Mechanical Properties and Biodegradability of LDPE Blends with Fatty-Acid Esters of Amylose and Starch

D. BIKIARIS,[1] J. ABURTO,[2] I. ALRIC,[2] E. BORREDON,[2] M. BOTEV,[3] C. BETCHEV,[3] C. PANAYIOTOU[1]

[1] Department of Chemical Engineering, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

[2] Ecole Nationale Superieure de Chimie, Laboratoire de Chimie Agro-Industrielle, 118 Route de Narbonne, 31077 Toulouse-Cedex, France

[3] Central Scientific and Research Laboratory, University of Chemical Technology and Metallurgy, 8, Kliment Ohridski Blvd., 1756 Sofia, Bulgaria

ABSTRACT: In the present article a series of low-density polyethylene (LDPE) blends with different amounts of fatty esters of amylose and starch, were prepared in a Haake-Buchler Reomixer. The tensile as well as the dynamic thermomechanical (DMTA) properties of the blends were measured. It was found that as the amount of the esters increases in the blends, the tensile strength and especially the elongation at break decrease nonlinearly. Scanning electron microscopy (SEM) was used to assess the interfacial adhesion between LDPE and the corresponding esters. The incompatibility of the blends was also verified with DMTA and differential scanning calorimetry (DSC). From the biodegradation studies of the blends during exposure in activated sludge, it was found that all esters are biodegradable, although to a much lesser degree compared to pure strach. The biodegradation rate of the composites is relatively small due to the low biodegradation rate of the pure esters. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1089–1100, 1999

Key words: LDPE; DMTA; SEM; DSC

INTRODUCTION

Biodegradable composites containing starch can be prepared in numerous ways. Native starch can be incorporated into the synthetic nonbiodegradable plastic as an additive,[1–8] or the plastic can be coextruded with starch[9] to prepare a composite more biodegradable than the pure thermoplastic or to increase the biodegradation rate of the synthetic polymer. Also, starch can be used together with fully biodegradable synthetic plastics,[10–15] producing a biodegradable blend of low cost. In some cases it was reported that the incorporation of starch can also increase the biodegradation rate of the synthetic biodegradable polymer.

Much effort has been focused upon polyethylene, which is the most widely used thermoplastic, especially for packaging applications. Its biodegradation rate has been extensively studied by Albertsson et al.[16–19] LDPE is generally regarded as a chemically "inert" polymer due to its long biodegradation time. Mixing with starch could, in a sense, enhance its biodegradation rate mainly due to the increase in polymer surface created after starch consumption by microorganisms. In such composites, additives like soaps of transition metals can also be added to speed up the thermooxidative degradation of LDPE,[20–23] or other compounds can be used to increase its photooxidation.[24] However, due to the hydrophilic nature of starch, most of the blends have poor mechani-

cal properties due to poor interfacial adhesion. Thus, the maximum tolerable amount of starch in these blends, usually, does not exceed 6–9% by weight.

One way to increase compatibility in starch/polyethylene blends is to use a compatibilizer containing groups capable of hydrogen bonding with starch hydroxyls. Ethylene/acrylic acid copolymers (EAA) is such an example[25–27] due to the hydrogen bonds that can be formed with the hydroxyl groups of starch.[28–31] Blends containing up to 40–50 wt % starch can be prepared in this way. The disadvantage of these blends is the lower biodegradation rate of the blends when they contain high amounts of EAA.[32] Recently, it was found that polyethylene-*g*-maleic anhydride copolymers (PE-*g*-MA) are most effective compatibilizers in LDPE/plasticized starch blends.[33,34] Their advantage is that blends with high amounts of plasticized starch can be prepared by using very small amounts of PE-*g*-MA and still retain satisfactory mechanical properties. The biodegradation rate was almost the same with uncompatibilized blends.

Another approach in achieving miscibility and improving adhesion of phases is to replace the hydrophilic —OH groups of starch with hydrophobic groups through an esterification reaction. Derivatized starches with octenyl–succinate,[35,36] octanoate,[37] dodecanoate,[38] and cholesterol[39] have been prepared and mixed with LDPE or HDPE thermoplastics. In a previous work of ours it has been found that octanoated starch with high degree of substitution is biodegradable.[40] In the present article decaoctanoated starch esters and a series of amylose esters were melt blended with LDPE to prepare blends containing high amounts of starch and still retaining satisfactory mechanical properties. Besides thermomechanical behavior, their biodegradability is also studied.

EXPERIMENTAL

Materials

The LDPE (Borealis) used was appropriate for packaging applications with a melt flow index of 2 g/10 min at 190°C. The potato native starch used in the acylation (esterification reaction) was provided by the INRA of Nantes, contained 19% amylose and 81% amylopectin. Corn amylose (70%) was purchased from Sigma Chemical Co. Starch and amylose esters were prepared as described in

our preceding article in this series[41] of articles according to the modified method of Mullen and Pacsu.[42] The esters are hereafter referred to as following: the octanoated, dodecanoated, and octadecanoated products are indicated by the prefix OC, DOD, and OCD, respectively. Modified starch or amylose are indicated by ST or AM, respectively, which follow the above prefixes. The degree of substitution is indicated by a number at the end. As an example, DODST2.7 means dodecanoated starch with a degree of substitution 2.7.

Melt Blending

LDPE was melt blended with the amylose or starch esters in a Haake-Buchler Reomixer model 600, equipment with roller blades and a mixing head with a volumetric capacity of 69 cm^3. Prior to mixing the esters, except deca-octanoated which has low melting point, were dried overnight in a vacuum oven at 60°C. Subsequently, the components were carefully premixed in appropriate amounts and fed into the Reomixer head. Mixing was performed at 170°C and 60 rpm for 15 min. For each system of LDPE/ester blends, five different levels of esters were used, namely, 10, 20, 30, 40, and 50 wt %. Melt temperature and torque were recorded during the mixing period. The blends, after preparation were milled and placed in tightly sealed vials to prevent any moisture absorption.

Blend Morphology

To study the morphology of the blends, thin films (about 130 ± 5 μm thickness each) were prepared, in a hydraulic press at 160°C and maximum pressure of 150 bar. In order to extract the starch or amylose ester from the blend, the films were placed in 250-mL round-bottom flasks and soaked for 24 h with 100 mL chloroform, at room temperature. Afterwards the films were washed carefully with chloroform and dried in a vacuum oven. Scanning electron microscopy observations were done with a JEOL microscope, model JSM-840A, on films coated with gold.

Mechanical Properties of Blends

The mechanical properties, such as tensile strength and elongation at break, were measured according to the ASTM D638 method on an Instron mechanical tester, Model 1122. 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 $Ca(NO_3)_2(4H_2O)$ 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 mode was used with 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 be made in the linear region of elasticity and without causing drawing effects. To specify this force, several stress–strain experiments were made beforehand. The static/dynamic force ratio was constant during the experiment. The testing was performed using about $8 \times 6 \times 0.3$-mm rectangular strips. The exact dimensions of each sample were measured before each scan.

Starch Ester Accessibility

About 0.3 g of LDPE/Octanoated starch blends in a form of thin films (130 ± 5 μm thick), were immersed in a 250-mL round-bottom flask containing 50 mL chloroform and soaked for 24 h at room temperature. Afterwards, the films were washed well with chloroform and dried until constant weight in a vacuum oven at 50°C. The percentage of the weight difference from the initial weight of the film relative to the final weight was defined as the accessible amount of octanoated starch in each blend.

Biodegradability of Blends

The polymer blends in a form of thin films 130 ± 5 μm thickness, were exposed to activated sludge in a wastewater treatment facility of a food company for 8 weeks. The rate of biodegradation was estimated as described previously.[38,41]

RESULTS AND DISCUSSION

In the present study, LDPE was melt blended with starch and amylose esters. The modification of polysaccharides by introducing long ester groups, is expected to increase the interfacial adhesion with LDPE. From a previous study it was found that similar blends have better mechanical properties compared to LDPE/plasticized starch blends.[37] The main goal of the work is to prepare blends of LDPE containing an amount of starch as high as possible while retaining much of the mechanical properties of pure LDPE. Figures 1 and 2 show the tensile strength and elongation at break of the blends, containing different amounts of starch and amylose esters.

In all blends the tensile strength decreases with increasing amount of starch or amylose esters. Blends containing octanoated and dodecanoated amylose with a degree of substitution of 2.7 (OCAM2.7 and DODAM2.7, respectively) show the greater losses in tensile strength for all compositions because of the very small tensile strength (about 0.7 MPa) of pure esters. On the contrary, blends with octanoated amylose with a low degree of substitution (d.s.) of 0.54 (OCAM0.54) and octadecanoated amylose with d.s. = 2.7 (OCDAM2.7), which have higher tensile strengths (1.8 and 3 MPa, respectively), the reduction in tensile strength is smaller. In fact, these blends containing even as much as 50 wt % of starch, lose only 20–25% of the initial tensile strength of pure LDPE.

The reduction in tensile strength for the blends containing OCAM2.7 and DODAM2.7 is even greater than for blends containing native amylose. In the later case, a high reduction was expected, due to the different polar nature of the two polymers. The granules of amylose do not melt during mixing with LDPE and, thus, most of the amylose remains in a filler form. On the contrary, amylose esters with low degree of substitution melt during the mixing process thus producing more homogeneous blends with LDPE.

The octadecanoated starches show a similar behavior to amylose esters. From Figure 1(b) it can be seen that blends containing OCDST with a low degree of substitution have higher tensile strength than the corresponding ones with a high degree of substitution. This happens also because pure OCDST1.8 has a higher tensile strength (3.1 MPa) than OCDST2.7 (0.7 MPa).

The effect of the ester type as well as the degree of substitution upon the elongation at break, is opposite to that observed in tensile strength. Blends that have the lower tensile strength have the higher elongation at break, and vice versa (Fig. 2). Thus, blends containing OCAM2.7 and DODAM2.7 have the highest elongation at break, and blends prepared with OCAM0.54 and OCDAM2.7 have the lowest. Pure amylose also has a negative effect on elongation at break, and its blends show very low values. But, even for the other blends, elongation at break decreases dramatically above 10

Figure 1 Tensile strength of (a) LDPE/amylose esters, and (b) LDPE/starch esters with different amount of the ester.

wt % of added ester. For blends prepared with esters such as OCAM0.54 and OCDAM2.7 this could be attributed to the very low elongation at

break of pure esters (9 and 19 %, respectively). The other esters however, such as OCAM2.7 and DODAM2.7, have elongation at break sim-

Figure 2 Elongation at break of (a) LDPE/amylose esters, and (b) LDPE/starch esters with different amount of the ester.

Figure 3   SEM microphotographs of LDPE/DODAM2.7 blends (a) 80/20, (b) 70/30, (c) 60/40, and (d) 50/50 w/w.

ilar or even higher than that of pure LDPE (600 and 1550, respectively), so the above explanation does not hold in this case. Thus, this behavior must be mainly attributed to the incompatibility of the two polymers. In all blends it seems that there is a minimum observed at a 40–50 wt % ester content. This is a typical behavior of incompatible systems. A similar minimum was also observed recently for LDPE/starch ester blends.[38]

The incompatibility of the blends was verified by studying their morphology with SEM (Fig. 3). In LDPE/DODAM blends containing 20 wt % DODAM, the size of the ester phase is between 5–30 μm. These relatively large values and the wide phase size distribution indicate a poor interfacial adhesion, and is a clear evidence that the two polymers are incompatible. The phase size also increases with increasing amount of the ester. Thus, in blends containing 30 wt % ester, larger (up to 100 μm) droplets are also observed. At 50 wt % ester content, it is difficult to determine the exact sizes, because DODAM produces a rather continuous phase. The same behavior also

appears in other esters with the same degree of substitution.

Comparing the esters with different degrees of substitution, it can be said that they give a similar blend morphology (Fig. 4). From the SEM microphotographs it can be concluded that the interfacial adhesion between the two polymers remains very poor even after esterification, although the polysaccharides have become more hydrophobic. This has a significant effect upon mechanical properties and especially elongation at break, which beyond 10 wt % of ester, is less than 200% for all studied blends. When comparing with LDPE/plasticized starch blends, it can be said that the phase size of the various esters is about the same to the phase size of plasticized starch.[34] It seems that, even in the case of the esters, a compatibilizer is needed, such as a polyethylene-g-maleic anhydride copolymer.

The incompatibility of the blends was also verified with DSC. In all thermograms of the blends, the melting point of LDPE was recorded. In those blends containing octadecanoated amylose or starch esters, a second melting peak at about

Figure 4 SEM microphotographs of (a) LDPE/OCDST1.8 70/30 w/w, and (b) LDPE/OCDST2.7 70/30 w/w.

32°C appears [Fig. 5(a)]. This peak is due to the melting of the ester phase, which is semicrystalline. In blends prepared with fully amorphous amylose esters, such as octanoated and dodecanoated with d.s. = 2.7, a glass transition appears at lower temperatures [Fig. 5(b)]. The melting points as well as the glass transition temperatures are about the same as those of the pure components—a further proof of incompatibility.

Dynamic Mechanical Analysis

The viscoelastic behavior of the blends was studied by a DMT analyzer. The temperature dependence of the dynamic mechanical properties is presented in Figures 6–11. To correctly analyze the spectra of the blends, it is useful to mention some features of the LDPE spectrum. Its loss tangent (tan δ) curve presents three relaxation peaks placed in the vicinity of −120°C (gamma),

0°C (beta), and 80°C (alpha transition). Their nature was reviewed by McCrumand and coworkers.[43] The gamma peak is associated with the relaxation of chains in the amorphous phase. The beta relaxation corresponds to the relaxation of branches. The alpha relaxation was first described as vibrational and reorientational motion within the crystals. Later, this relaxation has been interpreted as relaxation of the constrained molecules with reduced mobility located near the crystallites.[44,45] Concerning the glass transition of LDPE, both the gamma and beta relaxations

Figure 5 DSC thermograms of (a) LDPE/OCDAM2.7 50/50 w/w, and (b) LDPE/DODAM2.7 50/50 w/w.

Figure 6 DMTA spectra of LDPE/OCDAM2.7 blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

are quoted to have the properties of the glass–rubber transition. When the alkylidene content is low, the gamma peak is more prominent, whereas when the alkylidene content is high the major relaxation is the beta mechanism.

The addition of other substances to a pure polymer results in a very complex DMTA spectrum, which is sometimes difficult to interpret. Nevertheless, the dynamic mechanical analysis has proven to be a useful tool in investigating the inherent properties of polymer blends in relation to their end-use performance.

The DMTA spectra of LDPE.7 blends are shown in Figure 6. In all blends, the storage modulus E' decreases slowly, until $-25°C$. Afterwards, a very sharp drop appears. This can be attributed to the beta relaxation process, which is dominant in our case and has the properties of glass–rubber transition. It is observed that the value of E' decreases with increasing amount of OCDAM27. The blends become weaker due to the lower stiffness of the ester, which is in accordance with the tensile strength measurements discussed above. The reduction in E' due to the presence of the ester in the blends is more evident in the blend containing 50 wt % OCDAM2.7. Between 40–50°C a sudden decrease in E' is observed, similar to that of pure ester. Pure ester shows fast deterioration of E' with increasing temperature. The dynamic mechanical measurements of pure esters were possible only in a narrow temperature region. At low temperatures the samples became fragile and did not bear dynamic load while above 50°C they were in a liquid-like state.

The energy dissipation during the sinusoidal loading could be followed by the loss modulus E'' curves. The E'' spectrum of pure LDPE is composed of three broad relaxation peaks, reflecting the three relaxation phenomena described above. The presence of OCDAM2.7 does not significantly change the position of the gamma peak but its intensity varies without any clear tendency. In the region of beta relaxation, the increased content of OCDAM27 to 30 wt % decreases the peak intensity but does not displace the peak position. The beginning of the beta peaks could be at about $-13°C$. On the other hand, the alpha mechanisms is mostly affected by the ester content. It presents a clear trend to disappear with increasing the OCDAM27 content. As it could be seen from the E'' curve of the pure ester in this region, the ester is in a liquid-like state. In the DSC scan of the above ester a melting peak appears in this region and is attributed to melting of the long octade-

canoated ester side groups. It probably affects the spectrum of the blend, as the alpha peak is not evident in the curve of the blend with 50 wt % OCDAM27. The latter blend presents an E'' curve with a very broad and shifted to lower temperature beta peak, which is influenced by the relaxation phenomenon of pure ester below 0°C.

The tan δ spectra represent the damping properties of the material. It is possible to estimate the degree of compatibility if the relaxation peaks are well defined. In our case the pure ester shows only one broad peak with a maximum at about 13°C, which is very near to the beginning of melting. This phenomenon was not detected by DSC, because it is very close to the melting peak. This is why this melting peak is very broad (Fig. 5). Because the ester is semicrystalline, this peak could be attributed to a glass transition of the amorphous main chain of the starch ester. In tan δ curves, this peak overlaps in position with the beta peak of LDPE. Thus, from the DMTA data it is difficult to deduce information about the compatibility of the components in our case. The melting of OCDAM27 is, however, evident in the tan δ curves of the blends as a broadening of the alfa peak. Much more informative is the curve of the blend with 50 wt % OCDAM27. It shows two broad peaks. The first one between -13 and 0°C is probably the beta peak of LDPE, and the second one at 15°C is the peak of OCDAM27, as it has been observed in the pure ester. The assumption that the latter peak represents the glass transition of the pure ester is further enhanced by the fact that the corresponding octadecanoated starch ester shows exactly the same behavior (Fig. 7).

Examining the blends containing octadecanoated starch with lower degree of substitution (d.s. $= 1.8$) in Figure 8, it can be seen that the storage modulus is higher in all blends, compared to the corresponding ones of octadecanoated starch with a higher degree of substitution. This is also in accordance with the tensile strength measurements. The increased content of OCDST1.8 decreases the intensity of the E'' peaks without shifting the maximum of the peaks in the temperature scale. It is interesting to observe that in the blend with 50 wt % OCDST2.7 the alfa peak is overlaped in comparison with the blend with 50 wt % OCDST1.8. Obviously, the use of modified starch with a lower degree of substitution does not considerably change the relaxation behavior of the blend in comparison to that of pure LDPE. Thus, the tan δ curves of the blends with OCDST1.8 do not significantly differ from the curve of LDPE.

Figure 7 DMTA spectra of LDPE/OCDST2.7 blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

Figure 9 DMTA spectra of LDPE/OCAM2.7 blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

The DMTA spectra of LDPE/OCAM2.7 and LDPE/DODAM2.7 are similar (Figs. 9 and 10). At low temperatures, one can observe an overlapping of the curves of blends with 10 and 30 wt % ester.

At higher temperatures, the curves move apart. This effect is more pronounced in the case of LDPE/DODAM2.7. In both types of blends, how-

Figure 8 DMTA spectra of LDPE/OCDST1.8 blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

Figure 10 DMTA spectra of LDPE/DODAM2.7 blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

Figure 11 DMTA spectra of LDPE/Amylose blends: (a) storage modulus, (b) loss modulus, and (c) tan δ.

ever, at a 50 wt % ester content there is a drastic decrease in the dynamic mechanical properties.

The tan δ spectra of both pure OCAM2.7 and pure DODAM2.7 exhibit a relaxation peak at −35 and −38°C, respectively, which are very close to the glass transition temperatures of pure esters as were measured by DSC. At low temperature, the relaxation process in the ester influences the E'' spectra of LDPE/DODAM2.7 to a higher extent as compared to that of LDPE/OCAM2.7.

The above behavior is quite different in blends containing pure amylose (Fig. 11). In this case the storage modulus increases with increasing amount of amylose. But this behavior is the opposite to that observed for the tensile strength of the corresponding blends, in which the tensile strength decreases with increasing amount of amylose. Because amylose is in the form of granules, it behaves more like a filler. Thus, the storage modulus increases with added amount of amylose. On the other hand, the poor adhesion with the matrix disturbs the stress transfer and the granules of pure amylose could be regarded as stress concentrators or holes in the LDPE matrix.

According to Figure 11, loss modulus and tanä increase with increasing amounts of amylose in the blend. From the E' curve it can be seen that a new transition appears, with a maximum at about 50°C. A similar transition was also mentioned in starch anhydride functional polymer

blends and was attributed to the glass transition of the melted starch during the blending.[7,8,46] Shogren,[47] who studied extruded starch, attributed this transition to aging of the amorphous phase. However, by studying the octanoated and dodecanoated amylose esters, it can be seen that in the same area there is a sharp decrease in storage modulus. Tan δ also increases initially, but afterwards there is a sharp decrease, suggesting that in these esters the energy dissipated is much larger than the recovered one. Therefore, this transition involves group movements, which require significant amounts of energy. Most probably these esters pass from the viscoelastic to the viscous state within this region. This could explain why such a transition cannot be detected by DSC.

The transition due to material aging must be excluded in our case, because it is observed in materials studied immediately after their preparation. The transition temperature is also independent of the starch ester used. Also, the molecular reordering that takes place during aging, appears as an endothermic peak in the DSC scan. Such a peak was not observed in any of the DSC scans of the esters. A more detailed study is thus necessary to explain this phenomenon that takes place in amylose or starch granules as well as in their esters.

Biodegradation

As reported previously,[41] amylose and starch esters are biodegradable. But in blends with LDPE their biodegradation rate is much lower. The explanation is that only a small part of the existing ester is accessible to microorganisms in the blends. The remaining part is "buried" inside the LDPE matrix and it is protected from the microorganisms. To examine the accessibility of starch to microorganisms, the blends were treated with chloroform, which dissolves the esters.

As can be seen in Figure 12, the accessible amount of ester is very small in the blends with 10 and 20 wt % starch. This happens because in such low concentrations, most (95–80%) of the ester used, is covered by the LDPE matrix. Thus, only 5–20% of the total amount used is accessible to chloroform, leading to a small apparent biodegradation rate. Above a 30 wt % ester content, the accessible amount increases rapidly, and at 50 wt % almost the whole amount of the ester is accessible. In such blends, as can seen in Figure 3, the connectivity between the ester phases is high, and for this reason it is very difficult to judge which

Figure 12 Accessibility of the esters to the microorganisms in LDPE/amylose ester blends.

polymer constitutes the matrix and which the dispersed phase. To estimate the exact biodegradation rate of the blends, they were treated for different exposure periods in activated sludge. Figure 13 shows the weight loss of the LDPE/OCAM2.7 and LDPE/DODAM2.7 blends.

It is evident that the weight loss is very small, and depends mainly on the ester amount in the blend and on the exposure time. Blends containing OCAM2.7 have a higher biodegradation rate than the corresponding blends containing DODAM2.7.

This finding is attributed to the higher biodegradation rate that pure OCAM2.7 has compared to DODAM2.7 due to the bulkier ester side group of the later. The high weight loss of all blends containing 50 wt % of ester is in good agreement with accessibility results. But the biodegraded amount is much smaller than the accessible one, due to the low biodegradability of the esters. A similar behavior in weight loss was also found in LDPE dodecanoated starch blends, during soil burial.[40]

Except for the type of the ester groups, the biodegradation rate, as was expected, is also affected by the degree of substitution. Blends containing octadecanoated starch with d.s. = 1.8 appear to have about twice as high weight loss compared to the corresponding blends prepared with the same ester with a higher degree of substitution (Fig. 14). The substitution of hydroxyl groups due to the esterification reaction greatly reduces the ability of amylases to break the ether groups, and this difficulty increases as the degree of substitution becomes higher. The esters, however, remain partially biodegradable because of the fact that esterases can hydrolyze some of the ester groups, making the liberated hydroxyls accessible to amylases.

The changes in biodegradability become more evident in Figure 15 showing the weight loss of

Figure 13 Weight loss of LDPE/amylose ester blends during exposure in activated sludge: (a) LDPE/OCAM2.7, and (b) LDPE/DODAM2.7.

Figure 14   Weight loss of LDPE/OCDST blends during exposure in activated sludge: (a) OCDST1.8, and (b) OCDST2.7.

LDPE/pure amylose blends. The loss depends mainly on the amylose content, because it is fully biodegradable. In fact, above 30 wt % amylose the biodegradation rate is very high, especially in 50 wt % blends. At this concentration, about half of the added amylose was biodegraded after 8 weeks of exposure. This amount is about four to five times larger than the corresponding one in amylose ester blends (Fig. 13).

CONCLUSIONS

A series of LDPE/amylose or starch ester blends, have been prepared and extensively studied for

Figure 15   Weight loss of LDPE/amylose blends during exposure in activated sludge.

their thermomechanical and biodegradability behavior. It was found that, even after esterification of the polysacharides, their blends with LDPE have unsatisfactory mechanical properties at higher ester concentrations. This is due to the poor interfacial adhesion between LDPE and the esters, which results in an incompatible system. The amount of the ester in the blend plays an important role in the viscoelastic behavior of the blends, as was found by the DMTA study. By this study, some transitions in pure esters and specially in octadecanoated esters were detected, which could not be observed with the classical DSC technique. The biodegradation rate of the composites is very low, mainly due to the low biodegradation rate of the pure esters.

REFERENCES

1. Griffin, G. J. L. Br. Pat. 1,586,344 (1973).
2. Westhoff, R. P.; Otey, H. F.; Mehltretter, C. L.; Russell, C. R. Ind Eng Chem Prod Res Dev 1974, 13, 123.

3. Griffin, G. J. L. ACS Symp. Ser. No. 476; Rowell, R. M.; Schultz, T. P.; Narayan, R.; American Chemical Society: Washington, DC, 1992, p. 203.

4. Willett, J. L. U.S. Pat. 5,087,650 (1992).

5. Vaidya, U. R.; Bhattacharya, M. J Appl Polym Sci 1994, 52, 617.

6. Nie, L.; Narayan, R.; Grulke, E. A. Polymer 1995, 36, 2227.

7. Bhattacharya, M.; Vaidya, U. R.; Zhang, D.; Narayan, R. J Appl Polym Sci 1995, 57, 539.

8. Yang, Z.; Bhattacharya, M.; Vaidya, U. R. Polymer 1996, 37, 2137.

9. Kim, M.; Pometto, A. L. J Food Protect 1994, 57, 1007.

10. Shogren, R. L. Carbohydr Polym 1993, 22, 93.

11. Koenig, M. F.; Huang, S. J. Polymer 1995, 36, 1877.

12. Kotnis, M. A.; O'Brien, G. S.; Willett. J. L. Environ Polym Degrad 1995, 3, 97.

13. Otey, H. F.; Doane, M. W. In Starch Chemistry and Technology; Whistler, R. L.; Bemiller, J. M.; Paschall, E. F., Eds.; Academic Press: New York, 1984, 2nd ed., p. 389.

14. Lawton, J. W.; Fanta, G. F. Carbohydr Polym 1994, 23, 275.

15. Bastioli, C. In Degradable Polymers, Principles and Applications; Scott, G.; Gilead, D., Eds.; Chapman & Hall: London, 1995, 1st ed., p. 112.

16. Albertsson, A.-C. J Appl Polym Sci 1978, 22, 3419.

17. Albertsson, A.-C. Eur Polym J 1980, 16, 623.

18. Albertsson, A.-C.; Andersson, S. O.; Karlsson, S. Polym Degrad Stabil 1987, 18, 73.

19. Albertsson, A.-C.; Barenstedt, C.; Karlsson, S. J Appl Polym Sci 1994, 51, 1097.

20. Narayan, R.; Lafayette, W. Kunstoffe 1989, 79, 92.

21. Griffin, G. J. L. U.S. Pat. 4,983,651 (1991).

22. Sung, W.; Nikolov, Z. L. Ind Eng Chem Res 1992, 31, 2332.

23. Bikiaris, D.; Prinos, J.; Panayiotou, C. Polym Degrad Stabil 1997, 56, 1.

24. Scott, G. In Degradable Polymers, Principles and Applications; Scott, G.; Gilead, D., Eds.; Chapman & Hall: London, 1995, 1st ed., p. 169.

25. Otey, F. H.; Westhoff, R. P; Russell, C. R. Ind Eng Chem Prod Rec Dev 1977, 16, 305.

26. Otey, F. H.; Westhoff, R. P.; Doane, W. M. Ind Eng Chem Prod Rec Dev 1980, 19, 1659.

27. Jasberg, B.; Swanson, C.; Nelsen, T.; Doane, W. J Polym Mater 1992, 9, 153.

28. Fanta, G. F.; Swanson, C. L.; Doane, W. M. J Appl Polym Sci 1990, 40, 811.

29. Shogren, R. L.; Greene, R. V.; Wu, Y. V. J Appl Polym Sci 1991, 42, 1701.

30. Shogren, R. L.; Thompson, A. R.; Greene, R. V.; Gordon, S. H.; Cote, G. J Appl Polym Sci 1991, 47, 2279.

31. Fanta, G. F.; Swanson, C. L.; Doane, W. M. Carbohydr Polym 1992, 17, 51.

32. Allenza, P.; Schollmeyer, J.; Rohrbach, R. P. In Degradable materials, Perspectives, Issues and Opportunities; Barenberg, S. A.; Brash, J. L.; Navayon, R.; Redpath, A. E., Eds.; The First International Scientific Consensus Workship; CRC: Boca Raton, FL, 1990, p. 357.

33. Bikiaris, D.; Prinos, J.; Koutsopoulos, K.; Vouroutzis, N.; Pavlidou, E.; Frangis, N.; Panayiotou, C. Polym Degrad Stabil, to appear.

34. Bikiaris, D.; Panayiotou, C. J Appl Polym Sci, to appear.

35. Jane, J.-L.; Gelina, R. J.; Nikolov, Z. L.; Evangelista. R. L. U.S. Pat. 5,059,642 (1991).

36. Evangelista, R. L; Nikolov, Z. L.; Sung, W.; Jane, J.; Gelina, R. J. Ind Eng Chem Res 1991, 30, 1841.

37. Aburto, J.; Thiebaud, S.; Arlic, I.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. Carbohydr Polym, to appear.

38. Thiebaud, S.; Aburto, J.; Arlic, I.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. J Appl Polym Sci 1997, 65, 705.

39. Kang, B. G.; Yoon, S. H.; Lee, S. H.; Yie, J. E.; Yoon, B. S.; Suh, M. H. J Appl Polym Sci 1996, 60, 1977.

40. Bikiaris, D.; Pavlidou, E.; Prinos, J.; Aburto, J.; Arlic, I.; Borredon, E.; Panayiotou, C. Polym Degrad Stabil, to appear.

41. Aburto, J.; Arlic, I.; Thiebaud, S.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. J Appl Polym Sci, submitted.

42. Mullen, J. W.; Pacsu, E. Ind Eng Chem 1942, 34, 1209.

43. McCrum, E.; Read, B. E.; Williams, G. In Anelastic and Dielectric Effects in Polymeric Solids 3; John Wiley & Sons: London, 1967, p. 353.

44. Bershein, V. A.; Egorov, V. M. In Differential Scanning Calorymetry of Polymers 3; Ellis Horwood: New York, 1994.

45. Struik, L. C. E. Polymer 1987, 28, 1521.

46. Vaidya, R.; Bhattacharya, M.; Zhang, D. Polymer 1995, 36, 1179.

47. Shogren, L. Carbohydr Polym 1993, 19, 83.