Effect of Polyol 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 resins is a viscoelastic material and design of processing operations requires accurate data on the rheological properties of film-forming resins. Viscoelastic properties of resin resins can also show degree of plasticization of zein biopolymer by various plasticizers. Plasticization interactions have been investigated by differential scanning calorimetry (DSC), Mullen and Toluene [3] studied thermal properties of resinous proteins including gluten, gliadin, and zein and generated physical state diagrams based on DSC measurements and dynamic rheological properties. Tg 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 resin resins and films:

By dissolving zein (20% w/w) in aqueous ethanol 80% at (80°C), polyols (glycerol, sorbitol, mannitol) were added to the solution at 0.5 g, 0.7 g, 1 g of plasticizer. The resin was placed in a mixer for 20 minutes after stirring and water to obtain cohesive moldable resins. Resins were rolled and then pressed in hot press at (80°C, 25 MPa) between two metal surfaces to form film.

Oscillatory Dynamic Rheometry

Fourier rheometry, MCR-300 was used to determine storage (G'), loss modulus (G''), and complex viscosity (η*) of resin resins. Effect of temperature on viscoelastic properties of zein resin (loss factor tanδ) was investigated at three temperatures (25°C, 35°C, and 45°C).

Differential Scanning Calorimetry

DSC measurements were carried out in a DSC 801C PL. The Tg values were determined from the resulting thermograms at 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

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

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

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

![Fig. 2. Effect of temperature on loss factor of resin resins at 1 g plasticizer (g of zein level) at 1 Hz frequency.](image)

Thermal properties

Tg for resins containing various polyol levels and types were observed in 60-70°C range (Table 1). These Tg values were considerably lower than the values observed in resin resins plasticized by oleic acid (101.8°C) [5]. This was probably due to the hydrogen bonding and hydrophobic nature of polyols and hydrocarbons of oleic acid.

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Tg (°C)</th>
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<tbody>
<tr>
<td>sorbitol</td>
<td>64.8</td>
</tr>
<tr>
<td>mannitol</td>
<td>65.3</td>
</tr>
<tr>
<td>glycerol</td>
<td>66.8</td>
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</tbody>
</table>

CONCLUSION

Hastening effectiveness of resin 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 resin resins more than mannitol.

Glass transition temperatures of all samples were in 60-70°C range. These Tg values were considerably lower than the value observed in resin resins plasticized by oleic acid (101.8°C) [5]. There was not important difference between Tg of resins containing different polyols.

REFERENCES