

# Properties of octanoated starch and its blends with polyethylene.

J. Aburto<sup>a</sup>, S. Thiebaud<sup>a</sup>, I. Alric<sup>a</sup>, E. Borredon<sup>a</sup>, D. Bikiaris<sup>b</sup>, J. Prinós<sup>b</sup> and C. Panayiotou<sup>b\*</sup>

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

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

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Octanoated starch (OCST) was prepared by esterification of native starch with octanoyl chloride. The new material was characterised by <sup>1</sup>H NMR, FTIR, and elemental analysis. This showed that the esterification had proceeded to a degree of substitution of 2.7. The octanoated starch was subsequently mixed with low density polyethylene (LDPE) at various proportions in a Haake Rheomixer. Similar blends of LDPE were also prepared with plasticised starch (PLST) for comparison purposes. The thermomechanical properties were determined as a function of blend composition. The prepared LDPE/OCST blends show better mechanical properties compared to their respective LDPE/PLST blends. In particular, the elongation at breaking is significantly higher in the LDPE/OCST blends. The latter exhibit also a higher thermal stability and a low water absorption. Copyright © 1997 Elsevier Science Ltd. All rights reserved

## INTRODUCTION

In recent years, studies concerning the total or partial substitution of synthetic plastics in key applications by biodegradable materials have been increasing (Doane *et al.*, 1992). Although efforts to recycle used plastics in order to reduce their volume in landfills have been improved significantly, recycling would be neither practical nor economical for certain applications such as waste bags, agricultural mulch films, or food packaging. For this kind of application, plastics are expected to degrade into safe by-products under normal composting conditions. Replacement of petroleum based plastics with materials from agroresources, especially starch, is attractive from the standpoint of making the end product biodegradable. This replacement would permit us to conserve our petrochemical resources and to find out new non-food uses for starch. Starch is inexpensive, totally biodegradable, available in large quantities from certain crops (e.g. potato, maize) and is produced in greater quantities than current market demand (Shogren *et al.*, 1993).

Extended studies have been undertaken to replace

partially or totally synthetic plastics. Biodegradable plastics containing starch can be prepared in numerous ways. Native starch can be incorporated into the synthetic plastic as a filler (Griffin, 1992; Willett, 1992) or coextruded with starch (Kim and Pometto, 1994). However, due to the hydrophilic nature of starch, blends with hydrophobic plastics have poor mechanical properties due to poor interfacial adhesion. The maximum tolerable amount of starch in these blends usually does not exceed 6–9% by weight. The hydrophilicity of starch results in its inability to form a continuous phase with the synthetic polymer. This will most likely lead to stress concentration points, resulting in mechanical failure even at low tensile stresses. Conversely, smaller and well distributed phase domains will lead to mechanical behaviour that is more consistent with a homogeneous blend of two components (Simmons and Thomas, 1995).

One way to increase compatibility in starch blends is to use a compatibiliser containing groups capable of hydrogen bonding with starch hydroxyls. Poly(ethylene-co-acrylic acid) (EAA) is such a material (Otey *et al.*, 1977, 1980; Jasberg *et al.*, 1992). Its compatibility with starch is due to a helical V-type complex formation (Fanta *et al.*, 1990, 1992; Shogren *et al.*, 1991a, b, 1992). The disadvantage of these

\*To whom correspondence should be addressed.

blends is the lower biodegradation rate of EAA (Imam *et al.*, 1992).

Another approach in achieving miscibility and improving adhesion of phases is to replace the hydrophilic -OH groups of starch with hydrophobic groups through esterification. Derivatised starches with acetate (Parandoosh and Hudson, 1993), hydroxypropyl (Swanson *et al.*, 1988), alkyl siliconate (Griffin, 1978), octenyl-succinate (Jane *et al.*, 1991, Evangelista *et al.*, 1991), and fatty-acid esters (C<sub>4</sub>-C<sub>6</sub>) (Sagar and Merrill, 1995) have been prepared and mixed with LDPE.

In the present study, we have followed this latter approach but it was decided to use a longer chain ester of starch (C<sub>8</sub>). This modified starch is expected to exhibit an increased hydrophobic character due to the incorporation of long octenyl pendant groups. Native starch behaves like a brittle material having a high (30 MPa) tensile strength but a very low (4%) elongation at breaking (Stepto and Tomka, 1987; Schroetter and Enders, 1992). This behaviour makes it unsuitable for use in the usual plastic formulations (packaging materials, films, bags, etc.). OCST starch, on the other hand, is expected to show different mechanical properties due to the replacement of hydroxyl groups with ester groups. The hydrophobic character of OCST is, in turn, expected to enhance the compatibility of the modified starch with LDPE and, as a consequence, to improve the thermomechanical properties of the starch/LDPE blends.

The present work is the first part of a more extended study undertaken by our laboratories towards studying the thermomechanical behavior and biodegradability of systematically hydrophobised starch products.

## EXPERIMENTAL

### Materials

The potato starch used in the acylation was provided by INRA (Nantes). 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. Octanoyl chloride (Aldrich) was reagent grade; the pyridine and absolute ethanol were SDS anhydrous analytical grades. Low density polyethylene was an industrial grade from Alcudia.

### Synthesis of octanoated starch

The esterification of starch was carried out by the modified method of Mullen and Pacsu (1942). This method was preferred to the others reported in the literature, because it requires only a minimal amount of organic solvents in the synthesis reaction. In

addition, the organic solvents used minimise the starch degradation and act as catalysts. The general procedure of esterification was as follows. The starch was dried overnight in an oven at about 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. 15 ml of pyridine and 0.28 mol of octanoyl chloride were added and the reaction was allowed to proceed for 6 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 of absolute ethanol to precipitate the esterified starch and to eliminate any colour impurities. The product was washed twice with 200 ml of ethanol. The excess of ethanol was removed by an air stream and the starch ester was dried at 50°C overnight and its weight measured. The obtained octanoated starch was a pale yellow fluffy paste which solidified at 25°C to form a brittle thermoplastic material. The weight of dried octanoated starch was 7.6 g (weight increase 204% at 98% yield). The octanoated starch prepared by the above procedure was characterised using elemental analysis, NMR 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 starch were done in accordance with the modified method described by Thiebaud (1995). Octanoated 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 starch was melt blended with LDPE in a Haake-Buchler Reomixer 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 Reomixer. Mixing was performed at 170°C and 80 rpm for 15 min. The melt temperature and torque were recorded during the mixing period. A total of nine samples were prepared containing 5, 10, 15, 20, 25, 30, 40, 50 and 75 wt% octanoated starch respectively. Blends of LDPE/plasticised starch with the same starch content were also prepared in order to compare the properties of the two systems. The plasticised starch, which was used throughout this study, contained 35 wt% glycerine as plasticiser and was prepared by mixing the starch/glycerine mixture in the Reomixer at 170°C. Native starch used for plasticisation was previously dried at 150°C under

vacuum for 24 h to remove moisture. The blends, after preparation, were placed in tightly sealed vials to prevent any moisture absorption.

### FTIR measurements

FTIR spectra were acquired using a Biorad FTS-45A FTIR spectrometer. For each spectrum 64 consecutive scans with  $2\text{ cm}^{-1}$  resolution were averaged. Samples were measured in the form of thin films about  $70\text{ }\mu\text{m}$  thick, which were prepared by hot press molding.

### DSC measurements.

DSC measurements of samples were performed in a Shimadzu DSC-50Q fast quenching differential scanning calorimeter. Samples were placed in sealed aluminium cells, using a quantity of about 10 mg for each sample. Samples were initially heated by  $20^\circ\text{C}/\text{min}$  up to  $200^\circ\text{C}$  and immediately quenched to remove any previous thermal history. The samples were subsequently rescanned with a heating rate of  $20^\circ\text{C}/\text{min}$ .

### TGA measurements

TGA measurements were performed using a Shimadzu TGA-50 thermogravimetric analyser. Each sample was heated at a rate of  $20^\circ\text{C}/\text{min}$  up to  $650^\circ\text{C}$ .

### Water absorption measurements

Water absorption was measured by using  $3\times 8\text{ cm}$  film strips of  $80\text{ }\mu\text{m}$  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 per cent increase of the initial weight.

### Mechanical properties of blends

Measurements of the mechanical properties were performed on an Instron mechanical tester, Model 1122, according to the ASTM D638 method. Measurements were performed at a  $5\text{ mm}/\text{min}$  crosshead speed. Prior to measurement, the samples were conditioned at  $50\pm 5\%$  relative humidity for 24 h by placing them in a closed chamber containing a saturated  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged.

## RESULTS AND DISCUSSION

### Characterisation results

The  $^1\text{H}$  NMR peaks observed for OCST and their respective assignments are reported in Table 1. The elemental analysis of OCST gave the following results: C 65.8%, H 9.9%, O, 24.3% (the values as calculated from NMR are: C 66%, H 9.6%, O 24.4%). This corresponds to an approximate molecular formula of  $\text{C}_{27.9}\text{H}_{48.2}\text{O}_{7.7}$  for the prepared OCST. From this formula we were able to calculate the degree of substitution.

The degree of substitution (DS) for a starch derivative is defined as the moles of substituents of hydroxyl groups per D-glucopyranosyl structural unit of the starch polymer; with three hydroxyl groups per unit, the theoretical maximum DS is 3. For our sample, the value calculated from the above elemental analysis data was 2.7.

The contact angle found for octanoated starch was  $85^\circ$ . By using the same technique, poly(methyl methacrylate) exhibits a contact angle of  $86^\circ$ . This indicates that OCST has a similar degree of hydrophilicity to PMMA. Native starch does not give a measurable contact angle as water is readily absorbed by it upon contact.

The FTIR spectra of octanoated and native starch are shown in Fig. 1. In the native starch spectrum the characteristic broad peak of starch appears at  $958\text{--}1190\text{ cm}^{-1}$ . This peak is attributed to C–O bond stretching (Goheen and Wool, 1991). A strong broad band due to hydrogen bonded hydroxyls appears at  $3380\text{ cm}^{-1}$  and the symmetric C–H vibration band at  $2850$  and  $2920\text{ cm}^{-1}$ .

FTIR spectrum of OCST shows strong bands at  $1746\text{ cm}^{-1}$ ,  $2856\text{ cm}^{-1}$  and  $2927\text{ cm}^{-1}$ , which are attributed to stretching deformation of the ester carbonyl group and the methyl/methylene groups respectively. The strong band at  $3380\text{ cm}^{-1}$  (hydroxyl groups) of native starch decreases after the esterification reaction due to ester bond formation. The carbonyl overtone stretching band also appears at around  $3570\text{ cm}^{-1}$ .

### LDPE/octanoated starch blends.

The torque measurements for some LDPE/OCST blends during mixing are presented in Fig. 2. From the figure it is observed that the torque is stabilised after approximately 10 min of mixing, suggesting that good

**Table 1. NMR peaks and assignments for octanoated starch**

$\delta$ (ppm)	Group assignment	Number of H
0.81, t	–CH <sub>3</sub>	8
1.2, m	–CH <sub>2</sub> –	21.5
1.43, m	–CO–CH <sub>2</sub> –CH <sub>2</sub> –	5.5
2.26, m	–O–CO–CH <sub>2</sub> –	5.4
3.5–5.4, m	Glucose protons	7

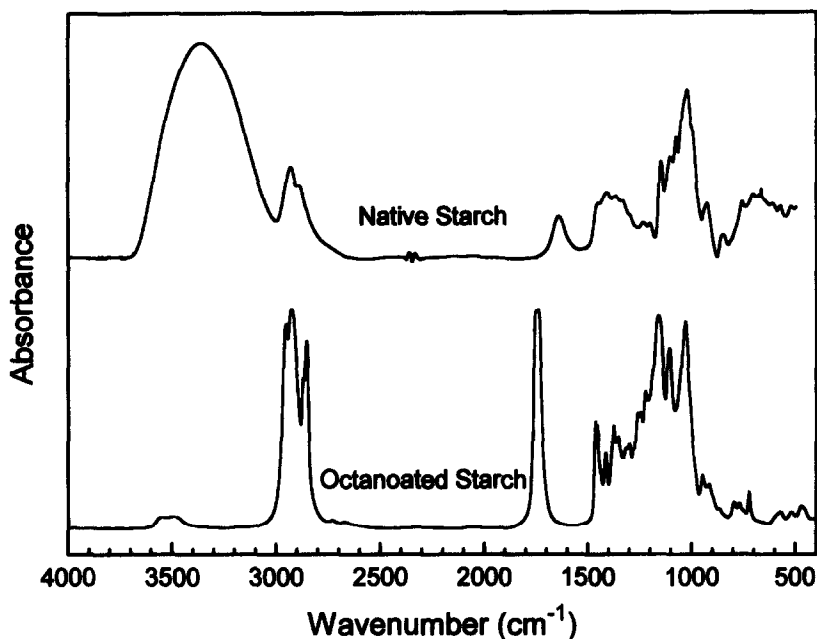


Fig. 1 FTIR spectra of native and octanoated starch.

mixing has occurred within this time period. The final torque decreases with increasing OCST content in the blends. This is due to the lower viscosity of the OCST melt as compared to that of LDPE. This causes a decrease in the melt viscosity of the blend as the OCST concentration increases.

Figure 3 presents the torque responses of two LDPE/OCST and two LDPE/PLST blends having the same starch content. As we can observe, the melt torque of LDPE/PLST also decreases with increasing PLST content in the blend. However, LDPE/OCST blends have significantly lower melt torques compared to

LDPE/PLST blends of the same starch content. This improved rheological behaviour is due to the substitution of -OH groups by the nonpolar and bulky octanoate groups, as this substitution leads to conformation changes in the starch molecule. In a previous study (Sagar and Merrill, 1995) it has been shown that the melt viscosity of esterified starches decreases with increasing molecular weight of the ester group. This can also be inferred from the melt temperature measurements presented in Fig. 4.

The melt temperature was defined as the final temperature of the melt in the rheomixer after

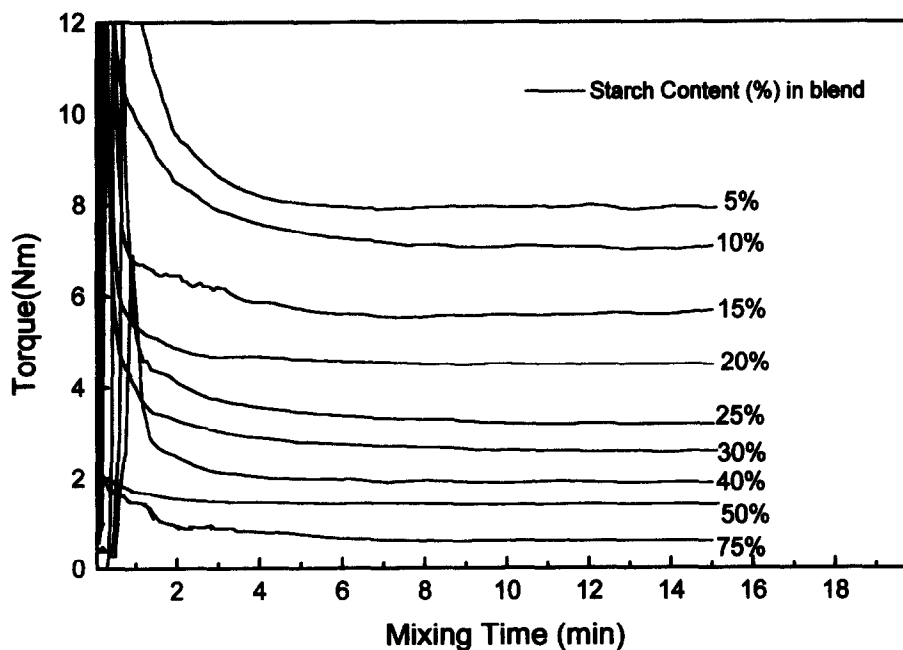


Fig. 2 Torque diagrams of LDPE/OCST blends.

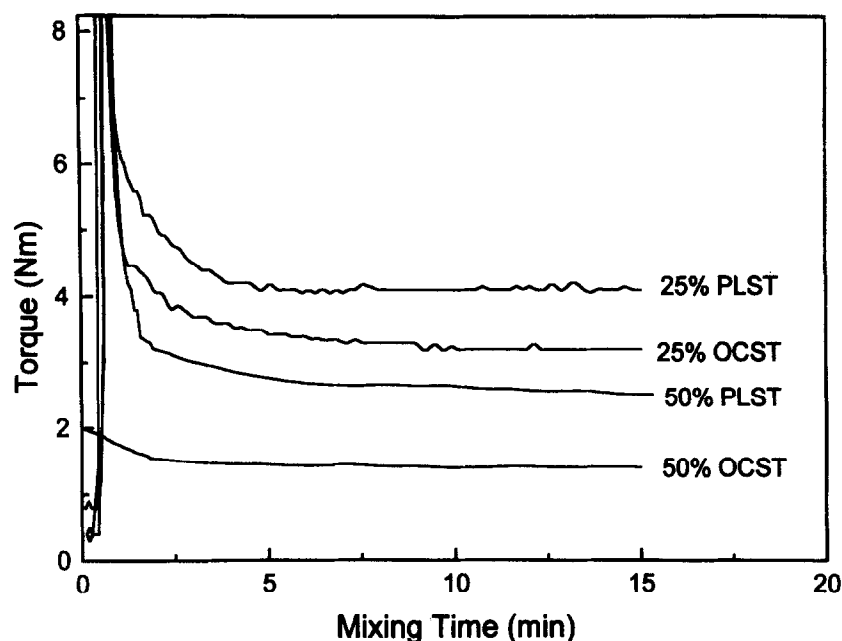


Fig. 3 Torque diagrams of LDPE/OCST and LDPE/PLST blends for starch contents of 25 and 50%.

stabilisation. This stabilisation is achieved after approximately 10 min of mixing time. In Fig. 4 it can be seen that the melt temperature for pure LDPE can rise up to 15°C above the setpoint temperature of the rheomixer (170°C). This increase is the result of friction created during mixing. For LDPE/OCST and LDPE/PLST blends, a decrease in melt temperature is observed with increasing starch (OCST or PLST) content. This is due to the lower melt viscosity of OCST and PLST compared to that of LDPE. This decrease is almost linear for starch contents up to 25 wt%. For higher starch

content the melt temperature is stabilised at approximately 1–2°C above the setpoint.

By comparing LDPE/OCST and LDPE/PLST blends, we can observe that the former show a lower melt temperature compared to the latter (for the same starch content). This observation is in accordance with the corresponding torque measurements, which show that LDPE/OCST blends have a lower melt torque compared to the torque of LDPE/PLST blends for the same starch content (Fig. 3). These two observations are in accordance with the fact that LDPE/OCST

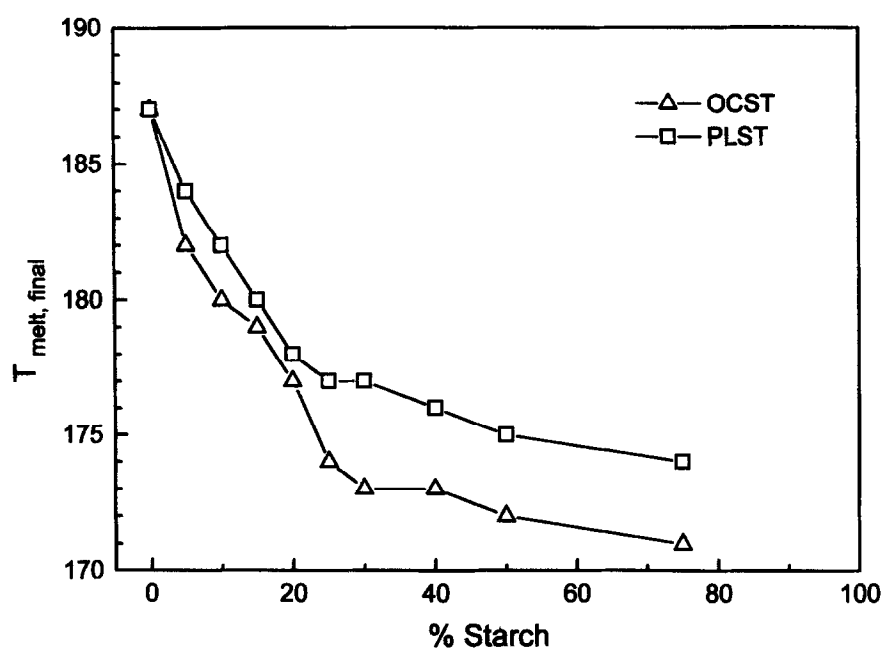


Fig. 4 Melt temperatures of LDPE/OCST and LDPE/PLST blends.

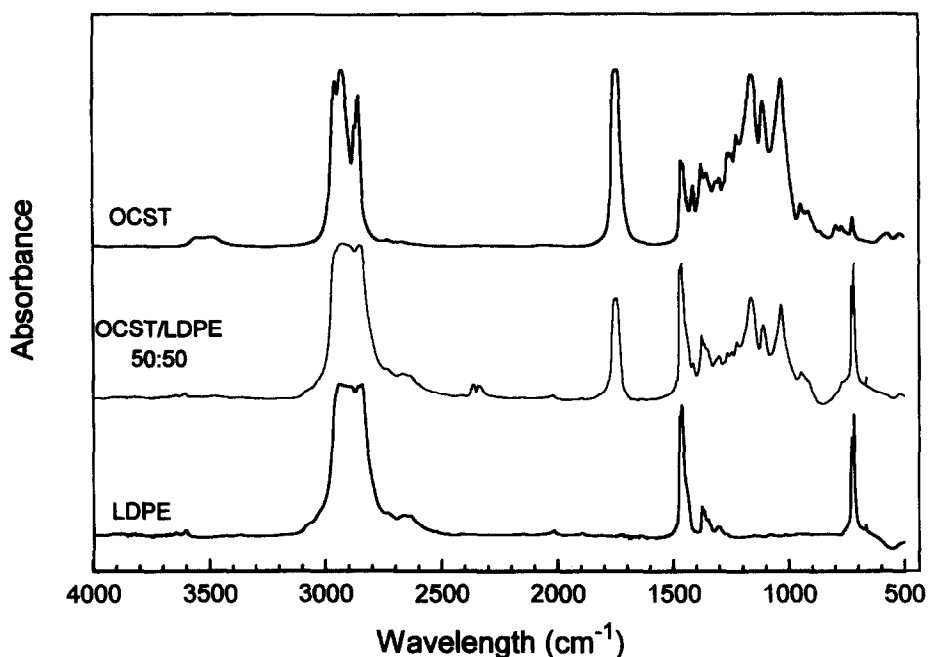


Fig. 5 FTIR spectra of OCST, LDPE and their 50:50 blend.

blends also present a lower melt viscosity compared to LDPE/PLST blends. The low melt viscosity makes these blends more easily processable compared to LDPE/PLST blends.

#### FTIR measurements

Figure 5 depicts the FTIR spectra of OCST, LDPE and a 50:50 blend of the two polymers. There are no significant differences observed in the spectrum of the blend (e.g. peak shifts) compared to the spectra for pure components—an indication that there are no strong intermolecular interactions between OCST and LDPE. This was expected since LDPE lacks any groups capable of developing such interactions (polar groups, hydrogen bond donors or acceptors, etc.). The only intermolecular forces expected to operate between LDPE and OCST are the weak van der Waals interaction forces (dispersion forces).

The only differences observed in the spectra for LDPE/OCST blends are in some peak intensities. Thus, there is an increase in intensity at  $958\text{--}1190\text{ cm}^{-1}$  (broad starch peaks) and at  $1746\text{ cm}^{-1}$  (ester carbonyl peak) with increasing OCST content. This was expected since both these peaks are attributed to OCST. For blends containing less than 50 wt% OCST there is no hydroxyl absorbance observed at  $3500\text{ cm}^{-1}$ .

#### DSC measurements

Native granular starch contains crystalline areas within the amylopectin (branched) component but the linear amylose is largely amorphous and can mostly be extracted in cold water (Swanson *et al.*, 1993). The

glass transition temperature and the melting point of dry native starch cannot be determined, because they lie above the decomposition temperature. However, with the addition of plasticisers such as water, dioles, glycerine, etc., there is a depression in both  $T_m$  and  $T_g$  and so they can be measured. Besides external plasticisers, bulky side groups can also act as internal plasticisers and effect plasticisation. In our samples it is expected that the octanoate side-chain groups will act in such a manner and will cause a decrease in  $T_g$  and  $T_m$ . It has been shown (Shogren, 1992) that amylose melts at a lower temperature compared to amylopectin and that the melting temperature depends on the water content of starch.

Figure 6 displays the DSC thermogram of octanoated starch. From the figure it is evident that octanoated starch is essentially a completely amorphous material, with  $T_g$  of  $40^\circ\text{C}$ . Obviously, the replacement of hydroxyl groups from hydrophobic octanoate groups has led to a total loss of crystallinity of the initially crystalline starch. The  $T_g$  found is in accordance with the  $T_g$  values for modified starch with lower ester side chains reported in the literature (Sagar and Merrill, 1995). In the above-mentioned study, it was found that the  $T_g$  of esterified starches decreases with increasing chain length of the acid used in esterification. Thus, the  $T_g$  of starch derivatives ranged from  $65^\circ\text{C}$  for starch butyrate to  $50^\circ\text{C}$  for starch hexanoate. Extrapolating these results to starch octanoate, it would be expected that  $T_g$  would be several degrees below  $50^\circ\text{C}$ , which is indeed the case. Caution must be exercised, however, in this extrapolation because the starch used in the previously mentioned study contained mainly amylose (70%),

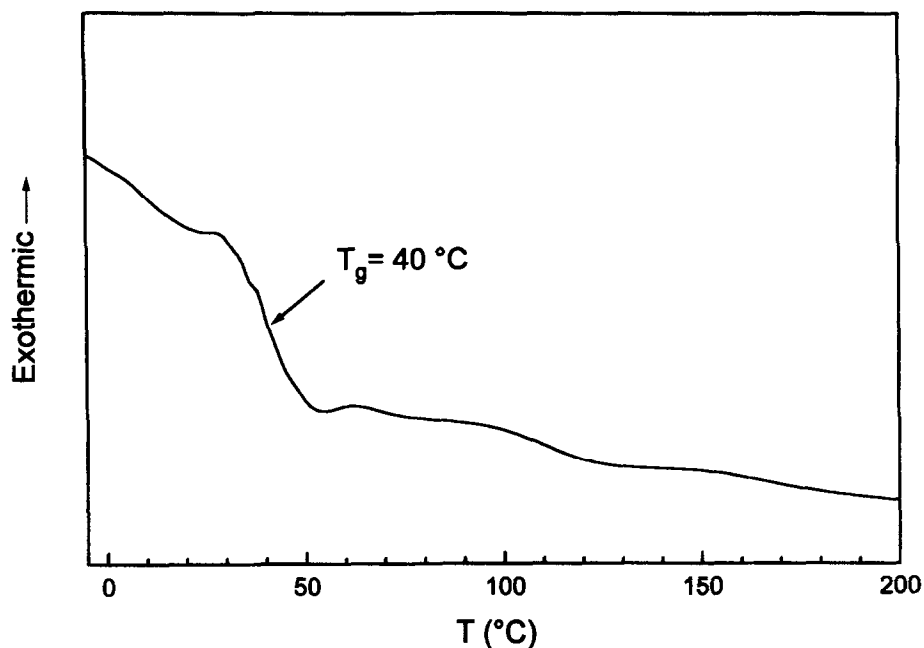


Fig. 6 DSC thermogram of octanoated starch.

while our sample was composed mainly of amylopectin. Amylopectin is a crosslinked polymer of high molecular weight and has higher  $T_g$  compared to amylose. To a great extent, the same behaviour must apply to the esterified derivatives as well. Thus, the  $T_g$  of OCST prepared from starch rich in amylose might be even lower than 40°C.

As far as LDPE/OCST blends are concerned, there are no significant differences observed in the DSC scans compared to those of pure components as is

shown in Fig. 7. Figure 8 depicts the melting point vs. OCST content for LDPE/OCST blends.

For polymer blends containing a crystallisable polymer, the Flory-Huggins interaction parameter,  $\chi_{12}$ , of the two polymers can be determined from melting point depression data using the well known Wang-Nishi formula:

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

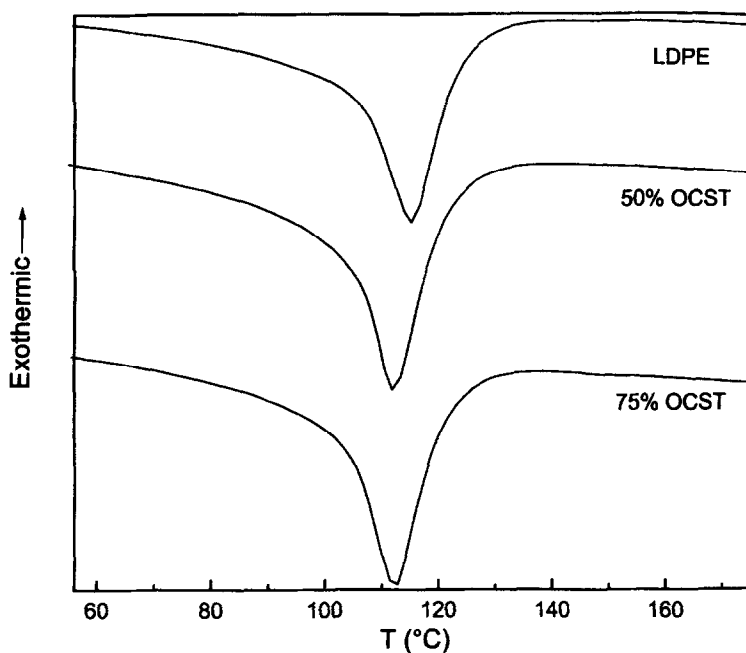


Fig. 7. Melting peaks of LDPE and LDPE/OCST blends.

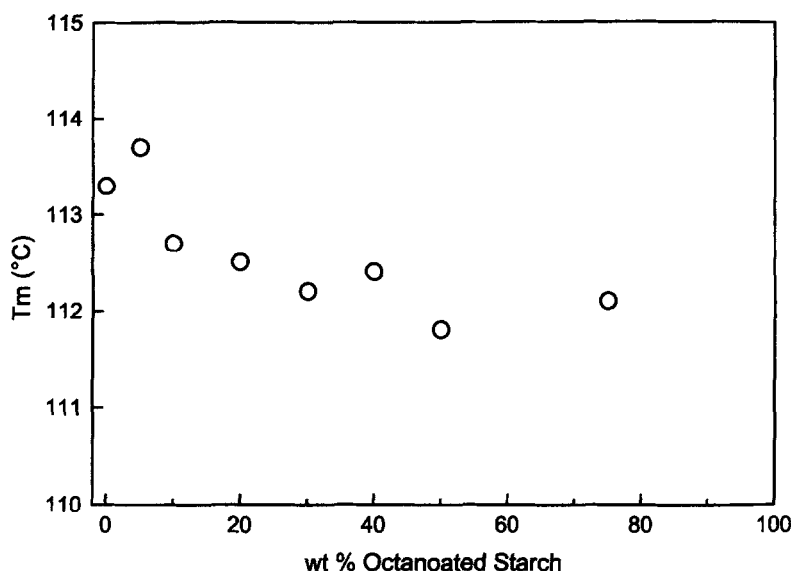


Fig. 8. Melting temperature vs. wt% OCST diagram for LDPE/OCST blends.

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 crystallisable component,  $\Delta H_f^0$  is the heat of melting, and  $\phi_2$  is the volume fraction of the crystallisable component. For miscible blends,  $\chi_{12}$  is expected to have a negative value, i.e.  $T_m < T_m^0$  (melting point depression). From Fig. 8 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. Concerning heat of melting, there are some differences observed in  $\Delta H_m$  of blends but there is no definite trend with composition in the calculated values.

From the above it can be concluded that no significant change can be observed for the melting behaviour of LDPE in the blends. Also, no decrease in the crystallinity of LDPE in the blends is observed. This is a further indication that LDPE is hardly miscible with OCST or that LDPE/OCST interactions are rather weak.

#### TGA measurements

When starch granules are heated under atmospheric conditions, they are thermally stable up to 200–230°C. Beyond 230–250°C, thermal degradation takes place, depending mainly on the water content of the starch.

Figure 9 presents the TGA thermograms of OCST and PLST along with LDPE. As observed, PLST has three weight loss stages whereas OCST has two such stages. The additional first stage observed in PLST is due to partial loss of the external starch plasticiser. Above 250°C the weight loss is mainly attributed to starch degradation. OCST shows two degradation stages. The first stage accounts for 85–90% of the weight loss, with the remaining 10–15% residue decomposing at higher

temperatures. These stages appear at higher temperatures compared to those of PLST.

This greater thermal stability of OCST compared to PLST is probably due to the low content of -OH in the former. A previous study (Morita, 1956) has shown that water is the main product of decomposition at temperatures below 300°C, formed by intermolecular or intramolecular condensation of starch hydroxyls. However, the onset of degradation in OCST still occurs at lower temperatures compared to that of LDPE.

Blends of OCST with LDPE show two decomposition stages as shown in Fig. 10. The first one (250–350°C) is due to starch decomposition and 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 (Nakatsuka and Andrady, 1992). Similar curves are obtained for LDPE/PLST as well, with the main difference being that PLST degradation starts at lower temperatures. Thermal degradation could take place during the thermal processing of starch and especially during extrusion, resulting in the formation of lower molecular weight starch molecules. This could seriously affect the mechanical properties of the final product. Colour development is another undesirable effect of degradation. The higher thermal stability of OCST is expected to minimise processing problems such as colour formation and loss of mechanical properties.

#### Mechanical properties.

Figure 11 presents the stress–strain curves recorded for pure OCST and its blends with LDPE. The corresponding curve for pure PLST is presented in the



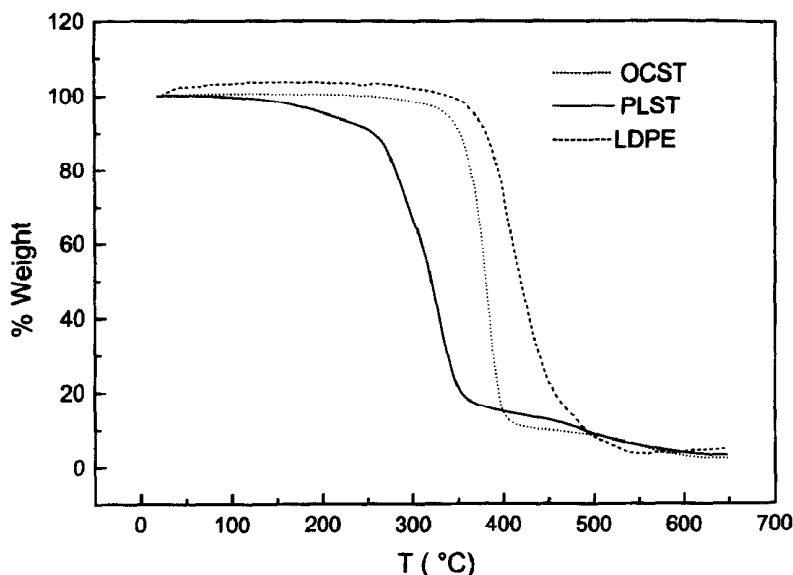


Fig. 9. TGA thermograms of OCST, PLST and LDPE samples.

same figure for comparison purposes. From the diagram it can be seen that OCST presents a yield point and its strength at the yield point is higher than its ultimate tensile strength. The opposite trend is observed for PLST and, as a result, PLST has a higher tensile strength, but a lower elongation at breaking compared to OCST. LDPE/OCST blends break without neck formation when the starch content is greater than 30 wt %. However, in blends containing less than 25 wt % OCST, necking is observed as shown in Fig. 11 for the samples containing 20 and 10 wt % OCST. From these stress-strain curves, the tensile strength and the elongation at break were determined.

Tensile strength and elongation at breaking values for OCST were found to be 0.61 MPa and 380%

respectively. It is evident that OCST has a rather poor tensile strength but a relatively high elongation at breaking. This is in accordance with the behaviour observed for other starch esters previously studied (Sagar and Merrill, 1995). Such a behaviour precludes the use of OCST as a thermoplastic material on its own.

Tensile strength measurements of LDPE/OCST blends and PLST are presented in Fig. 12. For both blend systems, tensile strength decreases with increasing starch content. For OCST blends, this decrease is *c.* 6% for every 5 wt % OCST added up to 25 wt % starch content. The respective rate of decrease for PLST blends is 8% for every 5 wt % PLST added. LDPE/OCST blends have better tensile strength properties compared to LDPE/PLST blends for starch contents below 50 wt %. Above

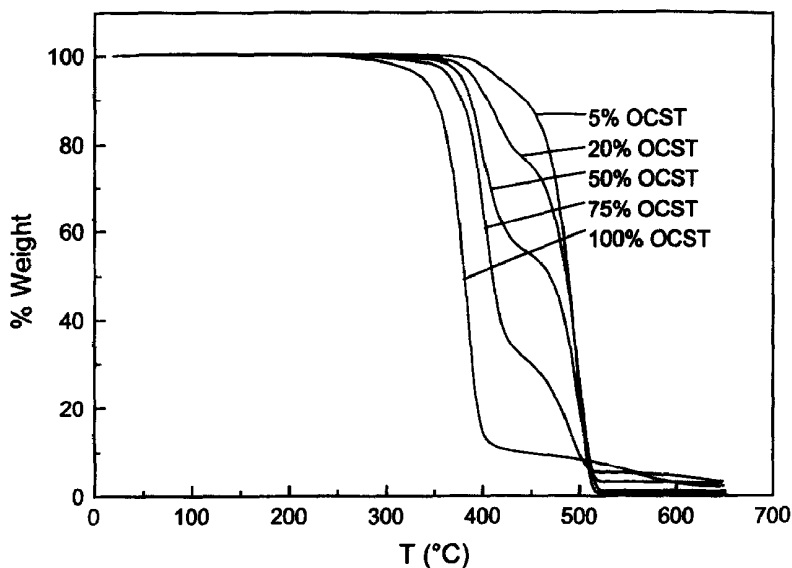


Fig. 10. TGA thermograms of LDPE/OCST blends.

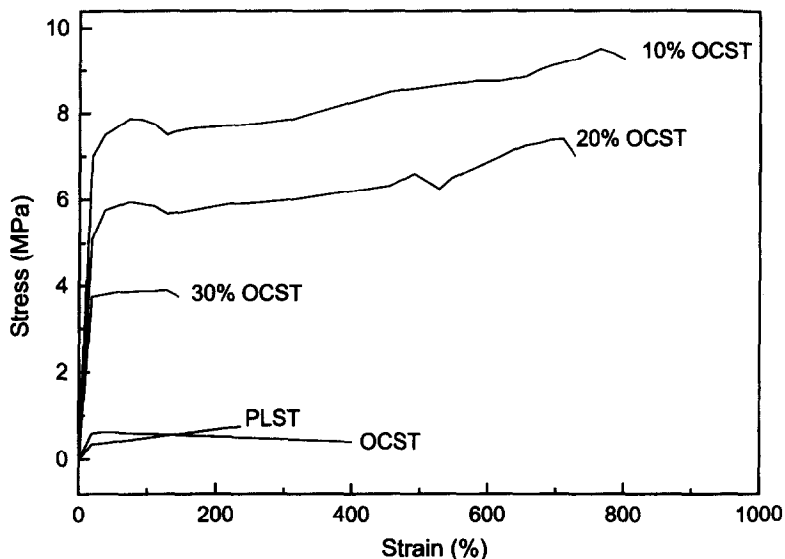


Fig. 11. Stress-strain curves for some samples.

this limit LDPE/PLST blends show higher tensile strength. This is largely due to the higher tensile strength of pure PLST compared to that of pure OCST.

The diagram of comparative elongation at breaking is presented in Fig. 13. In this diagram there is a distinct minimum observed for both blend systems in the middle of the composition range. This is a rather usual phenomenon observed in incompatible polymer blends. However, blends with OCST retain satisfactory elongation properties even for OCST contents up to 25 wt %, whereas in PLST blends the maximum tolerable starch content does not exceed 15 wt %. Above this point there is a rapid decrease in elongation at break.

The difference in elongation at break properties of the two blend systems is more pronounced in the composition range between 15 and 25% wt % in starch. These differences can be partly attributed to the higher

elongation at break of pure OCST compared to that of pure PLST. However, the elongation at break of the blends cannot be explained purely in terms of the different elongation properties of the pure components. Interfacial tension also plays an important role and it seems that the more hydrophobic OCST has drastically better adhesion properties with LDPE compared to PLST.

As a conclusion, LDPE/OCST blends show better mechanical properties compared to LDPE/PLST ones, especially in elongation at break. This means that larger amounts of OCST can be tolerated in blends with LDPE to give blends with acceptable mechanical properties.

#### Water absorption.

A major requirement for any material used in packaging formulations is minimal water absorption.

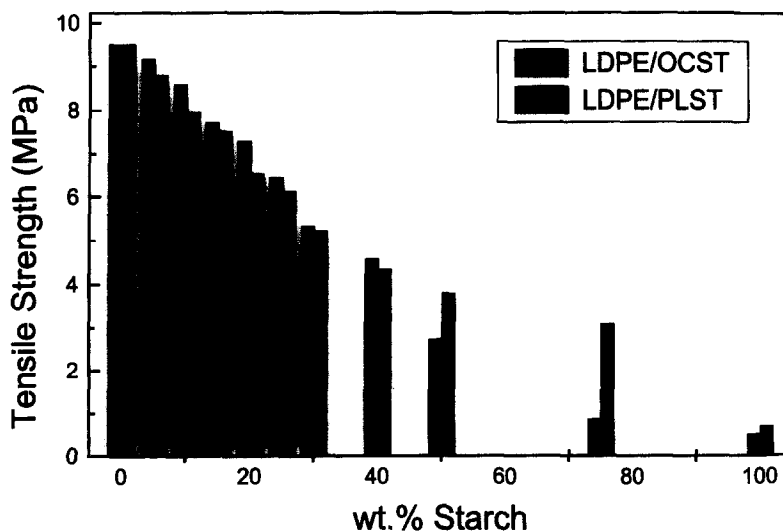


Fig. 12. Tensile strength of LDPE/OCST and LDPE/PLST blends.

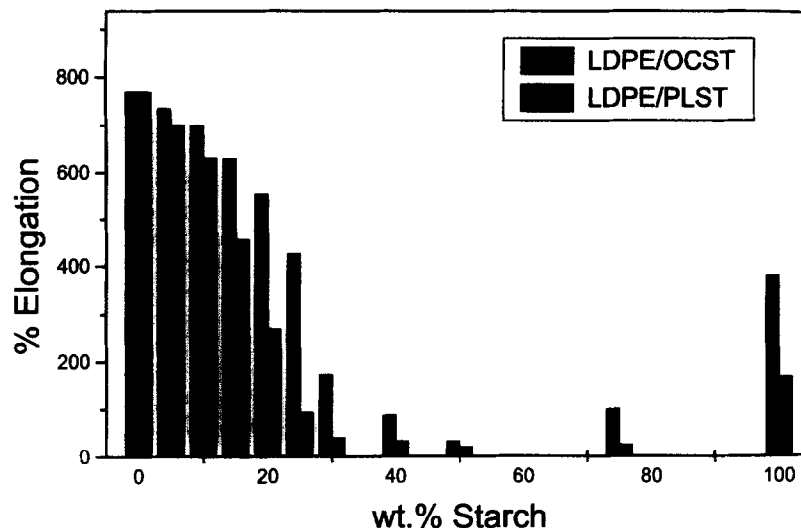


Fig. 13. Elongation at break of LDPE/OCST and LDPE/PLST blends.

Native starch in this respect is unsuitable as a blend component because it has a high hydrophilicity and can absorb large amounts of water. The problem remains in plasticised starch as well, with the additional problem of plasticizer leaching into the contained material. Octanoated starch, on the other hand, is expected to be less hydrophilic than either of the two aforementioned materials due to the low concentration of the highly hydrophilic hydroxyl groups.

The water absorption of LDPE/OCST blends vs. exposure time is presented in Fig. 14. From this diagram it is observed that only blends with an OCST content above 50 wt % show noticeable water absorption. Even for these samples the water absorption does not exceed 2.5%. This behaviour is in

accordance with contact angle measurements, which show that OCST is mainly hydrophobic with a hydrophobicity similar to that of PMMA. On the contrary, it was not possible to determine water absorption for the respective LDPE/PLST blends, since the films prepared for these blends disintegrated into small pieces within 1 day after immersion in water. This behaviour makes these OCST blends appropriate for packaging applications, where water absorption must be minimal.

#### ACKNOWLEDGEMENTS

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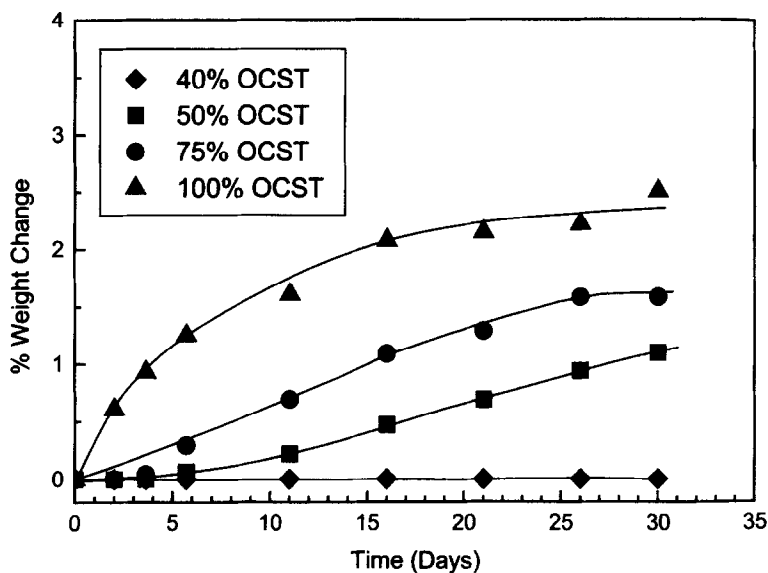


Fig. 14. % Water absorption by LDPE/OCST blends.

## CONCLUSIONS

In this study we have prepared a new thermoplastic, octanoated starch, and characterised it with a number of techniques. The degree of substitution of the modified starch was rather high (equal to 2.7) and, as a consequence, its degree of hydrophobicity was high as well. The new thermoplastic, when blended with LDPE, leads to products that exhibit interesting thermomechanical behavior. Compared to blends of LDPE with plasticised starch, these blends show higher thermal stability, higher elongation at break, and much lower water absorption. Regarding practical applications, however, one must keep in mind that the cost of the new thermoplastic is much higher compared to unmodified starch. The rate of biodegradation of the new thermoplastic is also expected to be slower than that of native starch. Work is underway in our laboratory for the evaluation of this biodegradation rate and other key thermomechanical properties of a series of systematically modified starches.

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