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

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INTRODUCTION

Zein is produced commercially from corn gluten meal (CGM) and has excellent film forming properties and can be used for fabrication of biodegradable films[1,2].

Zein resin is a viscoelastic material and design of processing operations requires accurate data on the rheological properties of film-forming resins. Viscoelastic properties of zein resins can also show degree of plasticization of zein biopolymer by various plasticizers. Protein-plasticizer interactions have been investigated by differential scanning calorimetry (DSC). Madeka and Kokini [3] studied thermal properties of cereal proteins including gliadin, glutenin, and zein and generated physical state diagrams based on DSC measurements and dynamic rheological properties. T_g is an important parameter in the study of synthetic polymers and biopolymers[4].

EXPERIMENTAL

Materials : Zein and other Materials were purchased from Merck.

Preparation of zein resins and flms

By dissolving zein (20% w/v) in aqueous ethanol 80% at (80°C). Polyoles (glycerol, sorbitol, manitol) were added to the solution at 0.5 g, 0.7 g, 1g of plasticizer/gram of zein. Zein-plasticizer dispersions were precipitated and 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.

Oscillatory dynamic rheometry

Paar physica, MCR300 was used to determine storage modulus (G'), loss modulus (G''), loss factor (tanδ) and complex viscosity(η*) of zein resins. Effect of temperature on viscoelastic property of zein resin (loss factor) investigated at three temperatures (25, 35, and 45°C).

Differential scanning calorimetry

DSC measurements were carried out in a DSC PL. The Tg values 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 DISCUSION

Rheological Properties

In zein resins plasticized by sorbitol and glycerol, storage modulus (G') and loss modulus (G'') decreased with increasing plasticizer level (Figure 1-A,C). This could be attributed to increase of biopolymer chain mobility and lubrication in resin matrix.

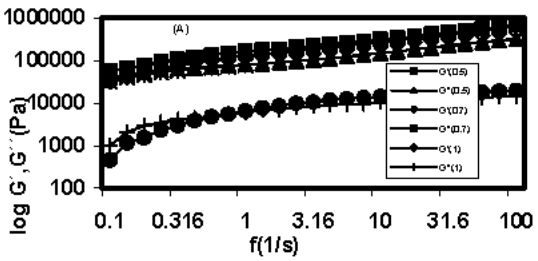

Fig1-Effect of Sorbitol plasticizer on G' and G''of zein resins at 25°C

In comparison with different plasticizers, sorbitol had the highest plasticization effect and could decrease G' effectively. In resins containing manitol, increasing in G' and G'' was observed when manitol level increased from 0.7 to 1 g/g of zein. This was probably due to rapid crystallization of manitol and the increase of stiffness of resin.

Effect of temperature on zein resin dynamic viscoelastic property (loss factor) investigated at three temperatures (25, 35, and 45°C) and is shown in fig.2. Resins containing sorbitol were influenced by temperature rising more than other resins. All samples showed decrease in tanδ with temperature increasing. This indicates that temperature affects viscose rigidity more than elastic rigidity.

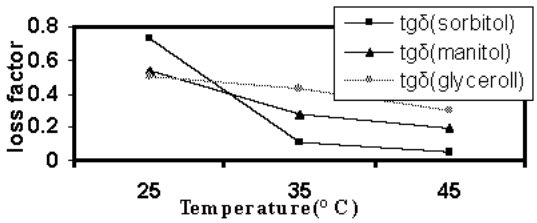

Fig. 2 Effect of temperature on loss factor of zein resins at 1 g plasticizer /g of zein level at 1Hz frequency.

Thermal properties

Tg for resins containing various polyol levels and types were observed in 60-70°C range (Table 1).These T_g values were considerable lower than the value observed in zein resin plasticized by oleic acid (101.8°C) [4]. This was probably due to the hygroscopic and hydrophilic nature of polyols and hydrophobic nature of oleic acid.

Table 1: Effect of plasticizers on T_g of zein resins

Plasticizer s	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

CONCLUSION

Plasticization effectiveness of zein resins could be verified by determination viscoelastic properties and thermal behavior of resins before film making from them. Zein films are generally brittle and require the addition of plasticizer.

Oscillatory tests showed sorbitol and glycerol could reduce rigidity of zein resins more than manitol.

Glass transition temperatures of all samples were in 60-70°C range. Theses T_g values were considerable lower than value observed in zein resin plasticized by oleic acid (101.8 °C) [9]. There was not importent difference between T_g of resins containing different polyols.

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