

Mechanical and Morphological Characterization of Starch/Zein Blends Plasticized with Glycerol

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Received 25 January 2005; accepted 9 October 2005

DOI 10.1002/app.23570

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends of starch and zein plasticized with glycerol were prepared by melting in a batch mixer at 160°C. Glycerol was used as plasticizer in contents ranging from 20 to 40 wt % with respect to the starch/zein matrix. These blends were characterized by mechanical tests, dynamic mechanical analysis, and optical microscopy. In tensile tests, the Young's modulus and ultimate tensile strength increased with increasing zein content for all compositions, whereas elongation at break decreased sharply with increasing zein content up to 20%, and it remained nearly constant at higher contents of zein, which increased the stiffness of the blends. On the other hand, increase in the glycerol

content caused a decrease in mechanical resistance of the blends. Storage modulus increased with increasing zein content and the $\tan \delta$ curves showed that the blends exhibited two distinct glass transitions, one for each component, indicating a two-phase system, confirming the morphological evidence of micrographs that displayed two separate phases. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4133–4139, 2006

Key words: blends; starch; zein; dynamic mechanical analysis; mechanical properties; natural polymers

INTRODUCTION

The use of natural renewable polymers, such as starch, proteins, and cellulose, in the production of biodegradable plastics is a growing field of research and industrial development.^{1–2} Much research has been carried out on natural polymers as substitutes for their synthetic counterparts, showing their great potential for many utilization in nonrecycled goods, such as trash and compost bags, films, and disposable diapers.^{3–4}

One of the most studied natural polymers for the production of biodegradable plastics is starch, the second largest component of biomass produced.⁵ Starch exists in a granular form in its natural state, but can behave like a thermoplastic material in the presence of plasticizers, such as water, glycerol, sorbitol, and others. In the temperature range between 90 and 180°C and under shear, it readily melts and flows, allowing it to be processed in injection, extrusion, and blow-

molding, similar to most conventional synthetic thermoplastic polymers.⁶ This material is named thermoplastic starch (TPS). Several attempts have been made to reduce the hydrophilic character of TPS, as this limits its use in a wide range of applications.^{7–10} These include modification reactions, filler addition, and blending with less polar polymers. Blends of TPS with synthetic polymers such poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl alcohol), and polyethylene have been studied.^{11–13} These blends show improved mechanical and water susceptibility properties compared to TPS, but do not lead to fully biodegradable materials. Recently, the development of fully biodegradable materials has gained more interest. There have been several reports in the literature on blends of starch with biodegradable polymers such as aliphatic polyesters like polycaprolactone, polylactic acid, poly(hydroxybutyrate-co-valerate) and polyesteramide.^{14–16}

An interesting alternative is to blend starch with zein, a corn protein, which has a hydrophobic character as a consequence of apolar amino acids, such as leucine, praline, and alanine.¹⁷ Zein is a completely amorphous polymer, which can be processed as a thermoplastic material in the presence of plasticizers with high boiling-points, such as triethylene glycol, glycerol, oleic acid, etc.¹⁸ Among these plasticizers, glycerol is most used for destructurezation of starch granules. Although glycerol has a hydrophilic nature

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Contract grant sponsors: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Pesquisa e Desenvolvimento (CNPq).

and, consequently, can cause an increase in the amount of water absorbed and also migrate out the film during its shelf life, we verified in preliminary experiments that the glycerol was a good plasticizer of starch/zein blends in the processing conditions used. Further work will be needed to fully understand the relationship between composition and properties of starch/zein blends plasticized with glycerol and the effect of glycerol on these blends. Thus, the objective of the present study is to investigate the effect of the composition of starch/zein blends plasticized with glycerol on their mechanical, dynamical mechanical properties and morphology.

EXPERIMENTAL

Regular corn starch containing 28 wt % amylose (Amisol 3408) was obtained from Corn Products Brasil (São Paulo, Brazil). Corn zein (protein) was purchased from Sigma–Aldrich [9010–66-6] and reagent grade glycerol was used as received.

Material processing

The starch/zein blends were prepared in different proportions. The glycerol content was 22, 30, and 40% by weight, with respect to the total mass of polymers (dry basis). The compositions used in this study were as follows:

- a. Compositions with 22% of glycerol in the weight proportions 0/100, 10/90, 20/80, 70/30, 50/50, 80/20, and 100/0 of starch/zein.
- b. Compositions with 30 and 40% of glycerol in the weight proportions 0/100, 20/80, 50/50, 80/20, and 100/0 of starch/zein.

Starch, zein, and glycerol were weighed separately, premixed in a beaker, and the mixture was processed in a Haake Rheomix 600p intensive mixer connected to a torque rheometer, at 160°C and 50 rpm, for 6 min. The mixtures obtained were pressed at 160°C with a clamp force of 5 ton for 5 min to produce 150 × 120 × 2.5 mm³ molded sheets. These specimens were conditioned at 22–25°C in relative humidity (RH) of 52–54% for 4 weeks prior to testing.

Water uptake

Specimens previously dried at 105°C overnight were weighed and conditioned in hermetic containers at 52–54% RH and (25 ± 2)°C, using a saturated Mg(NO₃)₂ solution, in conformity with ASTM E104 standard.¹⁹ The amount of water absorbed by the specimens during conditioning was determined by weighing them periodically until a constant weight

was attained. Water uptake (W) was then calculated as follows:

$$W(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where M_t is the mass at time t , and M_0 the initial dry mass before conditioning.

Tensile tests

The tensile tests were performed in an Instron 5569 universal test machine with a load cell of 50 kN. The specimens were prepared as specified in ASTM D638M²⁰ type II. For each material, at least five specimens were tested at a crosshead speed of 5 mm/min.

Dynamic mechanical analysis

Dynamical mechanical analyses were carried out in a Polymer Laboratories DMTA MK-II instrument, in accordance with ASTM D5023,²¹ using a three-point bending method. The dynamic storage modulus (E') and damping factor ($\tan \delta$) were measured as a function of temperature from –75 to 100°C, at a constant heating rate of 3°C/min and displacement amplitude of 64 μm, at a frequency of 1 Hz. The glass transition temperature (T_g) was determined as being the temperature correspondent to the maximum of the $\tan \delta$ peak for the main transition displayed in the $\tan \delta$ versus temperature curves.

Optical microscopy

Morphology of the blends was examined in thick films of about 50 μm, which were prepared by hot pressing. These films were stained with a solution of I₂ in aqueous KI and examined by phase contrast under a CBA Olympus optical microscope at 100× magnification.

RESULTS AND DISCUSSION

Water uptake

The results of the water uptake experiments are shown in Figure 1. The amount of water absorbed by the TPS at equilibrium increased with glycerol content, whereas for zein and starch/zein blends with more than 20% of zein (50/50 and 20/80), exudation occurred at glycerol contents higher than 22% (results not shown). Blends plasticized with 22% of glycerol exhibited water uptake values between those of pure plasticized components, i.e., a slight decrease in water uptake with increasing zein content. As glycerol is hydrophilic, it interacts with water and the hydrophilic groups of starch and zein. The strength of these interactions depends on the structure of these natural

polymers. Zein is composed of amino acids, many of which have nonpolar side groups, whereas starch has a more hydrophilic nature and can interact more strongly with water than zein does.

Tensile tests

Young's modulus (E), ultimate tensile strength (UTS), and elongation at break (ϵ) were determined from stress-strain curves obtained for the materials processed with 22, 30, and 40% of glycerol and are plotted against zein content in Figure 2. Young's modulus increased with zein content, whereas UTS increased only for zein contents higher than 50%. On the other hand, elongation at break decreased sharply with the addition of only 20% zein in the blends and remained approximately constant at higher contents. Zein is a brittle material and its presence favors a stiffer behavior of the blends. The presence of glycerol also affected the mechanical properties of these materials. For the TPS (100/0), E , UTS, and ϵ decreased with increasing glycerol content (Fig. 2). This effect is probably due to a decrease in the degree of interaction between starch chains, upon addition of more than 22% glycerol. The mechanical behavior of TPS depends on its structural development, which depends among other factors, on polymer-polymer and polymer-plasticizer interactions, as explained in the literatures.^{16,22-24} van Soest et al.²⁴ showed that at high plasticizer content, the TPS becomes weak in UTS and elongation at break decreases. This behavior was studied by infrared spectroscopy and was attributed to a low degree of interaction, especially through hydrogen bonds between starch molecules at high plasticizer contents.²⁴ The effect of plasticization on starch was intensified by the

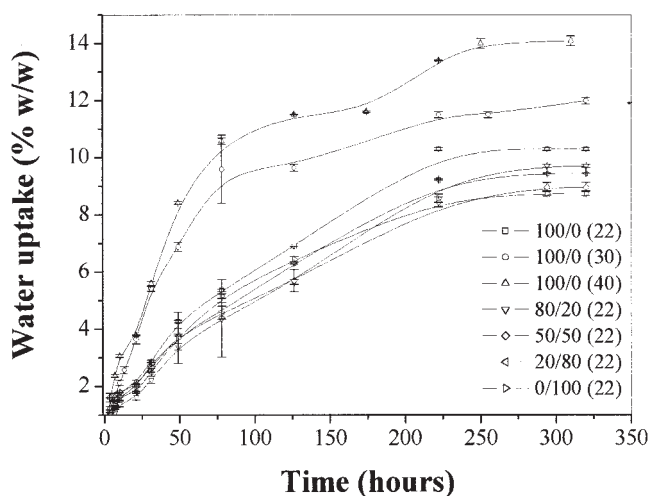


Figure 1 Water uptake at 52–54% RH versus time for TPS with 22, 30, and 40% of glycerol and for zein and starch/zein blends with 22% of glycerol. The numbers in brackets denotes the glycerol content.

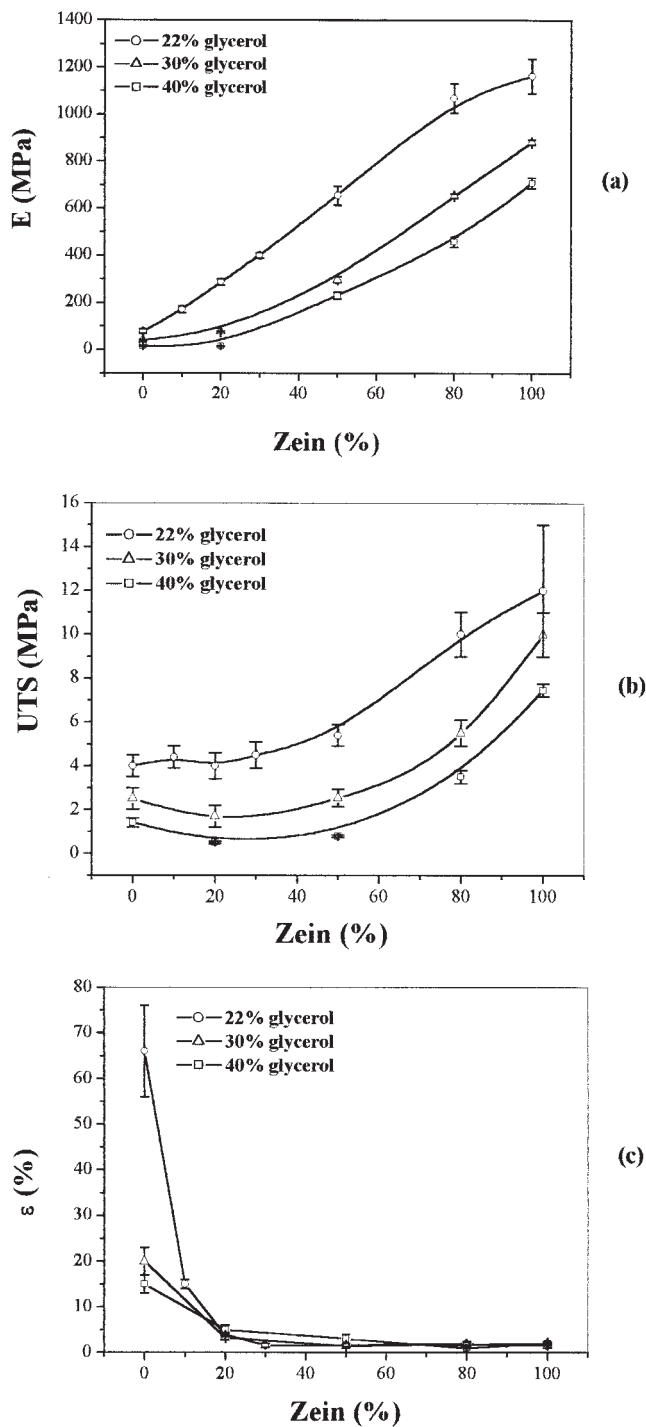
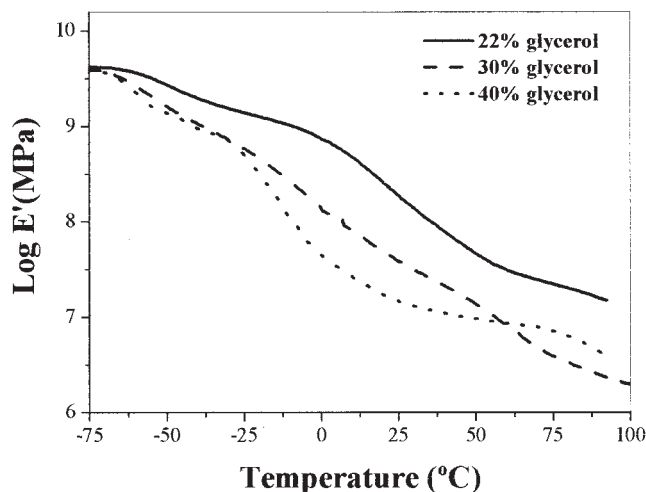
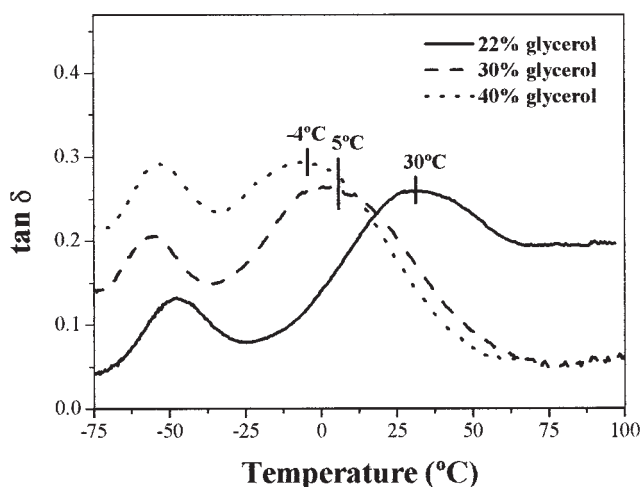


Figure 2 Effect of glycerol and zein contents in starch/zein blends on (a) Young's modulus (E), (b) UTS, and (c) elongation at break (ϵ).

amount of absorbed water, since it increased with increasing glycerol content. For zein and starch/zein blends, E and UTS decreased as glycerol content was increased, whereas the elongation at break remained approximately constant, probably due to the poor interaction between glycerol and zein. A similar effect was observed by Di Gioia et al.,²⁵ in which zein films



(a)



(b)

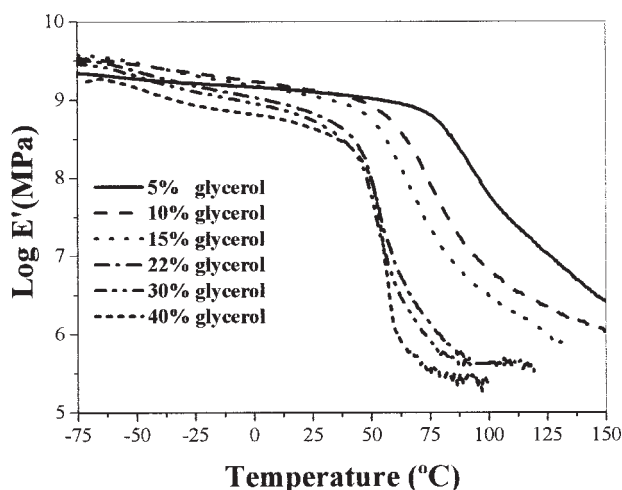
Figure 3 Storage modulus (E') (a) and damping factor ($\tan \delta$) (b) plotted against temperature for TPS with 22, 30, and 40% of glycerol content.

plasticized with octanoic acid showed small variation in elongation at break, when the plasticizer content was higher than 20%. The slight decreasing of water absorption with increasing zein content (for blends with 22% of glycerol), and exudation of plasticizer in the blends with 30 and 40% glycerol favored a brittle behavior in starch/zein blends.

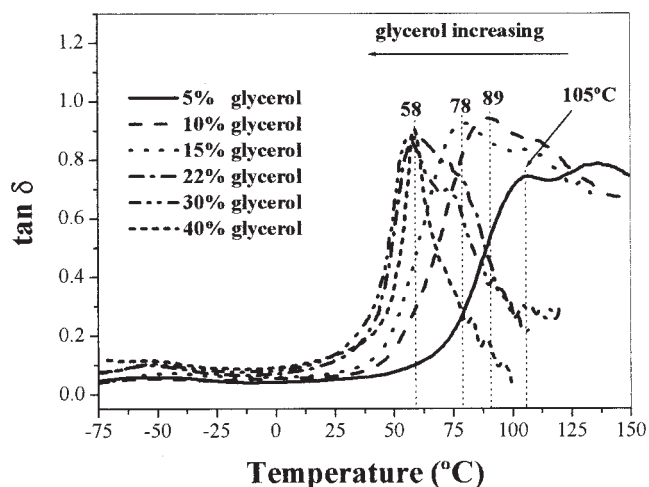
Dynamic mechanical analysis

Storage modulus (E') and damping factor ($\tan \delta$) curves are plotted against temperature, for TPS and plasticized zein with various amounts of glycerol, in Figures 3 and 4, respectively. TPS showed a gradual decrease in E' with increasing temperature (Fig. 3(a)).

This effect is due to crystalline domains acting as physical crosslinking agents and thus contributing to a moderate decrease in E' with rising temperature above the glass transition temperature, as observed in semicrystalline polymers.²⁶ On the other hand, the plasticized zein (0/100) exhibited a sharp decrease in E' above the glass transition temperature, which is typical of completely amorphous polymers.²⁷ The $\tan \delta$ curves for the TPS (Fig. 3(b)) show two maxima for TPS, the first at lower temperatures (ca. -53°C) and the second at higher temperatures. The low-temperature transition is attributed either to the glycerol itself or to glycerol-rich domains.²⁶ The transition at higher temperatures is due to the glass transition of TPS,



(a)



(b)

Figure 4 Storage modulus (E') (a) and damping factor ($\tan \delta$) (b) as a function of temperature for the plasticized zein with 5, 10, 15, 22, 30, and 40% of glycerol.

which is shifted from 30 to 5°C and to -4°C, as the glycerol content increases from 22 to 30% and to 40%, respectively. This transition is strongly dependent on plasticizer content and has also been observed in other studies.²³ Lourdin et al.²² showed that the T_g of starch decreases linearly with increasing glycerol content, from 5 to 30%. Dynamic mechanical analysis experiments were carried out on plasticized zein with 5, 10, 15, 22, 30, and 40% glycerol to analyze the effect of glycerol on the glass transition of zein. The plasticized zein also has three distinct maxima in the $\tan \delta$ curves (Fig. 4(b)). The low temperature peak coincides with that observed for TPS and can also be attributed to glycerol; at higher temperatures, one peak and a shoulder are observed, respectively, which reflect the glass transitions of the two zein fractions with different molecular weights, as reported by Wu et al.²⁸ When the glycerol content is higher than 15%, the effect of plasticization is more pronounced for both low and high molecular weight fractions of zein. As a consequence, two transitions that appeared clearly at lower plasticizer contents converged to a single transition, which in turn, is shifted to lower temperatures, confirming the higher plasticizing effect of glycerol. It is observed that when the glycerol content increases from 5 to 22%, the second transition temperature of zein is shifted from 104 to 63°C, whereas at higher glycerol contents, it remains approximately constant, indicating that the efficiency of plasticization of zein by glycerol reaches a limit around 22%, whereas the starch T_g decreases steadily with increasing glycerol content from 22 to 40%. These results are consistent with the water uptake experiment, where it was observed that at a glycerol content higher than 22%, zein showed exudation of glycerol. This suggests that the effect on zein of plasticization by glycerol is less than that on starch, probably due to their differentiated hydrophilic/hydrophobic characters.

Dynamic mechanical thermal analysis curves obtained for starch/zein blends plasticized with 22% of glycerol are presented in Figure 5. Comparison of the E' curves of the pure components with their blends showed that the blends containing up to 30% zein (90/10, 80/20, 70/30) showed the same behavior as TPS. On the other hand, the blends with 50 and 80% of zein showed a behavior similar to that of plasticized zein (0/100). The variation in storage modulus as a function of the composition suggests that a phase inversion may be occurring. It was also observed that the storage modulus increased with increasing zein content, indicating that its presence enhanced the stiffness of the blends, in agreement with the results obtained in tensile tests. Three maxima were observed in the $\tan \delta$ curves for the starch/zein blends in the temperature range from -80°C to 80°C. The first, attributed to glycerol, occurred at the same temperature for all blends (ca. -50°C), and the second and third

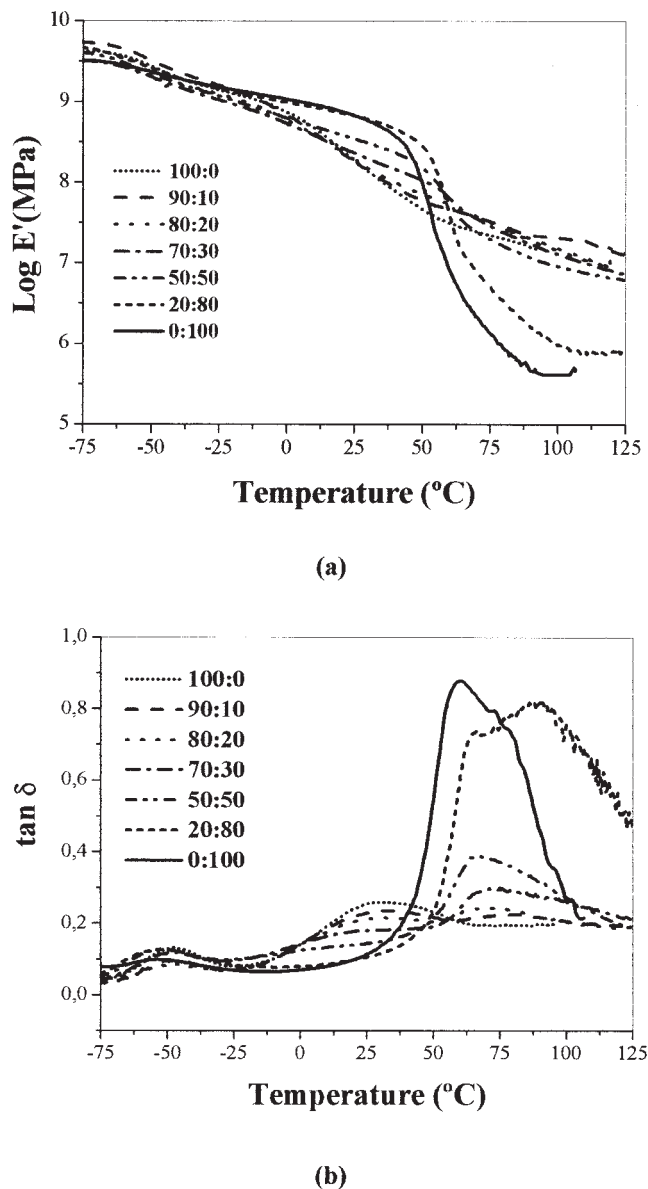


Figure 5 Storage modulus (E') (a) and damping factor ($\tan \delta$) (b) versus temperature for starch/zein blends with 22%.

ones at higher temperatures are due to the glass transition of TPS and zein, respectively (Table I). All blends exhibited two distinct glass transitions, one for each component (starch and zein). This type of behavior indicates that the starch/zein blends are immiscible; moreover, a decrease in the starch T_g and an increase in the zein T_g occurred in all blends. Probably, these shifts in glass transitions are due to the differences in hydrophilicity of starch and zein. As starch is more hydrophilic, the starch phase was more plasticized than the zein phase. One possible explanation is that, some glycerol or water may migrate from the zein phase (less hydrophilic) to the TPS phase (more hydrophilic), decreasing its T_g , and increasing that of zein.

Optical microscopy

Optical micrographs of the iodine/KI-stained thin films of 22% glycerol-plasticized blends are presented in Figure 6. Two distinct phases, a white zone for zein and a gray zone for starch, are clearly observed in all compositions, indicating that these blends are immiscible in the range of compositions studied. The morphology of immiscible blends depends on the composition, viscoelastic properties of the individual components, and the blending conditions.²⁷ At low concentrations, one polymer is dispersed as droplets in the other polymer. As the concentration of the dispersed phase is increased, the shape of the dispersed domains may change to fibrillar or lamellar. Further increase in the amount of the dispersed phase will lead to an increase in its continuity and a cocontinuous morphology is formed.²⁹ In the blend with 20% zein [Fig. 6(a)], irregularly sized and shaped domains of zein in a starch matrix were observed. The blend with 50% zein [Fig. 6(b)] showed the formation of a cocontinuous morphology and the blend with 80% zein [Fig. 6(c)] exhibited a dispersed starch phase within the zein matrix. The effect of composition on morphology has also been investigated in blends of TPS with other polymers.^{29,30} Walia et al.³⁰ observed a change in the morphology of TPS/poly(hydroxy ester ether) blends, where the blend with 25% TPS showed a dispersed phase and when the TPS content increased to 50%, a continuous phase was observed. Morphology plays an important role in the mechanical properties of immiscible blends. Tensile strength and Young's modulus are more dependent on matrix composition than elongation.

CONCLUSIONS

Results from tensile tests indicated that mechanical properties of starch/zein blends depend on both the glycerol and zein contents. Young's modulus and UTS

TABLE I
Glass Transition Temperature (T_g) Obtained from the Maximum of the $\tan \delta$ Curve for Thermoplastic Starch, Plasticized Zein, and Starch/Zein Blends with 22% Glycerol

Starch/zein ratio	Glycerol	DMTA		
		1st peak $\tan \delta$	2nd peak $\tan \delta$ (starch)	3rd peak $\tan \delta$ (zein)
100/0	22	-53	32	—
90/10		-50	31	78
80/20		-50	27	76
70/30		-49	20	72
50/50		-49	4	69
20/80		-50	—	63
0/100		-49	—	58

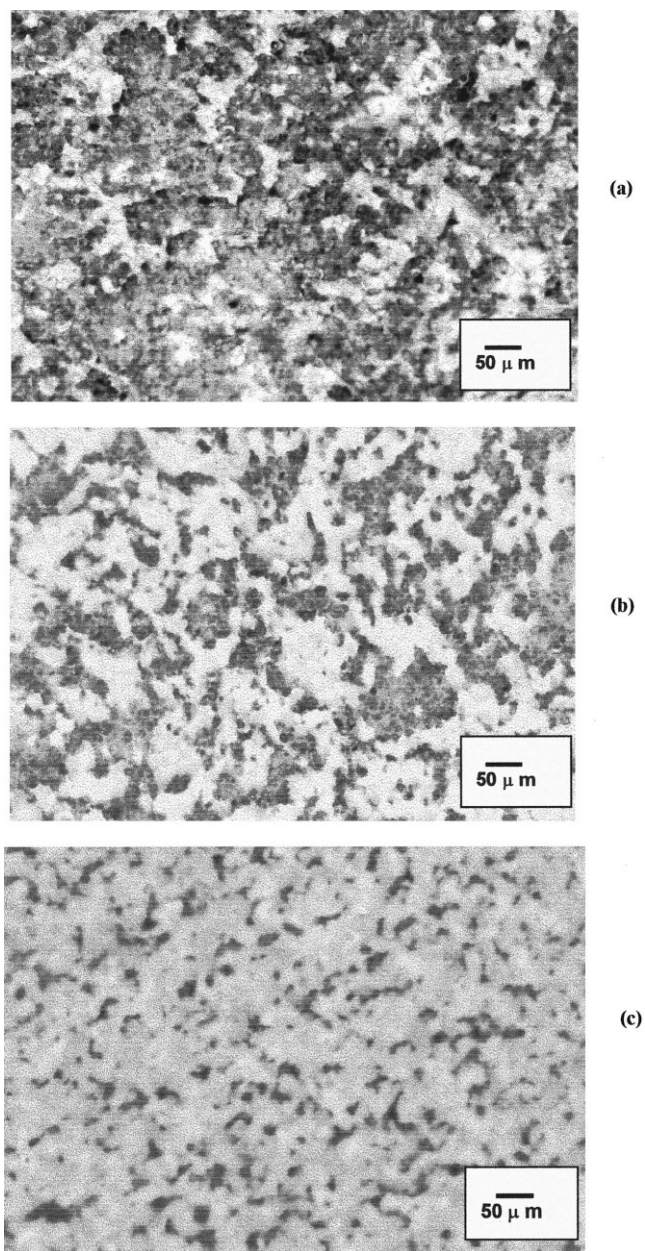


Figure 6 Optical micrographs of iodine/KI-stained thin films of starch/zein blends plasticized with 22% glycerol. (a) 80/20, (b) 50/50, and (c) 20/80.

increase with increasing zein content for all compositions, whereas elongation at break decreases sharply with addition of only 20% of zein in the blends and remains approximately constant at higher contents. On the other hand, the increase in glycerol content caused a decrease in mechanical resistance of the starch/zein blends. The storage modulus increased with increasing zein content. The $\tan \delta$ curves showed that blends exhibited two distinct glass transitions, one for each component. The dynamic mechanical analysis results are consistent with optical microscopy observations, indicating that starch/zein blends are

immiscible in the range of composition studied. In summary, the properties of starch/zein blends can be tailored to produce ecologically-friendly biodegradable materials by changing the relative compositions of these two natural polymers.

The authors acknowledge the support provided Corn Products Brasil for the donation of starch samples. The authors also thank Professor J. A. M. Agnelli of the Universidade Federal de São Carlos for allowing us to use the polymer-processing laboratory.

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