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Degradation of different polystyrene/thermoplastic starch blends buried in soil

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ABSTRACT

Blends of PS and TPS were prepared using two different plasticizers: glycerol or buriti oil by solvent casting technique. PS/TPS blends were submitted to degradation by soil burial tests in perforated boxes for 6 months and later analyzed by TG and CPMAS ^{13}C NMR. After degradation, blends with glycerol presented less stages of thermal degradation and NMR signals of minor intensity compared to the original blends. The presence of TPS at contents of 50% or greater improved the degradation of the blends. After 6 months, PS/TPS blends with buriti oil presented only one thermal degradation stage with a significant increase in mass loss. Moreover, all absorptions related to starch disappeared in NMR spectra after soil buried test, probably due to the consumption of starch by microorganisms. These results revealed that PS's degradability can be improved when TPS plasticized with buriti oil is added to it.

1. Introduction

A polymeric degradation is an irreversible process caused by factors that are answerable for the loss of its properties. In this process, in general, the scission of polymeric chains occurs and structural alterations take place by other mechanisms. The degradation of the majority of synthetic plastics in nature is a very slow process that involves environmental factors and microorganism activities. Polystyrene (PS) is a synthetic hydrophobic polymer with high molecular weight. In its natural form it is not biodegradable requiring for such process changes in its crystalline level, molecular weight and mechanical properties, which are responsible for its resistance to degradation (Arvanitoyannis & Biliaderis, 1999; Kiatkamjornwong, Sonsuk, Wittayapichet, Prasassarakich, & Vejjanukroh, 1999).

Studies of petrochemical polymer blend degradations (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; El-Rehim, Hegazy, Ali, & Rabie, 2004; Kiatkamjornwong et al., 1999; Morancho et al., 2006; Nakamura, Cordi, Almeida, Duran, & Mei, 2005; Psomiadou, Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1997; Ramis et al., 2004; Zuchowska, Steller, & Meissner, 1998) indicated that starch can speed up the degradation of polymers. Addition of starch to conventional synthetic polymers increases the porosity and the surface/content ratio of the blends and provides the waste of this additive for the microorganisms. As the microorganisms consume the surrounding starch, the plastic loses its structural integrity. This process can lead to the deterioration of the mechanical properties, facilitating the degradation for other mechanisms and thus allowing the attack of the polymeric matrix by microorganisms (Kiatkamjornwong et al., 1999; Zuchowska et al., 1998).

The result of the loss of integrity of polymeric matrix is an increase of its biodegradability. Blends of biodegradable and petrochemical polymers give origin to partially biodegradable materials that can effectively reduce the plastic garbage content for partial degradation.

Several plasticizers have been used with starch to convert it into thermoplastic starch (TPS), mainly water and glycerol (Chang, Karim, & Seow, 2006; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Tan, Wee, Sopade, & Halley, 2004). In this work we investigated a novel and natural plasticizer for starch: the buriti oil. Buriti (*Mauritia flexuosa* L.) is an abundant palm in the Amazonian Region of Brazil and supplies raw material for a variety of applications. Supercritical CO_2 extraction of the pulp of the buriti fruit released buriti oil fractions with a high concentration of oleic acid, tocopherols and carotenoids, especially β-carotene (Albuquerque et al., 2005; França, Reber, Meirelles, Machado, & Moreira, 1999).

The aim of this work was to compare the behavior of glycerol and buriti oil as plasticizers in PS/TPS blend degradations. Changes on the composition of such material exposed to natural microflora present in soil during indoor experiments were evaluated by solid-state ^{13}C NMR spectroscopy (CPMAS ^{13}C NMR). Weight loss as a function of degradation time was determined by thermogravimetry (TG).

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2. Experimental

2.1. Materials

PS ($\overline{M_w} = 280,000; \rho = 1.047\text{g ml}^{-1}$) was purchased from Aldrich Chemical Co. and glycerol from VETEC. Dried cassava (*Manihot esculenta Crantz*) starch with 74.70 ± 1.76% of amylopectin, determined by colorimetric analyzes (Chrastil, 1987) was used; buriti oil (ρ = 0.86 g ml^{-1}) extracted with supercritical CO_2 from the shell and the pulp of ripe fruits was courteously supplied by Dr. Moreira from Universidade Federal do Pará (UFPA), Brazil. Ethyl acetate (analytical grade) was also used.

2.2. Preparation of blends

TPS was obtained by mixing starch powder, water and glycerol or buriti oil in 50:15:35 (mass/vol/vol) ratios according to Famá, Flores, Gerschenson, and Goyanes (2006), with some modifications. The constituents were mixed for 30 min to obtain a paste which was transformed to TPS by heating at 95 °C in water bath with continuous stirring for 30 min.

PS and TPS were mixed in different ratios 0.9:0.1, 0.7:0.3, 0.5:0.5 and 0.3:0.7 (mass/mass) and then stirred (3 h, 50 °C) with ethyl acetate. The blends were prepared by conventional-casting technique using Teflon™ dishes as casting surfaces for at least 24 h at room temperature and vacuum (between 6.6×10^2–13.2×10^2 Pa). The obtained material, with 200–300 μm thickness was stored far from light to avoid the decomposition of the oil.

2.3. Degradation soil burial test

The soil burial tests started in December 2005 and continued for 6 months until June 2006. PS/TPS blends were buried in a perforated box to allow the samples to be attacked by the microorganisms and moisture. The box was buried at a depth of 7 ± 9 in. beneath the soil surface. After removal, all the samples were carefully washed in order to stop the degradation and the plastic sheets were stored in darkness until testing.

2.4. Thermogravimetry

Thermal degradation experiments were carried out using a thermogravimetric analyzer Shimadzu TGA-50. Temperature was raised from 25 to 600 °C, at a heating rate of 10 °C min^{-1} and under helium (50 ml min^{-1}) in order to determine the mass loss and decomposition temperature (T_d) of the blends. The T_d was ascertained from derivative thermogravimetric curves (DTG).

2.5. Solid-state ^{13}C nuclear magnetic resonance

Solid-state ^{13}C NMR spectra with cross-polarization and magic-angle spinning (CP/MAS NMR) were obtained using a Varian Mercury plus spectrometer operating at 75.46 MHz for ^{13}C. Hexamethylbenzene (HMB, 17.3 ppm) was used as an external reference. Samples were packed into 7-mm zirconia rotors and spun at 6 kHz. Spectra were acquired with 1.5 ms contact time, 4 s recycle delay, 0.05 ms acquisition time, 2000 scans and processed data done with Mestre-C 2.3 software.

3. Results and discussion

According to our previous paper (Schlemmer, Oliveira, & Sales, 2007), the PS/TPS blends with greater TPS content presented more thermal decomposition stages. The blends that have TPS content of 50% or greater have more decomposition stages showing a

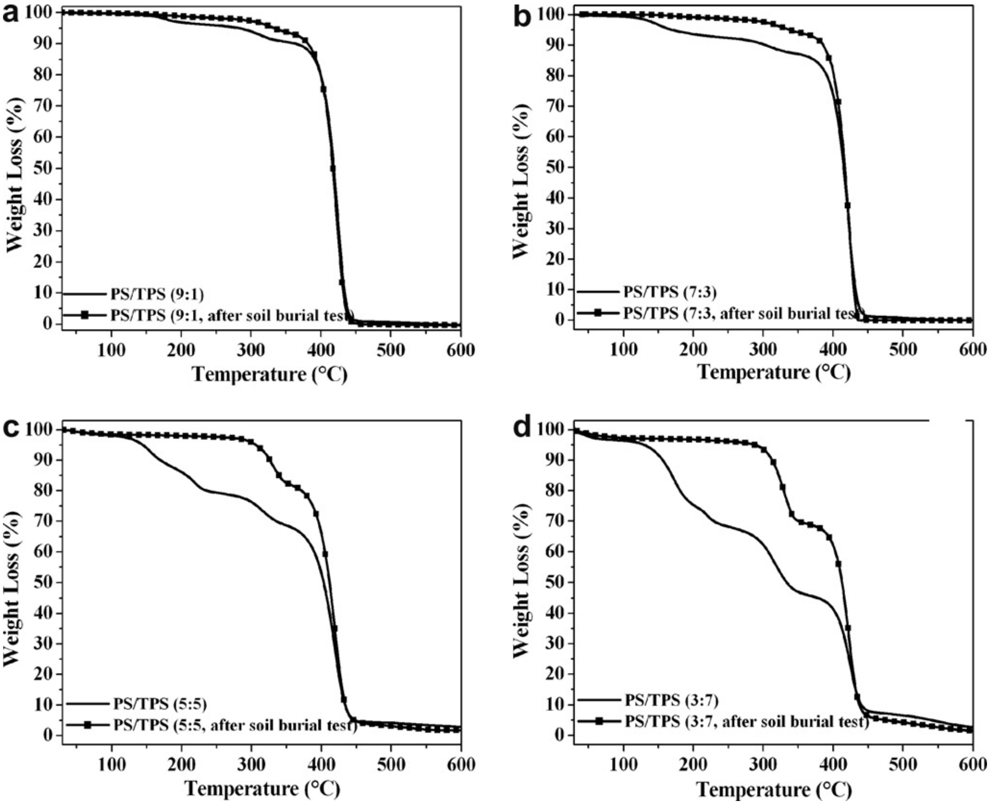

Fig. 1. TG curves for PS/TPS blends with glycerol, before and after 6 months of soil burial test.

decrease in the value of last T_d indicating the 'easier' thermal degradation. It was noticed that blends obtained with glycerol degrade in more stages and at inferior temperatures compared to those produced with buriti oil. The observed mass losses seem to be directly linked to the amount of starch in the blends.

After the 6 months of soil burial test, the growth of microorganisms on the plastic caused changes in some of its physical and chemical properties that can be detected by thermal analysis. From TG curves for PS/TPS blends with glycerol, before and after buried for 6 months (Fig. 1), it was verified that all the samples presented less stages of thermal degradation after the period of soil buried test. Thermal degradation stages related to TPS which occur at lower temperatures did not appear in TG curves after the test, indicating that the materials responsible for this degradation did not exist in blends anymore. Table 1 shows the T_d and weight loss percentage for all blends with glycerol.

It was observed that after soil burial test, degradation step near 308 °C (starch's T_d) is still present. However, the T_d values measured are shifted to greater temperatures, reaching up to 14 °C of difference in relation to the original samples. Moreover, in this stage there was an increase in the mass loss for blends with bigger TPS content. This data indicates that the part of sample that was not degraded during soil burial test had an increase in thermal stability probably due to some structural modification in TPS after degradation of its components.

The T_d4 values were associated with PS's thermal decomposition and remained practically unchanged (420–425 °C) after soil burial test, indicating that the PS structure is the same after 6 months. However, the mass loss percentage at this last stage of degradation was significantly greater for these blends, proportionally to TPS amount. Analysis of these data discloses that mass loss of PS stage increased in relation to TPS, indicating a possible consumption of the starch by microorganisms.

TG curves of PS/TPS blends with buriti oil (Fig. 2) presented less degradation stages after 6 months of soil burial test compared to blends with glycerol. For TG curves and data presented in Table 2, it can be said that TPS of blend in ratio (9:1) was consumed by microorganisms after soil burial test because thermal degradation stage associated with it does not appear in its curve. PS/TPS (7:3) blend showed few changes, before and after 6 months of buried.

Table 1
Data of decomposition temperature and percentual mass loss for PS/TPS blends with glycerol before and after soil burial test (B) for 6 months

Sample	T_d1 (°C)	Mass loss (%)	T_d2 (°C)	Mass loss (%)	T_d3 (°C)	Mass loss (%)	T_d4 (°C)	Mass loss (%)
PS/TPS (9:1)	173	3	–	–	317	5	424	89
PS/TPS (9:1) B	–	–	–	–	326	5	424	93
PS/TPS (7:3)	150	6	–	–	316	5	422	85
PS/TPS (7:3) B	–	–	–	–	321	3	420	94
PS/TPS (5:5)	158	11	218	8	319	10	420	64
PS/TPS (5:5) B	–	–	–	–	326	15	420	80
PS/TPS (3:7)	173	23	219	5	314	22	425	40
PS/TPS (3:7) B	–	–	–	–	328	28	423	65

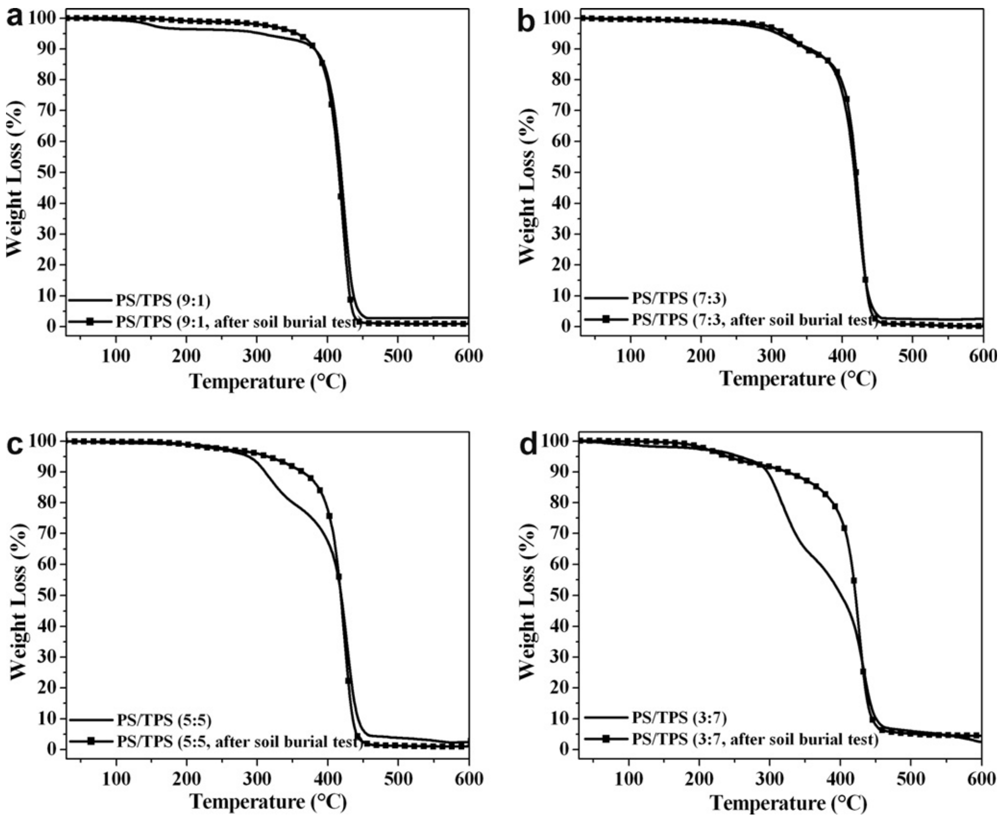

Fig. 2. TG curves for PS/TPS blends with buriti oil, before and after 6 months of soil burial test.

Table 2
Data of decomposition temperature and percentual mass loss for PS/TPS blends with buriti oil before and after soil burial test (B) for 6 months

Sample	T_d1 (°C)	Mass loss (%)	T_d2 (°C)	Mass loss (%)	T_d3 (°C)	Mass loss (%)	T_d4 (°C)	Mass loss (%)
PS/TPS (9:1)	146	3	–	–	–	–	424	93
PS/TPS (9:1) B	–	–	–	–	–	–	420	97
PS/TPS (7:3)	–	–	–	–	329	6	421	87
PS/TPS (7:3) B	–	–	–	–	335	9	420	87
PS/TPS (5:5)	–	–	255	2	318	16	428	75
PS/TPS (5:5) B	–	–	–	–	–	–	424	97
PS/TPS (3:7)	–	–	254	2	314	32	430	56
PS/TPS (3:7) B	–	–	227	6	–	–	426	86

Although the number of thermal degradation stages remains unchanged, it was observed an increase of 6 °C in T_d and the mass loss of the decomposition step associated with the starch also increased after soil burial test. After 6 months, TG curve of PS/TPS (5:5) blend presented only one thermal degradation stage, corresponding to PS degradation, with a significant increase in mass loss (30%). Thus, it can be conclude that all TPS with buriti oil was consumed by microorganisms. PS/TPS (3:7) blend presented a small thermal degradation stage around 227 °C that is characteristic of the TPS decomposition, and another step related to the PS decomposition.

PS shows T_d at 429 °C which is related to its depolymerization; below this temperature the decomposition is due to the TPS. Products of pyrolytic decomposition of starch and its fractions include carbon monoxide, water, volatile organic compounds and a carbonaceous residue (Tester, Karkalas, & Qi, 2004).

The PS and the native starch CPMAS ^{13}C NMR spectra are shown in Fig. 3a and b, respectively. In the PS spectrum, the resonances at 146 and 128 ppm are assigned to non-protonated and protonated aromatic carbons, respectively, and the methylene and methene carbon resonances are ascribed to the resonances at 41 and 46 ppm, respectively. In starch spectrum signals at 94–105 ppm and 56–60 ppm are attributed to C-1 and C-6 in hexapyranoses, respectively. The major signal intensity in all spectra around 64–75 ppm is associated with C-2, C-3 and C-5 (Atichokudomchau, Varavinit, & Chinachoti, 2004). The C-1 position of the glucose units exhibits characteristic chemical shift patterns that can reveal the nature of crystallinity in starch. For an A-type crystal, which has three nonidentical sugar residues, the C-1 peak exhibits a triplet pattern at ~102, 101 and 100 ppm whereas, for a B-type crystal, which has two nonidentical sugar residues, the C-1 becomes a doublet each at ~101 and 100 ppm. Our results for starch showed a duplet pattern indicating a B-type crystal. The two broad shoulders that appeared at 103 and 94 ppm could arise from the amorphous domains for C-1 and the broad resonance around 82 ppm from amorphous domains for C-4, which is accordance with literature (Atichokudomchau et al., 2004; Morgan, Furneaux, & Larsen, 1995).

The spectra of the blends are no more than a superposition of the spectra from starch and PS with plasticizer: glycerol or buriti oil. There is no detectable chemical shift difference or line shape change between the pure polymer and the polymer in the blend and thus the ^{13}C chemical shift itself cannot provide direct information about the interaction between PS, starch and plasticizer.

NMR spectra were recorded before and after degradation for each blend and showed an increase of intensity to signals relative to PS and decrease of intensity to signals relative to starch for PS/TPS blends with glycerol after degradation test. This is probably due to the consumption of starch by microorganisms. The peaks correspondent to starch diminished or disappeared completely for 50% and 70% of TPS. Nonetheless, for blends with buriti oil (Fig. 4), the major signal of starch spectrum diminished or disappeared for all concentrations, indicating that buriti oil is a plasticizer that improves starch degradation in relation to glycerol.

As microorganisms consume the surrounding starch the plastic will lose its structural integrity, enhancing other degradation mechanisms (Kiatkamjornwong et al., 1999). However, as the amount of starch is increased the degradability characteristics will increase.

4. Conclusions

The addition of starch to polystyrene plastics has been promoted as a technique to achieve biodegradability. From TG curves for PS/TPS blends with glycerol or buriti oil it was verified that all the samples presented less stages of thermal degradation after the period of soil buried test than the original ones. Furthermore, TG curves of PS/TPS blends with buriti oil presented even less degradation stages than blends with glycerol. The CPMAS ^{13}C NMR analyzes indicated that the blends of PS and TPS with glycerol or buriti oil were consumed in different levels after 6 months of buried test in soil. Blends with buriti oil showed more degradability compared to glycerol ones. Biodegra-

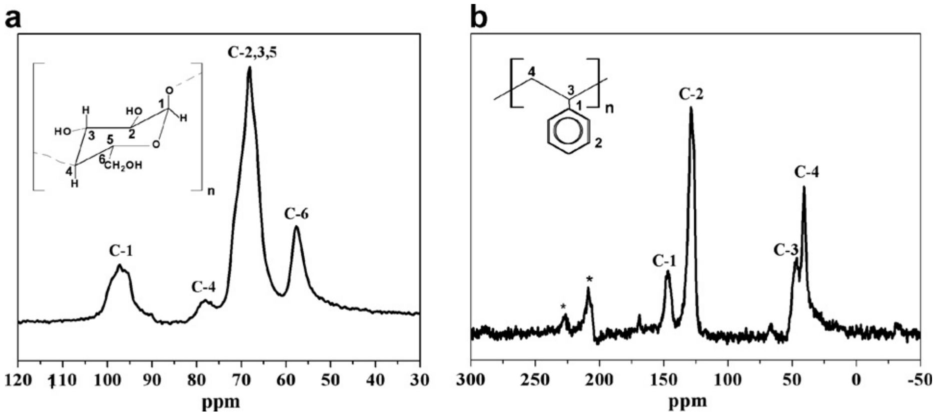

Fig. 3. CP/MAS ^{13}C NMR spectra of (a) native starch and (b) PS.

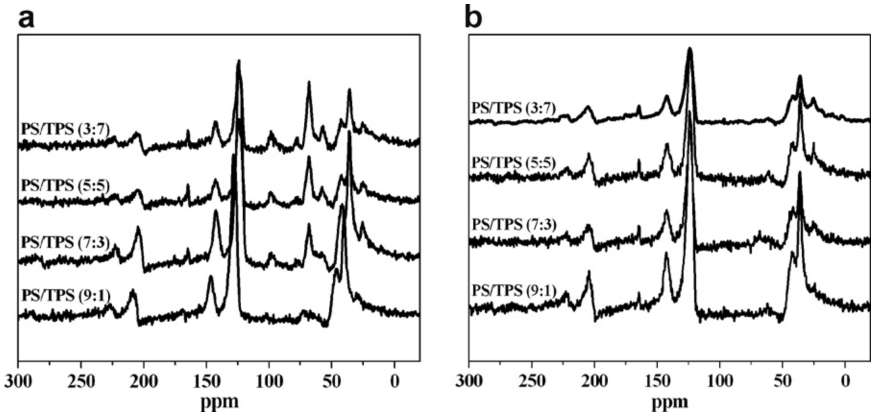

Fig. 4. CP/MAS ^{13}C NMR spectra of PS/TPS blends with buriti oil (a) before and (b) after 6 months of degradation in the soil.

dation mainly affects the starch, whose thermal stability increases, and has no significant effect on the PS.

The obtained results show that buriti oil, a natural raw material can be used as an environmentally-friendly alternative to other materials, and has superior properties compared to glycerol, the most used plasticizer for starch.

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