

Thermoplastic blends of corn gluten meal/starch (CGM/Starch) and corn gluten meal/polyvinyl alcohol and corn gluten meal/poly (hydroxybutyrate-co-hydroxyvalerate) (CGM/PHB-V)

Elisângela Corradini^{a,b,*}, José M. Marconcini^b, José A.M. Agnelli^a, Luiz H.C. Mattoso^b

^a Department of Materials Engineering, Federal University of São Carlos, 13560-905 São Carlos, SP, Brazil

^b National Nanotechnology Laboratory for Agriculture, Embrapa/CNPq, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 11 May 2010

Received in revised form 17 August 2010

Accepted 5 September 2010

Available online 15 September 2010

Keywords:

Biodegradable blends

PVAI

PHB-V

Starch

Corn gluten meal

ABSTRACT

Corn gluten meal/starch (CGM/Starch), corn gluten meal/polyvinyl alcohol (CGM/PVAI), and corn gluten meal/poly (hydroxybutyrate-co-hydroxyvalerate) (CGM/PHB-V) blends were prepared in different proportions. Glycerol was used as plasticizer. The blends were prepared by melting in a Haake torque rheometer, followed by hot compression molding. The morphology of the blends containing CGM showed changes as a function of variations in blend composition. Water absorption at equilibrium did not vary to any significant extent in response to the addition of PVAI or Starch to CGM, and decreased with increasing PHB-V content. Tensile tests showed that the addition of PVAI increased the flexibility of the blends, while the presence of PHB-V enhanced their rigidity, but slight changes in mechanical properties were observed with the addition of Starch to CGM. The dynamic mechanical analysis (DMA) results revealed that all the blends exhibited two different glass transitions, one for each component, indicating that these blends are immiscible in the compositional range of this study.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Proteins from cultivated crops such as soy, wheat and corn present a strong potential for the development of edible films or biodegradable plastics because they are nontoxic, biodegradable, and originate from renewable sources (Corradini, Imam, Agnelli, & Mattoso, 2009; Hernandez-Izquierdo & Krochta, 2008; Song & Zheng, 2009).

Corn gluten meal (CGM) is often obtained as an agricultural by-product of the starch processing industry. CGM is composed mainly of protein (60%), with a high percentage of hydrophobic amino acids, the remaining components being mainly water, fiber, and lipids (Lasztity, 1996). CGM is used mostly in animal feed, but it shows a strong potential for the development of biodegradable materials due to its thermoplastic properties (Beg, Pickering, & Weal, 2005). CGM can be extruded or injection-molded into biodegradable solid articles; however, gluten has poor processability compared to pure protein, starch or synthetic polymers (Wu, Sakabe, & Seiichiro, 2003) and shows significant limitations

in terms of mechanical properties (e.g., brittleness). Blending CGM with other polymers is one way of reducing cost and modifying materials. In this sense, CGM has been blended with polycaprolactone (PCL) to improve the melt flow index and properties of CGM (Aithani & Mohanty, 2006). The literature reports other attempts involving blends of wheat gluten with PCL (Finkenstadt, Mohamed, Biresaw, & Willett, 2008; Mohamed et al., 2008), maleic anhydride-modified polycaprolactone (John, Tang, & Bhattacharya, 1998), and poly (vinyl chloride) (Marais, Nguyen, Langevin, & Metayer, 2001).

The combination of CGM with other biodegradable polymers such as polyvinyl alcohol (PVAI), starch and poly (hydroxybutyrate-co-hydroxyvalerate) (PHB-V) may show a promising potential in the field of biodegradable plastics. The existence of polar and non-polar groups in CGM could lead to interactions between the polar groups of PVAI and starch and the nonpolar groups in PHB-V, rendering the blend mechanically viable. Additionally, blending CGM with these polymers may not only modify its mechanical properties but also improve its processability.

This paper describes the preparation of CGM/Starch, CGM/PVAI, CGM/PHB-V glycerol-plasticized blends by melt processing in an intensive mixer and the characterization of these blends. The resulting mixtures were hot compression molded, followed by characterization based on water absorption experiments, scanning electron microscopy (MEV), tensile tests and dynamic mechanical thermal analysis.

* Corresponding author at: National Nanotechnology Laboratory for Agriculture, Embrapa/CNPq, Rua XV de Novembro 1452, 13560-970 São Carlos, SP, Brazil. Tel.: +55 16 21072835; fax: +55 16 21072902.

E-mail address: elisangela@cnpdia.embrapa.br (E. Corradini).

2. Experimental

2.1. Materials

Hybrid corn starch containing approximately 27% amylose (commercially known as “amisol 3408”) and corn gluten meal (60–70% protein, 20% starch and 4% lipids) were kindly supplied by Corn Products Brazil, while polyvinyl alcohol (PVAL) with a degree of hydrolysis of 87–89% and viscosity of 23.0–27.0 mPa at 25 °C (commercially known as “DuPont™ Elvanol® 50–52”) was supplied by Petroquimil, and poly (hydroxybutyrate-co-hydroxyvalerate) (PHB-V) with Mw: 53,4837 g/mol and Mn: 24,5790 g/mol was donated by PHB Industrial. Analytical grade glycerol was purchased from Synth Reagents.

2.2. Material processing and characterization

Blends of corn gluten meal/starch (CGM/Starch), corn gluten meal/polyvinyl alcohol (CGM/PVAL) and corn gluten meal/poly (hydroxybutyrate-co-hydroxyvalerate) (CGM/PHB-V) were prepared in different proportions. The glycerol content was 20% in weight of the total mass of polymer (dry basis). The compositions used here contained 100/0, 75/25, 50/50, 25/75 and 0/100 of CGM/Starch, CGM/PVAL and CGM/PHB-V, respectively. The polymer powders were weighed separately, premixed in a beaker, and the resulting mixtures were processed by melting in a Haake torque rheometer at 150–160 °C, 50 rpm, for 6 min. The mixtures were pressed at 150 °C under 5 kgf for 5 min to produce 150 mm × 120 mm × 2.5 mm molded sheets. The resulting thermoplastic materials were then stored for four weeks at 25 ± 3 °C and 54 ± 3% of relative humidity, and characterized as follows.

2.2.1. Water absorption

Circular samples (11 mm in diameter and 2.5 mm thick), pre-dried overnight at 105 °C, were weighted and placed in hermetically closed containers with 54 ± 3% of relative humidity (RH) and 25 ± 2 °C, using a saturated Mg(NO₃) solution, as prescribed by the ASTM E 104 standard. The amount of water absorbed by the samples was determined by weighing them periodically until they reached a constant weight. The water absorption (*W*) of the samples was calculated as follows:

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

where *M_t* is the weight at time *t* and *M₀* is the dry weight before exposure to 54 ± 3% of RH.

2.2.2. Tensile tests

The tensile tests were performed in an Instron 5569 universal testing machine equipped with a load cell of 500 N. The samples were prepared according to the ASTM D638M standard, type II. At least 5 samples of each material were tested at a crosshead speed of 5 mm/min and 25 °C.

2.2.3. Dynamic mechanical analysis

Dynamic mechanical analyses were carried out in a TA Instrument DMA 500 analyzer, in accordance with the ASTM D-5023 standard, using the three-point bending method, a heating rate of 5 °C/min, an amplitude of 20 μm, and a frequency of 1 Hz.

2.2.4. Scanning electron microscopy (SEM)

SEM micrographs of the brittle surface of the blend samples were obtained with a Model DSM Zeiss Digital Scanning Microscope operating at 10–15 kV.

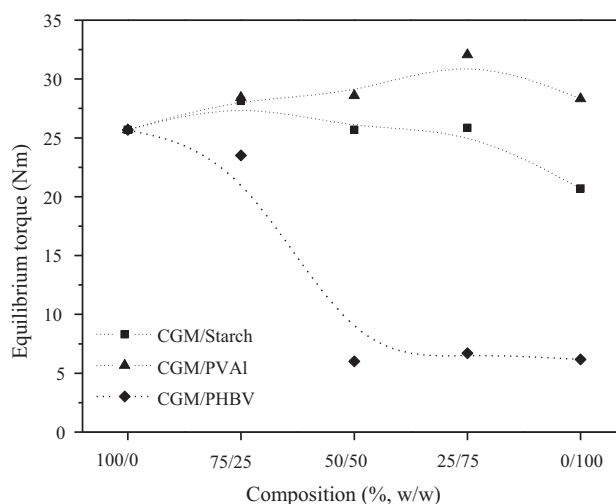


Fig. 1. Equilibrium torque values obtained after 6 min of mixing as a function of composition for the CGM/Starch, CGM/PVAL and CGM/PHB-V blends plasticized with 20% glycerol.

3. Results and discussion

Fig. 1 shows the equilibrium torque curves after 6 min as a function of the composition for the CGM/Starch, CGM/PVAL and CGM/PHB-V mixtures containing 20% of glycerol. Note that the equilibrium torque developed for the composition of CGM with glycerol (composition 100/0 Nm) was approximately 25 Nm. The compositions of Starch and PVAL with glycerol (0/100 of CGM/Starch and 0/100 of CGM/PVAL) presented torque values of 20 Nm and 28 Nm, respectively, which were close to that observed in the composition of CGM with glycerol. In contrast, the PHB-V with glycerol composition (0/100 de CGM/PHB-V) showed an equilibrium torque of about 6 Nm, which was much lower than that observed in the CGM/glycerol composition. These differences in the equilibrium torque of the individual polymers during processing with glycerol are directly proportional to their viscosities and can significantly influence the morphology of the respective blends.

The CGM/Starch and CGM/PVAL blends presented an increase in torque compared to the values observed for individual polymers. This synergic effect suggests the existence of interactions among the blend-forming polymers in the melted state. The curve for the CGM/PHB-V blends presented an S-shaped profile unlike that of the other two systems under study. This profile is typical of immiscible blends with a certain degree of interaction among polymers (Deanin, 1987).

A visual analysis indicated that the plasticity of the polymeric mass of CGM, obtained after processing in the torque rheometer, improved with the addition of any of the three polymers (Starch, PVAL or PHB-V).

The photographs in Figs. 2 and 3 show the fracture surface of the different CGM/Starch, CGM/PVAL and CGM/PHB-V compositions. The surfaces of the materials showed visible differences. The plasticized CGM (Fig. 2a) exhibited a very heterogeneous surface with various protein aggregates. This type of morphology was also reported by Finkenstadt et al. (2008). The thermoplastic starch (Fig. 2b) presented an apparently homogeneous surface, which suggests that complete destruction of the granular structure of the Starch occurred during processing, leading to a continuous phase. The glycerol-plasticized PVAL (Fig. 2c) presented a uniform and continuous surface with some roughness. Small holes were visible on the surface of the plasticized PHB-V (Fig. 2d), probably resulting from the immiscibility between glycerol and PHB-V. Morphologi-

Download English Version:

<https://daneshyari.com/en/article/1387113>

Download Persian Version:

<https://daneshyari.com/article/1387113>

[Daneshyari.com](https://daneshyari.com)