

Oxidative Degradations of Oxodegradable LDPE Enhanced with Thermoplastic Pea Starch: Thermo-Mechanical Properties, Morphology, and UV-Ageing Studies

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ABSTRACT: The abiotic UV-degradation behavior of oxodegradable LDPE was investigated in the presence of thermoplastic pea starch (TPPS) in this study. Oxodegradable LDPE was first melt-blended with thermoplastic pea starch (TPPS) using an internal mixing chamber to enhance the abiotic oxidative degradation of oxodegradable LDPE. Because of their different affinity, maleated polyethylene was added as compatibilizer. Tensile properties, thermal properties, and morphology of resulting melt-blends were determined at different content in TPPS. High content in TPPS (40 wt %) could be readily added to oxodegradable LDPE without affecting the tensile properties of resulting melt-blends. UV-

ageing studies on compatibilized TPPS/oxodegradable LDPE melt-blends were carried out by Attenuated Total Reflectance infrared spectroscopy (ATR-FTIR), Dynamic Thermomechanical Analyses (DMTA) and Differential Scanning Calorimetry (DSC) under abiotic conditions. These results suggested a synergistic effect on the UV-ageing of TPPS-based melt-blends provided by both components during the first stage of UV-irradiation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 489–496, 2011

Key words: oxodegradable LDPE; pea starch; melt-blends; synergistic association; UV-ageing

INTRODUCTION

The world's annual consumption of plastic materials is increasing at a growing rate of ~ 6%, reaching 180 MTons in 2000. Totally, 64% of these plastic materials are composed of polyethylenes (PE), and are mainly used for short-time applications (e.g., packaging). However, being nonbiodegradable, these plastic materials exhibits a extremely long end-life time with, as a consequence, the accumulation of plastic wastes in the environment due to their inherent hydrocarbon backbone, rendering them insensitive to biological attacks.

Adding suitable pro-oxidants have shown to induce abiotic oxidation reactions to PEs when discarded of. After thermal or UV-exposures, this leads to the formation of low molecular weight polymers bearing oxygenated functions including aliphatic carboxylic acids, alcohols, aldehydes and ketones. These so-called oxodegradable PEs are ultimately metabolized by the action of microorganisms in compost or in soil.^{1–3} However, even though the propensity of oxodegradable PEs to be degraded in these active environments is recognized, oxodegradable PEs cannot be considered as a biodegradable material, i.e., being mineralized at minimum 90 wt % by the action of organisms over 180 days.^{4–7} In contrast, oxodegradation involves a two-stage process carried out over ~ 2 years; (i) an abiotic oxidative degradation, and (ii) the subsequent (bio)degradation of oxidized products in the presence of microorganisms. The rate-determining step of the process is the abiotic oxidative degradation, requiring suitable prooxidants for acceptable lifetimes of oxodegradable LDPE during (bio)degradation in compost or in soil.¹ However, the process does not proceed very rapidly even at elevated temperatures,

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not allowing to quote oxodegradable LDPE as biodegradable materials.

In this work, oxodegradable low density polyethylene (LDPE) was melt-blended with thermoplasticized pea starch to enhance the abiotic oxidative degradation of oxodegradable LDPE. Merlin et al. showed that UV irradiation of starch resulted in chain scissions and radical generations on the glucosidic ring.⁸ These features suggest us that these radicals so-generated from starch could synergistically enhance the abiotic oxidative degradation reactions, and ultimately the (bio)degradation rate of oxodegradable LDPE.

Pea starch represents an interesting structural platform in the design of sustainable plastics because of its inherent biodegradability and large abundance.^{9–12} Pea starch is available as a by-product derived from protein extraction, and can be considered as relatively cheap compared with other types of renewable resources like corn.¹³ For packaging applications, the use of thermoplastic starch is preferred. Starch plasticization consists to “destructure” starchy granules in the presence of plasticizers as glycerol.^{14–20}

Developing melt-blends derived from oxodegradable LDPE and thermoplastic pea starch (TPPS) with satisfactory thermomechanical properties depends on the control over interfacial adhesion between the different component phases.²¹ The current method to improve the interfacial adhesion between hydrophobic LDPE and hydrophilic plasticized starch is to use maleic anhydride-grafted polyethylene (MA-g-PE) as a compatibilizer.^{22,23}

Hence, this work aims at reporting the elaboration of oxodegradable LDPE and thermoplastic pea starch (TPPS) compatibilized with MA-g-PE to study their behavior under abiotic UV-degradation. In the first step, oxodegradable LDPE/TPPS-based melt-blends were prepared in an internal mixing chamber. Tensile properties and morphology of these TPPS-based melt-blends were evaluated at different content in TPPS. UV-ageing studies were subsequently carried out by ATR-FTIR spectroscopy, DMTA, and DSC to evaluate the UV-degradation of oxodegradable LDPE with thermoplastic pea starch under abiotic conditions.

EXPERIMENTAL

Materials

LDPE used for the preparation of oxodegradable LDPE was provided by TOTAL PETROCHEMICALS with MFI = 0.7 g/10 min. (190°C–2.16 kg). Light-induced prooxidant was kindly supplied by Symphony Plastics Ltd, UK, while maleic anhydride-grafted polyethylene (MA-g-LDPE) was produced by Dupont (Fusabond MB528D). Pea starch

was obtained from Cosucra groupe Warcoing SA, Belgium with a dry content of 85 wt %, including 60.7 wt % amylopectin, 35.7 wt % amylose, 3.4 wt % fiber, and 0.24 wt % protein, as determined by colorimetric methods and Proskey and DUMAS methods. The average particle size of pea starch was less than 50 μm as determined by gravimetry on vibrating sieves (pore sieves ranging from 50 to 700 μm). Glycerol (99%) was obtained from Sigma-Aldrich Belgium with a water content of 0.1 wt % as determined by Karl-Fisher analysis.

Preparation of oxodegradable LDPE

Oxodegradable LDPE was prepared using an internal mixer at 160°C for 5 min after addition of 1 wt % light-induced prooxidant to neat LDPE.

Thermoplasticization of pea starch

Thermoplastic pea starch (TPPS) was obtained by hand-mixing pea starch with 50 parts of glycerol and 10 parts of distilled water. After an overnight storage, the resulting mixture was introduced into a Brabender-type internal chamber (using elastomer-type screws) at 110°C and at a shearing rate of 100 rpm for 10 min.

Thermoplastic pea starch/oxodegradable LDPE melt-blends

Oxodegradable LDPE was hand-mixed with different contents in TPPS. The resulting mixtures were then introduced into a Brabender-type internal mixer at 160°C and at a shearing rate of 75 rpm for 10 min. Films or plates were then obtained by hot-pressing at 160°C under 150 bars for 4 min, followed by a cooling cycle at 15°C under 80 bars for 5 min.

Characterizations

Tensile properties were measured at 20°C on a Lloyd LR 10 K tensile tester with dumbbell-shaped specimens obtained from compression molded samples following ASTM D638 type V method. All tensile data were the average of five independent measurements; the relative errors are reported as well. Dynamic thermomechanical properties (DTMA) were determined using a thermodynamic mechanical analyzer (DMTA) in sinusoidal mode on thick films (0.5 mm) obtained by compression-molding. A differential scanning calorimeter (DSC) 2920 from TA Instruments under nitrogen was used to determine the thermal transitions of thermoplastic pea starch-based melt-blends. A Jeol 5500 LV scanning electron microscope (SEM) was used to observe the cryo-fractured surfaces of the composites at an

TABLE I
Tensile Properties of Oxodegradable LDPE/TPPS Melt-Blends at Different TPPS Contents as Compatibilized or Not with 10 wt % MA-g-PE

Entry	Composition in TPPS (wt %)	Composition in MA-g-PE ^a (wt %)	Young's Modulus (MPa)	Tensile strength (MPa)	Break elongation (%)
1	–	–	230 ± 44	12.7 ± 0.4	280 ± 20
2	20	0	320 ± 37	7.3 ± 0.9	45 ± 16
3	20	10	311 ± 67	11.5 ± 0.8	250 ± 40
4	30	0	366 ± 11	7.1 ± 0.8	60 ± 20
5	30	10	345 ± 15	10.7 ± 0.9	214 ± 80
6	40	0	314 ± 35	6.1 ± 0.7	21 ± 7
7	40	10	227 ± 49	9.5 ± 0.2	140 ± 40
8	50	0	360 ± 16	5.0 ± 0.7	10 ± 2
9	50	10	288 ± 27	10.4 ± 0.7	35 ± 2

^aComposition in MA-g-PE fixed with respect to the polyolefinic part.

accelerated voltage up to 20 kV and various magnifications. A spectrometer BIO-RAD Excalibur FTIR equipped with a micro-ATR Harrick Split Pea TM from SAFIR Cie was used to determine the chemical composition of the TPPS-based blends. The spectra recorded between 4000 and 700 cm⁻¹ were obtained by simple internal reflection from the sample directly deposited and pressed on the surface of a hemispherical silicon crystal.

RESULTS AND DISCUSSION

Pea starch was plasticized in the presence of water (10 parts by starch) and glycerol (50 parts by starch) before melt-blending with oxodegradable LDPE. The effect of TPPS content on the tensile properties of oxodegradable LDPE/TPPS-based melt-blends was studied (Table I). Totally, 10 wt % maleated polyethylene (MA-g-PE) as a compatibilizer was added in these melt-blends. This weight fraction of MA-g-PE was optimized in the case of melt-blends between neat LDPE and TPPS (results not shown here). For the sake of comparison, the tensile properties of neat LDPE are provided (Entry 1, Table I).

From Table I, we can observe that the tensile properties of oxodegradable LDPE and nonadded LDPE are almost identical. Only 1 wt % prooxidant was added in the case of oxodegradable LDPE, and therefore this amount is not enough to significantly affect the tensile properties of corresponding LDPE matrix.

When considered oxodegradable LDPE-based melt-blends in the absence of MA-g-PE, the ultimate properties of the resulting melt-blends decrease gradually with the content of TPPS, while their Young's modulus increases regularly with the content of TPPS. The latter feature indicates a reinforcing effect provided by TPPS.

In perfect agreement with the literature,^{22,23} adding MA-g-PE as a compatibilizing agent (10 wt %

with respect to the polyolefinic part) maintains the ultimate properties identical to those of the corresponding noncompatibilized LDPE/TPPS melt-blends up to 40 wt % TPPS. At higher TPPS content (50 wt %), the ultimate elongation recorded for the resulting melt-blends significantly drops down (see Entries 9 and 10, Table I). It is worth noting that the Young's modulus of oxodegradable LDPE/TPPS melt-blends is almost identical after addition of MA-g-PE. These same observations are made in the case of melt-blends derived from neat LDPE (not shown here). These results show that high amount of pea starch (plasticized) up to 30 wt % can be associated with oxodegradable LDPE, enhancing the biosourced fraction within the resulting melt-blends.

Morphological studies confirmed the enhanced interfacial adhesion between both partners after addition of MA-g-PE (Fig. 1). After cryofracture, the presence of free TPPS nodules, visible together with some voids (more likely resulting from the removal of TPPS nodules during the cryofracture test), is observed in the case of noncompatibilized blends. This was much more highlighted after immersion in an acidic solution of HCl (5M) allowing the selective hydrolysis of plasticized starch fraction. Accordingly, the TPPS nodules located at the surface vanished with the presence of increasingly large voids all along the immersion time. Such morphology is related to the lack of interfacial adhesion between hydrophilic TPPS and hydrophobic oxodegradable LDPE. During the cryofracture test, the stress propagates mainly across the interface between nonmiscible partners of the corresponding melt-blends. In the case of compatibilized melt-blends, no void at the surface is observed, even after three days of immersion in the acidic solution. This fully confirms the improvement of interfacial adhesion between oxodegradable LDPE and TPPS as a result of the grafting of MA-g-PE onto the TPPS particles, i.e., via reaction between the polysaccharide/glycerol hydroxyl

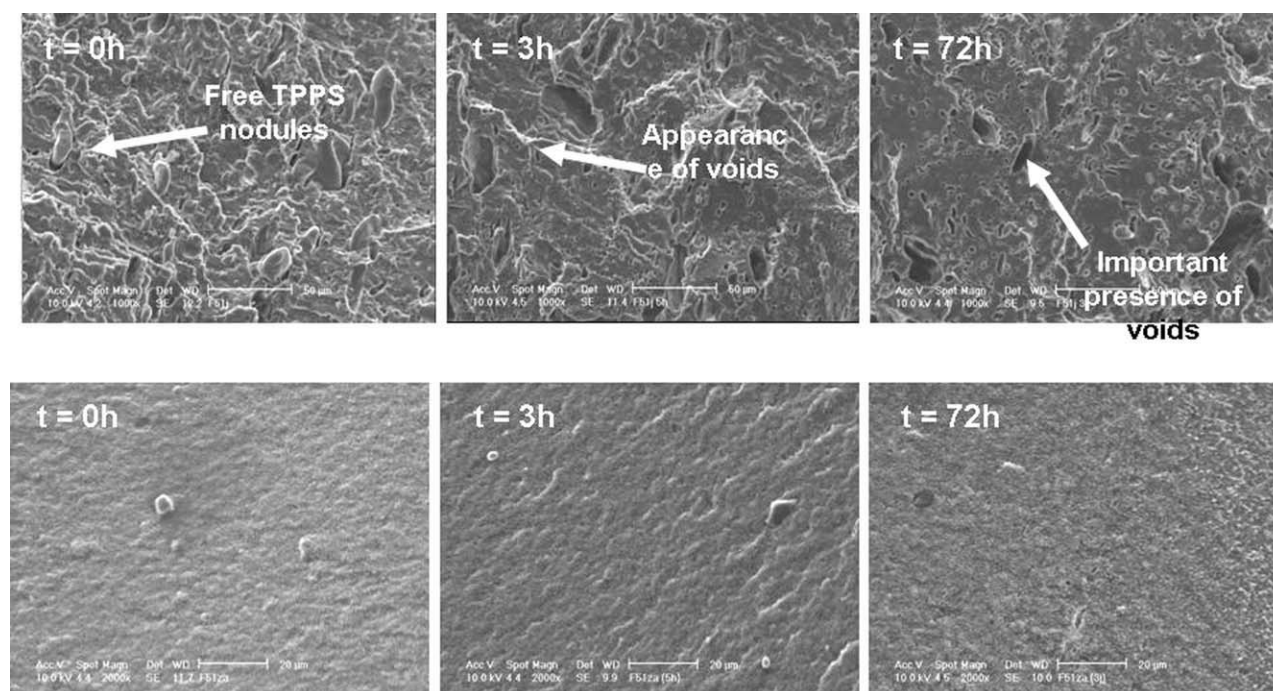


Figure 1 SEM images of oxodegradable LDPE/TPPS melt-blends (30 wt % TPPS) without (a) and with (b) 10 wt % MA-g-PE. Cryofracture surface after immersion aqueous HCl - 5M for 3 h and 72 h (Entries 5,6 - Table I).

functions and the cyclic carboxylic anhydride pending along the MA-g-PE chains. As a consequence, the stress fracture propagated mainly through the polymeric matrix, leading to a more cohesive fractures.

Since the objective of this work is to evaluate the effect of adding TPPS on the abiotic oxidative degradation reactions of oxodegradable LDPE, UV-ageing studies were performed on oxodegradable LDPE and oxodegradable LDPE/TPPS melt-blends containing 30 wt % TPPS and 10 wt % MA-g-PE as compatibilizer (see Entry 6, Table I). These samples were melt-compressed to make films with a thickness of 0.5 mm, and were then subjected to UVA radiation (400–315 nm). The films were placed at 20 cm distance of the lamp and each week the films were turned back to allow weekly irradiation for each side of these samples. Figure 2 shows the normalized ATR-FTIR spectra of oxodegradable LDPE aged for seven weeks.

ATR-FTIR spectroscopy is an interesting technique that allows characterizing samples through a thickness of a few micrometers with absorbance in the broad mid-infrared spectrum. Because of the high penetration of infrared radiations, ATR-FTIR can monitor UVA damage to the deep-surface of the materials. From Figure 2, it comes out that a broad carbonyl band associated with the stretching of aldehyde and/or carboxylic esters ($1733\text{--}1700\text{ cm}^{-1}$), as well as γ -lactone functions ($\sim 1780\text{ cm}^{-1}$) appeared starting from the second week of UVA radiation.

The relative intensity of the carbonyl bands increases with irradiation time. These functions are actually generated by the photodegradation of the polyolefinic part promoted by the prooxidant. This leads to the homolytic cleavage of C—C bond of LDPE, preferably at branching points of LDPE (Scheme 1). The resulting radicals can react with atmospheric oxygen with the formation of an unstable hydroxyperoxides, directly decomposing into various carbonyl/hydroxyl products.²

In the case of oxodegradable LDPE/TPPS melt-blends, although the characteristic peaks are

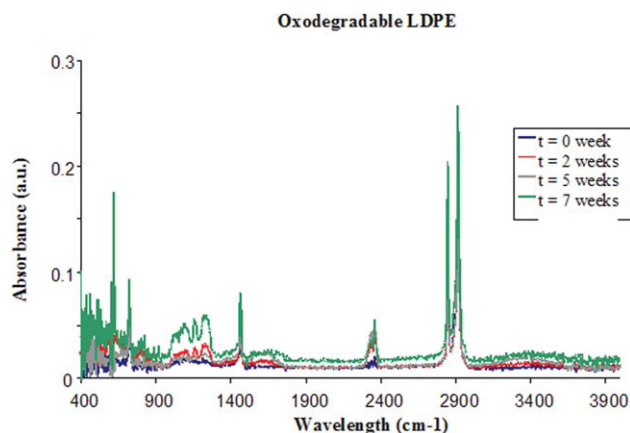
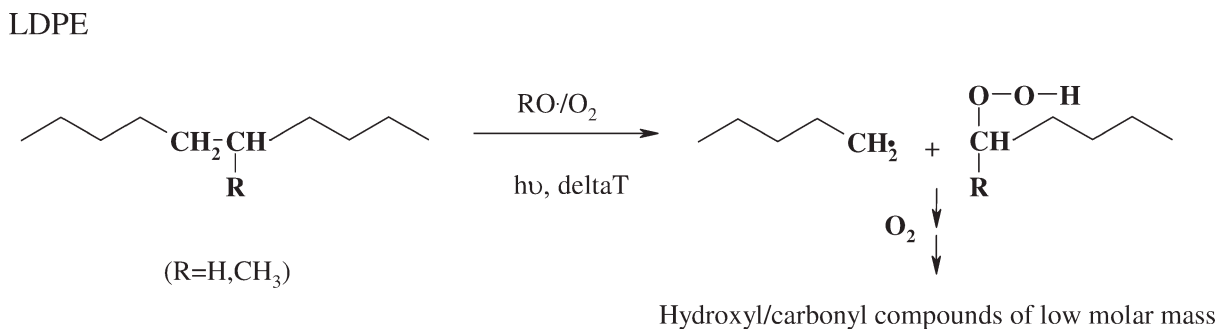


Figure 2 ATR-FTIR spectra of oxodegradable LDPE films after seven weeks of UVA irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



Scheme 1 Formation of carbonyl functions through peroxidation of oxodegradable LDPE.

partially hindered by the infrared profile of plasticized starch, the presence of carbonyl functions resulting from the photo-oxidative degradation are still observed after two weeks of UVA irradiation (Fig. 3). The intensity of this carbonyl band also increases with irradiation time. This indicates that the part of oxodegradable LDPE can be degraded under the photo-oxidative conditions in the presence of TPPS.

In contrast, the presence of the carbonyl bands is not observed, even after seven weeks of radiation, in the case of neat LDPE, i.e., not added with prooxidant (not shown here). This is a good agreement with the literature, showing that the effect of UV exposure, in the field or in the artificial environments, was not significant after only 243 days at room temperature.³

The effect of UV-ageing on the DMTA properties of oxodegradable LDPE and compatibilized oxodegradable LDPE/TPPS melt-blends was determined. The DMTA technique was appropriated to clearly distinguish the degradation of both polymeric partners within the blends in function of time. Figure 4 shows the time-dependence of storage modulus, E' , and tan delta of oxodegradable LDPE UV-aged for 13 weeks. Tan delta corresponds to the dissipating

factor, defined as the ratio between the loss modulus, E'' , and the storage modulus, E' . At low temperature (usually below glass transition temperature), the molecular motion of polymeric segments is strongly restricted. The polymeric segments behave as an ideal spring, where the stored energy is not released as heat. This leads to a stiff material with a high storage modulus. When the temperature increases, some parts of polymeric chains are able to move freely. This transition is related with a release of mechanical energy (viscous release), depending mainly on E'' . After a 13-week irradiation under UVA, throughout the temperature range studied, the DTMA results show that E' of oxodegradable LDPE increases with irradiation time while the amplitude of tan delta decreases with the irradiation time. In the case of tan delta, there is a particular transition at $\sim 60^\circ\text{C}$, corresponding to the beginning of the melting for oxodegradable LDPE. This transition decreases with irradiation time. In perfect agreement with the literature,² such behavior can be explained by the preferential formation of shorter polyolefinic chains, starting from the branching points of oxodegradable LDPE matrix. The photo-oxidation of oxodegradable LDPE²⁴ proceeds through an induction period, in which oxygen uptake is responsible for

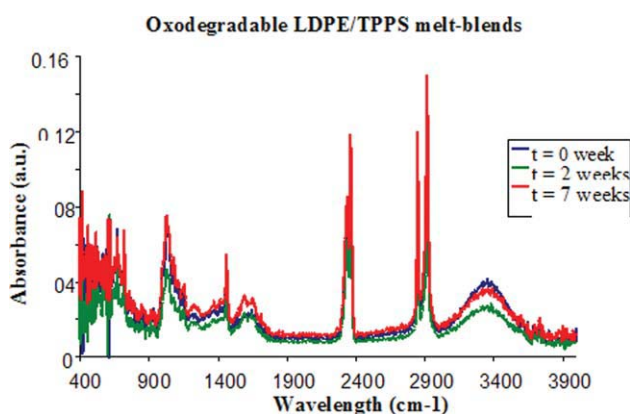


Figure 3 ATR-FTIR spectra of oxodegradable LDPE/TPPS melt-blends after seven weeks of UVA irradiation (TPPS content = 30 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

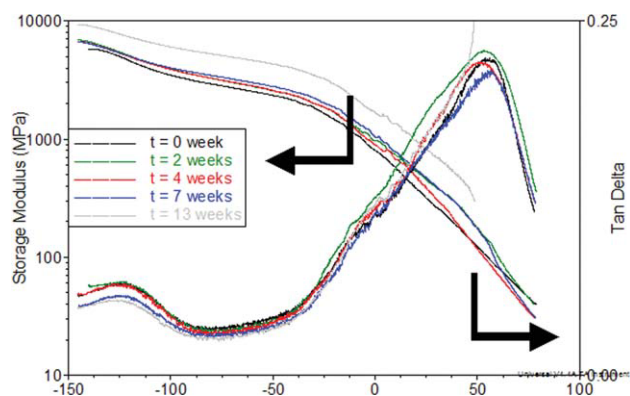


Figure 4 Storage modulus and tan delta of oxodegradable LDPE after 13 weeks of UVA irradiation (amplitude = $30\ \mu\text{m}$, frequency = 3Hz, from -120 to 80°C at a heating rate of $3^\circ\text{C}/\text{min}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Time-Effect of UV-Ageing on Melting Enthalpy (ΔH_m) and Melting Temperature of Oxodegradable LDPE (from -40°C to 200°C at a Heating Rate of $10^\circ\text{C}/\text{min}$ - 2nd Scan)

Entry	Time (weeks)	ΔH_m (J/g)	T_m ($^\circ\text{C}$)
1	0	85	111
2	2	90	112
3	5	92	112
4	11	110	111
5	13	120	112
6	17	99	112
7	25	75	112

the formation of oxygenated products including hydroperoxides, peroxides, and so on. The resulting linear chains are able to organize more easily leading to higher extent of crystallization at longer irradiation time. It results that the crystallinity degree of oxodegradable LDPE increases with time as confirmed by DSC analyses (Table II).

For instance, the melting enthalpy increases from 98 to 122 J/g after seven weeks of irradiation, confirming the enhancement of crystallinity degree for oxodegradable LDPE. At longer irradiation times (beyond 13 weeks), the storage modulus of oxodegradable LDPE starts decreasing, whereas the amplitude of tan delta increases with the irradiation time (Fig. 5). Under these conditions, oxodegradable LDPE gets more brittle as a result of the polyolefinic chain cleavages. This is supported by DSC analyses where the crystalline degree of oxodegradable LDPE decreases at longer irradiation times (Fig. 7, Table II).

In the case of the oxodegradable LDPE/TPPS melt-blend, there is an additional transition observed at ca. -43°C (Fig. 6). This is ascribed to the glass transition temperature for the TPPS part. The ampli-

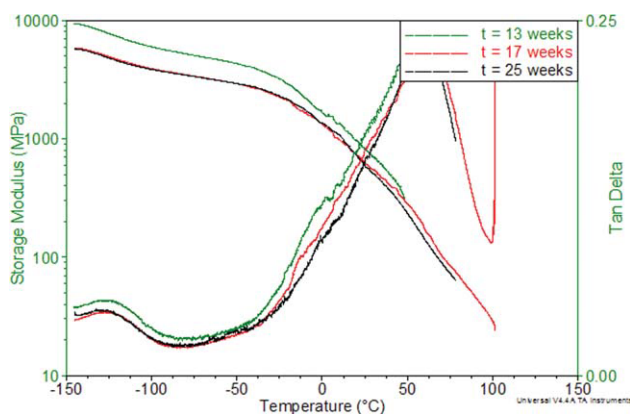


Figure 5 Storage modulus and tan delta of oxodegradable LDPE after 25 weeks of UVA irradiation (amplitude = $30\ \mu\text{m}$, frequency = 3 Hz, from -120 to 80°C at a heating rate of $3^\circ\text{C}/\text{min}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

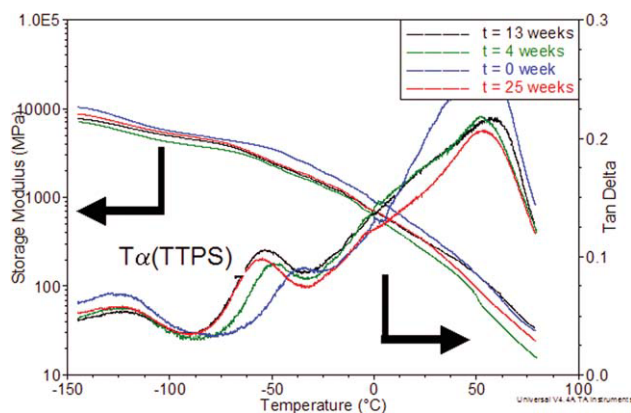


Figure 6 Storage modulus and tan delta of compatibilized oxodegradable LDPE/TPPS melt-blends after 25 weeks of UVA irradiation (TPPS content = 30 wt %; amplitude = $30\ \mu\text{m}$, frequency = 3Hz, from -120 to 80°C at a heating rate of $3^\circ\text{C}/\text{min}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tude and the temperature of this transition decrease at longer irradiation times due to the preferential cleavage of α (1-4) and α (1-6) bonds of the polysaccharidic chains.²⁵ This leads to a decrease of the relative molecular weight of starch macromolecules, and therefore a drop of the glass transition temperature of plasticized starch.

Regarding the fraction in oxodegradable LDPE within the melt-blends, almost the same observations can be achieved as those of oxodegradable LDPE alone: UV-degradation of oxodegradable LDPE starting through its branching points, and then through the main polyolefinic backbone.²⁴ However and interestingly enough, UV-degradation of oxodegradable LDPE is quite accelerated in the presence of TPPS (Table III).

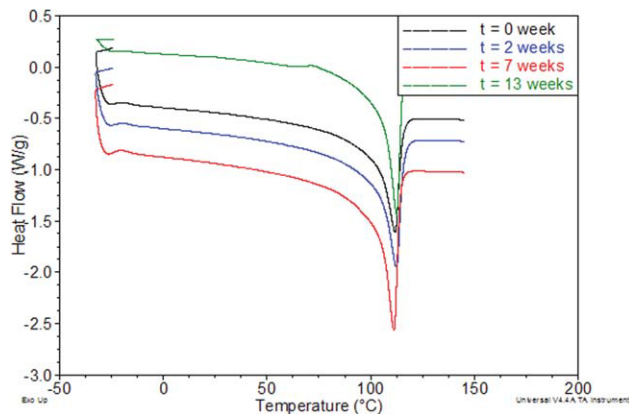


Figure 7 DSC thermograms of oxodegradable LDPE UV-exposed at different intervals of time (from -40 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ —2nd scan). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3

Melting Enthalpy (ΔH_m) and Melting Temperature of Compatibilized Oxodegradable LDPE/TPPS Melt-Blends at Different Times of UVA Irradiation (TPPS Content = 30 wt% ; from -40°C to 200°C at Heating Rate of $10^\circ\text{C}/\text{min}$ —Second Scan)

Entry	Time (weeks)	ΔH_m (J/g)	T_m ($^\circ\text{C}$)
1	0	70	111
2	2	68	111
3	5	71	111
4	11	72	110
5	13	64	111
6	17	63	110
7	25	58	111

By comparison with oxodegradable LDPE alone (13 weeks), UV degradation occurring through the main polyolefinic backbone started earlier, i.e., after 11 weeks according to the time-evolution of melting enthalpy for the polyolefinic fraction within the melt-blend.

Again and by comparison with the literature, the process is more faster as compared with the photo-oxidation degradation of LDPE in this stage.²⁴ The obtained results showed that there is a synergistic effect on the oxidation process of the oxodegradable LDPE/TPPS blends when exposed to UV-sunlight. This means that photo-radiation could induce oxidation reaction enhanced and could accelerate the biodegradability rate of LDPE/starch blends by creating oxodegradable LDPE/starch that is more susceptible to biotic reactions.

CONCLUSIONS

This article was devoted to highlight the synergistic association of oxodegradable LDPE with thermoplasticized pea starch under UV-ageing. Melt-blends between thermoplasticized pea starch and oxodegradable LDPE, compatibilized or not with maleic anhydride-grafted polyethylene (MA-g-PE), were prepared using an internal mixing chamber. Tensile properties, morphology, and thermomechanical properties of resulting melt-blends were studied. Tensile properties show that oxodegradable LDPE and TPPS have some affinity, as evidenced by the smooth decrease of ultimate properties for the resulting melt-blends at different TPPS content. When MA-g-PE is used as a compatibilizer, the tensile properties of the resulting melt-blends were significantly enhanced up to a high content of TPPS close to 40 wt %. This allows valorizing pea starch (plasticized or not) as a biosourced material at high content in polymeric compositions. DMTA and DSC studies were performed on oxodegradable LDPE and compatibilized oxodegradable LDPE/TPPS melt-blends (30 wt % TPPS) after a 25-week UV-

ageing study to clearly distinguish the contribution of both polymeric partners in the oxodegradable LDPE/TPPS melt-blends. It results that oxodegradable LDPE or in combination with TPPS underwent photo-oxidative degradations as promoted by prooxidant added into LDPE. During the first weeks, the thermomechanical properties of oxo-degradable LDPE show that the crystallinity of the olefinic matrix increases with UV-irradiation time, due to the preferential cleavage of branching points of LDPE. After 13 weeks, the UV-degradation proceeds directly through the main backbone, leading to a decrease of crystallinity degree. When TPPS is added, starch is also subject to degradations as some preferential cleavages of these α (1-4) and α (1-6) bonds. This leads to a decrease in amplitude and intensity according to the glass transition of plasticized starch fraction. In the case of oxodegradable LDPE part, the same behavior is observed, except that the degradation of oxodegradable LDPE is somehow accelerated in the presence of TPPS. Clearly and even though some faster degradation (under UVA irradiation) is observed in presence of plasticized pea starch, it does not mean that the resulting investigated oxodegradable LDPE/TPPS melt-blends can be considered as biodegradable polymeric materials in terms of the norms discussed in the introduction section, e.g., following the international standards, i.e., ASTM D6400-04 and EN 13432.

References

- Chiellini, E.; Corti, A.; D'Antone, S. *Polym Degrad Stab* 2007, 92, 1378.
- Wiles, D. M.; Scott, G. *Polym Degr Stab* 2006, 91, 1581.
- Bonhomme, S.; Cuer, A.; Delort, A. M.; Lemaire, J.; Sancelme, M.; Scott, G. *Polym Degrad Stab* 2003, 81, 441.
- Bajer, K.; Kaczmarek, H. *Polimery (Warsaw)* 2007, 52, 13.
- Jenck, J. F.; Agterberg, F.; Droscher, M. *J. Green Chem* 2004, 6, 544.
- Gu, J. G.; Gu, J. D. *J Polym Environ* 2005, 13, 65.
- Lucas, N.; Bienaime, C.; Belloy, C.; Queneudec, M.; Silvestre F., Nava-Saucedo, J. E. *Chemosphere* 2008, 73, 429.
- Merlin, A.; Fouassier, J. P. *Makromol Chem* 1981, 182, 3053.
- Meier, M.; Metzger, J.; Schubert, U. S. *Chem Soc Rev* 2007, 11, 1788.
- Clark, J.; Budarin, V.; Deswarte, F.; Hardy, J.; Kerton, F.; Hunt, A.; Luque, R.; Macquarrie, D.; Milkowski, K.; Rodriguez, A.; Samuel, O.; Tavener, S.; White, R.; Wilson, A. *Green Chem* 2006, 10, 853.
- Ratnayake, W. S.; Hoover, R.; Shahidi, F.; Perera, C.; Jane, J. *Food Chem* 2001, 74, 189.
- Naguleswaran, S.; Vasanthan, T. *Food Chem* 2010, 118, 627.
- Ratnayake, W. S.; Hoover, R.; Warkentin, T. *Starch/Stärke* 2002, 54, 217.
- Fishman, M. L.; Coffin, D. R.; Konstance, R. P. *Carb Polym* 2000, 41, 317.
- Forssell, P. M.; Mikkila, J. M.; Moates, G. K. *Carb Polym* 1997, 34, 275.
- Narayan, R. In *Polymers from Agricultural Coproducts*, Fishman, M. L.; Friedman, R. B.; Huang, S. J., Eds.; Am Chem Soc Symp Ser: Washington, 1994; 575, p. 2.

17. Shorgen, R. L.; Fanta, G. F.; Doane, W. M. *Starch/Stärke* 1993, 45, 276.
18. Forssell, P.; Mikkila, J.; Sourtti, T. J. M. S. *Pure Applied Chem A* 1996, 33, 703.
19. Van Soest, J.; Benes, K.; de Witt, D. *Polymer* 1996, 37, 3543.
20. Nayak, P. *Macromol Chem Phys C* 1999, 39, 481.
21. Barlow, J. W.; Paul, D. R. *Polym Eng Sci* 1984, 24, 525.
22. Chandra, R.; Rustgi, R. *Polym Degrad Stab* 1997, 56, 185.
23. Bikiaris, D.; Panayiotou, C. *J Appl Polym Sci* 1998, 70, 1503.
24. Abd El-Rehim, H. A.; Hegazy, E. S.; Ali, A. M.; Rabie, A. M. *J Photochem Photobiol A: Chem* 2004, 163, 547.
25. Bertolini, A.; Mestres, C.; Colonna, P. *Starch/Stärke* 2000, 52, 340.
26. Raquez J.-M.; Nabar, Y.; Narayan, R.; Dubois, P. *Int Polym Process* 2007, 22, 463.
27. Kummerer, K. *Green Chem* 2007, 9, 899.
28. Raston, C. *Green Chem* 2005, 7, 57.