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ORIGINAL PAPER

The effect of thermoplastic starch on the properties of HDPE/TPS blends during UV-accelerated aging

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Abstract The influence of thermoplastic starch (TPS) on the properties of UV-irradiated TPS/high-density polyethylene (HDPE) blends was investigated. Changes in chemical structure, molecular weight, crystallinity, and mechanical properties, as a function of exposure time, were determined using FTIR-spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and tensile tests. The inclusion of TPS influence neither the evolution of carbonyl index nor the molecular weight reduction of HDPE/TPS. In contrast, the presence of TPS in the blends increased the fusion enthalpy because of starch retrogradation. This increasing resulted in a corresponding increase of Young's modulus of HDPE/TPS blends.

Keywords Thermoplastic starch · Polymer blends · Photodegradation · Carbonyl index · Molecular weight · Crystallinity · Tensile properties

Introduction

When polyethylene (PE) films, such as those used in agriculture, are exposed to heat and UV irradiation in the presence of oxygen, their mechanical properties would

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usually deteriorate [1]. Changes in mechanical performance have been related to changes in chemical and molecular structure which are reflected in modifications in crystallinity and mechanical properties [1–4]. Recent work has been focused on the effect of the addition of granular starch on the photodegradation of PE [5–7]. In an early work, Albertsson et al. studied the effect of corn starch and a prooxidant on the photooxidation of LDPE films and they found that incorporating only starch did not influence the susceptibility of the material to photolysis [5]. A further work of the same research group reported that LDPE with corn starch demonstrated a lower degradation rate than that of pure LDPE [6]. In a more recent work, Ratanakamnuan and Aht-Ong found that photodegradation rate increased and tensile properties decreased with the addition of banana starch in LDPE/banana starch films [7]. Melt blending of TPS with synthetic polymer, such as polyethylene, has been considered an excellent alternative for the development of low-cost, sustainable materials [8–11]. Blends obtained in such works are available for commercial application such as blown films for packaging bags or agricultural uses due to the unusual high ductility reported [9, 10]. During melt blending of TPS particles, in contrast to granular starch, they can undergo deformation, breakup and coalescence, and consequently blend morphology can be controlled by certain processing parameters [8]. Moreover, the addition of softer TPS-dispersed particles has resulted in ductile blends when blended with LDPE [9, 10]. The purpose of this work is to evaluate the influence of TPS on the photodegradation of HDPE films.

Experimental

Materials

Two different high-density polyethylene resins, HDPE8007 (MFI = 8.3 g/10 min, PE830) and HDPE17450 (MFI = 17 g/10 min, PE1700), from Dow Chemical were used. Corn starch was obtained from Arancia Corn Products (Guadalajara, México). Glycerol from Proquisa Chemical Products (Saltillo, México) was used as plasticizer.

Preparation of HDPE/TPS films

In order to obtain masterbatches of different HDPE/TPS blends having 30 wt% TPS, an extrusion system composed of a 9 zones co-rotating twin-screw extruder (TSE, ZSK30 from Werner & Pfleiderer) and a single-screw extruder (SSE, KTS-100 from Killion) was used [12]. HDPE was melted in the SSE, which was connected to the barrel zone 5 of TSE. Temperature profile of SSE was from 80 to 180 °C and screw speed of 116 rpm. On the other hand, a suspension of starch/glycerol/water (48:32:20) was added to the feeding zone of TSE to prepare TPS. Almost all water was extracted from TPS at zone 4 and, finally, a practically water-free TPS was blended with HDPE from the zones 6–9. Pelletized samples were stored in metalized bags to avoid contact with environment moisture. HDPE/TPS blends containing 10 wt% TPS were prepared from those having 30% using the same TSE configuration but with a temperature profile between 150 to 180 °C.

Films of the HDPE/TPS blends having an average thickness of 1 ± 0.02 mm were prepared using the SSE. Temperature profile for PE830/TPS blends was 140 to 190 °C and for die and rollers 190 and 80 °C, respectively, while for PE1700/TPS blends, it was 140 to 180 °C and 180 and 80 °C for die and rollers, respectively. Roller speed was maintained at 1.0 mm min^{-1}.

Accelerated aging of HDPE and HDPE/TPS blends

Films HDPE/TPS specimens were exposed to UV light ($\lambda = 340$ nm) using the weathering tester equipment, model QUV Q-Panel. Evaluations were carried out according to cycle A (4 h of condensation at 50 °C and 8 h of UV light at 60 °C) of ASTM D-4329-05 standard method.

FTIR

Chemical changes of aged HDPE/TPS films were measured by infrared spectroscopy (IR) using a Nicolet 710. Samples were scanned in transmission mode at a wavelength range of 4,000–400 cm^{-1} using a resolution of 0.5 cm. Carbonyl index (CI), analyzed at 1,722 cm^{-1}, was calculated by Eq. 1:

$$\mathrm{CI} = \frac{A_{1722}}{A_{728}} \tag{1}$$

where A_{1722} and A_{728} are the intensity wavelengths of carbonyl and $–\mathrm{CH}_2–$ groups characteristic of PE macromolecule, respectively.

Differential scanning calorimetry (DSC)

Differential scanning calorimeter measurements were performed on a DSC 2920 TA Instruments under nitrogen atmosphere. About 10 mg of each sample was weighed, placed in standard aluminum pan, and heated from 30 to 190 °C at a rate of 10 °C/min. Degree of crystallinity (X_c) was calculated by Eq. 2:

$$X_\mathrm{c} = \frac{[\Delta H_\mathrm{m}]}{\Delta H_\mathrm{m}^\mathrm{o}} \times 100 \tag{2}$$

where ΔH_m is the melting enthalpy of the sample and $\Delta H_\mathrm{m}^\mathrm{o} = 293.6\ \mathrm{J\ g^{-1}}$ represents the theoretical melting enthalpy of HDPE at 100% crystallinity [13].

Molecular weight

Molecular weight (M_w) was measured by gel permeation chromatography (GPC) using an Alliance model GPCV-2000 equipped with two linear columns (a column 103 Å, and a guard column STYRAGEL), refractive index, viscometer, and light scattering sensors. Tests were performed at 140 °C using 1,2,4 trichlorobenzene as eluent.

Mechanical properties

Films HDPE/TPS tensile samples were tested according to the ASTM D638-97 at 15 mm min^{-1} on a universal machine (4301 Instron) equipped with a 500 N load cell and data acquisition system. The average values of Young's modulus and elongation at break were calculated from at least 10 measurements.

Results and discussion

Oxidation evolution

Chemical changes of films of HDPE and HDPE/TPS induced by UV exposure were evaluated by FTIR. Considering that FTIR spectra of both polyethylenes and their blends are similar, discussion will be carried out on the films prepared with PE 1700. In the case of unexposed PE1700 films, a weak peak related to the presence of carbonyl impurities is observed at 1,722 cm^{-1} (Fig. 1a). After exposure to UV radiation, the intensity of carbonyl peak increased as a consequence of PE oxidation. In the case of the unexposed PE1700/TPS films, the starch fingerprint regions (1,162, 1,116, 1,023, and 937 cm^{-1}) and the broad band at around 3,400 cm^{-1} associated with hydroxyl groups can be observed (Fig. 1b). There were also two weak peaks at 1,722 and 1,654 cm^{-1}, the former is associated with carbonyl impurities and the latter is related to water bonded with starch molecules [14, 15]. The intensity of the peak at 1,654 cm^{-1} shows a surprisingly dramatic increasing after 3 days of UV exposure, which could be related to the water uptake during the condensation period of UV exposure [14, 15]. As observed in the PE1700 films, PE1700/TPS blends also show a gradual increase of carbonyl peak at 1,722 cm^{-1} by UV oxidation with time.

The carbonyl indexes (CI) of the films of PE1700 and PE1700/TPS blends were calculated to obtain quantitative information of the oxidation evolution (Fig. 2). Before exposure to UV light, both the PE1700 and PE1700/TPS blends show CI at 0.02 and 0.06, respectively, which are probably related to the presence of carbonyl impurities and chromophores. The first 3 days of exposure for PE1700 shows that the CI has an increasing rate of ca. 0.003 CI unit/day [16]. From 3 to 18 days there is an almost constant oxidation rate of ~0.01 CI unit/day. But for the period of 18 to 25 days, a higher oxidation rate of 0.017 CI unit/day is observed. In the case of PE1700/TPS blend films, a similar trend in oxidation rate in the period between 3 and 25 days (~0.01 and 0.016 CI units/day, respectively) is noticeable. During the first 3 days, however, there is a marked increasing in the oxidation rate of 0.023 CI unit/day, which is probably related to the high water uptake observed by FTIR at 3 days of UV exposure (Fig. 1b). Considering the oxidation rate from 3 to 25 days of exposure, it seems that there is no influence of the presence of TPS on the oxidation rate of PE1700 as observed by Albertsson et al. [5].

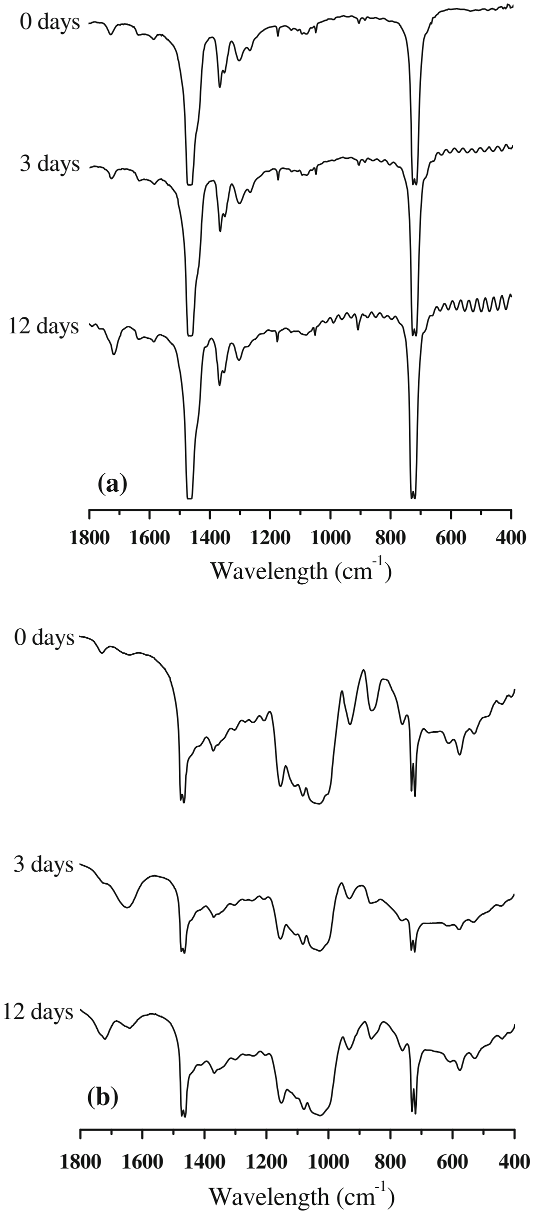

Fig. 1 FTIR spectra of **a** PE1700 and **b** PE1700/TPS blends with 30 wt% TPS content, exposed to UV irradiation for 0, 3, and 12 days

Molecular weight

Changes in molecular weight (M_w) of the films prepared with both PE830 and PE1700 and their blends showed similar trends, by that reason, Fig. 3 depicts only the evolution of M_w of PE830 and PE830/TPS (10 and 30 wt% TPS) films. Before UV irradiation, M_ws for PE830 and the two PE830/TPS blends were 8.2, 8.6, and

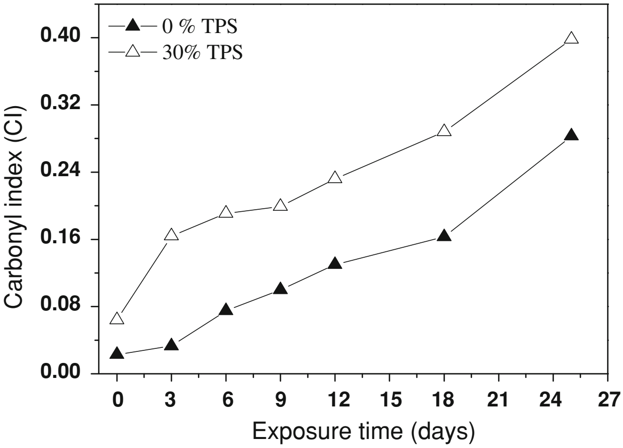

Fig. 2 CI of photoaged (*filled triangle*) PE1700 and (*open triangle*) PE1700/TPS blends with 30 wt% TPS content

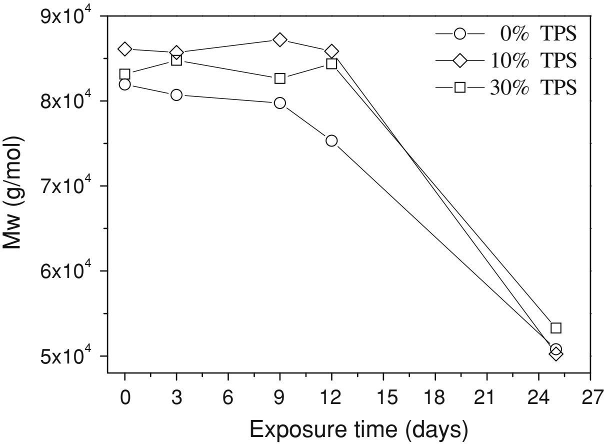

Fig. 3 M_w of photoaged (*open circle*) PE830 and PE830/TPS blends with 10 wt% (*open diamond*) and 30 wt% (*open square*) TPS content

8.3×10^4 g mol^{-1}, respectively. The higher M_ws of both the PE830/TPS blends are due to the different processing of each film. PE830 underwent only one processing step (film extrusion), while the PE830/TPS blend with 30% TPS went through two processing steps (melt blending in the TSE and film extrusion), and the PE830/TPS blend with 10% TPS underwent three steps (melt blending at 30% TPS, dilution with more PE in the TSE, and film extrusion). UV irradiation shows almost no effect on the M_w of the PE830 film during the first 9 days, whereas M_w of both PE830/TPS blends is unchanged for 12 days. After 25 days of UV exposure, M_w of all three films drop to about 5.2×10^4 g mol^{-1} due to PE photodegradation. As also observed in the oxidation evolution, it seems that the presence of TPS has no effect on the PE's M_w of the UV-irradiated films.

Structural changes

DSC measurements were performed to evaluate the effect of UV exposure on the changes of the crystalline fraction of HDPE and HDPE/TPS blend films. Melting temperature (T_m) of the unexposed PE830 films exhibits a maximum at 135.2 °C and decreases to 134.2 and 133.5 °C after 3 and 12 days of exposure, respectively (Fig. 4a). Broadening of DSC curves seems to be also dependent on UV exposure time. Similar behavior is also observed for PE830/TPS films having 30 wt% TPS in which T_m decrease from 135.5 °C before exposure to 134.7 and to 132.9 °C after 3 and 12 days, respectively. It should be noted that the DSC curve at 12 days was wider in the case of the blend (Fig. 4b).

Enthalpy of fusion (ΔH_m) is calculated from the area under the melting peak and is a useful way to quantify the amount of ordered regions in semicrystalline polymers [17]. Figure 5 shows the effect of UV irradiation on the ΔH_m values of PE830 and PE830/TPS blends having 10 and 30% TPS. Unexposed samples exhibit a reduction of ΔH_m, which is inversely proportional to the TPS content (206, 194, and 135 J g^{-1} for PE830 and PE830/TPS blends having 10 and 30% TPS, respectively). UV-irradiated PE830 samples show a dramatic reduction of ΔH_m from 206 J g^{-1}, before UV exposure, to 198 and 162 J g^{-1}, after exposure for 3 and 12 days, respectively. Conversely, PE830/TPS blends having 10 and 30 wt% TPS show different trends. In the former, ΔH_m seems to remain constant after 12 days of UV exposure, while in the later, ΔH_m increases 15 J g^{-1} after the same period of time.

The ΔH_m results clearly show that exposure to UV radiation produces structural changes in the PE films. Some authors have reported increasing crystallinity (X_c) of LDPE and HDPE during thermal and UV aging [2, 4, 6, 18] while other authors have found that crystallinity of LDPE decreases during aging [6, 17, 19].

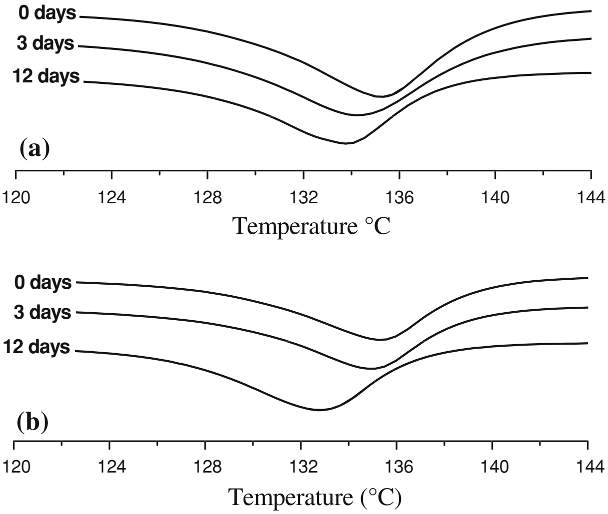

Fig. 4 DSC thermograms of **a** PE830 and **b** PE830/TPS blends with 30 wt% TPS content, exposed to UV irradiation for 0, 3, and 12 days

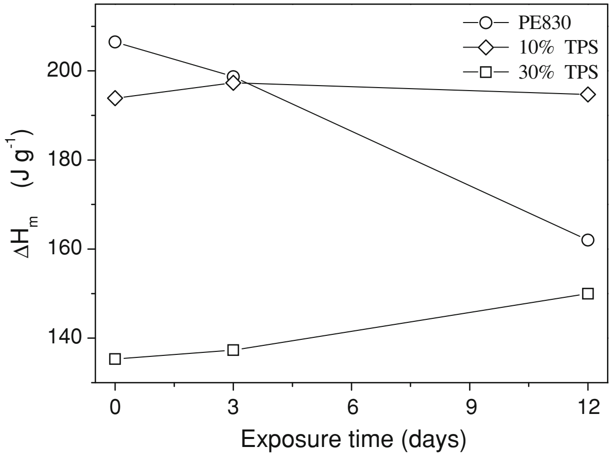

Fig. 5 ΔH_m of photoaged PE830 (*open circle*) and PE830/TPS blends with 10 wt% (*open diamond*) and 30 wt% (*open square*) TPS content

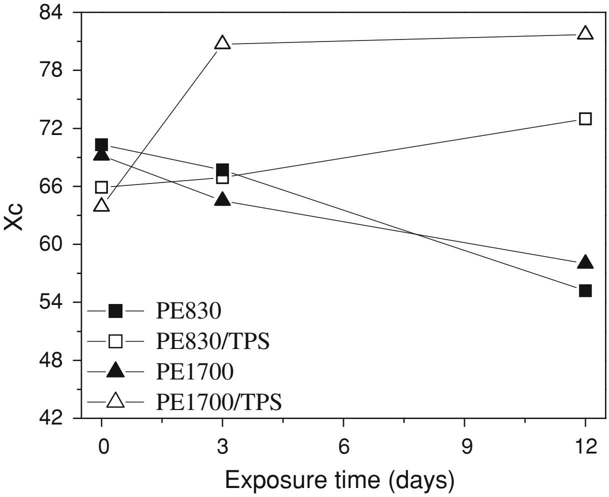

Fig. 6 X_c of photoaged PE830 (*filled square*), PE1700 (*filled triangle*), PE830/TPS (*open square*) blends with 30 wt% TPS and PE1700/TPS (*open triangle*) blends with 30 wt% TPS

Crystallinity increasing has been related to chain scission of polyethylene amorphous regions during UV irradiation [2, 18]. Conversely, decreasing X_c of PE samples has been related to the formation of functional groups such as hydroxyl, ketones, and branching during photodegradation [17]. In the present work, X_c of both PE830 and PE1700 decreases during exposure to UV irradiation, from about 70% before exposure to about 57% after 12 days (Fig. 6). Lower X_c could be related to the formation of functional groups (Fig. 2) considering that M_w of PE remained unchanged during this period of time (Fig. 3). X_c of unexposed PE830/TPS

(30% TPS) films was 66% and it increases progressively after 3 and 12 days of UV irradiation up to 73%, i.e. 3% higher than unexposed PE830 and 16% higher than PE830 films photodegraded for 12 days. In the case of PE1700/TPS (30% TPS) blend, X_c shows an important shift (16%) during the first 3 days of UV exposure. This unexpected increase is coincident with the large water uptake observed by FTIR (Fig. 1). TPS is a nonequilibrium amorphous material that exhibits time-dependent structure and properties when stored above T_g [20]. During aging, starch chains undergo a reorganization process known as retrogradation which is characterized by the increase of crystallinity and, consequently, the stiffness of TPS materials [20, 21]. T_g of the TPS used in this work is about −54 °C [22]. During accelerated degradation of PE/TPS films, as mentioned above, samples were exposed in cycles of 8 h of UV irradiation at 60 °C and 4 h of condensation

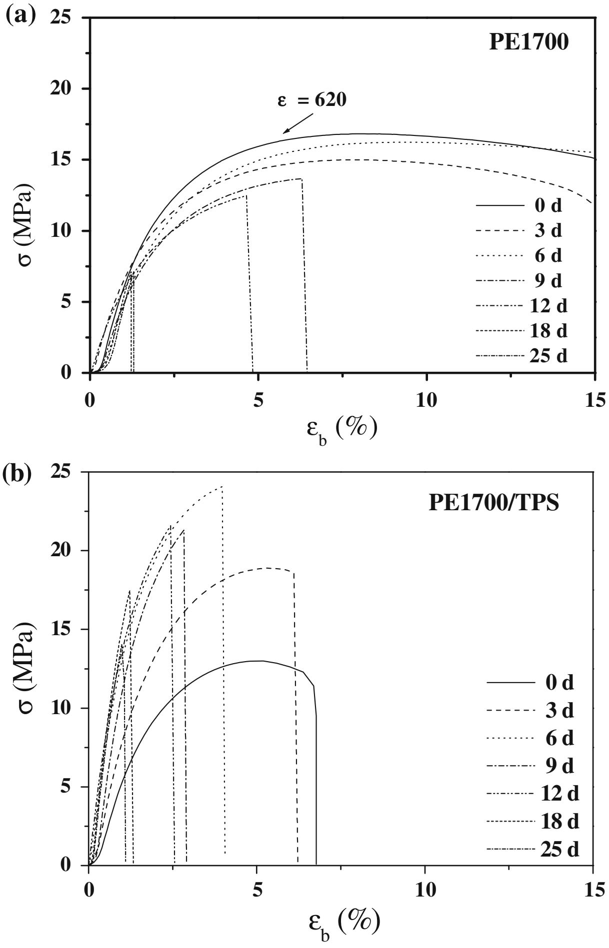

Fig. 7 The change of tensile diagrams as a function of exposure time (0, 3, 6, 9, 12, 18, and 25 days) of **a** PE1700 and **b** PE1700/TPS blends with 30 wt% TPS content

(ca. 100% relative humidity) at 50 °C, which are well above the T_g of TPS. After 3 days of UV irradiation, an important increase of water bonded to starch molecules was observed by FTIR in PE/TPS blends (Fig. 1). Water is an excellent plasticizer for starch and unpublished results from our research group have shown that retrogradation process progresses faster as water content increases. In those results, it was observed that retrogradation produced a large melting signal between 120 and 150 °C and a large increase in tensile strength and Young's Modulus (E). For these reasons, it can be concluded that the increment of crystallinity in PE/TPS blends was produced by the retrogradation of TPS during UV aging.

Mechanical properties

Curves of stress–strain (σ–ε) of PE1700 and PE1700/TPS (30%) are depicted in Fig. 7. Both stress and strain of PE1700 films decrease during UV aging. Strain at break (ε_b) decreases from 6.2 to about 0.05 during the first 12 days of UV exposure even though M_w remains almost constant. Maximum stress also decreases during aging, which is in good agreement with the reduction of crystallinity observed in Fig. 6. The addition of 30 wt% TPS, even before UV irradiation, results in very fragile films that show ε_b below 0.1. While PE1700 resulted in lower stress, PE1700/TPS shows important stress increments during aging. The stress at break at 6 days is two times higher than the unexposed films. Stiffening of PE/TPS can be related to the crystallinity increasing produced by starch retrogradation.

Stiffening produced by retrogradation of starch also affects the evolution of E as a function of UV irradiation (Fig. 8). E of PE1700 depicts a gradual reduction during aging. The presence of TPS diminishes the drop of E values during UV irradiation (10% TPS) or even increases it for the first 6 days at short times E (30% TPS). These results confirm the important effect of starch retrogradation on the performance of HDPE/TPS during aging at high energy and high relative humidity environment.

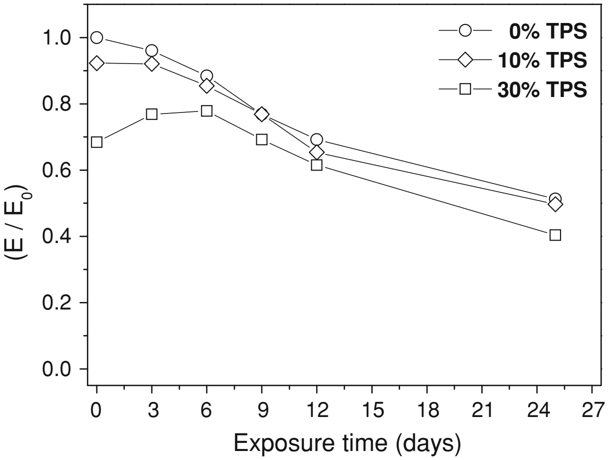

Fig. 8 Relative Young's Modulus (E/E_0) of photoaged PE1700 (*open circle*) and PE1700/TPS blends with 10 wt% (*open diamond*) and 30 wt% (*open square*) TPS content

Conclusions

Thin films of HDPE and HDPE/TPS blends were exposed to UV irradiation in order to analyze the effect of the presence of TPS on the photodegradation of HDPE. Evaluation of oxidation rate and molecular weight of HDPE showed that there is almost no effect of TPS on the photodegradation mechanisms of HDPE. Conversely, the presence of TPS has an important influence on the mechanical performance of HDPE/TPS blends due to the increment of ΔH_m during aging. Increment of ΔH_m was related to the retrogradation process of starch molecules during accelerated aging. These results evidenced the important effect of starch retrogradation on the performance of HDPE/TPS blends during aging at high energy and high relative humidity environment.

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References

1. Sebaa M, Servens C, Pouyet J (1992) Natural and artificial weathering of low-density polyethylene (LDPE): calorimetric analysis. J Appl Polym Sci 45:1049–1053. doi:10.1002/app.1992.070450614
2. Jabarin SA, Lofgren EA (1994) Photooxydative effects on properties and structure of high-density polyethylene. J Appl Polym Sci 53:411–423. doi:10.1002/app.1994.070530404
3. Briassoulis D (2006) Mechanical behavior of biodegradable agricultural films under real field conditions. Polym Degrad Stab 91:1256–1272. doi:10.1016/j.polymdegradstab.2005.09.016
4. Fayolle B, Collin X, Audouin L, Verdu J (2007) Mechanism of degradation induced embrittlement in polyethylene. Polym Degrad Stab 92:231–238. doi:10.1016/j.polymdegradstab.2006.11.012
5. Albertsson AC, Griffin GJL, Karlsson S, Nishimoto K, Watanabe Y (1994) Spectroscopic and mechanical changes in irradiated starch filled LDPE. Polym Degrad Stab 45:173–178. doi:10.1016/0141-3910(94)90134-1
6. Erlandsson B, Karlsson S, Albertsson AC (1997) The mode of action of corn starch and a prooxidant system in LDPE: influence of thermooxidation and UV-irradiation on the molecular weight changes. Polym Degrad Stab 55:237–245. doi:10.1016/S0141-3910(96)00139-5
7. Ratanakamnuan U, Aht-Ong D (2006) Photobiodegradation of low-density polyethylene/banana starch films. J Appl Polym Sci 100:2725–2736. doi:10.1002/app.23048
8. St-Pierre N, Favis BD, Ramsay BA, Ramsay JA (1997) Processing and characterization of thermoplastic starch/polyethylene blends. Polymer 38:647–655. doi:10.1016/S0032-386(97)81176-7
9. Favis BD, Rodriguez F, Ramsay BA (2003) Polymer compositions containing thermoplastic starch. US Patent 6,506,657
10. Rodriguez-Gonzalez FJ, Ramsay BA, Favis BD (2003) High performance LDPE/thermoplastic starch blends: a sustainable alternative to pure polyethylene. Polymer 44:1517–1526. doi:10.1016/S0032-3861(02)00907-2
11. Taguet A, Huneault MA, Favis BD (2009) Interface/morphology relationship in polymer blends with thermoplastic starch. Polymer 50:5733–5743. doi:10.1016/j.polymer.2009.09.055
12. Tena-Salcido CS, Rodríguez-González FJ, Méndez-Hernández ML, Contreras-Esquivel JC (2008) Effect of morphology on the biodegradation of thermoplastic starch in LDPE/TPS blends. Polym Bull 60:677–688. doi:10.1007/s00289-008-0903-0
13. Peacock AJ (2000) Handbook of polyethylene. Marcel Dekker Inc, New York
14. Kauráková M, Belton PS, Wilson RH, Hirsch J, Ebringerová A (1998) Hydration properties of xylan-type structures: an FTIR study of xylooligosaccharides. J Sci Food Agric 77:38–44. doi:10.1002/(SICI)1097-0010(199805)77

15. Kauráková M, Wilson RH (2001) Developments in mid-infrared FT-IR spectroscopy of selected carbohydrates. Carbohydr Polym 44:291–303. doi:10.1016/S0144-8617(00)00245-9
16. Yang R, Ying L, Yu J, Wang K (2006) Thermal oxidation products and kinetics of polyethylene composites. Polym Degrad Stab 91:1651–1657. doi:10.1016/j.polymdegradstab.2005.12.013
17. Kaczmarek H, Oldak D (2006) The effect of UV-irradiation on composting of polyethylene modified with cellulose. Polym Degrad Stab 91:2282–2291. doi:10.1016/j.polymdegradstab.2006.04.024
18. Roy PK, Surekha P, Raman R, Rajagopal C (2009) Investigating the role of metal oxidation state on the degradation behavior of LDPE. Polym Degrad Stab 94:1033–1039. doi:10.1016/j.polymdegradstab.2009.04.025
19. Albertsson AC, Karlsson S (1993) Environment-adaptable polymers. Polym Degrad Stab 41:345–349. doi:10.1016/0141-3910(93)90082-T
20. Shi R, Liu Q, Ding T, Han Y, Zhang L, Chen D, Tian W (2007) Ageing of soft thermoplastic starch with high glycerol content. J Appl Polym Sci 103:574–586. doi:10.1002/app.25193
21. Chinnaswamy R, Hanna MA, Zobel HF (1989) Microstructural, physiochemical, and macromolecular changes in extrusion-cooked and retrograded corn starch. Cereal Foods World 34:415–422
22. Rodriguez-Gonzalez FJ, Ramsay BA, Favis BD (2004) Rheological and thermal properties of thermoplastic starch with high glycerol content. Carbohydr Polym 58:139–147. doi:10.1016/j.carbpol.2004.06.002