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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

EVALUATION ON MICROSTRUCTURE OF BIODEGRADABLE CORN STARCH/CITRUS PECTIN BLENDS PREPARED FROM MELTED STATE

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Citrus pectin (PEC) and thermoplastic starch (TPS) were blended by melt blending through Haake Rheomix and plasticizer glycerol aiming the development of biodegradable materials for agricultural and packaging applications. X-ray diffraction in conjunction with thermogravimetric analysis indicated an immiscible state of the polymers in blend. Results obtained from the mechanical tensile tests of blend indicated a significant increase in elongation at break with drastic decrease in tensile strength and elastic modulus over neat polymers. Application of the simple linear additive rule for mechanical properties has evidenced antagonism in the polymer blend. From these results we have assumed that TPS gives a plasticizer effect on PEC matrix, enabling new applications in agricultural and packaging areas as plasticized materials of higher ductility.

Introduction

Environmental impact of the large volume of petroleum-derived plastic has led to search for new alternatives to replace them with eco-designed polymeric materials[1]. Pectin (PEC) is a biodegradable, renewable and anionic natural polymer with complex structure, consisting mainly of poly(α-(1→4)-D-galacturonic acid) segments chain whose acid units are partially esterified with methanol (called methyl-esterification degree, DM)[2]. PEC is the major component of the residues from agriculture citrus fruit, notably in Brazil, one of the largest producers of orange juice in the world. In this context, PEC shows great potential for the development of new biodegradable films for agricultural and packaging applications.

As a good route to balance the cost-effective issue and get new materials that has good performances, PEC can be submitted to the polymer blending with starch an inexpensive, biodegradable and renewable polymer. Starch is composed of a mixture of amylose and amylopectin, both consisting of 1,4 α-D-glucopyranose repeating units[3]. When processed in the presence of water, plasticizers and at elevated temperatures and shear in the extruder, starch melts and flows like synthetic polymers[4]. Due to this, thermoplastic starch (TPS) is the most commonly used natural polymers for manufacturing biodegradable thermoplastic films and have been richly utilized in blend formulations to improve the processability of other natural polymers, keeping the biodegradability of the final material[5,6].

The objective of this work was to develop biodegradable polymer blends from corn starch and citrus pectin with a focus on microstructural characterization and mechanical properties of these polymeric materials.

Experimental

Materials

Regular corn starch Amidex 3001 (content of amylose ~28%) was a gift of Corn Products Brasil Ltda. Standardized pectin (DM = 8.4%) was acquired from CPKelco (Limeira, Brazil). All of the other chemicals were of analytical grade and were used without additional purification.

Blending Process

Plasticization of polymers was performed in a Haake Rheomix OS4. Glycerol and deionized water were utilized as plasticizers at 20 wt% and 30 wt% for all formulations, respectively. Stearic acid was used as processing agent at 1 wt%. The processing was realized at 130°C, 160 rpm during 4 min. The compounds obtained were pressed into rectangular bar and 1-mm thick films by compression molding at 140°C for 7min. The samples were dried at 35°C for 24h and put in a sealed environmentally controlled instrument container for 2 days. The condition inside the container was controlled at 50% RH and 25°C according to standard ASTM D618[7].

Scanning Electron Microscopy (SEM)

Samples were prepared by cryogenic fracture and fixed onto specimen supports. After gold coating procedure, micrographs of fractured surface were registered in magnification of 500x using a Zeiss DSM 960 microscope. The measures were realized in the secondary electron mode and accelerating voltage of 17kV.

X-ray Diffraction (XRD)

XRD analyses were carried out with a Shimadzu diffractometer using a Cu Kα (λ = 0.154nm) radiation generated at 30KV and 30mA. The diffraction patterns for blend films were obtained at room temperature in the range of 2θ between 5 and 55° with scan speed of $2°.min^{-1}$.

Thermogravimetric Analysis (TGA)

Thermal profiles (TG and DTG curves) were obtained in Q500 equipment, TA instruments. Mass samples around 8-10mg were placed in platin panel and heated from 25 to 600°C, at heating rate of $10°C.min^{-1}$ under dynamic atmosphere of nitrogen with flow rate of $60mL.min^{-1}$. The equipment was previously calibrated with a zinc pattern.

Mechanical tests

The mechanical properties Tensile Strength (TS) (MPa), Elastic Modulus (ME) (MPa) and Elongation at Break (EB) (%) were determined according to standard ASTM 638[8]. The stress-strain curves were obtained using a universal testing machine EMIC DL-3000 with a 50kN load cell. Specimens Type II were fixed by grips with an initial distance of 100mm and stretched at speed of $50mm.min^{-1}$. Eight specimens were utilized to establish the average values of properties.

Results and Discussion

The SEM micrographs of neat TPS and PEC and its blend are presented in Figure 1. The SEM image of neat TPS shows a homogeneous and smooth surface with some rounded domains associated to starch granules that were not entirely disrupted in the thermomechanical process.
The SEM image of neat PEC shows a homogeneous and rougher surface, suggesting that a full matrix was obtained from processing of natural pectin. For TPS/PEC blend 50/50, the image was similar to PEC. A characterization in terms of phases was difficult due to the low contrast between TPS and PEC obtained by SEM. But the micrograph of blend suggests that the TPS and PEC polymers were well distributed in material.

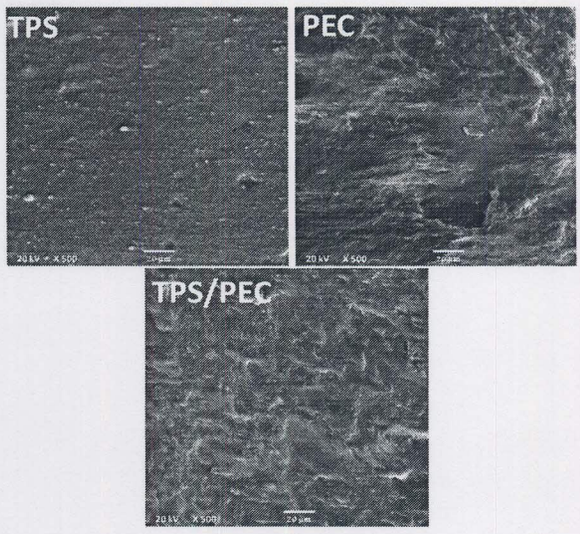

Figure 1: SEM micrographs of neat TPS and PEC polymers and TPS/PEC blend 50/50.

The presence of crystallinity as well as crystal type into TPS, PEC and TPS/PEC blend were investigated by X-ray diffraction, as shown in Figure 2. In diffractogram of PEC it can be seen a large band between 10 and 45° of 2θ, which is a typical diffraction profile of poor crystalline materials.

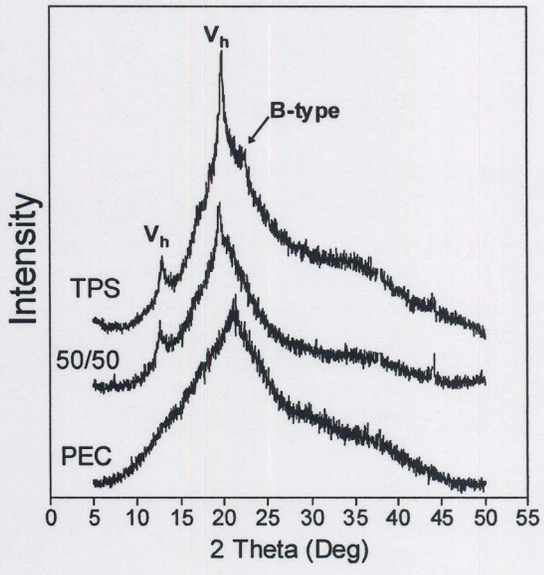

Figure 2: X-ray diffractogram of neat TPS and PEC polymers and TPS/PEC blend 50/50.

Native starch can be formed by A, B, and C crystalline forms, whose structure are largely described in excellent literatures[3,9]. When the starch granules are disrupted by heat and shear force during processing, amylose, an essentially linear polymer will dissociate out of the granules, and was shown to crystallize into several single helical crystal structures (V_a, V_h, and E_h-type). The V- and E-type structures are typical of the complexes formed between amylose and fatty acids, but the formation of E_h-type rather than V_h-type structure is favored by low extrusion water content and

high extrusion temperature[10]. Amylopectin which is a branched polymer always crystallizes into the B-type crystallinity structure during ageing of the TPS[11].

There are two principal sharp peaks in diffractogram of TPS, with the 2θ at 12.9° and 19.9°, and it was classified to be V_h-type structure of amylose. This is plausible because stearic acid it was used at 1wt% in processing. In addition, was observed a small shoulder with 2θ at 23.3° in diffractogram which can be associated with residual B-type structure of native starch or re-crystallization of amylopectin in TPS matrix. The diffractogram for TPS/PEC blend, indicate an overlap of patterns of the pure polymer matrices, with principal peaks concerning to the V_h-type strucuture of TPS. Once the crystallization of amylose did not prevented after blending process with pectin, the diffractogram evidences that TPS/PEC system is a multiphasic polymer blend.

The TG/DTG curves for TPS, PEC and TPS/PEC blend under nitrogen atmosphere are showed in the Figure 3. All materials presented a mass loss around 20wt% between 50 and 170°C, which can be attributed to the water and glycerol elimination. Neat polymeric materials showed only a second step of mass loss. For PEC this step was between 180 and 270°C with maximum at 227°C, while for TPS was between 274 and 374°C with maximum at 317°C.

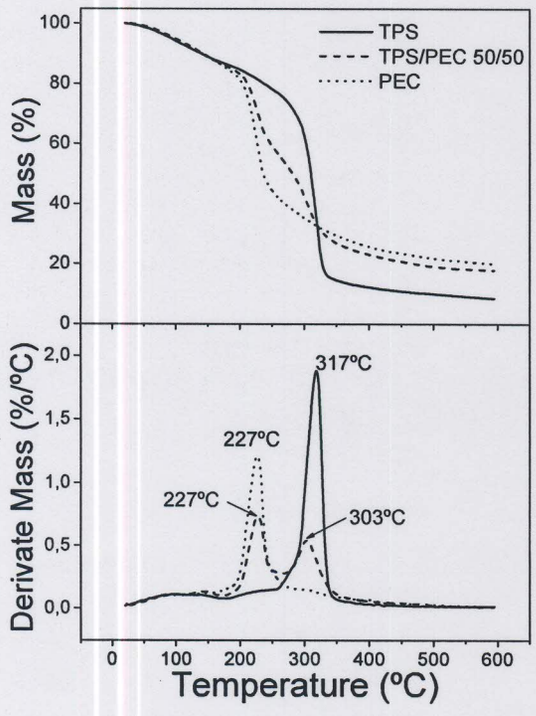

Figure 3: TG curves (up) and DTG curves (down) of neat TPS and PEC polymers and TPS/PEC blend 50/50. Heating rate of 10°C.min^{-1} and nitrogen atmosphere.

These steps can be related to the despolymerization and degradation of polysaccharides in a non-oxidative process, leading to the formation of aromatic and aliphatic complex compounds, liberation of CO_2, H_2O, CO and formation of carbonaceous residue[12]. In this case, thermal parameters show that corn starch is a more thermostable natural polymer than citrus pectin.

TG/DTG curves of TPS/PEC blend clearly presented two steps of mass loss above 170°C, which are compatibles with the steps of decomposition for neat TPS and PEC. It is a typical profile of immiscible polymer blends. However, the maximum signaled at 317°C for TPS was shifted to 303°C, indicating some degree of interaction between TPS and PEC phases in the blend.

The mechanical behaviors resulted from microstructure of plasticized materials are illustrated in strain-stress curves of Figure 4. The average values of the mechanical properties of neat PEC were 7 MPa for TS, 5 % for EB and 212 MPa for ME, respectively. For neat TPS these values were 0,8 MPa, 30% and 10 MPa, respectively. The results clearly showed that net PEC displays a more brittle behaviour then compared to TPS.

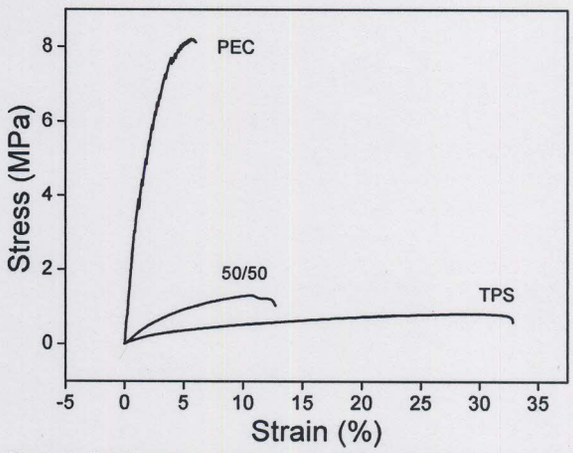

Figure 4: Strain-stress curves of neat TPS and PEC polymers and TPS/PEC blend 50/50. All materials contain plasticizer glycerol at 30wt%.

The addition of starch at a mass content of 50 wt% significantly increased the EB of PEC matrix to 12 %, while decreased the TS to 2 MPa and ME to 38 MPa. Assuming that the TPS/PEC blend follows the addition law, the following linear model for mixture between two components can be written to represent the mechanical properties of this system[13]:

$$\hat{y} = b_1x_1 + b_2x_2$$

where $\hat{y}$ is the value of the response, b_1 and b_2 are the model parameters and x_1 and $x2$ are the mass fraction of the components. For the mechanical properties TS, EB and ME, the linear model is rewritten as:

$$TS\ (\text{MPa}) = 7x_{PEC} + 0{,}8x_{TPS}$$

$$EB\ (\%) = 5x_{PEC} + 30x_{TPS}$$

$$ME\ (\text{MPa}) = 213x_{PEC} + 10x_{TPS}$$

where the model parameters are the values of the properties of neat TPS and PEC.

For TPS/PEC blend 50/50 ($x_1=x_2=½$) the addition law predicts for TS, EB and ME the values 4 MPa, 17,5% and 112 MPa, respectively. A comparison between experimental and predicted data reveals that mechanical properties of TPS/PEC blend show a high deviation from addition law, with strongly antagonistic interactions. For TS and ME properties, experimental values were much lower, but for EB the value was closed to the addition law. From these results we have assumed that TPS gives a plasticizer effect on PEC matrix, resulting in biodegradable polymer blends of higher ductility.

Conclusions

Biodegradable polymer blends were successfully prepared from citrus pectin and corn starch. The results of this study showed that starch/pectin blends are multiphasic materials with crystalline structure concerning mainly to the V_h-type strucuture of amylose in thermoplastic starch phase. The mechanical behaviour of the blend follows an antagonistic pattern with an increase of ductility of pectin improved by presence of starch in the blend. These properties enable new uses of starch/ pectin blends in agricultural and packaging applications.

Acknowledgements

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