content of PCL was increased to 60% from 50% in the blend system so that it can be compared with some other synthetic plastics. A comparison of some properties of the two blends is shown in Table 12.

Table 12: *Comparison of properties between 50% PCL based blend and 60% PCL based blend*

Blend Composition	**Tensile Strength (MPa)**	**% elongation**
50:50 PCL: GHCl modified CGMP	10 ± 1.61	462 ± 33.3
60:40 PCL: GHCl modified CGMP	17 ± 1.13	598 ± 15.6

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal. All compositions are in wt%.

The blend with 7.5% GHCl was found to be the best in the overall properties under the present experimental conditions. The resulting blend with 60% PCL showed improvement in its mechanical properties as shown in Table

12 and Figure 29. The tensile strength, percent elongation and modulus improved by 70%, 29% and 28% respectively.

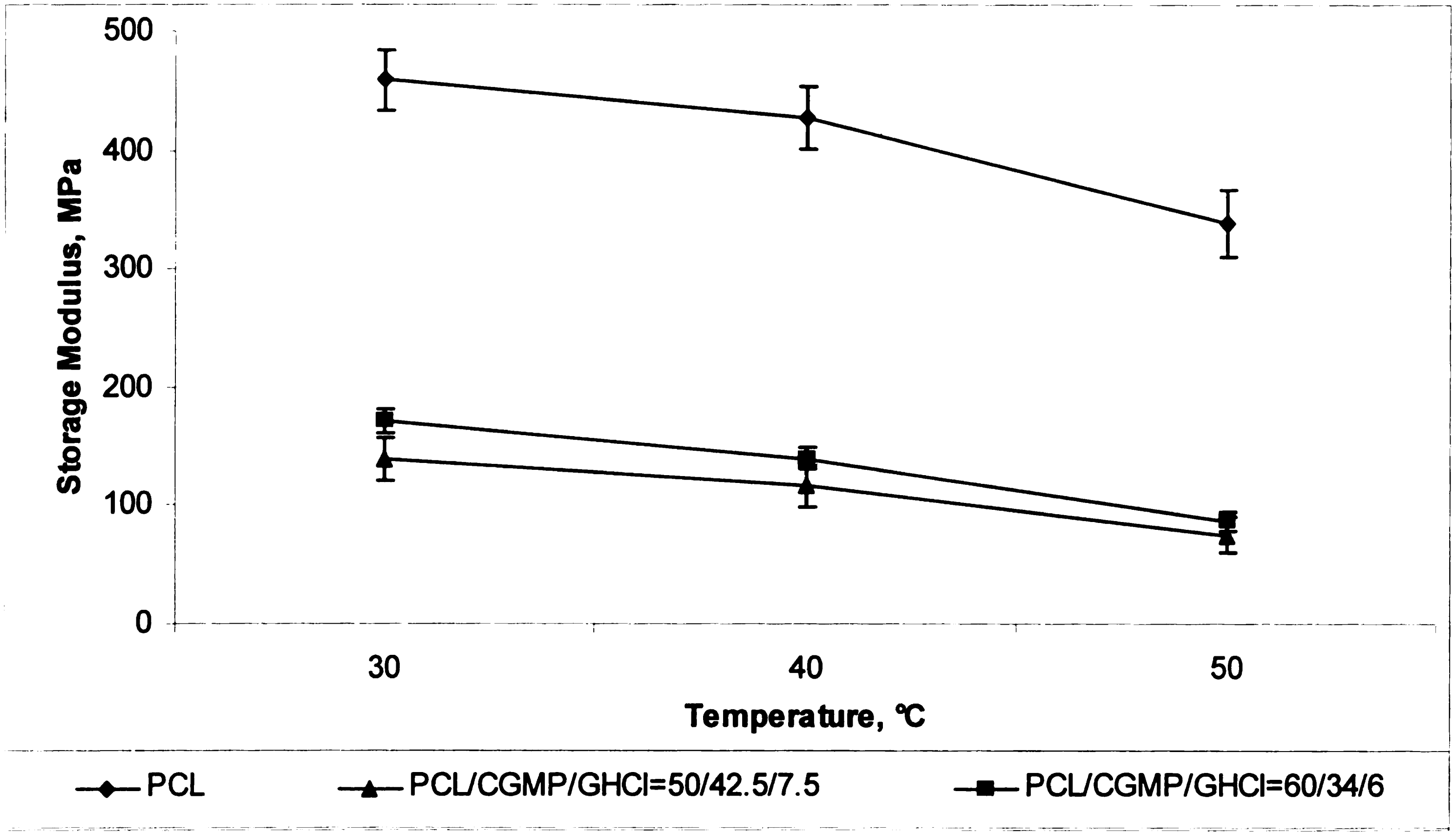


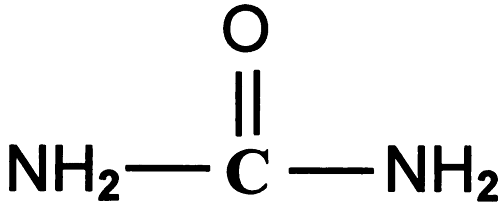
Figure 29: *Storage modulus of PCL and its blends.*

Note: GHCl is guanidine hydrochloride and CGMP is the plasticized corn gluten meal. All components are in wt%

Chapter 5

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

We have successfully developed injection molded biodegradable plastic formulations from the blends of corn gluten meal based bioplastic and PCL. The choice of the ratio of components, the melt processing temperature and the screw speed of the extruder all affected the overall properties of the resulting biodegradable polymer blends. The uniqueness of the present investigation is the chemical modification with GHCl, which has resulted in a biodegradable plastic having a high percent elongation that show potential applications for biodegradable packaging. Among the different blends tested, the blend with 7.5% GHCl produced the best results under present experimental conditions. Further increase in the PCL content, i.e. from 50 to 60% in the final blend improved the overall mechanical properties of the blend. We were successful in making a new class of biodegradable plastic from PCL-based blend with the maximum permissible content of a renewable resource as well as inexpensive by-product like corn gluten meal. The result shows the immense potential for designing and engineering new value-added and eco-friendly bio-based materials from the by-products of corn based industries. The morphological analysis revealed increased homogeneity between PCL and CGM phases in the presence of GHCl. Urea (see Figure 30), which has some similarity in structure to GHCl (see Figure 13) can be evaluated as a replacement for GHCl in order to reduce the overall cost of the blends.



$$NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

***Figure 30:** Chemical structure of Urea*

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