

Effect of Polyolic Plasticizers on Rheological and Thermal Properties of Zein Resins

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A B S T R A C T

One of the zein film forming methods is thermomoulding by hot press. Pure zein film is very brittle and plasticizers can improve its mechanical and film making properties. In this research, polyols (glycerol, sorbitol, and manitol) at three levels (0.5, 0.7 and 1 g/g of zein resin) were used separately as a plasticizer and for determining their plasticization effectiveness the rheological and thermal properties of zein resin samples were studied. Sorbitol and glycerol had good plasticizing effects and could decrease viscoelastic modulus of zein resin considerably, but manitol was not as effective as them. Resins containing manitol remained rigid and had unfavorable chalky appearance. The effects of plasticizers on thermal properties of resin were investigated by DSC at -100 to 150°C. No crystallization and melting peaks related to zein resin and plasticizers were observed. Thermograms showed that polyolic plasticizers and zein resin remained a homogeneous material throughout the cooling and heating cycles. As well as, at glass transition temperature, there is not any significant difference among zein resins containing various plasticizers. The T_g of different resins were at 60 -70°C. This was probably due to similar molecular weight of the selected polyols. In addition, after initial decreasing of T_g of resin, subsequent increase of plasticizer levels did not cause considerable reduction in it.

Key Words:

zein resin;
edible film;
polyolic plasticizer;
viscoelastic;
mechanical properties;
thermal properties.

INTRODUCTION

Over the past 30 years, considerable research effort has been devoted to the usages of edible films and coatings for food packaging [1,2]. An edible coating or film is defined as a thin, continuous layer of edible material formed or placed on or between foods or food components. The aim of recent reserches is to produce natural

biopolymer-based coating materials with specific properties, which may be eaten together with the foods. Their function is to provide a barrier to mass transfer (water, gas, and lipids), serve as a carrier of food ingredients and additives (pigments, flavours, antioxidants, and antibiotics), and/or provide mechanical protection [1-3]. As

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well as, the increase of nondegradable synthetic material usage in food packaging has enhanced environmental pollution in the world and plastic recovering methods have several defects and problems. Replacing conventional synthetic packaging with biodegradable biopolymers, in certain applications, can be a way to reduce the usage of non-renewable resources and decrease the wastes through their biological recycling to the biosystem [3,4].

Zein (prolamin of corn) is located in small round particles, 1-2 μm in diameter, called protein bodies in maize endosperm, and it constitutes 47% of the total protein in corn [5,6]. Zein is produced commercially from corn gluten meal (CGM). CGM is a co-product material that is obtained during starch production from corn by ethanolic extraction. CGM has low price and is used mainly for animal feeding [7,8]. However, zein is an expensive product and thus extraction of zein and production of biodegradable film from it would produce important economic benefits [5,7,9]. Zein has excellent film forming properties and can be used for fabrication of biodegradable films. Zein biofilm is formed through the development of hydrophobic, hydrogen, and limited disulfide bonds between zein chains [3-10].

Cuq et al. [1] classified the technologies used for preparation of protein-based materials in two broad groups: (i) wet (or solvent) processes based on the dispersion or solubilization of proteins in a solvent medium and (ii) dry processes based on the thermoplasticity of proteins at low moisture content. The wet process is generally preferred to form edible preformed films, or coatings of food products by dipping, brushing, or spraying of protein solution. Films were also prepared by a combination of wet and dry processes involving the preparation of a mouldable resin of zein and plasticizers which was later formed into a film by drawing or heat process [11,12]. Resin film forming method can be an alternative for wet method due to better mechanical and barrier properties [10-12].

Zein resin is a viscoelastic material and design of its processing operations requires accurate data on the rheological properties of its film-forming property. Viscoelastic properties of zein resin can also show degree of plasticization of zein biopolymer by various plasticizers. Viscoelastic properties of materials are generally measured by transient (stress relaxation and

creep tests) and dynamic methods. The dynamic test is performed with applying a small sinusoidal oscillatory shear strain (or stress) and measuring the resulting stress (or strain).

Protein-plasticizer interactions have been investigated by differential scanning calorimetry (DSC). Madeka and Kokini [13] studied thermal properties of cereal proteins including gliadin, glutenin, and zein and generated physical state diagrams based on DSC measurements and dynamic rheological properties. They reported that the first few percentages of water resulted to a dramatic decrease in the glass transition temperature (T_g) of zein and gliadin. However, the effect decreased significantly once moisture content increased to ~15%. Glass transition temperature (T_g) of polymer diminishes with increasing of the low molecular plasticizer levels in film matrix and decreases with decreasing of the molecular size of the applied plasticizer. T_g is increased by increasing of cross-linking between polymer chains [11-13]. T_g is an important parameter in the study of synthetic polymers and biopolymers. For example, it is expected that the permeation of gas and vapor molecules through a film will be higher above T_g . The T_g values are also important for determination of compression moulding and extrusion temperatures.

Polyoles are natural plasticizers for biopolymer however they have not been used as a plasticizer for zein film making. The objectives of this study are to determine the effects of polyolic plasticizers on the viscoelastic and thermal properties of zein resins.

EXPERIMENTAL

Materials

Zein, regular grade, was obtained from Freeman Industries Inc. (Tuckahoe, N.Y.). Other Materials, e.g., glucose, galactose, fructose, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were purchased from Merck. Ethanol 95% was obtained from Razi Corporation and then ethanol 80% was prepared from it.

Preparation of Zein Resins and Films

Zein dispersions were obtained by dissolving zein (20 w/v%) in warm (80°C) aqueous ethanol 80%. Polyoles (glycerol, sorbitol, and manitol) were added to

the solution at 0.5 g, 0.7 g, and 1g of plasticizer/g of zein and stirred in a mixer at 300 rpm for 10 min. Zein-plasticizer dispersions were precipitated by the addition of a seven fold volume of cold water (5°C) as the result of hydrophobic aggregation. Resins were collected as soft solids and kneaded in a mixer for separation of remaining alcohol and water to obtain cohesive mouldable resins.

Resins were rolled and then pressed in hot press (80°C, 25 MPa) between two metal surfaces to form zein films. Films were dried at room conditions for 48 h.

Oscillatory Dynamic Rheometry

Dynamic small strain amplitude oscillatory experiments were conducted to determine viscoelastic properties of zein resins. The dynamic test is performed by applying a small sinusoidal oscillatory shear strain (or stress) and measuring the resulting stress (or strain). In small strain amplitude oscillatory technique, a sinusoidal varying strain ($\gamma = \gamma_0 \sin(\omega t)$) is applied to a sample, where γ is the strain, γ_0 is the strain-amplitude (i.e., the maximum applied deformation), ω is the frequency of oscillations and t is the time.

Application of a small strain, assures that material response is in the linear viscoelastic range, the range within which the stress is proportional to the applied strain. The stress response of linear viscoelastic material to a sinusoidal strain input is given by following equation:

$$\tau = \gamma_0 G' \sin(\omega t) + \gamma_0 G'' \cos(\omega t) \quad (1)$$

The frequency dependent functions G' and G'' are shear elastic modulus (storage modulus or elastic rigidity) and shear viscose modulus (loss modulus or viscose rigidity), respectively. G' is a measure of the energy stored and subsequently released per cycle of deformation per unit volume and obtained from:

$$G' = \tau_0 \cos \theta / \gamma_0 \quad (2)$$

G'' is a measure of the energy dissipated as heat per cycle of deformation per unit volume and obtained from the following equation.

$$G'' = \tau_0 \sin \theta / \gamma_0 \quad (3)$$

where θ is phase angle between strain and stress.

The loss factor (loss tangent or damping factor) ($\tan \delta$) denotes relative effects of viscous and elastic components in viscoelastic behaviour:

$$\tan \delta = G'' / G' \quad (4)$$

where δ is phase lag angel. The complex modulus (total rigidity) is also used to describe dynamic test data and obtained from:

$$G^* = \tau_0 / \gamma_0 = \sqrt{G'^2 + G''^2} \quad (5)$$

Similarly, complex viscosity (η^*) can also be defined in terms of real (η') and imaginary (η'') parts of viscosity:

$$\eta^* = \sqrt{\frac{G'^2}{\omega} + \frac{G''^2}{\omega}} = \sqrt{\eta' + \eta''} \quad (6)$$

where η' is known as dynamic viscosity or in phase component of complex viscosity and η'' which does not have specific name related to elastic rigidity or out of phase component of complex viscosity.

A dynamic strain rheometer with cone and plate geometry (Paar physica, MCR300 Messtechnik GmbH, Stuttgart, Germany) (radius 5 cm, cone angle 0.02 rad, gap 53 μm) was used to determine storage modulus (G'),

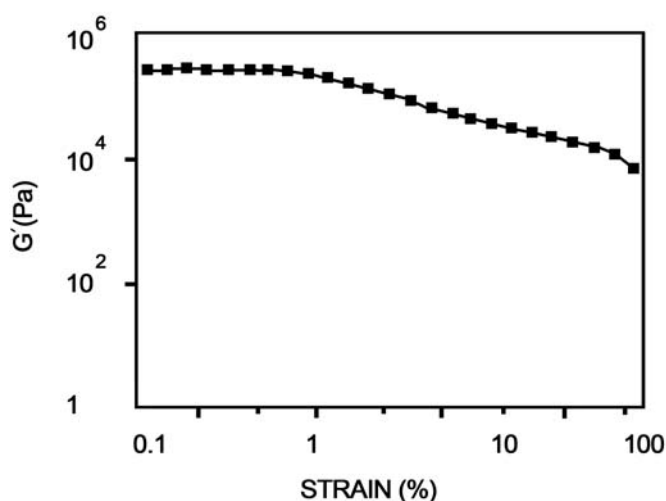


Figure 1. Determination of linear viscoelastic range of zein resin by strain sweep at 1 Hz frequency and 25°C.

loss modulus (G''), loss factor ($\tan\delta$) and complex viscosity (η^*) of zein resins. The dynamic frequency scans performed from 0.1 to 100 rad/s. The temperature was elevated and controlled by an air-heating oven which was part of the rheometer. Effect of temperature on viscoelastic property of zein resin (loss factor) investigated at three temperatures (25, 35, and 45°C).

Differential Scanning Calorimetry

The DSC measurements were carried out in a DSC PL Polymer Laboratories, UK. Calibration was based on pure indium and sapphire. An empty Aluminum pan was used as reference. Samples (~0.03 g) were scanned at a rate of 10°C/min between temperature ranges of -100°C to 150°C. The glass transition temperatures were determined from the resulting thermograms as the midpoint between onset and end temperatures of step changes in heat flow observed

during heating and identified as second-order transitions.

RESULTS AND DISCUSSION

Rheological Properties

Before oscillatory testing of zein resins samples, the extent of the linear viscoelastic region was determined by performing a strain sweep at a fixed frequency of 1Hz (Figure 1). The behaviour illustrated in Figure 1 is typical of many viscoelastic materials: the storage modulus remains constant in the linear range and decreases above a critical shear strain. A dynamic frequency sweep was conducted by applying oscillation amplitude within the linear region (about 0.1% of strain) over a frequency range between 0.1 to 100 Hz.

The effects of different polyolic plasticizers at three

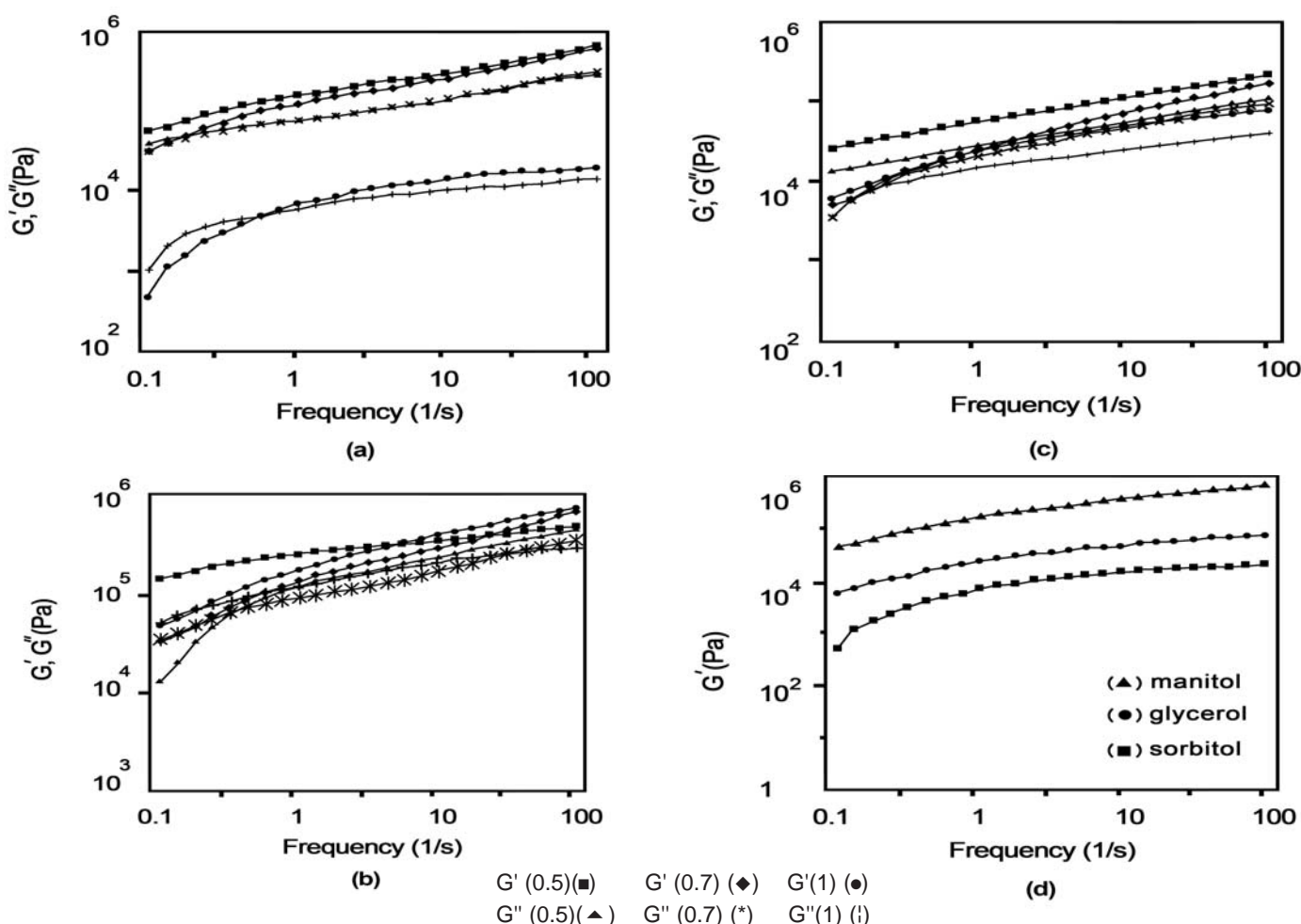


Figure 2. Effect of plasticizer types and levels (g plasticizer/g of zein) on G' and G'' of zein resins at 25°C: (a) Sorbitol, (b) Manitol, (c) Glycerol, and (d) comparison between different plasticizers at 1 g plasticizer/g of zein.

levels (0.5, 0.7, and 1 g of plasticizer/g of zein) on the viscoelastic properties are shown in Figures 2, 3, and 4. In zein resins plasticized by sorbitol and glycerol, storage modulus (G') and loss modulus (G'') decreased with increasing plasticizer level (Figures 2a -2c). This could be attributed to increase of biopolymer chain mobility and lubrication in resin matrix. Plasticizers are used to depress the glass-transition temperature of the polymers and decrease viscoelastic modulus [14-16]. Plasticizers dissolve in the polymer, separating chains from each other and facilitating chain movement and increasing flexibility [10,11,17]. Thus, sorbitol and glycerol could perform plasticization process effectively. In comparison with different plasticizers, sorbitol had the highest plasticization effect and could decrease G' effectively (Figure 2d).

In zein resins containing sorbitol, increase plasticiz-

er from 0.5 to 0.7 g/g of zein had not considerable effect on G' and G'' values. In resins containing manitol, increasing in G' and G'' was observed when manitol level increased from 0.7 to 1 g/g of zein (Figure 2b). This was probably due to rapid crystallization of manitol and the increase of the stiffness of resin. In all samples, G' values were higher than G'' values that indicates zein resins tend to be more solid viscoelastic than liquid viscoelastic.

Complex viscosity (η^*), that is measure of total rigidity, decreased with increasing plasticizer levels from 0.5 to 1g plasticizer /g of zein in resins containing sorbitol and glycerol (Figures 3a-3c). In zein resins containing manitol, η^* decreased with increasing manitol from 0.5 to 0.7 g/g of zein, but in higher level (1 g/g of zein) reverse effect was observed and η^* increased again (Figure 3b). This was attributed to increase of

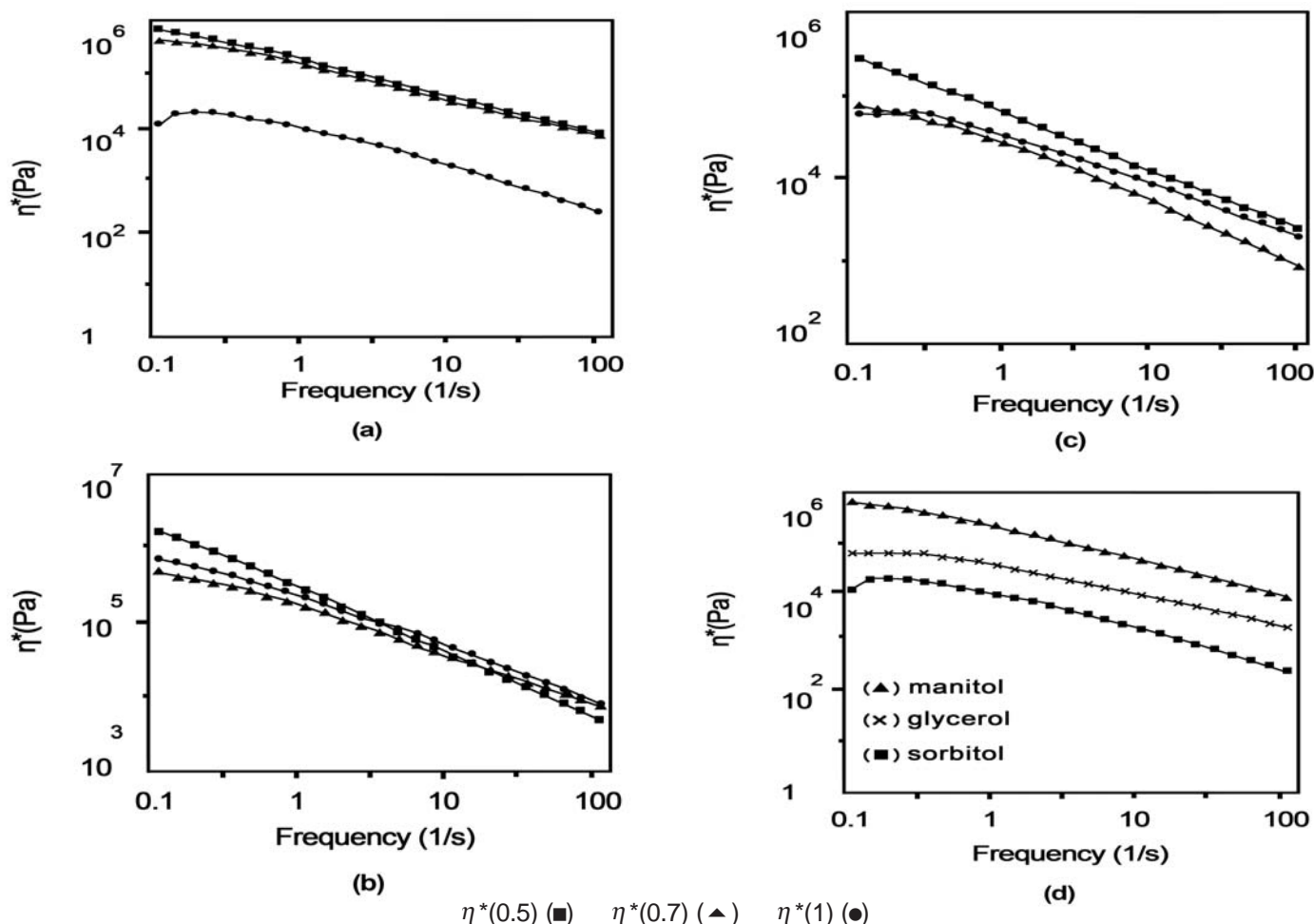


Figure 3. Effect of plasticizer types and levels (g plasticizer/g of zein) on complex viscosity (η^*) zein resins at 25°C: (a) Sorbitol, (b) Manitol, (c) Glycerol, and (d) comparison between different plasticizers at 1 g plasticizer/g of zein.

solid material and anti-plasticization effect. As shown in Figure 3d, in comparison with different resins, resins containing sorbitol had the lowest η^* . Loss factor ($\tan\delta$), that is the measure of viscose rigidity to elastic rigidity ratio, increased with increasing of plasticizer levels from 0.5 to 1g/g of zein in resins containing sorbitol and glycerol (Figure 4a-4c). This indicated that elastic modulus (G') was influenced more than viscose modulus (G'') by polyolic plasticizers. In zein resins containing manitol, $\tan\delta$ increased with increasing manitol from 0.5 to 0.7 g/g of zein but increasing more in plasticizer level had not considerable effect on loss factor. As shown in Figure 4d, in comparison within different resins, resins containing sorbitol had the highest loss factor. It means that sorbitol could decrease elastic modulus more than the other two polyolic plasticizers.

Effect of temperature on zein resin dynamic vis-

coelastic property (loss factor) investigated at three temperatures (25, 35, and 45°C) and is shown in Figure 5. Resins containing sorbitol were influenced by temperature rising more than other resins. All samples showed decrease in $\tan\delta$ with temperature increasing. This indicates that temperature affects viscose rigidity more than elastic rigidity.

Thermal Properties

DSC Thermograms of polymer-plasticizer mixture show plasticizer's compatibility with biopolymer and effectiveness of plasticization process. DSC Thermograms for zein resins are shown in Figure 6. Exothermic small peaks were observed at -0.24, -0.45, and -0.3 °C for sorbitol, manitol, glycerol, respectively, and attributed to crystallization of residual water in resins matrix. Sharp and first-order transition peaks were not found in heat-

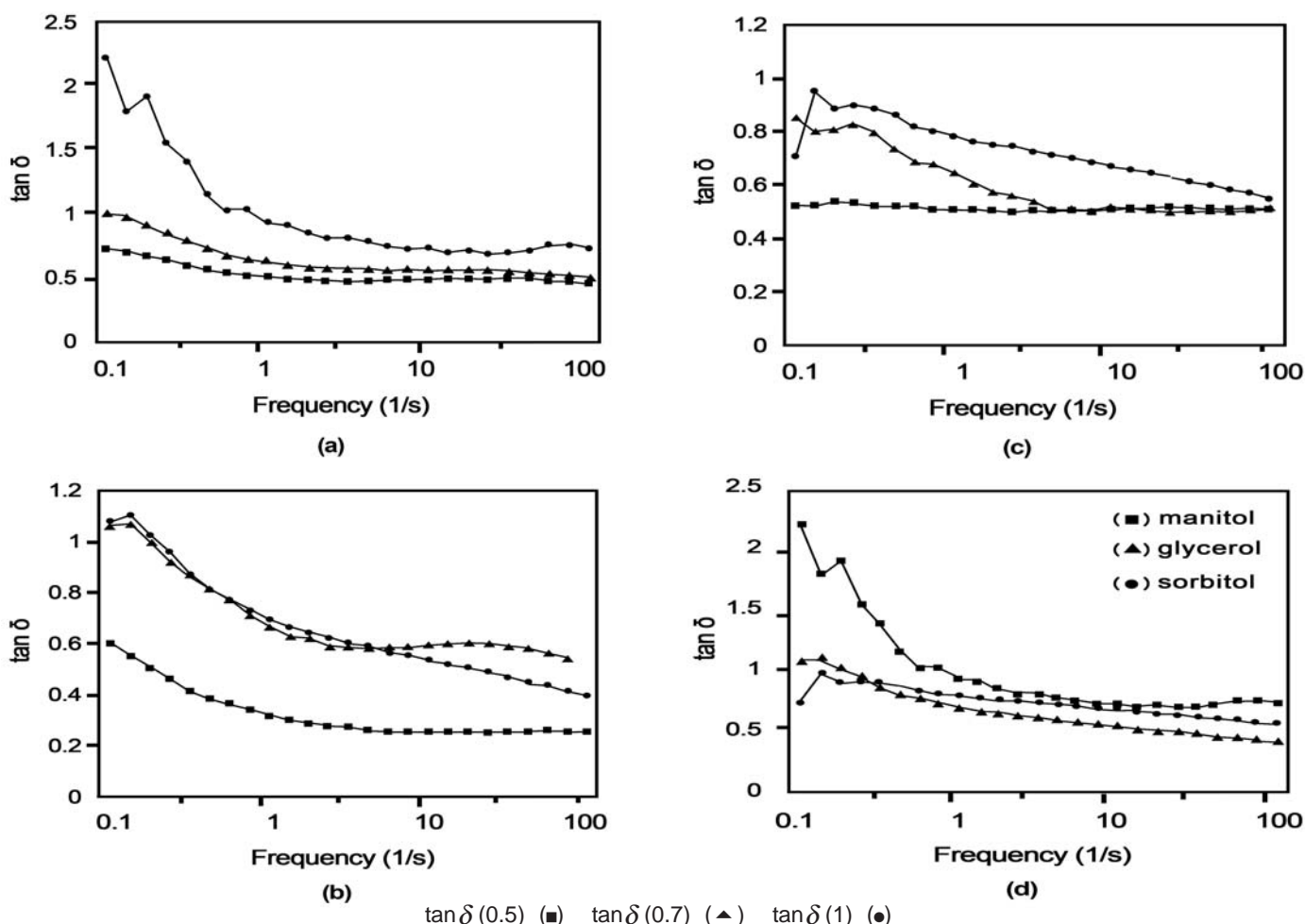


Figure 4. Effect of plasticizer types and levels (g plasticizer/g of zein) on loss factor ($\tan\delta$) of zein resins at 25°C: (a) Sorbitol, (b) Manitol, (c) Glycerol, and (d) comparison between different plasticizers at 1 g plasticizer/g of zein.

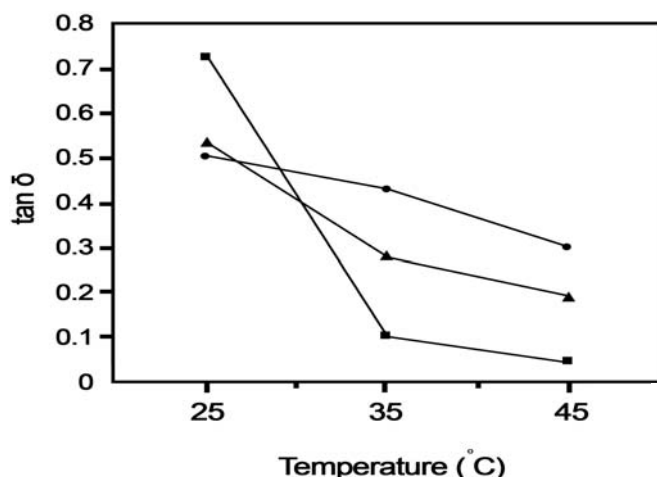


Figure 5. Effect of temperature on loss factor of zein resins at 1 g plasticizer /g of zein level at 1Hz frequency.

ing and cooling scans of zein resins for the temperature range scanned (-100 to 150°C). No peaks related to melting and crystallization of plasticizers and zein biopolymer were observed. Thermograms suggested that polyolic plasticizers and zein remained a homogeneous material throughout the cooling and heating cycle, because phase separation of plasticizers from zein (separated glass transition temperature or melting and crystallization peaks) was not observed this was in agreement with Wang et al. research work [12].

If polymer and plasticizers are immiscible, the mixture will exhibit two T_g corresponding to the two pure phases. In fact, this is a way of checking phase in amorphous blends. Wang et al. [12] studied the effect of processing methods on thermal behaviour of zein films by differential scanning calorimetry (DSC). Films containing 41% oleic acid were prepared by:

- 1) Dissolving plasticizers in casting ethanol solutions and pouring on flat surfaces.
- 2) Extrusion of zein resins (prepared by cold water precipitation of ethanol solutions of zein and oleic acid). Extruded samples were collected as ribbons.
- 3) Non-extruded resin films were prepared by stretching resins by hand over the rims of cylindrical container and allowed to dry at room temperature.

Some of the zein films were treated by hot rolling or hot press. DSC Thermograms for unheated zein films showed endothermic peaks centered at about 27°C, which were attributed to melting of oleic acid. DSC Thermograms also showed large oleic acid melting

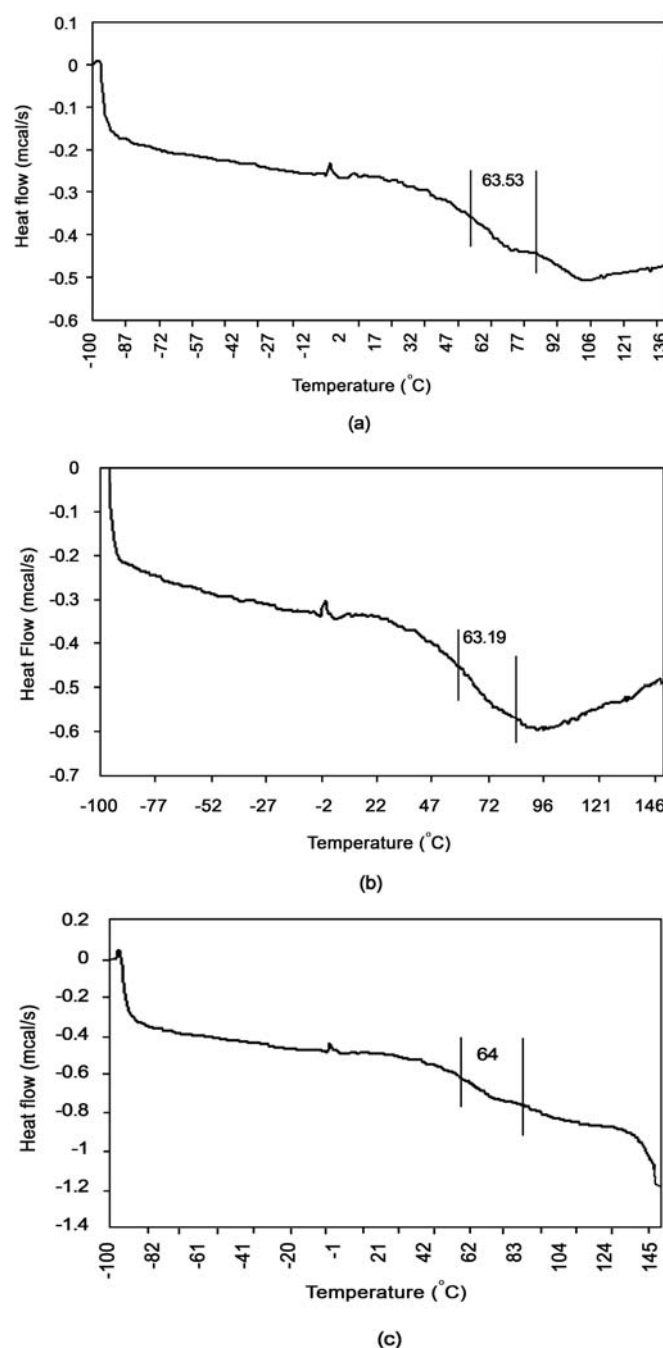


Figure 6. Typical differential scanning calorimetry thermograms of zein resins containing plasticizers (0.5 g/g of zein): (a) Sorbitol, (b) Glycerol, and (c) Mannitol.

peaks for cast films, smaller peaks for resin films (extruded and non-extruded), and no apparent peaks for heat-treated samples. It suggested that the resin formation process enhanced zein-oleic acid interactions and promoted plasticization thus reducing phase separation. It is believed that the layered structure of resins is able

to bind larger amounts of oleic acid than cast films. In our works melting and crystallization peaks was not observed, even in unheated zein resin. This suggested that resin production increased interaction between polyols and zein in the resins, which possibly led to higher structural organization. Preventing from phase separation in resin films leads to increased film toughness by allowing microstructure development and orientation [11].

Santosa and Padua [15] observed a broad endothermic peak centered at $\sim 87^{\circ}\text{C}$ in DSC Thermograms of granular zein. They attributed enthalpy changes to break up of hydrogen bonds and other molecular associations and protein unfolding (denaturizing). In contrast, the zein sheets' thermograms did not show any of these feature that attributed to the heat induced conformational changes during resin forming. The term glass transition refers to the temperature (or the temperature range) at which, a glass polymer begins to soften to rubbery state and flow, whereas below T_g , polymers exist in a glassy, rigid state [12,15]. Glass transitions in biopolymer are not sharp, and the glass transition temperature (T_g) may be reported as the onset, middle, or end point. Glass transition temperature for resins containing various polyol levels and types were observed in $60\text{--}70^{\circ}\text{C}$ range (Table 1). These T_g values were considerably lower than the value observed in zein resin plasticized by oleic acid (101.8°C) [11]. This was probably due to the hygroscopic and hydrophilic nature of polyols and hydrophobic nature of oleic acid.

Water acts as an important plasticizer depressing T_g in biopolymer films, for example water plasticization of most biological materials causes T_g depression from $\sim 200^{\circ}\text{C}$, for anhydrous high molecular weight polymers such as starch and gluten, to -10°C [13]. Magoshi et al. [16] have measured the glass transition temperature (T_g) of zein at various moisture contents and reported its decrease from 139°C to 47°C when water content

increased from 0 to 6.6%. Similarity between the glass transition temperature (T_g) values for various zein resins suggests that thermal behaviour at high temperatures was not affected by the type of polyolic plasticizers. This was probably due to similar molecular weight of selected polyols. After initial lowering of T_g of zein, subsequent increase of plasticizer levels did not cause great reduction in zein T_g . Magoshi et al. [16] have measured the glass transition of anhydrous zein at $162\text{--}165^{\circ}\text{C}$. Therefore, polyols can decrease T_g of zein, effectively.

CONCLUSION

Plasticization effectiveness of zein resin could be verified by determination viscoelastic properties and thermal behavior of resin before film making from it. Plasticization process is necessary for producing of suitable zein films which are generally brittle and require the addition of plasticizer.

Polyolic materials are edible plasticizers and are found in the most of fruits naturally. Oscillatory tests showed sorbitol and glycerol could reduce rigidity of zein resin more than manitol. Zein resins containing sorbitol and glycerol had lower G' , G'' and η^* values than resins containing manitol. Manitol had low compatibility with zein and crystallized rapidly thus, it did not show good plasticizing effect.

Zein resin production process caused loss in crystallization ability of zein. Thus, crystallization peaks were not observed. Glass transition temperatures of all samples were in the range $60\text{--}70^{\circ}\text{C}$. These T_g values were considerably lower than the value observed in zein resin plasticized by oleic acid (101.8°C) [9]. There was not important difference between T_g of resins containing different polyols. This is attributed to the similar molecular weights of polyols.

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Table 1. Effect of plasticizers on T_g of zein resins.

Plasticizer \ level (g plasticizer/g zein)	0.5	0.7	1
Sorbitol	64.8	63.53	61.58
Manitol	65.31	64.06	67.36
Glycerol	67.61	63.19	61.81

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