Microwave-assisted modification of starch for compatibilizing LLDPE/starch blends

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A B S T R A C T

Modification of activated cassava starch (S) was performed by using octenyl succinic anhydride (OSA) at different starch/OSA ratios under microwave radiation. FTIR and titration results indicated that, within a reaction time of 7 min, degrees of substitution (DS) of about 0.045 may be achieved with 20% OSA. Subsequently, linear low density polyethylene/starch (LLDPE/S) blends were prepared employing succinylated starches (S-*g*-OSA) as compatibilizers. The morphology and mechanical properties of LLDPE/S blends with and without compatibilizer were compared. It was observed that the addition of 10% of compatibilizer with respect to the dispersed phase content led to a reduction of the starch phase size and to an improvement of the blends mechanical properties.

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1. Introduction

The polyolefins industry is still a very dynamic business, where linear low density polyethylene (LLDPE) plays a key role. LLDPE has a wide range of applications in the production of films, injection molding, and rotational molding. About 75% of LLDPE is used in films, world over. This is because of its excellent mechanical properties and high draw-down ratio compared to LDPE at the same density (Selke, Culter, & Hernandez, 2004). In injection molding, for example, LLDPE grades, which are stiffer and more resistant to impact and distortion at elevated temperatures, replace many of the LDPE and HDPE grades. In addition, low temperature impact properties are superior to those of polypropylene. However, the use of polyolefins, in general, causes serious environmental concerns because they are not biodegradable; i.e., they are not biodegraded by the microorganisms present in the environment. Even though recycling has become an alternative, not all post-consumer products may be recycled and, in some cases, this process is not economically sustainable. The waste management problem has prompted the development of, at least, partially degradable plastics, a fact that may be achieved by blending with a biodegradable filler, which can effectively reduce the volume of plastic waste by partial degradation (Nakamura, Cordi, Almeida, Duran, & Mei, 2005; Pedroso & Rosa, 2005; Walker, Tao, & Torkelson, 2007).

Starch is a renewable, biodegradable hydrophilic polymer that has been employed as filler in blends with different synthetic materials up to a certain amount (Bastioli, 2005; Pascente, Már-

quez, Balsamo, & Müller, 2008), and sheets or films can be made by conventional processes (Bastioli, 2005; Fakirov & Bhattacharyya, 2007). In the case of polyethylenes (PE), the high interfacial tension when blending them with starch must be reduced in order to ensure homogeneity at microscopic level and to obtain suitable mechanical properties (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Garg & Jana, 2007; Nakamura et al., 2005). In order to achieve this, the use of a modified starch as a component of the blend offers an approach to meet the performance requirements. Swanson, Westhoff, and Doane (1988) examined the effect of adding modified starch on films of LDPE and poly(ethylene-*co*-acrylic acid) (EAA) blends; they observed that the presence of hydroxypropyl derivates of starch led to materials with improved elongation and tensile strength. Such a kind of modified starch was also used in the works of Kim, Ki, and Park (2002, 2003), in which also the addition of short pulp fiber as reinforcement and glycerol as plasticizer was reported. Nakamura et al. (2005) reported that samples of LDPE containing acetylated cassava starches exhibited an improvement in the mechanical properties when compared to LDPE/unmodified starch blends. On the other hand, Garg and Jana (2007) observed that the addition of a crosslinked starch to LDPE increased the tensile strength and elongation of LDPE/starch blends in comparison to blends containing glycerol modified starch; LLDPE/S blends compatibilized with crosslinked and glycerol modified starch produced smoother films.

The work of Evangelista, Nikolov, Sung, Jane, and Gelina (1991) is, up to our knowledge, the only work that has reported studies on blends prepared with LLDPE and octenyl succinate modified starch. They compared the properties of blends including modified starch with those of blends prepared with native corn starch. In all cases,

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the first ones showed higher tensile strength and elongation values than the corresponding blends where the starch was not modified. Nevertheless, the authors prepared the blends with only one modified starch, in which the degree of substitution was not reported.

Modification of starch with alkenyl succinic anhydrides has been of interest because this modification disrupts hydrogen bonding between starch molecules and reduces starch retrogradation, while imparting an amphiphilic character (Bhosale & Singhal, 2006). These modified starches could find application as compatibilizers in PE/starch blends; they can be prepared by treating starches with different alkenyl succinic anhydrides such as octenyl, dodecenyl, and octadecyl succinic anhydrides. The length of the alkenyl group and the degree of substitution will ultimately determine the extent of hydrophobic character of the modified starch. Among this kind of modifications, starch modified with octenyl succinic anhydride (OSA) has been known for a long time (Bao, Xing, Phillips, & Corke, 2003; Bhosale & Singhal, 2006; Cadwell & Wuzburg, 1953; He, Song, Ruan, & Feng, 2006; Thirathumthavorn & Charoenrein, 2006). The methods for preparing OSA starch were patented by Cadwell and Wuzburg (1953), in which the reaction is performed under mild alkaline conditions. Acid-treated starches derivatized with OSA have been also reported (Billmers & Mackewicz, 1997; Shogren, Vishwanathan, Felker, & Gross, 2000; Thirathumthavorn & Charoenrein, 2006). More recently, Bhosale and Singhal (2006) optimized reaction conditions for the successful modification of both amaranth and waxy corn starches (Jeon, Viswanathan, & Gross, 1999). All reactions that can be found in the literature have been performed adding OSA in starch/water slurries in conventional reactors with reaction times of hours. Recently, an alternative method for the modification of starches has been reported by Moorthy (2004), Jyothi, Rajasekharan, Moorthy, and Sreekumar (2005), and Biswas, Shogren, Kim, and Willett (2006) who have used microwave radiation to carry out the modification of starch with succinic anhydride in very short times such as minutes. The aim of this work is to perform the chemical modification of cassava starch with octenyl succinic anhydride under microwave radiation and to compare the effect of starches with different degrees of substitution (DS) as compatibilizers for LLDPE/S blends.

2. Materials and methods

2.1. Materials

Linear low density polyethylene (Venelene 11S1) was obtained from Polinter, CA (MFI = 2.50 dg/min, $\rho = 0.917$ g/cm^3), and cassava starch (S) was kindly supplied by PDVSA, San Tomé (18% amylose). Octenyl succinic anhydride (OSA) was purchased from Aldrich. All chemicals were analytical grade.

2.2. Preparation of modified starches

2.2.1. Modification of cassava starch with OSA in aqueous media (S-g-OSA$_s$)

This reaction was carried out following the procedure described by Bhosale and Singhal (2006). Five grams of native cassava starch were introduced in a glass reactor with 20 ml of distilled water under stirring. The pH of the slurry was adjusted and maintained throughout the reaction at a value of 8.0 ± 0.4 with a NaOH solution by using a ThermoOrion pH meter (USA). To this mixture, 3% (A1) and 20% (A2) OSA with respect to the starch weight was added drop wise during 2 h and the reaction was carried out for 24 h. After the reaction, the pH was brought to 6.5 by adding HCl. The reaction product was washed with ethanol and dried under vacuum for 48 h.

2.2.2. Modification of cassava starch with OSA under microwave radiation (S-g-OSA$_{mw}$)

The procedure we used was based on the work of Jyothi et al. (2005) with some modifications. Before the reaction in the microwave, a 25% suspension of native cassava starch in water was prepared at room temperature and the pH adjusted to 8.5 ± 0.1 in order to activate the hydroxylic groups of the starch. The starch was then filtered, dried under vacuum during 48 h, and stored for the subsequent reactions.

Activated starch was impregnated with distilled water (1 ml for each 5 g of starch) in a glass reactor; once the starch was dispersed, the corresponding amount (w/w) of OSA was added for the reaction (B1: 10%, B2: 20%), and the mixture was homogenized with an electrical hand mixer. Afterwards, the glass reactor was introduced in the microwave and subjected to the first heating cycle. The reactions were performed by applying three heating cycles of 2 min and a final heating cycle of 1 min in a DAEWOO domestic microwave oven (KOR-860A model, China) regulating the potency at 360 W. In the period between the cycles, which was of 40 s, the mixture was agitated. After finishing the reaction, a 100 ml solution of the product was prepared with equal parts of water and ethanol, and the pH was brought to 6.5 ± 0.1. Then, the modified starch was filtered and washed with ethanol. The solid was dried under vacuum for 48 h.

2.3. Characterization methods

2.3.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded with a Nicolet Magna IR 760 spectrometer (Madison, USA) with a resolution of 4 cm^{-1} and 64 scans, and wavenumber range between 400 and 4000 cm^{-1}. The data were analyzed by using the OMNIC Utility version 3.0. Discs were obtained by mixing dried starch with analytical grade KBr.

2.3.2. Determination of the degree of substitution (DS)

DS is the average number of hydroxyl groups substituted per anhydroglucose (AGU) unit. The DS of OSA starch (S-g-OSA) was determined using a titration method. Thus, 5 ml of a 0.5 M aqueous NaOH solution was added to a suspension of S-g-OSA (1 g of S-g-OSA in 10 ml distilled water for non-hydrophobic products and 1 g of S-g-OSA in 10 ml dimethylsulfoxide for hydrophobic products) and maintained under stirring for 24 h at room temperature. Then, excess of alkali was titrated with a 0.5 M aqueous HCl solution, using phenolphthalein as indicator. A blank suspension of native unmodified starch was also titrated.

DS was determined from % OSA substitution as follows (Bhosale & Singhal, 2006):

$$\%OSA = \frac{(V_{blank} - V_{sample}) \times 0.1 \times N \times 100}{W} \tag{1}$$

where V_{blank} is the HCl volume required for blank titration (ml), V_{sample} the HCl volume for sample titration (ml), W the weight of sample employed (g), and N the normality of the HCl solution. Thus,

$$DS = \frac{162 \times \%OSA}{21,000 - (209 \times \%OSA)} \tag{2}$$

where 162 is the molecular weight of the starch anhydroglucose unit (g/mol), 209 the molecular weight of the octenyl succinic group (g/mol), and 21,000 is 100 × molecular weight of the octenyl succinic group. All measurements were done in duplicate.

2.3.3. Preparation of the blends

Linear low density polyethylene/native cassava starch blends (100/0, 90/10, 80/20, 70/30, and 60/40), LLDPE/S blends, were prepared by melt-extrusion, after having dried the starch under vacuum at 40 °C for 48 h. The mixing was performed in an ATLAS

laboratory scale screw extruder (ATLAS Electric Devices Co., Chicago, USA) at 190 °C and with a screw speed of 60 rpm. LLDPE was processed once before preparing the blends and, then, each blend was extruded three times to improve homogeneity. Finally, the extruded filaments were cut into pellets.

LLDPE/S/S-g-OSA blends with the following compositions were prepared: 90/10/1, 80/20/2, 70/30/3, 60/40/4, where the amount of S-g-OSA was always 10 wt.% with respect to the disperse phase of native cassava starch. Before the extrusion of the blends, S-g-OSA and native starch were blended in a first step. Melt-extrusion of these blends was carried out under the conditions previously indicated for LLDPE/S blends.

2.3.4. Tensile tests

Compression-molded sheets were prepared from neat LLDPE and blends at 190 °C in a Carver Laboratory Press (Model C, Wisconsin, USA). Dumbell-type samples were cut from the sheets in order to carry out tensile tests in a JJ Tensile Testing Machine T-5003 (USA) according to the ASTM D638 standard procedure, at a deformation rate of 50 mm/min. Measurements were done in eight replicates.

2.3.5. Scanning electron microscopy (SEM)

To evaluate the dispersion in the LLDPE/S and LLDPE/S/OSA-g-S blend systems the different samples were analyzed with a PHILIPS SEM 505 Scanning Electron Microscope (Eindhoven, The Netherlands). The samples were fractured in liquid nitrogen and the fracture surfaces were gold plated. From the images, average sizes and size distributions of the dispersed phase were calculated. Number average diameters (D_n) of the particles were obtained using the following equation: (Arnal, Matos, Morales, Santana, & Müller, 1998; Chandrasekhar, 1943).

$$D_n = \frac{\sum n_i d_i}{\sum n_i} \qquad (3)$$

where n_i is the number of particles of diameter d_i.

2.3.6. Differential scanning calorimetry (DSC)

Samples for differential scanning calorimetry (DSC) were punched from the compression-molded sheets. Small disc samples were cut (5.0 ± 0.2 mg) and encapsulated in aluminum pans. A Perkin-Elmer DSC7 (Massachusetts, USA) was used to study the thermal behavior of all compositions under ultra high purity nitrogen atmosphere. The instrument was calibrated with indium and tin. "Standard" scans were performed by heating the samples at 150 °C for 3 min; then, they were cooled down to −10 °C at 20 °C/min and finally they were heated from −10 °C to 190 °C at 20 °C/min.

3. Results and discussion

3.1. Preparation and characterization of modified starches

The compatibility between LLDPE and starch needs to be improved, and a possible way of achieving this goal is the introduction of aliphatic chains within the starch by modifying it with octenyl succinic anhydride (OSA) (see Fig. 1). Due to the fact that the reactions reported in the literature have been carried out in starch/water slurries in conventional reactors with reaction times of hours (Bao et al., 2003; Bhosale & Singhal, 2006; Cadwell & Wuzburg, 1953; He et al., 2006; Thirathumthavorn & Charoenrein, 2006), we decided to perform the modification by means of microwave radiation; nevertheless, we also modified starch using the conventional method for comparison purposes. In both cases, an activation step is needed; this step takes place when NaOH is added to an aqueous starch slurry; under these conditions the reactive sites (hydroxyl groups) are transformed into alkoxide groups, which are more reactive. Based on previous works of Bhosale and Singhal (2006), Jyothi et al. (2005), and Chi et al. (2007) we used a pH of 8.5 ± 0.2; lower values are not enough for the nucleophilic attack on the anhydride and higher values promote the hydrolysis of the modifying agent. Once the starch has been activated, the corresponding reagents may be added.

Fig. 2 shows the FTIR spectrum of native starch (S); the bands at 575, 765, and 862 cm^{-1} are due to the C–C stretching and C–H bending vibrations of the glucosidic ring. In the fingerprint region between 900 and 1500 cm^{-1} the bands located at 930, 1014, 1082, and 1159 cm^{-1} correspond to –C–O–C– bonds in the anhydroglucose unit (Fang, Fowler, Sayers, & Williams, 2004). The band at 1648 cm^{-1} originates from tightly bound water present in starch (Hatakeyama & Hatakeyama, 2004; Kakurakova & Wilson, 2001), and those observed at 2923 and 3421 cm^{-1} are due to the characteristic vibrations of C–H and –OH bonds. In Fig. 2 the spectrum of conventionally modified S-g-OSA$_s$ may be also observed. It must be remarked that reactions A1 and A2 were performed in a 25% aqueous starch suspension at a pH of 8.5 during 24 h. In this spectrum two new signals may be clearly appreciated, one at 1571 cm^{-1} corresponding to the non-symmetric deformation of the carboxylate (–COO^{-}) group and the other one at 1724 cm^{-1} due to the ester carbonyl stretching (Chi et al., 2007). All these results confirm the reaction of OSA into the starch backbone. These signals, characteristic of the OSA modification, were also taken into account to corroborate the microwave-assisted chemical modification.

The FTIR spectra of the products resulting from reactions B1 and B2, performed under microwave radiation, are also presented in Fig. 2. In order to carry out these reactions we employed the method used by Jyothi et al. (2005) to modify starch with succinic anhydride; however, we performed a previous activation step, as described in the experimental part, to increase the reactivity of starch towards OSA. Again, the bands at 1571 and 1724 cm^{-1} confirm the chemical modification when the OSA content was varied from 10% to 20%. At this point, it should be remarked that we tried to perform the modification reactions by activating native starch in the solid state, directly in the microwave; nevertheless, the degree of substitution was very low and we decided to carry out the activation in a separate step.

Once the presence of the functional groups was corroborated, we determined the degree of substitution (DS) of the different products to study the influence of the modification method (conventional vs. microwave) and the effect of the relative percentage of OSA to starch. The degree of substitution is the average number of hydroxyl groups substituted per anhydroglucose unit (AGU).

Most of the reactions found in the literature allowed a maximum level of OSA of 3% according to FDA restrictions for preparing modified food starches (Bhosale & Singhal, 2006). Bhosale and Singhal (2006) studied the variation of the DS with the increase of OSA up to 3% (dry basis of starch) and obtained one of the highest DS reported in the literature for the conditions we also used to perform reaction A1; they obtained values of about 0.022, which varied slightly depending on the starch type. As may be observed in Table 1, which shows the DS results obtained after titration, we obtained a similar DS (0.024) under such conditions. It must be pointed out that He et al. (2006) investigated the effect of amylose content on DS, observing an increase of the DS by increasing the amylose content, but even with 39.6% of amylose they obtained a DS of just 0.030.

Since our product will be destined to be used as compatibilizer in polymer blends, we performed reactions using higher amounts of OSA. From Table 1, it can be observed, when comparing reactions A1 and A2, that the DS increases in about 30% when the
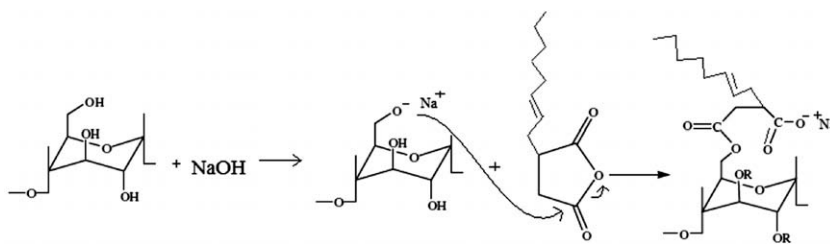
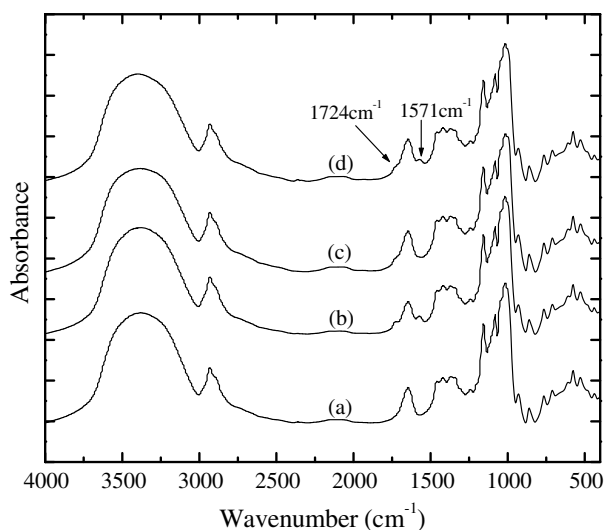**Fig. 1.** Schematic representation of the reaction that takes place between starch and OSA.

Fig. 2. FTIR spectra of (a) S, (b) S-g-OSA$_s$ (A1), (c) S-g-OSA$_{mw}$ (B1), and (d) S-g-OSA$_{mw}$ (B2).

Table 1
Degree of substitution (DS) obtained for the different products

Reaction	OSA content (% w/w)	Average DS
A1	3	0.024 ± 0.002
A2	20	0.032 ± 0.001
B1	10	0.032 ± 0.001
B2	20	0.045 ± 0.001

OSA concentration varied from 3% to 20%; this is due to a greater availability of OSA molecules in the vicinity of the immobile starch hydroxyl groups; however, it should be mentioned that such an increase is not so high as the increase observed when the OSA concentration changes from 1% to 3% (Bhosale & Singhal, 2006).

With respect to the reactions carried out under microwave radiation, it is observed that when the OSA concentration increased from 10% to 20%, the DS increased in about 30%; a DS of 0.045 was obtained; this is one of the highest values that has been obtained with OSA when compared with other works published in the literature in starches with similar amylose contents. The increase of DS when adding a higher amount of OSA is due, as was previously discussed, to a higher probability of OSA to reach the alkoxide groups. In Table 1 it may be analyzed the influence of the preparation method when the OSA concentration was 20%; it is clear that the use of microwave radiation leads to an increase in the efficiency of the reaction of about 30% since the DS varies from 0.032 to 0.045. Furthermore, such higher DS is obtained after 7 min of reaction compared with reaction times of hours needed using the conventional method. This is the result from the almost instantaneous and homogeneous "in core" heating of the reagents under microwave radiation (Hayes, 2002; Jyothi et al., 2005).

S-g-OSA has been reported to be an effective emulsifier due to its dual functional hydrophilic and hydrophobic groups. A simple experiment that demonstrates how the introduction of the octenyl chain changes the interfacial properties of modified starch consisted in adding the same amount of S and S-g-OSA into a vial containing distilled water. It could be observed that native starch, due to its higher affinity for a polar solvent, is easily dispersed in water. On the other hand, S-g-OSA forms aggregates on the surface of the liquid and could not be dispersed in water even by vigorous stirring, a fact that indicates its hydrophobic character.

Once the modified starches were characterized, we proceeded with the preparation of LLDPE/Starch blends using S-g-OSA as compatibilizer.

3.2. LLDPE/starch blends

3.2.1. Thermal and morphological behavior

Table 2 shows the relevant transition temperatures and enthalpies extracted from the cooling runs performed in the DSC after erasing thermal history and the subsequent heating runs for LLDPE/S and LLDPE/S/S-g-OSA$_{mw}$ blends (DS = 0.045). The enthalpies have been normalized by the weight fraction of LLDPE in the blends. The thermal properties of neat LLDPE and the LLDPE component in the blends are very similar considering the experimental errors involved in the measurements. Therefore, it appears that starch is completely immiscible with LLDPE as expected and previously reported in the literature (Evangelista et al., 1991; Kim, 2003; Nakamura et al., 2005; Pedroso & Rosa, 2005; Willett, 1994), and even after the addition of S-g-OSA$_{mw}$ no significant changes on the LLDPE matrix from the calorimetric point of view are produced. The invariance of the crystallization temperatures (T_c) indicates that the cassava starch is not a nucleating agent for LLDPE.

Scanning electron microscopy (SEM) demonstrated that the LLDPE/S blends exhibit a classical two phase morphology, as

Table 2
Thermal transitions obtained for the LLDPE component in LLDPE/S and LLDPE/S/S-g-OSA$_{mw}$ blends obtained from DSC scans (20 °C/min).[a]

Sample	T_{c_o}	T_{c_p}	ΔH_c	T_{m_o}	T_{m_p}	ΔH_m	X_c
LLDPE/S	(°C)	(°C)	(J/g)	(°C)	(°C)	(J/g)	(%)
100/0	107.6	104.2	127	118.3	124.3	139	48
90/10	107.5	104.8	130	117.8	123.6	144	49
80/20	107.4	104.9	128	117.8	123.8	137	47
70/30	107.0	104.5	131	117.5	122.8	132	45
60/40	107.6	105.7	122	118.5	122.9	138	47
LLDPE/S/S-g-OSA$_{mw}$							
100/0/0	107.6	104.2	127	118.3	124.3	139	48
90/10/10	107.3	104.3	106	117.4	123.2	125	43
80/20/10	107.3	104.6	109	117.1	122.9	129	44
70/30/10	107.6	104.8	107	117.7	122.6	123	42
60/40/10	107.2	104.5	107	118.0	123.0	124	42

[a] T_{c_o}, T_{c_p}: onset and peak crystallization temperatures. T_{m_o}, T_{m_p}: onset and peak melting temperatures. ΔH_c, ΔH_m: latent heat of crystallization and melting. X_c: crystallinity percentage.

shown in Fig. 3, typical of immiscible blends. The starch dispersed droplets do not show any signs of adhesion to the LLDPE matrix as indicated by the clean holes left on the fracture surfaces explored or by the polished surface of the starch droplets. Nevertheless, the quality of the dispersion obtained is good considering the immiscibility of the components.

For comparison purposes, the effect of two compatibilizing agents on the morphology of the blends was studied by SEM. The first one was S-g-OSA$_s$ prepared in aqueous media with a DS of 0.024 and the second, another S-g-OSA$_{mw}$ but prepared by the microwave-assisted method with a DS of 0.045. The presence of an aliphatic chain in the chemical structure of the compatibilizing agent is expected to improve the dispersion and/or the adhesion in between the phases, since it should diffuse to the interphase. The higher the DS, the higher is the probability of compatibilization. Fig. 3 shows SEM micrographs for compatibilized 80/20 blends. Fig. 3c shows the morphology of the 80/20/2 LLDPE/S/S-g-OSA$_s$ (DS = 0.024) blend where the two phase morphology, even though appears very similar to that of the uncompatibilized blend, exhibits some starch particles that were broken after the cryogenic fracture (see, for example, the white circle). On the other hand, upon increasing the degree of substitution, some other signs of morphological change were apparent and are highlighted with white circles in Fig. 3d, which corresponds to a 80/20/2 LLDPE/S/S-g-OSA$_{mw}$ (DS = 0.045) blend; some irregularities on the surface of the starch dispersed phase can be observed, as well as some plastic deformation at the interfaces may indicate enhanced interactions between the two phases. Similar results were obtained for all compositions.

The effect of the compatibilizer on the blend morphology is quantitatively assessed by determining the size distribution of starch particles. Fig. 4 shows the particle size distribution for the 80/20 blends with and without compatibilizer. The highest frequency or the most frequently encountered particle size for all blends is in the range 8–10 μm. Nevertheless, it is only in the blend that contains S-g-OSA$_{mw}$ that a high frequency in the smallest particles of sizes 6–8 μm is obtained. This result is another evidences indicating that S-g-OSA$_{mw}$ is indeed acting as a compatibilizer for the LLDPE/S blend by reducing the particle size of the dispersed starch phase and may also prevent coalescence. Additionally, the largest particles within the distribution in the LLDPE/S blends, i.e., 18–20 μm, disappear for the compatibilized blends. The number average diameter, D_n, of the particles was reduced from ~13 to ~10 μm; i.e., 23%.

3.2.2. Tensile properties

Amorphous starch at low moisture contents displays a glass transition, T_g, at much larger values than room temperature; therefore, it behaves as a glassy polymer and it is not surprising that it acts as a rigid load (Jang, Huh, Jang, & Bae, 2001; Nakamura et al., 2005; Pedroso & Rosa, 2005; Walker et al., 2007; Willett, 1994) and causes an increase in the elastic modulus of the LLDPE matrix. Fig. 5 shows that the elastic modulus, E, increased as the amount of starch in the blends is higher; however, the addition of a compatibilizer caused no significant effects on this property. On the other hand, Fig. 6 shows the impact of adding starch on the yield properties of LLDPE. The tensile strength clearly decreases as the
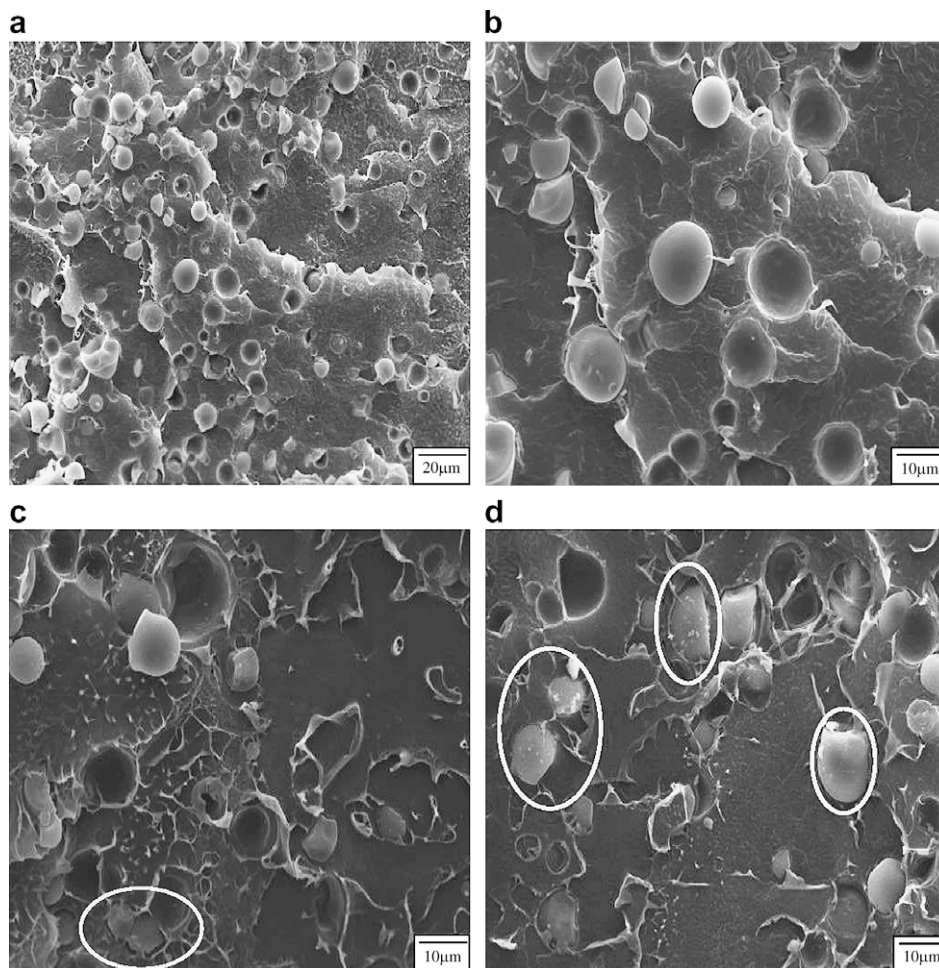

Fig. 3. SEM micrographs of the cryogenically fractured surface of (a and b) 80/20 LLDPE/S blend, (c) 80/20/2 LLDPE/S/S-g-OSA$_s$ (DS = 0.024) blend, and (d) 80/20/2 LLDPE/S/S-g-OSA$_{mw}$ (DS = 0.045) blend.
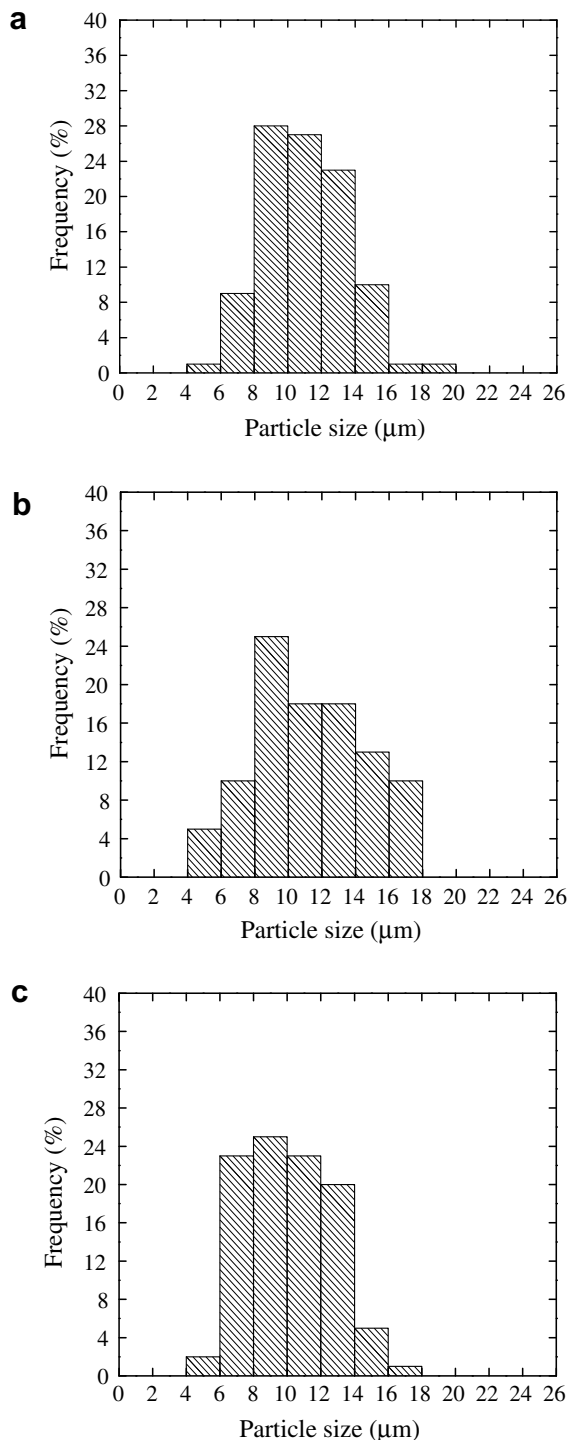
a

b

c

Fig. 4. Particle size distribution for the 80/20 blends (a) without compatibilizer and with compatibilizers (b) S-g-OSA$_s$ and (c) S-g-OSA$_{mw}$.
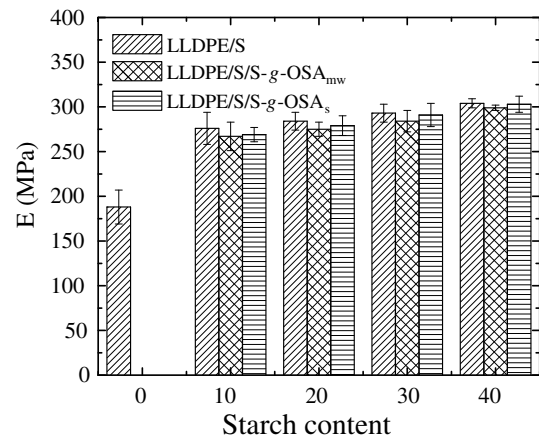

Fig. 5. Young modulus of the LLDPE/S and LLDPE/S/S-g-OSA blends.

LLDPE. A similar effect was obtained on the strain to yield. There is no doubt that the S-g-OSA$_{mw}$ has a significant impact on the yield properties of the blends, especially in those with lower starch contents (i.e., 10% and 20%); it must be remembered that the DS value for this compatibilizer is 0.045. Since with S-g-OSA$_s$ no effect was obtained, the most likely explanation is that in that case the DS (which was only 0.024) was not enough to induce compatibilization.

The ultimate properties, or stress and elongation at break are presented in Fig. 7. In this case, starch addition causes a decrease in both parameters and the compatibilization does not improve the properties except in the case of the 90/10 blend where a slight improvement was obtained as compared to the uncompatibilized blend when the S-g-OSA$_{mw}$ was employed. The ultimate properties in the case of ductile materials are not as critical as the yield properties, since the application of a ductile material will be limited by the appearance of any sign of plastic deformation. Also, the rupture properties largely depend on any defects that the specimens may have as a consequence of processing or preparation (such as die punching).

Finally, the toughness of the materials in tension was evaluated by determining the area under the experimental engineering stress–strain curves. Fig. 8 shows that the blends compatibilized with S-g-OSA$_{mw}$ (with a DS = 0.045) exhibit toughness values under tension that are 15–20% larger than uncompatibilized blends. One can speculate that such improvement in toughness under tension could also be reflected in a higher impact resistance, a possibility that would need corroboration and that will be subject of forthcoming studies.

4. Conclusions

Cassava starch was successfully modified with octenyl succinic anhydride by means of a microwave-assisted reaction in solid state, after having activated native starch under alkaline conditions. Degrees of substitution as high as 0.045 may be obtained after only 7 min of microwave irradiation. In comparison to native cassava starch, the modified starches exhibited less hydrophilicity, property that allowed their use as compatibilizers in LLDPE/starch blends. Its addition in the blends led to enhanced interactions between the two phases and to an increase of the blend toughness when compared with the blend without compatibilizer.

The LLDPE/starch blends exhibited an increase in Young modulus due to the rigid character of the filler, and a reduction in tensile strength with increasing starch content attributed to a poor interfacial adhesion. However, the mechanical properties were signifi-
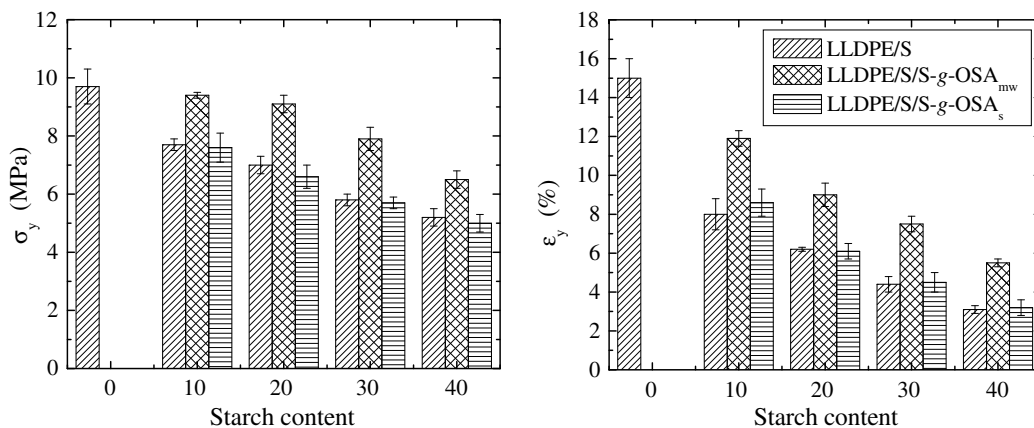
content of starch increases reflecting the immiscibility and lack of adhesion between the LLDPE and starch. However, a very clear improvement in the yield stress (in between 10% and 15% improvement, depending on composition and always beyond the uncertainties indicated by the error bars) was observed when S-g-OSA$_{mw}$ (i.e., the compatibilizer with the highest DS) was added to the blend. In fact, the improvement is so good that in the cases of the 90/10/1 and 80/20/2 blends compatibilized with S-g-OSA$_{mw}$ the stress at yield values are basically the same as that of neat

Fig. 6. Yield stress and strain as a function of starch content for the indicated LLDPE/S and LLDPE/S/S-*g*-OSA blends.
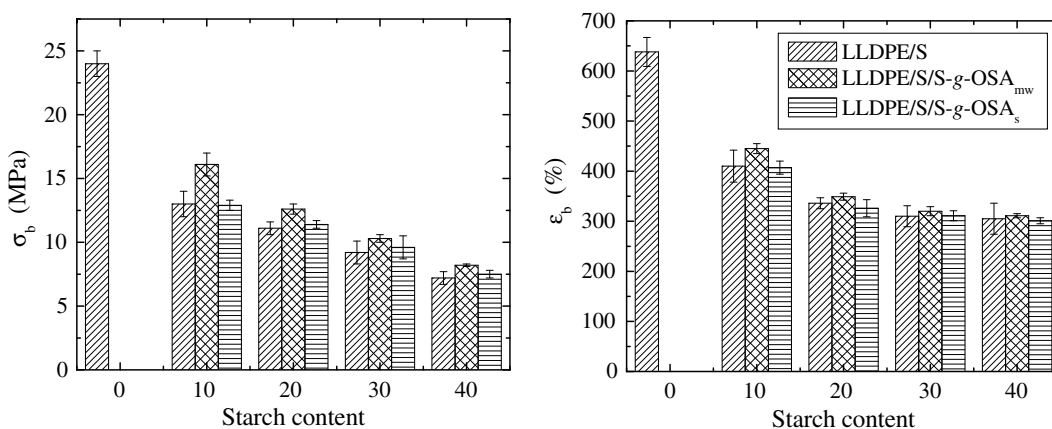

Fig. 7. Stress and elongation at break as a function of starch content for the indicated LLDPE/S and LLDPE/S/S-*g*-OSA blends.
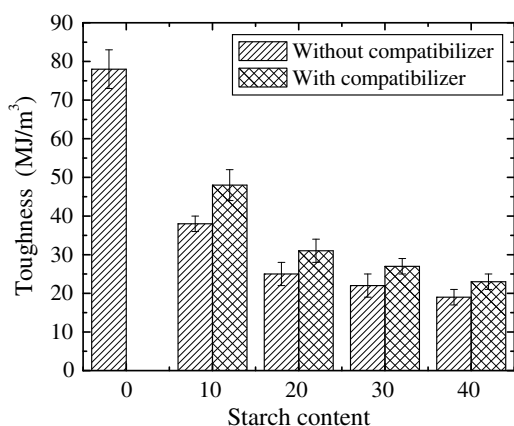

Fig. 8. Toughness under tension as a function of starch content for the indicated LLDPE/S and LLDPE/S/S-*g*-OSA blends.

cantly improved by adding 10% of S-*g*-OSA with DS = 0.045. In fact, the improvement was so good that in the 90/10/1 and 80/20/2 blends compatibilized with S-*g*-OSA$_{mw}$ the stress at yield is basically the same as that of neat LLDPE.

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