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Application of Differential Scanning Calorimetry to Evaluate Thermal Properties and Study of Microstructure of Biodegradable Films

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Abstract The glass transition temperature (T_g) and melting temperature (T_m) of gelatin–starch films were determined using differential scanning calorimetry. Also, the microstructure was observed using scanning electron microscopy (SEM) and the crystalline structure by means of X-ray diffraction (XRD). The effect of starch and glycerol concentrations in films on the thermal properties was evaluated through response surface methodology (RSM). The highest values of T_m were obtained at starch concentration intervals of (0.26 to 0.54) %w/w and glycerol concentrations lower than 0.5 (%w/w). On the other hand, the T_g values diminished as the glycerol concentration increased. Mathematical models for both transitions were fitted to the experimental data. The micrographs obtained by SEM show the influence of glycerol in the microstructure of the films, being more "gummy" as the content of the plasticizer increased. The XRD patterns of the films demonstrate the existence of some pseudo-crystalline regions in the biodegradable materials.

Keywords Biodegradable films · DSC · SEM · XRD

1 Introduction

The development and characterization of biodegradable films have increasingly attracted the attention of many scientists, mainly due to the large variety of applications

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[1]. Additionally, the production and use of biodegradable films help to decrease the environmental impact of highly polluting petroleum-based plastics [2].

Proteins and carbohydrates are two of the most important kind of materials used for the manufacture of biodegradable films. In addition to being produced on a large scale and at a low cost, these types of biopolymers may produce films with good physicochemical properties. Proteins produce films with good barriers to gases, and carbohydrate-based films have excellent mechanical properties [3,4]. However, if the film is produced mixing carbohydrates and proteins, its final properties will be better in comparison with those of a single component. In the case of packaging materials, thermal properties such as the glass transition temperature (T_g) and the melting temperature (T_m) are very important since they determine the interval of temperatures in which materials can be used [5].

Plasticizers are substances of low molecular weight, and when they are incorporated into the polymeric matrix, they increase film flexibility and elasticity [2]. Also, it has been reported that the plasticizers affect thermal properties such as T_g and T_m of edible or biodegradable films. According to Arvanitoyannis et al. [6,7], the addition of plasticizers into the films results in lower values of T_g and T_m and lower crystallinities.

In this investigation, the melting temperature (T_m) and glass transition temperature (T_g) were determined in gelatin–starch biodegradable films by differential scanning calorimetry (DSC). The effect of some variables in the elaboration of these films, such as glycerol and starch concentrations, was evaluated using response surface methodology (RSM). Also, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the films.

2 Experimental

Biodegradable films were prepared following the method proposed by Aguilar-Mendez et al. [8]. Aqueous solutions with selected amounts of gelatin, starch, and glycerol were prepared in accordance with the experimental design (Table 1). The solutions were heated ((90 ± 2) °C) and mixed with a magnetic stirrer on a hot plate for 30 min.

Table 1 Experimental design and results

Test	Starch content (%w/w)	Glycerol content (%w/w)	T_g (°C)	T_m (°C)
1	0.2	0.2	80	194
2	0.6	0.2	71	193
3	0.2	0.8	62	192
4	0.6	0.8	55	193
5	0.12	0.5	68	193
6	0.68	0.5	61	194
7	0.4	0.08	80	194
8	0.4	0.92	61	193
9	0.4	0.5	64	194
10	0.4	0.5	63	194
11	0.4	0.5	65	195
12	0.4	0.5	66	195
13	0.4	0.5	67	194

Each solution was spread onto polyethylene casting plates and dried at (30 ± 2) °C in an oven. Finally, the films were detached from the casting plates and conditioned at (50 ± 2) % relative humidity using a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$. DSC measurements were performed using a Pyris 1 calorimeter (Perkin Elmer, USA). The samples (3 mg) were weighed into aluminum pans and heated from 30 °C to 220 °C at a rate of $5\,°C \cdot min^{-1}$. In all measurements an empty pan was used as a reference. X-ray diffraction patterns were obtained using a Siemens D5000 X-ray diffractometer (30 kV, 20 mA) with Cu Kα radiation ($\lambda = 1.5418$ Å). The microstructure of the films was characterized with a scanning electron microscope (SEM, JEOL JSM-6390LV, Rigaku, Japan).

3 Results and Discussion

3.1 Differential Scanning Calorimetry

Figure 1 shows typical thermograms of the different materials used in this investigation. It is possible to observe that the films elaborated with mixtures of starch–gelatin presented values of T_m higher than those for starch and gelatin alone. In accordance with RSM (Fig. 2), the highest values of T_m were obtained at starch concentration intervals of (0.26 to 0.54) %w/w and glycerol concentrations lower than 0.5 %w/w (Fig. 2a). On the other hand, the T_g values diminished as the glycerol concentration increased (Fig. 2b). According to Arvanitoyannis et al. [6], polyols, such as glycerol, interact with starch and gelatin polymers favoring hydrogen bonding formation and decreasing the interactions between polymer chains. This behavior leads to lower interaction energies between polymer chains. The results were statistically evaluated using variance analysis, and they showed a significant F value ($P < 0.05$). The mathematical models obtained for T_m ($R^2 = 0.77$) (Eq. 1) and T_g ($R^2 = 0.96$) (Eq. 2) were

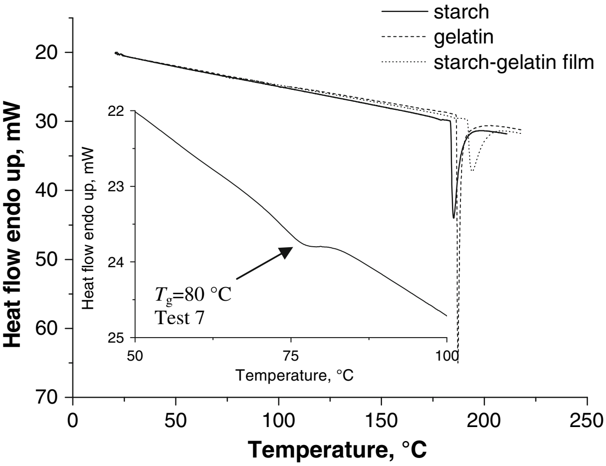

Fig. 1 Thermograms of starch, gelatin, and starch–gelatin film

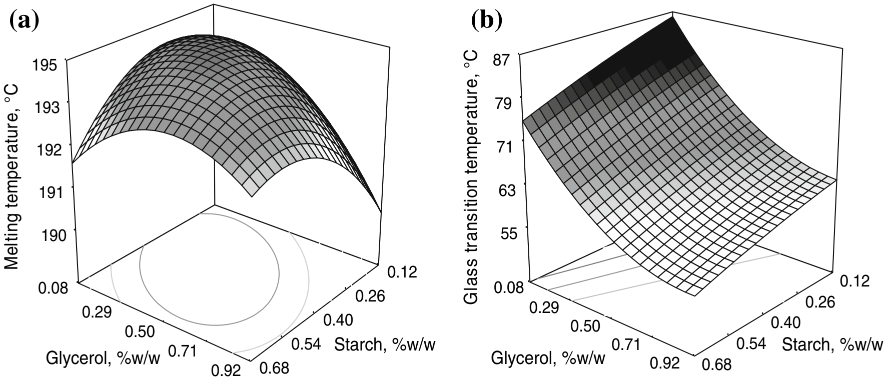

Fig. 2 Response surface graphs for (**a**) melting temperature and (**b**) glass transition temperature

properly fitted to the experimental data. X_1 and X_2 are starch and glycerol contents, respectively.

$$T_\mathrm{m} = 192.53 + 8.22X_1 + 1.63X_2 - 14.37X_1^2 - 6.39X_2^2 + 8.33X_1X_2 \quad (1)$$

$$T_\mathrm{g} = 92.34 - 14.86X_1 - 58.32X_2 - 6.56X_1^2 + 29.58X_2^2 + 7.08X_1X_2 \quad (2)$$

where X_1 is the starch content and X_2 is the glycerol content.

3.2 X-ray Diffraction

The technique of XRD was applied to observe the crystal structure of biopolymers and biodegradable films. The spectrum obtained for corn starch (Fig. 3a) shows a characteristic pattern reported in the literature (JCPDS-ICDD 39-1911); the peaks correspond to amylopectin (pseudo-crystalline), which presents some granular structure in corn starch [9]. The diffraction pattern for gelatin (Fig. 3b) shows a peak at $2\theta = 20.6°$ which has already been reported. Other authors have found small peaks at $2\theta = 7°$ to $8°$ [10].

On the other hand, in the XRD pattern of a biodegradable film (Fig. 3c) a peak appears more clearly defined at $2\theta = 22°$. Due to the formation of hydrogen bonds between gelatin and glycerol, the peak shifts to larger scattering angles. Therefore, it is possible to suppose that there are pseudo-crystalline regions in the films due to the gelatin–glycerol and gelatin–starch interactions.

3.3 Scanning Electron Microscopy

The results of microstructure studies with SEM shows the characteristic structure of corn starch (Fig. 4a), with polyhedral form for the most part; and also some spherical granules could be seen. Figure 4b shows a micrograph of gelatin with an amorphous form. During the process of film forming, both biopolymers were mixed and the final microstructure of the starch–gelatin film is shown in Fig. 4c, d. In these figures (test 2),

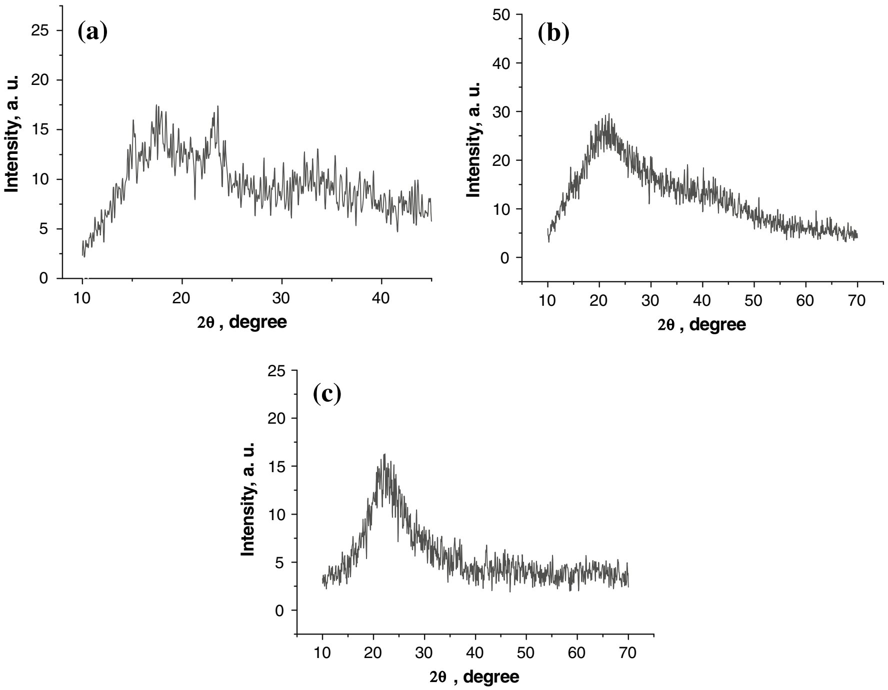

Fig. 3 X-ray diffraction patterns for (**a**) corn starch, (**b**) gelatin, and (**c**) biodegradable film

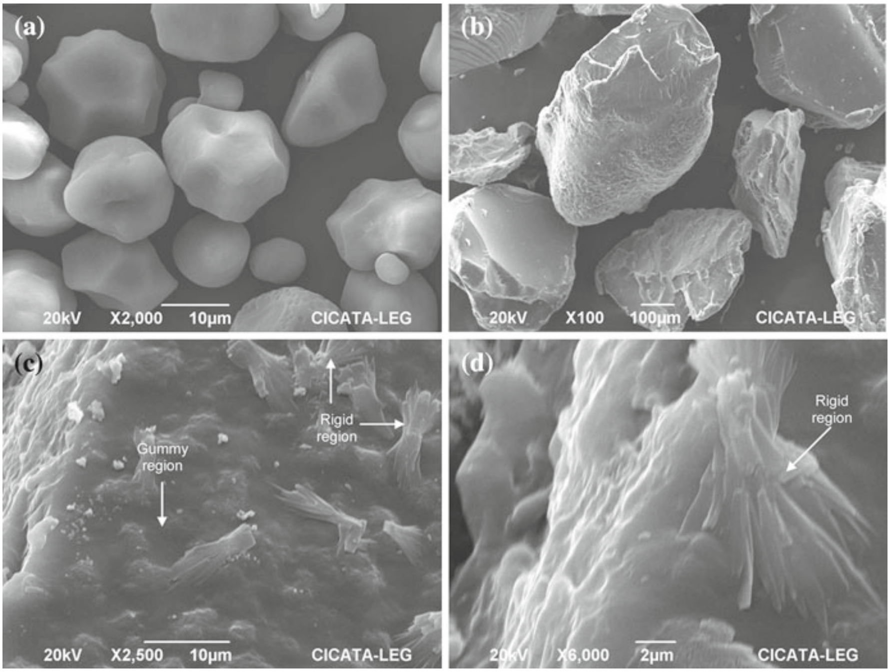

Fig. 4 SEM micrographs for (**a**) corn starch, (**b**) gelatin, and (**c, d**) biodegradable film

it is possible to observe some rigid (crystalline structure) and "gummy" regions. The glycerol content influenced the film microstructure significantly since, as it increased, the films present major "gummy" regions and vice versa. These results agree with those obtained for T_g and T_m.

4 Conclusions

In this investigation it was possible to obtain biodegradable films with different thermal properties depending on the elaboration conditions. The glycerol concentration influenced significantly the thermal properties, since it diminished the values of T_g and T_m of the biodegradable films. These results were corroborated with the results of microstructure investigations. The XRD technique demonstrated pseudo-crystalline regions in the starch–gelatin films and it is possible to suppose that the interactions between glycerol and gelatin are shown in the micrographs by shifts in scattering angles.

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