

Properties and Microstructure of Plasticized Zein Films

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ABSTRACT

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A new method for preparation of zein films involving plasticization of zein with oleic acid to form an intermediate moldable resin was presented. The resin was stretched over rigid frames to form thin membranes that were set in flexible films. The objective of the study was to investigate the effect of film preparation method on film properties. Tensile properties, microstructure, and thermal behavior of zein films plasticized with oleic acid were investigated for films prepared by conventional casting from ethanol solutions and by stretching of plasticized resins. Cast films were stiff and brittle, whereas resin films showed more

flexibility and toughness. Differential scanning calorimetry thermograms of cast films indicated phase separations were generated when heated that were not observed for resin films. Microstructure images showed a higher degree of structure development and orientation in resin than in cast films. Glass-transition temperatures of resin films were measured at -94 and 104.4°C , indicating the film remained flexible through a wide temperature range. Resin film flexibility and toughness were attributed to effective plasticization that led to fiber formation and orientation.

Environmental concerns about use of nondegradable plastics for packaging and disposable consumer goods has led to intensification of research to develop biodegradable packaging materials. Several biological polymers have drawn research attention because of their film-forming abilities. Examples include starch, the fermentation products poly-(3-hydroxybutyrate)-co-(3-hydroxyvalerate), and synthetic polymers of lactic acid (Glover 1993, McCarthy-Bates 1993, Moore 1993, Albertsson and Karlsson 1994, Andreopoulos and Theophanides 1994, Anonymous 1995, Krochta and de Mulder-Johnston 1997). Zein, the prolamine of corn, was investigated for its potential use as a structural material in packaging applications (Lai et al 1997). Zein, abundant in corn gluten meal, an underutilized by-product of the corn-refining industry.

Zein is located in small round particles, 1–2 μm in diameter, called protein bodies in maize endosperm. Three distinct fractions, α , β , and γ zein, have been identified by differential solubility in aqueous alcohol solutions (Esen 1987). Commercial zein is a mixture of proteins with different molecular sizes, solubility, and charge (Turner et al 1965). Customarily, zein is extracted with warm aqueous alcohol and precipitated with chilled water. Commercial preparations usually contain only the α fraction of zein (Matsumura et al 1997). α -Zein is a polypeptide with a molecular weight between 21,000 and 25,000. A structure containing nine α -helix regions was proposed for α -zein by Argos et al (1992) based on hydration potential, polarity, and secondary structure. Commercial zein contains high concentrations of α -helix structure in alcohol-water solutions (Danzer et al 1975). Earlier work by Timasheff (1970) indicated that certain solvents, such as ethanol, may enhance the α -helix structure of zein. Conformational changes induced by solvent treatment have been studied by Augustine and Baiaru (1986, 1987).

The film-forming properties of zein have long been recognized (Reiners et al 1974). Zein is used in the formulation of coatings for nuts, confectioneries, and pharmaceutical tablets. It functions as an oxygen, lipid, and moisture barrier (Winters and Deardorff 1958, Kanig and Goodman 1962, Mendoza 1975, Andres 1984). Interest in the development of edible and biodegradable films (Krochta and de Mulder-Johnston 1997) has driven research on the formation of free-standing zein films (Guilbert 1986; Aydt and Weller 1988; Aydt et al 1989; Gennadios and Weller 1990; Gennadios et al 1993, 1994; Wu 1995).

Preparation of zein films generally involves casting alcohol solutions on inert, flat surfaces. Formed films are peeled off after the solvent has evaporated (Gennadios and Weller 1990). Films also have been prepared from acetone solutions (Yamada et al 1996). Zein films are brittle, and thus, plasticizers are needed to improve their flexibility. Kanig and Goodman (1962) added oleic acid to casting solutions, Mendoza (1975) and Aydt and Weller (1988) used glycerol as plasticizer, and Wu (1995) used lactic acid. An alternative method to prepare zein films that involves plasticization of zein by forming an emulsion with oleic acid followed by precipitation of the protein-lipid mixture to form a soft moldable resin was reported by Lai (1997). The plastic resin was stretched over rigid frames to obtain thin membranes that set into flexible films.

The objective of this study was to study the effect of film preparation method on the properties of zein films plasticized with oleic acid. Mechanical properties, microstructure, and thermal behavior of zein films prepared by casting from solutions and stretching of resins were investigated.

MATERIALS AND METHODS

Zein, regular grade, was obtained from Freeman Industries Inc. (Tuckahoe, NY). Other materials included oleic acid, $\text{C}_{18:1}$ 90% (Aldrich, Milwaukee, WI); ethyl alcohol (Midwest Grain Products, Pekin, IL); and $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (EM Science, Gibbstown, NJ).

Cast films were obtained by dissolving zein to 16% (w/v) in warm (75°C) aqueous ethanol at 75%. Oleic acid was added to the solution at 0.5 g of oleic acid/g of zein and stirred for 10 min. The emulsion was cooled to room temperature and cast on a nonstick surface. Films were allowed to dry at room temperature and ambient relative humidity and peeled off after 24 hr. Resins were obtained from zein-oleic acid emulsions prepared as described above and precipitated by the addition of a sevenfold volume of cold (5°C) water. Resins were collected as soft solids and kneaded in a Brabender Farinograph (C. W. Brabender Co., Hackensack, NJ). Films were drawn from the moldable mass and stretched over circular container rims (16 cm dia). Films were allowed to dry at room temperature and ambient relative humidity. Moisture content of films was determined from moisture sorption isotherms (Lai and Padua, *in press*).

Tensile measurements for tensile strength, elongation, Young's modulus, and toughness were performed with an Instron testing system (model 1011, Instron Engineering Corp., Canton, MA). Samples were cut from the central region of zein films into dumbbell-shaped specimens and preconditioned for 48 hr at 25°C and 50% rh inside desiccators containing saturated solutions of calci-

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um nitrate (Aydt et al 1991). A micrometer was used to monitor film thickness. Averages of 10 measurements were recorded. Testing protocols followed ASTM Standard D638-91, type I (ASTM 1994). Film strips were placed in the pneumatic grips of the testing machine, which were set at an initial separation of 115 mm. Crosshead speed was set at 5 mm/min. At least 14 specimens for each treatment were tested.

Scanning electron microscopy (SEM) was used to examine the surface of zein-oleic acid films. Samples were mounted directly on stubs with double-coated carbon-conductive tabs (Ted Pella Inc., Redding, CA) and coated with 60% gold and 40% palladium with a 35 mA current in a sputter coater (Polaron SEM Coating Systems, Mountain View, CA) for 1 min. Samples were observed with a scanning electron microscope (Zeiss DSM 960, Thornwood, NY) with an accelerating voltage of 5, 7, or 10 kV.

An atomic force microscope (AFM) (Explorer model, Topo-Metrix, Santa Clara, CA) also was used to observe the surface of zein-oleic acid films. AFM images were obtained with a 14.9- μ m air scanner on sample surfaces in constant force mode.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer DSC-7 (Perkin-Elmer Cetus, Norwalk, CT) calibrated with indium. An empty pan was used as reference. Films were freeze-dried and kept in a desiccator before scanning. Weighed samples of 20–25 mg were placed in aluminum pans and pressure-sealed. Samples were scanned from –20 to 175°C at 10°C/min. Additional scanning at very low temperature was performed from –120 to 20°C with liquid nitrogen. Glass-transition points were determined by finding the midpoint of the change in the heat capacity of films.

The two-tail Students' *t* test was used to analyze the difference between means of tensile test data for cast and resin films. A confidence level of 95% ($P < 0.05$) was used.

RESULTS AND DISCUSSION

Films prepared by stretching zein resins had an average thickness of 0.040 ± 0.0059 mm. Resin films were translucent to transparent, smooth surfaced, flexible, pliable, and creased when folded. Cast films had an average thickness of 0.092 ± 0.0093 mm. Cast films were translucent, had a glossy surface on one side and a dull surface on the other, and were bendable, but they did fracture when folded. Moisture content was 4% for resin films and 6% for cast films.

Tensile Properties

Typical stress-strain curves for cast and resin zein films are shown in Fig. 1. Zein was plasticized with oleic acid at the same mass

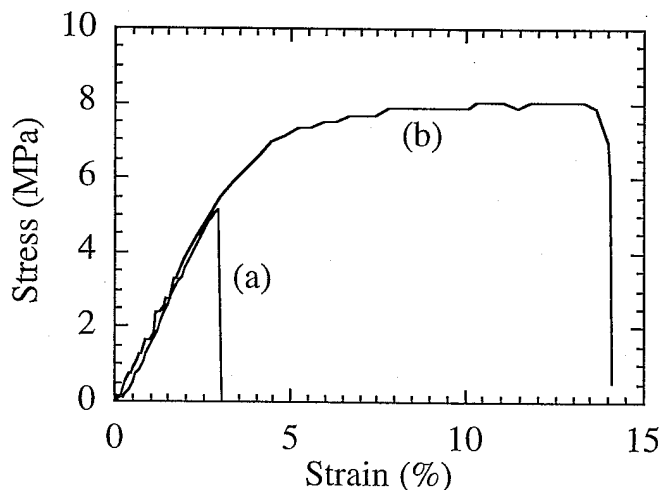


Fig. 1. Typical tensile-strain curves of zein films prepared from casting solutions (a) and resins (b).

ratio (0.5 g of oleic acid/g of zein) for both types of film. Cast films were brittle and exhibited an essentially linear relationship between stress and strain. Resin films were tougher than cast films. Tensile properties of cast and resin films are summarized in Table I. Significant differences ($P < 0.05$) were found between cast and resin films for tensile strength, strain at break, elastic modulus, and material toughness. In general, resin films showed better mechanical properties than cast films. Resin films had higher ultimate tensile strength and increased percent elongation. The elastic modulus was determined from the slope of the stress-strain curve, for which only the linear region was considered. Elastic moduli of resin films was lower than those of cast films. Toughness, calculated as the energy required for breaking divided by the volume of specimen tested, was much higher for resin films due to increased tensile strength and percent elongation.

Plasticizers were used to depress the glass-transition temperature of polymers and lower their modulus. Plasticizers dissolved in polymer, separating chains from each other and facilitating chain movement (Sperling 1992). Tensile tests suggested that oleic acid was a more effective plasticizer in resin films than in cast films. Although cast films remained largely stiff and brittle, the low modulus of resin films indicated effective plasticization.

Microstructure

Differences in film morphology were investigated by SEM. Micrographs of resin films (Fig. 2A–C) show aligned protein fibrils embedded in a continuous material, arrangements of oriented ribbon-like structures of zein, and entanglements of ribbon-like strands of zein, respectively. The three types of morphology were observed in the same sample. Zein fibers similar to those shown in Fig. 2A were observed by Lawton (1992), who related them to the development of viscoelasticity in zein-starch doughs. The effect of stretching was apparent in Fig. 2B, where orientation was induced by applied stress. Oriented morphology was observed in the middle region of films along the direction of drawing. The seemingly entangled morphology in Fig. 2C may be the result of nonhomogeneous stretching, which was observed toward the rim of films. The nonuniformity of orientation might be related to stress gradients in the sample.

Zein film formation mechanisms are not well understood. However, a study on wheat dough (Orth et al 1973) reported the formation of glutenin fibers in bread dough and related them to gluten elasticity. The same report noted that glutenin from different varieties of wheat exhibited different morphology, i.e., fibrous and ribbon-like or filmy structures. Fibrous structures in bread dough were thought to be responsible for dough elasticity, whereas less elastic glutenin from durum wheat was characterized by flat ribbon-like structures and filmy material. Gluten also fibrillated and showed orientation when drawn. By stretching films of vital wheat gluten and observing them under crossed polarizing light, Slade et al (1988) found oriented microcrystalline microfibrils with diameters near 0.5 μ m embedded in a viscous, orienting amorphous matrix (Levine and Slade 1990).

Zein has been described as a globular protein in many systems. Using a laser scanning electron microscope, Yamada et al (1996) found zein molecules as aggregates of small globules in aqueous ethanol solution. However, the globular particles observed by

TABLE I
Tensile Properties of Zein Films Prepared from Casting Solutions and Stretched Resins^a

Preparation Method	Tensile Strength (mPa)	Strain Break (%)	Elastic Modulus (mPa)	Toughness (mPa)
Cast	6.81 (1.89)	3.18 (0.86)	317.12 (23.18)	0.081 (0.03)
Resin	8.68 (1.03)	11.89 (3.14)	267.19 (46.55)	0.829 (0.19)

^a Values in parentheses indicate standard deviation.

Yamada et al (1995) were different from the fiber-like structures in the zein-starch dough system observed by Lawton (1992). The current morphology studies of zein resin films suggest that after precipitation from alcohol solutions and mechanical treatment zein particles merge with each other to form fibrillar structures. However, further research is necessary to elucidate the fiber formation mechanism.

Figure 3 shows micrographs of cast films. The glossy side of films in Fig. 3A were featureless, except for pinholes that may come from the cast-supporting surface. The reverse side (Fig. 3B) showed deposition of globular formations in an irregular pattern.

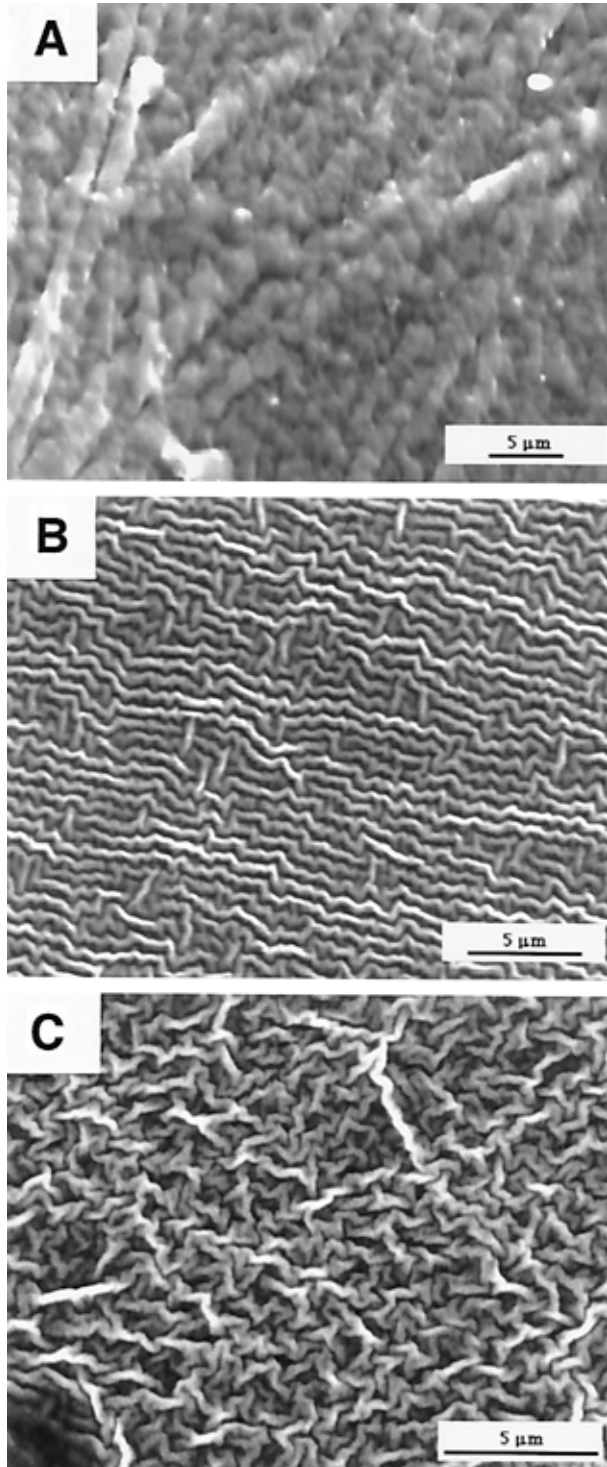


Fig. 2. Scanning electron micrographs of zein films prepared from resins, showing structural features: **A**, aligned protein fibers; **B**, oriented protein ribbons; and **C**, protein ribbon entanglements.

The glossy side of films is thought to consist of zein deposited from the casting solution during the drying process. Globules on the reverse side of films are believed to be oleic acid separated from the zein matrix by the evaporating solvent. However, further research is necessary to determine the composition of film layers. The heterogeneity of cast films plasticized with fatty acids has been observed by several researchers (Kester and Fennema 1989, Vojdani and Torres 1989, McHugh and Krochta 1993, Torres 1994, Park et al 1996). Distinct fatty acid layers were found in cast films due to the instability of the emulsions formed between fatty acids and proteins or polysaccharides. Irregularity of puckered zein cast films also was observed by Foulk and Bunn (1994).

Structure development and orientation of stretched resin films also was observed by AFM in Fig. 4A. AFM images of cast films presented in Fig. 4B show uniform deposition of components with no salient structural features. Microstructure images of resin and cast films suggests that the increased toughness of stretched resin films over cast films results from the formation of oriented fibrils and ribbon-like structures when the resin is mechanically worked and stretched. Cast films appear to show phase separation between zein and oleic acid and no evidence of structure development. Uniform deposition of zein in cast films may explain their surface gloss.

Differential Scanning Calorimetry

DSC thermograms for resin and cast films are shown in Fig. 5. Sharp first-order transition peaks were found in heating and cooling scans of cast films. Peaks observed at 7.1°C were attributed to

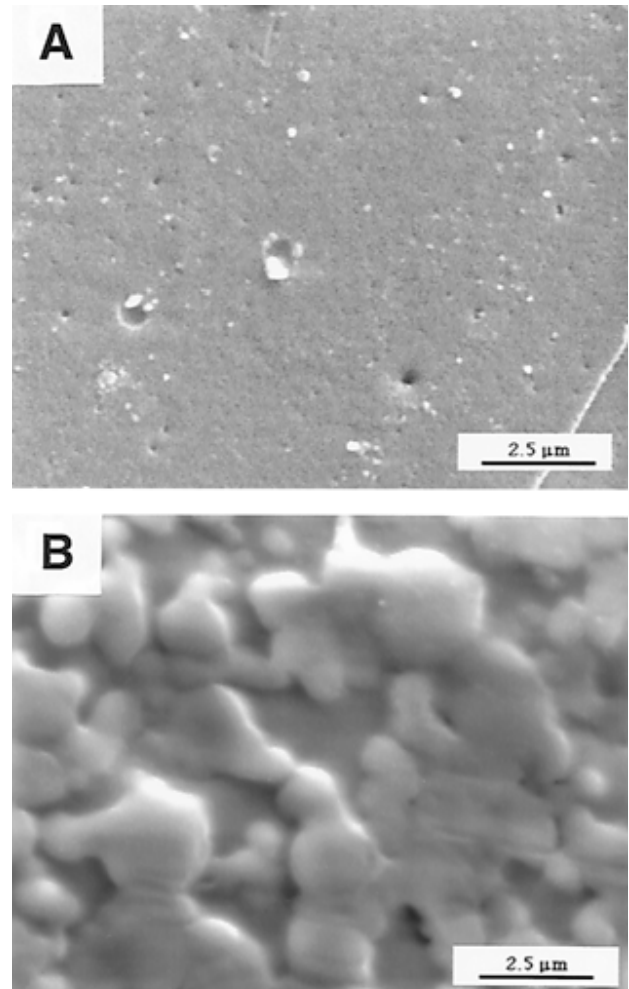


Fig. 3. Scanning electron micrographs of zein films prepared by casting of ethanol solutions: **A**, surface of the lower layer of film; and **B**, globular deposits on the upper layer of film.

melting of oleic acid, and those at -0.9 and -4.3°C were attributed to crystallization of oleic acid (Kobayashi et al 1986, Suzuki and Ogaki 1985, Sato and Suzuki 1986). Resin films showed no first-order transitions for the temperature range scanned. Cast film

thermograms indicated separation of oleic acid from zein when heated. Phase separation may explain the brittleness of cast zein films. Resin film thermograms suggest that oleic acid and zein remained a homogeneous material throughout the cooling and heating cycle. Preventing phase separation in resin films leads to increased film toughness by allowing microstructure development and orientation. High-temperature glass transitions for resin and cast films were observed at 104.4 and 101.8°C , respectively. The similarity between the gelatinization temperature (T_g) values for cast and resin films suggests that thermal behavior at high temperatures was not affected by the plasticization method.

Low-temperature thermograms of resin film showed a glass transition at -94°C (Fig. 6). Low-temperature T_g values for wheat glutenin and gliadin fractions were studied by Hosney et al (1986), Cocero and Kokini (1991), de Graaf et al (1993), and Roos (1995). The observed low T_g temperature for zein resin films in this study was in reasonable agreement with the prediction of de Graaf et al (1993) for glutenin plasticized with water at the same molar fraction. Cherian et al (1995) studied the thermochemical behavior of cast gluten-glycerin-sorbitol films and found a glass-transition temperature of -42°C . The low-temperature T_g of zein resin films was perhaps due to transitions in an amorphous oleic acid phase.

CONCLUSIONS

Forming processes affected mechanical and thermal properties of zein films. Films cast from ethanol-water solutions showed little elongation, resulting in stiff, brittle materials. Films drawn from resins showed a higher elongation percent and produced tougher and more flexible films. Differences in mechanical properties between the two types of films were attributed to microstructure development and orientation. Stretched resin films formed fibers and ribbon-like structures in contrast to deposition of solids without distinguishable patterns in cast films. DSC thermograms of resin films missed the melting and crystallization peaks for oleic acid present in cast film thermograms. This suggested increased interaction between oleic acid and zein in the resin films, which possibly led to higher structural organization. The T_g temperature of resin films was measured at -94°C , indicating the film remained flexible at frozen storage temperatures.

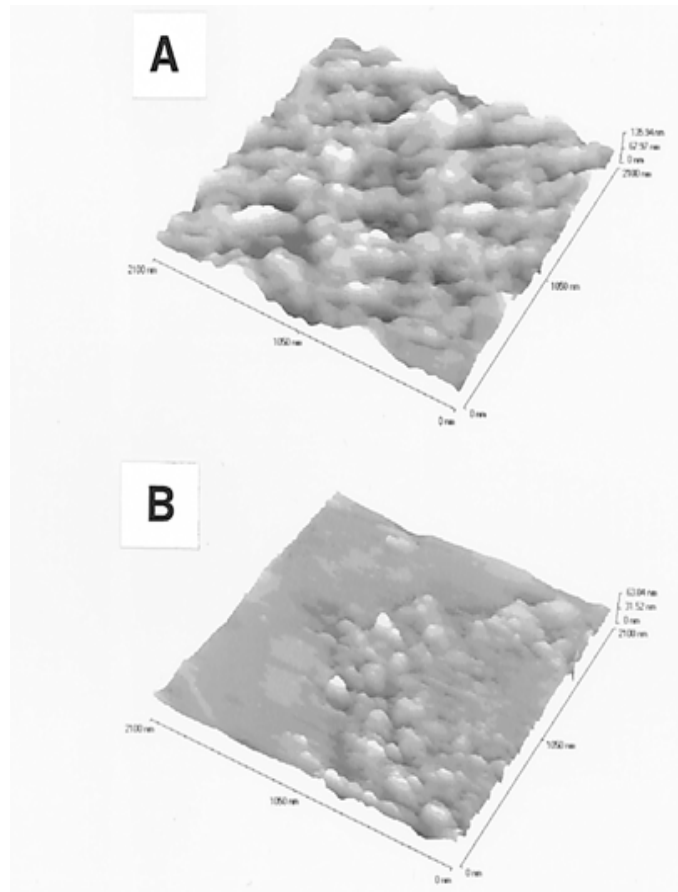


Fig. 4. Atomic force surface micrographs of zein films prepared from resins (A) and casting solutions (B).

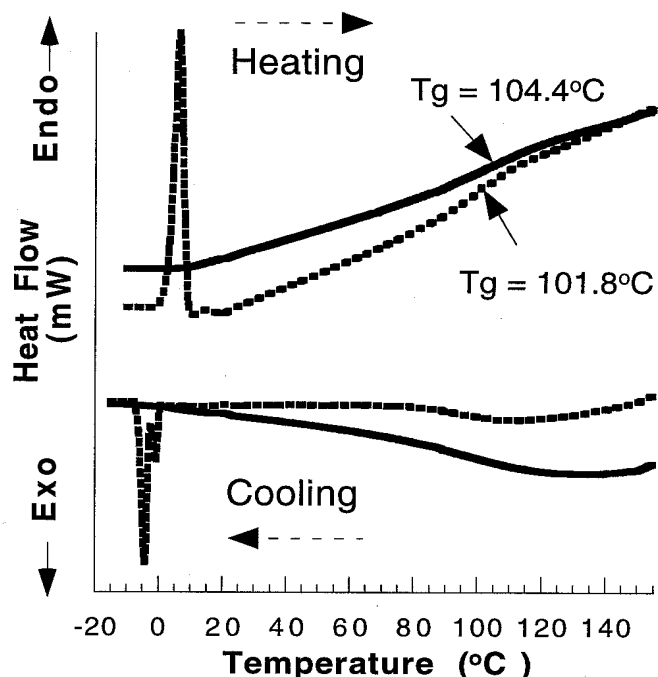


Fig. 5. Differential scanning calorimetry thermograms of zein films prepared from resins and casting solutions. Solid lines represent thermograms of resin films; dotted lines represent thermograms of cast films.

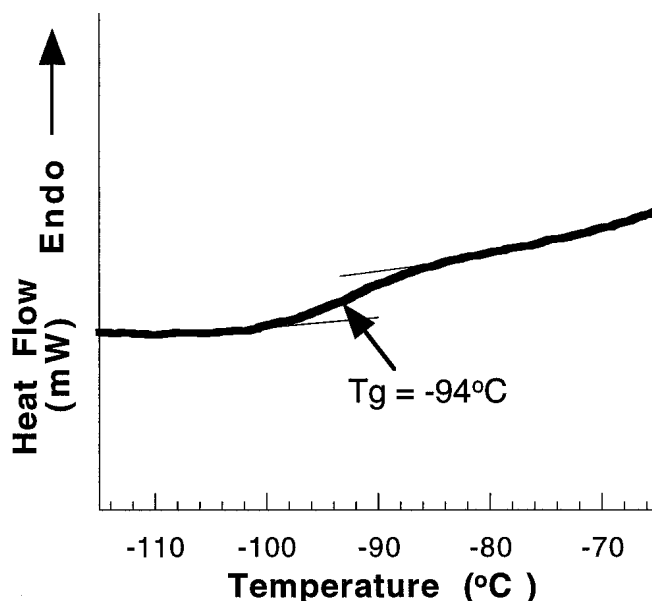


Fig. 6. Differential scanning calorimetry thermograms of zein resin films performed at low temperatures.

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