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Effect of flaxseed meal on the dynamic mechanical properties of starch-based films

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ABSTRACT

Starch (S)–flaxseed meal (FM) biofilms were prepared from potato and maize starch by incorporating FM up to 15% (dry solid basis) and using glycerol as plasticizer. The dynamic mechanical properties, tensile properties and water vapor permeability (WVP) of these films were measured. The storage modulus of both the starch (control) and starch–FM films decreased as temperature increased. Tan δ increased initially in all the films with increase in temperature until a peak value was reached which allowed the determination of glass transition temperature (T_g). Both tensile strength and Young's modulus of the starch–FM films increased with increase in the FM content. The WVP of the potato starch–FM films first increased to 2.261 ($\times 10^5$ g m^{-2} h^{-1} Pa^{-1}) when FM content increased to 5% and decreased down to 1.832 ($\times 10^5$ g m^{-2} h^{-1} Pa^{-1}) with further increase in the FM content to 15%. While the WVP values of the corn-starch and corn starch–FM films were not significantly ($p > 0.05$) different. The incorporation of FM increased the tensile strength, decreased the % elongation at break and increased the T_g.

1. Introduction

Starch and starch-based materials will be increasingly used in the future due to their greater availability, inherent biodegradability, low cost and desirable performance. For these reasons, starch generates a greater interest and it is considered as a promising alternative to synthetic polymers for packaging applications. However, the use of thermoplastic starch is limited in industrial applications, owing to its low resistance to mechanical stress and relative humidity. A number of studies have been undertaken on starch/polymer blends in applications such as packaging film and agricultural mulch (Stenhouse et al., 1997; Vaidya et al., 1995; Chen et al., 1997; Gáspár et al., 2005). A limited number of studies have also been undertaken regarding the use of natural fibers, micro-fibrils and regenerated cellulose fibers in association with starch (Averous, 2004; Curvelo et al., 2001; Dufresne et al., 2000; Funke et al., 1998).

Flaxseed is an important oilseed in the world. China is the second largest producer of flaxseed, after Canada, representing 20% of the world production (Agriculture and Agri-Food Canada, Bi-weekly Bulletin, 2007). It is mainly used to produce flaxseed oil for industrial applications such as paints, linoleum, varnishes, inks, and cosmetics (Green and Marshall, 1984). Most of the cellulose fibers and proteins are concentrated in flaxseed meal, which is a by-product of flaxseed-milling industry (Bhatty, 1993). Because of the high concentration of cellulose fibers in flaxseed meal, it can be used as a source of cellulose fibers for preparing reinforced or composite starch films. Cellulosic fibers from agricultural residues such as banana (Cherian et al., 2008; Zuluaga et al., 2009), wheat straw, and soy hulls (Alemdar and Sain, 2008) have already been produced and characterized. Starch itself is very brittle and posssess poor mechanical properties for packaging applications. However, by blending with plasticizers, such as glycerol or xylitol, elongation (E) can be improved significantly, but tensile strength (T) is negatively impacted (Muscat et al., 2012; Fu et al., 2011). The improvement in the mechanical behavior of a polymer from stiff/brittle to soft/flexible is due to increase in the molecular mobility (Stein and Greene, 1997). The glass transition temperature (T_g) of starch-based films can be affected by the presence of small molecular plasticizers (Kalichevsky et al., 1992). Currently, studies are mostly confined to the investigation of the steady state mechanical properties of starch and starch-based films (Dias et al., 2010; Reis et al., 2008; Araujo-Farro et al., 2010).

The dynamic mechanical analysis (DMA) is one of the proven methods used to determine the viscoelastic properties of materials. In this research, tensile (in tension mode) tests with temperature sweeps were applied to the starch–flaxseed meal composite films to obtain the storage modulus versus temperature data.

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Determination of the glass transition temperature (T_g) of the starch-based composite is important for ascertaining its stability at elevated environmental temperatures. A more common method of determining T_g of polymer composites is the DMA which defines T_g in terms of mechanical properties (Ghanbarzadeh and Oromiehi, 2009; Thakhiew et al., 2010).

In this study, we have successfully produced starch-based films containing flaxseed meal. The physicochemical properties such as water vapor permeability (WVP) and glass transition temperature (T_g) were also determined and analyzed. We have also characterized the tensile and viscoelastic properties of these films in order to provide technological basis for extending the applications of flaxseed meal in food packaging industry.

2. Materials and methods

2.1. Materials

Commercial grade potato starch (Amylose starch 19.1%) and maize starch (Amylose starch 24.7%) were purchased from Xinghua Starch Plant (Beijing, China). Flaxseed meal (FM) was purchased from a local market in Henan Province of central China. A grinder (B-400, Büchi Labortechnik AG, Switzerland) was employed to pulverize the flaxseed meal to pass a 80-mesh screen. Both the starch and flaxseed meal were dried in a convective oven at 105 ± 2 °C for 12 h to remove the excess moisture content. The dried samples were kept in a sealed desiccator until analysis.

2.2. Film preparation

Film forming solutions had 10% (w/w) total solids in all the cases. The ratio of (starch + FM) to the plasticizer (glycerol) was also maintained at 70:30 in all the cases (Table 1). The proportion of FM and starch in the starch–FM blend was varied as presented in Table 1. The blend of FM, glycerol and starch in water was stirred for 5 min at 14,000 rpm using a high speed dispenser (IKA® T25 digital, Staufen, Germany) to prepare the suspension. Afterwards, this suspension was heated at 95 °C for 30 min in a water bath. The suspension was constantly stirred at 300 rpm while it was being heated. Finally, these film forming suspensions were poured uniformly in glass Petri dishes having 14 cm in diameter. These Petri dishes (containing the film forming suspensions) were then put in a ventilated room at about 30 ± 2 °C for 30 h. The starch films (P0, Table 1) prepared without flaxseed meal were served as control sample.

2.3. Tensile test

Films were conditioned at 25 °C and 52.9% relative humidity using saturated magnesium nitrate solution. The conditioning was carried out for a week before testing. Sample thickness was measured using a micrometer with a sensitivity of 1 μm. The tensile stress at yield point (σ_y), tensile strength (σ_b) and percentage elongation at yield point (P.E.Y.) were determined using a Universal Testing Machine (INSTRON-4411 analyzer, Instron Inc., UK) according to ASTM D882-97 (1997) method. The dimension of the film samples was 15 mm (width) × 100 mm (length) in these tests. Then, the film sample was fixed using a clamp and the tensile test was conducted with a tensile speed of 25 mm/min until fracture. The tensile stress and the elongation length were recorded at fracture point. The reported results are the average values of five samples (n = 5). Young's modulus was calculated from the tensile stress–strain plots by the computer software. Duncan's multiple range test ($P < 0.05$) was used to determine the significance of differences between the means.

Table 1
The proportion of flaxseed meal, cellulose fibers, starch, water and thickness values.[a]

Samples	FM (g)	Starch (g)	Glycerol (g)	Water (g)	Thickness (mm)
P0	0	7.00	3.00	90.00	0.279 ± 0.002
P5	0.5	6.50	3.00	90.00	0.354 ± 0.004
P10	1.0	6.00	3.00	90.00	0.335 ± 0.005
P15	1.5	5.50	3.00	90.00	0.301 ± 0.003
M0	0	7.00	3.00	90.00	0.278 ± 0.003
M5	0.5	6.50	3.00	90.00	0.245 ± 0.005
M10	1.0	6.00	3.00	90.00	0.261 ± 0.001
M15	1.5	5.50	3.00	90.00	0.242 ± 0.002

Values represent the mean ± standard deviation; n = 3.
[a] P refers to potato starch film; M refers to maize starch film; 0, 5, 10 and 15 refer to flaxseed meal (FM) content (%).

2.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical measurements were conducted using a Q800 Dynamic Mechanical Analyzer (TA Instruments, New Castle, USA) using a film tensile clamp at single-frequency scanning mode of 0.35 Hz (angular frequency x = 2.2) and a heating rate of 2.0 °C/min over a temperature range from 40 °C to 140 °C. Constant amplitude of 5 μm was applied in all the DMA experiments. The samples were subjected to a cyclic strain of 0.05%. This strain value was sufficiently small to ensure that the mechanical response of the specimen was within the linear viscoelastic regime. The temperature of both the sample and the instrument was equilibrated to 40 °C before all these tests. All necessary thermal and mechanical calibrations of the instrument were performed before the experiments according to the operation manual (TA Instruments, 2004). The Poisson ratio was maintained at 0.38 and the data were acquired in terms of storage modulus E', the loss modulus E'' and the ratio of these two parameters, $\tan\delta = E''/E'$.

2.5. Water vapor permeability (WVP)

The water vapor permeability tests were conducted using the ASTM E96-00 method with some modifications (ASTM, 1996). The permeation cell (glass beaker) had an internal diameter of 23.84 mm and an external diameter of 25 mm (exposed area: 5.68 cm^2). The cell contained 5 ml of deionized water. After that, the permeation cell along with the film sample was sealed over a circular opening of glass beaker and was stored at 25 °C in desiccators maintained at 0% RH. The extent of water vapor transport across the film was determined from the weight reduction of the permeation cell. Changes in the weight of the cell were recorded to the nearest 0.0001 g and weighed daily for 10 days. Thickness of each film was measured with a micrometer at ten randomly selected points before the permeation tests. Three replicate samples were analyzed (Table 1). The WVP ($\times 10^5$ g m^{-2} h^{-1} Pa^{-1}) was calculated using Eq. (1):

$$WVP = \left(\frac{WVTR}{PS(RH_1 - RH_2)}\right) \times x \quad (1)$$

where $WVTR$ is the rate of water vapor transfer (g d^{-1}) which was determined from the slope of mass loss (g) versus time (d) line (g d^{-1}), S is the cell area (m^2), P (kPa) is the saturation vapor pressure of water at the test temperature (25 °C), RH_1 is the relative humidity in fraction inside the permeation cell (RH_1 = 0.529), RH_2 is the fraction of relative humidity in the desiccators (RH_2 = 0.000), and x is the average thickness of the film (mm).