

LDPE/Starch Blends Compatibilized with PE-*g*-MA Copolymers

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Received 17 November 1997; accepted 13 February 1998

ABSTRACT: In the present study, low-density polyethylene (LDPE) and plasticized starch (PLST) blends, containing different percentages of PLST, were prepared. In these blends, two different polyethylene/maleic anhydride graft (PE-*g*-MA) copolymers containing 0.4 and 0.8 mol % anhydride groups, respectively, were added as compatibilizers at 10 wt % PLST. The compatibilization reaction was followed by FTIR spectroscopy. The morphology of the blends was studied using scanning electron microscopy (SEM). It was found that as the amount of anhydride groups in the copolymers increases a finer dispersion of PLST in the LDPE matrix is achieved. This is reflected in the mechanical properties of the blends and especially in the tensile strength. The blends compatibilized with the PE-*g*-MA copolymer containing 0.8 mol % anhydride groups have a higher tensile strength, which in all blends, even in those containing 20 and 30 wt % PLST, is similar to that of pure LDPE. The biodegradation of the blends followed the exposure to activated sludge. It was found that the compatibilized blends have only a slightly lower biodegradation rate compared to the uncompatibilized blends. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1503–1521, 1998

Key words: polyethylene; starch; poly(ethylene-*g*-maleic anhydride); compatibilization; biodegradation

INTRODUCTION

Over the last 50 years, synthetic plastics have become the major new materials replacing the traditional ones such as paper, glass, steel, and aluminum in many applications. Thus, the total volume of plastics production nowadays exceeds that of steel.¹ Their main advantages are that they can be easily formulated, producing materials with desirable properties that are light in weight and cheap to produce and with low-energy requirements for their transport and especially for their production. But plastics also have some disadvantages, mainly, the nonbiodegradability

of most of them, causing many environmental problems associated with plastic disposal after their usage.

Polymer recycling is an environmentally attractive solution, but the results in a worldwide scale have not been too successful so far. The biggest percentage of recycling has been achieved in some European countries, mainly due to an efficient combination of mechanical and chemical methods for plastics recovery. A variety of mechanical methods for recycling plastics has already been developed² and a large portion of the recycled plastics can be used for energy production.³ Significant progress has been achieved in the last few years in the technology of chemical recycling of plastics as well. This includes the melting and depolymerization of plastics into their corresponding monomers which can be reused. Already, major companies such as BASF,

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Contract grant sponsor: EU/DG XI; contract grant number: LIFE# A127-01208.

Journal of Applied Polymer Science, Vol. 70, 1503–1521 (1998)
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VEBA, and BP have developed the necessary know-how and they are investing in this technology by building new plants.⁴ Nevertheless, it is calculated that worldwide only 1% of the produced plastics is recycled,⁵ whereas the remaining part, especially of plastics used for packaging materials, ends up in municipal burial sites. It is estimated that plastics compose approximately 7.2 wt % (20% by volume) of the total litter, contributing significantly to the problem of litter management.

Thus, in the last 20–30 years, there has been an increased interest in the production and use of fully biodegradable polymers with the main goal being the replacement of nonbiodegradable plastics, especially those used in packaging materials. Such biodegradable plastics which are commercially available are polycaprolactone, polyhydroxyalkanoates, and especially poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate (Biopol[®]), poly(lactic acid), poly(butylene succinate), and poly(butylene succinate-*co*-adipate) (Bionolle[®]), poly(vinyl alcohol), and poly(ethylene glycol). However, although many of the above-mentioned polymers possess the required properties and can be used for the production of blown film and injection -molded articles, they are not widely used due to their high cost. Biodegradable polymers are estimated to be four to six times more expensive than polyethylene or polypropylene, which are the most widely used plastics for packaging applications.

Many research and industrial attempts have been focused on the use of natural biopolymers such as starch, cellulose, lignin, chitin, and chitosan, which are also fully biodegradable. In addition, these materials are also very cheap and they are produced from renewable, natural sources. However, the above biopolymers are unsuitable for most uses in the plastics industry: They are susceptible to water absorption, they are formulated by using special techniques, and the final products have poor physical properties. Some approaches to overcome these problems include chemical modification by simultaneously changing their hydrophilic character to hydrophobic. Such examples are cellulose and starch esters.^{6–8} But in most cases, these modified biopolymers still have inferior mechanical properties and the cost for their esterification is high.

Starch has a high biodegradation rate and in the early 1970s Griffin had the idea to use granular starch as a filler in polyethylene in order to increase the biodegradability of the resulting material.⁹ It was also used as an additive in biode-

gradable synthetic polymers in order to decrease their cost¹⁰ as well as in nonbiodegradable polymers like PVC and ABS,¹¹ EAA,¹² EVA, and PP.¹³ Most of starch applications, however, are focused on polyethylene. The latter is widely used as packaging material and as mulch film in agricultural applications. In both cases, recycling of the plastic is very difficult. As a result of these efforts, in the last few years, several commercial products have been developed, most of them containing low amounts of starch.¹⁴ Increasing the amount of starch causes a decrease in both tensile strength and elongation at break. As a result, the produced materials lose their ability to produce blown films. This decrease arises from poor adhesion between starch and low-density polyethylene (LDPE) due to the different polar character of starch and LDPE. To increase the incorporated amount of starch, the latter can be surface-treated with a hydrophobic additive¹⁵ or a compatibilizer can be used.

The ethylene–acrylic acid (EAA) copolymer is the most effective compatibilizer so far, but it must be used in high amounts in order to obtain satisfactory mechanical properties. Otey et al. produced blown films containing up to 40–50 wt % gelatinized starch along with EAA and ammonia.^{16,17} The carboxylic groups of EAA can form V-type complexes with starch,^{18,19} increasing the ability to use higher amounts of starch. But in this case, it was found that EAA inhibits the rate of starch biodegradation.²⁰ On the other hand, EAA has an accelerating effect on the thermooxidative degradation of LDPE/starch blends when used in low amounts together with a prooxidant.²¹

Similar complexes like EAA can also be formed with the hydroxyl groups of the polyethylene–vinyl alcohol (EVOH) copolymer.²² As a result, materials with a high amount of starch can be produced. Also, the addition of EVOH can increase the processability and injection moldability of plasticized starch.²³ Poly(vinyl alcohol), however, is water-soluble, thus limiting the use of such materials in aquatic environments.

In the last few years, increased interest has appeared in the use of starch together with polymers containing reactive groups. Such polymers are the styrene–maleic anhydride (SMA) copolymer and the ethylene propylene-*g*-maleic anhydride copolymer (EPMA).^{24–26} In the present study, two polyethylene-*g*-maleic anhydride (PE-*g*-MA) copolymers containing 0.4 and 0.8 mol % anhydride groups were used. The main objective

was to test the compatibilization capacity of these materials in LDPE/plasticized starch (PLST) blends.

EXPERIMENTAL

Materials

The LDPE (Borealis) used was appropriate for packaging applications with a melt flow index of 2 g/10 min at 190°C. PE-*g*-MA copolymers containing 0.4 and 0.8 mol % anhydride groups (as measured by titration with an alcoholic NaOH solution) was kindly supplied by DuPont (Canada) under the trade names MB-158 (melt flow index 1.1 g/10 min at 190°C) and MB-110 (melt flow index 32.5 g/10 min at 190°C), respectively. The native corn starch containing 30 wt % amylose and 70 wt % amylopectin was supplied by Amylum (Greece). It was plasticized with 25 wt % glycerol in a Haake–Buchler Reomixer at 180°C for 10 min and will be referred to hereafter as PLST.

Melt Blending

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 cm³. Prior to mixing, the polymers and especially PLST and PE-*g*-MA were dried separately by heating in a vacuum oven at 80°C for 24 h. The components were physically premixed before being fed into the Reomixer. Mixing was performed at 180°C and 60 rpm for 15 min. For the LDPE/PLST blends, five different levels of PLST were used, namely, 5, 10, 15, 20, and 30 wt %. In these blends, two different PE-*g*-MA copolymers containing 0.4 and 0.8 mol % anhydride groups were used as compatibilizers, at an amount of 10 wt % based upon PLST. Melt temperature and torque were recorded during the mixing period. After preparation, the blends were milled and 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 4 cm⁻¹ resolution were coadded. Samples were measured in the form of thin films about 70 ± 2 μm; thick, which were prepared by hot-press molding.

Blend Morphology

The morphology of the blends was studied with scanning electron microscopy (SEM), using a JEOL microscope Model JSM-840A. For this reason, a thin film from each blend was prepared in a hydrolytic press, about 120 ± 3 μm; thick. To remove the PLST from the blend, the films were treated with hot water in 80°C for 24 h. Afterward, the films were coated with gold and observed by SEM.

Mechanical Properties of Blends

Measurements of the mechanical properties such as tensile strength (at break) and elongation at break were performed according to the ASTM D638 method on an Instron mechanical tester, Model 1122. The films of the samples (about 150 ± 5 μm; thick) were prepared in a hydrolytic press at 170°C. Measurements were done using a 5-mm/min crosshead speed. Prior to the measurements, the samples were conditioned at 50 ± 5% relative humidity for 24 h by placing them in a closed chamber containing a saturated Ca(NO₃)₂ · 4H₂O solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Dynamic Thermomechanical Analysis

The dynamic thermomechanical properties of the blends were measured with a Rheometrics Scientific analyzer Model MK III. The tensile method was used at a frequency of 1 Hz, a strain level of 0.071%, and a range of temperature from –120 to 100°C. The heating rate was 3°C/min. The static force was chosen so that the experiments were made in the linear region of elasticity and without causing drawing effects. To specify this force, several stress–strain experiments were made beforehand. Also, the ratio of the static-to-dynamic force was constant during the experiment. The testing was performed using about 8 × 6 × 0.3-mm rectangular strips. The exact dimensions of each sample were measured before the scan.

Water-Absorption Measurements

Water absorption was measured using 30 × 80-mm film strips of 120 ± 2-μm; thickness according to the ASTM D570-81 method. Water-absorption measurements were performed by soaking the samples in distilled water. At regular

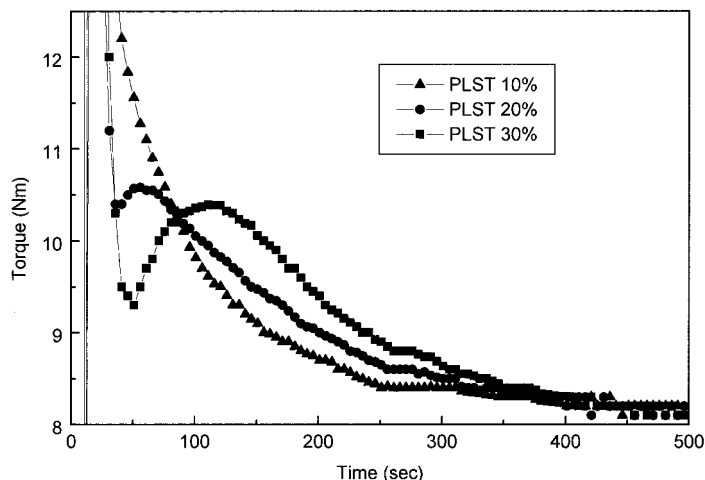


Figure 1 Torque curves of LDPE/PLST compatibilized blends.

time intervals, each sample was removed from the water tank, dried by wiping with blotting paper, and subsequently weighted to determine the water uptake. The samples were placed back in the water after each measurement. The water absorption was calculated as the weight difference and is reported as percent increase of the initial weight.

Sample Biodegradability

The polymer blends in the form of thin films of $120 \pm 2 \mu\text{m}$; thickness were exposed to activated sludge in a wastewater treatment facility of a food treatment plant for 8 weeks. The test permitted us to evaluate the rate of aerobic biodegradability by measuring the weight loss and mechanical properties of the studied samples after 2, 4, 6, and 8 weeks of exposure to activated sludge. The temperature of the sludge was constant during the 8 weeks ($25 \pm 1^\circ\text{C}$) and the pH was about 7. In these blends, the compatibilizer level was fixed at 10 wt % PLST.

The measurements performed to follow the biodegradation of the samples were the following:

- Sample weighting to measure the starch weight loss. In fact, in all samples after immersion in activated sludge, there is a weight increase due to the water absorption. We defined weight loss as the difference between the water absorption in pure water and in activated sludge at the same exposure time. In the second case, due to the starch consumption of the microorganisms, the percent

water absorption is always lower than in pure water.

- Scanning electron microscopy. The surfaces of the film specimens after removing them from activated sludge were dried in a vacuum oven at 70°C for 24 h and coated with gold to avoid charging under the electron beam.
- Mechanical measurements such as tensile strength and elongation at break were as described before.

RESULTS AND DISCUSSION

Figure 1 shows the torque curves of the LDPE/PLST blends containing also the compatibilizer with 0.8 mol % anhydride groups. The compatibilizer was added at 10 wt % based on the PLST level.

In uncompatibilized blends, it was observed that the torque decreases as the amount of PLST increases in the blend.²⁷ This behavior arises from the lower melt viscosity that PLST has compared to LDPE (about 20 times lower as deduced from the melt flow index at 190°C). However, in our compatibilized samples, the torque magnitude seems to have the opposite behavior initially and stabilizes after 400 s of mixing, remaining unchanged afterward. In the blend with 10 wt % PLST, the torque decreases continuously until it becomes stable, while in the blend with 20 wt % PLST, there is a small increase after the initial melting of the materials. This phenomenon is

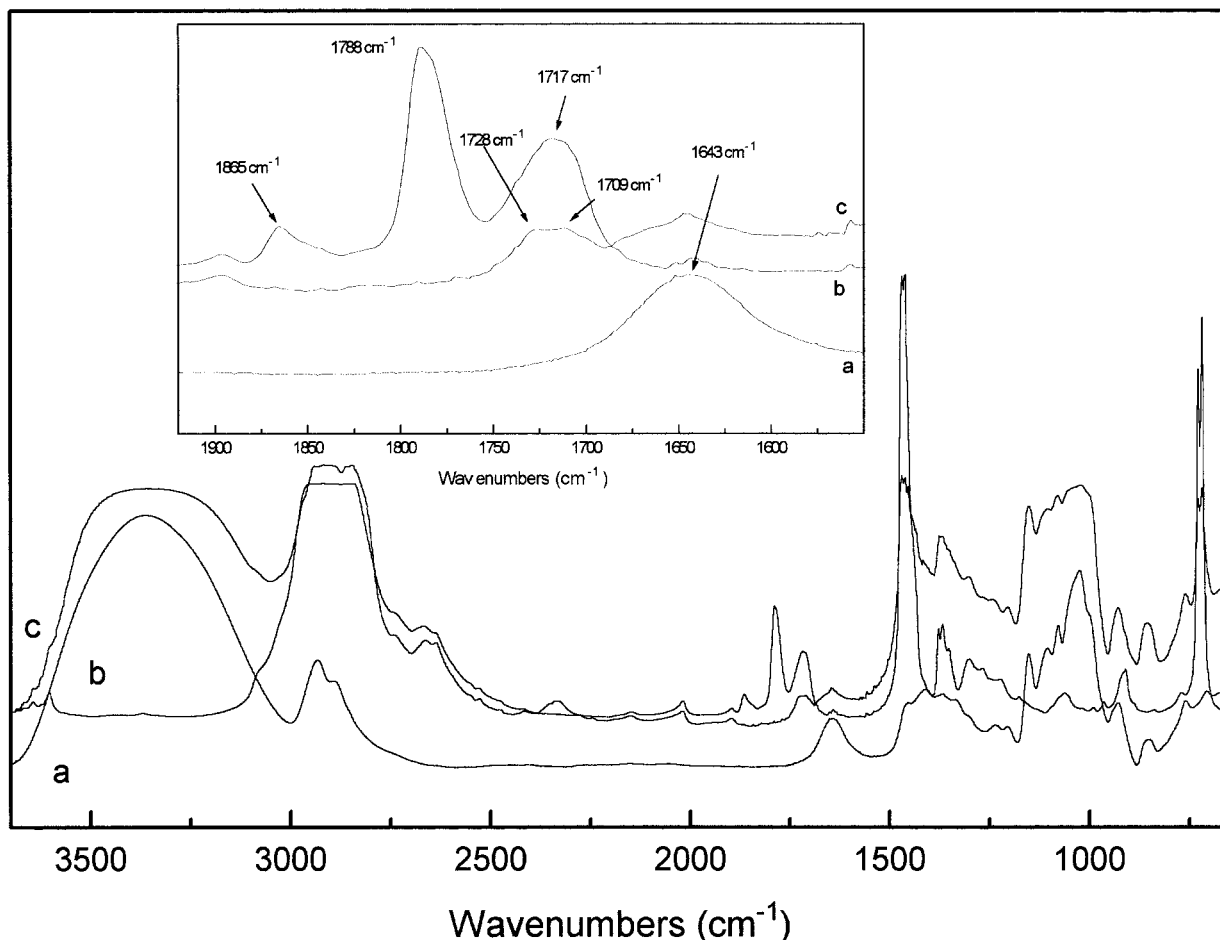


Figure 2 FTIR spectra of (a) PLST, (b) PE-*g*-MA, and (c) compatibilized LDPE/PLST 70/30 w/w blend.

more pronounced in the blend prepared with 30 wt % PLST, where a peak in torque appears. Such an increase in the torque is expected in reactive blends^{28,29} and is attributed to the reaction between the chemically reactive groups of the materials. In our case, these groups are the anhydride groups of the compatibilizer and the hydroxyl groups of either the starch or glycerin. For this reaction, branched and crosslinked macromolecules are produced which have a higher melt viscosity compared to linear macromolecules. In the blend containing 10 wt % PLST, this peak cannot be observed since the concentration of the reactive groups is very small (the total amount of PE-*g*-MA is 1 wt %). Thus, the amount of branched or crosslinked macromolecules produced is not enough to cause a torque increase as is the case in blends containing 20 and 30 wt % PLST. As the amount of starch increases, a higher amount of PE-*g*-MA is used and therefore a larger

amount of branched and crosslinked macromolecules is produced. The presence of these macromolecules must be the reason why the torque does not decrease with an increasing amount of starch in the blends. A similar increase in torque by increasing the amount of starch was also observed when starch was blended with polymers containing reactive groups such as SMA copolymers.²⁶

From the observation of the torque curves, it is concluded that the reaction is essentially complete within the first few minutes, since after the initial increase in torque, observed during the first 100 s of mixing, the torque subsequently decreases gradually until the final stable value. This indicates that, essentially, all the anhydride groups have reacted, possibly due to the large excess of hydroxyl groups. To verify this assumption and to estimate the amount of anhydride that has reacted, the blends were studied with FTIR spectroscopy (Fig. 2).

In the spectra of PLST, the characteristic broad peak at $960\text{--}1190\text{ cm}^{-1}$, which is attributed to C—O stretching, is present, along with the hydroxyl group peak at $3000\text{--}3600\text{ cm}^{-1}$. The spectrum of the copolymer used as the compatibilizer shows the characteristic peaks of the anhydride group at 1865, 1788, and 1717 cm^{-1} .³⁰ In the blend produced, the peaks at 1865 and 1788 disappear and a broad peak at 1728 cm^{-1} is formed, attributed to ester groups formed by the reaction of the hydroxyl groups with the anhydride groups. There is also a small peak at 1709 cm^{-1} due to the carboxyl groups which are simultaneously produced by the above reaction. Thus, examination of the FTIR spectra of the blends indicates that the anhydride groups of the compatibilizer have reacted.

In the PE/starch blends, containing EAA as the compatibilizer, it was found that the carboxylic groups of EAA can form hydrogen bonds with the hydroxyl groups of starch. This can also be verified from the FTIR spectra by the peak at 2674 cm^{-1} , which is attributed to O—H stretching in a hydrogen-bonded carboxyl dimer.³¹ In our blends, a carboxylic group is formed for each reacting anhydride group. These groups could also enhance hydrogen bonding, thus enhancing the compatibilization capacity of the copolymer. But a similar absorption is also detected at the same spectral region due to the carbonylic groups of anhydride, and as a result, any peak due to hydrogen bonding is masked. On the contrary, a broad peak was observed at 1702 cm^{-1} which can be attributed to hydrogen-bonded carbonyls. This area is more characteristic of hydrogen-bond formation. This peak, however, is very weak and the spectral noise makes its definite assignment to hydrogen bonding difficult.

Blends Morphology

In polymer blends, it is necessary to study the morphology of the final product since most of its properties, especially its mechanical properties, depend on it. In most cases, the major component of the blend forms the matrix, whereas the minor component is the dispersed phase. Thus, in the LDPE/PLST blends, PLST is expected to be the dispersed phase. As a result, after treatment with hot water, PLST will be removed, leaving cavities in the places where it was initially present. In Figure 3, the SEM microphotographs of uncompatibilized blends are presented.

By examining the morphology of the blends, it can be seen that the size of the starch phase increases with an increasing amount of PLST. Thus, in the blends with 10 wt % PLST, the average size is about $8\text{ }\mu\text{m}$; whereas in the blends with 20 wt % PLST, it becomes about $33\text{ }\mu\text{m}$; It is remarkable that in blends containing less than 15 wt % PLST there is a fine dispersion and homogeneity of PLST in the LDPE matrix. The large sizes of the PLST phases produced, especially in the blend containing 30 wt % PLST, suggest that the adhesion between PLST and LDPE is very poor and the two polymers are strongly incompatible. The interfacial tension is very high, leading to the phase separation of the two polymers in the melt state.

When in the above blends the PE-*g*-MA copolymer containing 0.4 mol % anhydride groups is added as the compatibilizer (with 10 wt % PE-*g*-MA based on the PLST content), the size of the PLST phase decreases compared to the respective uncompatibilized blends. This is more pronounced in the blends containing 20 and 30 wt % PLST, which also become more homogeneous. The above is evidence that the interfacial tension has been decreased. Branched and crosslinked macromolecules that are produced by the reaction between PE-*g*-MA and PLST act as emulsifiers. They contain different parts, each one compatible with one of the two polymers. This structure gives them the ability to place themselves in the interface of LDPE-PLST during melt blending. The result is a reduction in the interfacial tension between the two polymers and a finer distribution of PLST in all the compatibilized blends (Fig. 4).

The decrease of the size of the PLST phase seems to be strongly affected by the amount of anhydride groups that the compatibilizer contains. Thus, in the blends in which the PE-*g*-MA used contains 0.8 mol % maleic anhydride, the reduction of the PLST phase size is larger (Fig. 5). The phase size in all compatibilized blends is lower than $5\text{ }\mu\text{m}$; and is detectable only in higher magnification. This better dispersion arises from the higher amount of branched or crosslinked copolymers that are produced, since this PE-*g*-MA copolymer has more anhydride groups available to react with the hydroxyls.

By carefully examining the SEM microphotographs of the blends, we conclude that the size of the PLST phase is not uniform. While most of the droplets have a size close to a mean value, there are also much larger and much smaller ones. This is better presented in Figure 6, showing the size

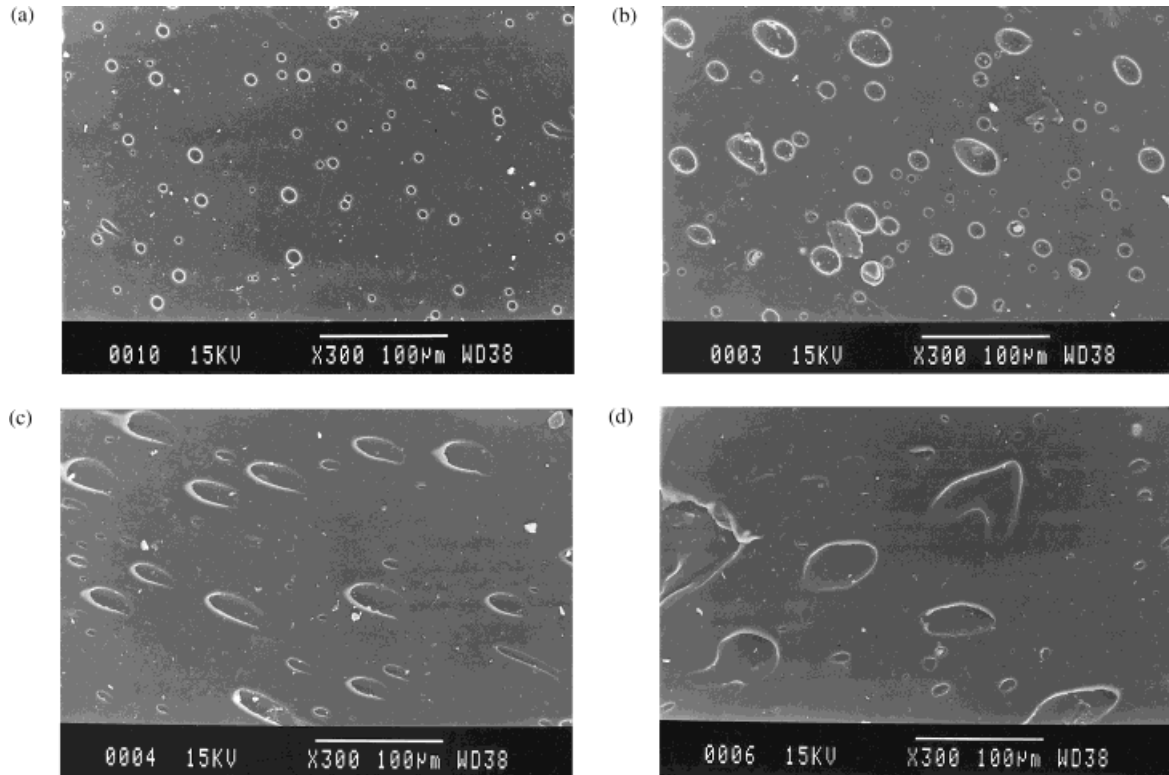


Figure 3 SEM microphotographs of uncompatibilized LDPE/PLST blends: (a) 90:10; (b) 85:15; (c) 80:20; (d) 70:30 w/w.

distribution and the deviation from the mean value for all blends prepared, as calculated from the SEM photographs.

In the uncompatibilized blends, it can be seen that, as the amount of PLST increases in the blend, the deviation of the phase size from the mean value is increasing. Thus, in the blend containing 30 wt % PLST except from the large-sized droplets (about 90 μm), there are also small ones (about 20 μm). These measurements confirm that in the incompatible blends after phase separation each component has the tendency to aggregate, forming large phases, especially in blends containing almost equal amounts of each component. When PE-*g*-MA is added as the compatibilizer in the above blend, the size range of the phases decreases. By comparing the compatibilized blends, we can conclude that the size reduction is larger in the blends where the compatibilizer with the larger content of anhydride was used. It is also remarkable that the phase size does not exceed 3 μm , even in blends with high PLST content, while most PLST domains are approximately about 1 μm in size.

By examining blends in which the PE-*g*-MA with the higher content of anhydride was used as the

compatibilizer, we can see that for blends containing 5 and 10 wt % PLST the phase size is larger compared to that of the blends containing larger amounts of PLST. In fact, it is similar even to the phase size of the blends in which the PE-*g*-MA with the lower content of anhydride was used. It is probable that in addition to the anhydride content the frequency of the reacting groups also plays an important role in phase-size reduction. Since the compatibilizer is used at a 10% level based on the starch, in blends containing high amounts of starch, the reactive groups of the compatibilizer have a much higher probability to react. This higher probability would imply that blends with even higher starch content could be prepared by using higher amounts of the compatibilizer.

Mechanical Properties

Figure 7 shows the variation of the tensile strength in the LDPE/PLST blends that were prepared. In the uncompatibilized blends, there is a continuous reduction in tensile strength as the amount of PLST increases. This behavior can be explained by examining the SEM micrographs of

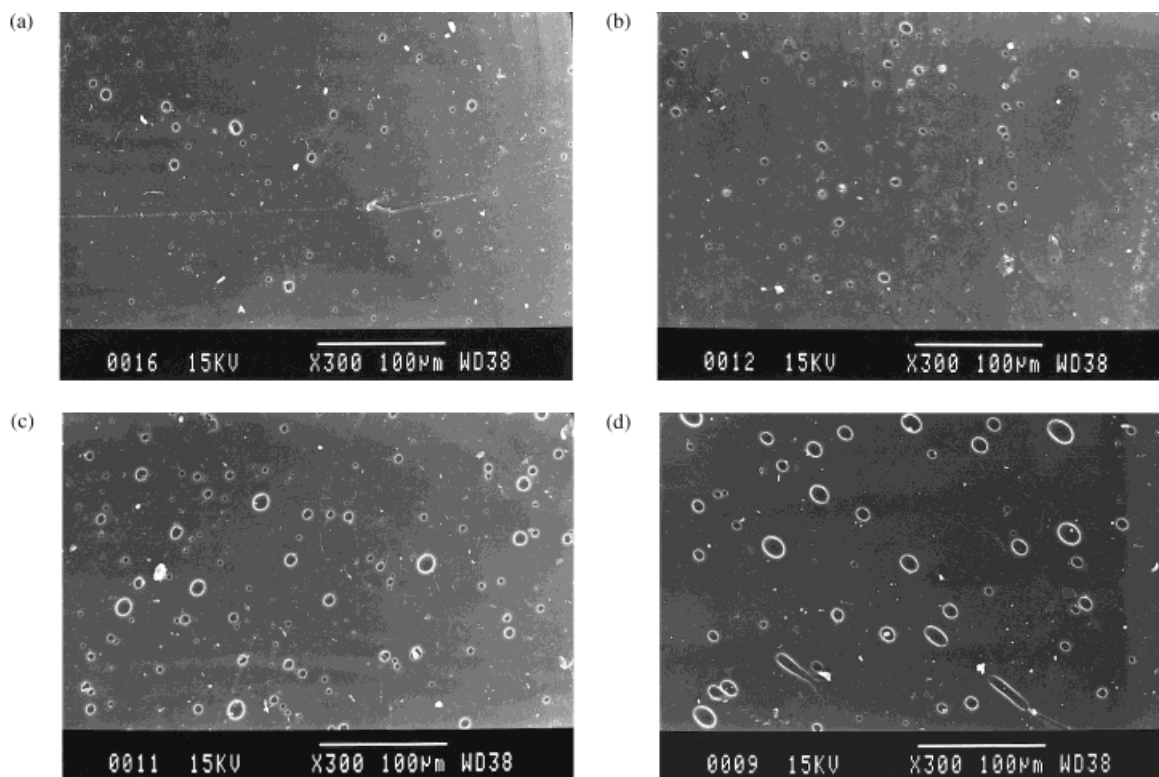


Figure 4 Compatibilized LDPE/PLST blends with PE-*g*-MA, containing 0.4 mol % anhydride groups: (a) 90:10; (b) 85:15; (c) 80:20; (d) 70:30 w/w.

the respective blends. Due to the increase in phase size that occurs in higher contents of PLST, blends containing 20 and 30 wt % PLST show the lowest tensile strength. Thus, it can be said that the incompatibility between the two polymers greatly affects the mechanical properties of the blends. Another possible explanation is that PLST has a smaller contribution to the tensile strength of the blends, since it has a very low tensile strength (about 1 MPa). This is mainly due to the glycerine which as a plasticizer lowers the tensile strength of the starch, as this high reduction of the tensile strength of PLST is also responsible for the starch degradation that takes place during the plasticization, due to the high temperatures and shear forces used.³² If water is used for the starch destructurezation, the tensile strength was reported to be about 30–40 MPa.^{33,34} But in this case, elongation at break is very small (about 4%).

In addition to a plastisized form, starch can also be used in polymer blends as a filler in a granular form. But the addition of granular starch in LDPE has the same result, as is the case of PLST, namely, the reduction of tensile strength. In fact,

this reduction follows the general trend of filler addition in polymer composites³⁵ and it has been reported that the reduction becomes more pronounced with increasing starch granular size.³⁶ In a previous work, we found that higher amounts of starch can be incorporated with LDPE when it is used in a thermoplastic (plasticized) form.³⁷ This was the main reason for using thermoplastic starch in the present work.

The compatibilized blends have a quite different behavior. In the blends that were compatibilized with PE-*g*-MA containing 0.4 mol % anhydride groups, a decrease in tensile strength was observed as the amount of PLST increased. This decrease, however, is smaller compared with the corresponding decrease in the uncompatibilized blends. Even in the blends with 20 and 30 wt % PLST, the decrease is only 4.5% of the initial LDPE's tensile strength. The absolute value of the tensile strength for all compatibilized blends is, of course, higher compared with the strength of their uncompatibilized counterparts. Furthermore, the finer dispersion of PLST in the blends, prepared with the compatibilizer containing 0.8 mol % anhydride groups, is reflected more strongly in the tensile strength of

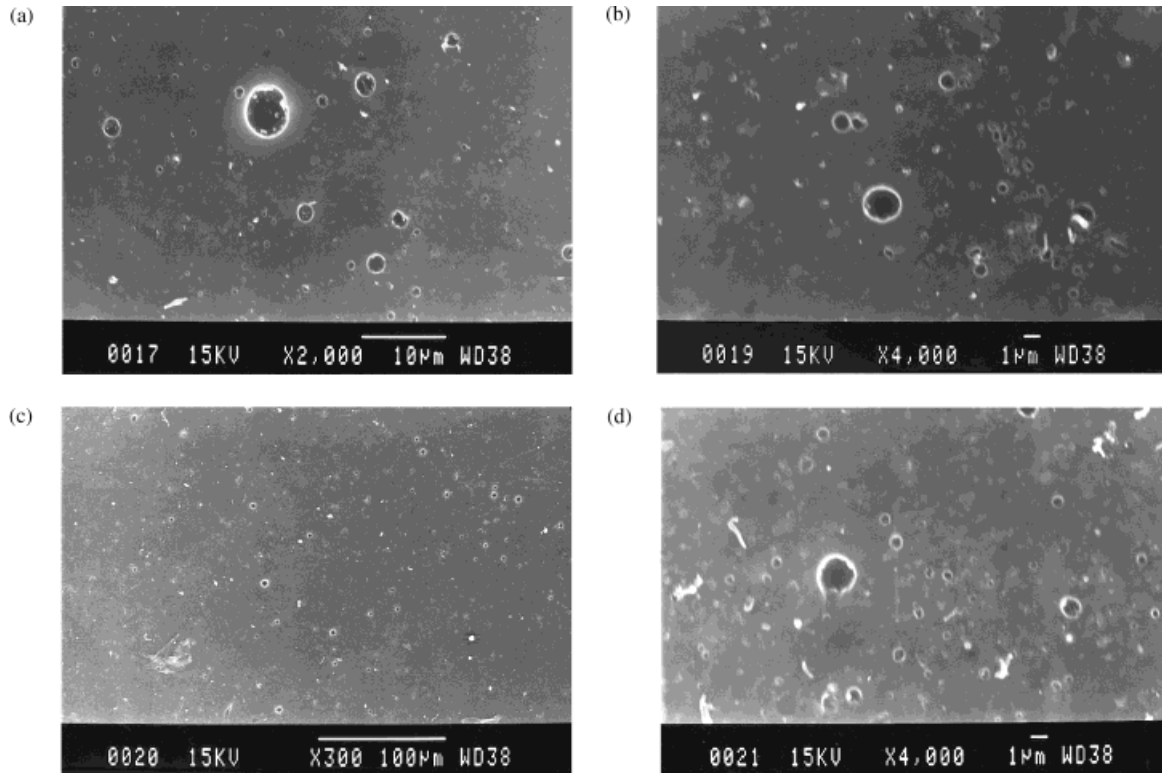


Figure 5 Compatibilized LDPE/PLST blends with PE-g-MA containing 0.8 mol % anhydride groups: (a) 90:10; (b) 85:15, (c) 80:20; (d) 70:30 w/w.

these blends. There is no decrease, but, in fact, the tensile strength remains almost stable: Even the blend containing 30 wt % PLST has the same tensile strength as that of pure LDPE.

The compatibilized blends also exhibited an increase in the elongation at break compared to

the uncompatibilized ones. The trend is similar to that of the tensile strength. In the uncompatibilized blends, the reduction of the elongation at break increases with an increasing amount of PLST. In the compatibilized blends, the increase is higher in the blends compatibilized with the

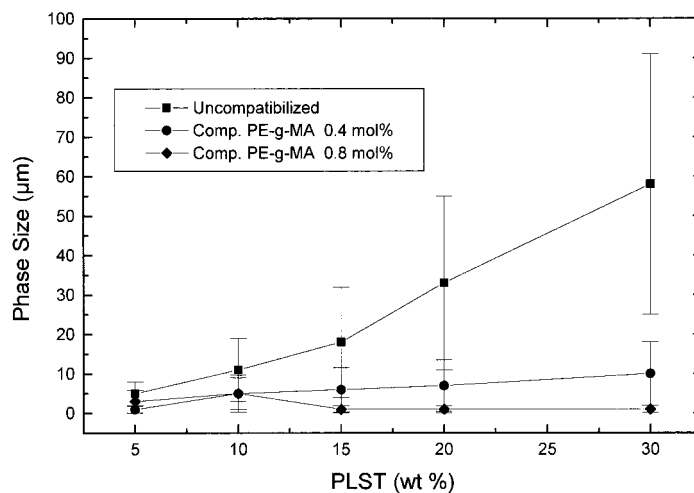


Figure 6 Size range of PLST phase in uncompatibilized blends.

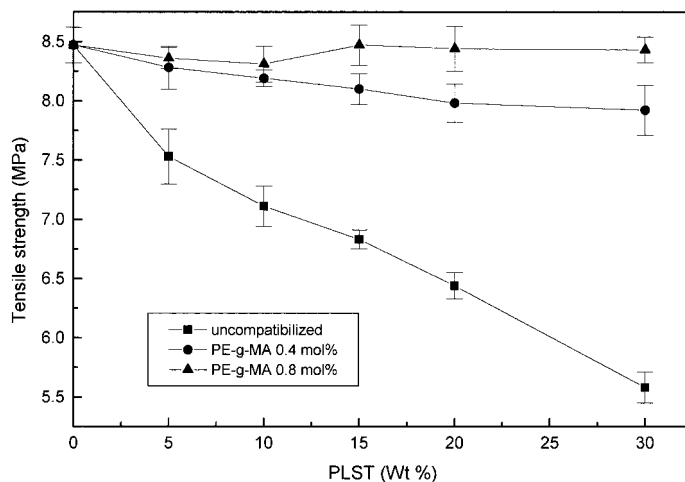


Figure 7 Tensile strength of LDPE/PLST blends.

copolymer richer in anhydride groups. However, the elongation at break still remains lower compared to that of pure LDPE (Fig. 8).

From the above measurements of the mechanical properties, we can conclude that PE-*g*-MA copolymers are effective compatibilizers for LDPE/PLST blends. Only very small amounts, 0.5–3.0 wt %, are needed, leading to a large improvement of mechanical properties and especially tensile strength. Other compatibilizers and especially EAA must be used in very high amounts in order to produce comparable results. It is evident that the mechanical properties strongly depend on the dispersion and phase size of PLST in the LDPE matrix. As the size of the dispersed phase becomes smaller, an increase in mechanical properties and especially in tensile

strength is observed. A small contribution to this behavior may be due to the presence of branched or crosslinked macromolecules that are produced by the reaction of the compatibilizer and the PLST macromolecules. These macromolecules have higher tensile strength, compared to the linear ones, but lower elongation at break. Their presence could also explain, in part, why the increase in elongation at break was not as evident as in the tensile strength of the blends.

Dynamic Mechanical Analysis (DMTA)

Dynamic mechanical analysis is a very useful technique for studying the viscoelastic response of the polymers as well as their blends in a wide range of temperatures. DMTA is able to detect

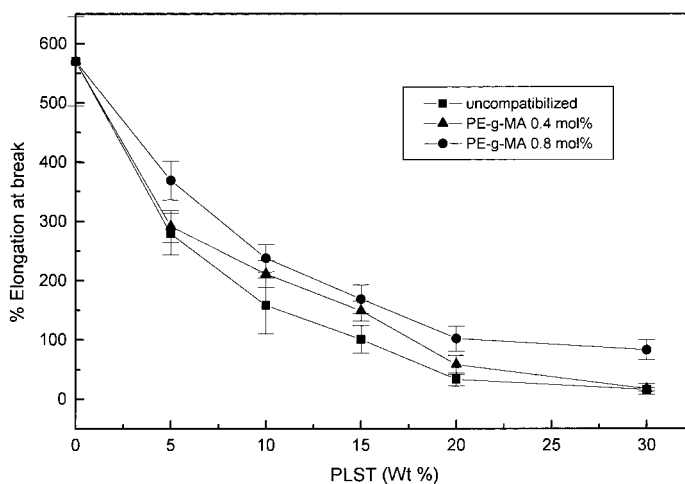


Figure 8 Elongation at break of LDPE/PLST blends.

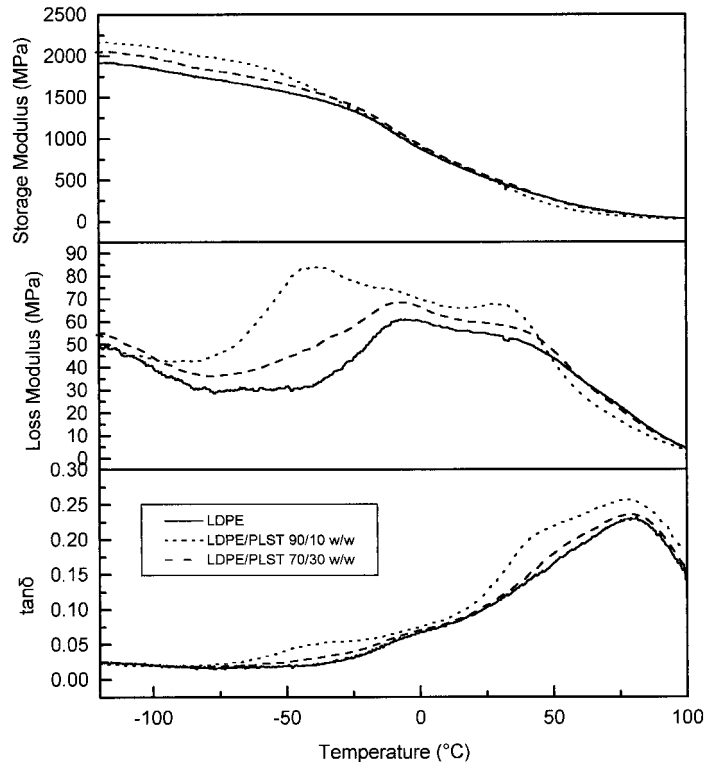


Figure 9 DMTA thermograms of uncompatibilized blends: (a) storage modulus; (b) loss modulus; (c) $\tan \delta$.

transitions such as glass transitions or secondary transitions arising from molecular motions of side groups or small segmental motions. The sensitivity of this method is about 2000 times higher than that of DSC.³⁸ In Figure 9, the DMTA thermographs of uncompatibilized LDPE/PLST blends are presented.

As can be seen, the change in the storage modulus G' with temperature is rather complex. At temperatures lower than -25°C , G' increases with an increasing amount of PLST in the blend. In this temperature region, most of the molecular motions are "frozen in"; it can be said that the blends behave like a rigid filled system. On the contrary, this trend diminishes with increasing temperature, and at temperatures higher than 50°C (the rubbery plateau), it is reversed. This can be attributed to the lower viscosity of PLST as compared with LDPE. The above behavior is the opposite to that observed in similar blends prepared with granular starch and the EPMA copolymer.³⁸ The storage modulus for temperatures above 0°C in the latter was higher when the amount of starch in the blend was increased, since granular starch behaves as a filler at these temperatures.

The changes are more pronounced in the loss modulus (G'') and the loss tangent, $\tan \delta$. LDPE, which has a glass transition between -80 and -120°C and also a secondary transition between -25 and $+10^{\circ}\text{C}$. Unfortunately, PLST was very brittle at low temperatures due to the freezing procedure and all our attempts to measure the thermomechanical behavior of PLST for comparison failed. But, as can be seen from the thermographs of the blends, there is a clear relaxation between -75 and -15°C with a maximum at about -36°C . This is more pronounced in the blend containing 30 wt % PLST and must be attributed to the glass transition of PLST. The T_g of granular starch is estimated to be about 210°C (ref. 39) or 230°C (refs. 40 and 41) as calculated from extrapolated data. A direct measurement of its T_g is not possible because it is very close to the degradation temperature of starch (about 225 – 250°C). The T_g of plasticized starch depends linearly on the water content³² or the amount and the kind of plasticizer used. According to Salla and Tomka,³⁹ the glass transition of a glycerol-plasticized starch was in the range of -40 to -50°C . At the same temperature range, a small transition was detected with DSC in our pure

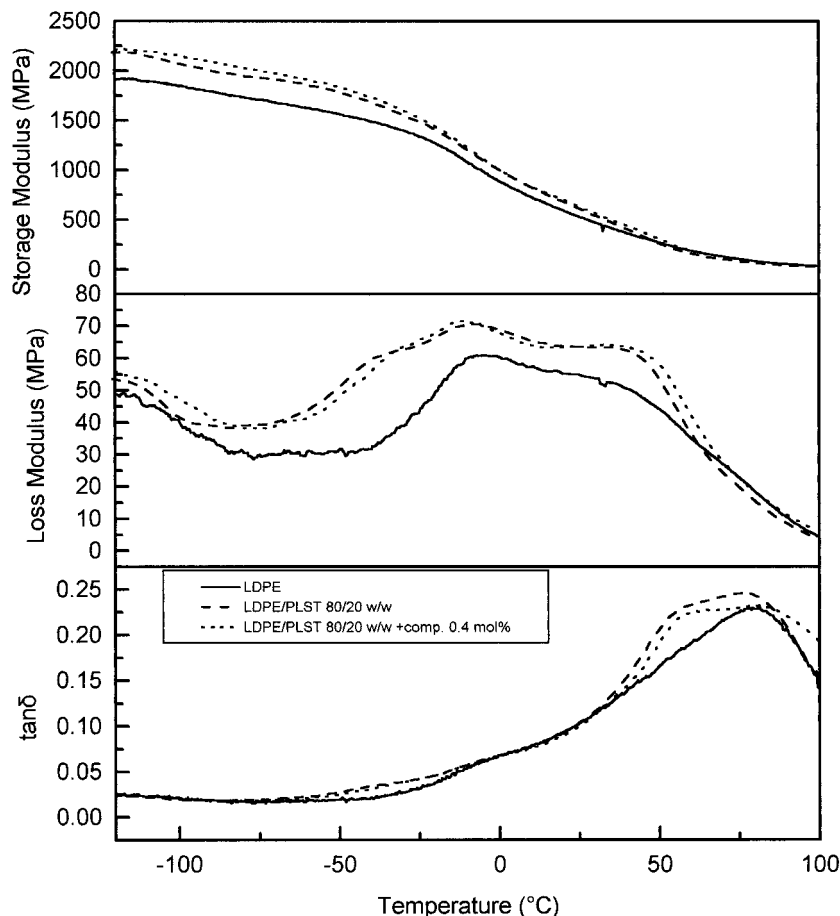


Figure 10 DMTA thermograms of compatibilized blends: (a) storage modulus; (b) loss modulus; (c) $\tan \delta$.

PLST sample. Thus, the maximum, which appears in the DMTA thermographs at about -36°C , must be attributed to the T_g of PLST, taking into account that the T_g determined by DMTA is always higher compared to that determined by DSC. This difference between the two methods depends, of course, on the frequency that was used during the DMTA measurements.

A very weak transition also appears between 15 and 60°C , which is similar to that mentioned by Vaidya et al.³⁸ in granular starch/EPMA blends and was attributed to the glass transition of starch. But in our plasticized starch, its glass transition lies at a lower temperature. Thus, this transition could be attributed to a melting process. It is well known that starch is a mixture of amylose, which is mainly amorphous, and amylopectin, which is crystalline. In native starch, their melting points can be measured only in the presence of high amounts of water, which acts as a plasticizer.^{42,43} But from the DSC experiments,

no melting point was detected in our PLST samples at this temperature region. A similar transition, which was detected by DSC and DMTA in extruded starch containing a high amount of water,⁴² was attributed to the enthalpy relaxation (physical aging) of amorphous starch. Perhaps a similar relaxation takes place also in our PLST samples.

In the compatibilized blends, the behavior is similar to that mentioned for the uncompatibilized blends as can be seen in Figure 10. The only difference is in the value of the storage modulus which is higher in the compatibilized blends. This higher rigidity possibly arises from the branched and crosslinked macromolecules that are produced by the reaction between PE-*g*-MA and PLST.

Biodegradation

The aim of our work was to prepare LDPE/PLST blends containing high amounts of PLST and still

Table I Water Absorption of LDPE/PLST Blends

Time (days)	Percent Weight Increase During Immersion in Distilled Water														
	Uncompatibilized Blends PLST (%)					Compatibilized Blends with PE-g-MA 0.4 mol % PLST (%)					Compatibilized Blends with PE-g-MA 0.8 mol % PLST (%)				
	5	10	15	20	30	5	10	15	20	30	5	10	15	20	30
4	1.6	3.3	3.4	4.5	10.8	1.6	2.2	4.4	6.9	8.8	1.6	3.0	4.5	7.4	9.9
7	1.9	4.1	4.2	5.4	11.4	1.8	3.4	5.3	8.6	11.4	1.6	4.3	5.4	9.9	14.1
10	2.5	4.6	5.0	6.7	10.9	2.1	4.2	6.5	10.5	13.1	2.3	4.9	7.1	11.6	16.5
14	2.6	5.2	6.0	7.6	10.8	2.6	5.0	7.6	12.3	14.0	2.9	5.6	8.8	13.0	16.8
21	3.4	6.8	7.1	9.1	11.2	3.0	6.1	9.1	13.4	14.5	3.6	6.7	11.5	14.6	17.1
28	3.7	6.3	8.1	9.3	10.6	3.9	6.5	9.8	14.6	15.0	4.6	7.8	12.4	16.5	17.7
42	4.9	6.8	10.0	10.7	11.0	5.0	8.2	12.5	14.9	16.7	5.7	9.3	13.6	19.7	20.0
56	6.4	7.4	10.1	11.2	11.5	7.0	8.3	15.6	16.1	17.4	8.2	11.4	17.8	19.8	20.1

have satisfactory mechanical properties. For this reason, PE-g-MA was used as a compatibilizer. As was mentioned earlier, the reaction of anhydride groups with starch hydroxyls results in the production of branched and crosslinked macromolecules. These macromolecules could have a negative effect on the biodegradation rate. In linear polyolefins, it was found that microorganisms can degrade oligomers like triacontadecane ($C_{32}H_{66}$),⁴⁴ but in branched macromolecules, even lower molecular weight molecules are not degraded by microorganisms.⁴⁵ The carboxylic groups produced by the reaction could also have a negative effect upon the biodegradation rate. For the above-mentioned reasons, a biodegradation study of our systems is essential.

One of the most frequently used methods for estimating the biodegradation rate is the weight loss of the samples. Since the biodegradation during soil burial is a slow and time-consuming process (more than 1 year may be required), we decided to measure the biodegradation rate during exposure to activated sludge. However, since starch is a hydrophilic substance, the weight loss data must be corrected for possible water uptake during the exposure. Thus, the samples were first placed in distilled water to determine their water uptake. In Table I, the weight increase of the uncompatibilized as well as of the compatibilized blends, during the time of exposure in distilled water, is shown.

As can be seen, the weight increase in the uncompatibilized blends depends on the time of exposure and the PLST content of the blend. The highest rate for water absorption was observed during the first 5–10 days for all the blends and

especially those with high PLST contents. The uptake rate was slowed afterward. The compatibilizers have a positive contribution to water absorption, and as the amount of anhydride groups increases, the rate becomes higher. Thus, the blends compatibilized with the PE-g-MA copolymer containing 0.8 mol % anhydride groups absorb the highest amount of water. This behavior can be attributed to the production of the carboxylic groups which are hydrophilic in nature and the resulting blends become more hydrophilic than do the uncompatibilized ones. Also, as more carboxylic groups are produced, greater amounts of water can be absorbed. The water absorption of native starch and starch plasticized with glycerol was extensively studied by Sala and Tomka³⁹ and is out of the scope of this work.

In Figure 11 is shown the weight loss of the uncompatibilized blends with the exposure time in activated sludge. The weight loss is insignificant for blends containing 5 and 10 wt % PLST. Only above 20 wt % PLST is there a small loss which becomes larger in the blend with 30 wt % PLST. The maximum weight loss is about 13% of the initial weight. The same behavior was also observed in the compatibilized blends (Fig. 12). Again, only in the blends with 20 and 30 wt % PLST was there a significant weight loss.

The weight-loss measurements suggest that the compatibilized blends have slightly lower degradation rates than those of the corresponding uncompatibilized ones. Furthermore, in compatibilized blends, the biodegradation rate decreases as the content of anhydride groups increases in the copolymers. One possible explanation for this behavior is that the branched macromolecules

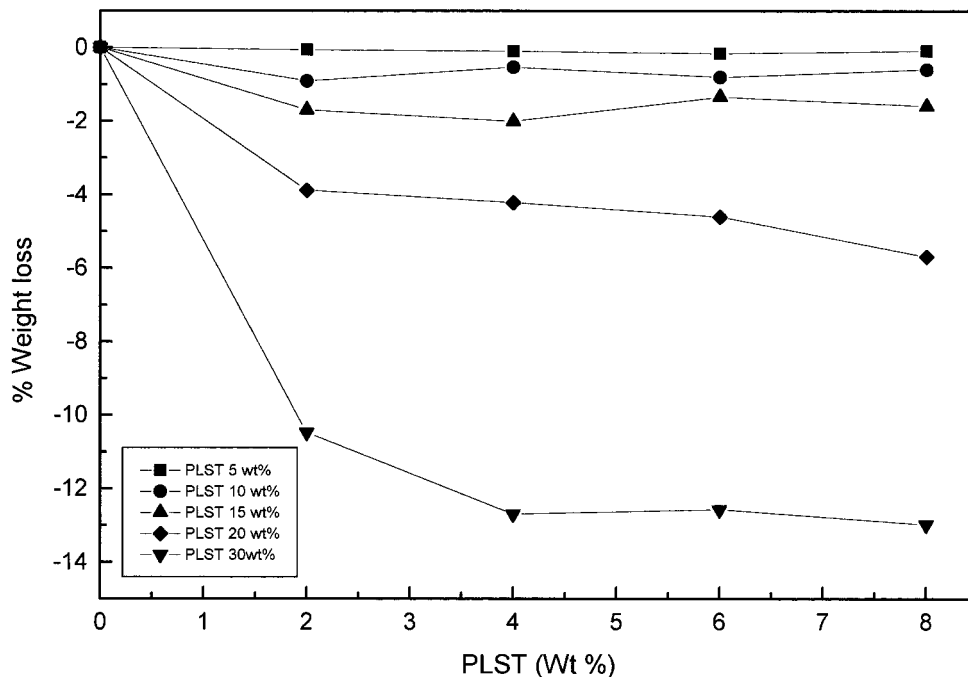


Figure 11 Weight loss of uncompatibilized blends.

which are produced by the reaction between PE-g-MA and PLST have a lower biodegradation rate than that of the linear ones. Thus, in the blends

compatibilized with the PE-g-MA copolymer containing 0.8 mol % anhydride groups, where a higher amount of branched macromolecules are

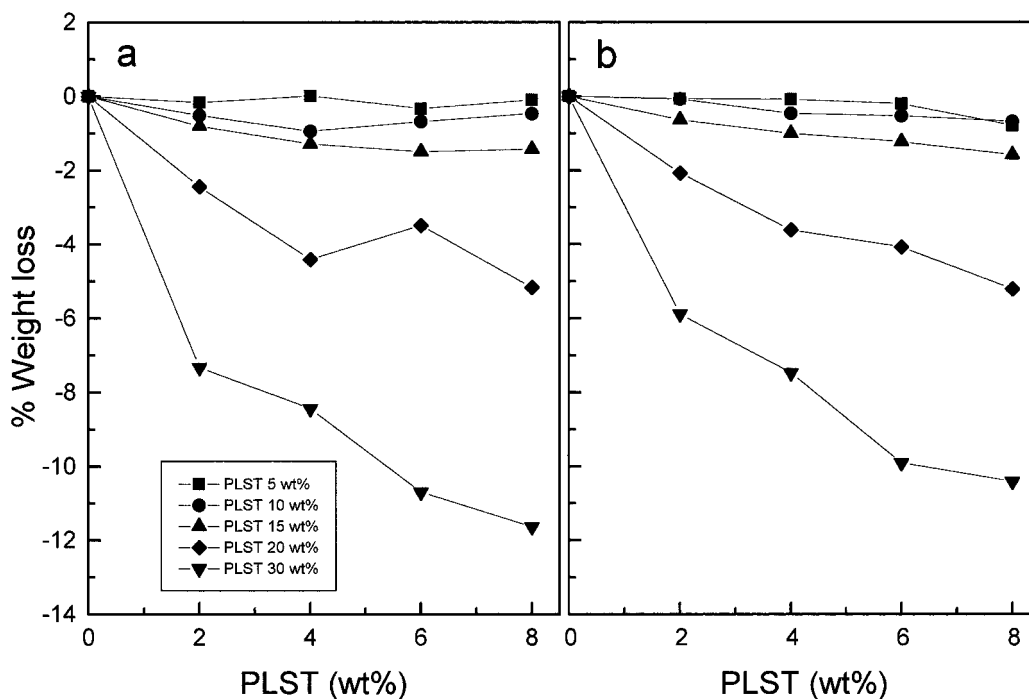


Figure 12 Weight loss of blends compatibilized with PE-g-MA containing (a) 0.4 mol % anhydride groups and (b) 0.8 mol % anhydride groups.

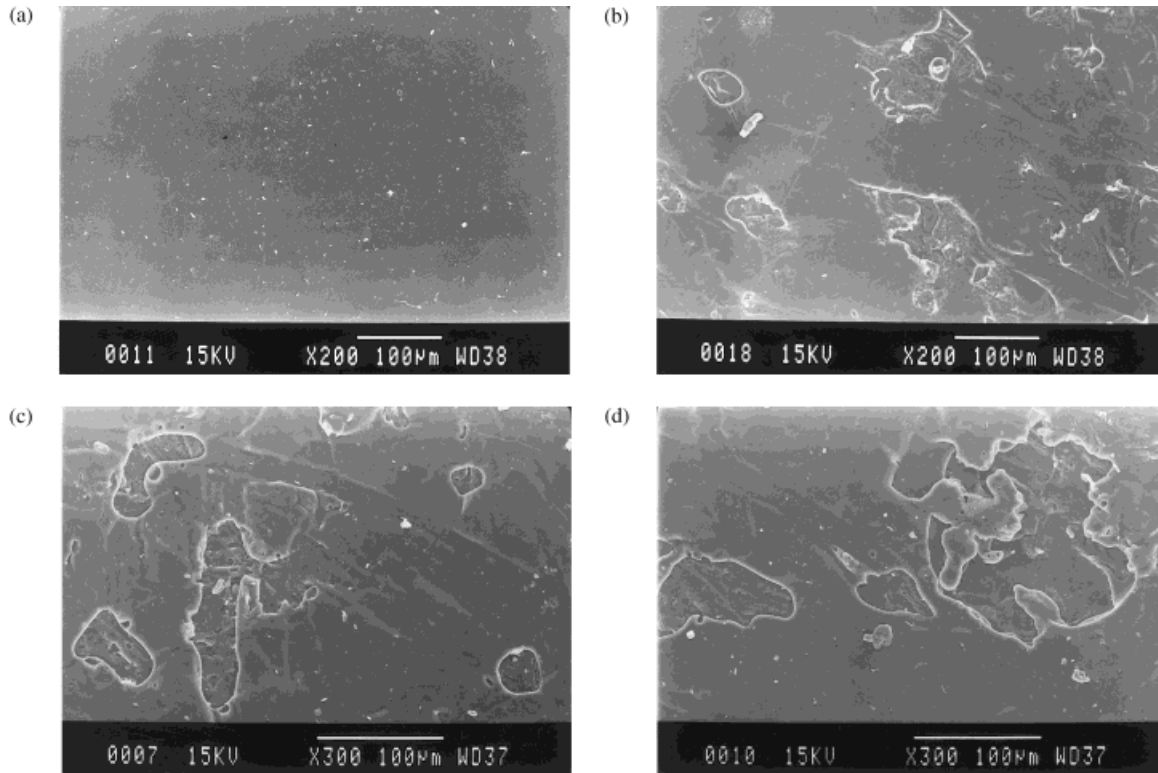


Figure 13 SEM microphotographs of a 70:30 LDPE/PLST blend during exposure in activated sludge after (a) 0 weeks, (b) 2 weeks, (c) 6 weeks, and (d) 8 weeks of exposure.

produced, the lowest biodegradation rate is observed. However, even in this case, the degree of branching is very small and takes place only in a small part of the starch macromolecules. In fact, although starch already contains a high degree of branched macromolecules (amylopectin), it remains biodegradable.

Another possible explanation for the lower biodegradation rate is the finer dispersion of the PLST component in the LDPE matrix due to the compatibilization. The connectivity of the PLST phase is the major factor affecting starch accessibility according to the scalar percolation theory as applied in LDPE/starch blends.⁴⁶ This connectivity is obviously disrupted in compatibilized blends. Applying the scalar percolation theory in our case, the critical amount of starch after which the connectivity starts to increase is around 30 wt % PLST. Also, due to the finer dispersion, lower amounts of PLST are placed on the film surface. Since this is the amount of starch accessible to microorganisms, larger amounts of PLST inside the LDPE matrix are protected from biodegradation. What is important, however, is that this reduction in the biodegradation rate, when using

the PE-g-MA copolymer as the compatibilizer, is not significant, and this is an additional advantage of this particular compatibilizer.

To determine the source of the weight loss, the biodegraded samples were studied by SEM. The microphotographs for the uncompatibilized blend containing 30 wt % PLST for different exposure times are shown in Figure 13. Before the microbial attack, the surface of the film is clear and homogeneous. After 2 weeks [Fig. 13(b)] exposure, some holes appear and the boundaries between the PLST phases and the LDPE matrix are becoming clear. The consumption of the starch is continued during the 6th week, and by the 8th week, relatively large holes appear, suggesting extensive starch consumption. These microphotographs prove that starch is the main carbon source for the microorganisms while the LDPE matrix remains unaffected.

From the molecular weight measurements after soil burial on similar LDPE blends, it was found that LDPE remains unaffected.⁴⁷ This happens because the molecular weight of the LDPE macromolecules is several hundred thousands, whereas microbes can primarily act on the edges

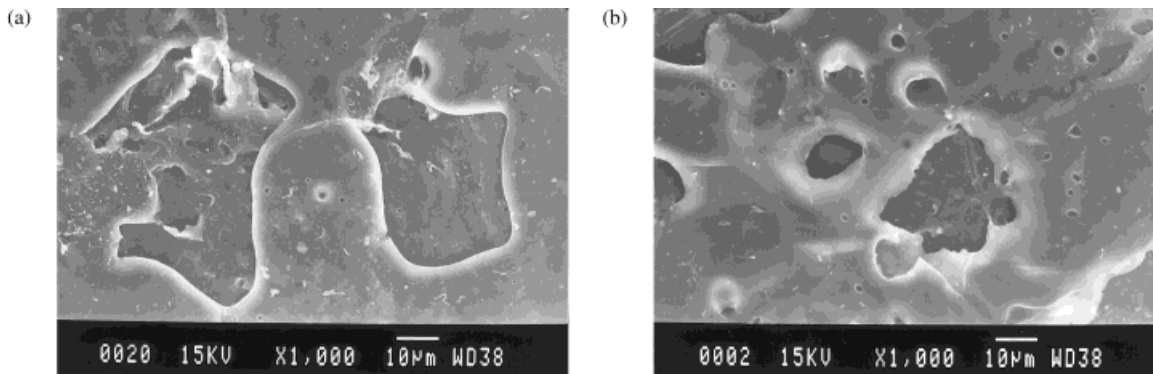


Figure 14 SEM microphotographs during exposure in activated sludge of a compatibilized 70:30 LDPE/PLST blend with PE-g-MA containing (a) 0.4 mol % anhydride groups and (b) 0.8 mol % anhydride groups.

of the macromolecules and can consume macromolecules with a molecular weight up to 450. However, it has been reported that higher molecular weight ethylene oligomers with molecular weights of 540, 740, and 1140 can be degraded when they are blended with starch.⁴⁸ This is evidence that the consumption of starch and the holes that are created increase the surface of the LDPE, and as a result, the microorganisms can attack the LDPE matrix more easily, creating

favorable conditions for the consumption of polyethylene oligomers.

The lower biodegradation rate that the compatibilized blends show is very difficult to be detected by SEM microphotographs as can be seen in Figure 14. The only difference with the uncompatibilized blends is the smaller size of the holes. This is due to the fact that, as the morphology study has shown, in the compatibilized blends the PLST phase size is smaller.

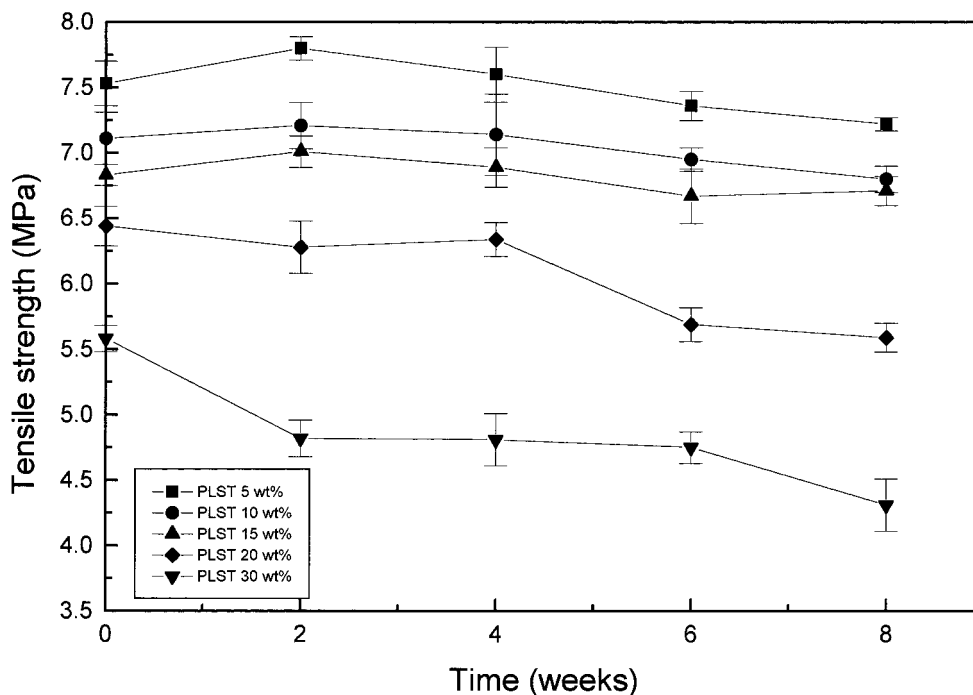


Figure 15 Tensile strength of uncompatibilized blends during exposure in activated sludge.

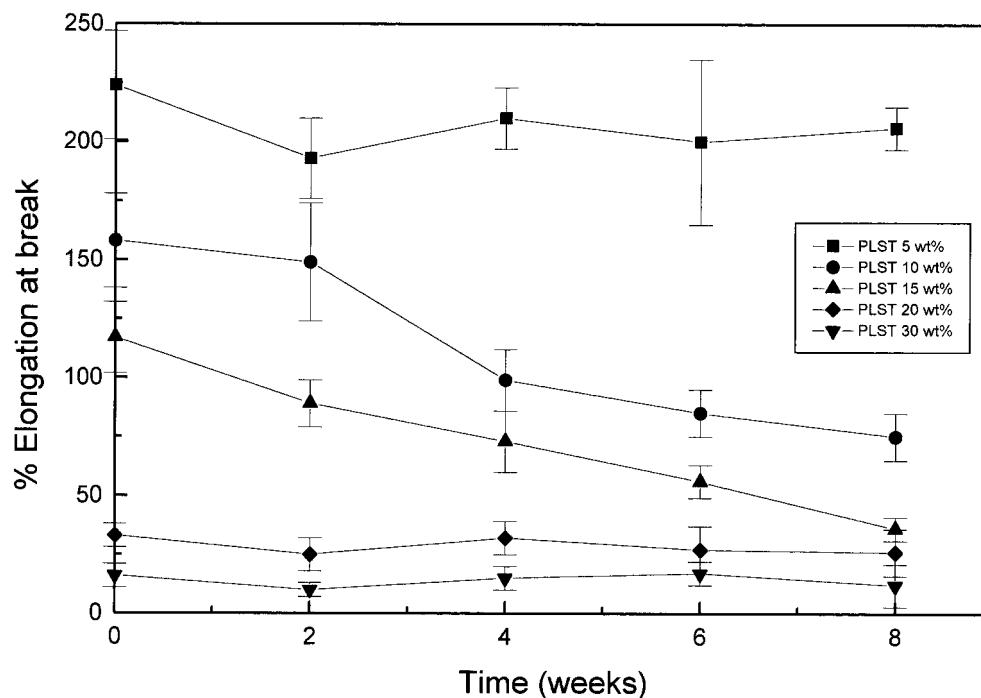


Figure 16 Elongation at break of uncompatibilized blends during exposure in activated sludge.

Because of the holes created on the surface of the films by starch consumption, the mechanical properties of the material decrease with the biodegradation time. Indeed, such a decrease is observed in the tensile strength (Fig. 15) as well as in the elongation at break (Fig. 16).

The decrease in tensile strength is larger in blends containing 20 and 30 wt % PLST and it becomes more evident with the exposure time. This is in accordance with weight-loss measure-

ments which show greater weight losses for these particular blends. In lower amounts of PLST, the tensile strength remains essentially unaffected.

The elongation-at-break properties during the exposure time show a different trend. In this case, a high decrease appears in the blends with the smaller PLST amounts (10 and 15 wt %). In the blend with 5 wt % PLST, the starch consumption is too small for any decrease in the mechanical properties to be detectable. Also, in the blends

Table II Variation of Tensile Strength of Compatibilized Blends During Exposure Time in Activated Sludge

Time (Weeks)	Tensile Strength (MPa)									
	Compatibilized Blends with PE-g-MA 0.4 mol %					Compatibilized Blends with PE-g-MA 0.8 mol %				
	PLST (wt %)					PLST (wt %)				
	5	10	15	20	30	5	10	15	20	30
0	8.28	8.19	8.10	7.96	7.92	8.26	8.31	8.47	8.44	8.43
2	8.29	7.96	8.01	7.94	7.73	8.22	8.24	8.33	8.27	8.18
4	8.35	7.90	7.87	7.83	7.37	8.09	8.14	8.09	8.17	8.05
6	8.23	7.84	7.76	7.60	7.42	8.19	8.13	8.03	7.89	7.96
8	8.12	7.86	7.74	7.49	7.11	8.13	8.09	8.07	7.84	7.86

Table III Variation of Elongation at Break of Compatibilized Blends During Exposure Time in Activated Sludge

Time (weeks)	Percent Elongation at Break									
	Compatibilized Blends with PE-g-MA 0.4 mol %					Compatibilized Blends with PE-g-MA 0.8 mol %				
	PLST (wt %)					PLST (wt %)				
	5	10	15	20	30	5	10	15	20	30
0	257	211	149	58	17	369	238	169	102	83
2	258	150	65	28	27	381	213	106	58	49
4	246	117	56	36	25	312	196	95	46	26
6	210	130	33	33	20	276	192	81	38	27
8	156	106	49	24	23	269	162	70	40	30

with 20 and 30 wt % PLST, where the starch consumption is very high, the decrease in the elongation at break is very small. This arises mainly from the very low elongation at break that these blends have and, thus, the variation is very difficult to detect. A similar trend in the variation of the mechanical properties is also observed in the compatibilized blends, as shown in Tables II and III.

CONCLUSIONS

In the present study, it has been shown that LDPE/PLST blends containing high amounts of PLST (up to 30 wt %), which retain to a great extent the tensile strength of LDPE, can be prepared. This is possible by using the PE-g-MA copolymer as a compatibilizer. In fact, the blends compatibilized with PE-g-MA containing 0.8 mol % anhydride groups have the same tensile strength as that of pure LDPE. Another important finding is that this compatibilizer does not affect to a great extent the biodegradation rate of the material. However, the production of blown films from such blends requires a high elongation at break. The branched and crosslinked macromolecules that were produced during the compatibilization reaction had a negative effect upon the elongation at break. A possible way to overcome this problem could be the addition of an elastomer along with the compatibilizer. A combination of the two compatibilizers could produce blends containing high amounts of plasticized

starch and also retaining satisfactory mechanical properties for blown-film production.

The authors are thankful to Drs. M. Botev and C. Betchev for their assistance in the DMTA measurements.

REFERENCES

1. J. Guillet, in *Degradable Polymers, Principles and Applications*, 1st ed., G. Scott and D. Gilead, Eds., Chapman and Hall, London, 1995, pp. 216–246.
2. W. Michaeli and M. Bittner, *Chem. Ing. Tech.*, **64**, 422 (1992).
3. T. Geiger, H. Knopf, G. Leistner, R. Romer, and H. Seifert, *Chem. Ing. Tech.*, **65**, 703 (1993).
4. M. Lee, *Chem. Br.*, **Jul.**, 515 (1995).
5. K. Udipi and A. M. Zolotor, *J. Polym. Sci. Polym. Symp.*, **75**, 109 (1993).
6. J. M. Mayer, G. R. Elion, C. M. Buchanan, B. K. Sullivan, S. D. Pratt, and D. L. Kaplan, *J. M. S. Pure Appl. Chem. A*, **32**, 775 (1995).
7. A. D. Sagar and E. W. Merrill, *J. Appl. Polym. Sci.*, **58**, 1647 (1995).
8. S. Thiebaud, J. Aburto, I. Alric, E. Borredon, D. Bikiaris, J. Prinos, and C. Panayiotou, *J. Appl. Polym. Sci.*, **65**, 705 (1997).
9. G. J. L. Griffin, Brit. Pat. 1,586,344 (1973).
10. M. A. Kotnis, G. S. O'Brien, and J. L. Willett, *J. Environ. Polym. Degrad.*, **3**, 97 (1995).
11. G. J. L. Griffin, U.S. Pat. 4,125,495 (1978).
12. F. H. Otey, R. P. Westhoff, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.*, **16**, 305 (1977).
13. J. L. Willett, U.S. Pat. 5,087,650 (1992).
14. R. L. Evangelista, Z. L. Nikolov, W. Sung, J.-L. Jane, and R. J. Gelina, *Ind. Eng. Chem. Res.*, **30**, 1841 (1991).

15. J.-L. Jane, R. J. Gelina, Z. Nikolov, and R. L. Evangelista, U.S. Pat. 5,059,642 (1991).
16. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 592 (1980).
17. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res.*, **26**, 1659 (1987).
18. G. F. Fanta, C. L. Swanson, and W. M. Doane, *J. Appl. Polym. Sci.*, **40**, 811 (1990).
19. R. L. Shogren, R. V. Greene, and Y. V. Wu, *J. Appl. Polym. Sci.*, **42**, 1701 (1991).
20. S. H. Imam, S. M. Gould, M. P. Kinney, A. M. Ramsay, and T. R. Tosteson, *Curr. Microbiol.*, **25**, 1 (1992).
21. D. Bikiaris, J. Prinos, and C. Panayiotou, *Polym. Degrad. Stab.*, **56**, 1 (1997).
22. C. Bastioli, in *Degradable Polymers, Principles and Applications*, 1st ed., G. Scott and D. Gilead, Eds., Chapman and Hall, London, 1995, pp. 112–137.
23. E. R. George, T. M. Sullivan, and E. H. Park, *Polym. Eng. Sci.*, **34**, 17 (1994).
24. L. Nie, R. Narayan, and E. A. Grulke, *Polymer*, **36**, 2227 (1995).
25. Z. Yang, M. Bhattacharya, and U. R. Vaidya, *Polymer*, **37**, 2137 (1996).
26. U. R. Vaidya and M. Bhattacharya, *J. Appl. Polym. Sci.*, **52**, 617 (1994).
27. J. Aburto, I. Arlic, E. Borredon, D. Bikiaris, J. Prinos, and C. Panayiotou, *Carbohydr. Polym.*, to appear.
28. Ch. Tselios, D. Bikiaris, J. Prinos, and C. Panayiotou, *J. Appl. Polym. Sci.*, **64**, 983 (1997).
29. W. E. Baker and M. Sallem, *J. Appl. Polym. Sci.*, **28**, 2057 (1987).
30. D. L. Pavia, G. M. Lampmann, and G. S. Kriz, in *Introduction to Spectroscopy*, Saunder, Philadelphia, 1979.
31. G. C. Pimentel and A. L. McClellan, in *The Hydrogen Bond*, Freeman, San Francisco, 1960, p. 83.
32. P. Forssell, J. Mikkila, T. Suortti, J. Seppala, and K. Poutanen, *J.M.S. Pure Appl. Chem. A*, **33**, 703 (1996).
33. R. F. T. Stepto and I. Tomka, *Chimia*, **41**, 76 (1987).
34. J. Schroeter and H. J. Endres, *Kunststoffe*, **82**, 1086 (1992).
35. J. L. Willett, *J. Appl. Polym. Sci.*, **54**, 1685 (1994).
36. S. Lim, J.-L. Jane, S. Rajagopalan, and P. A. Seib, *Biotechnol. Prog.*, **8**, 51 (1992).
37. J. Prinos, D. Bikiaris, S. Theologidis, and C. Panayiotou, *Polym. Eng. Sci.*, to appear.
38. U. R. Vaidya, M. Bhattacharya, and D. Zhang, *Polymer*, **36**, 1179 (1995).
39. R. M. Sala and I. A. Tomka, *Angew. Makromol. Chem.*, **199**, 45 (1992).
40. K. J. Zeleznak and R. C. Hosenev, *Cereal Chem.*, **64**, 121 (1987).
41. P. D. Orford, R. Parker, S. G. Ring, and A. C. Smith, *Int. J. Biol. Macromol.*, **11**, 91 (1989).
42. R. L. Shogren, *Carbohydr. Polym.*, **19**, 83 (1992).
43. R. L. Shogren, G. F. Fanta, and W. M. Doane, *Starch/Starcke*, **45**, 276 (1993).
44. T. F. Cooke, *J. Polym. Eng.*, **9**, 171 (1990).
45. J. E. Potts and A. Clendinning, in *The Biodegradability of Synthetic Polymers*, NJ, 1973.
46. J. S. Peanasky, J. M. Long, and R. P. Wool, *J. Polym. Sci. Part B Polym. Phys.*, **29**, 565 (1991).
47. R. G. Austin, in *Degradable Materials, Perspectives, Issues and Opportunities*, S. A. Barenberg, J. L. Brash, R. Navayon, and A. E. Redpath, Eds., *The First International Scientific Consensus Workshop*, CRC, Boca Raton, FL, 1990, pp. 357–376.
48. D. Raghavan, *Polym. Plast. Technol. Eng.*, **34**(1), 41 (1995).