

# Properties of Fatty-Acid Esters of Starch and Their Blends with LDPE

S. THIEBAUD,<sup>1</sup> J. ABURTO,<sup>1</sup> I. ALRIC,<sup>1</sup> E. BORREDON,<sup>1</sup> D. BIKIARIS,<sup>2</sup> J. PRINOS,<sup>2</sup> C. PANAYIOTOU<sup>2</sup>

<sup>1</sup> Ecole Nationale Supérieure de Chimie, Laboratoire de Chimie Agro-Industrielle, 118 Route de Narbonne, 31077 Toulouse-Cedex, France

<sup>2</sup> Department of Chemical Engineering, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

Received 1 November 1996; accepted 22 November 1996

**ABSTRACT:** In the present study, starch octanoates OCST1.8 and OCST2.7 with degrees of substitution (d.s.) of 1.8 and 2.7, respectively, and dodecanoate DODST2.7 (d.s. = 2.7), were prepared by esterification of native starch with fatty acid chlorides. Our analyses, including elemental analysis, FTIR, contact angle, DSC, and TGA measurements confirmed the esterification reaction of starch and the degree of substitution. The ester group was found to act like an internal plasticizer, with an increase in the number and the size of fatty acyl chains grafted onto starch. These starch esters were mixed with low density polyethylene (LDPE) at various proportions in a Haake Rheomixer. Water and moisture absorption, thermal and mechanical properties, and biodegradation were investigated as a function of blend composition. The DODST2.7/LDPE blends showed, in general, better thermal stability and higher elongation, but lower tensile strength and water absorption, than did corresponding OCST/LDPE blends. The addition of starch esters to LDPE led to a very slow rate of biodegradation of these blends. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 705–721, 1997

**Key words:** modified starch; LDPE; blends; biodegradation

## INTRODUCTION

Starch is an abundant, inexpensive, renewable, and fully biodegradable natural raw material which has generated a renewed interest in its use as a component in plastic formulations, as testified by an impressive amount of literature in recent years. Indeed, the total or partial substitution of synthetic plastics with materials from agroresources, especially unmodified starch, is attractive from the standpoint not only of being a cheap filler, but also of providing biodegradation properties to the final product. Degradable plas-

tics are very important as part of the solution to the waste management problem. Municipal solid waste consists of ~7.2% by weight or 18% by volume of plastics. The greatest part of this plastic waste derives from packaging formulations for which recycling is neither practical nor economical.

However, starch by itself is unsuitable for most uses as a plastic because of its poor physical properties (mechanical properties, dimensional stability). Some approaches to overcoming these problems include chemical modification, addition of plasticizers, or blending with other synthetic polymers.<sup>1</sup> In this last case, the hydrophilic character of starch leads to poor adhesion with the synthetic polymer. Thus, the addition of granular starch to polyolefins, such as polyethylene, leads to a reduction of the elongation and tensile strength.<sup>2</sup> On the contrary, a homogeneous blend of two compo-

Correspondence to: C. Panayiotou (cpanayio@mailhost.ccf.auth.gr).

Contract grant sponsor: Science and Technology National Council of Mexico (CONACYT).

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/040705-17

nents with small and well-distributed phase domains could improve the mechanical behavior.<sup>3</sup>

Therefore, in order to enhance the compatibility between two immiscible polymers, a reactive functional group can be introduced into synthetic polymers, being capable of hydrogen bonding with starch hydroxyls. For example, polyethylene copolymerized with acrylic acid,<sup>4–11</sup> vinyl alcohol,<sup>12,13</sup> C1-6 alkylacrylates, C1-6 alkyl methacrylates, vinyl acetate,<sup>14</sup> or mixed with oxidized polyethylene,<sup>15</sup> were used for compatibilization with starch. But the biodegradability of these materials may be uncertain or low.<sup>16,17</sup>

Another method to improve miscibility and adhesion of phases in starch–polyethylene blends is the chemical modification of the hydroxyl groups of starch with a hydrophobic compound. Recently, according to Swanson, Westhoff, and Doane,<sup>18</sup> the mechanical properties of the blends polyethylene–poly(ethylene-*co*-acrylic acid)–hydroxypropyl or acetyl derivatives of starch were improved when compared to those of pure (unmodified) starch. A process was proposed by Griffin<sup>19,20</sup> for making low density polyethylene blown films containing native or modified starches and autooxidants such as unsaturated fatty acids and their derivatives. Octenyl succinate starch metal ion complexes were combined with polyethylene to create a plastic which is biodegradable, retaining also satisfactory tensile strength, surface structure, texture, and moisture resistance.<sup>21,22</sup>

From a study of the properties of starch esters (butyrate, valerate, hexanoate), Sagar and Merrill<sup>23</sup> showed that the ester groups act like an internal plasticizer, with an increase in the size of fatty acid chain. The resulting starch esters behave like thermoplastic materials.

Following the proposition of Sagar and Merrill<sup>23</sup> we have decided to produce longer chains of starch esters (octanoate and dodecanoate) by chemical modification of the latter, and blend them with low density polyethylene (LDPE). Water absorption, mechanical, and thermal properties and interfacial adhesion are expected to be better compared to LDPE–starch blends. The biodegradability, however, of these blends is expected to be drastically reduced. In a preliminary study<sup>24</sup> we presented some properties of LDPE–OCST 2.7 (octanoated starch with d.s. = 2.7), but no results of biodegradability were reported. In the present study we extended this work by producing octanoated starch with d.s. = 1.8 (OCST 1.8), in order to examine the effect of the degree of substitution on the properties of the LDPE/

OCST blends. We have also prepared dodecanoated starch with a d.s. = 2.7 (DODST 2.7) in order to study the effect of the chain length on the above properties.

## EXPERIMENTAL

### Materials

The potato starch used in the acylation was provided by the INRA of Nantes, France. The potato starch contained 19% amylose and 81% amylopectin on a dry basis and had a moisture content of 14% by weight. The amount of proteins and lipids in this starch was insignificant. The octanoyl and dodecanoyl chloride (Aldrich) were reagent grade; the pyridine and absolute ethanol were SDS anhydrous analytical grades. LDPE was an industrial grade from Borealis.

### Synthesis of Starch Esters

The esterification of starch was carried out by the modified method of Mullen and Pacsu.<sup>25</sup> This method was preferred to others reported in the literature, because it requires only a minimal amount of organic solvent in the synthesis reaction. In addition, the organic solvent used minimized the starch degradation and acted as a catalyst. The general procedure of esterification was as follows: the starch was dried overnight in an oven at 105°C to remove moisture (final moisture <2%). The dried starch (2.5 g) was then placed in a two-necked flask equipped with a mechanical stirrer and a condenser. Fifteen mL of pyridine and the appropriate amount of octanoyl chloride (0.07 mol for OCST 1.8, 0.14 mol for OCST 2.7) or of dodecanoyl chloride (0.28 mol) were added. The reaction was allowed to proceed for 3 h at 115°C. Upon completion of the reaction, the mixture was cooled and poured with vigorous stirring into a glass beaker containing 200 mL absolute ethanol to precipitate the esterified starch and to eliminate any color impurities. The product was washed twice with 200 mL ethanol. In the case of dodecanoated starch (DODST 2.7), hot ethanol was used to perform the purification. The excess of ethanol was removed by an air stream and the starch ester was dried at 50°C overnight and weighed. The OCST 1.8 was a white powder, while DODST 2.7 was a pale yellow amorphous solid. The weight of dried OCST 1.8 was 4.7 g (weight increase 88% at 78% yield) and dried DODST 2.7

was 10 g (weight increase: 232% and 100% yield). These starch esters, prepared by the above procedure, were characterized by using elemental analysis and IR spectroscopy.

### Contact Angle Measurement

The contact angle formed between a water droplet placed upon a material surface is a measure of the hydrophobicity of the material. Contact angle measurements of octanoated and dodecanoated starch were done in accordance with the modified method described by Thiebaud.<sup>26</sup> Octanoated and dodecanoated starch films were prepared by hot press molding at 100°C and 150 kg/cm<sup>2</sup> pressure for 5 min.

### Melt-Blending

Octanoated or dodecanoated starch was melt-blended with LDPE in a Haake–Buchler Rheomixer model 600, with roller blades and a mixing head with a volumetric capacity of 69 cm<sup>3</sup>. Prior to mixing the polymers were dried in a vacuum oven by heating at 80°C for 24 h. The components were physically premixed before being fed into the Rheomixer. Mixing was performed at 160°C for dodecanoated starch and 180°C for the octanoated starch with the lower degree of substitution (1.8). Mixing was conducted at 80 rpm for 15 min. Melt temperature and torque were recorded during the mixing period. A total of 8 samples were prepared containing 5, 10, 15, 20, 30, 40, 50, and 75 wt % starch ester, respectively. The blends, after preparation, were placed in tightly sealed vials to prevent any moisture absorption.

### FTIR Measurements

FTIR spectra were acquired in a Biorad FTS-45A FTIR spectrometer. For each spectrum 64 consecutive scans with 2 cm<sup>-1</sup> resolution were averaged. Samples were measured in the form of thin films ~70 μm thick, which were prepared by hot press molding.

### Thermal Analysis

DSC measurements of samples were performed in a Shimadzu DSC-50Q Fast Quenching Differential Scanning Calorimeter. Samples were placed in sealed aluminum cells, using a quantity of ~10 mg for each sample. The samples were initially heated with a heating rate of 20°C/min

up to 200°C in a nitrogen atmosphere and immediately quenched to remove any previous thermal history. The samples were subsequently rescanned with a heating rate of 20°C/min and from these thermograms the melting temperatures and heats of fusion were calculated. TGA measurements were performed in a Shimadzu TGA-50 Thermogravimetric Analyzer. Each sample was heated with a heating rate of 20°C/min in a nitrogen atmosphere up to 650°C. Prior to thermal analysis, the samples were dried in a vacuum oven at 80°C for 24 h.

### Water and Moisture Absorption

Water absorption was measured by using 3 × 8 cm film strips of 80 μm thickness according to the ASTM D570-81 method. Water absorption measurements were performed by soaking the samples in distilled water. At regular time intervals, each sample was removed from the water tank, dried by wiping with blotting paper, and subsequently weighed to determine water uptake. The samples were placed back in water after each measurement. The water absorption was calculated as the weight difference and is reported as percent increase of the initial weight.

For the moisture absorption the dried samples were placed for 30 days in an enclosure containing an aqueous solution of 33.2% sulfuric acid at 25°C in order to obtain a relative humidity of 70%.<sup>27</sup> The moisture absorption was calculated as the weight difference and is reported as percent increase of the initial weight.

### Mechanical Properties of Blends

Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed on an Instron mechanical tester, Model 1122, according to the ASTM D638 method. Measurements were done using a 5 mm/min crosshead speed. Prior to measurements, the samples were conditioned at 50 ± 5% relative humidity for 24 h by placing them in a closed chamber containing a saturated Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

### Biodegradation

The polymer blends in a form of thin films of 130 ± 2 μm thickness were exposed to activated

**Table I Elemental Analysis and Contact Angles of the Starch Esters**

Sample	C (%)	H (%)	O (%)	Molecular Formula	Contact Angle (°)
OCST1.8	62.86	9.36	27.78	C <sub>20.4</sub> H <sub>36.4</sub> O <sub>6.8</sub>	87
OCST2.7	65.8	9.9	24.3	C <sub>27.6</sub> H <sub>47.8</sub> O <sub>6.7</sub>	92
DODST2.7	71.35	11.15	17.5	C <sub>38.4</sub> H <sub>69.4</sub> O <sub>6.7</sub>	95

sludge in a wastewater treatment facility of a food company for 4 weeks. The test permitted us to determine the rate of aerobic biodegradability by measuring the weight loss and mechanical properties of the studied samples after 1, 2, 3, and 4 weeks of exposure to activated sludge. The temperature of the sludge was constant during the 4 weeks ( $25 \pm 1^\circ\text{C}$ ) and the pH  $\sim 7$ .

## RESULTS AND DISCUSSION

### Characterization of Starch Esters

The elemental analysis of starch esters gave the results shown in Table I. In the table are also shown, for comparison purposes, the results for the OCST 2.7 sample studied previously.<sup>24</sup>

The degree of substitution (d.s.) for a starch derivative is defined as moles of substituents of hydroxyl groups per D-glucopyranosyl structural unit of the starch polymer; with three hydroxyl groups per unit, the theoretical maximum d.s. is three. The results from the elemental analysis showed that three products of starch esters were synthesized (Table I): starch octanoate with a degree of substitution of 1.8 (OCST 1.8) and 2.7 (OCST 2.7), and starch dodecanoate with a degree of substitution of 2.7 (DODST 2.7). We will compare the properties of these esters alone or in blends with LDPE and with starch octanoate with a degree of substitution of 2.7 (OCST 2.7).<sup>24</sup>

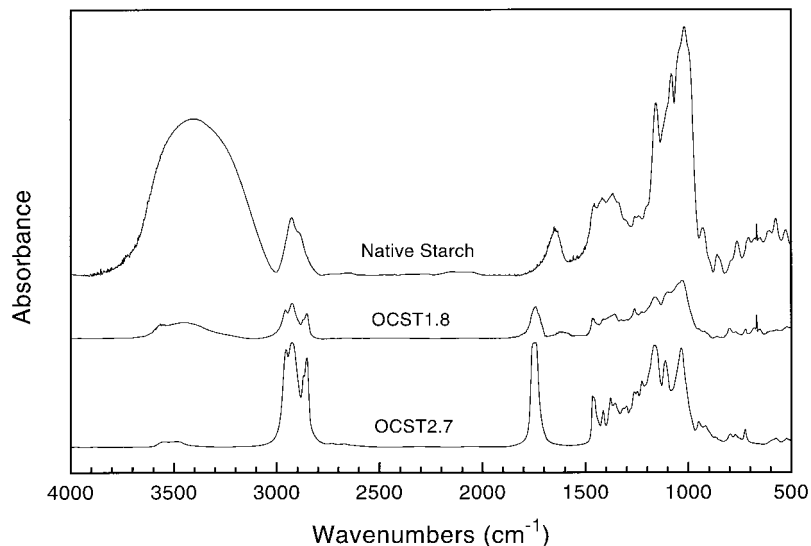
The contact angle increases with increasing carbon chain length and d.s. (Table I) as expected, because of the hydrophobic character of the grafted chains. The carbon chains conformation and remaining helicoidal structure of starch in the starch esters prevent the formation of hydrogen bonds between free OH groups of starch esters and molecules of water, resulting in higher hydrophobicity.

The FTIR spectra of native and esterified starches with octanoyl chloride (Fig. 1) confirm the esterification of starch, as the strong ester carbonyl band appears at  $1746\text{ cm}^{-1}$  in the final products.

In the native starch spectrum, the characteristic broad peak ( $958\text{--}1190\text{ cm}^{-1}$ ) is attributed to C—O bond stretching.<sup>28</sup> Another strong broad band due to hydroxyl bond stretching appears at  $3000\text{--}3600\text{ cm}^{-1}$ . This peak intensity decreases after esterification of starch with fatty acid chlorides. The higher the degree of substitution is, the greater is the decrease in the band intensity, as it can be observed for the octanoated starches with degrees of substitution 1.8 and 2.7. Likewise, the bands at  $1746\text{ cm}^{-1}$  and  $2800\text{--}2950\text{ cm}^{-1}$ , corresponding to the deformations of the ester carbonyl group and the methyl/methylene groups, respectively, increase with the degree of substitution of hydroxyl groups. The intensity of the band at  $2800\text{--}2950\text{ cm}^{-1}$  increases also with increasing carbon chain length of the starch esters. Thus its intensity is greater in the dodecanoated starch sample, compared to the octanoated one with the same degree of substitution (Fig. 2).

As far as the thermal behavior (DSC measurements) is concerned, DODST and OCST, with a degree of substitution of 2.7, are essentially amorphous materials, with measurable glass transition temperatures (Fig. 3). A melting point cannot be determined, as no melting peak appears in the thermograms. In fact, the chemical modification of hydroxyl groups, such as the esterification with fatty acid chlorides, leads to a loss of crystallinity of the initially crystalline starch. Indeed, native granular starch contains crystalline areas within the amylopectin (branched) component, whereas the linear amylose is largely amorphous. The  $T_g$  and  $T_m$  of dry native starch cannot be determined because they lie above the decomposition temperature.

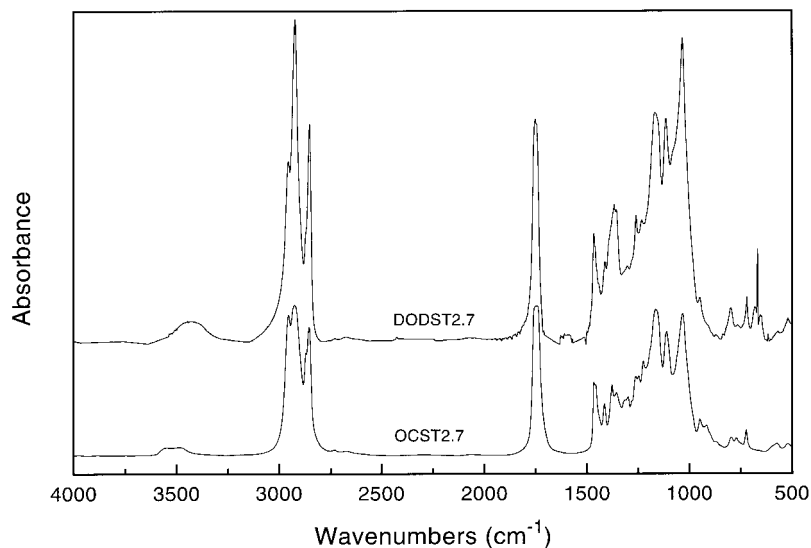
The  $T_g$  values of esterified starches decreased with increasing carbon chain length of the acid chloride used in esterification. Thus the DODST 2.7 has lower  $T_g$  than the OCST 2.7, being  $25^\circ\text{C}$  and  $40^\circ\text{C}$ , respectively. This is because the longer carbon chain acts as a more efficient internal plasticizer. This is in accordance with the literature, as the  $T_g$  of starch derivatives ranged from  $65^\circ\text{C}$  for starch butyrate to  $50^\circ\text{C}$  for starch hexanoate.<sup>23</sup>



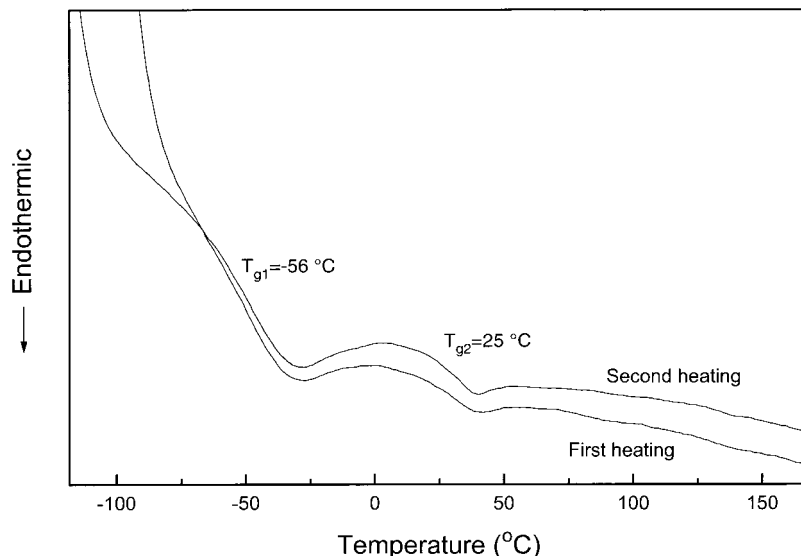
**Figure 1** FTIR spectra of native and octanoated starches.

Our samples (OCST 2.7 and DODST 2.7) showed lower  $T_g$ , as expected. However, caution must be exercised in this extrapolation, because the starch used in the previously mentioned study mainly contained amylose (70%), while our samples are mainly composed of amylopectin. Amylopectin is a branched polymer of a high molecular weight and has a higher  $T_g$  compared to amylose.<sup>28</sup> To a great extent, the same behavior must apply to the esterified derivatives as well. Thus, the  $T_g$  of starch octanoate and dodecanoate prepared from starch rich in amylose would be even lower than the ones determined in the present study.

We may notice that the DSC thermogram of DODST 2.7 displays two distinct glass transitions. The first one is observed at  $-56^\circ\text{C}$  and the second at  $25^\circ\text{C}$ . It is possible that the derivatized amylopectin and amylose molecules might be phase-separated to some extent. Given that the almost linear amylose molecules have an architecture very different from the amylopectin, there could well be a great difference in their glass transition temperatures.<sup>23</sup> It is well known that pure amylopectin has a higher  $T_g$  than the amylose, which is linear. The first glass transition ( $-56^\circ\text{C}$ ) may be attributed to the linear amylose macro-



**Figure 2** FTIR spectra of starch esters with a degree of substitution of 2.7.



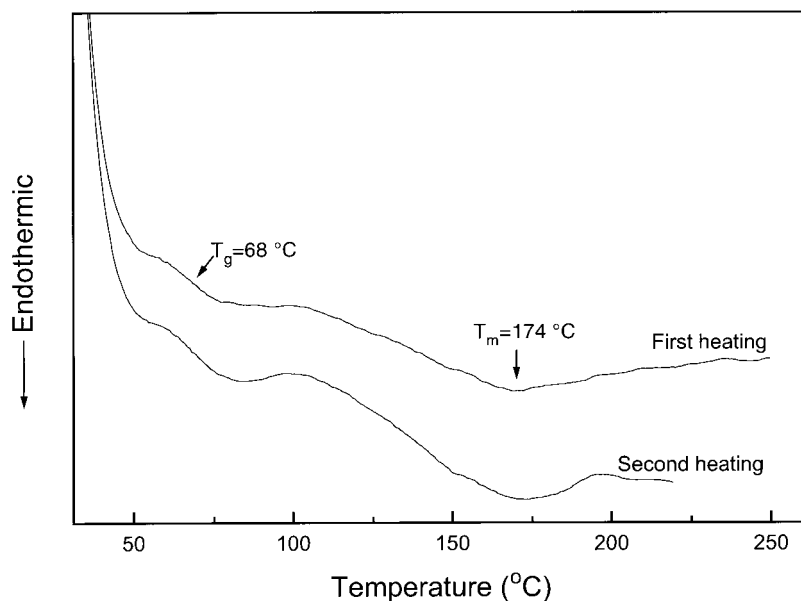
**Figure 3** DSC thermogram of starch dodecanoate (DODST2.7).

molecules, and the second to the amylopectin, which, as a branched (and more crystalline) polymer, has a higher  $T_g$ .<sup>29</sup>

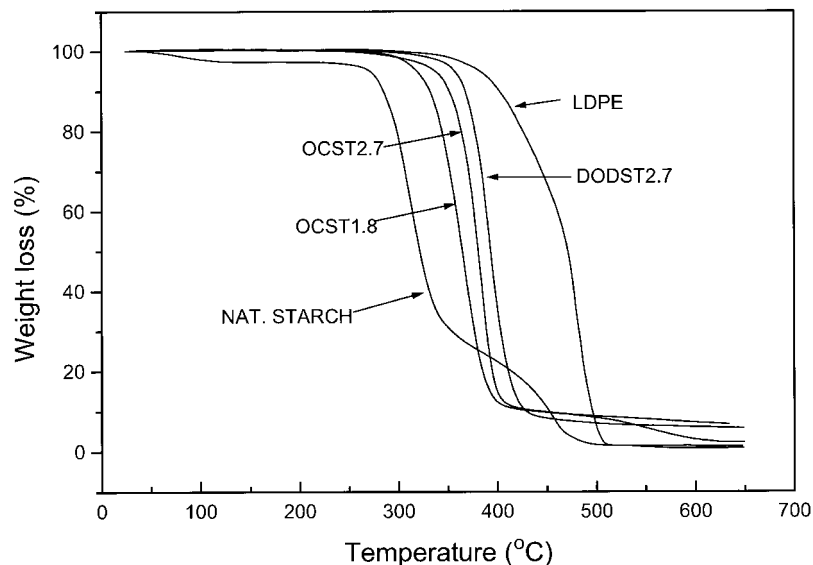
The DSC thermogram of OCST 1.8 (Fig. 4) exhibits two transition temperatures. The lower one (68°C) is attributed to a glass transition and the second, a very broad endothermic peak with maximum temperature 174°C, is attributed to melting. This may be due to the partial replacement of hydroxyl groups of starch by the bulkier groups, leading to a reduction in its hydrogen bonding

ability and making the formation of crystals more difficult. Also, the broadness of the melting endotherm can be explained by the formation of less perfect crystals. For octanoated starches with different degrees of substitution,  $T_g$  depends also on the degree of substitution. Thus, OCST 1.8 is a semicrystalline material and has a  $T_g$  of 68°C, whereas OCST 2.7 has a  $T_g$  of 40°C. This is because the starch becomes more amorphous as the degree of substitution increases.

The thermogravimetric analysis (Fig. 5) has



**Figure 4** DSC thermogram of starch octanoate (OCST1.8).



**Figure 5** TGA thermograms of starch, LDPE, and starch esters.

shown that the esterification of starch increases its thermal stability. Indeed, when starch granules were heated under nitrogen atmosphere, they were thermally stable up to 250°C. On the contrary, the thermal degradation of esterified starches took place only after 300°C. It must be noticed that unmodified starch contained ~2 wt % moisture even after heating under vacuum for 24 h. This is because natural starch is very hydrophilic and can absorb up to 14 wt % of moisture under normal room conditions and considerably more when the relative humidity approaches 100%. The greater thermal stability of starch esters compared to neat starch is probably due to the low content of hydroxyl groups in the former. A previous study<sup>30</sup> has shown that water is the main product of decomposition at temperatures < 300°C formed by intermolecular or intramolecular condensation of starch hydroxyls. Thus, the higher degree of substitution has a positive effect on the thermal stability of the esterified product (compare OCST 1.8 with OCST 2.7). A beneficial influence of increasing carbon chain length of the ester on thermal stability was also observed. But, in all cases, the onset of degradation still occurred at lower temperatures than that of LDPE.

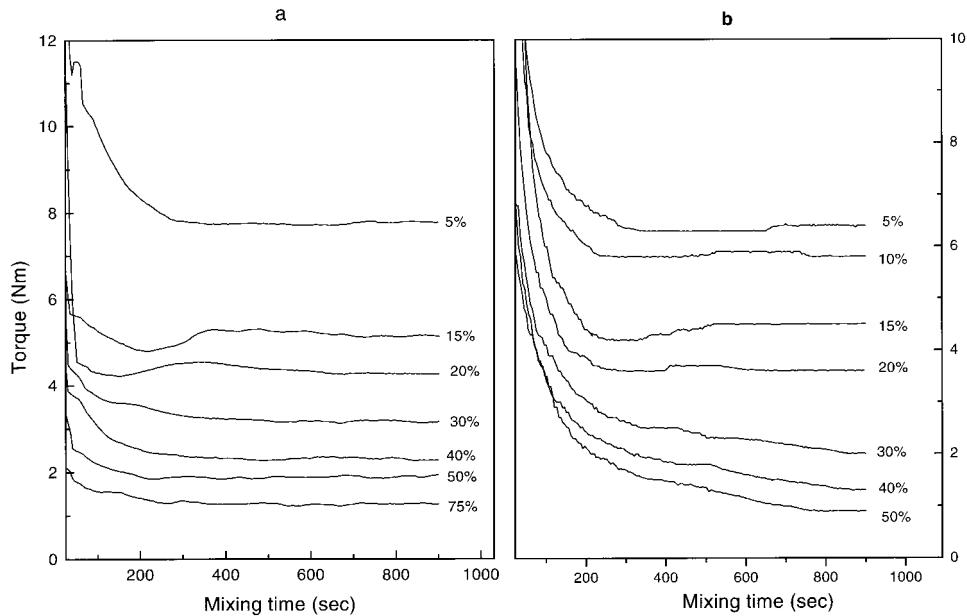
## Characterization of LDPE/Starch Ester Blends

### Torque and Melt Temperature Measurements

The torque measurements for LDPE/DODST 2.7 and LDPE/OCST 1.8 blends during mixing at dif-

ferent temperatures are presented in Figure 6. The torque was stabilized after ~10 min of mixing, suggesting that good mixing has occurred within this time period. The final torque decreased with increasing starch ester content in the blends. This phenomenon can be explained by the lower melt viscosity of esterified starch compared to that of LDPE. These changes in the behavior of the ester melts, especially their viscosities, are mainly due to the internal plasticization provided by these ester groups, as well as the changes in the conformation of the starch molecules caused by these bulky side groups. Indeed, the melt viscosity of esterified starch decreases with increasing molecular weight of the ester group.<sup>23</sup>

In the above measurements, the melt temperature was defined as the final temperature of the melt in the rheomixer after stabilization. This stabilization was achieved after ~10 min of mixing (Fig. 7). As can be observed, the melt temperature can reach 10–12°C above the temperature setpoint of the rheomixer (160°C for DODST 2.7/LDPE and 180°C for OCST 1.8/LDPE). This increase is the result of friction created during mixing which generates heat. In both cases, a decrease in melt temperature was achieved with increasing starch ester content. This is also due to the lower melt viscosity of esterified starches compared to that of LDPE. Comparable results for the torque and the melt temperature were obtained for LDPE/OCST 2.7 blends in our previous study.<sup>24</sup>

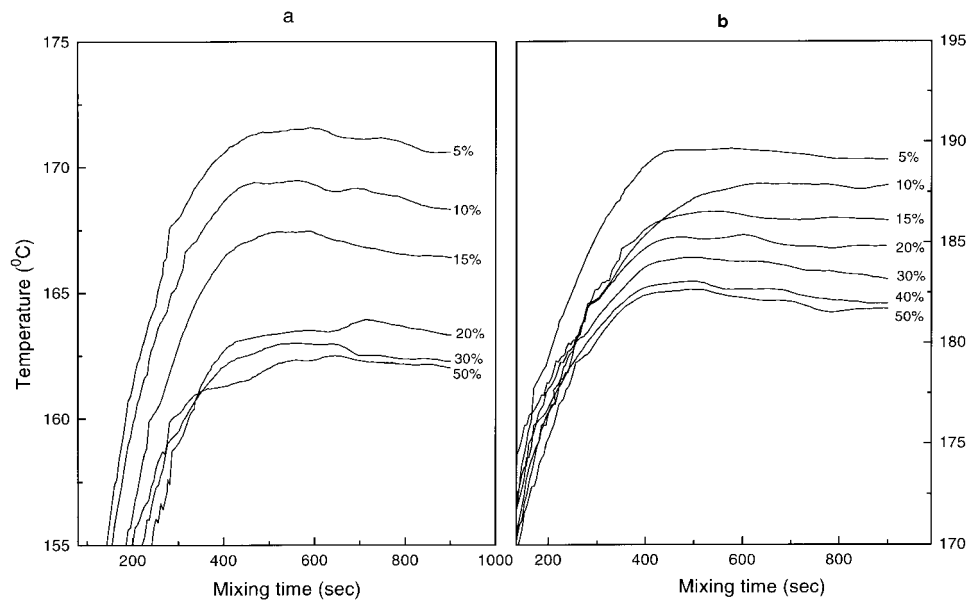


**Figure 6** Torque diagrams of (a) LDPE/DODST2.7 and (b) LDPE/OCST1.8 blends for various starch ester contents.

### Thermal Analysis of the Blends

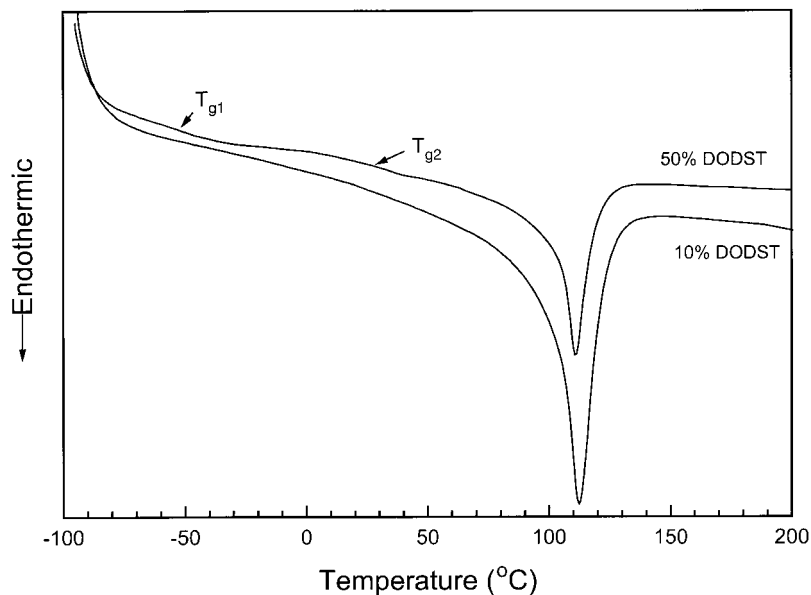
**DSC Measurements.** The DSC thermograms of LDPE/starch esters blends presented no significant differences compared to those of pure components. In the OCST blends a clear melting peak

of LDPE can be observed as well as in starch-rich blends (with >30 wt % of OCST), where a very weak endothermic peak appears with a maximum near 173°C. This is attributed to the melting of OCST which, even after the blend preparation, still remains semicrystalline. The same was observed in blends with DODST. In the



**Figure 7** Melt temperatures diagrams of (a) LDPE/DODST2.7 and (b) LDPE/OCST1.8 blends for various starch ester contents.





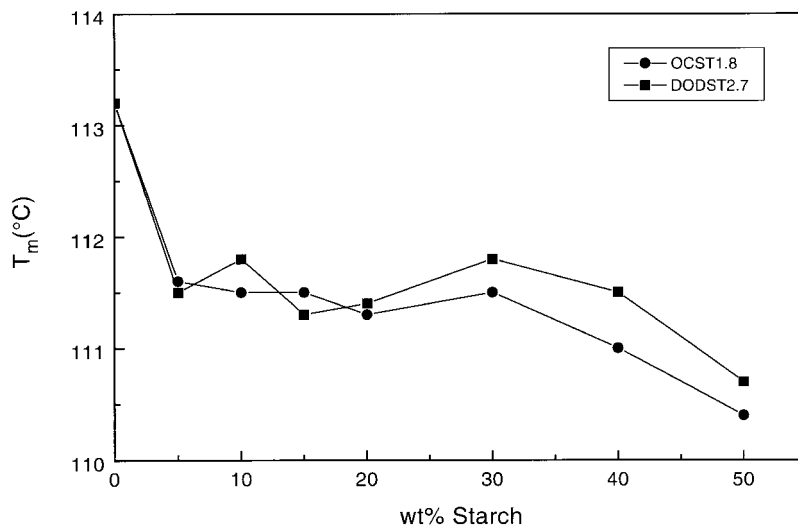
**Figure 8** DSC thermograms of DODST/LDPE blends for various starch ester contents.

blends with >30 wt % of DODST, besides the LDPE melting peak, the two glass transitions of DODST were also detected, as can be seen in Figure 8, where the blends with 10 and 50 wt % of DODST are compared. In the blend with 10 wt % of DODST only the melting of the LDPE was detected, because of the very low starch content.

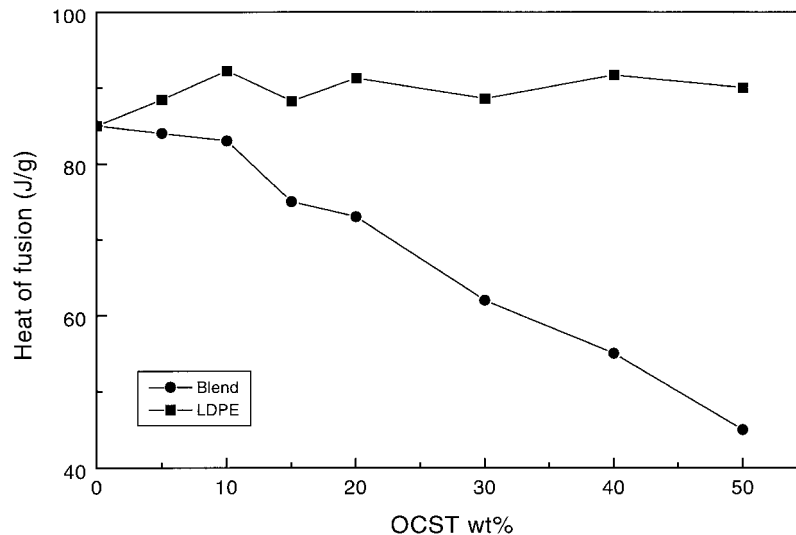
The melting points of LDPE were determined in all blends and are presented in Figure 9 as a

function of starch ester content. As can be seen, only a small decrease of the melting temperatures of the LDPE in blends, compared to that of pure LDPE, is observed. If blends are compared, there is only a small difference in melting point for blends between 10 and 50 wt % starch content, which is well within experimental error.

For polymer blends containing a crystallizable polymer, the Flory–Huggins interaction parameter,  $\chi_{12}$ , of the two polymers can be determined



**Figure 9** Melting point versus starch ester content in LDPE/DODST2.7 and LDPE/OCST1.8 blends (determined from DSC scans).



**Figure 10** Heat of fusion of LDPE/OCST1.8 blends and heat of fusion of LDPE in these blends.

from melting point depression data using the well known Wang–Nishi formula:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_f^0 V_1} \chi_{12}(1 - \phi_2)^2$$

where  $T_m$  and  $T_m^0$  are the melting points of the crystalline polymer in the blend and in the pure state, respectively,  $V_2$  is the molar volume of the repeat unit of the crystallizable component,  $\Delta H_f^0$  is its heat of melting, and  $\phi_2$  is the volume fraction of the crystallizable component. For miscible blends,  $\chi_{12}$  is expected to have a negative value, that is  $T_m < T_m^0$  (melting point depression). From Figure 9 it can be seen that there is only a small depression in  $T_m$ , but no apparent trend is observed as a function of composition. This fact suggests that the interaction parameter between the two polymers has a near-zero negative value.

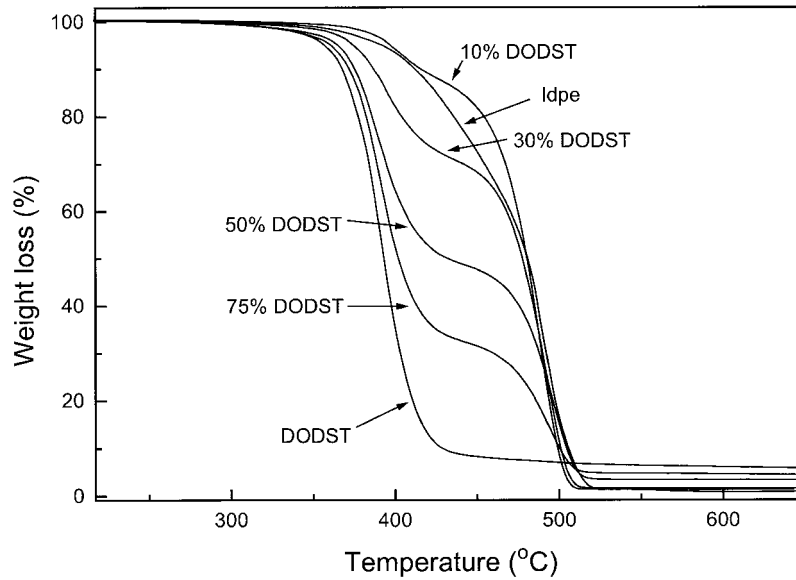
The same conclusions were drawn from the fusion heats data of the melting peaks (Fig. 10). There is an expected decrease in heat of fusion as the amount of LDPE decreases with increasing starch content. But, when the heats of fusion are corrected, taking into account the LDPE content in the blends, it is evident that there are no significant changes in the crystallinity of LDPE, as the heat of fusion lies between 85 and 87 J/g. It can be concluded that LDPE is hardly miscible with starch esters. Interactions between these two polymers are rather weak in nature.

**TGA Measurements.** The blends of LDPE with esterified starches showed two decomposition stages, as presented in Figures 11 and 12, for the blends with DODST and OCST, respectively. The first one (300–400°C) is due to starch decomposition, as it starts and finishes at the same temperatures as the pure esterified starches. The second, appearing at higher temperatures, is due to LDPE decomposition. Since the two steps are well separated, it is possible to determine the starch content of the blends from the weight loss of the first stage. However, this method is applicable only for relatively low starch contents.<sup>31</sup>

From these thermograms it can be seen that the blends with 10 wt % of esterified starch have the highest stability and it seems that the decomposition of LDPE is shifted to slightly higher temperatures than pure LDPE.

### Mechanical Properties

Tensile strength and elongation at break values were determined from stress–strain curves of each sample of LDPE-esterified starches and neat components. The pure esterified starches OCST and DODST with the same degree of substitution, 2.7, showed a weak ultimate tensile strength value of 0.61 and 0.65 MPa, respectively. But the elongation at break of the latter is much higher, namely, 1500% compared with the OCST, which has only a 380% elongation. The rather poor tensile strength and high elongation at break for starch esters is in accordance with the behavior

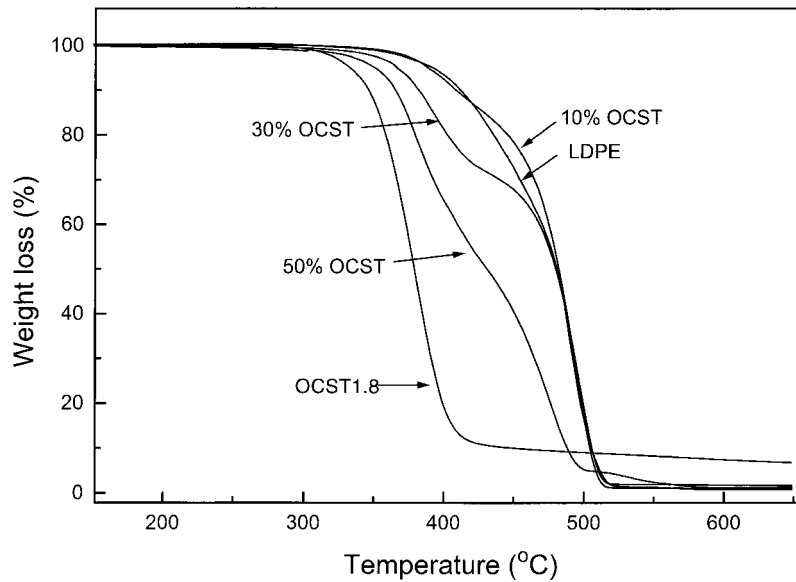


**Figure 11** TGA thermograms of LDPE/DODST2.7 blends for various starch ester contents.

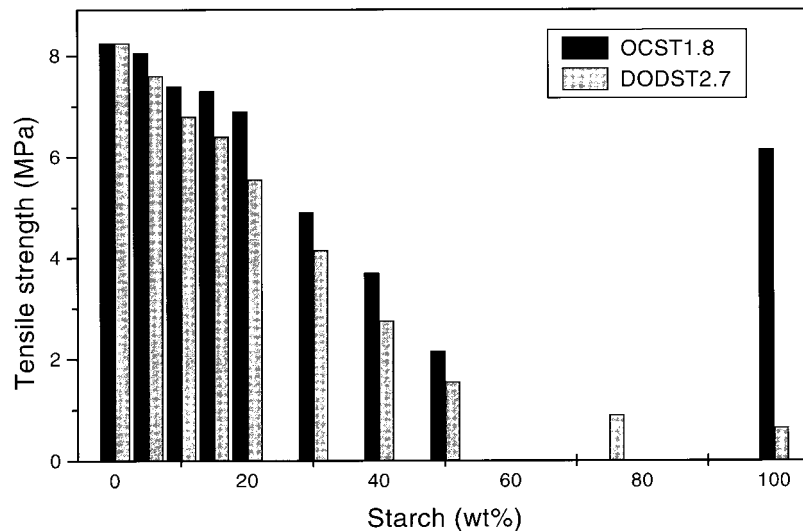
observed for other starch esters previously studied.<sup>23</sup> This can be attributed to the internal plasticization provided by the fatty ester groups, and the higher elongation of DODST is further evidence that the dodecanoic ester acts as a better plasticizer than the octanoic one.

However, OCST with a degree of substitution

of 1.8 behaved differently from the samples with a higher degree of substitution of 2.7.<sup>24</sup> Its tensile strength and elongation at break values were found to be 6.15 MPa and 11%, respectively. Thus, it behaves more like a brittle material, and these values are closer to the unmodified starch which, as mentioned previously, has a tensile strength



**Figure 12** TGA thermograms of LDPE/OCST1.8 blends for various starch ester contents.

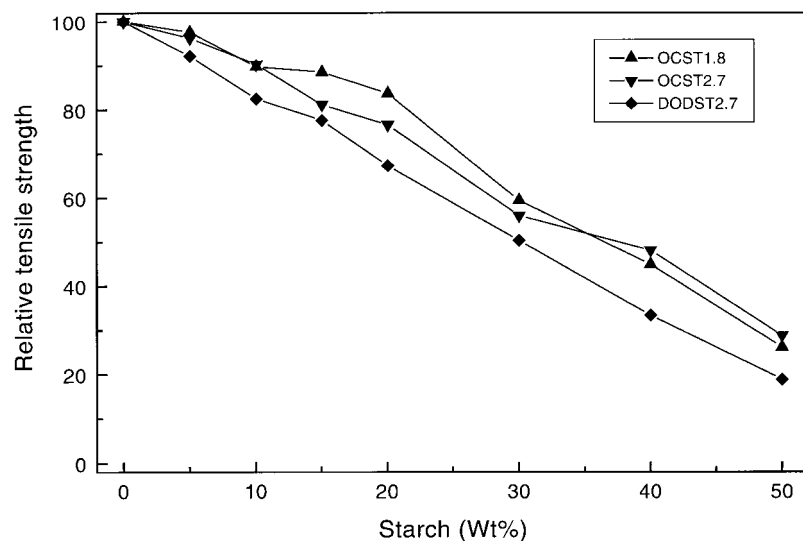


**Figure 13** Tensile strength at break of LDPE/DODST2.7 and LDPE/OCST1.8 blends.

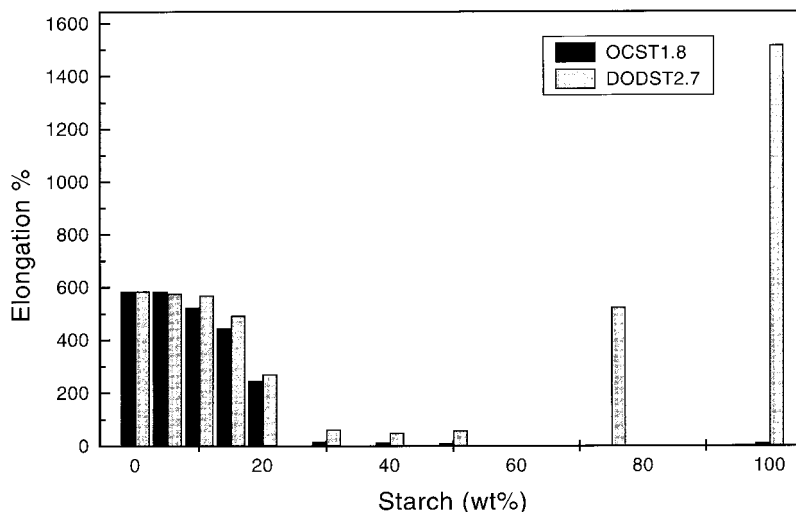
of 30 MPa and an elongation at break of 4%.<sup>32</sup> Comparing OCST esters with different degrees of substitution, it can be seen that tensile strength decreases and the elongation at break increases with an increasing degree of substitution. This is because starch with higher content of fatty ester groups becomes more plasticized and also loses its crystallinity.

In Figures 13 and 14 the tensile strength at break and the relative tensile strength values of LDPE–starch ester blends are presented. As observed, the tensile strength decreases with in-

creasing starch ester content in the blends. For blends with DODST, the decrease is monotonic, but for blends with OCST a minimum is observed. These blends also have better tensile strength than blends with DODST of the same starch content (Fig. 13). This behavior probably appears because OCST with degree of substitution 1.8 has a higher tensile strength than DODST. LDPE/OCST1.8 blends have slightly better tensile strength properties compared to the LDPE/OCST2.7, as can be seen in Figure 14. For all blends, the tensile strength is satisfactory up to



**Figure 14** Relative tensile strength at break of LDPE/DODST2.7, LDPE/OCST2.7, and LDPE/OCST1.8 blends.



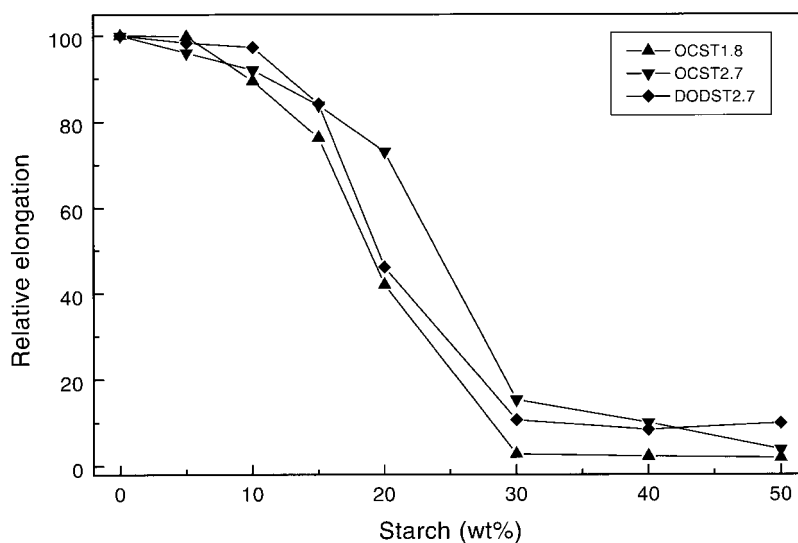
**Figure 15** Elongation at break of LDPE/DODST2.7 and LDPE/OCST1.8 blends.

15 wt % starch content and for OCST blends with up to 20 wt % starch content, where they still retain 80% of pure LDPE tensile strength. At higher ester starch contents the decrease is larger, especially in blends with 50 wt % of starch.

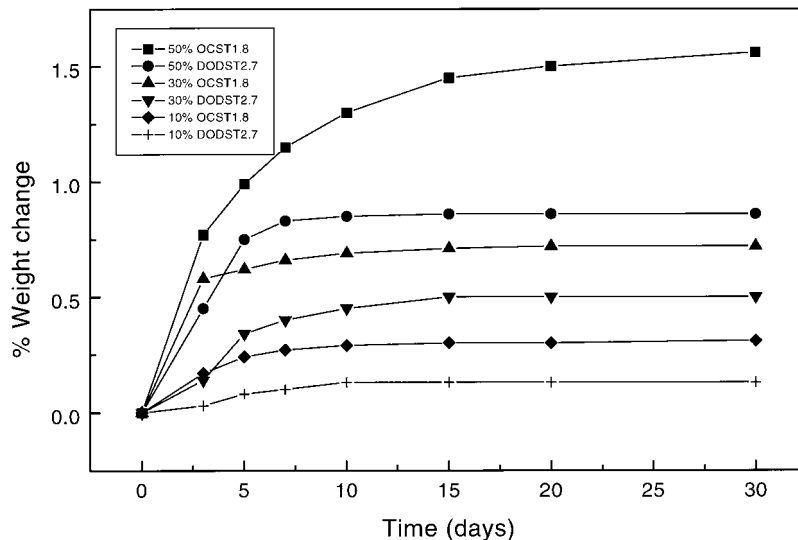
The same conclusions can be reached when elongations at break of the blends are compared (Figs. 15 and 16). The elongation at break for OCST1.8 decreases with increasing amount of starch ester in the blends. The behavior of the DODST2.7 blends is somewhat different. It can be seen that the percent elongation initially decreases to a minimum at ~30–50% DODST2.7, but starts to increase again. This is a rather usual

phenomenon observed in incompatible polymer blends. This could, in theory, also be observed in OCST1.8 blends, but as can be seen in Figure 15, OCST1.8 has a very low elongation at break. Nevertheless, in all cases, blends in the low starch content range retain satisfactory elongation properties for starch ester contents up to 15 wt %.

Comparing the three different blend systems, there are no great differences observed between them, as far as mechanical properties are concerned, for low starch content. It seems that the degree of substitution or the chain length of the ester group does not play any significant role in the mechanical properties. This is probably due



**Figure 16** Relative elongation at break of LDPE/DODST2.7, LDPE/OCST2.7, and LDPE/OCST1.8 blends.



**Figure 17** Absorption water (%) diagram of LDPE/OCST1.8 and LDPE/DODST2.7 blends.

to the fact that their blends with LDPE are still incompatible, as with its blends with unmodified starch.

DODST2.7 blends, however, show superior percent elongation properties compared to other starches for contents  $>50\%$  in starch. This must be attributed mainly to the high elongation at break value of pure DODST2.7.

All the esterified starches can be used for preparation of blends with LDPE destined for packaging usage and containing up to 15–20 wt % of starch. This amount is higher than the amount of the unmodified starch (6–9 wt %) which can be incorporated in industrial LDPE/STARCH blends with satisfactory mechanical properties.<sup>21</sup>

#### Water and Moisture Absorption

The plot of water absorption versus time for LDPE/starch ester blends is shown in Figure 17. LDPE/OCST1.8 blends absorb more water than LDPE/DODST2.7, as expected. Indeed, the higher degree of substitution of the starch dodecanoate and the more hydrophobic side chains make the blends less sensitive to water. Their absorption increases with increasing starch ester content, but for all samples it remains quite low. This behavior is in accordance with contact angle measurements.

Concerning the moisture absorption in relative humidity of 70%, the results (Table II) confirm that OCST1.8/LDPE blends are less hydrophobic than DODST2.7/LDPE ones.

These two tests show that esterification renders starch more hydrophobic, which would lead to an enhancement of dimensional stability in blends (less swelling) by reducing the possibility of hydrogen bond formation between hydroxyl groups in the starch and water, that is, by reducing the water uptake. In addition, esterification of starch with fatty acid chlorides makes the blends with LDPE appropriate for packaging applications, where water absorption must be minimal.

#### Biodegradation

From recent studies of biodegradation of polyethylene–starch blends,<sup>1,27</sup> it appears that microbes consume starch, creating pores in the plastic that increase the surface area of the polyethylene matrix, and provide opportunities for its degradation. The study of biodegradation, however, of starch esters in blends has not been undertaken yet in the open literature. In other natural polymers, like cellulose, which is also fully biodegradable, it has been found that biodegradability depends on the degree of substitution. Cellulose acetate with a degree of substitution  $<2.5$  is fully biodegradable.<sup>33</sup> However, cellulose acetate butyrate [almost totally substituted cellulose with d.s. (butyrate) = 2.58 and d.s. (acetate) = 0.36] showed no weight loss during 12 months of immersion in activated sludge.<sup>34</sup>

The biodegradation of LDPE/starch ester blends was followed by the weight loss (Fig. 18) due to removal of the starch component by micro-

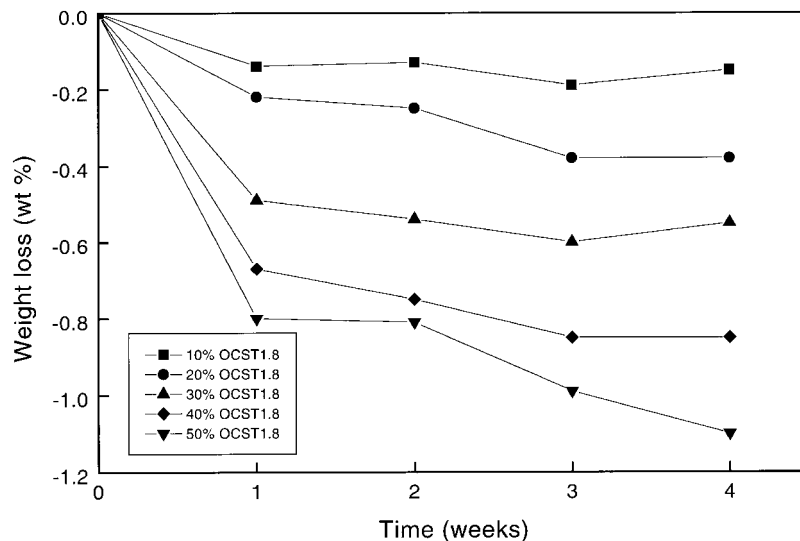
**Table II Moisture Absorption (%) of LDPE/OCST1.8 and LDPE/DODST2.7 Blends After 30 Days Exposure to 70% Relative Humidity**

Starch Ester Content (%) in Blends with LDPE	Moisture Absorption (%) of OCST1.8	Moisture Absorption (%) of DODST2.7
10	0.15	0.11
20	0.16	0.12
30	0.21	0.13
40	0.23	0.14
50	0.30	0.15
75	—	0.20

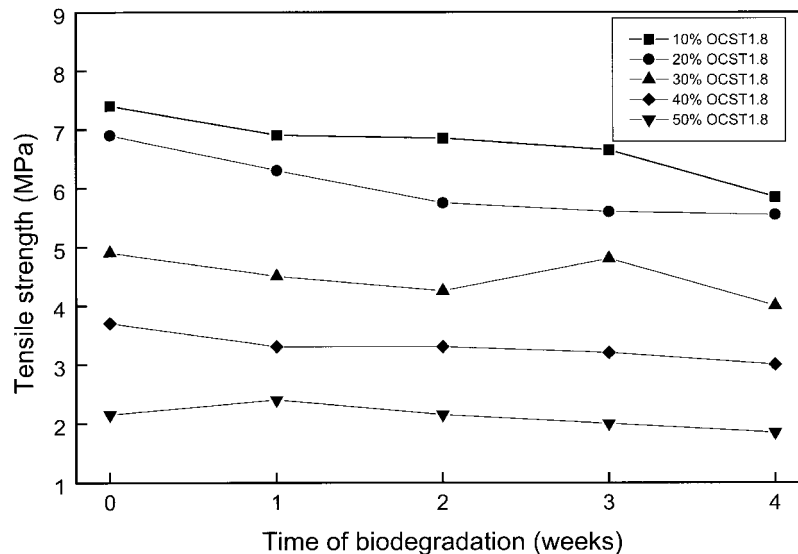
organisms and mechanical properties measurements (Fig. 19). From the weight losses diagram it can be observed that, as the amount of the OCST in the blends increases, the weight loss also increases. The blend with 50 wt % of OCST lost ~1.1 wt % during the test period of 4 weeks. About the same were the results in the LDPE/DODST blends, with the difference that the weight loss was less. Thus, the blend with 50 wt % of DODST lost ~0.85 wt % during the same period. These results indicate that the rate of biodegradation, if any, is very slow and the rate is probably greater for OCST with 1.8 degree of substitution.

After 4 weeks of exposure to activated sludge, there were no significant changes in the mechanical properties of samples (Fig. 19). There is only a small reduction in tensile strength as well as in elongation at break for all the blends during the exposure period.

Very small changes in mechanical properties were found, however, in LDPE blend with 6 wt % of pure starch for a 10-month accelerated biodegradation period in inoculum.<sup>35</sup> Thus, the 4 weeks' exposure time in activated sludge for our blends may be insufficient. Octanoated starch with a degree of substitution 1.8 may be biodegradable, because more than one-third of the hydroxyl groups are unmodified. This sample remains more hydrophilic than the respective samples of starch with a 2.7 degree of substitution. Also, the high amylopectin/amylose ratio in our starch sample could have an inhibiting effect on the biodegradation of blends. It was observed by Bhattacharya et al.<sup>29</sup> that starch (with 70% amylose)/styrene maleic anhydride blends were a little more biodegradable than those containing starch composed only of amylopectin. However, our results are not conclusive as regards these two remarks. Further experiments must be conducted in order to test these



**Figure 18** Weight loss of LDPE/OCST1.8 blends during exposure in activated sludge.



**Figure 19** Tensile strength of LDPE/OCST1.8 blends during exposure in activated sludge.

hypotheses, possibly, a biodegradation study of pure starch esters with different degrees of substitution.

## CONCLUSIONS

The esterification of starch with fatty acid chlorides enhances its thermoplastic character and its mechanical properties, increases its thermal stability, and renders it hydrophobic. These increases are higher when the carbon chain length is longer and the degree of substitution of starch esters is higher. Also, the tendency of starch to swell in water is eliminated by this chemical modification. The new thermoplastic materials obtained after mixing starch esters and LDPE exhibit interesting properties. The dimensional stability of LDPE/starch ester blends is enhanced compared to that of LDPE/unmodified starch blends. Blends of LDPE/starch esters retain satisfactory mechanical properties for starch ester contents up to 15–20%. Their thermal stability decreases with the starch ester content, although it is definitely improved compared to that of LDPE/unmodified starch blends.

The biodegradability of the blends was tested for a 4-week period in activated sludge. The rate of biodegradation observed was very slow. The biodegradation of the pure modified starches needs to be determined, in order to explain the

very slow rate of biodegradation of their composites with LDPE.

However, comparing the properties of LDPE/starch ester blends and the cost of their production, commercial applications will probably be limited. Continuing efforts, however, may provide fully biodegradable starch-based thermoplastic materials, which possess water resistance and strength properties suitable for developing environmentally friendly materials.

The authors wish to thank the Science and Technology National Council of Mexico (CONACYT) for financial support. Also, the Greek company Heitoglou Bros. is acknowledged for their kind permission to use the wastewater treatment facilities of their plant.

## REFERENCES

1. C. L. Swanson, R. L. Shogren, G. F. Fanta, and S. H. Imam, *J. Environ. Polym. Degrad.*, **1**, 155 (1993).
2. J. L. Willett, *J. Appl. Polym. Sci.*, **54**, 1685 (1994).
3. S. Simmons and E. L. Thomas, *J. Appl. Polym. Sci.*, **58**, 2259 (1995).
4. F. H. Otey, R. P. Westhoff, and C. R. Russell, *Ind. Eng. Chem. Prod. Rec. Dev.*, **16**, 305 (1977).
5. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Prod. Rec. Dev.*, **19**, 1659 (1980).
6. B. Jasberg, C. L. Swanson, T. Nelsen, and W. M. Doane, *J. Polym. Mater.*, **9**, 153 (1992).



7. G. F. Fanta, C. L. Swanson, and W. M. Doane, *J. Appl. Polym. Sci.*, **40**, 811 (1990).
8. G. F. Fanta, C. L. Swanson, and R. L. Shogren, *J. Appl. Polym. Sci.*, **44**, 2037 (1992).
9. R. L. Shogren, R. V. Greene, and Y. V. Wu, *J. Appl. Polym. Sci.*, **42**, 1701 (1991).
10. R. L. Shogren, A. R. Thompson, R. V. Greene, S. H. Gordon, and G. Cote, *J. Appl. Polym. Sci.*, **42**, 2279 (1991).
11. R. L. Shogren, A. R. Thompson, F. C. Felker, R. E. Harry-O'kuru, S. H. Gordon, R. V. Greene, and J. M. Gould, *J. Appl. Polym. Sci.*, **44**, 1971 (1992).
12. G. F. Fanta and E. B. Bagley, in *Encyclopedia of Polymer Science Technology*, Suppl. 2, H. F. Mark and N. M. Bikalis, Eds., Wiley-Interscience, New York, 1977, p. 665.
13. E. R. George, T. M. Sullivan, and E. H. Park, *Polym. Eng. Sci.*, **34**, 17 (1994).
14. J. L. Willett, U.S. Pat. 5,087,650 (1992).
15. J. L. Jane, A. W. Schwabacher, S. N. Ramrattan, and J. A. Moore, U.S. Pat. 5,115,000 (1992).
16. S. H. Imam, J. M. Gould, M. P. Kinney, A. M. Ramsay, and T. R. Tosteson, *Cur. Microbiol.*, **25**, 1 (1992).
17. P. Allenza, J. Schollmeyer, and R. P. Rohrbach, in *Degradable Materials: Perspectives, Issues and Opportunities*, S. A. Barenberg, J. L. Brash, R. Narayan, and A. E. Redpath, Eds., CRC Press, Boca Raton, FL 1990.
18. C. L. Swanson, R. P. Westhoff, and W. P. Doane, *Proceedings of the Corn Utilization Conference II*, National Corn Growers Association, St. Louis, 1988.
19. G. J. L. Griffin, U.S. Pat. 4,016,117 (1977).
20. G. J. L. Griffin, U.S. Pat. 4,021,388 (1977).
21. R. L. Evangelista, Z. L. Nikolov, W. Sung, J.-L. Jane, and R. J. Gelina, *Ind. Eng. Chem. Res.*, **30**, 1841 (1991).
22. J.-L. Jane, R. J. Gelina, Z. L. Nikolov, and R. L. Evangelista, U.S. Pat. 5,059,642 (1991).
23. A. D. Sagar and E. W. Merrill, *J. Appl. Polym. Sci.*, **58**, 1647 (1995).
24. J. Aburto, I. Alric, E. Borredon, D. Bikiaris, J. Prinós, and C. Panayiotou, *Carbohydr. Polym.*, to appear.
25. J. W. Mullen and E. Pacsu, *Ind. Eng. Chem.*, **34**, 1209 (1942).
26. S. Thiebaut, Ph.D. Thesis, Order number 1087, INP Toulouse, France.
27. R. E. Wilson, *Ind. Eng. Chem.*, **13**, 326 (1921).
28. S. M. Goheen and R. P. Wool, *J. Appl. Polym. Sci.*, **42**, 2691 (1991).
29. M. Bhattacharya, U. R. Vaidya, D. Zhang, and R. Narayan, *J. Appl. Polym. Sci.*, **57**, 539 (1995).
30. H. Morita, *Anal. Chem.*, **28**, 64 (1956).
31. S. Nakatsuka and A. L. Andrady, *J. Appl. Polym. Sci.*, **45**, 1881 (1992).
32. R. F. T. Stepto and I. Tomka, *Chimia*, **41**, 76 (1987).
33. R. A. Gross and J.-D. Gu, *J.M.S.-Pure Appl. Chem.*, **A32**, 613 (1995).
34. G. Tomasi and M. Scandola, *J.M.S.-Pure Appl. Chem.*, **A32**, 671 (1995).
35. R. G. Austin, in *Degradable Materials: Perspectives, Issues and Opportunities*, S. A. Barenberg, J. L. Brash, R. Narayan, and A. E. Redpath, Eds., CRC Press, Boca Raton, FL 1990.