

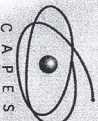
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XII INTERNATIONAL
MACROMOLECULAR COLLOQUIUM

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7th INTERNATIONAL SYMPOSIUM ON
NATURAL POLYMERS AND COMPOSITES

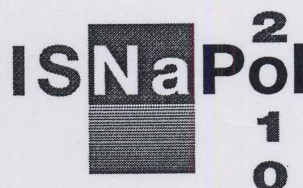
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NATURAL POLYMERS AND COMPOSITES

FOREWORD

It is a great pleasure for us to welcome all the participants of the **XII International Macromolecular Colloquium and the 7th International Symposium of Natural Polymers and Composites**. We are very pleased with your contributions which are very important to the success of the Meeting. During this time, researchers will have the opportunity to initiate and enhance fruitful interactions among different institutions around the world working in the field of Polymer Science and Technology. We hope this Meeting will also offer a good opportunity to improve the research on the field of natural polymer-based materials and composites developed in Brazil.

Without your participation and specially the contribution of those presenting the 30 lectures, 34 oral sessions and 411 posters it would not be possible to organize this Meeting. We would like to acknowledge also the support from BRASKEM, CAPES, CNPq, FAPERGS, FAPESP, Petrobras and PROPESQ-UFRGS and the participation of the exhibitors dpUnion, Instrutécnica, Polimate and Reoterm.

We wish all the participants lots of interesting discussions and important stimulus for their further work and a pleasant stay in Gramado.

Organizing Committee



MECHANICAL PROPERTIES OF BLENDS OF CORN GLUTEN MEAL (CGM) WITH POLYVINYL ALCOHOL (PVAL), STARCH AND POLY(HYDROXYBUTYRATE-CO-HYDROXYVALERATE) (PHB-V)

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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. The glycerol content was 20% in weight of the total mass of polymers (dry basis). The blends were prepared by melting in a Haake torque rheometer, followed by hot compression molding. 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 DMA results revealed that the CGM/Starch, CGM/PVAL and CGM/PHB-V blends exhibited two different glass transitions, one for each component, indicating that these blends are immiscible in the compositional range of this study.

Introduction

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 [1]. CGM is used mostly in animal feed, but it shows a strong potential for the development of biodegradable materials due to its thermoplastic properties [2-4]. 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 and characterized by tensile tests.

Experimental

Material

Material: 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% (commercially known as "DuPont™ Elvanol® 50-52") was supplied by Petroquimil, and poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-V) was donated by PHB Industrial. Analytical grade glycerol was purchased from Synth Reagents.

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 weighted separately, premixed in a beaker, and the resulting mixtures were processed by melting in a Haake torque rheometer at 150°C-160°C, 50 rpm, for 6 min. The mixtures were pressed at 150°C under 5 kgf for 5 minutes to produce 150mm X 120mm X 2.5mm 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.

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 [5]. At least 5

samples of each material were tested at a crosshead speed of 5mm/min and 25°C.

Results and Discussion

Figure 1 shows the values of Young's modulus (E), ultimate tensile strength (σ_r), and deformation at break (ϵ_r) for the different compositions of CGM/Starch, CGM/PVAI and CGM/PHB-V processed with 20% glycerol. Note that the addition of PHB-V and PVAI caused a significant increase in the values of ultimate tensile strength (σ_r) of the blends containing CGM. For example, the CGM/PVAI 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 (Starch). The mean values of σ_b for the 25/75, 50/50 and 75/25 compositions varied in the range of 2.9-5MPa (CGM/Starch), 3.1-9.2 MPa (CGM/PVAI) and 3.8-9.2 MPa (CGM/PHB-V). The deformation at break (ϵ_r) of plasticized CGM (CGM) increased with the addition of PVAI. The CGM/PVAI 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 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/PVAI 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 PVAI 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/PVAI 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 PVAI to CGM favors flexibility, while the addition of PHB-V favors rigidity. JOHN et al. (1997) reported that CGM/Polycaprolactone (PCL) blends with 65% gluten and 35% PCL presented values of ultimate tensile strength of 5 MPa and elongation at break of 8%. Aithani & Mohanty [6] 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. [7] reported a 20% increase in ultimate tensile strength with the introduction of 30% of wood powder in a glycerol-plasticized CGM matrix.

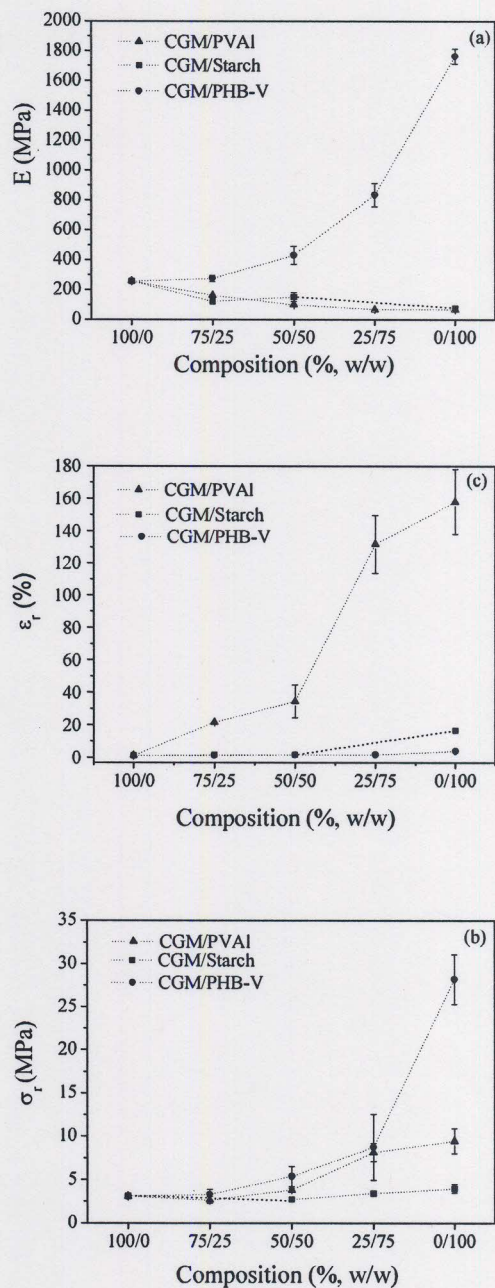


Figure 1 – Young's Modulus (E) (a), ultimate tensile strength (σ_r) (b), and elongation at break (ϵ_r) (c) as a function of composition of the CGM/Starch, CGM/PVAI and CGM/PHB-V blends plasticized with 20% glycerol

In another study [4], sisal, coconut and jute fibers were added 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 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/PVAI 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/PVAI and CGM/PHB-V blends, but lower values of elongation at break.

Conclusions

Blends of PVA, PHB-V and Starch with gluten were obtained in a wide range of compositions. 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 PVAI in the blends with CGM.

Aknowledgements

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