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Mechanical properties and biodegradation of thermoplastic starches obtained from grafted starches with acrylics

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ABSTRACT

The mechanical properties and rate of biodegradation of thermoplastic starch obtained from acrylic grafted starch were evaluated. Thermoplastic starch from ungrafted starch (TPS) and grafted starch (TPGS) were obtained by mixing ungrafted or grafted starch with water and glycerol in a mixer camera. The TPS and TPGS with starch-g-PMMA behave as rigid materials with a high Young's modulus. However, TPGS with starch-g-(PBA-co-PMMA) showed less rigidity. Using dynamic mechanical analysis (DMA), an increase in the flexibility of starch was observed due to the addition of a plasticizer. The susceptibility of TPS and TPGS to biodegradation was evaluated with *Aspergillus niger*. Good fungus growth was observed after 45 days of incubation on TPS probes, whereas lower fungus growth was observed on TPGS probes. Starch biodegradation was confirmed by minor decomposition temperatures obtained by TGA, which indicated a decrease in the molecular weight of the starch due to enzymatic attack.

1. Introduction

Over the last several years, there has been a considerable increase in research related to biodegradable polymers due to problems associated with non-degradable residues derived from plastic. Although some biodegradable polymers such as polycaprolactone and polyhydroxyalcanoate have good properties and characteristics for films or materials produced by injection, they are too expensive to be used in common disposable products, such as packaging, bottles and containers, which are the main items that lead to pollution from plastics (Ma, Chang, Yu, & Stumborg, 2009; You, Li, Gao, Yu, & Zhao, 2003). On the other hand, starch is a natural polymer with greater use in biodegradable products due to its low cost, abundance and biodegrability (Famá, Gerschenson, & Goyanes, 2009; Qiao, Tang, & Sun, 2011; Shang, Fu, Chen, & Yang, 2009; Sugih, Drijfhout, Pichioni, Jansssen, & Heeres, 2009). Starch granules have different sizes and forms derived from their biological source. Starch can be circular, elliptical, oval or polygonal (Acosta, Villada, Torres, & Ramírez, 2006). Starch is composed of amylose and amylopectin, which are polymeric chains. These starch constituents have the same repetitive unit but different molecular weights. Additionally, amylose is a linear polymer while amylopectin is ramified. In the presence of plasticizer (water or other hydrophilic compounds), starch can be considered a thermoplastic material because it can be processed with heat and mechanical energy (Chaléat, Halley, & Truss, 2007; Raphaelides, Dimetreli, Exarhopoulos, Kokonides, & Tzani, 2011; Sankri et al., 2010; Teixeira, Da Róz, Carvalho, & Curvelo, 2007; Thunwall, Boldizar, & Rigdahl, 2006). During processing, the starch granules break and yield an amorphous mass. Depolymerization (macromolecular rupture) of amylose and amylopectin also occurs (Guan & Hanna, 2006).

However, thermoplastic starches (TPS) have poor mechanical properties and are sensitive to humid environments. Thus, the chemical modification of starch or blending with natural or synthetic polymers is necessary to improve these properties and compete with non-biodegradable plastics (Mano, Koniarova, & Reis, 2003; Rahman, Sin, Rahmat, & Samad, 2010; Rodriguez-Gonzalez, Ramsay, & Favis, 2004; Shujun, Jiugao, & Jinglin, 2006; Tena-Salcido, Rodríguez-González, Méndez-Hernández, & Contreras-Esquivel, 2008). One way to develop TPS with improved properties includes the modification of starches through grafting with synthetic polymers. Graft copolymerization has been used as an important technique for the modification of physical and chemical properties of polymers. Thus, with grafted starch, it is possible to modify properties such as the elasticity, absorbency, ionic interchange capacity, thermal resistance and microbiological resistance (Celik, 2006; Rahman et al., 2000).

In this work, thermoplastic starch made from grafted starch (TPGS) was obtained, and the mechanical and thermal properties of the material were compared to thermoplastic starch obtained with ungrafted material (TPS). Biodegradation of the modified materials with *Aspergillus niger* was also studied.

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2. Experimental

Corn starch was acquired from Productos de Maíz S. A. de C.V. (México City, México). Methyl methacrylate (MMA) and butyl acrylate (BA) monomers were obtained from Aldrich (Milwaukee, WI) and were passed through an Aldrich column to remove inhibitors. Poly(methyl methacrylate) and poly(butyl acrylate)-co-poly(methyl methacrylate) grafted starches were obtained as granules, according to a procedure reported in the literature (Vera-Pacheco, Vázquez-Torres, & Canché-Escamilla, 1993). The reactions were carried out in 20 L stainless steel reactor equipped with a stirrer, a condenser and a temperature control. Nitrogen was purged into the reactor to remove the presence of oxygen during the reaction. 750 g of starch was suspended in 5.4 l of water during 90 min. Then, 750 g of monomer (MMA or MMA-BA mixture) was added and after 5 min a solution of ceric ammonium nitrate (CAN) in HNO_3 0.1 N (23.9 g CAN/471 ml HNO_3 0.1 N). After 5 h of reaction at 30 °C, the slurry was filtered and the grafted granules were washed with ethanol and dried under vacuum at 50 °C. The grafted granules were extracted with acetone for 24 h, filtered to remove homopolymer and were then dried under vacuum at 50 °C. The grafting percentage was determinate by the following formula (Rahman et al., 2000):

$$\text{grafting percentage} = \frac{\text{weight of grafted polymer}}{\text{weight of copolymer(starch-g-polymer)}} \times 100$$

2.1. Production and characterization of the thermoplastic starch

Thermoplastic materials with grafted (TPGS) and ungrafted (TPS) starch were obtained with water and glycerol added as plasticizers. The ratio of starch (or grafted starch) to glycerol to water was 70/10/20 or 70/20/10. The starch was first blended with water and followed by glycerol in a ribbon mixer and stored overnight. The mixtures were manually fed into a Brabender Plasticorder II roller mixer for 10 min at 170 °C and 40 rpm. The blend was milled using a Brabender knife mill to the reduce particle size. These particles were moulded at 170 °C in a Carver Laboratory press at 10,000 lb to obtain samples for mechanical and biodegradation experiments.

The tensile tests for TPS and TPGS were conducted with a Shimadzu AG-I universal machine following ASTM D882-09 (2009) method. The test was conducted at a crosshead speed of 12.5 mm/min with an initial separation grip of 125 mm. The samples (175 mm × 10 mm × 0.5 mm) were cut from the 0.5 mm hot-pressed moulded sheets. The analyses were performed after equilibrating the samples (3 days at 23 ± 2 °C) at 50 ± 5% relative humidity.

The storage modulus and Tan delta curves of samples were obtained on a Perkin Elmer DMA7 mechanical dynamic analyzer, working in tension mode at 1 Hz with preload of 0.1 N. The heating rate was of 5 °C/min and temperature range was of -100 to 170 °C. The samples (15 mm × 2 mm × 0.5 mm) were cut from the 0.5 mm hot-pressed moulded sheets. The analyses were performed after equilibrating the samples (3 days at 23 ± 2 °C) at 50 ± 5% relative humidity.

2.2. Hydrolytic degradation of thermoplastic starch

Rectangular sections (3 mm × 5 mm × 3 mm) of TPS or TPGS were cut of probes. In order to evaluate the continuity of starch in these samples, hydrolytic degradation was carried out in a solution of HCl 6N at 60 °C for 12 h or until total disintegration of the samples.

2.3. Biodegradation of thermoplastic starch

The TPS and TPGS were biodegraded according to the ASTM standard G21-96 (2002). The culture was prepared without a carbon source and sterilized by autoclaving at 121 °C for 25 min. One layer of the medium was left to solidify in Petri dishes. The starch or grafted starch samples were distributed over this layer. A second layer of the medium containing a suspension of *A. niger* spores was poured onto the Petri dishes. This procedure allowed the samples to be maintained between the two layers of the semisolid medium. The Petri dishes were kept at room temperature in the dark. The growth of the fungus was evaluated by visual observation at 4, 8, 12 and 45 days of incubation. The samples were removed from the Petri dishes, washed with a sodium hypochlorite solution and dried at room temperature for 24 h in a vacuum oven at 60 °C to achieve a constant weight.

2.4. Characterization of thermoplastic starch after biodegradation

A Jeol SEM 6360 scanning electron microscope was used to examine the surface and surface fractures of thermoplastic starch after biodegradation. To minimize damage and to improve contrast, the samples were coated with a gold film before examination. Thermogravimetric analysis (TGA) of samples was performed with a Perkin Elmer TG7 thermogravimetric balance with a heating rate of 10 °C/min and a temperature range of 50–600 °C under a nitrogen atmosphere.

3. Results and discussion

Grafted polymerization was conducted on granular starch at 30 °C using ceric ammonium nitrate as initiator. It can be observed in Fig. 1, that grafted starch maintained a granular form after the grafting reaction with a notable increase of average size due the grafted polymer. These results are similar to the reported by other authors (Fanta & Shogren, 1997; Moreno-Chulim, Barahona-Pérez, & Canché-Escamilla, 2003). As the reaction was carried out at a low temperature, there is a low swelling of the granule and the radical is formed mainly on the granular surface and the polymer or copolymer is grafted on this surface. The grafting percentage was determined to be 45% and 44% to PMMA or PBA-co-PMMA, respectively, indicating that the starch is the main component in the grafted starch granule.

The starch granules lost their granular structure in the presence of plasticizer when they were processed under heat and high shear stress conditions (i.e., extrusion or blending processes). The last process has been used in this work for the production of thermoplastic ungrafted starch (TPS) and thermoplastic grafted starch (TPGS). TPS or TPGS was achieved through the blending starch or grafted starch with glycerol and water as plasticizers in a mixer camera.

3.1. Mechanical properties and morphology of thermoplastic starch

The effect of the grafted polymer on the mechanical properties of thermoplastic starch is shown in Fig. 2. In this figure, the TPS has characteristics of a rigid material, with a high modulus and low elongation at break. The TPS has a Young's modulus equal to 660 MPa and tensile strength of 7.5 MPa. The TPGS has lower mechanical properties in comparison to TPS, and these values diminish with an increase in the PBA content (rubber polymer) in the grafted copolymer. The TPGS with starch-g-PMMA has a modulus and tensile strength of 420 MPa and 5 MPa, respectively. The TPGS with starch-g-(25PBA-co-75PMMA) has a modulus of 40 MPa and tensile strength of 2 MPa. This behaviour can be rationalized if we consider TPGS as blends of ungrafted and grafted starch with the ungrafted starch as continuous phase. This mixture is present after granular destruction occurs during processing. The incorporation of PBA, a rubber-like polymer, on grafted starch results in a

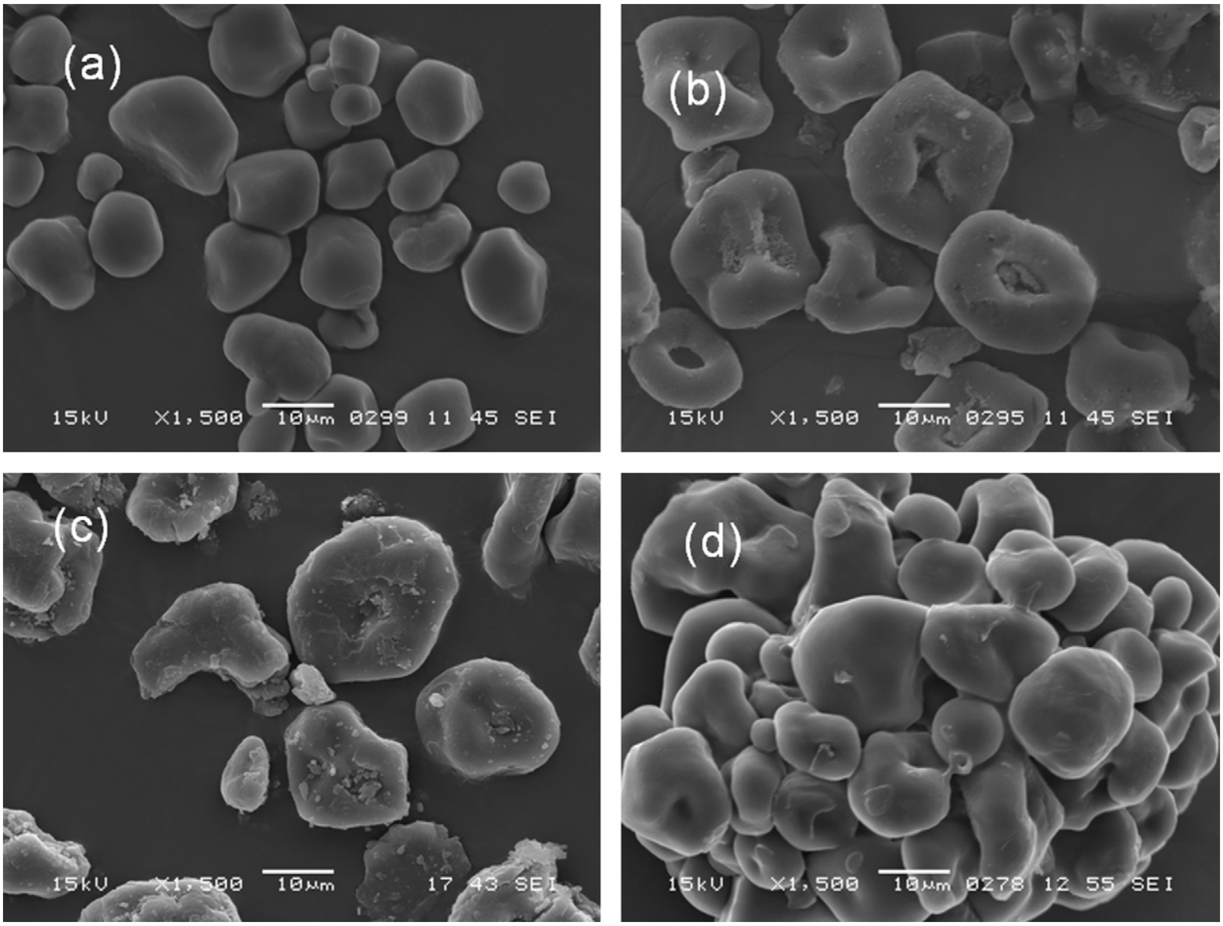

Fig. 1. SEM micrographs of granular starch (a) unmodified, (b) PMMA-grafted, (c) 25PMMA-co-75PBA-grafted and (d) 50PMMA-co-50PBA-grafted.

lower modulus material. Thus, TPGS with starch-g-(PBA-co-PMMA) shows lower mechanical properties when compared to TPS or TPGS with starch-g-PMMA.

The destruction of granular structure is evidenced from the fracture surface of the tensile probe microphotography, obtained by the use of a scanning electron microscope (Fig. 3). The form of flaws in the materials depends on the grafted polymer and the glycerol content. TPS (Fig. 4a) and TPGS with PMMA grafted starch (Fig. 4b) showed a smooth fracture indicating behaviour typical of brittle materials. The TPGS with PBA-co-PMMA grafted starch showed less brittle behaviour and depressions existed on the fracture surface. The presence of depressions indicated the effect of PBA-co-PMMA grafted starch on the thermoplastic starch phase. The continuity of ungrafted starch in the TPGS was confirmed by the disintegration of the samples when they were exposed to acid degradation. It is well known that acid hydrolysis to starch involves the random cleavage of glycoside bonds producing from oligosaccharides to glucose units, and this hydrolysis has been used to recover the grafted polymer at starch-g-polymer samples (Gurruchaga, Goñi, Valero, & Guzmán, 1993) or to determinate the continuity of the starch phase in TPS blended with PE (Tena-Salcido et al., 2008).

3.2. Dynamic mechanical analysis of TPS and TPGS

Fig. 4 shows the effect of the grafted polymer or copolymer on the storage modulus and the Tan delta curves of thermoplastic starch and thermoplastic grafted starch. The TPS showed a decrease in the storage modulus (Fig. 4a) in a range from 35 to 65 °C, with a

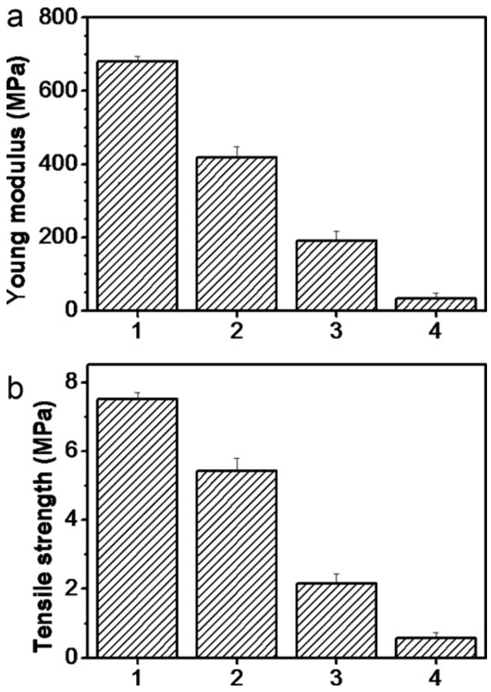

Fig. 2. Effect of grafted polymer on the mechanical properties of thermoplastic starch with a formulation of 70/20/10 (starch or grafted starch)/glycerol/water: (1) ungrafted starch, (2) starch-g-PMMA, (3) starch-g-(25PBA-co-75PMMA), and (4) starch-g-(50PBA-co-50PMMA).

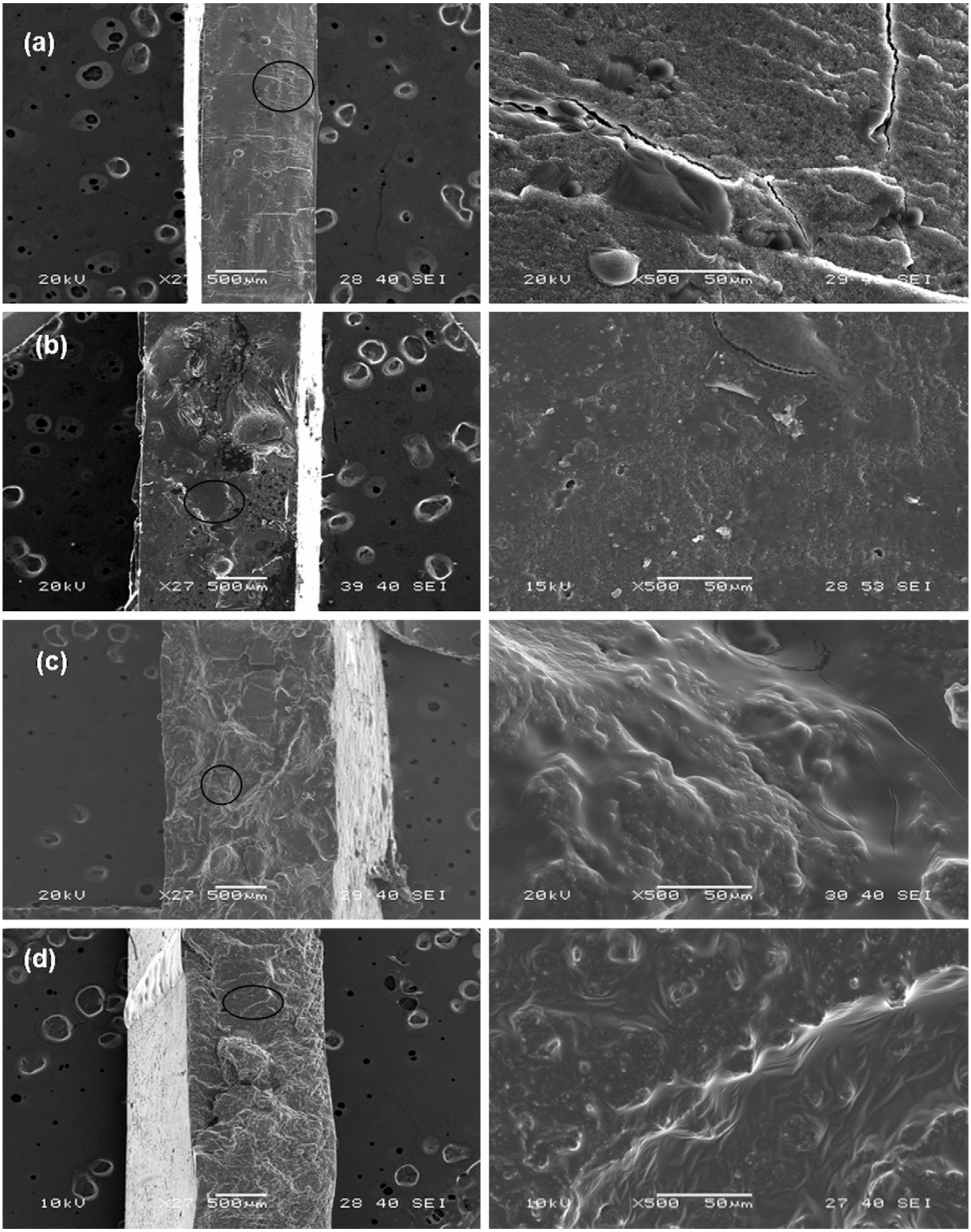

Fig. 3. SEM micrographs of the ruptured surface of thermoplastic ungrafted starch (TPS) and thermoplastic grafted starch (TPGS): (a) ungrafted starch, TPGS with (b) starch-g-PMMA, (c) starch-g-(25PBA-co-75PMMA), and (d) starch-g-(50PBA-co-50PMMA).

maximum at 50 °C in the Tan delta curve (Fig. 4b). This behaviour can be attributed to the glass-vitreous transition temperature (Tg) of plasticized starch. It has been reported that plasticizers increase the free volume or molecule mobility of the polymer by reducing H-bonding between polymer chains. This leads to a transition, Tg, that occurs at lower temperatures when compared to unplasticized starch. Unplasticized starch has a Tg that is higher than its degradation temperature (Mathew & Dufresne, 2002). It can be observed that the drop in the storage modulus is more pronounced for TPGS in comparison to TPS, and a drop modulus until three orders of magnitude is observed. This diminish can be attributed to the TPGS that are more flexible material than the TPS matrix due the higher plasticization of the ungrafted starch matrix, and it is in accordance with the behaviour of the mechanical properties of these materials. This drop of modulus occurs in range interval between −10 to 170 °C and −60 to 90 °C for TPGS with PMMA and PBA-co-PMMA grafted starch, respectively. The Tan delta curves of TPGS obtained with PMMA grafted starch show a peak with

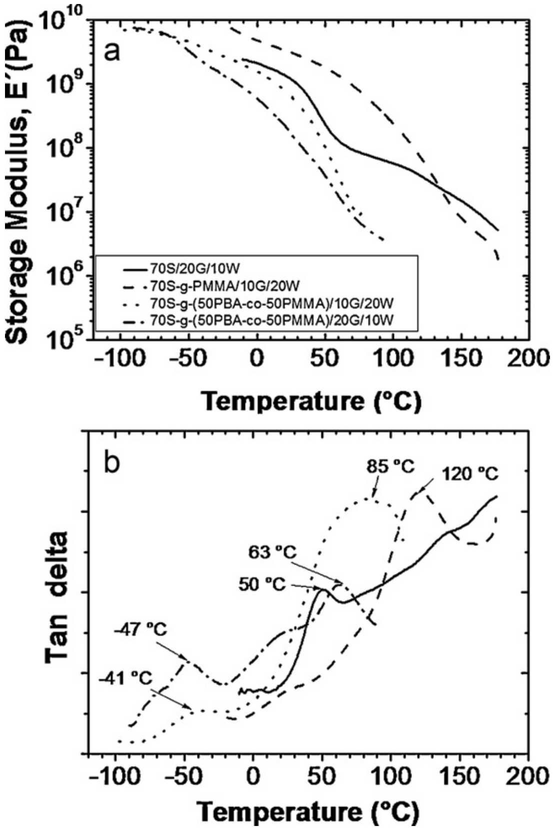

Fig. 4. (a) Storage modulus *versus* temperature and (b) tan δ *versus* temperature of TPS and TPGS obtained using relation (starch or grafted starch)/glycerol/water of 70/10/20 or 70/20/10.

maxima at 120 °C, which is attributed to the Tg of PMMA. In this curve, the Tg of plasticized starch appears as a shoulder at 25 °C. TPGS obtained with 50PBA-co-50PMMA grafted starch and 10 or 20% of glycerol shows two peaks, one at 85 or 63 °C and other −41 or −47 °C attributed to the copolymer rich in PMMA and in PBA, respectively. These copolymers are formed during the grafted PBA-PMMA copolymerization onto starch. In this case, the higher reactivity and solubility in water of PMMA over PBA, led to the brief polymerization of PMMA in a first step of grafted copolymerization onto granule starch, and results in a grafted copolymer with a higher PMMA content. After the major consumption of PMMA a copolymer rich in PBA is formed. The displacement of the Tg of these copolymers to lower temperatures with the increase of glycerol can be attributed to the plasticization of the PBA-co-PMMA grafted starch.

3.3. *Thermogravimetic analysis of thermoplastic starch*

In thermogravimetric analysis (TGA) of thermoplastic starch, the loss of mass due to volatilization of degradation products was monitored as a function of temperature. The thermogravimetric (TG) curves and the derivative thermogravimetric (DTG) curves of thermoplastic starches are shown in Fig. 5. The TPS thermogravimetric curve showed two decompositions. The first loss of mass (20%), in the range of 100–309 °C, was attributed to a loss of water and glycerol from the samples. The second loss of mass (53%), in the range of 309–358 °C, was attributed to thermal degradation of amylose and amylopectin. The TPS was degraded completely at 600 °C and the maximum decomposition temperature (T_{dmax}) was observed at 330 °C (indicated by a maximum peak in the DTG curves, Fig. 5b).

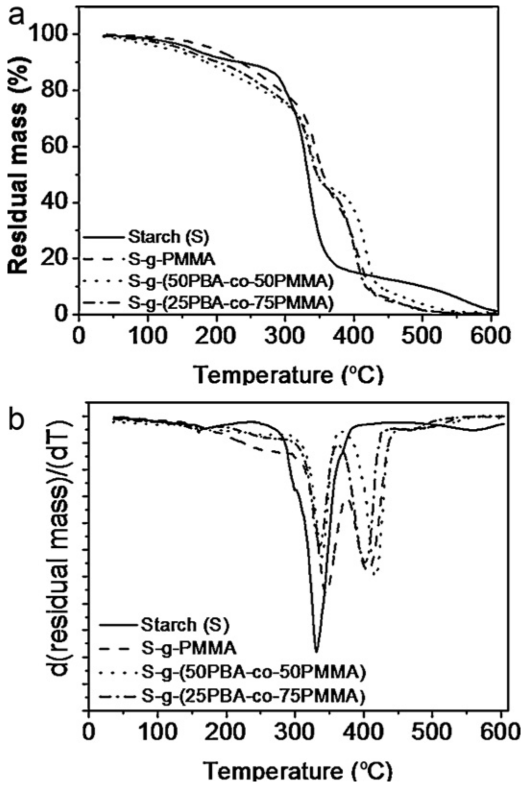

Fig. 5. Thermogravimetric and derivative thermogravimetric curves of thermoplastic starch (TPS) and thermoplastic grafted starch (TPGS).

The TG curves of TPGS were similar and independent of the polymer or copolymer grafted to starch. Three decomposition zones were observed. The first zone with a loss of mass of 22% occurred in the range of 100–328 °C and was attributed to the loss of water and glycerol from the samples. The second zone (25–35% loss mass) occurred at 328–365 °C and was due to the decomposition of starch. The third loss of mass (32–38%) was observed at 405–440 °C and was attributed to the grafted polymer. In Fig. 1b, the starch peak in the DTG curves of TPGS is slightly shifted to higher temperatures with respect to TPS, indicating the higher thermal stability of the grafted starch due to the presence of the grafted polymer (Celik, 2006; Fares, El-Faqeeh, & Osman, 2003). The higher thermal stability of PBA with respect to PMMA results in a higher T_{dmax} value. The value of T_{dmax} increases as the PBA content in the grafted copolymer increases.

3.4. *Growing fungus*

Fig. 6a–c displays the Petri dish with TPS and TPGS after biodegradation with *A. niger*. In all samples, the presence of mycelium (white zones) and spores (black zones) was observed, indicating that the fungus grew in the Petri dish on starch present in TPS or TPGS as a carbon resource. A greater amount of white zones was present in TPS samples when compared to TPGS samples. This indicates a minor feasibility of TPGS samples to fungal attack. A greater amount of black zones and a higher production of spores are observed when the more flexible copolymer (50PBA-co-50PMMA), is grafted to starch which indicates the limited growth and development of fungus. This behaviour can be attributed at the polymer or copolymer grafted starch can form a thin film on the probe's surface that reduces the access of fungus to ungrafted starch and limits their growth. This film formation has been reported in other blends of thermoplastic starch-polymer too (Vikman, Hulleman, Van der Zee, Mylärinen, & Feil, 1998). The SEM micrographs of surface's

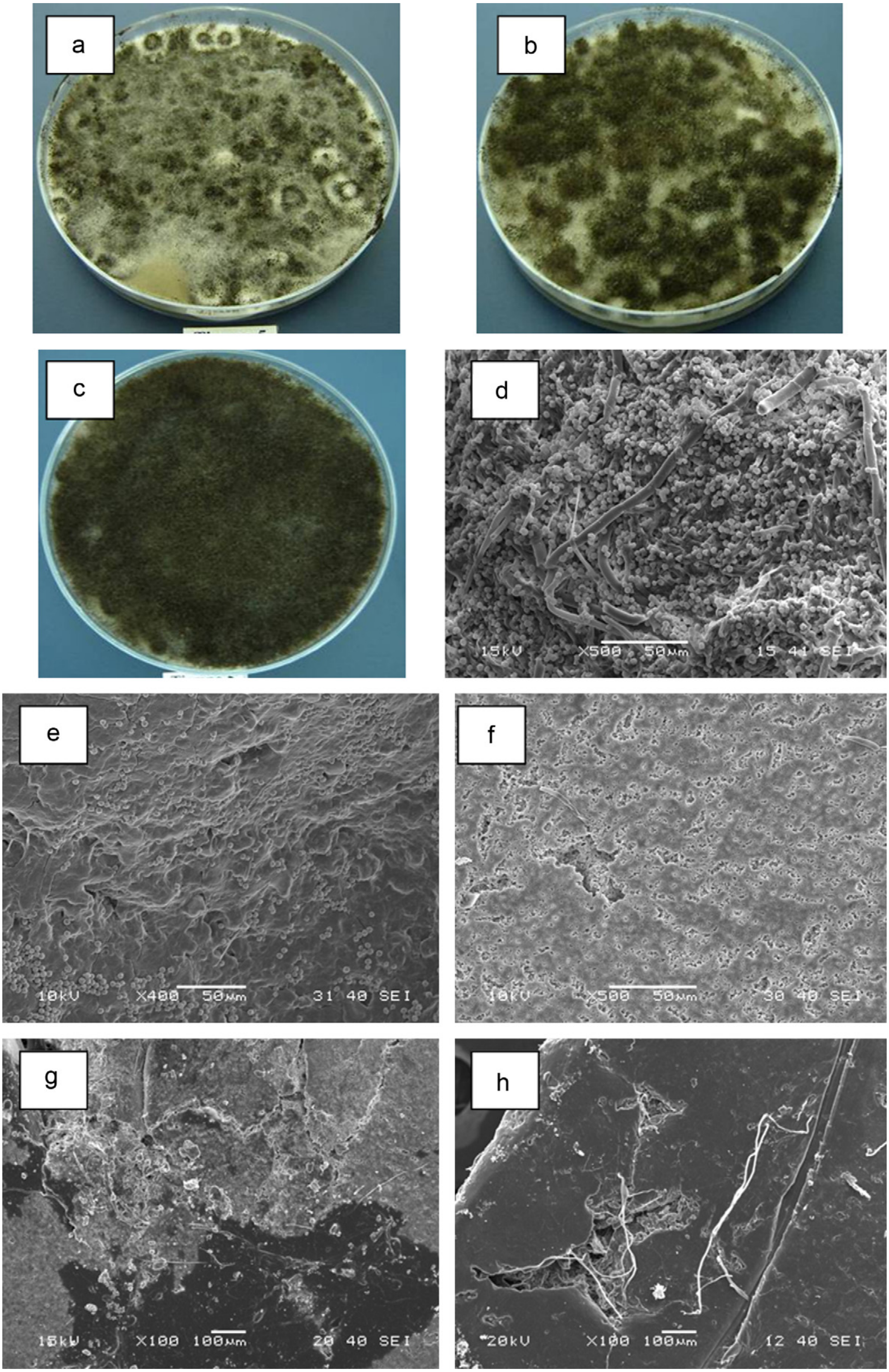

Fig. 6. Growth of *A. niger* over the Petri dishes and surface's probe of the thermoplastic starch after 45 days of culturing. Preti dishes: (a) TPS samples; TPGS samples with (b) starch-g-PMMA or (c) starch-g-(50PBA-co-50PMMA). Surface's probes: (e) TPS samples; TPGS samples with (d) and (e) starch-g-PMMA, (f) starch-g-(25PBA-co-75PMMA), and (g) starch-g-(50PBA-co-50PMMA).

probe (Fig. 6d–h) of the TPS or TPGS corroborate this assumption. In these figures the presence of both hyphae and spores is visible on the surface of TPGS with starch-g-PMMA probes (Fig. 6d) indicating the growth of fungus but after removal of the fungus, a good attack is observed on the surface probe of TPS (Fig. 6e) and poor attack is observed on the surface probe of TPGS (Fig. 6f–h). Due the minor viscosity of (PBA-co-PMMA)-g-starch in comparison with PMMA-g-starch, the first produces a more continuous film and these materials showed the lower accessibility of the fungus attack to ungrafted starch. The limited access to ungrafted starch in the TPGS probe was confirmed too, when the probes were degraded by acid solutions. The TPGS probes obtained with starch-g-(PBA-co-PMMA) required great times to disintegrate in comparison with TPGS probes obtained using starch-g-PMMA.

3.5. Biodegradation of TPS and TPGS

In Fig. 7, the effect of time on starch biodegradation in TPS and TPGS can be observed. The samples have an initial loss of mass due to the diffusion of glycerol into the agar. This behaviour explains how the fungus was able to grow on the entire surface of the Petri dish. The TPS probes lost mass more quickly than TPGS probes due to the accessibility of *A. niger* to the ungrafted starch in TPS. After 12 days of incubation, the TPS sample lost 60% of its weight. A weight loss of 30% and 20% was observed for TPGS obtained from starch-g-PMMA and starch-g-(50PBA-co-50PMMA), respectively. It has been reported that *A. niger* produces amylase and glucoamylase enzymes that can degrade amylose and amylopectin to glucose (MacKenzie, Jeenes, Gou, & Archer, 2000).Due the disintegration of the samples by the biodegradation of the ungrafted starch matrix, thermogravimetric analysis was used to follow the changes in ungrafted starch due the enzymatic attack. Fig. 8 shows the derivative thermogravimetric analysis (DTGA) curves of TPS and TPGS after 12 and 45 days of biodegradation. TPS after 12 days of biodegradation showed two peaks at 260 and 320 °C. The first peak can be attributed to the production of dextrins (anhydrous glucose chains with a low molecular weight) of varying molecular weight, which are generated due to starch degradation. The second peak can be attributed to starch non-biodegraded. It has been reported that the biodegradation of starch by *A. niger* occurs by the random rupture of ether linkages in amylase and amylopectin or by the rupture of ether linkages in the extreme chain. In the first case, more short chains are obtained. In the second case, there is little effect on the size of the chain (Moreno-Chulim et al., 2003). The DTGA curves of TPS after 45 days of biodegradation show only a peak at 235 °C, indicating major degradation of starch to dextrins, which is due to fungal attack. Similar behaviour is observed in TPGS samples where starch is degraded by the fungus. Due to the fact that grafted polymers (PMMA or PBA-co-PMMA) are not biodegradable, their maximum decomposition temperature (Td$_{max}$) were similar to the maxima observed in non-biodegraded TPGS.

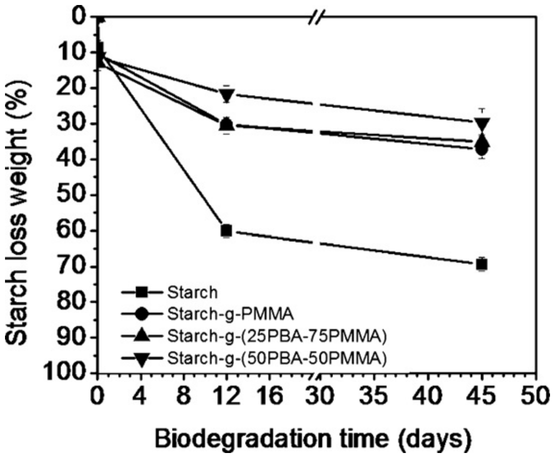

Fig. 7. The effect of incubation time on the weight loss of TPS and TPGS samples obtained using (ungrafted starch or grafted starch)/glycerol/water (70/20/10) relation.

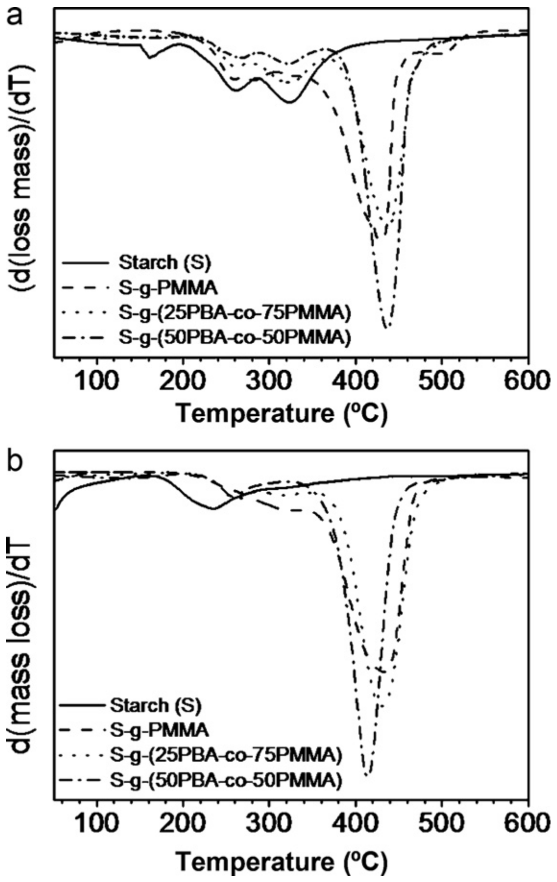

Fig. 8. Thermogravimetric and derivative thermogravimetric curves from TPS and TPGS after (a) 12 days and (b) 45 days of inoculation with *A. niger*.

4. Conclusions

The mechanical properties of thermoplastic starch can be modified by the use of grafted polymers. The use of rigid (PMMA) and rubbery polymers (PBA) increases the flexibility of thermoplastic grafted starch (TPGS) in comparison to thermoplastic starch (TPS) and allowed for the preparation of a wide range of materials by modifying the ratio of PBA/PMMA in the grafted copolymer.

A. niger can use the starch present in thermoplastic grafted starch as a carbon source and their growth depends on the grafted polymer. Flexible polymers limit the accessibility of the fungus to starch and reduce the rate of starch biodegradation. The biodegradation of starch was evidenced in the loss of mass in TPS and TPGS samples and in the reduction of chain length (dextrin production) due to enzymatic attack as observed at thermogravimetric analysis of biodegrade samples.

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