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Kris Eugene Spence
Iowa State University

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Biodegradable plastic made from
dialdehyde starch and zein

by

Kris Eugene Spence

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE

Department of Food Science and Human Nutrition
Major: Food Science and Technology

Signatures have been redacted for

Signatures have been redacted for privacy

Iowa State University
Ames, Iowa

1994

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LIST OF SYMBOLS

$^{\circ}\text{C}$	degree Celsius
cm^{-1}	wavenumber
CO_2	carbon dioxide
g	gram
g/cm^3	gram/cubic centimeter
GPa	gigapascal
H_2SO_4	sulfuric acid
kV	kilovolt
M	moles/liter
mg	milligram
mm	millimeter
mm/Hg	millimeters of mercury
MPa	megapascal
N	normality
NaOH	sodium hydroxide
NaHSO_3	sodium bisulfite
Pa	pascal
μm	micrometer
w/w	weight/weight
w/v	weight/volume

INTRODUCTION

In the last few years we have seen an increased emphasis on both environmental awareness and preservation. Humankind's heightened concern about their environmental surroundings has led to changed attitudes about acceptable waste, waste reduction and waste elimination. In addition, much publicity has been focused on the effect of disposable consumer goods in the waste management system. Disposable polymeric materials add to handling and disposal space problems in both refuse collection and landfills and contribute to serious environmental pollution when not properly disposed. Of particular concern is the slow decomposition of these materials under natural conditions (Bugorkova et al. 1991). Landfilling is the most common method of disposing of Municipal Solid Waste (MSW) in the U.S. with approximately 75% of the MSW being landfilled (Moore, 1992). The scheduled closings of over two-thirds of U.S. landfills by the year 2000, has only heightened the concern. Over 21.9 billion pounds of plastic durable materials were discarded in 1992 (Anon., 1994). Although plastics only make up 15-20% by volume (4-7% by weight) of materials in landfills, their resistance to degradation makes their lasting presence obvious (Rivard et al., 1991; Moore, 1992). Leading European Community countries have already passed legislation limiting the use of non-degradable packaging. A 1987 Italian law, since repealed due to its strict limitations, required all plastics used in nondurable goods to be degradable and Denmark has banned nonrecycleable plastic beverage containers and PVC since

1987. In addition, the United Nations has moved to prevent ocean dumping of plastic wastes through the 1973 Maritime Pollution Law of the Sea Agreement. Similar laws may be expected in the U.S. soon (Evans and Sikdar 1990). It has been estimated that worldwide concerns about the environment will push the demand for degradable plastics past 3200 million pounds by the year 2000. Plastics that are biodegradable will dominate the degradable plastics market (1100 million pounds) with photodegradable plastics and bio-/photodegradables making up the remaining portion (Anon. 1992). In North America the demand for degradable plastics is expected to grow 17% per year (Lindsay, 1992). In addition, the Japanese have formed a biodegradable plastics society with over 70 member companies to meet an expected market for biodegradables which they estimate at 4 billion U.S. dollars by the year 2000. Recent research efforts to develop polymeric alternatives to petroleum-based products have centered on natural polymers as starting materials. Along these lines, one solution is the development of degradable products from renewable resources whose functional life can be controlled. The methods of control vary from immediate disintegration in water to reuse as animal feed to photodegradation. However, biodegradability is currently the most desirable means of control.

LITERATURE REVIEW

Development of degradable polymers

The rush to develop degradable plastics in the late 1980's led to a variety of materials and claims. Starch filled petroleum-based polymers were the first to be marketed but failed to meet consumer degradation expectations. In light of the need and large demand for these products, a variety of new polymers have entered the degradable plastics arena. Many utilize starch as the primary polymer while others produce microbially derived lactic acid polymers or polyhydroxybutyrate-valerate (PHBV) from carbohydrate fermentation. These microbially produced polymers and others currently face obstacles such as the difficulty to obtain or process the polymers and their high market cost compared to petroleum based polymers. Renewable crop polymers like corn starch, zein, soy protein and cellulose are not only readily available, but they also have the advantage of possessing a molecular structure which is easily degraded. Structural differences between synthetic polymers and natural polymers prevent or severely limit microbial degradation of the synthetics. Studies with ^{14}C -labeled polyethylene in soil, measured for CO_2 evolution, showed a conversion rate of less than 2% per year (Albertsson, 1978). Therefore, the use of natural polymers which can already be utilized by microorganisms is a logical step and should be investigated as a solution to this problem. In particular, emphasis should be placed on polymers derived from renewable resources. For these reasons, we have

chosen to determine whether a biodegradable material could be prepared from corn starch and zein, a corn protein. Objectives of this study were to improve the water resistance and mechanical properties of this polymer over existing starch-based materials. Our approaches include the use of dialdehyde starch, an oxidized starch product, and zein as the base ingredients for our compression molded plastics.

Dialdehyde starch

Dialdehyde starch (DAS) is the unique product formed from the oxidation of native corn starch with periodate. Native corn starch is a natural polymer consisting of 1,4- α -linked glucopyranose units with 1-6- α -linked branches. Oxidation of starch with periodate has been known for many years. Jackson and Hudson (1937) elucidated the reaction mechanism of periodic acid on the starch molecule. The reaction involves a high degree of specificity, with the periodic acid cleaving the bond between the C2-C3 atoms on the pyranose ring. This bond cleavage generates a carbonyl from a hydroxyl group on each of the two carbons. Thus the pair of aldehydes leads to the name dialdehyde and in the reaction on starch, a polymer, the product is referred to as polymeric dialdehyde starch, (PDS). The reaction and a unit of the polymeric product structure is given in Figure 1. Mehltreeter et al. (1957) demonstrated that the iodate produced from the oxidation reaction could be regenerated electrolytically back to periodate in reaction cells and allow for a continuous and cost effective means of oxidation on a large scale. Pfeifer et al. (1960) later proposed a semi-continuous process in which the

periodate is regenerated in a separate cell. The product of this oxidation reaction is white and has the appearance of corn starch. The dialdehyde starch shows no birefringence, is insoluble in cold H_2O , is soluble in hot H_2O , and gives no color reaction with iodine (Newton and Pechham, 1944).

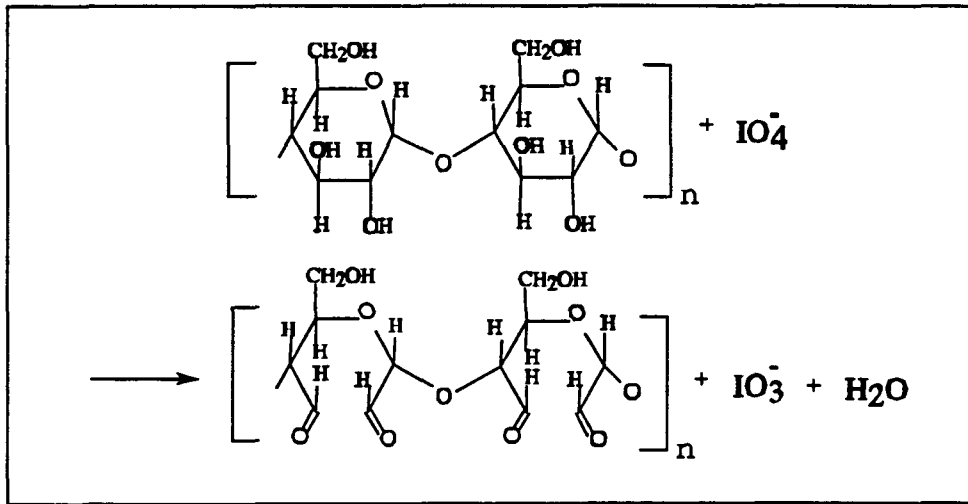


Figure 1. Reaction of periodate on two anhydroglucosyl units of starch shows specific cleavage between carbons 2 and 3 to form the dialdehyde.

The reaction produces iodate from periodate and no further reaction takes place. Thus, the reaction may be monitored by quantifying the reactants or products. In addition to the cleavage of the C2-C3 bond, other parts of the pyranose unit may also react with the oxidant. Terminal residues, formerly primary alcohols, become formaldehyde and formic acid is formed from the internal and secondary hydroxyl groups (Davidson, 1967). Dialdehyde starch, however, does not always exhibit two free aldehydes. It has been shown that the modified group

exists in the hemialdal and intermolecular hemiacetal linkages (Guthrie, 1961; Mehltreeter, 1963). This change in conformation does not effect the reactivity of the hydroxy groups. Many researchers have shown that the hemialdal and hemiacetal linkages are weak and may be readily reactive towards amines, bisulfite, hydroxyl groups, hydrazines, and hydrazones (Mehltreeter, 1967). The functionality of the dialdehyde groups was of great interest to some researchers in the 1950's and 1960's. Many of those investigations were directed toward industrial applications such as paper wet strength, wood glue and even medicinal uses (Mehltreeter, 1985). Filachione et al. 1956, Fein and Filachione (1957), and Nayudamma et al. (1961) showed that both calfskin and collagen could be tanned with dialdehyde starch. Other studies reacted dialdehyde starch to urea, casein, wheat and zein (Sloan et al., 1956; Weakley et al, 1961; Chatterji and Arnold, 1965; and Kalia, 1965). The examination of the reaction between dialdehyde starch and amino acids, peptides and proteins has proved to be quite interesting. Both the nature of the bonds formed and the utility of the reaction has been investigated. Studies of particular importance are those which determined where the crosslinks formed between the aldehydes and protein groups and also the effects this crosslinked structure had on the particular product's physical properties. It is noteworthy that the crosslinked network formed is characterized in many applications to either improved strength, decreased solubility or both. These properties are also indicative of the type of molecular bonding taking place. One study which outlines this crosslinking was performed by Schmandke and Hartmann

(1976), who examined the effects of dialdehyde starch on the shear strength of spun sunflower protein/casein fibers and field bean protein/casein fibers. Their results demonstrated that shear strength increased with the percent dialdehyde starch used. A series of reports by Schwenke et al. beginning in 1975 characterized the physical and chemical properties of casein and other proteins after modification with dialdehyde starch. Mechanical and swelling properties of the crosslinked protein and dialdehyde starch gels showed that crosslinking proceeds relatively fast to irreversibly block the basic amino groups (Schwenke et al., 1978). Similarly, Marzona (1983) treated wheat gluten with dialdehyde starch and determined the free amino acid composition and the products solubility in urea bisulfate, alkali and chymotrypsin. The crosslinking decreased both the chemical and enzymatic solubility. Comparing treated to untreated gluten, Marzona was able to hypothesize that lysine and arginine were the most reactive at 22°C and after the temperature was increased to 100°C phenylalanine and tyrosine participated in the reactions. A Schiff base was offered as the probable interchain bonding structure. Chatterji and Arnold (1965) also investigated the crosslinking in wheat gluten and dialdehyde starch. Their experimental methods showed which aldehyde in the dialdehyde is linked to the protein. Since the products of reduction with borohydride and acid hydrolysis on the crosslinked material was erythritol and glyoxal rather than a glycolaldehyde, they determined that the aldehyde on the third carbon must be free. The described structure is supported by other work which has demonstrated the second carbonyl group to be the most reactive.

Mester (1955) provided evidence for the C2 reactivity by observing that a diphenyl-formazan is formed when diazotized aniline and pyridine are reacted with dialdehyde starch.

Zein

Zein is the major storage protein and most abundant protein in corn. Zein makes up 39-52% of the total corn protein (Wilson, 1987). An endosperm-specific protein, zein resides in protein bodies of 1.5 - 1.8 μm diameter in the kernel (Wilson, 1987). Based on the Osborne and Mendel sequential extraction method for separation of protein groups, zein is categorized as a prolamin; soluble in aqueous alcohol. Zein is low in ionized amino acids, high in nonpolar amino acid, and the high proportion of hydrocarbon group chains results in its hydrophobic characteristics (Paulis, 1982; Pomes, 1971). Specific amino acid analyses show that zein lacks tryptophan and lysine, is low in threonine and valine and has just enough cysteine to form sulfhydryl bonds between chains (Wilson, 1987). Zein is also characterized by higher amounts of glutamine and asparagine correlating to a greater amount of ammonia (Paulis, 1982). Pomes (1971) accounted for the reactive groups of zein as shown in Table 1. Based on circular dichroism, 59% of zein is considered to exist in an α -helix (Wilson, 1987). Magoshi et al. (1992) have shown, using x-ray diffraction, that a zein film cast from aqueous alcohol is amorphous and in random coil formation. Their further study with DSC (differential scanning calorimetry) showed a glass transition at 165°C and thermal degradation above 320°C.

Table 1. The reactive groups of zein protein.

Reactive Groups	mole/mole of zein
Amide	53
Amine	1
Carboxyl	4
Hydroxyl	24
Phenolic	8

Protein and starch plastics

Both zein and dialdehyde starch have been studied for a variety of industrial uses. Particularly important to this study are their uses in adhesives and plastic articles or films. Starch has previously been used as an additive to petroleum-based thermoplastics to make them degradable. The starch is first treated with silicones to make it hydrophobic and then added to the petroleum polymers at 7-15 volume percent. An autooxidant agent is often added. Gelatinized starch has also been reacted with poly(ethylene-co-acrylic acid) and linear low-density polyethylene to produce a flexible and transparent film (Evans and Sikdar, 1990). In the past, zein has been limited to paper coating, but research shows that as a film it has advantages over casein. When cured with formaldehyde, zein produces a tough film which absorbs only 10% moisture when immersed in H₂O long enough to obtain equilibrium (Swallen, 1941).

Solubilities

Oxidation of starch causes a change in solubility. While corn starch is often

dispersed in butanol-saturated water, KCl, CaCl₂, LiCl, and NaOH, dialdehyde starch is only soluble in these solutions at low oxidation levels (Roberts, 1961). Sloan et al. (1956) reported that for highly oxidized starches, piperidine, pyridine, and dimethoxy tetraethylene glycol were ineffective solvents at temperatures up to 100°C. Only glycerol and aqueous chloral hydrate dispersed all levels of oxidized starch. Alkaline solutions are not acceptable because of rapid degradation and depolymerization at high pH (Whistler et al., 1959; Launer and Tomimatsu, 1961; Plunkett, 1968).

Zein, as previously mentioned, is soluble in aqueous alcohol. About 80% of zein, α -zein, is soluble in 95% ethanol and the remaining 20%, β -zein, is dissolved in 60% ethanol. Zein may also be dissolved in quaternary ammonium hydroxide solutions, and sodium or potassium hydroxide solutions at 0.02 and 0.2 N. Zein is water soluble only in the pH range of 11.3 - 12.7, however, in alkaline solutions zein will gel upon standing (Reiners et al., 1973). Alcohol-solubility affords zein a unique place among industrially utilized proteins. Alcohol solutions of zein have been used in wood finishes, flexographic inks, and as a release coating in medicinal tablets (Pomes, 1971).

Compression molding

Compression molding was the first major method of processing plastics and is the most common method for molding thermosets. Compression molding is categorized as a high pressure process using pressures of 5 - 50 MPa. In metric units pressure and stress are measured in the unit called pascal (Pa) which is

equal to one Newton per square meter (N/m^2). One MPa (megapascal) is equal to 10^6 Pa or 10^6 N/m^2 . In compression molding the material is compressed in a two-part closed mold between the platens of the molding machine. In this process of molding, both mold surfaces are heated and conduction alone melts the material (Powell, 1983). Heat and pressure are used to cure the plastic over a desired length of time. Granular thermoset material first melts and then becomes fluidized to fill the mold. Further heating leads to a material that is crosslinked or "set". Due to the low viscosity of thermosets, some material passes into the space between the mold plates to form a flash, a thin sheet of material, which must be removed from the final product. Industrial scale processing of thermosets may be made more time and labor efficient by employing multi-cavity molds or transfer molding (Rosato and Rosato, 1990).

Crosslinked polymers

Polymers connected in a three-dimensional network are said to be crosslinked. The transformation from linear chains to a network produces many physical and chemical changes. Monomers or polymers with a sufficient number of reactive groups in proximity to each other may react forming a juncture. The linked chains restrict molecular motion (Seymour and Carraher, 1984). In highly crosslinked polymers the chains cannot flow past each other and solvent molecules cannot enter the structure, therefore, the polymer is tough, hard, infusible and insoluble. This increase in interchain forces also produces an increase in the glass transition temperature (Bolker, 1974). Thus, crosslinked polymers are set

irreversibly and are unaffected by changes in temperature (Hall, 1989). Polymers which cannot be melted and re-melted are known as thermosets. These polymers differ from thermoplastics which reversibly soften when heated. Polymers with aldehyde groups, which can crosslink with other functional groups, usually exhibit the behavior of thermosets (Billmeyer, 1959).

Properties of plastics

Although polymers have a large variety of chemical structures, they have common features which define their physical properties. As large macromolecules, with a molecular weight range of $10^3 - 10^7 \text{ g mol}^{-1}$, the chain conformation and mobility play a major role in their properties (Hiemenz, 1984). Plastics are described as polymers with properties between those of elastomers and fibers, being both flexible and hard (Seymour and Carraher, 1984). Conventional testing of plastics includes analysis for mechanical properties, water or solvent resistance, and specific gravity. Perhaps the most fundamental information used to characterize plastics is derived from the stress-strain curve produced during a tensile test. A tensile test measures the resistance to pulling stress. Stress is defined as the force per unit area applied to the specimen. Any change in length, more precisely deformation per unit length, of the specimen as a result of this stress is called strain. The stiffness of a material is measured as the ratio of stress to strain and is the slope of the straight-line portion of a stress-strain diagram. This value is known as Young's Modulus or the modulus of elasticity. The yield strength is defined as the amount of stress which will produce a small amount of

permanent deformation (Dieter, 1986). Some materials demonstrate a sharp yield point on their stress-strain curves, but in most cases the transition from elastic to plastic behavior is gradual. Therefore, the yield point is often arbitrarily defined with a line constructed parallel to the elastic part of the stress-strain curve but displaced to the right an amount equivalent to a strain of 0.2 % (Brick et al., 1977). The linear portion of the curve up to the yield point is known as the elastic region in which strain is fully recoverable. Past the yield point bond stretching becomes bond breaking making elastic recovery impossible and leading to fracture. Polymers possessing low molecular mobility due to close packing, crystallinity, or crosslinking have very small elastic strains. Since polymers with greater elastic strain require more energy for deformation, they are capable of absorbing more energy upon impact without failure and therefore have a greater application value (Seymour and Carraher, 1984).

Fracture behavior of plastics

Fracture is the fragmentation of a material under stress as the result of bonds breaking along the plane defined by the growing fracture surfaces (Berry, 1964; Tager, 1972). Fracture begins with crack initiation followed by crack propagation. Crack initiation may depend upon a number of variables including: temperature, surface features, and state of stress (Dieter, 1986). When and how crack initiation through fracture occurs defines the two types of fracture. Ductile fracture features plastic deformation past the yield point due to regrouping of the individual elements prior to crack propagation (Tager, 1972). Brittle fracture arises

suddenly with rapid crack propagation and no deformation, usually limited to 1% strain or less (Powell, 1983). Brittle fracture occurs near or at the elastic limit of the material and is preceded only by recoverable strain. The stress-strain curve of a brittle material is linear, showing no yielding before fracture. It is this propensity for sudden and unpredictable failure which should be prevented for most applications. Polymers below their T_g (glass transition temperature), or those with bulky side groups or crosslinking exhibit brittle fracture. These conditions inhibit polymer chain disentanglement (Powell, 1983). The Griffith theory of brittle fracture explains that numerous micro-cracks in a brittle material allow localized stress concentrations causing crack propagation at a stress below the theoretical value. Griffith noted that, "A crack will propagate when the decrease in elastic strain energy is at least equal to the energy required to create the new crack surface" (Dieter, 1986). A tensile stress does not initiate any cracks but is needed for crack propagation. Voids, aggregates, or cracks produced during or post-molding may act as initiation sites and thus processing should be designed to avoid irregularities. Brittle behavior also may often be identified at the fracture surface. Unique surface features mark the dislocations along the crack front and often produce geometric imprints around the point (flaw) of stress concentration (Wolock and Newman, 1964).

Additives

Additives are often necessary to effect positive changes in the modulus, workability or solubility of polymers. Plasticization is one of the most important

methods of polymer modification. Plasticization consists of the addition of smaller molecules, solids or liquids, to the polymer to improve its elasticity or processability. As a result, all properties of the polymer are affected through an increased flexibility and mobility of the molecular structures (Tager, 1972).

Plasticizers act to lower the melt viscosity, elastic modulus and glass transition temperature (T_g) of the plastic by reducing intermolecular forces. A good plasticizer should be nonvolatile, compatible and efficient at less than 10% addition.

Some traditional plasticizers have recognized toxicity problems i.e. polychlorinated biphenyls and phthalic acid esters, and have been discontinued (Seymour and Carraher, 1988). Water and glycerol are two non-toxic plasticizers which may be utilized. Another group of common plastics additives are the antioxidants. These compounds are added specifically to retard the degradation of the polymer.

Oxidation is often responsible for the degradation of polymers through generation of free radical chain reactions. Antioxidants suppress the oxidation rate by scavenging free radicals (Kelen, 1983). Many natural antioxidants found in plants are derivatives of phenol and hindered phenols (Seymour and Carraher, 1988).

Butylated hydroxy toluene (BHT) and Irganox 1010 are a hindered phenolic antioxidants commonly used in plastics processing (Allen and Edge, 1992). Sodium bisulfite is a disinfectant which can also be used as an antioxidant.

Biodegradation

What defines "degradable" or "biodegradable" came to the forefront with the marketing of the starch-filled petroleum based polymers whose degradation was

initiated by microorganisms attacking the starch molecules and breaking up the polymer into smaller pieces. Concerns were expressed over the fate of the remaining polymer after starch biodegradation. However, no accepted definition for "degradable" existed at the time. Different claims by manufacturers caused a closer examination by scientists, legislatures and consumer groups. Meetings of those involved in degradable polymer research produced a number of definitions. A degradable polymer can be defined as "a polymer that undergoes changes in chemical structure which result in a loss of physical properties...if the loss of its properties is due, at least in part, to a biological agent (microorganism or enzymes)" (David, 1992). In 1991 the Second International Workshop on Degradable Materials met to share research approaches and to develop a consensus for defining degradable and biodegradable. From the conference the following definitions were proposed: "Polymer degradation is a deleterious change in the properties of a polymer due to a change in the chemical structure" and a "Biodegradable polymer is a polymer in which the degradation is mediated at least partially by a biological system" (Ottenbrite, 1992). Also in 1991, the ASTM (American Society for Testing and Materials) Committee D20 on Plastics approved the following definitions:

Degradable plastic, n. - "A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard methods appropriate to the plastic and the application in a period of time that determines its classification."

Biodegradable plastic--"..in which the degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi, and algae."

Biodegradation is therefore restricted to degradation by microorganisms. Biodegradation of polymers may be qualitatively measured by several methods. In the soil burial method, samples are buried in soil outdoors or in the laboratory and checked after an elapsed time for weight changes or loss of mechanical properties. Other tests place the plastic material in nutrient medium, inoculate with fungi or bacteria and measure colony growth. However, none of these methods can give quantitative degrees of decomposition. For quantitative determinations, both the biological oxygen uptake and the production of carbon dioxide can be measured (Kelen, 1983). ASTM has recently developed standard test methods for measuring the aerobic biodegradation in activated-sludge-wastewater (ASTM D 5271-92) and in compost (ASTM D 5338-92). Similarly, aerobic biodegradation may be measured by CO₂ evolution under controlled laboratory conditions in a soil biometer as will be shown in this thesis.

MATERIALS AND METHODS

Starch modification

Normal corn starch was a gift of American Maize (Hammond, IN). Polymeric dialdehyde starch was purchased from Sigma Chemical Company (St.Louis, MO) and zein was purchased from Freeman Industries (Tuckahoe, NY). Dialdehyde starch was prepared by oxidation of normal corn starch following the procedure of Mehltreeter (1964). The entire reaction procedure was carried out in a fume hood. The starch was oxidized with 0.11M sodium meta-periodate solution added dropwise over a period of one hour to the continuously stirred starch slurry. The amount of sodium meta-periodate was adjusted to produce the various degrees of oxidation. After a 24 hour reaction time, the starch was filtered in a Buchner funnel and washed 6 times in distilled water. Following the second wash the pH was adjusted to 7.0 with 0.5N NaOH. Two final washes with acetone completed the modification procedure. The starch was dried overnight in a forced air oven at 50°C. All other chemicals were reagent grade and used without further purification.

Starch modification analysis

Fourier Transform Infrared (FTIR) was investigated as a means of more rapid detection for oxidation. FTIR spectroscopy scans were performed on KBr disks of both the unmodified and modified starches. Starch was ground in a mortar and pestle and dried in a vacuum oven at 30 mm/Hg at 50°C for 48 hours and then immediately added to KBr. The starch concentration in the disk was 0.3%. The disks were prepared from exactly 100 mg of the KBr and starch mixture

added to a hand press.

Degree of oxidation was determined chemically by colorimetric measurements of the phenylhydrazone formed by addition of p-nitrophenylhydrazine in glacial acetic acid to a solution of dialdehyde starch. Absorbencies at 445 μm were measured against a like-treated starch blank. Percent oxidation was calculated by adjusting the absorbance reading to a mg/ml basis and dividing by 467.7, the absorbance of 100% oxidation (Wise and Mehltreeter, 1958).

Preparation of the starch-zein mixtures

For the plastic mixture, zein (1 part) was added to methanol (75% w/v) and dissolved. Any additives to be included were added at this step. Dialdehyde starch (3-7 parts) was folded into the solution to form a dough-like mixture. The dough was thoroughly hand-mixed (under the fume hood) and spread into a foil lined glass dish. The methanol was allowed to evaporate for 2-3 hours in the fume hood before being placed in the forced air oven to dry overnight (10-12 hours) at 50°C. The dried material was ground in electric mill (UDY Corp., Fort Collins, CO). The moisture was adjusted to the desired level (9-12%) by placing the powdered material into a humidity chamber (Figure 2). Moisture content was measured prior to molding on a moisture analyzer (Sartorius Moisture Analyzer, Goettingen, FRG).

Additives

Plasticizers were added to the mixture to determine their effects on both processing and final product quality. Glycerol, sorbitol, and ethylene glycol were

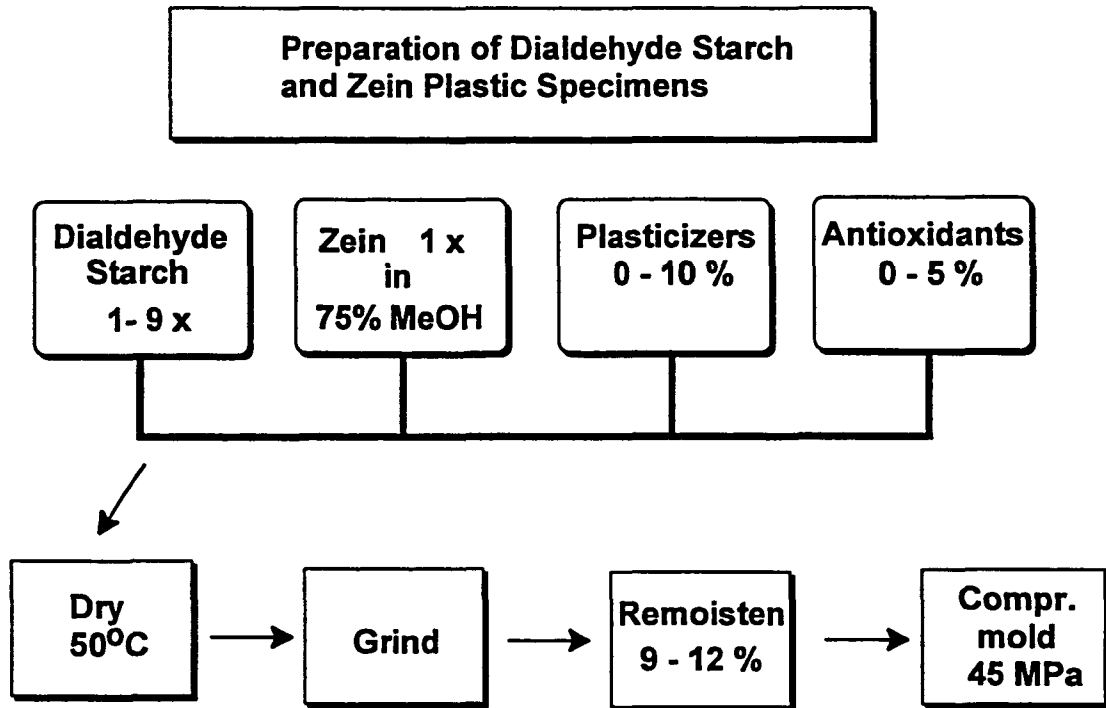


Figure 2. Flow chart for the preparation of dialdehyde starch and zein plastic material and specimens.

tested at either 1%, 5%, or 10% by weight to the zein-methanol solution prior to starch addition. Antioxidants were added to minimize side reactions during processing. Irganox 1010 (CIBA-GEIGY, Hawthorne, NY), an industrial antioxidant, was used in a trail run for antioxidants and was thoroughly mixed into the sample material (1% w:w) as a powder just prior to molding. The other antioxidants, BHT (butylated hydroxytoluene) (UOP, Des Plaines, IL) and sodium bisulfite (NaHSO_3) (Fischer Scientific, Pittsburgh, PA), were incorporated at 1%, 3% and 5%, by weight and were each dissolved in methanol and added to the zein during the material preparation procedure.

Specimen molding

The ground, powdery material was compression molded in molds designed to produce a Type I specimen (ASTM standards D638-86). Type I applies to specimens of less than 7mm thickness with the following dimensions: overall length 165mm, gage length 50mm and narrow width 13mm. For each tensile bar, 16 g of material was placed in the mold cavity and leveled with a spatula. Compression molding temperatures for the different samples ranged between 108°C and 160°C with the temperature controlled within 2°C for each set of replicates. A pressure of 45 MPa was used for all specimens.

Specimen property testing

Tensile bars were tested according to ASTM D638-86, Standard Test Method for Tensile properties of Plastics. Before testing, specimens were conditioned for ≥ 40 hours at 50% relative humidity. The tensile bars were placed

in the grips of the Instron Model 4502 testing system (Park Ridge, IL) with a gauge length of 115mm and a crosshead speed of 5mm/min. and measured for tensile strength, percent elongation at yield, and yield strength at peak. Young's Modulus (modulus of elasticity) was calculated by the Instron. For each treatment 5 or more specimens were tested. The average test values and standard deviations were recorded.

The ASTM standard test method D570-81 was modified slightly and employed for water absorption measurements. The same broken tensile bars obtained from mechanical testing were first conditioned in an oven at 50°C for 24 hours. The specimens were then cooled in a desiccator and weighed. Each specimen was immersed in a petri dish containing 40ml of distilled water. After 2 hours, each specimen was removed from the dish, blotted dry to remove surface water, and weighed. The specimens were immediately re-immersed and weighed again at 24 hours total immersion time. A 24 hour re-drying and weighing of the specimens was performed and the soluble matter loss was calculated. In accordance with the ASTM method, the 24 hour water absorption was taken as the weight gain from immersion plus any soluble loss. Values were reported in percent of water absorption based on total weight.

Apparent and bulk density measurements were made following ASTM standard method D 792-86. Weight differences were measured for conditioned rectangular pieces of tensile bars before and during suspension in kerosene and/or mineral oil using a Mettler 33360 density determination kit (Hightstown, NJ). The

known specific gravity of the kerosene and mineral oil was 0.803 g/cm^3 and 0.866 g/cm^3 , respectively.

For all data the standard deviation is given in parentheses following the mean (average) value.

Surface features

The flat surface and tensile fracture surfaces of the tensile specimens were examined at 20 kV on a JOEL JSM-35 scanning electron microscope (SEM) (Tokyo, Japan). Samples were mounted on brass discs and sputter coated with a platinum/palladium alloy (60/40) and stored in a desiccator. Micrographs were taken using Polaroid 615 positive/negative film.

Biodegradation studies

A respirometric system measures the mineralization of polymer carbon to CO_2 . The ASTM Method D 5338-92, a method using composting conditions, was chosen as the model for a soil test. No ASTM method for soil biodegradation has yet been approved.

A respirometer was designed to measure the mineralization of the DAS and zein polymers in a natural soil environment. The basic design of the respirometric system consisted of pretraps, the soil reactor, and a CO_2 posttrap as shown in Figure 3. Air from a laboratory air line was controlled to a flow rate of 15 ml/min. The air was bubbled through 4 - 1 L pretraps containing approximately 500 ml of distilled water, 2N NaOH, 2N NaOH, and 2N H_2SO_4 , respectively, which acted to clean, humidify and remove CO_2 from the incoming air. Tubing then directed the

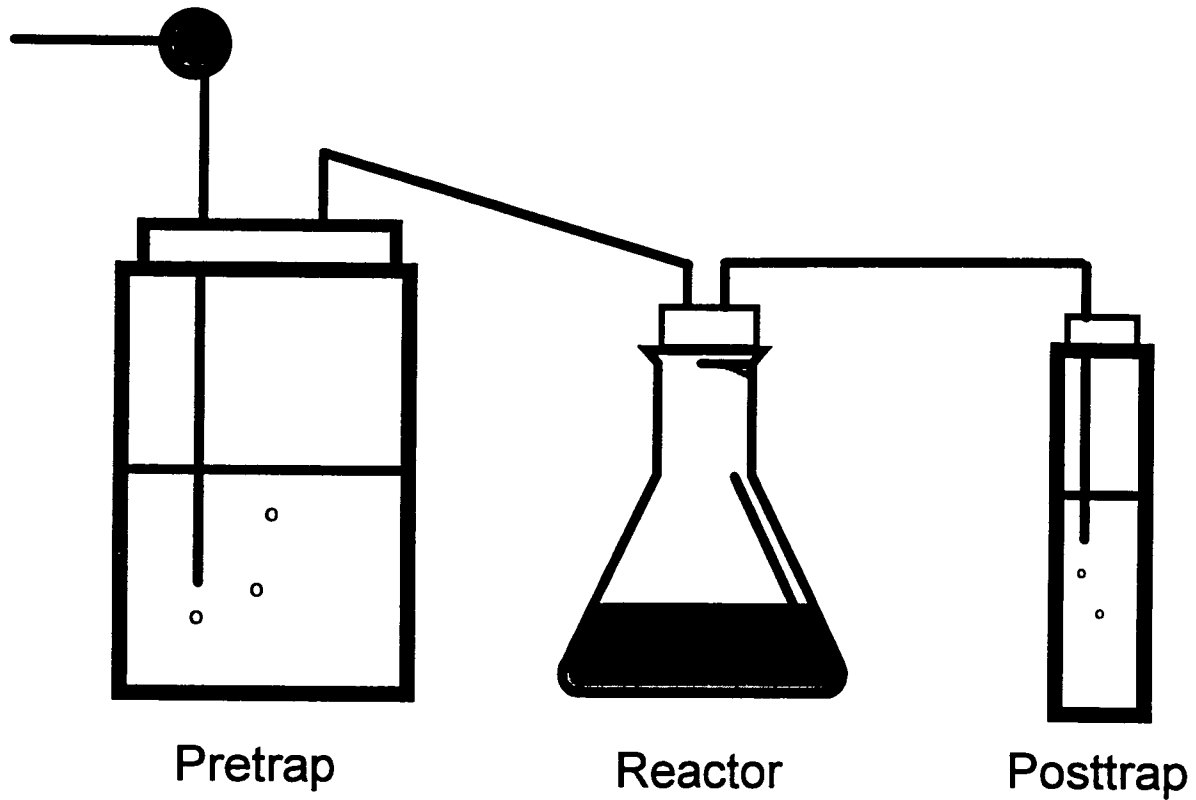


Figure 3. Diagram showing the main components of the respirometer. The pretrap removes CO_2 from and sterilizes the incoming air. The reactor contains the the soil and ground polymer for biodegradation. The posttrap captures CO_2 evolved from polymer mineralization.

air flow to each of the 35 reactors. Each reactor was a pre-sterilized 400 ml dilution bottle with an inlet and outlet in the stoppered top. A 100 g homogenous mixture of soil (Hyponex All Purpose potting soil, Hyponex Corp., Marysville, OH) and sand (1:1 w/w), along with 10 g of sample, except controls, was added to each reactor bottle. The moisture content of the soil and sand was 25%. The soil mix was used without further treatment and no analysis of the indigenous microbial population of the soil was performed. Five replicates were prepared for each of the six samples and the control (soil and sand without any polymer added) were maintained in a water bath at 25°C for 180 days. Temperature and water circulation were controlled by an Immersion Circulator Model 70 (Fischer Scientific, Pittsburgh, PA). Twice during the study, on days 30 and 98, 10 ml of sterilized distilled water was added to each reactor to maintain a humid environment for microbial growth. Prior to the water addition, the airflow to the reactors was increased for 3 minutes to purge any CO₂ in the headspace into the posttrap. A posttrap test tube containing 10 ml of NaOH solution trapped the CO₂ produced by each reactor in the form of sodium carbonate. The test tubes were periodically changed and the NaOH solution from each tube was titrated twice, first rapidly to pH 8.3 with 0.9 N HCl and second to pH 4.2 with standardized 0.4 N HCl, using two DL Mettler 12 autotitrators (Mettler Instruments, Hightstown, NJ). During the acid-base titration the sodium carbonate was converted to bicarbonate and then the bicarbonate was neutralized to carbonic acid with CO₂ volatilization. The titration was carried out potentiometrically and the end point calculation performed

by the autotitrator gave the milliequivalents of carbon in the sample. The degree of polymer biodegradation was taken to be the difference between the average CO_2 value of the reactors with samples and the controls. These values were then converted to percent biodegradation based upon the amount of carbon evolved divided by the theoretical carbon amount of each sample. In addition, it should be noted that the normality of the NaOH used in the posttraps was changed during the 180 days of analysis. From initiation through the 35th day, 2N NaOH was used. At day 36 through day 57, a 10N NaOH solution was used and 4 N NaOH was used from the 58th day to the test completion.

RESULTS AND DISCUSSION

Starch modification analysis

The reactivity of DAS depends on the degree to which it is oxidized. Following the modification of corn starch, two methods were attempted to quantify the degree of starch oxidation. Determining the number of aldehyde functional groups present or the degree to which the polymer was modified was an important concern. Fourier transform infrared (FTIR) was investigated for use as a rapid method. The C=O stretching frequency of the carbonyl group in aldehydes and ketones occurs at 1730-1665 cm^{-1} and an aldehydic C-H stretch occurs at 2720 cm^{-1} and 2820 cm^{-1} . FTIR was conducted using periodate oxidized corn starch of various degrees of oxidation. As noted earlier, DAS is expected to be in hemialdal or hydrated form under normal conditions. However, Spedding (1960) demonstrated in a study of periodate oxidized cellulose films that absorbance at 1734 cm^{-1} changed from a shoulder to a distinct peak with increased oxidation and oven heating. In an effort to reduce any hydration of the aldehyde groups, ground corn starch, DAS (10% oxidized) and PDS were dried in the vacuum oven at 50 °C for 48 hours and rapidly prepared into pellets. Again, no increase in the carbonyl peak was noted (Figure 4). Although these results show that FTIR may not be used for characterization of oxidation levels in starch, they do agree with earlier work by Rowen et al. (1951) on oxidized cellulose. Rowen and coworkers could find no change in the spectrum for oxidized and native cellulose in the C=O

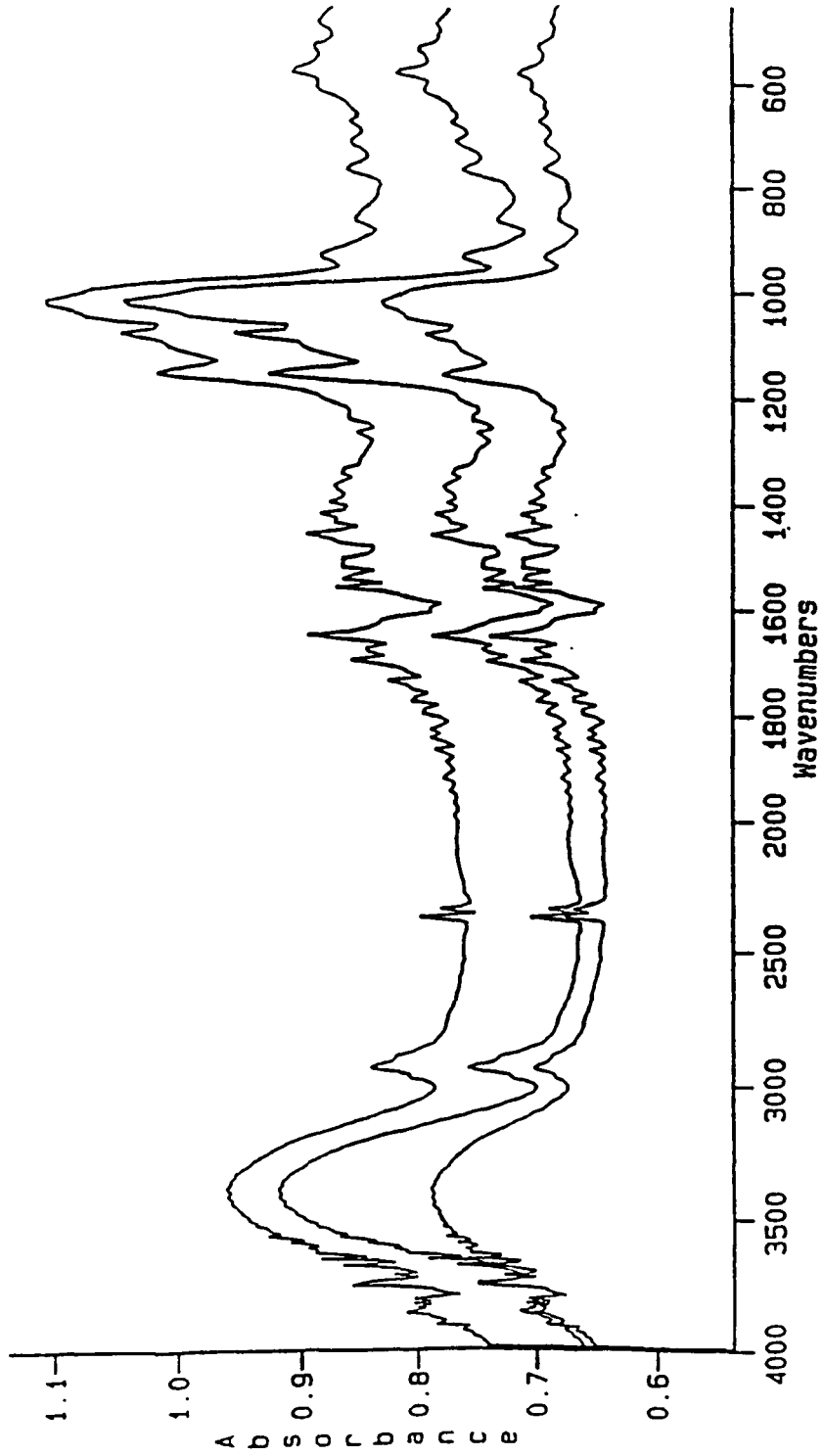


Figure 4. FTIR scans of corn starch and two dialdehyde starches (mole ratio periodate to AGU of 0.017 and 0.033) from top to bottom, respectively, in KBr pellet (0.3%) after drying 48 hours in vacuum oven.

stretching region and they suggested this resulted from hydration of all the aldehyde groups. They did, however, note changes due to the cleavage of anhydroglucose rings ($1000\text{-}1250\text{ cm}^{-1}$).

Chemical measurements of oxidation using the procedure of Wise and Mehltreeter (1958) produced more satisfactory results. The red precipitate of the phenylhydrazone was formed after a slightly longer period on the steam bath than described in the method. The precipitate was easily washed and collected in ethanol for colorimetric analyses. The results of selected samples confirmed modification procedures.

Early molding trials

As the methods for molding these polymers were developing, initial failures were caused by incomplete melting of the powder or polymer sticking inside the mold. Many aspects of processing had to be adjusted or characterized before the actual study could begin. Concerning the mold, a piece of 0.3 mm teflon sheeting was placed between the mold base and the mold frame to prevent sticking and large flash formation by filling the gap. Once the specimen was removed, the mold was initially only cooled to approximately 70°C before refilling. This caused the edges and lower half of the product to remain in a powdery state. It became obvious that using a hot or warm mold was not suitable for molding starch-based plastics. The starch exposed to the warm surfaces would lose moisture. Insufficient moisture reduced gelatinization and melt flow which caused molding failure. For all specimens thereafter, the molds were cooled to less than 40°C

before being reused. In addition, leveling the sample in the mold cavity before molding was also important. If the mixture was not evenly spread throughout the cavity, an end or the middle section may not receive enough pressure to produce the plastic material. Unmolded ends were a common problem in the beginning, but careful filling of the mold solved this problem. In order to prevent warping in the specimens after removal from the mold, the mold needed to be cooled to less than 60°C and the specimen placed under another object while cooling to room temperature. Finally, the removal of the flash, if any, warranted careful attention. As mentioned in the literature review, thermosets and crosslinked polymers commonly produced brittle fracture. A common mechanism of brittle fracture is small cracks on the surface. Fine abrasive paper (100 grit) was used in the longitudinal direction to remove the flash edge. This was followed by a Scotch Brite fine sanding pad (3M, St.Paul, MN) to reduce cracks and smooth the surface.

Effects of moisture content

Water is an effective plasticizer and plays an important role in the plasticization of starch and proteins. Dialdehyde starch (0.017 mole ratio periodate/ AGU) and zein (4:1 w/w) with 5% glycerol was adjusted to 4 different moisture contents, 9.3%, 10.0%, 11.2% and 12.0%, and compression molded into specimens at 113°C. As moisture content increased, the tensile properties of the specimens decreased. From 9.3% to 12.0% moisture, the tensile strength of the material decreased by 57%. Elongation decreased with increased moisture from 2.02% to 0.97% over the same interval (Table 2). Interestingly, the water

absorption of the specimens decreased with increasing moisture content in the mixture. Specimens with 9% moisture content gave absorption values of 48.6% whereas specimens with 12% moisture only absorbed 37.9%. This decrease in water absorption in specimens with increasing moisture content has been noted by others working with natural polymer plastics. Paetau (1993) described a decrease in water absorption for soy protein plastics from 133% to 98% as the moisture was increased from 7.1% to 16.9%, respectively. In addition, increased moisture acted as a plasticizer enabling molding temperatures as low as 108°C.

Table 2. Effect of moisture content on the mechanical properties and water absorption of DAS and zein (4:1) compression molded at 113°C.

Moisture content (%)	Tensile strength (Mpa)	Elongation (%)	Water Absorption (%)
9.3	16 (1.0)	2.0 (.2)	49.0 (2.0)
10.0	11 (2.0)	1.3 (.2)	43.0 (2.0)
11.2	11 (3.0)	1.5 (.4)	38.6 (0.9)
12.0	7 (2.0)	1.0 (.1)	38.0 (1.0)

In the case of DAS and zein plastic the higher moisture content may allow for more complete starch gelatinization and protein gelling and thus lead to more opportunities for crosslinking to occur. This crosslinking decreases water absorption. Another explanation for the decrease in water absorption is that the increased hydration of the polymers, protein and dialdehyde starch, diminished

their absorption of more water. Increased hydration at higher initial moisture contents would reduce water absorption rates during the 24 hour testing. Results of the mechanical testing show increased moisture may have lowered strength values by interfering with the matrix and/or through holes left behind after evaporation during the molding process. These holes would serve as areas for stress concentration. In addition, using the same total weight of material per specimen lead to more water and less polymer in the higher moisture samples. Even with greater gelatinization and some increase in crosslinking, the decrease in polymer material and the increase in moisture content would reduce tensile strengths and elongations. However, the relatively small decrease in water absorption resulting from increased moisture content is minimally important when compared to the decrease in tensile properties produced by the excess moisture.

Effects of oxidation and temperature

The effects of starch oxidation and molding temperature on tensile strength were examined. Unmodified and dialdehyde (DAS) corn starch were mixed with zein at a 4:1 ratio and 5% glycerol (tot. wt.) was added. The DAS used was produced with various degrees of oxidation. The mole ratio of periodate to AGU was 0.017, 0.033 and 0.05 to correspond to ≈ 1 aldehyde unit for every 30, 15, and 10 anhydroglucopyranosyl units, respectively. Specimens were compression molded at a 9% moisture content at 3 temperatures (113°C, 118°C and 128°C) at 45 MPa. Tensile strength increased with increasing degree of oxidation (Figure 5) The specimens molded at 128°C displayed less tensile strength indicating some

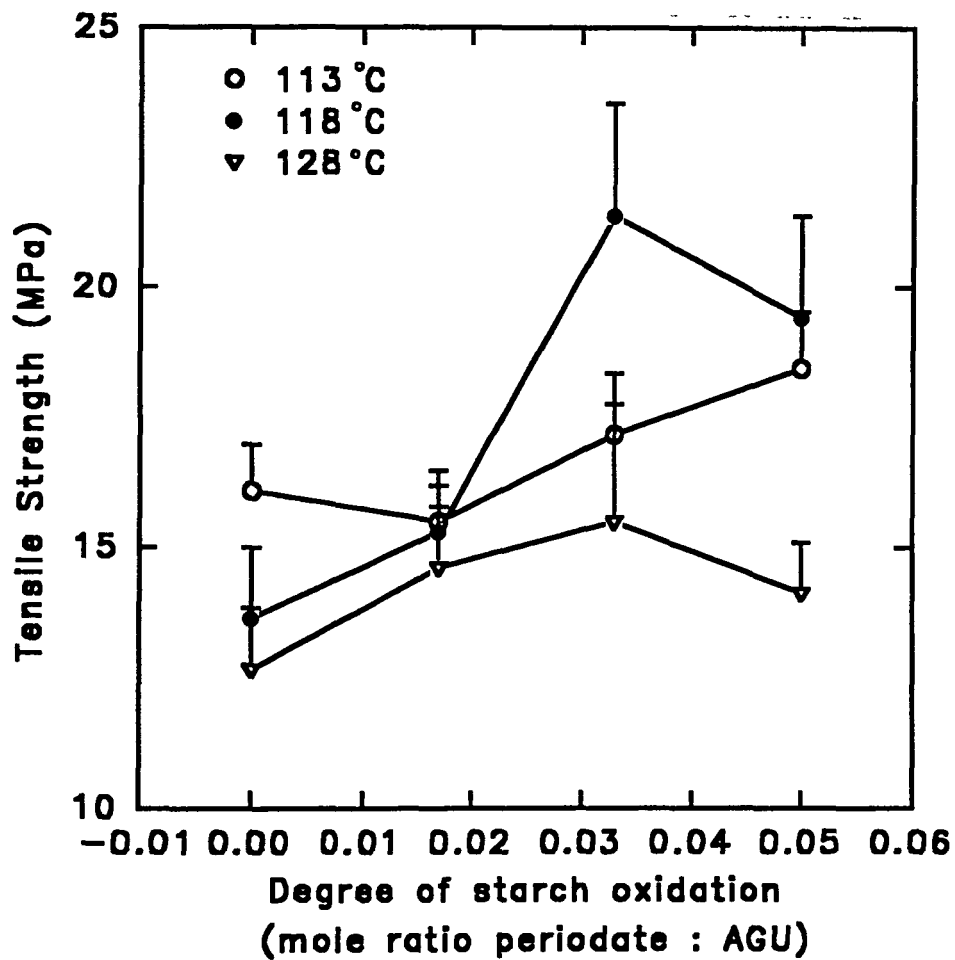


Figure 5. Effects of molding temperature and degree of starch oxidation on the tensile strength of DAS and zein plastic.

thermal degradation might take place at that temperature. The effect of oxidation and temperature were less obvious on the elongation values. The narrow range of elongation percentages, from 1.5% to 2.3%, is shown in Figure 6. Likewise, the modulus of elasticity or Young's modulus also demonstrates little variance with one exception. That exception is DAS (mole ratio 0.033) and zein (4:1 w/w) compression molded at 118°C which gives a modulus of 1.9 GPa (Figure 7). The water absorption of these specimens also decreased with degree of oxidation and molding temperature (Figure 8). Molding at 128°C did not, however, negatively impact water resistance but rather led to a decrease in water absorption over 24 hours immersion.

Polymeric dialdehyde starch was also mixed with the zein. Water absorption of specimens of PDS and zein (4:1 w/w) with 10% moisture and molded at 126°C was only 2.6% after the 24 hour immersion with a negligible water solubles (weight) loss (0.40%). The specimens, very dark in color, showed no sign of swelling or deformation during the immersion. The tensile strength was 49 MPa and the elongation was 4.3%. Additional specimens were also prepared using polymeric dialdehyde and starches with lower degrees of oxidation in which the level of oxidation had been measured colorimetrically. Comparisons of the specimens demonstrated the enhanced water resistance of the highly oxidized starch and zein plastic. An almost 87% increase in tensile strength was also a benefit to the higher crosslinking (Table 3). The high water resistance of polymeric dialdehyde and zein specimens prompted further study of this property.

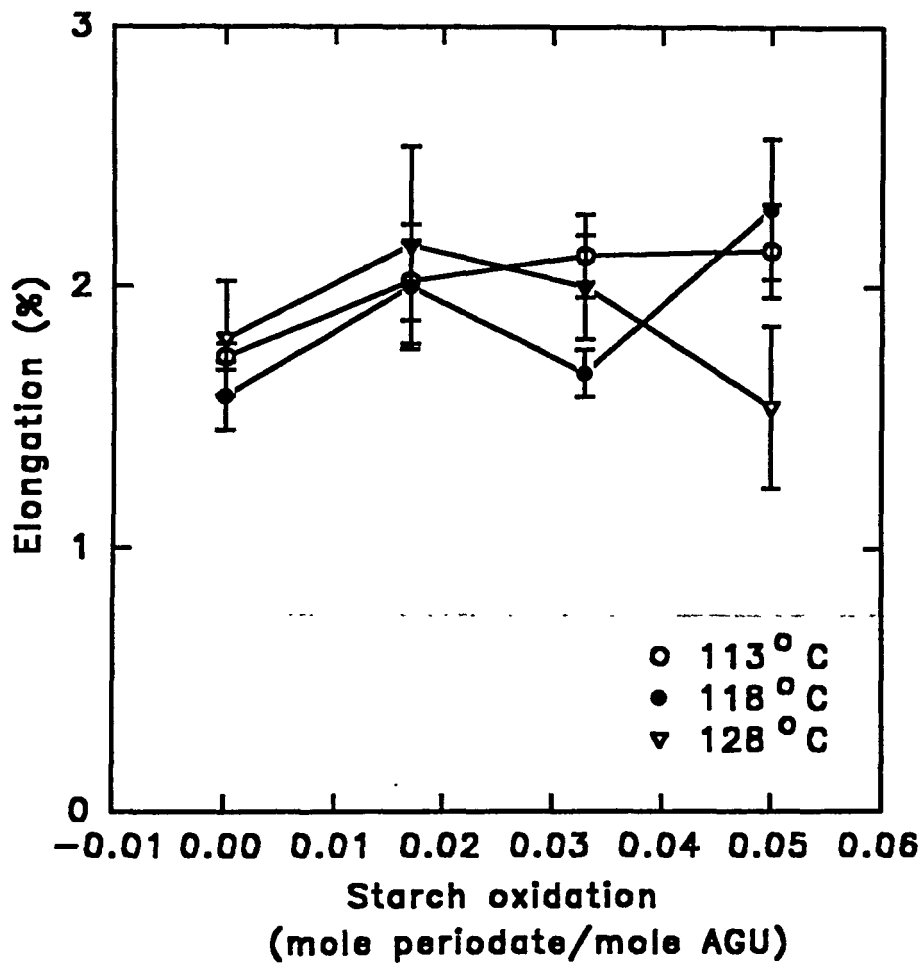


Figure 6. Effects of molding temperature and degree of starch oxidation on the percent elongation of DAS and zein plastics.

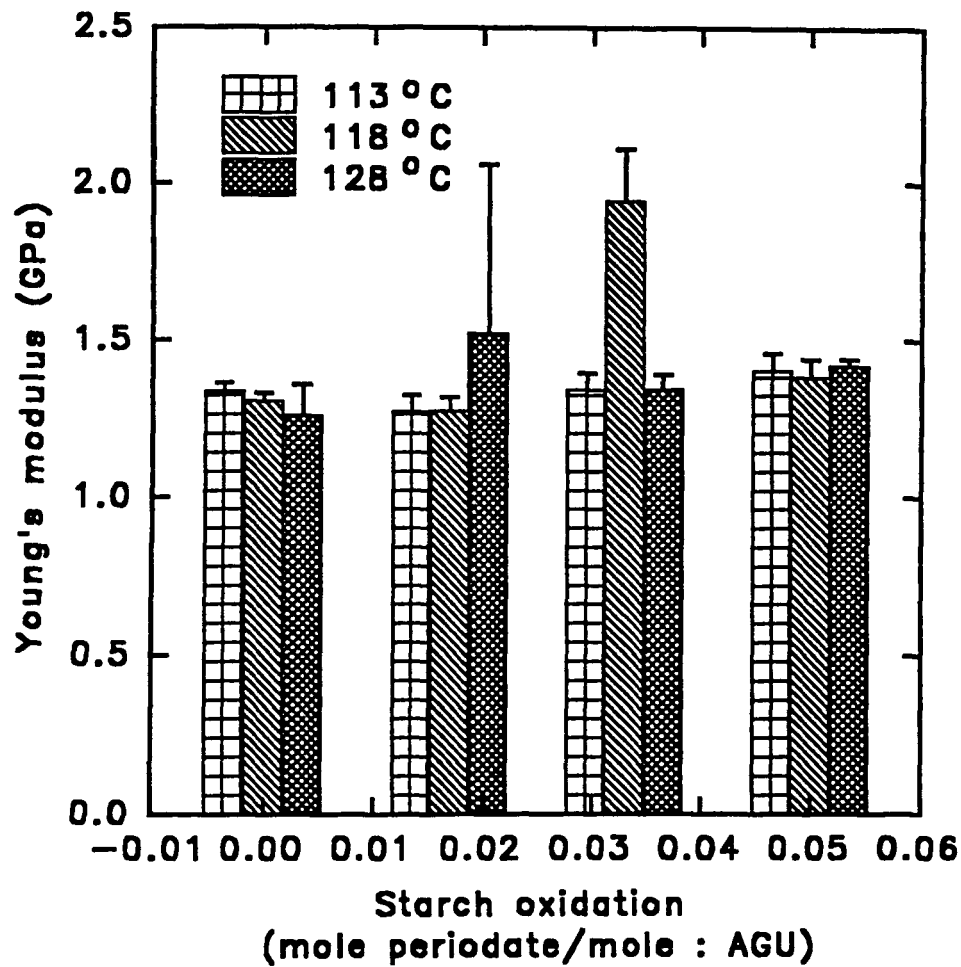


Figure 7. Effects of molding temperature and degree of starch oxidation on the Young's modulus of DAS and zein plastics.

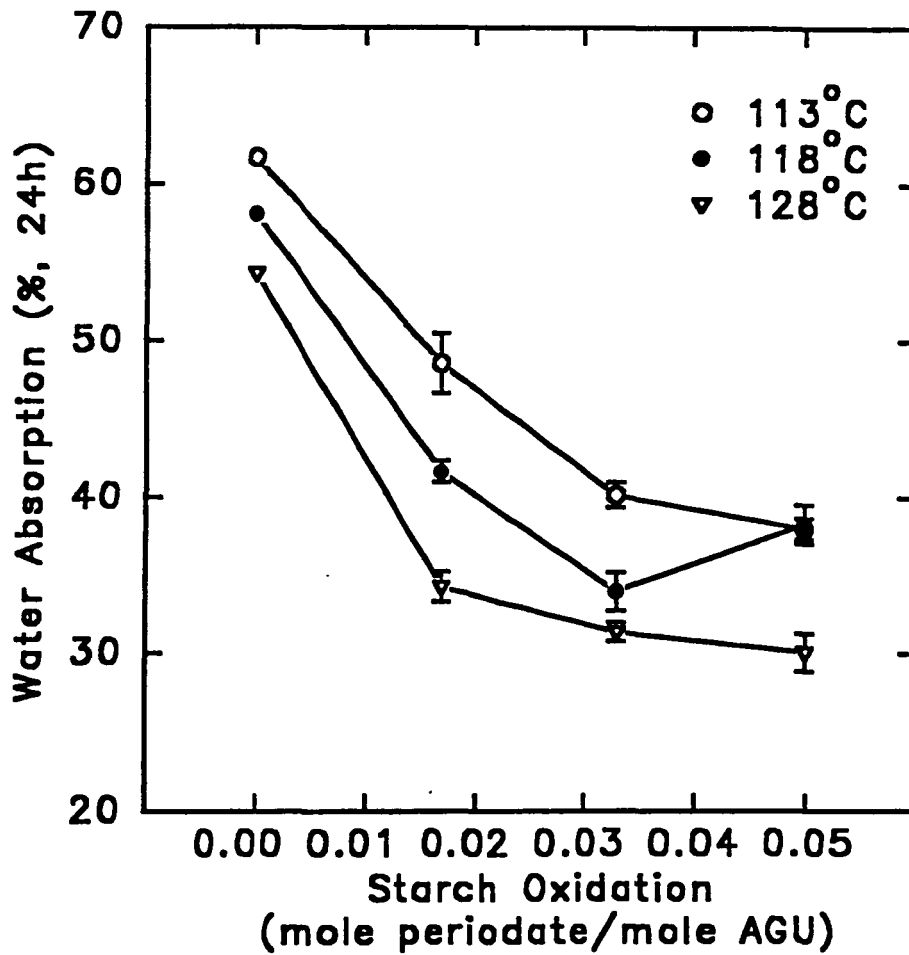


Figure 8. Effects of molding temperature and degree of starch oxidation on 24 h water absorption.

Table 3. Dialdehyde starch and zein (3:1 w/w) without glycerol, molded at 135°C and 9% moisture content.

Starch Oxidation (%)	Tensile strength (MPa)	Elongation (%)	Young's Modulus (GPa)	Water Absorption (% , 24h)
0	19 (2.0)	2.3 (.2)	1.28 (.07)	42.6 (2.3)
1	20 (1.0)	2.5 (.1)	1.39 (.06)	26.9 (1.1)
5	22 (2.0)	2.75 (.09)	1.54 (.07)	26.5 (.3)
9	19 (2.9)	2.0 (.3)	1.56 (.05)	29.7 (1.1)
90	38 (3.9)	4.0 (.5)	1.77 (.11)	5.3 (.3)

PDS and zein (4:1 w/w) tensile bars were immersed in distilled water for an extended time to follow water absorption. These specimens demonstrated an increased resistance to swelling and water uptake even after 24 hours. After 20 days the sample had a water absorption of only 30.8%; a value unmodified or lesser oxidized samples had reached in approximately 24 hours (Figure 9). At the 20 day mark specimens showed signs of mold beginning to grow on the surface and most were discarded. However, a specimen was left in its petri dish for an additional 104 days. Mold covered the water surface, but upon inspection the specimen still maintained a defined, yet swollen, shape. The specimen was removed and rinsed free of mold and the soft outer layer. It was weighed, dried and then re-weighed for solubles loss measurement. Even immersed in a covered petri dish of standing water, the specimen continued to absorb water and

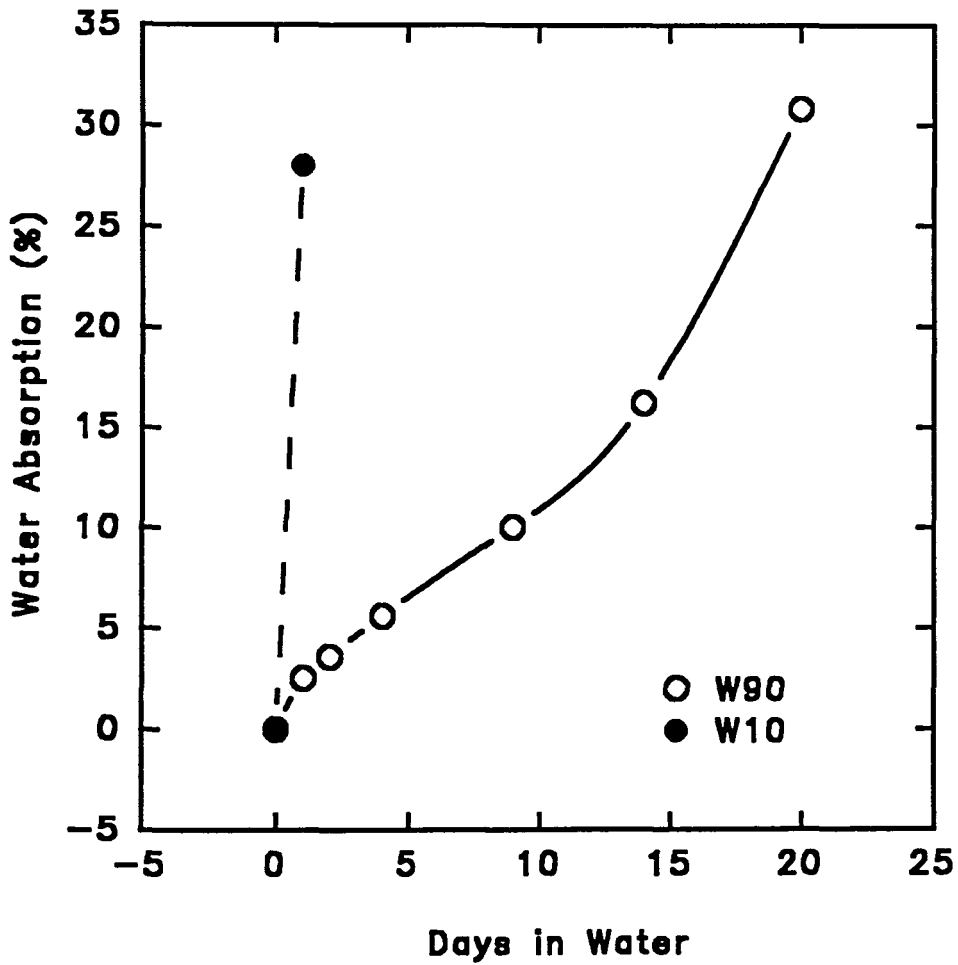


Figure 9. Long term water absorption of polymeric dialdehyde and zein (4:1/w:w) specimens (W90) versus 10% oxidized starch and zein (4:1/w:w) sample (W10).

disintegrate with the help of microorganisms. The total water absorption for the 124 day period could be estimated at 83.4%, including the weight loss of 57.5%.

The immersion of specimens for water absorption testing demonstrated the ability of the crosslinked dialdehyde starch and zein plastic to resist deformation in water or high humidity environments. Specimens of compression molded corn starch and zein swelled considerably, became more pliable and often disintegrated in the water absorption tests. Dialdehyde starch and zein plastic specimens retained the tensile bar shape and resisted swelling when immersed up to 24 hours in water.

The effect of molding temperature on the plastics was evident from the first few trials. Certainly temperature was important in obtaining the right melting conditions for the samples. If the temperature was too low the product was a loosely connected mass still in the powdery state. Too high of a temperature, generally above 140°C, the specimens blistered and thermally degraded. Increased water content, as a plasticizer, allowed lower temperatures to be used for molding but excess moisture rarely had a beneficial effect on the properties of the specimens. Raising the temperature almost always increased the water resistance, or decreased the water absorption, of the material. Since increased temperature and/or increased starch oxidation resulted in specimens with darker color it was plausible to attribute both the color and decreased water solubility to crosslinking and other chemical reactions, such as Maillard reaction, promoted by the increase in temperature. The effect of temperature on the mechanical

properties of the material was less defined than for water resistance. This could be attributed to the brittle behavior of the material in which fracture is governed by flaw size rather than the structural or chemical make-up of the polymer.

The optimum temperature range for the DAS and zein plastics molding was 118°C to 135°C depending on the sample composition. Specimens of DAS of low oxidation showed some evidence of thermal degradation at 128°C (Figures 5, 6 and 7) and a greatest tensile strength at 118°C. However, specimens with a higher degree of starch oxidation (90%) could not be properly molded at 118°C at 9% moisture content. At molding temperatures below 125°C these samples were not completely molded, particularly on the ends of the tensile bars. Figure 10 illustrates the decrease in mechanical properties of highly oxidized starch and zein plastics at 140°C.

Effects of glycerol and other plasticizers

Water resistance of polymeric dialdehyde and zein specimens was negatively effected by the addition of glycerol to the mixture. Tensile bars were made from DAS and zein mixtures with and without glycerol. DAS and zein specimens prepared with other plasticizers, such as sorbitol (1%) and ethylene glycol (1%), had lower mechanical properties and water resistance than those with glycerol. Examples of molding conditions and mechanical properties of the specimens are shown in Table 4. Other examples include DAS and zein (4:1) with 9% moisture content and compression molded at 128 °C displayed a tensile strength of 15.5 MPa with 5% glycerol and 22.8 MPa without glycerol in the

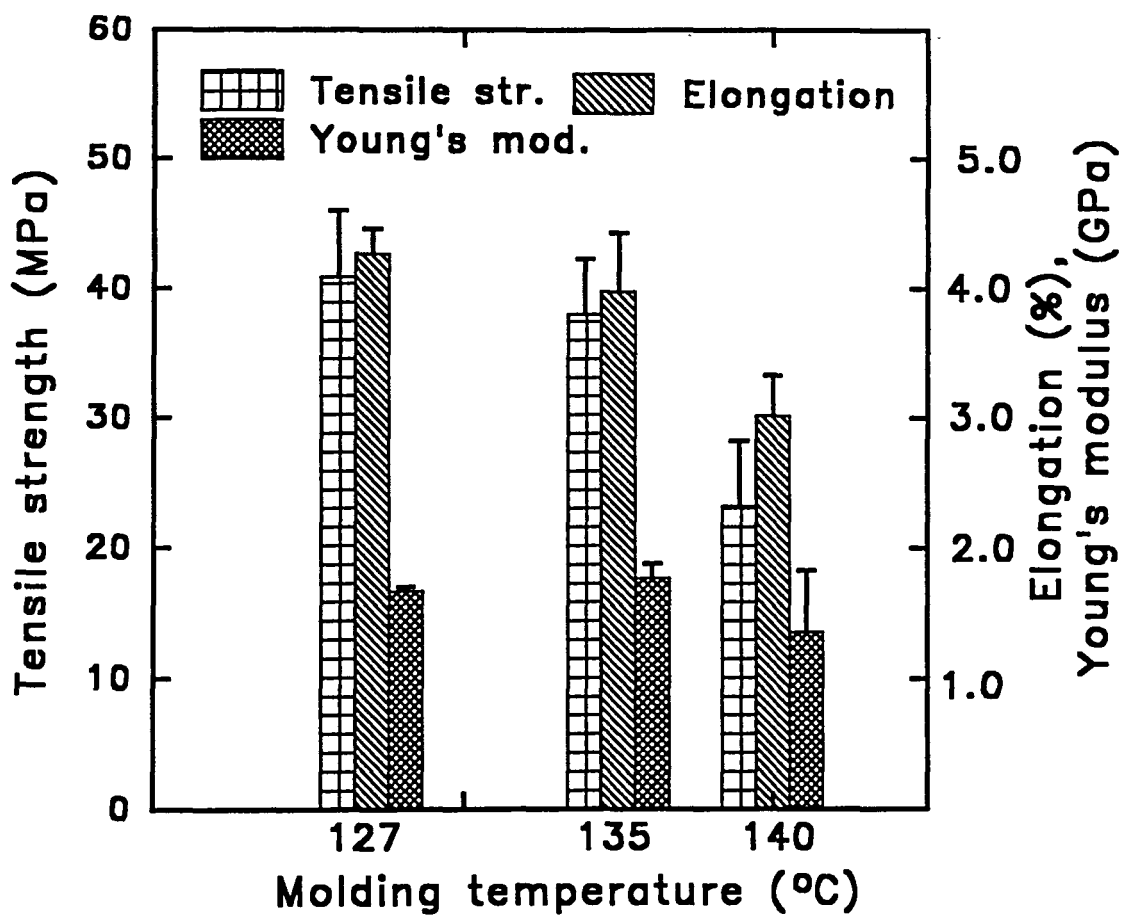


Figure 10. Effect of molding temperature on the mechanical properties of highly oxidized starch and zein plastics molded with 9% moisture.

Table 4. Effect of glycerol on tensile properties and water absorption of molded polymer specimens.

Oxidation %	Molding temp. °C	Moisture %	Plasticizer	Tensile strength MPa	Elongation (%)	Young's modulus (GPa)	Water absorption (%)
6.7	118	10	Glycerol 5%	15 (2)	2.1 (.4)	1.22 (.04)	37.1 (.6)
6.7	128	10	Glycerol 5%	17 (7)	2.38 (.08)	1.22 (.06)	32.0 (2)
6.7	119	10	None	19 (2)	2.1 (.2)	1.52 (.06)	28.2 (.6)
6.7	128	10	None	20 (1)	2.1 (.2)	1.48 (.03)	21.7 (.5)
90	135	9	None	48 (5)	3.6 (.4)	1.97 (.02)	2.7 (.6)
90	135	9	Glycerol 5%	32 (4)	3.2 (.2)	1.77 (.12)	8.0 (1)
90	135	9	Glycerol 10%	32 (3)	3.7 (.6)	1.57 (.18)	21.2 (.9)

mixture. Likewise, the water resistance also increased from an absorption of 31.4% down to 21.7% for the specimens with and without glycerol, respectively. The 24 hour water absorption of polymeric dialdehyde and zein also increased by 50% with 5% glycerol added to the material. The specimens showed only a minimal increase in solubles loss from 2.2% to 4.1%. Results were similar at 10% glycerol content for both the tensile strength and elongation which decreased.

Effects of zein

Plastic specimens showed increasing elongation and water absorption with increasing zein content. Although zein prevents the specimens from disintegrating, the specimens did swell and absorb more water as the concentration rose. In samples of lower oxidation with 5% glycerol, water absorption was measured for 15%, 20% and 25% zein contents. The specimens with 20% zein gave the lowest water absorption (Figure 11). Polymeric dialdehyde and zein (in PDS to zein ratios of 9:1, 4:1, 2:1 and 1:1) specimens without glycerol also demonstrated preferred properties at 20% zein concentration. Water absorption increased from 4.5% to 19.6% for PDS and zein ratios of 9:1 and 1:1, respectively. Percent elongation increased with zein concentration while tensile strength was decreased at higher zein concentrations. (Figures 12 and 13). Solubles loss was minimal for all the samples.

Effects of antioxidants

Other additives, antioxidants, were also added to the polymeric dialdehyde and zein (4:1) composition. An antioxidant used in petroleum plastics, tradename

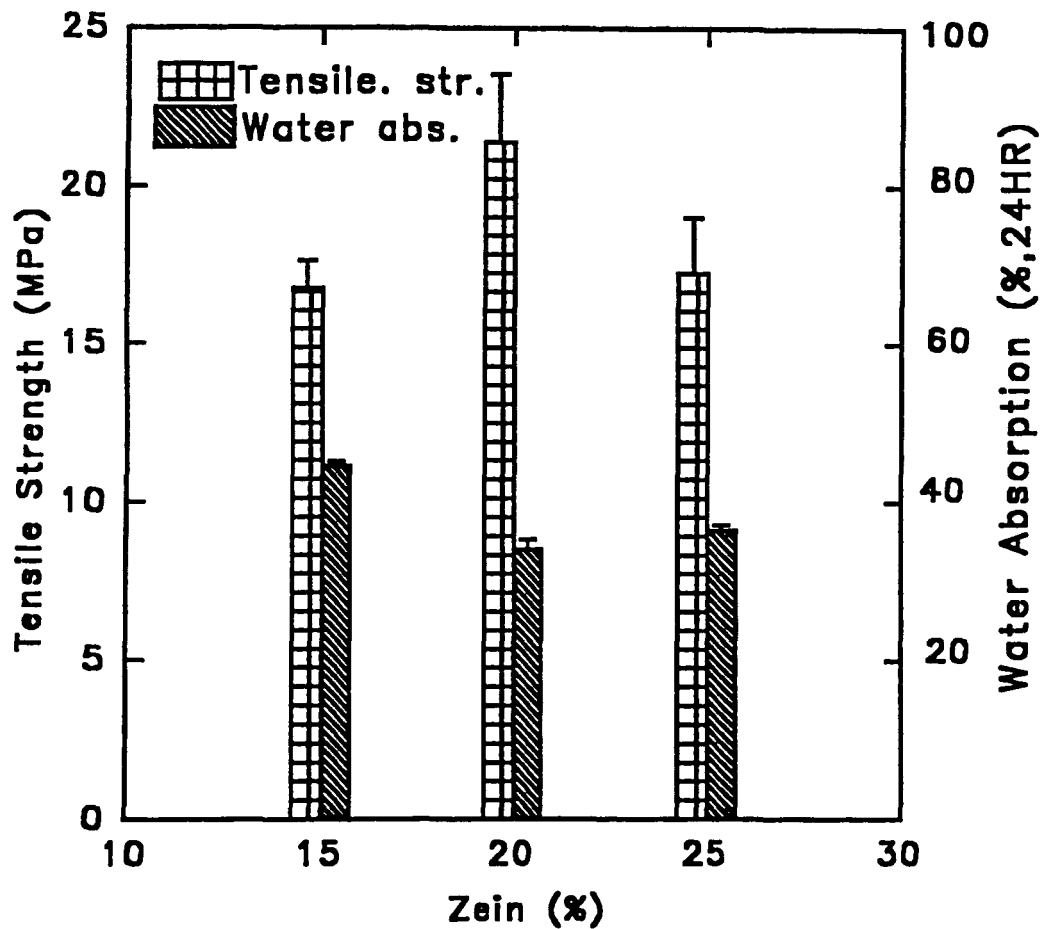


Figure 11. Effect of zein concentration on the tensile strength and water absorption of dialdehyde starch starch and zein (4:1/ w:w) molded with 5% glycerol and 9% moisture content.

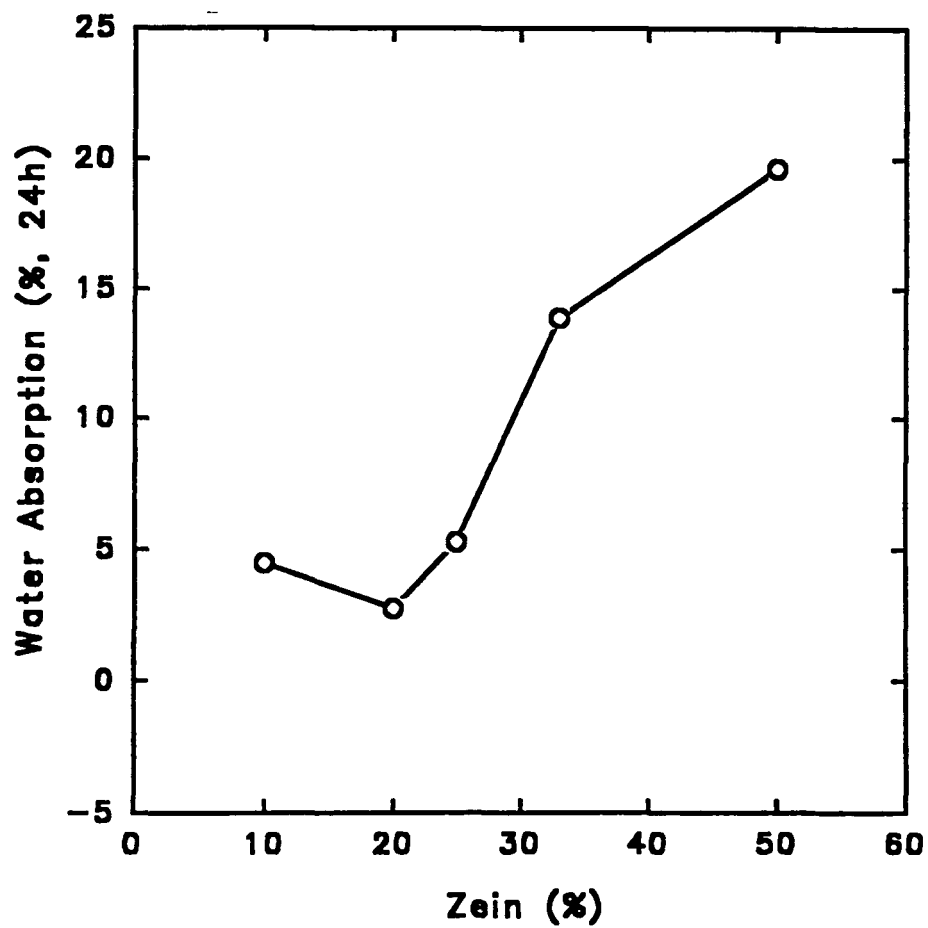


Figure 12. Effect of zein concentration on the 24 hour water absorption of polymeric dialdehyde starch (90% oxidized) and zein (4:1/ w:w) molded 9% moisture content.

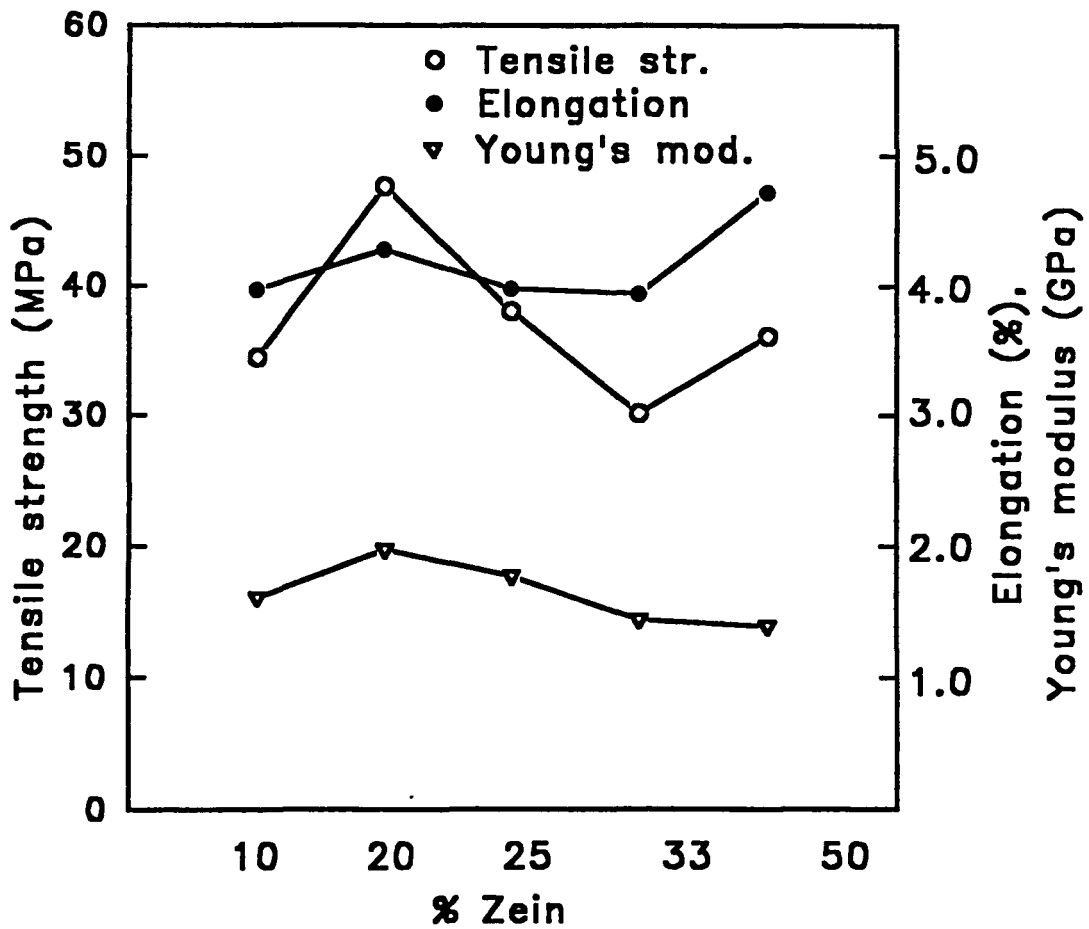


Figure 13. Effect of zein concentration on the mechanical properties of polymeric dialdehyde starch (90% oxidized) and zein (4:1/ w:w) molded with 9% moisture content.

Irganox 1010, was added to the material post-grinding at 1% by weight. The material was molded at 9% moisture and 135°C. Tensile strength was improved by the antioxidant at 42.3 MPa. Water absorption and solubles loss increased only slightly. BHT and sodium bisulfite were solubilized in methanol and incorporated into the material preparation at 1%, 3% and 5%. All samples were compression molded at 9% moisture and 135°C. BHT displayed a minimal effect on the mechanical properties of the specimens at all 3 levels of addition. There was only a slight decrease in coloration of the finished product. However, it is possible that BHT may form a benzoquinone or stilbene quinone in the stabilization of the polymer at high thermal processing, the later of which gives a yellow or brown color (Allen and Edge, 1992). The change in average tensile strength over the 1% to 5% incorporation range was only slight. A subtle increase in elongation was noted. Water absorption measurements also displayed minimal variations. The effect of sodium bisulfite (BIS) was quite the opposite (Figure 14). A drastic decrease in mechanical properties followed the addition of the bisulfite. At the 5% level the bisulfite containing specimen had a tensile strength of only 23.1 MPa compared with 48 MPa of the sample without bisulfite. In conjunction water absorption increased from 8.1% to 33.4% for 1% and 5% bisulfite incorporation, respectively. The difference in water absorption for the BIS compared to BHT shows the importance of the crosslinking reaction toward water resistance (Figure 15). The reactions between aldehydes and proteins have been studied well. A couple of workers have also studied DAS reactions with proteins and amino acids.

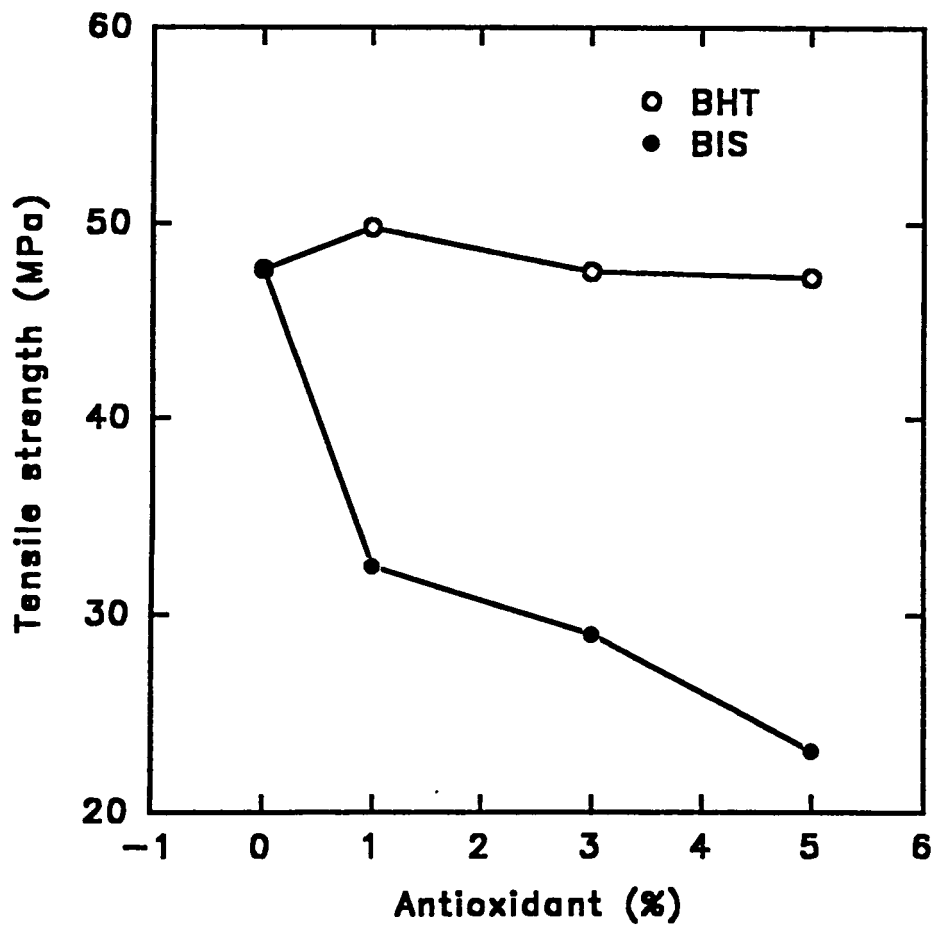


Figure 14. Effect of antioxidants, BHT and sodium bisulfite, on the tensile strength of dialdehyde starch (90% oxidized) and zein (4:1) molded with 9% moisture content.

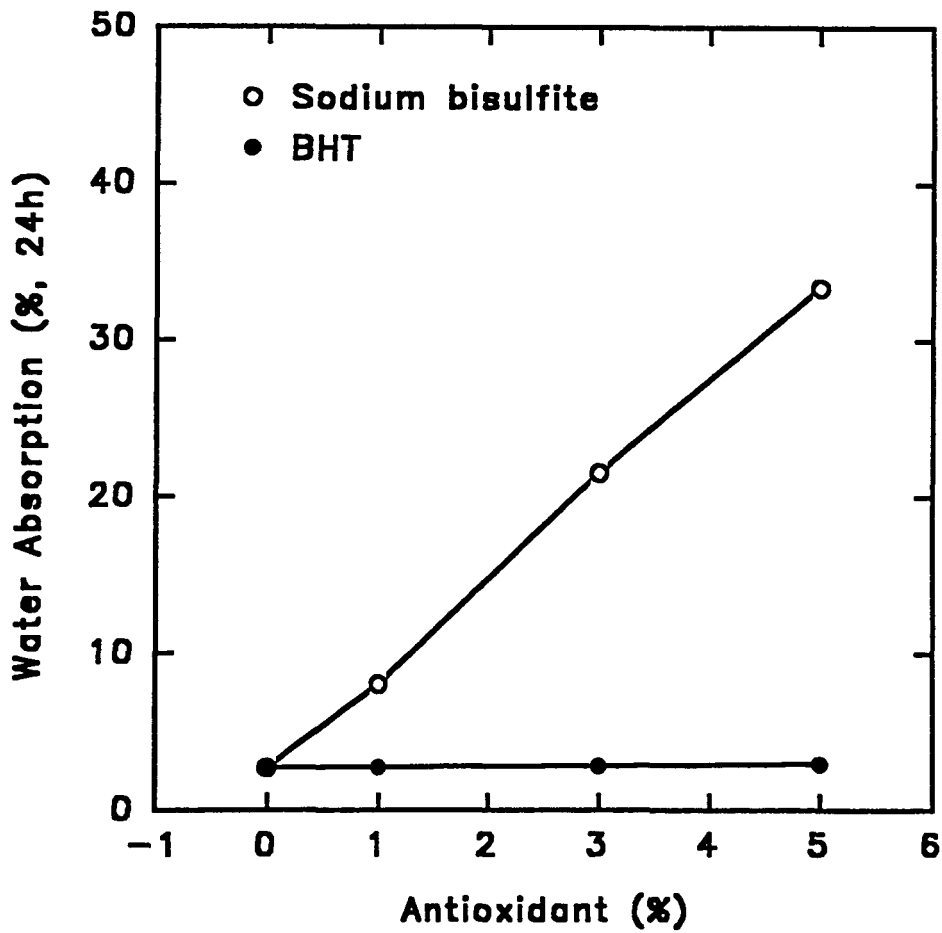


Figure 15. Effect of antioxidants, BHT and sodium bisulfite, on the 24 hour water absorption of dialdehyde starch (90% oxidized) and zein (4:1) molded with 9% moisture content at 135°C.

Sloan (1956) reacted DAS with urea and were able to determine that crosslinks formed between the protein and DAS by determining moles of urea that reacted. Chatterji and Arnold (1965) studied wheat gluten and DAS showing that fewer number of carbonyl groups remained free after the reaction. Sodium bisulfite was used in this study to examine its effect on the crosslinking reaction and on the processing and properties of the plastic produced. The bisulfite groups reacted with the aldehyde groups of DAS which were then no longer free to form crosslinks with the zein. As a result, the bisulfite treated specimens were much lighter in color than those without the bisulfite. The probable formation of Schiff bases was absent, thus the reduction in brown color. The comparison of these two reactions of the antioxidants lends much support to the mechanism of crosslinking reactions that have been proposed.

Stress-strain curves

A representative stress-strain curve for the PDS and zein (4:1/w:w) plastic is shown in Figure 16. The curve deviated from linearity very soon after the load is applied and yielding occurred at a yield stress of 5 MPa. Fracture for these specimens, at an average load of 178.2 (21) Kg, was sudden and without noticeable deformation or necking. The elongation for the specimens was 3.9 (0.5)%. This type of fracture behavior was typical for all samples and specimens tested.

Surface and fracture features

Both the surface and fracture end of the tensile bars were examined

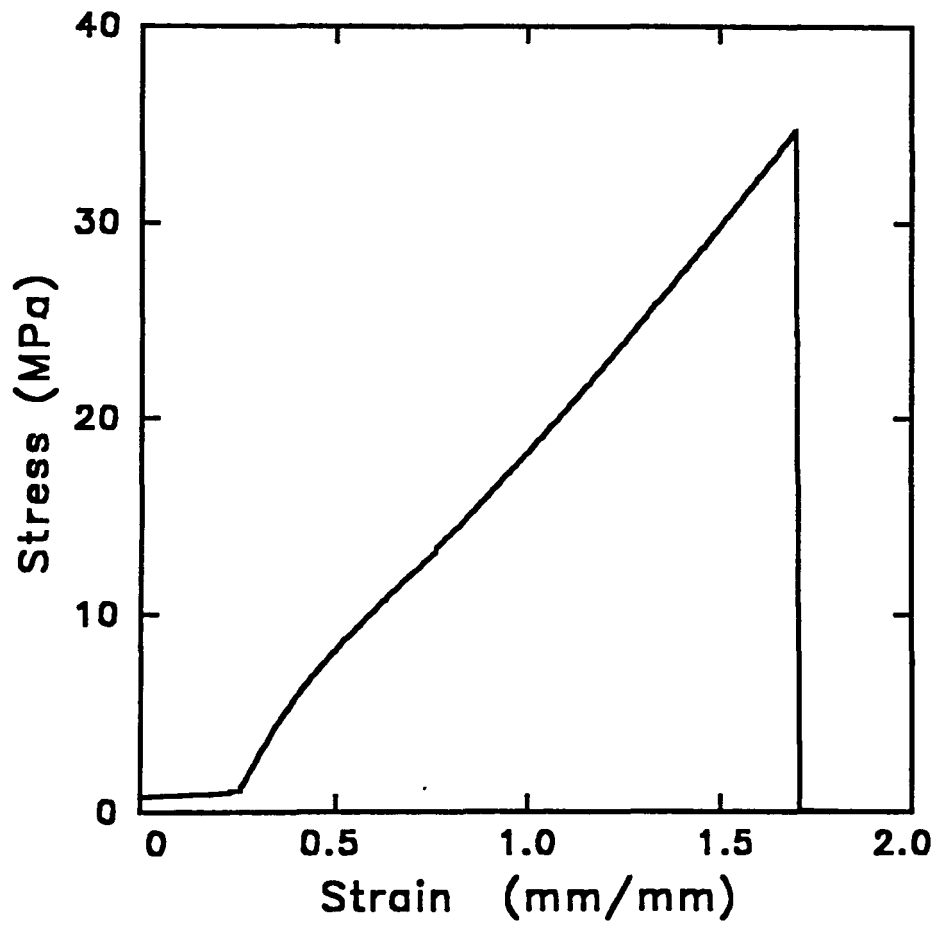


Figure 16. Typical stress-strain curve of DAS and zein plastics.

following mechanical testing. Fractography has the potential to reveal many characteristics about the material. Fracturing begins at flaws in brittle material and identification of these flaws can aid in determining process success as well as potential improvements. Although the dialdehyde starch and zein plastic displayed some yielding, many fracture ends of specimens had the mirror surface region surrounded by a rough surface radiating outwards that is typical for brittle fracture (Figure 17). The dark color of the specimens prevented identification of the flaw. Comparing the surface features proves quite interesting. Polymeric dialdehyde and zein polymers, 1:1 and 4:1 (w:w), show differences on the surface at a magnification of 300x (Figure 18). Specimens were examined after molding and after water immersion and re-drying. The higher zein concentration (50%) displays a rather smooth surface after molding. Following 24 hours immersion in water and redrying, the surface shows numerous holes and pits. The specimen with 20% zein, however, is less homogenous on the surface and shows a mostly smooth surface with some minor rough and porous areas. Cross-sections of the specimens do not display this porosity. The removal of these porous regions from the surface could eliminate cracks or stress concentration zones and enhance the strength of the material. After exposure to water, the 20% zein surface begins to display cracks and was very porous with large pitted areas. The cracks in the material are the artifacts of shrinkage after redrying. The porous regions following water immersion and redrying show the areas where soluble losses occurred. The porous regions may also provide a view of the microstructure of the material,

Figure 17. Scanning electron micrograph of the fracture surface features of a tensile specimen. The stress concentration zone and radial cracks are characteristic of brittle fracture (bar=200 μ m).

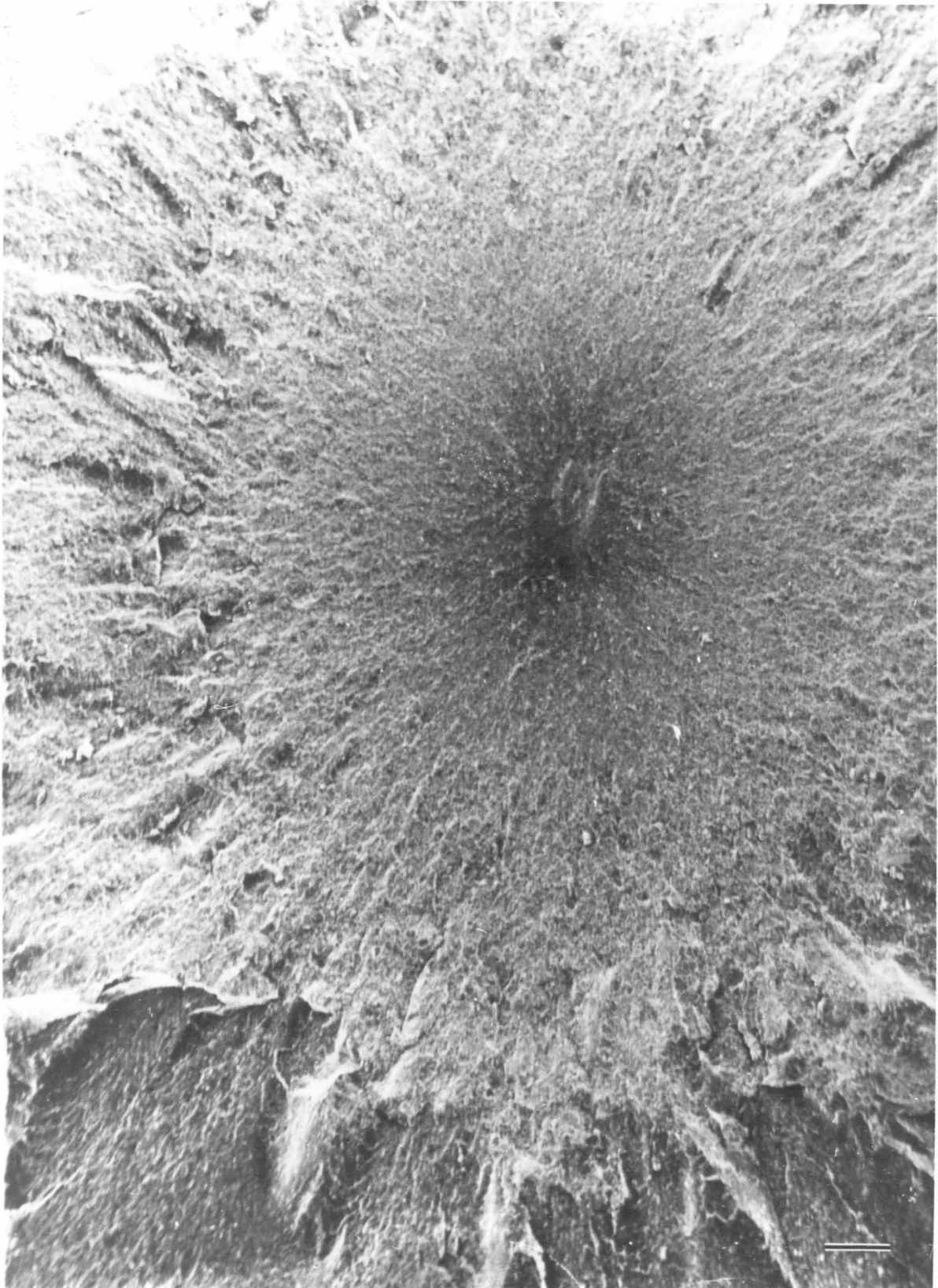
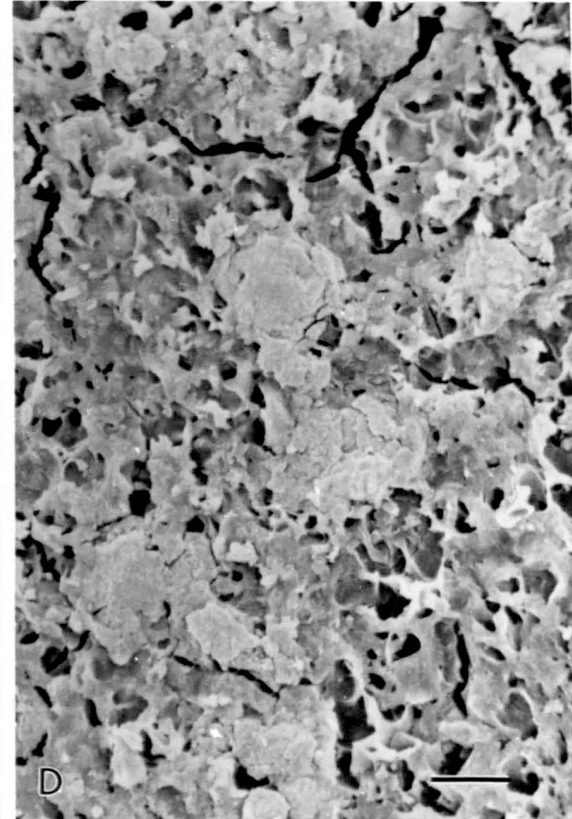
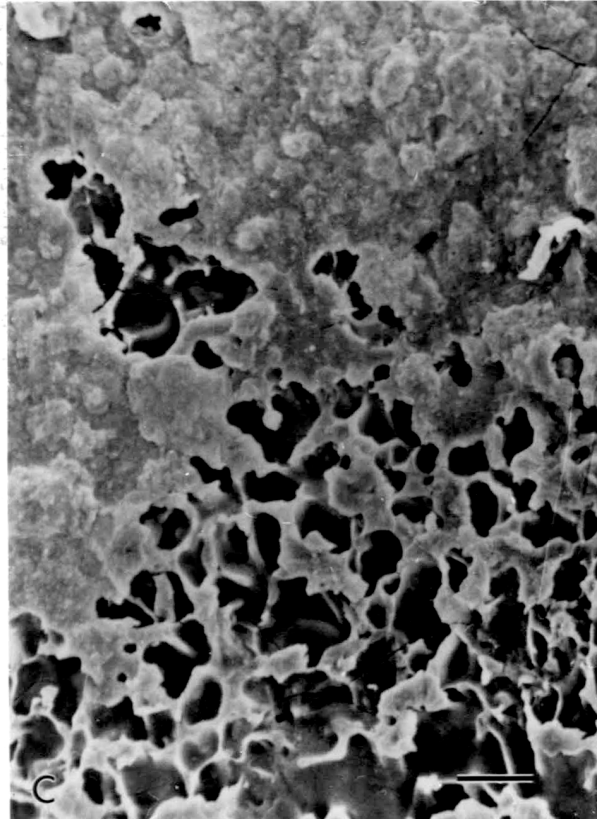
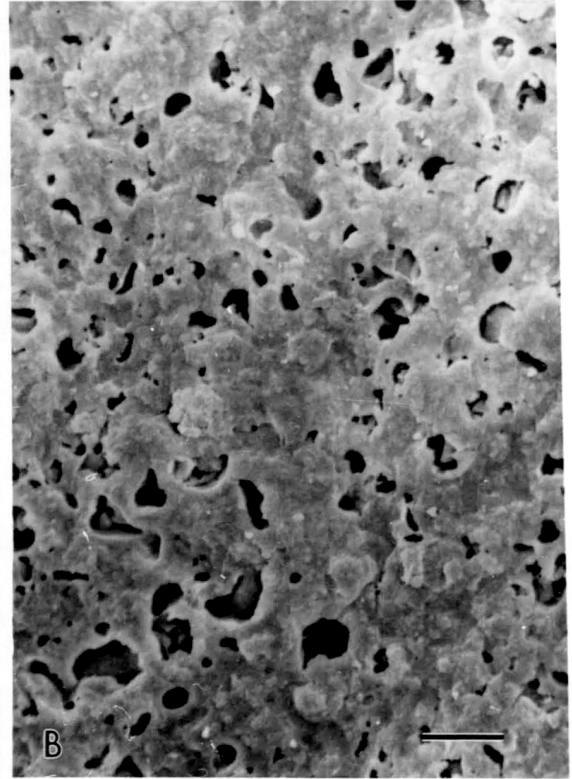
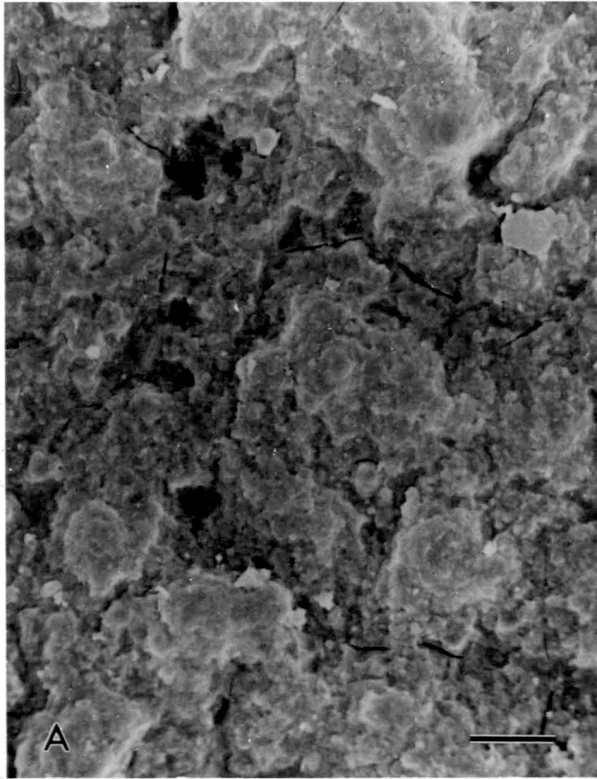


Figure 18. Scanning electron micrographs of the flat surface features of tensile specimens made from different ratios of polymeric dialdehyde starch and zein (1:1 top, 4:1 bottom), A and C = after molding, B and D = after 24 hour water immersion and re-drying (bar=20 μ m).



although the structure could be disturbed in the vacuum process of applying the SEM coating prior to examination. The surfaces of the two examples shown are representative of most specimens and are indicative of the role zein plays in water resistance.

Specific gravity and comparisons to petroleum plastics

The specific gravity of several representative specimens are given in Table 5. The average specific gravity was 1.43 g/cm³ for DAS and zein polymers. The specific gravity was consistent for all samples and did not differ with degree of starch oxidation or zein concentration. The value for corn starch (unmodified) and zein polymer was 1.40 g/cm³. Comparisons to synthetic petroleum-based polymers shows that DAS and zein polymer had a higher specific gravity than either Type III high density polyethylene, general purpose polystyrene or Nylon Type 6 with 0.96 g/cm³, 1.04 g/cm³, 1.14 g/cm³, respectively (Shah, 1984) (Table 6).

Table 5. Representative measurements of specific gravity.

Sample #	Sample description	Liquid	Specific gravity g/cm ³
1	corn starch and zein (4:1)	kerosene	1.40
2	DAS (1% oxid.) and zein (3:1)	mineral oil	1.43
3	DAS (9% oxid.) and zein (3:1)	mineral oil	1.43
4	PDS and zein (3:1)	mineral oil	1.43
5	PDS and zein (4:1)	kerosene	1.43

Table 6. Comparison of dialdehyde starch and zein plastic to petroleum plastics.

Property	High dens. PE type III (HDPE)	Styrene (general purpose)	Nylon type 6 (general purpose)	Dialdehyde starch and zein (4:1)
Specific gravity	0.96	1.04	1.14	1.43
Water absorption (24h) %	<0.01	0.03-0.2	1.7-1.8	2.6-25
Tensile strength MPa	22-29	34-70	65-86	15-49
Elongation %	700-1000	1-2.3	30-220	2-4.3

The higher density of DAS and zein plastic, compared to the petroleum plastics, demonstrated that the molecular chains of the two component polymers are very closely packed. The stiffness and low elongation of the plastic were related to this close packing and subsequent crosslinking. The moderate tensile strength range and minimal elongation of the DAS and zein plastic most resembles that of styrene. The DAS and zein plastic's tensile strengths ranged from 15 MPa to 49 MPa and were therefore in between the ranges of 22-29 MPa and 65-86 MPa of HDPE and Nylon 6, respectively. The water absorption values for the DAS and zein plastic were higher than those given for the petroleum plastics. The water absorption ranged from 2.6% to 25% and could be controlled by varying the amount of crosslinking and processing conditions.

Biodegradation

Studies of biodegradation of starch, starch-based polymers and starch-filled

polymers by a variety of methods have shown that starch is rapidly degraded by microorganisms. Using a sludge-waste water system, Raghavan et al. (1993) demonstrated that a 1 g starch sample placed into the inoculated solution was 95% degraded in 4.2 days. By measuring CO₂ evolution, biomass increase and soluble starch they were able to determine that 60% of the carbon was accounted for by CO₂ and 35% of the carbon was in the biomass. Results of the 180 day soil degradation study show a similar CO₂ evolution percentage for the corn starch and DAS and zein plastics at the point of test stoppage. Figure 19 displays the results graphically while Table 7 provides the numerical data for all samples.

Table 7. Totals for respirometric measurements after 180 days

Sample Name	Sample description	180 day total carbon (mg)	Degradation (%)
CS	10 g corn starch	3264.50	63.5
PDS	10 g polymeric dialdehyde starch	870.23	9.6
Zein	10 g Zein	4266.97	63.1
P90	10 g polymeric dialdehyde starch and zein (3:1) polymer	2253.08	37.3
P5	10 g dialdehyde starch (5% oxidized) and zein (3:1) polymer	3355.61	60.1
P1	10 g dialdehyde starch (1% oxidized) and zein (3:1) polymer	3095.14	54.7
None	Control, no polymer added	442.69	---

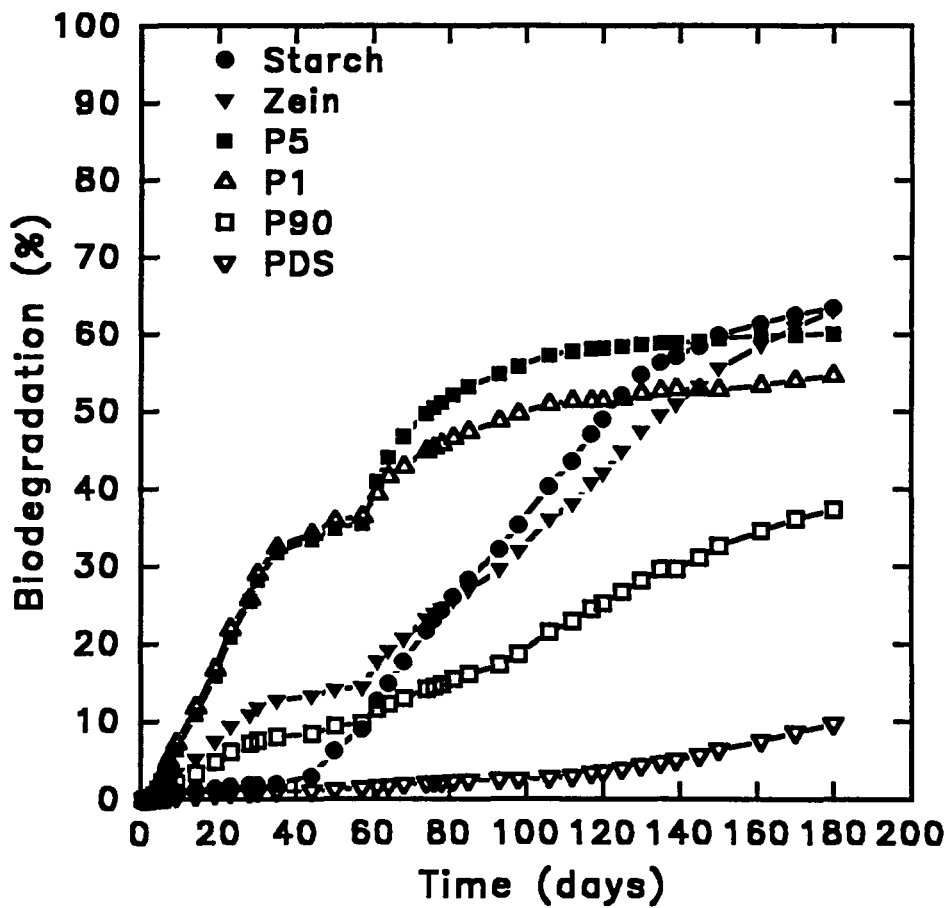


Figure 19. Biodegradation represented as percentage of carbon evolved as CO_2 in soil respirometers over 180 days for native starch and zein, polymeric dialdehyde starch (PDS), and ground DAS and zein plastic. The plastics were molded from dialdehyde starch of various oxidation levels and zein (3:1) with 9% moisture at 135°C . P90= PDS and zein, P5= DAS (5% oxidized) and zein, P1= DAS (1% oxidized) and zein.

Both corn starch and zein showed good biodegradation; reaching 63.5% and 63.1% carbon evolved as CO₂, respectively. However, the corn starch reactors did not begin to show any degradation until after day 30. DAS and zein plastics (3:1 w/w) were also shown to be biodegradable. The plastics samples were labeled P90, P5 and P1, with the number following the letter P representing the percentage of starch oxidation. P1 and P5 mineralization reached 54.7% and 60.1% by the 180th day. P90 exhibited limited degradation at 37.3% mineralization. If 35% of the carbon in these samples went to biomass then the total biodegradation would reach or exceed 90% for all but the PDS and P90 samples.

For the DAS and zein compression molded plastics the gelatinized starch and denatured protein served as rich carbon and nitrogen sources for the microbial population growth. In the dialdehyde starch and zein plastics, zein made up 25% of the polymer by weight but accounted for 32.6% of the carbon in the material. Samples P5, P1 and zein showed the most rapid rate of CO₂ evolution during the first 30 days. It is evident from these results that nitrogen availability greatly enhanced the initial rate of biodegradation. The lack of CO₂ evolution for corn starch during the first 30 days is believed to be due to the size of the sample relative to the amount of soil. A 10 g sample of starch in 100 g of soil could possibly absorb enough moisture to significantly reduce the water activity of the environment and thus prohibit microbial growth. This is supported by the fact that CO₂ evolution began to increase after the first addition of water. In terms of the microorganisms present, it is also possible that potting soil has an indigenous

population that are lignin or cellulosic degrading and thus had to adapt to the starch. In addition, the starch was in the form of granules which are more impervious to enzymatic attack. Polymeric dialdehyde starch showed very limited degradation which was related to the modified structure of the product.

Biodegradation under these conditions with no inoculum of microorganisms is assumed to be harsher than other testing methods using sewage or compost which have a large number of natural flora. The mineralization of the dialdehyde starch and zein in less than 6 months in the limited soil environment is therefore noteworthy considering its resistance to moisture.

CONCLUSIONS

The use of polymeric dialdehyde and zein has produced a plastic with a much improved water resistance over other starch-based plastics. The use of plasticizers neither improved tensile properties nor water resistance for compression molded product. Glycerol had a hygroscopic effect on the specimens at all levels of incorporation. The use of the hydrophobic protein allowed for a product which retains its shape upon exposure to moisture. However, increased zein concentration over 20% did lead to greater water absorption. Addition of antioxidants may improve the color of the material. The polymer has been shown to be degradable in an aerobic soil environment. The advantages of water resistance and improved tensile strength of this plastic over other starch-based technologies may lead to numerous industrial applications.

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