Promotion

UFRGS

Associação Brasileira de Polímeros

Sponsors

Braskem

Support

CAPES

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

Embrapa
Instrumentação Agropecuária

FACULDADE DE ENGENHARIA QUÍMICA
UNICAMP

Fapergs

FAPESP
Fundação de Amparo à Pesquisa do Estado de São Paulo

Instituto de Química de São Carlos

BR
PETROBRAS

pro pesq
Pró-Reitoria de Pesquisa - UFRGS

UFRGS
UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

Exhibitors

UNION

Instrutécnica

POLIMATE

ReoTerm
INSTRUMENTOS CIENTÍFICOS

ISSN 2178-4043

ISNaPol 2010

7th INTERNATIONAL SYMPOSIUM ON NATURAL POLYMERS AND COMPOSITES

Elisângela

XII INTERNATIONAL MACROMOLECULAR COLLOQUIUM

September 7th - 10th, 2010
Hotel Serra Azul
Gramado/RS - Brazil

XII INTERNACIONAL
MACROMOLECULAR COLLOQUIUM

ISNaPol 2010
7th INTERNATIONAL SYMPOSIUM ON
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

BIODEGRADATION, MECHANICAL AND THERMOGRAVIMETRIC CHARACTERIZATION OF THERMOPLASTIC STARCH (TPS).

Rodrigo Tonelli[1], Adriana de Campos[1], Luiz H. C. Mattoso[1]; Sandra M. M. Franchetti[2]; José M. Marconcini[1*]

[1]Laboratório Nacional de Nanotecnologia para o Agronegócio (LNNA), Embrapa Instrumentação Agropecuária (CNPDIA) – São Carlos, SP – marconcini@cnpdia.embrapa.br
2 Departamento de Bioquímica e Microbiologia –UNESP –Rio Claro-SP

Thermoplastic starch (TPS) is a polymer is obtained plasticizing starch with a plasticizer like a glycerol. In this work, it was studied mechanical, thermogravimetric and biodegradation of TPS. The biodegradation experiment was realized following the ASTM D5338-98 norm, with composted soil, in order to use a variety of microorganisms able to degrade the thermoplastic starch (TPS), which it is a biopolymer. The microbial activity of soil was measured by titrations, calculating CO2 originated from the microbial digestion. The more CO_2 emition represents a higher microbial activity in the soil and, consequently, higher biodegrability of the studied polymer. In this case, the TPS suffered a high biodegradation after 41 days of the study.

Introduction

World demand for synthetic polymers has increased each year. The concern about the impact generated by these materials is increasing along with the intense and irresponsible use of non-biodegradable materials. Nowadays, studies are focused on the development of intelligent and sustainable alternatives, and this is increasing every day. An alternative highly effective and almost no environmental impact are the natural polymers[1]. Starch, for example, can be transformed into polymer matrix widely used and still be a biodegradable material.[1]

Synthetic polymers have been developed to the point where can be designed microstructures, and molecular weight and molecular weight distribution can be controlled. However, the mesoscopic structure within the starch granule has evolved to suit the plant's own needs and is therefore much more complex. Starch is a polysaccharide produced by mostly higher order plants as a means of storing energy. It is stored intracellularly in the form of spherical granules 200-100 μm in diameter. Most commercially available starches such as grains are isolated from the corn, rice and wheat, and from tubers such as potato and cassava (tapioca). Physically, most native starches are semi-crystalline, having a crystallinity of about 20-45% [1]. Amylose and the branching points of amylopectin form amorphous regions. The short-branched chains in the amylopectin are the main crystalline component in granular starch. Crystalline regions are present in the form of double helices with a length of ~ 5 nm. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The molecular weight of amylopectin is about 100 times higher than that of amylose. The ratio of amylose/amylopectin depends upon the source and age of the starch, and it can also be controlled by the extraction process employed. Starch granules also contain small amounts of lipids and proteins.

Starch is a versatile and cheap raw material with numerous applications, e.g. as thickener, texturizer, and adhesive. The starch biopolymers are packed in semi-crystalline granules that are insoluble in cold water. For almost any application the ordered granule structure is disrupted by heating with water. This process is known as gelatinization or melting.[1]

The objectives of the present work were the characterization of corn thermoplastic starch films by thermogravimetric analysis and mechanical properties as also its biodegradability.

Experimental

Samples Prepare:

Thermoplastic starch (TPS) was obtained by components mixture prior to feeding the extruder, the following weight proportions: glycerol 18 %, water 10 %, 0.2 % stearic acid and 72.8% starch.

Starch mixture was extruded in a co-rotation twin-screw extruder 18mm L/D=40 ZSK18 Coperion. The screw rotation speed was 200 rpm and temperature profile was 140 to 160 ^{0}C. With the samples into pellets, the film samples was obtained in a single screw extruder AX Plastics, with speed rotation of 150 rpm and temperature range of 120 - 130 ^{0}C. The extruded films had a thickness of about 0.65 mm. Test specimens was obtained, following ASTM standard D882-09, as follow size: 15 mm wide and 80 mm in length.

Thermoplastic starch characterization (TPS)

Tensile Mechanical Testing:

Samples extruded in the form of films were evaluated in mechanical properties of tensile strength. Tensile tests were performed in a EMIC DL3000, following the ASTM D882-09. The tests were carried out with speed of 5 mm / min and load cell of 50 kgf.

Thermogravimetry:

Thermo oxidative degradation temperature of TPS samples was evaluated using thermogravimetry technique using TA Q500 (TA Instruments) under the following conditions: weight 10.00 ± 0.50 mg; atmosphere of synthetic air, flow 60 mL min^{-1}; heating rate: 10 °C min^{-1}; temperature range: 25 °C to 600 °C and platinum port sample.

Composted Soil Prepare:

Soil samples were collected in a region that contained soil with litter. Soil was added to 25% by weight of earthworm compost commercially.
Distilled water was put on soil composted until it reached 50% moisture by weight.

Composted Soil Characterization

Chemistry Analysis:

Composted soil used in the biodegradation test was chemically analyzed by the Plants and Soil Chemistry Analysis Laboratory of UFSCar.

Soil Composted Microbiology:

Composted soil microbiology was analyzed using 1 mL of inoculum in the following media: PCA and PDA, to verify the microorganisms (fungi and bacteria) present in the composted soil.

Biodegradation Test:

The test was performed according to ASTM 5338-98, using 600 g of soil composted, already humidified, in bottles of 2L. The temperature was controlled so that it will remain around 30 °C. Soil composted received continuous aeration without CO_2 and humidified air. The evolution of CO_2 was analyzed by the method of titration, using HCl 0.2 M, potassium hydroxide 20 mL and 1 mL of barium chloride 0.5 M. For this method, was used an automatic titrator TitroLine Easy.

Results and Discussion

Thermoplastic starch characterization:

Table 1 shows the values of Young's modulus (E), tensil strenght (σ_r) and elongation at break (ε_r) of thermoplastic starch.

Sample	*Tensile strenght (σ_r) (MPa)*	*Elongation at break (ε_r) (%)*	*Elastic modulus (E) (MPa)*
TPS	*0,65±0,07*	*63,89±8,31*	*64,62 ± 2,39*

Table 1 - Young's modulus (E), tensil strenght (σ_r) and elongation at break (ε_r) of thermoplastic starch.

It is observed that the homopolymer has poor capacity to support stress. This study is important to understand the behavior of this polymer for future studies such composites and understand the behavior of this polymer in biodegradation studies.
This way, it was study the thermo oxidative of thermoplastic starch (Figure 1).

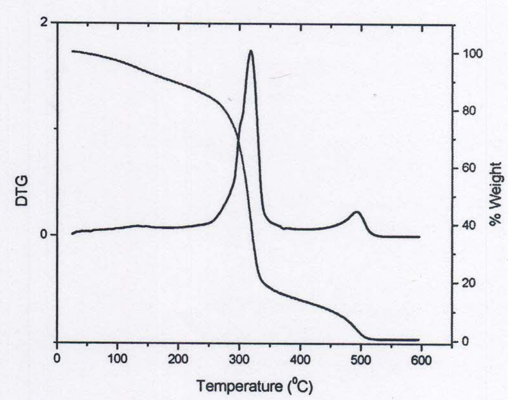

Figure 1- Thermo oxidative analysis and DTG of thermoplastic starch.

Weight loss at temperatures between 25 and 130 °C is attributed to the evaporation of water. Starch has one decomposition peak with a maximum degradation rate occurring at 316 °C.
This polymer, thermoplastic starch, was put in composted soil to study its biodegradation.
The composted soil used in the biodegradation test was chemically analyzed in order to understand the inoculum used. Chemical characteristics are presented in table 2.

pH	C	N	P_2O_5	K_2O	CaO	MgO	SO_4	C/N
6.3	8.3	0.5	0.04	0.14	0.52	0.21	0.21	16.6

Table 2 - Chemistry Analysis of Composted Soil, in weight %.

It was observed that the C/N ration is according of biodegradability standard.
Compostec soil microorganisms were analyzed, using bacteria and fungi mediums. The study shows that

there are more bacteria than fungus in the composted soil used in this test (Table 3).

Bacteria (UFC/mL)	Fungus (UFC/mL)
72×10^{-3}	4×10^{-3}

Table 3- Counting of microorganisms (bacteria and fungi)

Figure 2 shows the variety of microorganisms of composted soil used for biodegradation test.

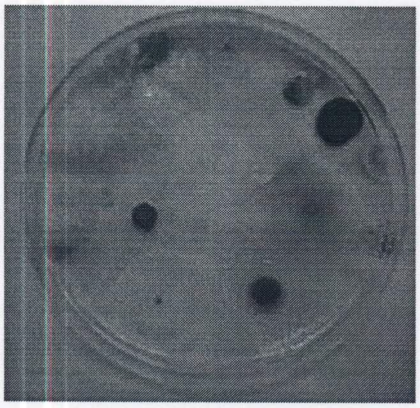

Figure 2- Microorganisms present in composted soil.

Figure 3 shows CO_2 evoluted each day, in weight, from TPS biodegradation in composted soil during 41 days. According ASTM 5338-98 standard[3], TPS films is approved by biodegradation test. Results showed that this material is highly biodegradable. After 4 days, it was occurred an enhanced in CO_2 emission, because adaptation phase (lag phase) of microorganisms growing was finished. In this study, microorganism life phases must be described as follow: Steady state phase occurred from 9 to 21 day, followed by death phase from 21 to 24 day and recovering phase from 24 to 41 day.

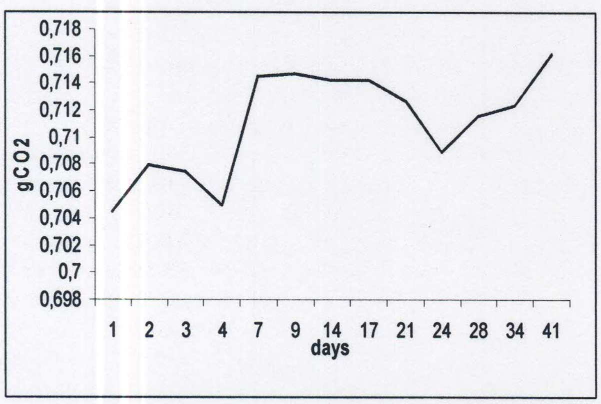

Figure 3- CO_2 evoluted each day, in weight, from TPS biodegradation in composted soil.

Conclusions

The results of the biodegradation showed that the thermoplastic starch, obtained by extrusion, has a high degree of biodegrability. TPS was rapidly consumed by microorganisms in the soil and metabolized into smaller time periods, according ASTM 5338-98 standard.
These characteristics of the TPS allow it to be used as sustentable alternative with low environmental impact.

Acknowledgements

The authors wish to thank Corn Products for supplying corn starch used in this study. The financial and technical support of EMBRAPA, CNPq Process N^0 483265/2007-1, FINEP/MCT, and FAPESP Process N^0 2008/08264-9 are also gratefully acknowledged.

References

1. Papers in Journals: Liu H., Xie F., Yu L., Chen L., Li L. Thermal processing of starch-based polymers, Progress in Polymer Science 2009, 34, Elsevier, p. 1348-1368.
2. Papers in Journals: R. Ling; M. Yoshida; P.S. Mariano *J. Org. Chem.* 1996, *61,* 4439.
3. ASTM D 5338-98 Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions.
4. Papers in journals: Guinesi, L.S.; Róz, A.l.; Corradini, E.; Mattoso. L.H.C.; Teixeira, E.M.; Curvelo A.S. Thermochimica Acta, 447, p.190 2006.
5. Theses: F. H. Dutra, Tese de Doutorado, Universidade Federal do Rio Grande do Sul, 1995.
6. Books without editor: E. Haslam, *Shikimic Acid Metabolism and Metabolites,* John Wiley & Sons, New York, 1993.
7. Books with editor: J. G. Buchanan; H. Z. Sable in *Selective Organic Transformations,* B. S. Thyagarajan, Ed.; Wiley-Interscience, New York, 1972; Vol. 2, 1-95.
8. Patents: F. R. Lyle, U.S. Patent 5 973 257, 1985; *Chem. Abstr.* 1985, *65,* 2870.
9. Congress abstracts: O. Barbosa in Anais do 10° Congresso Brasileiro de Catálise, Salvador, 1999, Vol. 1, 343.