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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)

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ABSTRACT

Corn gluten meal/starch (CGM/Starch), corn gluten meal/polyvinyl alcohol (CGM/PVAl), 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 PVAl or Starch to CGM, and decreased with increasing PHB-V content. Tensile tests showed that the addition of PVAl 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.

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 (PVAl), starch and poly (hydroxybutyrate-co-hydroxyvalerate) (PHB-V) may show a promising potential in the field of biodegradable plastics. The existence of polar and nonpolar groups in CGM could lead to interactions between the polar groups of PVAl 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/PVAl, 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.

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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 "DuPontTM 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), predried 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 $Mg(NO_3)$ 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 M_0 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.

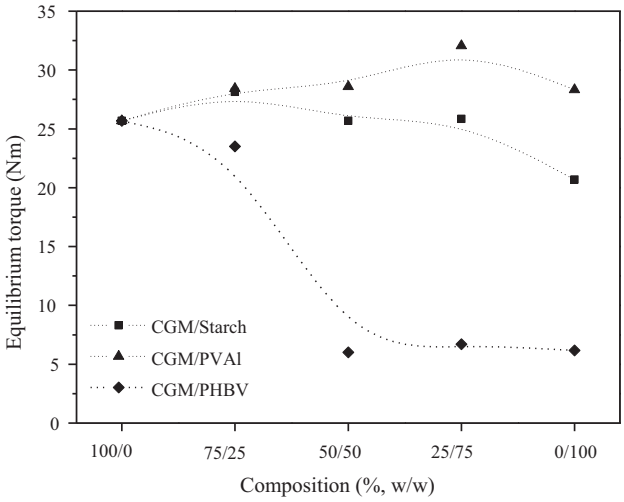

Fig. 1. Equilibrium torque values obtained after 6 min of mixing as a function of composition for the CGM/Starch, CGM/PVAl and CGM/PHB-V blends plasticized with 20% glycerol.

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-

cal variations were found as a function of the mass composition of the blends' components (Fig. 3). These changes in the blends' morphologies are related to differences in the viscosity of each polymer during processing, as indicated by the torque behavior. Immiscible blends normally exhibit dispersed phase/matrix type morphology (Mekhilef & Verhoogt, 1996; Moreira, Cairo, & Soares, 2002). The polymer that is present in the largest quantity forms the continuous phase (matrix) and the other polymers in smaller quantities form the dispersed phase. The morphologies of the 75/25 CGM/PVAl, CGM/Starch and CGM/PHB-V compositions showed some similarities with that of the plasticized CGM (Fig. 2a), while the morphology of the 75/25 GM/PVAl, CGM/Starch compositions presented some similarities with that of the respective polymer in larger quantity. However, the 25/75 CGM/PHB-V composition clearly showed a two-phase morphology with spherical domains of gluten dispersed in the continuous phase of PHB-V. The formation of this type of morphology is common in immiscible polymer blends when their components present significantly different viscosities.

It was also found that the CGM/PVAl blends presented a better dispersion of the polymers than the CGM/Starch and CGM/PHB-V blends. The presence of cracks and faults in the CGM/Starch 25/75 and CGM/PHB-V 25/75 compositions indicate weak interfacial adhesion between phases.

Fig. 4 shows absorption curves of equilibrium water as a function of composition for the CGM/Starch, CGM/PVAl, and CGM/PHB-V blends plasticized with 20% glycerol. The values of absorption at equilibrium were as follows: gluten – $7.99 \pm 0.04\%$, PHB-V – $0.25 \pm 0.02\%$, PVAl – $8.53 \pm 0.08\%$, and starch – $9.98 \pm 0.08\%$. The absorption properties of polymers are determined principally by their hydrophilicity and hydrophobicity balance. Starch and PVAl have more intense hydrophilic properties than gluten and PHB-V due to the OH groups in their structures, while gluten has amphoteric characteristics (hydrophilic/hydrophobic) and PHB-V possesses a highly hydrophobic structure. The addition of PVAl or starch to the blends with gluten caused no major variation in water absorption, while the addition of PHB-V triggered the opposite effect, i.e., reduction of water absorption in blends containing gluten.

Fig. 5 shows the values of Young's modulus (E), ultimate tensile strength (σ_r), and deformation at break (ε_r), which were calculated from the stress–strain curves for the different compositions of CGM/Starch, CGM/PVAl and CGM/PHB-V processed with 20% glycerol. Note that the addition of PHB-V and PVAl caused a significant increase in the values of ultimate tensile strength (σ_r) of the blends containing CGM. For example, the CGM/PVAl and CGM/PHB-V blends in the 50/50 composition showed an increase of 34% and 74%, respectively, in relation to the plasticized CGM (composition 100/0). In the case of the CGM/Starch blends, the tensile strength showed a non-significant variation with the addition of starch. The mean values of σ_r for the 25/75, 50/50 and 75/25 compositions varied in the range of 2.9–5.0 MPa (CGM/Starch), 3.1–9.2 MPa (CGM/PVAl) and 3.8–9.2 MPa (CGM/PHB-V). The deformation at break (ε_r) of plasticized CGM (CGM) increased with the addition of PVAl. The CGM/PVAl 50/50 blend showed an increase of approximately 900% in the value of ε_r in relation to the plasticized CGM. The addition of PHB-V or Starch in the blends with CGM did not

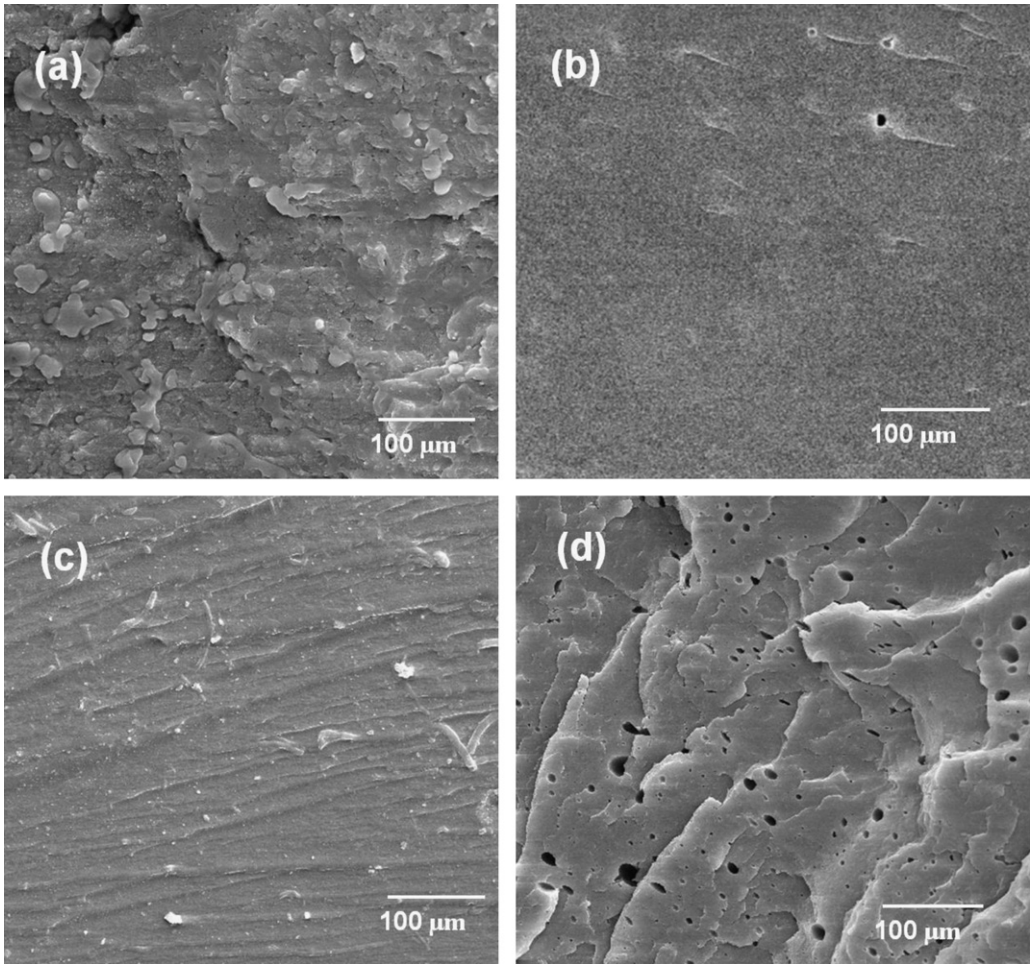

Fig. 2. SEM images of the surfaces of thermoplastic materials containing 20% glycerol: (a) CGM, (b) Starch, (c) PVAl, and (d) PHB-V.

lead to a significant variation in the values of ε_r. The mean values of ε_r for the compositions of 25/75, 50/50 and 75/25 of CGM/TPS, CGM/PVAl and CGM/PHB-V varied from 2.0% to 3.0%, 22% to 132% and 1.3% to 1.7%, respectively. The increase of PHB-V content in the blends with gluten caused the modulus of elasticity (E) to increase, while the addition of PVAl or starch to the blends with CGM did not lead to a significant variation in the values of E. The mean values of E for the compositions 25/75, 50/50 and 75/25 of CGM/TPS, CGM/PVAl and CGM/PHB-V varied in the range of 121–151 MPa, 162.5–67.2 MPa and 275–834 MPa, respectively. These results indicate that the addition of PVAl to CGM favors flexibility, while the addition of PHB-V favors rigidity.

John et al. (1998) reported that CGM modified/Polycaprolactone (PCL-MA) blends with 65% gluten and 35% PCL-MA presented values of ultimate tensile strength of 5 MPa and elongation at break of 8%. Aithani and Mohanty (2006) prepared CGMP blends (plasticized corn gluten meal) modified with guanidine hydrochloride (GHCl) and PCL. Their results indicated that the presence of GHCl caused a significant increase in elongation at break compared with the CGMP/PCL composition. Their 50/42.5/7.5 PCL/CGMP/GHCl blend presented E, σ_r, and ε_r values of 6.5 MPa, 450 MPa and 500% MPa, respectively. Wu et al. (2003) reported a 20% increase in ultimate tensile strength with the introduction of 30% of wood powder in a glycerol-plasticized CGM matrix. In another study, Corradini et al. (2009), added sisal, coconut and jute fibers as reinforcement in a biodegradable polymer matrix composed of starch, CGM and glycerol. The composites reinforced with 30% of coconut, jute and sisal fibers presented values of σ_b in the range of 7.0–9.0 MPa, while the

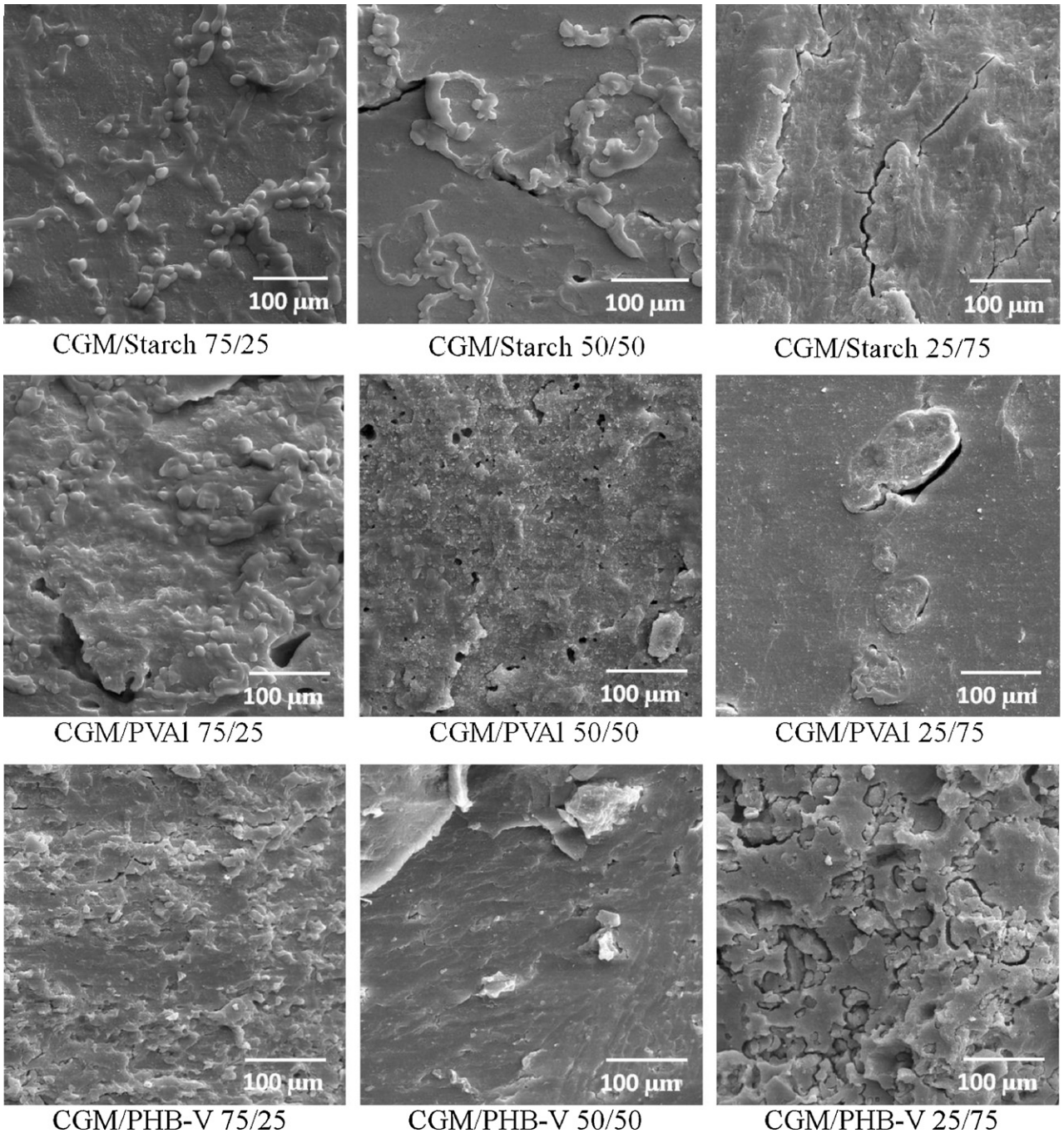

Fig. 3. SEM images of the surfaces of the 25/75, 50/50 and 75/25 CGM/Starch, CGM/PVAl and CGM/PHB-V compositions containing 20% glycerol.

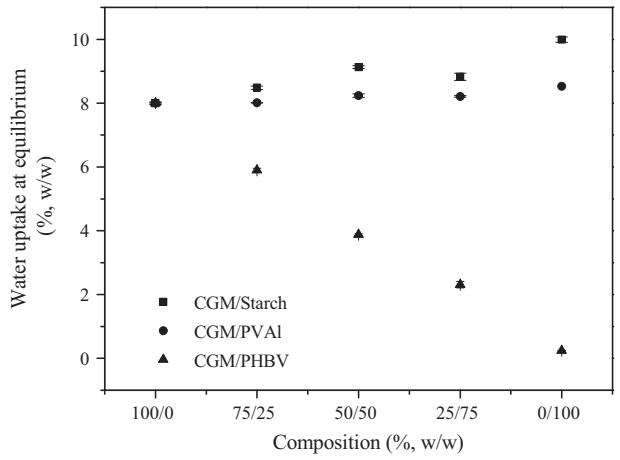

Fig. 4. Water absorption at 54 ± 3% RH as a function of composition in the CGM/Starch, CGM/PVAl and CGM/PHB-V blends plasticized with 20% glycerol.

values of E exceeded 1500 MPa and the values of ε were lower than 2%.

Comparing these values against the results obtained with the blends under study, it was found that, in some compositions, the CGM/PVAl and CGM/PHB-V blends presented values of E and σ_r close to those of the CGM/PCL and PCL/CGMP/GHCl blends, while the CGM/Starch blends exhibited lower mechanical properties in the compositions studied here. It was also found that the CGM composites with natural fibers presented higher values of E and σ_b than the CGM/PVAl and CGM/PHB-V blends, but lower values of elongation at break.

Fig. 6a–c shows the curves of the storage modulus (E') and damping factor ($\tan\delta$) as a function of temperature for the CGM/Starch, CGM/PVAl and CGM/PHB-V blends, respectively. The CGM, Starch, PVAl and PHB-V polymers plasticized with glycerol presented two transitions, the first in the range of −61 °C to −51 °C corresponding to the glass transition (Tg) of glycerol (Tg_{Gly}) or regions rich in glycerol (Lourdin, Bizot, & Colonna, 1997) and the second at around 78 °C, 32 °C, 1.1 °C and 21 °C, corresponding to the Tg of CGM (Tg_{CGM}), starch (Tg_{starch}), PVAl (Tg_{PVAl}) and PHB-V (Tg_{PHB-V}), respectively. The compositions of 25/75, 50/50 and 75/25 of GM/Starch, CGM/PVAl and CGM/PHB-V presented three glass transitions: the first was attributed to glycerol, while the second and third corresponded to the Tg of the respective polymers (Table 1). The presence of two transitions indicates that the blends under study are immiscible, although variations were found in the Tg of the polymers. These variations may be related to specific interactions between the blend-forming polymers as well as interactions between the polymers and glycerol. In the case of CGM/Starch blends, all the compositions showed a significant decrease in the Tg of Starch, although this decrease was less pronounced with increasing concentrations of Starch. This type of behavior may be related with the differences in the hydrophilicity of Starch and CGM. Starch is more hydrophilic than CGM, and the Starch phase may be more plasticized than the CGM phase. This behavior was also found in the glycerol-plasticized starch/zein system (Corradini, De Medeiros, Carvalho, Curvelo, & Mattoso, 2006). An explanation for this is that part of the glycerol or water may have migrated from the gluten phase (less hydrophilic) to the starch phase (more hydrophilic), reducing its Tg. When the dispersed phase is Starch, a large part of the glycerol is concentrated in this phase, and the 50% and 75% increase in starch content probably led to a better distribution of glycerol in the Starch phase. It was also found that the Tg of gluten did not change when the Starch content was low, but increased when the starch content increased from 25% to 50% and 75%, probably due to the migration of glycerol to the starch phase. In the

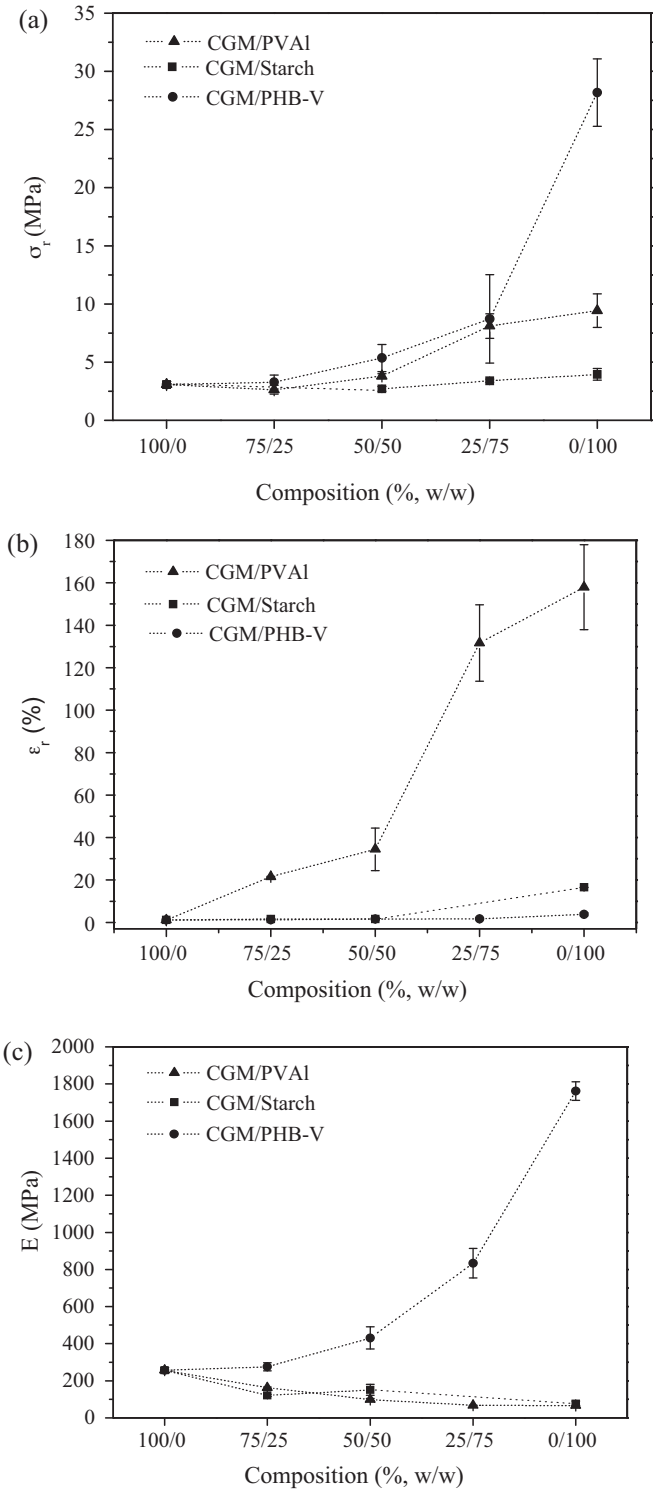

Fig. 5. Ultimate tensile strength (σ_r) (a), elongation at break (ε_r) (b) and Young's Modulus (E) (c) as a function of composition of the CGM/Starch, CGM/PVAl and CGM/PHB-V blends plasticized with 20% glycerol.

case of the CGM/PVAl blends, the same behavior was observed in the blend with 25% PVAl, but the blends with higher PVAl contents showed an increase in the Tg of PVAl similar to that of partially miscible systems. These results indicate the presence of two effects, i.e., the effect of the plasticizer prevails at low PVAl contents, while the effect of the interaction between the polymers prevails at higher PVAl contents. In the case of the CGM/PHB-V blends, the Tg of PHB-V did not change significantly, indicating low interaction between

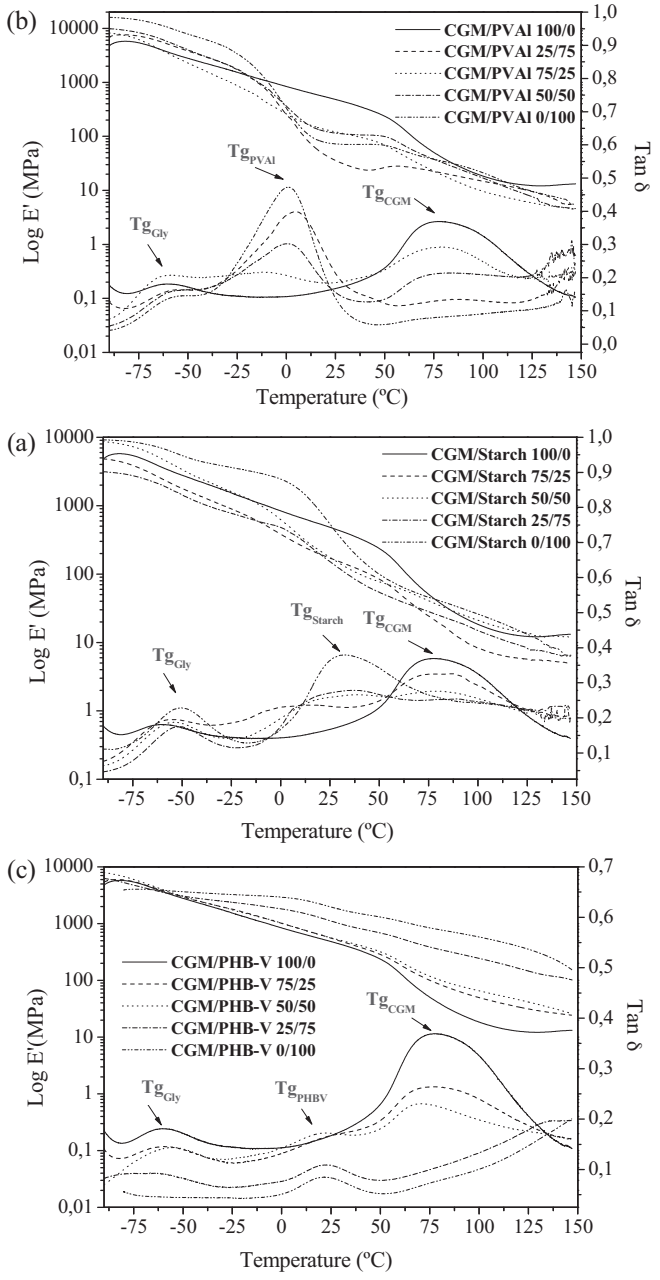

Fig. 6. Storage modulus (E') and damping factor ($\tan\delta$) as a function of temperature in blends plasticized with 20% glycerol: CGM/Starch (a), CGM/PVAl (b), and CGM/PHB-V(c).

CGM and PHB-V, although there was a variation of the Tg of CGM for 50/50 and 75/25 CGM/PHB-V compositions. This variation in Tg_{CGM} may be related to the non-homogeneous distribution of glycerol between the PHB-V and CGM phases, as discussed for the CGM/PVAl and CGM/Starch blends. The Tg of CGM was not clearly detectable in the 25/75 CGM/PHB-V composition, but the SEM results clearly showed the existence of phase separation, indicating the immiscibility of this composition. A comparison of the E' curves indicates that the values of E' at around 25 °C decreased in response to the addition of starch or PVAl, while the presence of PHB-V caused the values of E' to increase. This finding indicates that starch contributed to decrease the rigidity while PHB-V caused the opposite effect, i.e., it increased the rigidity of gluten. This behavior is consistent with the results obtained from the flexural tests.

Table 1
Glass transition (Tg) of the CGM/Starch, CGM/PVAl and CGM/PHB-V blends containing 20% glycerol, calculated from the maximum of the tan δ curve.

Composition CGM/TPS	1st peak tan δ Tg_{Gly}	2nd peak tan δ Tg_{Starch}	3rd peak tan δ Tg_{CGM}
100/0	−61	–	77
75/25	−55	1.5	77
50/50	−53	19.6	79
25/75	−51	23	90
0/100	−51	32	–
Composition CGM/PVAl	**1st peak tan δ Tg_{Gly}**	**2nd peak tan δ Tg_{PVAl}**	**3rd peak tan δ Tg_{CGM}**
100/0	−61	–	78
75/25	−62	−7,5	78
50/50	−60	1.9	74
25/75	−61	5.1	85
0/100	−58	1.1	–
Composition CGM/PHB-V	**1st peak tan δ Tg_{Gly}**	**2nd peak tan δ Tg_{PHBV}**	**3rd peak tan δ Tg_{CGM}**
100/0	−61	–	78
75/25	−61	20	74
50/50	−58	20	69
25/75	−62	22	–
0/100	–	21	–

4. Conclusions

Blends of PVAl, PHB-V and starch with gluten were obtained in a wide range of compositions. The blends of gluten with PVAl, PHB-V and starch were immiscible in the compositions studied here. The addition of PVA to gluten favored flexibility, while the addition of PHB-V increased the rigidity. Starch had a less significant effect on the mechanical properties than PHB-V and PVAl in the blends with CGM. The addition of PVAl or starch to the blends with gluten caused only a minor variation in water absorption, while the addition of PHB-V produced the opposite effect, reducing their water absorption. These results are interesting, since they demonstrate the possibility of using gluten combined with PVAl and PHB-V in the development of new materials with good mechanical properties and higher water resistance, without loss of their characteristics of biodegradability.

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