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Evaluation of Biodegradability of Different Blends of Polystyrene and Starch Buried in Soil

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Summary: Polystyrene/cornstarch blends were prepared by melt-processing in the presence of maleic anhydride (MA), using an internal mixer as reactor. Scanning electron microscopy (SEM) was used to visualize the blends morphology. Addition of MA contributed to improve interfacial adhesion between the two phases. Soil burial tests were used to investigate biodegradability. Results from samples weight loss, as a function of incubation time, revealed that the increase in the content of starch contributed to increase biodegradability. The results showed that the microbial activity inside the specimens was accelerated in the first 15 days of evaluation. Photographs of the films showed significant differences after 30 days of incubation in soil. SEM was also used to evaluate biodegradation, and revealed fractured surfaces covered with a heterogeneous microorganism community.

Keywords: reactive processing; soil biodegradation; starch/PS blends; thermoplastics

Introduction

In the last decades, the production and use of synthetic polymers has increased the amount of plastic waste mainly in developing countries. Attempts have been made to solve this problem, including the development of biodegradable polymers from natural sources.[1] Biodegradable polymers can be converted into environmentally friendly products, and are considered as an alternative to minimize plastic waste disposal in landfills.[2]

Starch is totally biodegradable in a wide variety of environments, and may be used in the development of materials for specific market demands. Furthermore, starch is an inexpensive product, available worldwide from many sources.[1] Addition of starch to conventional synthetic polymers increases the porosity of the blend after consumption of the starch phase by microorganisms. As the microorganisms consume the starch phase, the synthetic polymer loses its structural integrity, enhancing other degradation mechanisms, with deterioration of mechanical properties.[3] Eventually, this process can allow the attack of the polymer synthetic matrix, and lead to the degradation of the synthetic polymer.[3,4]

This concept of biodegradation has found its main application in blends of minor amounts of starch with synthetic polymers, in which the latter constitutes the continuous phase so that the blend can be melt-processed to form films or plastics with synthetic polymer-like properties.[5] The introduction of natural polymers such as starch into blends with petrochemical plastics such as polystyrene (PS) constitutes a form of secondary recycling. PS has been extensively used for packaging, and is resistant to microorganism attack. However, lack of adhesion between the polysaccharide and the synthetic polymer matrices gives poor final properties. Starch and hydrophobic polymers are immiscible, and simple mixing produces blends with separate phases.[6] To improve compatibility

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and adhesion between the two immiscible polymers, interfacial modification may be achieved by modifying the polymer matrix itself. Grafting a reactive moiety onto the polymer matrix can be used; this moiety reacts with the starch macromolecules.[7] Coupling agents containing reactive functional groups generate in situ the formation of block or graft copolymers at the interface by melt-blending.[8]

Maleic anhydride (MA) has been grafted onto many different hydrophobic polymers to produce functional polymers. The use of MA-grafted polymers was found to improve strength, modulus, and elongation by helping to form a co-continuous phase in polymer blends. Maleated polymers can act as compatibilizers between nonfunctional polymers and starch.[2]

In the present work, PS/starch blends were prepared by melt-processing in the presence of MA, using an internal mixer as reactor. The morphology features of PS/starch blends were investigated by scanning electron microscopy (SEM). Soil burial tests and SEM were used to evaluate the biodegradability of the blends.

Experimental Part

Materials

Regular corn starch (CS) composed of 26 – 30% amylose and 74 – 70% amylopectin, with less than 0.5% gluten, and 12 wt% moisture content was supplied by Corn Products Brazil (São Paulo, SP, Brazil). Analytical grade glycerol, MA, and dicumyl peroxide were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, RJ, Brazil). Crystal PS N2560 ($\rho = 1.05\,g/cm^3$) was supplied by Innova S.A. (São Paulo, SP, Brazil).

Preparation of Blends

CS and glycerol were premixed in a conventional mixer (Ika Works, Wilmington, NC, USA) for 10 minutes, and maintained in tightly sealed bags for 2 days at 4 °C. Plasticized CS and PS were mixed in different ratios PS/CS of 80:20, 60:40 and 40:60 (wt/wt).

Processing of Blends

Following a central composite design, processing of blends was carried out at different temperatures and rotor speeds for 10 min in a Rheomix 600 internal mixer equipped with counter-rotating "roller" type rotors and in line with a Haake Rheocord 9000 torque rheometer (Karlsruhe, Germany). The processing temperature and rotor speed followed a central rotational experimental design, described below. After preparation, the blends were placed in tightly sealed bags to prevent any moisture absorption.

Films Preparation

The samples obtained by processing were submitted to compression-molding in a Carver laboratory press, at 120 °C for 20 min, followed by cooling for 5 min. The resulting films were 2 mm in thickness.

Soil Burial Biodegradation Test

Biodegradation of PS/starch blends were evaluated by soil burial test under laboratory conditions (average temperature of 23 °C). Black subsoil was enriched with 30 wt% bovine manure. The pH of soil was 6.9. Samples were cut into pieces with 25 mm × 25 mm × 2.0 mm dimensions, weighed (1.0 ± 0.1 g), and buried in plastic containers (10 L) filled with soil, previously passed through a 2 mm sieve. Every 15 days, for a period of 60 days, three replications of each sample were taken out of the container, cleaned with a smooth brush, and weighed. The average weight was considered. The soil moisture content (20 wt%) was maintained during the period of the test. Weight loss of the specimens with time was used to evaluate degradation. A digital camera was used to image the films before and after incubation in soil for 30 days.

Scanning Electron Microscopy

The morphology of the samples was observed with a Jeol electron microscope, model JSM-5610LV (Akishima-shi, Japan) at acceleration voltage of 15 kV. Samples were fractured and the fractured surfaces were vacuum-coated with gold before measurements.

Experimental Design and Statistical Analysis

A central composite design of second order was constructed on three levels of three independent variables; temperature, rotor speed and starch content.[9] The design comprised twelve combinations of variable levels, with four replications at the central point (Table 1). The parameters ranges were chosen on the basis of preliminary experiments, performed in the internal mixer. The response variable was the weight loss of the specimens buried in soil.

Table 1.
Coded levels for the central composite design

Independent variables	Levels		
	−1	0	+1
Temperature (°C)	160.0	170.0	180.0
Rotor speed (rpm)	40.0	50.0	60.0
Starch content (wt%)	20	40	60

A second-order polynomial model for dependent variables was established to fit the experimental data. The analysis of variance (ANOVA) was carried out using

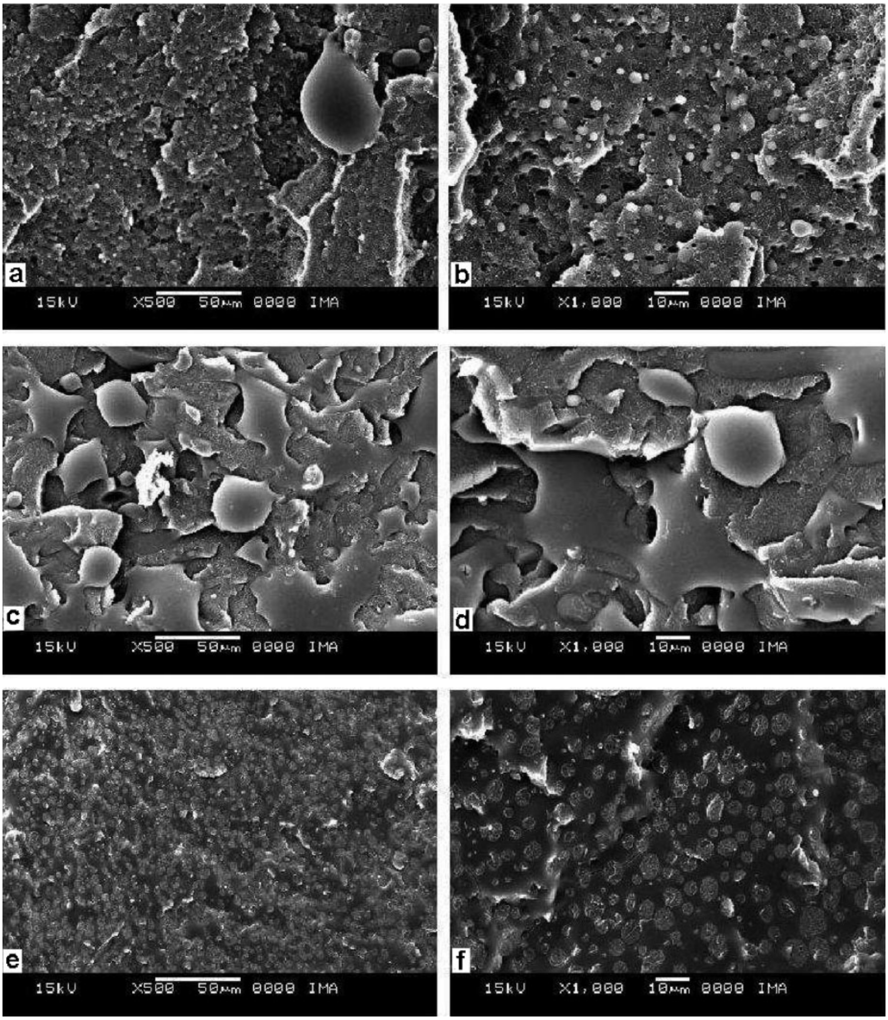

Figure 1.
SEM images for fractured surfaces of PS/starch blends with different starch contents: 20 wt% (a–b), 40 wt% (c–d) and 60 wt% (e–f).

Statistica for Windows 6.0 (Statsoft Inc., Tulsa, OK, USA) to determine the significance at the 5% ($P \leq 0.05$) level, for linear, quadratic and interaction effects.

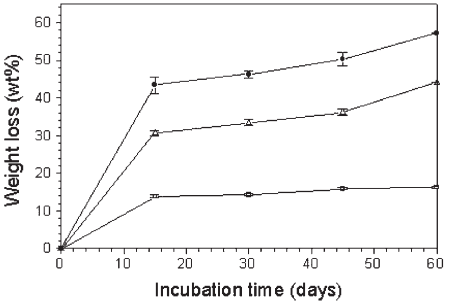

Figure 2.

Weight loss as a function of time for PS/starch blends with (■) 20 wt% starch, (Δ) 40 wt% starch, and (•) 60 wt% starch.

Results and Discussion

The morphology of PS/starch blends was evaluated by SEM as a function of starch content. Figures 1a and 1b show micrographs of fractured surfaces of the PS/starch blend with 20 wt% starch. In these figures, the rough PS matrix is filled with nearly spherical starch particles. In Figure 1b, the small size of these particles, and the absence of starch remnants, allow to conclude that the processing conditions were efficient to completely melt granular starch. In this figure, the well-dispersed starch particles are 1 to 5 μm in diameter. A different morphology may be observed in Figures 1c and 1d for the blend with 40 wt% starch. In this case, larger particles with irregular shapes are revealed. Coalescence is evidenced by the reduction in the amount of small particles and the increase in the number of elongated particles. Phase inversion occurred for blends with higher starch concentrations. In Figures 1e and 1f, SEM micrographs for the PS/starch blend with 60 wt% starch are shown. The PS dispersed phase appears as nearly spheroidal particles with 2–10 μm in diameter. In all these samples, addition of MA contributed to improve interfacial adhesion between the two phases. Some authors argued that the presence of a plasticizer,

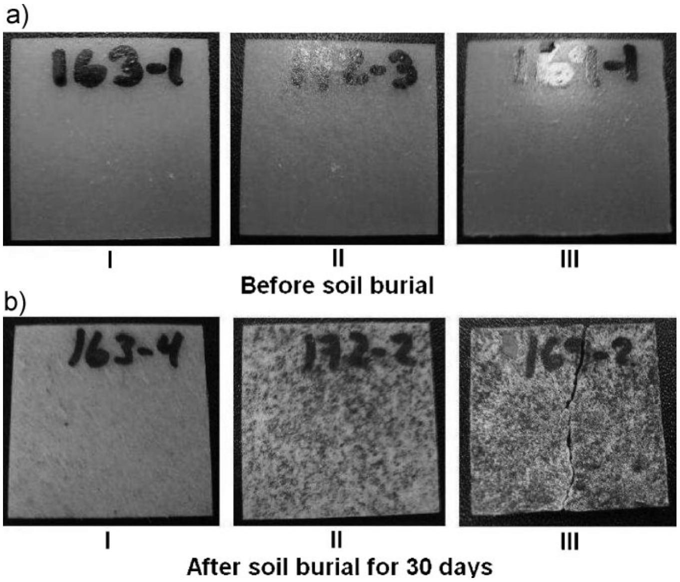

Figure 3.

Photographs for PS/starch blends with 20 wt% (I), 40 wt% (II) and 60 wt% (III) starch contents, before (a) and after (b) soil burial.

such as glycerol, could interfere with the starch/ MA interaction.[7] However, this kind of behavior seems not to have affected PS/ plasticized starch blends.

Biodegradation experiments are of fundamental importance for the production of environmentally friendly materials.[10] Soil burial tests, monitored by weighing the samples as a function of incubation time, are considered useful methods to evaluate the biodegradability of materials.[11] In this work, tests were carried out at room temperature, and followed by weighing specimens, after being buried in composted soil. The variation in weight loss for three different PS/starch blends is shown in Figure 2. The total weight losses for the specimens with 20, 40, and 60 wt% starch were 16, 39 and 57 wt%, respectively. Figure 2 shows that the weight loss increases with increasing starch content. According to some authors, as the amount of the dispersed starch phase is increased, interconnection and continuity are enhanced.[12] Thus, for the blend with the highest starch content, a small amount of

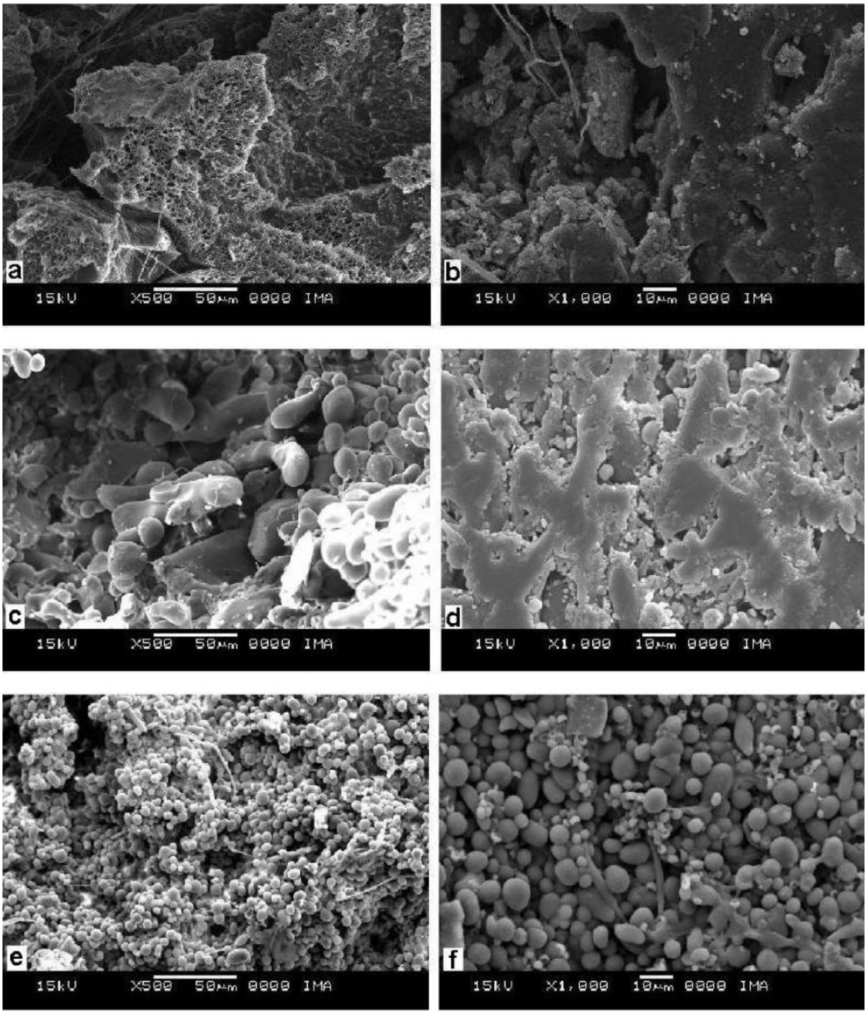

Figure 4.
SEM images for fractured surfaces of PS/starch blends with 20 wt% (a–b), 40 wt% (c–d) and 60 wt% (e–f) starch contents, after incubation for 60 days.

the synthetic polymer is present to exert some kind of protection from microorganisms. For MA-g-LLDPE/starch blends, other authors also found that the rate of degradation depended on starch content, and that the higher the starch content, the higher was the degree of degradation.[5]

Figure 2 shows that the biodegradation rate for PS/starch blends reached its highest value along the first 15 days of incubation, mainly for the blend with 60 wt% starch. The microbial activity decreases after that period, mainly for the mixture with 20 wt% starch. This result seems to indicate that, at least under these conditions, the starch fraction is the only one to be biodegradated. On the other hand, the low biodegradation rate determined for the sample processed with starch at a 20 wt% composition may be attributed to the limited accessibility of the starch phase to microorganisms.

Figure 3 shows photographs for PS/starch blends before and after incubation for 30 days. For the blends processed with 20 wt% of starch (Figure 3a-I and 3b-I), the specimens showed a gradual change in color, probably because of water absorption during soil burial; however, no change in shape was observed for the specimens. As the starch content was increased, even after only 30 days, changes in color, thickness, surface roughness, and increasing erosion were visually observed as starch biodegradation progressed (Figure 3b-II and 3b-III).

SEM was used to confirm the effects of microorganism inoculation on fractured surfaces of PS/starch blends (Figures 4 a-f). For the blends with 20 and 40 wt% starch, which were melt-processed according to the experimental design at 180 °C and 170 °C, respectively, SEM results revealed very degraded surfaces with many holes and cracks, as a consequence of the preferential removal of the starch phase. These holes and cracks produced by biodegradation have random shapes, typical of materials degraded in soil.[13] For the blend with 60 wt% starch (Figures 4e and 4f), the fractured surface is completely covered by the characteristic heterogeneous bacterial community, observed previously for starch alone.[11]

Conclusion

The biodegradability of PS/cornstarch blends were investigated along 60 days of incubation in soil, by determining the samples weight loss. The blends were prepared by melt-processing with different starch contents. As the starch content was increased, phase inversion was observed. The biodegradation results showed that with increasing starch contents, the total weight loss increased. The rate of bacterial growth depended on the relative ease with which the starch phase could be accessed by microorganisms.

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