Characterization of EVA/PLA Blends When Exposed to Different Environments

I. Moura • G. Botelho • A. V. Machado

Abstract

EVA/PLA blends compatibilized with EVA-g-PLA grafted copolymers synthesized by reactive extrusion, through transesterification reaction between ethylene-vinyl-acetate (EVA) and polylactide (PLA) using titanium propoxide ($Ti(OPr)_4$) as catalyst, were characterized when exposed to different environments. Stability to UV radiation was assessed exposing the samples to a Xenon lamp, which simulates the sun UV spectrum and the biodegradability was evaluated by biochemical oxygen demand (BOD) in a closed respirometer. Exposed samples were removed periodically and analyzed by several analytical techniques, such as, FTIR, DSC, rheology and tensile tests. The results obtained evidenced that UV radiation induces structural modifications, which affect substantially rheological and mechanical properties. Moreover, the blend with higher amount of copolymer exhibits lower photo durability and greater biodegradability. From the environmental point of view, these new materials are very promising for application with short lifetime, like packaging.

Keywords Ethylene-vinyl-acetate • Polylactide • Durability • Copolymer

Introduction

Polymers produced from the raw materials of agricultural production chain or by action of microorganisms are biologically degradable. Therefore, these polymers rapidly gain economic importance due to the increasing demand for saving fossil raw materials and its contribution for a healthier environment [1].

Aliphatic polyesters have been widely used in a wide range of applications due to their capability to biodegrade in natural environments [2], including packaging materials and agricultural mulch films. Among them, polylactide (PLA) is the most used biodegradable polymer, due to its properties such as, low density, easy manufacturing, corrosion and resistance, which provides to this polymer a high potential [3]. Besides biodegradation it is also important to assess the stability to UV radiation. Therefore, many studies concerning bio and photodegradation of PLA have been recently reported [4-7].

PLA photodegradation studies reported the occurrence of two degradation mechanisms. The first involves a photolysis reaction leading to breakage of the backbone $C-O$ bond. The second one includes photodegradation of PLA leading to the formation of hydroperoxide and its subsequent degradation to compounds containing carboxylic acid and diketone end groups. Thus, when biodegradable polyesters are exposed to

environment, biodegradation, photodegradation as well as hydrolitic degradation might occur [2, 8-10].

Even though PLA is biodegradable and has relevant properties, during lifetime it has to fulfill similar specifications, in terms of thermal and mechanical properties, as conventional plastics [11]. To achieve these properties it is necessary to develop ecological friendly materials based on PLA and non-biodegradable polymers, which can be photo and biodegradable.

A good candidate to be blended with PLA is EVA, since it has excellent flexibility, fracture toughness, light-transmission properties, adhesion to other organic/inorganic materials together with long lifetime [12-14]. However, due to their incompatibility, EVA and PLA can not be successfully blended without significant reduction on mechanical properties. Hence, many attempts were made to improve the interaction between EVA and PLA, aiming to produce materials with improved properties [15, 16]. Moura et al. [16] synthesised compatibilized blends with EVA-g-PLA grafted copolymers as an alternative material to overcome the lack of properties that biodegradable plastics present during life-cycle. These new materials exhibited similar properties to conventional non-biodegradable polymers and higher biodegradability.

Since during lifetime and after become waste EVA/PLA blends can be exposed to sunlight, heat, oxygen, moisture and microorganisms, it is of great importance to investigate the durability of these materials when exposed to these conditions.

Ideally, polymers should be tested in real time and with realistic in-service environments, but this would require long exposure times [17]. It is also known that the results obtained with weathering units with a light distribution that comprises UV light above 300 nm can be used to simulate natural UV radiation [18, 19]. Thus, this study aims to evaluate the durability of EVA/PLA blends when exposed to UV radiation and microorganisms. The UV stability was carried out in Xenon Test 150 S chamber, which simulates the sun UV spectrum under accelerated atmosphere conditions. Biodegradation was assessed by biochemical oxygen demand (BOD) in a closed respirometer. Samples were collected along time and characterized by several analytical techniques (FTIR, DSC, rheology and tensile tests).

Experimental

Materials

Ethylene-vinyl-acetate copolymer (EVA) (Escorene Ultra Lot. 61E466) with 28wt% of vinyl acetate ($\overline{\boldsymbol{Mn}} = 18{,}000$ g mol^{-1}), supplied from Exxon was used as a synthetic non-biodegradable polymer and polylactide (PLA) ($\bar{M}\boldsymbol{n} = 22{,}000$ g mol^{-1}) supplied by Sigma Aldrich was used as a biodegradable polyester. Titanium propoxide ($Ti(OPr)_4$) from Sigma Aldrich was used as a transesterification catalyst.

Synthesis of EVA/PLA Compatibilized Blends with EVA-g-PLA Graft Copolymers

EVA/PLA blends were prepared in a Haake batch mixer (Rheocord 90; volume 50 cm^3), equipped with two rotors running in a counter-rotating way. The procedure was previously described in Moura et al. [16], and the compositions used are showed in Table 1. The amount of PLA and $Ti(OPr)_4$ was varied in order to investigate the effect of catalyst amount on both, copolymer formation and their photodegradation. Therefore, samples containing three different amounts of copolymer were prepared.

UV Stability Experiments

The accelerated weathering of EVA, PLA and EVA/PLA blends were carried out in a XenoTest 150 S chamber from Heraeus (Original Hanau) equipped with a filtered Xenon lamp with an intensity of $60 Wm^{-2}$ according to standard procedures [20]. The light of the Xenon lamp was filtered under $\lambda > 300$ nm with an UV window combined with six IR filter glasses. The XenoTest creates an accelerated environment of the natural weathering conditions, simulating materials behaviour during its lifetime.

The specimens used in these experiments, with dimensions 135×45 mm, were cut from thin films (about 50μ m thick), previously prepared by compression moulding at 160°C. The samples were removed at 100,400 and 700 h (4, 17 and 30 days, respectively) of exposure and characterized by the analytical techniques indicated below.

Biodegradability Evaluation

Biodegradation tests were performed in aqueous environment under aerobic conditions according to the standard ISO 14851:1999 (determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium), which postulates a method quantify the biochemical oxygen demand (BOD) in a closed respirometer. This procedure was previously described in Moura et al. [21].

Material Characterization

FTIR Spectroscopy

Chemical modifications that occur on materials were followed by infrared spectroscopy. All spectra (16 scans, nominal resolution of $4\ cm^{-1}$) between $4{,}000 - 500\ cm^{-1}$ were acquired before and after photodegradation using a Jasco spectrometer.

Table 1 Composition of the prepared samples

Sample	EVA (wt%)	PLA (wt%)	Catalyst (wt%)	EVA-g-PLA (wt%)
EVAPLA0	60.0	40.0	0.0	0.0
EVAPLA0.9	59.5	39.6	0.9	8.0
EVAPLA1.9	59.5	38.6	1.9	25.0

Thermal Measurements

Thermal behaviour of all samples was recorded using TA Instruments differential scanning calorimeter (DSC 2920). Samples weighing about 10 mg were heated from 25 to 200°C at a heating rate of 10°C/min, cooled down to room temperature at the same rate, in order to eliminate the thermal history of the materials. Then, they were heated again until 200 °C and cooled to room temperature at the same heating rate. Experiments were performed under liquid nitrogen with a flux of 50ml/min to prevent further oxidative degradation of samples during heat.

The crystallinity degree (X_c) was calculated by the ratio of ΔH_f (the apparent melt enthalpy measured from the DSC curves as melting enthalpy per gram) corresponding to the component and ΔH_f^0 (the melt enthalpy per gram of the component in its completely crystalline state, being 44.0 and 93.6 J/g for EVA and PLA, respectively), according to the following equation:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \quad (1)$$

Rheological Properties

Oscillatory rheological measurements of original polymers and prepared samples were carried out in an TA instruments AR-G2 rotational rheometer using a parallel-plate geometry. The gap and diameter of the plates were 1 mm and 4.0 cm , respectively. A frequency sweep was carried out to determine the complex viscosity (η^*) and storage modulus (G'). The experiments were performed at a processing temperature of 160°C, in a frequency range from 0.01 to 100 Hz under constant strain.

Mechanical Properties

The mechanical properties of the homopolymers and EVA-g-PLA copolymers nonexposed and submitted to accelerated weathering were characterized using stress-strain experiments in a ZWICK equipment.

The tensile experiments were carried out with a deformation rate of 5.0 mm/min at room temperature and relative humidity of 50%. The tests were performed on 2.5 cm × 0.8 cm rectangular samples in a longitudinal direction.

At least 6 specimens of each sample were tested. The thickness of every specimen was measured with a pachymeter Mitutoyo with an accuracy of 0.025 mm .

Results and Discussion

Blends compatibilization was achieved by EVA-g-PLA grafted copolymers, which obtained through a transesterification reaction catalysed by a titanium alkoxide derivative according to the mechanism shown in Fig. 1 [16].

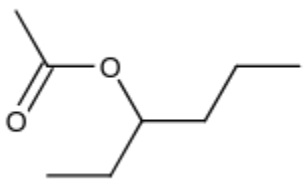
The structural changes that occurred during durability tests of EVA, PLA and prepared copolymers, when exposed to UV radiation, was evaluated by FTIR. FTIR spectra of EVA nonexposed and submitted to accelerated weathering over 100, 400 and 700 h (Fig. 2) evidenced notable changes in some functional groups after irradiation. The enlargement absorption shoulder at around 1,175 cm^{-1} and the absorption band at 1,715 cm^{-1}, corresponding to the carbonyl ($C = O$) stretching, are associated to the formation of ketone and lactone groups, respectively. According to previous studies [13, 22], these groups might be formed during the acetaldehyde process in Norrish photolysis reaction (Fig. 3a) or even during the water deprivation reaction of the hydroperoxyde (Fig. 3b) [23, 24]. The carbonyl vibration observed around 1,760 cm^{-1} is due to lactone formation, over back-biting process in the vinyl acetate units by the acetate groups, as shown in Fig. 3c [13, 22]. Additionally, several new absorption bands appeared in the range of $910 - 990$ cm^{-1}, which were attributed to insaturations of vinyl ($-CH = CH_2$) and vinylene bonds ($-CH = CH-$) [13].

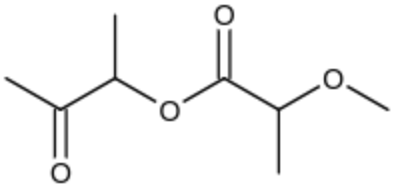
Photo-chemically induced degradation starts from vinyl acetate groups (VAc) located in the amorphous regions, which have a major influence on EVA photodegradation [13, 22]. Therefore the changes in FTIR along degradation time can be explained by the VAc content of the EVA used (28wt%).

Studies concerning EVA photodegradation have also reported that during degradation a competition between crosslinking and chain scission takes place, being the later dominant [25-29].

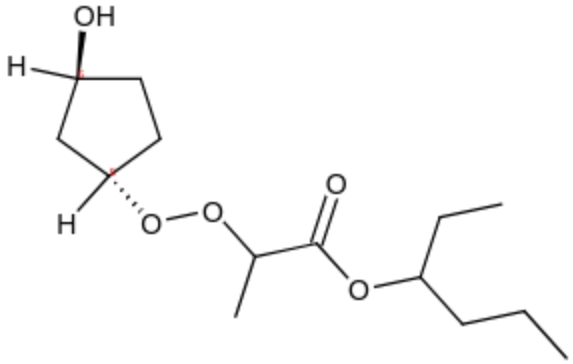
The spectrum of nonexposed PLA shows a band corresponding to ester overtone at $3{,}400 - 3{,}600$ cm^{-1} and a peak associated with hydroxyl groups between $3{,}600 - 3{,}700$ cm^{-1}. CH -assymetric and CH -symmetric stretches appear at 2,920 and 2,850 cm^{-1}, respectively. PLA exposed to accelerated weathering along time (Fig. 4), shows a growth of the absorption bands at $3{,}400 - 3{,}700$ cm^{-1} (Fig. 4a), resulting from an increase of hydroxyl groups resulting from oxidation. Moreover, CH stretch bonds also undertake some modifications. The results obtained are in agreement with literature [2, 8-10, 30], which reported that PLA undergoes structural modifications, when submitted to UV radiation. Gardette et al. [9] and Tsuji et al. [2] reported that PLA degrades through chain scission and hydrolysis by rain/water and/or moisture. PLA absorbs water, which results in hydrolysis of the ester linkages, which leads to chain scission of the long PLA molecules and consequently, low molecular weight oligomers formation [9]. The structural PLA changes detected such as, $C = C$ bonds and hydroperoxides formation can be explained by the published Norrish II mechanism (Fig. 5) [30].

Fig. 1 Reaction mechanism of copolymer formation (adapted from [16])





PLA



PLA segment ended by acetate group

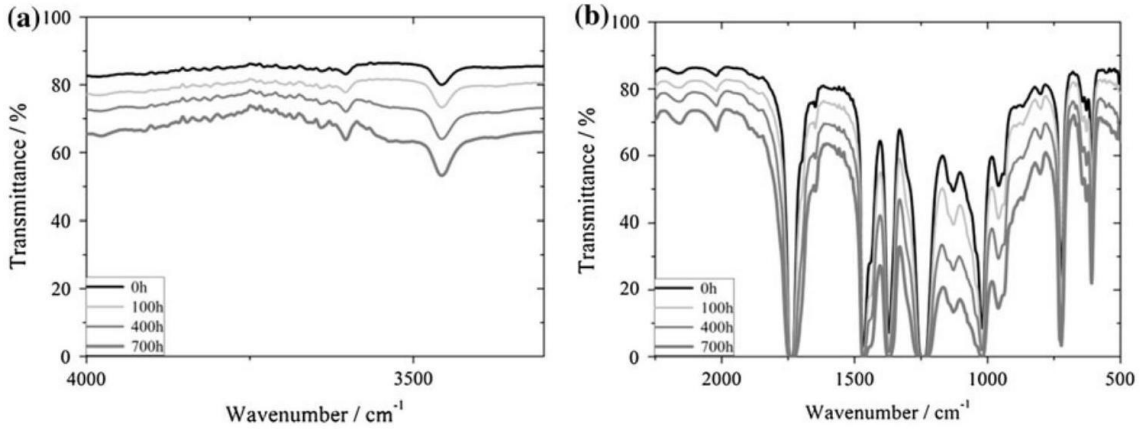


Fig. 2 FTIR spectra of EVA exposed to UV radiation **a** hydroxyl region and **b** carbonyl region

Figure 6 depicts the FTIR spectra of the copolymers samples before and after 100, 400 and 700 h of accelerated weathering. All exposed samples (EVAPLA0, EVAPLA0.9 and EVAPLA1.9) exhibit an increase of the absorption band at $3{,}400 - 3{,}700\ cm^{-1}$ and an enlargement of the absorption band at $1{,}700 - 1{,}800\ cm^{-1}$, corresponding to hydroxyl and carbonyl groups of PLA and EVA, respectively. When FTIR spectra of all samples are compared it is clear that similar chemical changes occurred. In the hydroxyl region ($3{,}400 - 3{,}700\ cm^{-1}$) it is possible to observe an increase along degradation time, but it

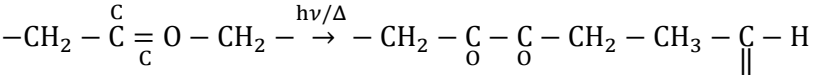
becomes more evident after 700 h of exposure time for samples EVAPLA0.9 and EVAPLA1.9.

Figure 6b, d, f (carbonyl region) depict a broad absorption band with a maximum at 1,750 cm^{-1}. All samples present similar evolution, but this band becomes broader at 700 h namely for EVAPLA1.9 sample. As stated before, these modifications can be attributed to ketone and lactone formation, which can be created via acetaldehyde evolution, hydroxide breaking down and via back-biting process (Fig. 3).

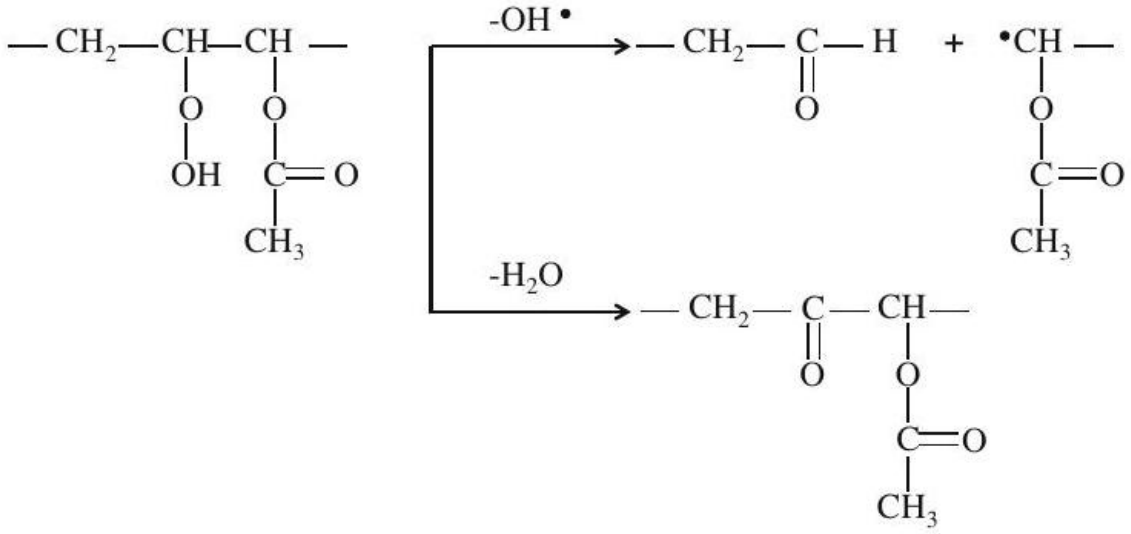
Even though the chemical changes observed are similar for both samples, the qualitative analysis of the spectra suggests that the chemical modifications are more pronounced for EVAPLA1.9, which can be associated to higher copolymer amount (25.0wt%) [16]. The difference can be attributed both to its more branched/crosslinked structure and to the higher number of ester groups of EVA linked to PLA chains [16].

Rheological characterization was conducted to obtain more details of the effect of UV exposure on the polymer structure, mainly chain scission. The analysis of complex viscosity (η^*) and storage modulus (G′) was performed for original polymers and prepared samples along exposure time. Figure 7a and b present the values of η^* and G', at low frequency (0.1 Hz), along aging time. Even though all materials have a similar trend, differences can be noticed. The complex viscosity of EVA decreases significantly during the initial 100 h of exposure (4.2E4 to 2.1E3 Pa.s). Then, both viscosity and storage modulus change slightly from 100 to 400 h and until 700 h a considerable variation was detected (1.9E3 to 1.6 E 2 Pa. s and 9.2 E 1 to 7.3 E 0 Pa , respectively). These results confirm that chain scission occurred during UV exposure and it was the main reaction during the initial 100 h and after 400 h of exposure. Between 100 and 400 h it seems that no significant changes occurred, what can be explained by the competition between chain scission and crosslinking reactions.

(a)



(b)



(c)

$$CH_2 - CH_2 - CH_I^{CH} - C \overset{h\nu/\Delta}{\rightarrow} - CH$$

Fig. 3 a Ketone formation via acetaldehyde evolution, b Ketone formation via hydroxide breaking down and **c** Lactone formation via back-biting process

The PLA viscosity also decreases with the increase of exposure time. It changes from 3.6 E 3 to 7.8E1 Pa. s during the initial 100 h , indicating the occurrence of chain scission. After this period both viscosity and storage modulus are almost constant. Contrarily to EVA, the rheological behavior suggests that PLA chain scission is less noticeable.

In accordance with the trend observed by FTIR, the decrease in viscosity after 700 h exposure time, is more pronounced for EVAPLA1.9 (from 5.6E4 to 2.4E0 Pa.s), followed by EVAPLA0.9 (from 1.4E4 to 2.4E0 Pa.s) and finally EVAPLA0 (1.6E4 to 7.4E1 Pa.s). As explained before, since this sample (EVAPLA1.9) has a more branched structure and higher amorphous regions, chain scission is more noticeable.

The storage modulus has a similar trend. Again, these results confirm that EVAPLA1.9 suffers higher chain scission when exposed to similar conditions.

It is also clear that the pseudoplastic behavior of the samples decrease after UV exposure. Once more, this behaviour can be explained by the chemical changes that take place during degradation. The rheological measurements corroborate that the sample with higher copolymer amount is more prone to chain scission during exposure to UV radiation.

EVA and PLA are both semi-crystalline polymers and the initial crystallinity degree (X_c) is about 26.4 and 27.5%, respectively. Tables 2 and 3 show the values of melting temperature and X_c obtained for all samples tested, before and after exposed 700 h to accelerated weathering. As it can be seen in Table 2, while the melting temperature of EVA is approximately constant until 400 h , the crystallinity degree becomes higher along exposure time. This behavior can be attributed to chain scission, as observed by rheological measurements, and the formation of ketone structures with lower steric hindrance enhances the chain mobility. The increase in crystallinity can also be explained according to Liu et al. [31], by intra and inter-molecular entanglement in molecules renders easy the rearrangement and/or recrystallization during aging.

Comparing the melting temperature and crystallinity degree of EVA with the one of PLA, the first was almost constant and minor changes occurred for the later, only enlarge 9% after 700 h of exposure time. This would be expected from the rheological results. This small increase in X_c can be due to the rearrangement of the amorphous PLA segments, which resulted from chain scission, into crystalline phase [30, 32].

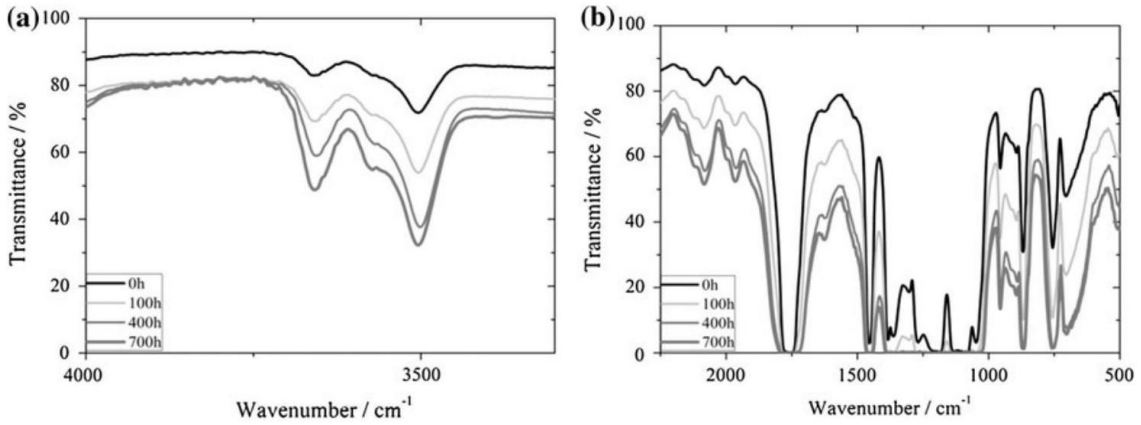
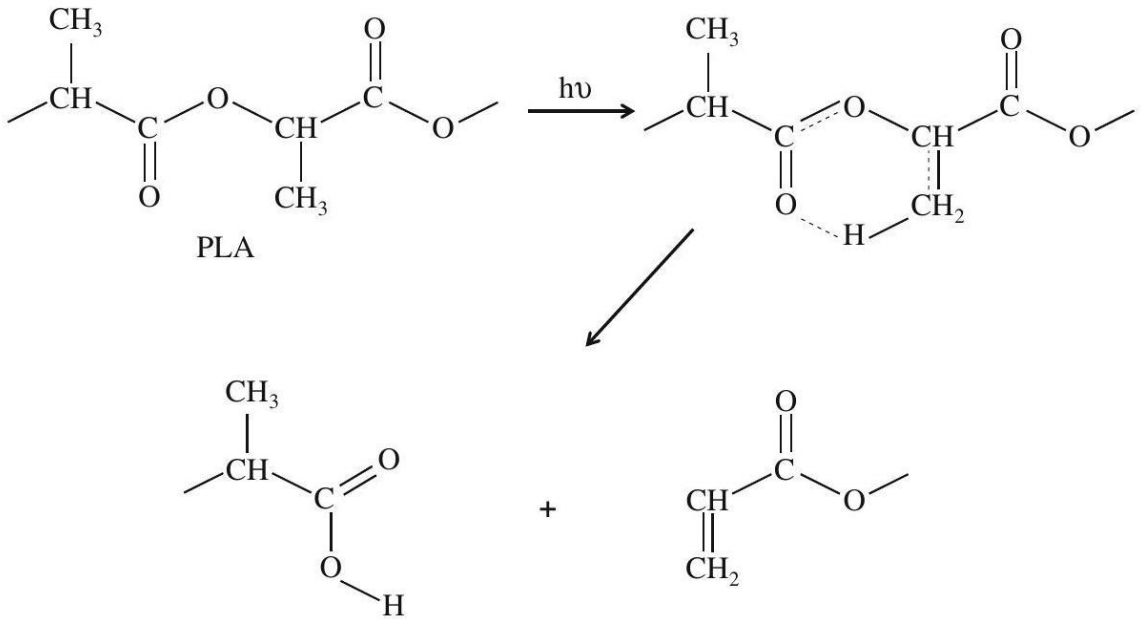


Fig. 4 FTIR spectra of PLA exposed to UV radiation a hydroxyl region and b carbonyl region

Fig. 5 Photodegradation of PLA via Norrish II mechanism [29]



Prepared blends exposed to accelerated weathering, exhibit similar melting temperature along the time in both phases, only a decrease is observed at 700 h (Table 3). This is in agreement with changes in molecular weight, a strong decrease was noticed for EVAPLA0.9 and EVAPLA1.9 between 400 and 700 h . However, an increase of X_c along time occurs, mainly in EVA phase. Moreover, the overall increase of X_c is more pronounced for samples containing a higher copolymer amount. Thus, X_c after 700 h of exposure is slightly higher for EVAPLA1.9 than EVAPLA0.9. This is in agreement with FTIR and rheological results, where the major changes occurred for EVAPLA1.9. This behavior can be explained by the higher content of copolymer in EVAPLA1.9 sample.

Since embrittlement point is regarded as a significant point to assess the maximum extent of polymeric degradation, it was determined from the plots of the crystallinity data. Figure

8a, b depict the embrittlement point of EVA, PLA and EVAPLA1.9, respectively. It can be observed that the exposure period was enough to result in polymers embrittlement. From EVA FTIR spectrum (Fig. 2), the fast enlargement of carbonyl absorption band is noticed during the first 100 h of exposure. After that, the rate of enlargement in carbonyl absorption slows down. Conversely, for PLA and in accordance to Norrish II mechanism, changes in hydroxyl groups, and modifications in CH stretch bonds increases slowly until 400 h and faster from 400 to 700 h of exposure time. Therefore, the slow increase in X_c until 400 h , can be associated to PLA photodegradation via a bulk erosion mechanism and after by chain scission.

Comparing the embrittlement points of EVA and PLA, there is no doubt that for short degradation times the former undergoes higher molecular modifications, i.e., the degree of chain length reduction during this period is particularly high for EVA, what can be mirrored in X_c (see Table 2).

Figure 8b indicates that when the copolymer is present in large amount (25.0wt%) the embrittlement of the material was reached rapidly. An exposure time of 100 h is enough to obtain significant changes, which can be related with their more branched/crosslinked structure due to copolymer formation and more amorphous regions, which favors the oxygen and radiation penetration.

It is well known that changes in chemical structure and morphology are responsible for the deterioration of tensile properties, in particular, elongation at break (ε) and modulus. To follow the mechanical behavior, tensile tests (tensile strength, elongation at break and Young modulus) were performed for original polymers and prepared samples with different exposure time (Fig. 9). EVA is a polymeric material that exhibits a flexible behavior before exposure and becomes more fragile after degradation. Until 100 h of exposure an increase can be observed for tensile strength, Young modulus and elongation at break and after that time a decrease along exposure occurs. After 700 h of exposure it has an elongation at break lower than 250%, which means that it lost about 30% of this property. Similar behavior occurred for tensile and modulus. These changes can be associated to both chain scission and increase in crystallinity (Table 3). Even though, a lost of 30% of mechanical properties is significant, according to literature the material can be used until it lost 50%. Jin et al. [12], in a study with two EVAs with lower VA content, observed similar evolution of mechanical properties during exposure. However, both EVAs investigated became fragile after 400 h exposure.

A reduction in mechanical properties was also observed for PLA (Fig. 9b). Tensile properties decrease with increasing exposure time. After 700 h, PLA has a decrease of 60% for elongation at break, 40% for tensile strength and 65% for Young modulus. These results indicate that the chemical modifications that occurred due to UV radiation had a significant effect on PLA properties. Moreover,

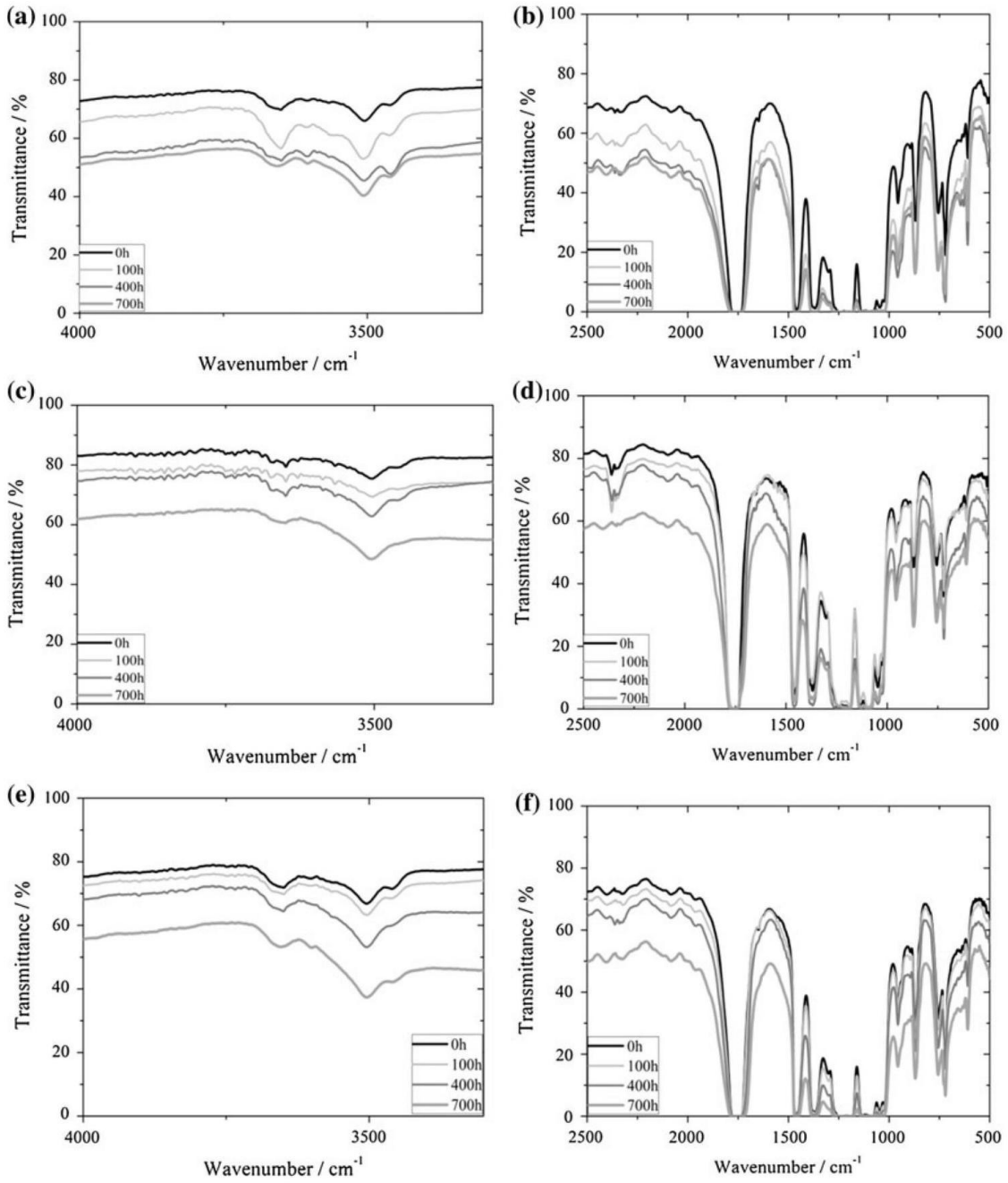


Fig. 6 FTIR spectra of the samples exposed to UV radiation: hydroxyl region (**a**, **c**, **e**) and carbonyl region (**b**, **d**, **f**) corresponding to EVAPLA0, EVAPLA0.9 and EVAPLA1.9, respectively

the PLA used in the present work has a lower $\bar{M}n$ ($\bar{M}n = 22{,}000\ \mathrm{g\ mol^{-1}}$), which can explain a significant decrease in tensile properties, namely elongation at break during photodegradation.

Figure 9c depicts changes in tensile properties of the sample EVAPLA1.9. A huge reduction in the mechanical properties can be observed, being more pronounced for elongation at break. After the irradiation period the elongation at break, tensile and Young modulus decrease from

43 to 3%, 7 to 4 MPa and 116 to 79 MPa , respectively. This behavior is in agreement with FTIR, DSC and rheological results, higher chain scission promotes a significative decrease of the mechanical properties. Therefore samples EVAPLA1.9 exhibited lower durability under UV radiation.

The biodegradability was characterized by biochemical oxygen demand, which is expressed as the amount of 0_2 consumed during biodegradation divided by their theoretical oxygen demand (ThOD). The values of the theoretical

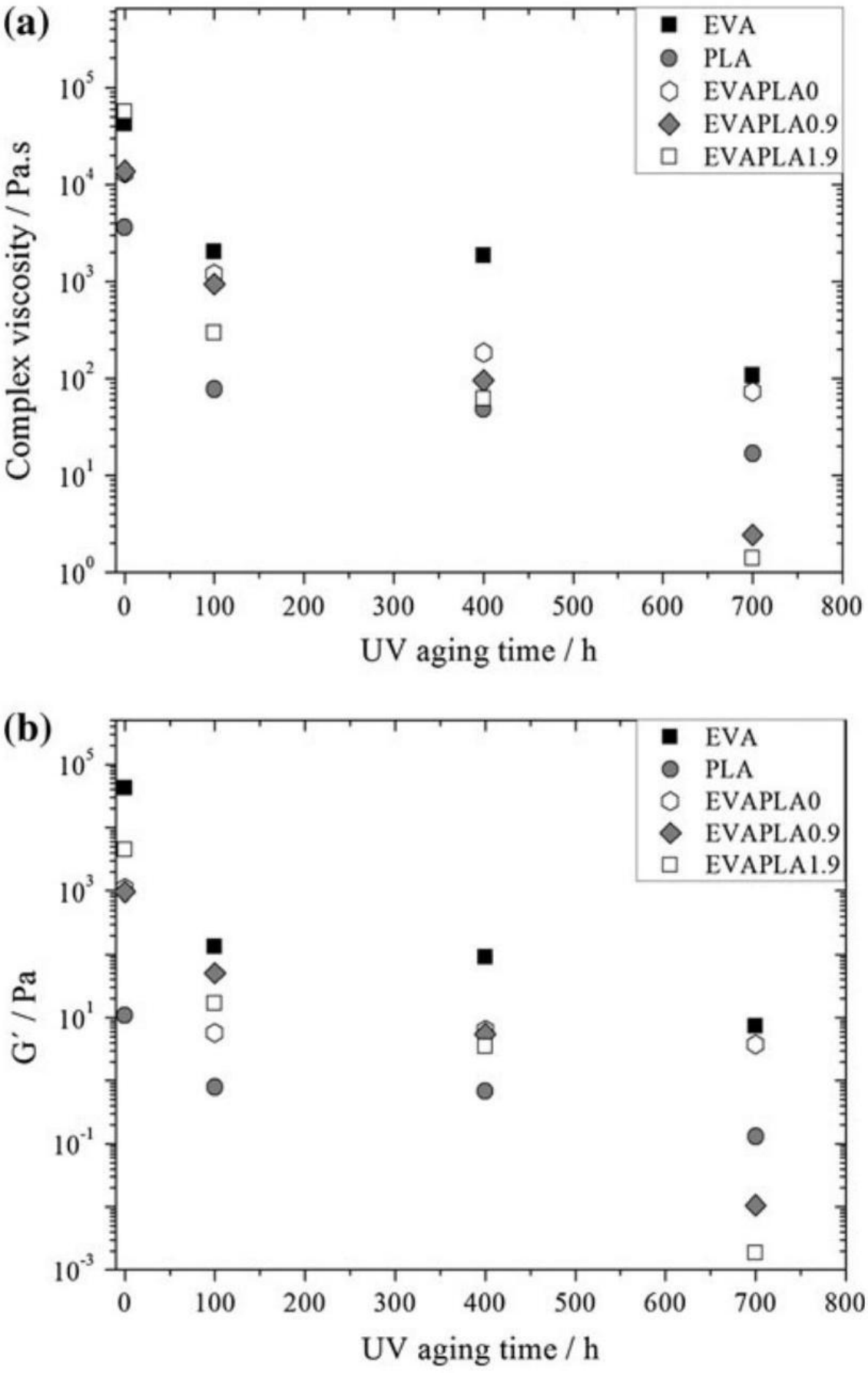
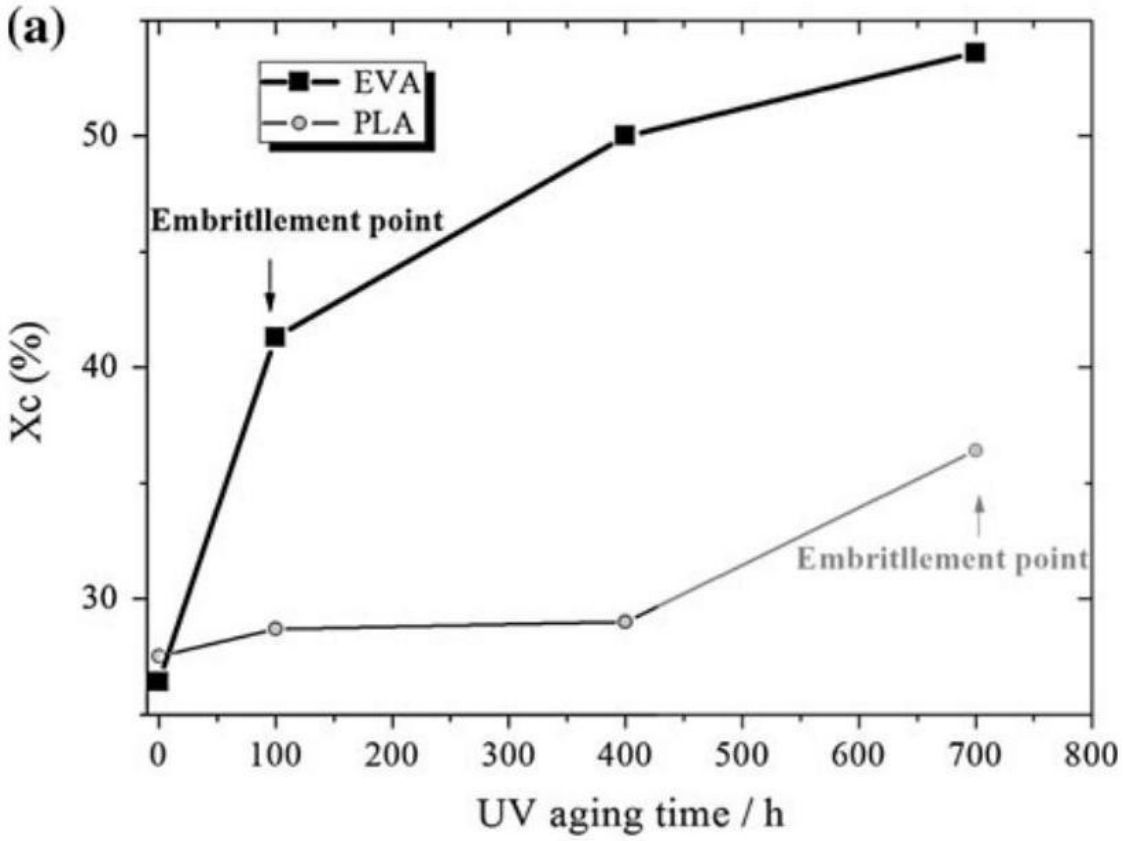

(a)
Complex viscosity / Pa.s
UV aging time / h
EVA
PLA
EVAPLA0
EVAPLA0.9
EVAPLA1.9
(b)
G′ / Pa
UV aging time / h
EVA
PLA
EVAPLA0
EVAPLA0.9
EVAPLA1.9

Fig. 7 Rheological behaviour of all samples as function of aging time, a complex viscosity and b storage modulus

Table 2 Melting temperature (Tm) and degree of crystallinity (Xc) of neat polymers

Time (h)	Tm(°C)/Xc(%)			
	0	100	400	700
EVA	87/26	87/41	88/50	91/54
PLA	154/28	153/29	153/29	152/36

oxygen demand were calculated based on elemental analysis of each sample. Table 4 shows the results after 60 days of biodegradation. As expected between the neat


(a)
EVA
PLA
Embritllement point
Embritllement point
Xc (%)
50
40
30
0
100
200
300
400
500
600
700
800
UV aging time / h

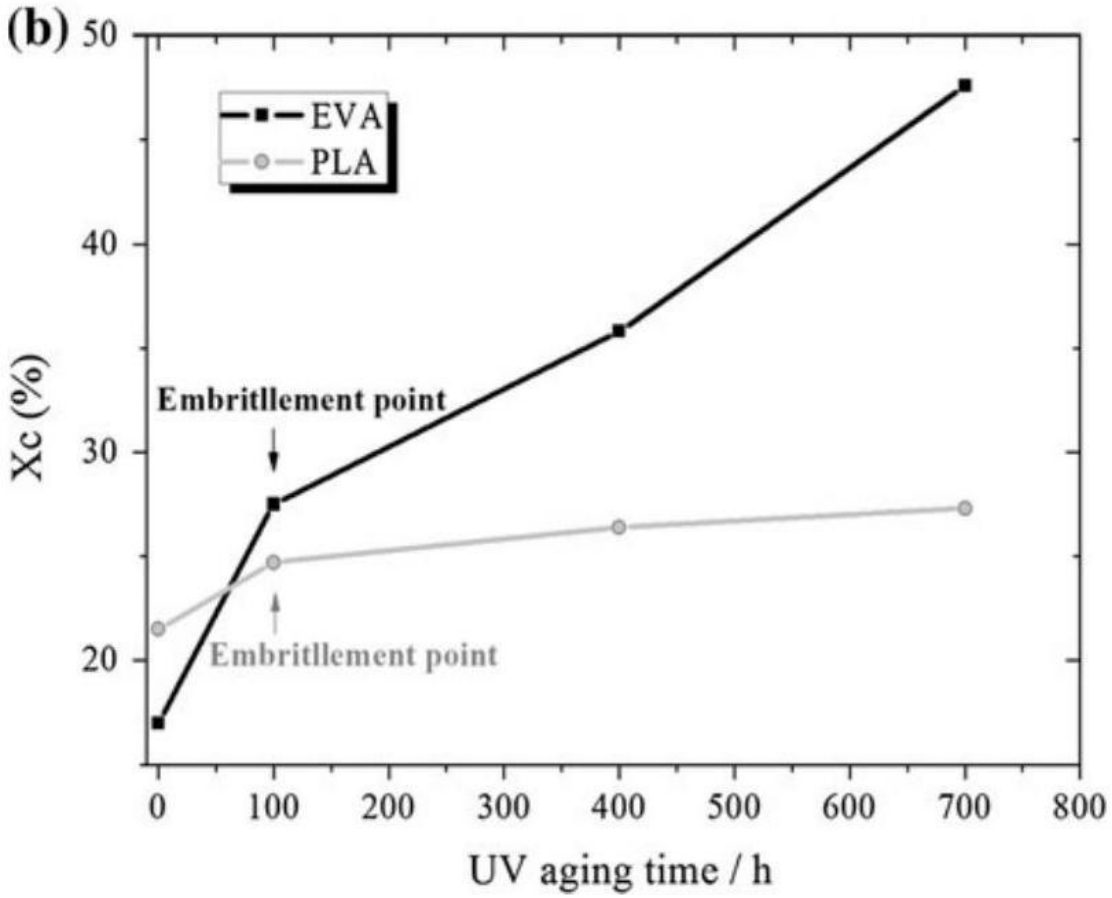
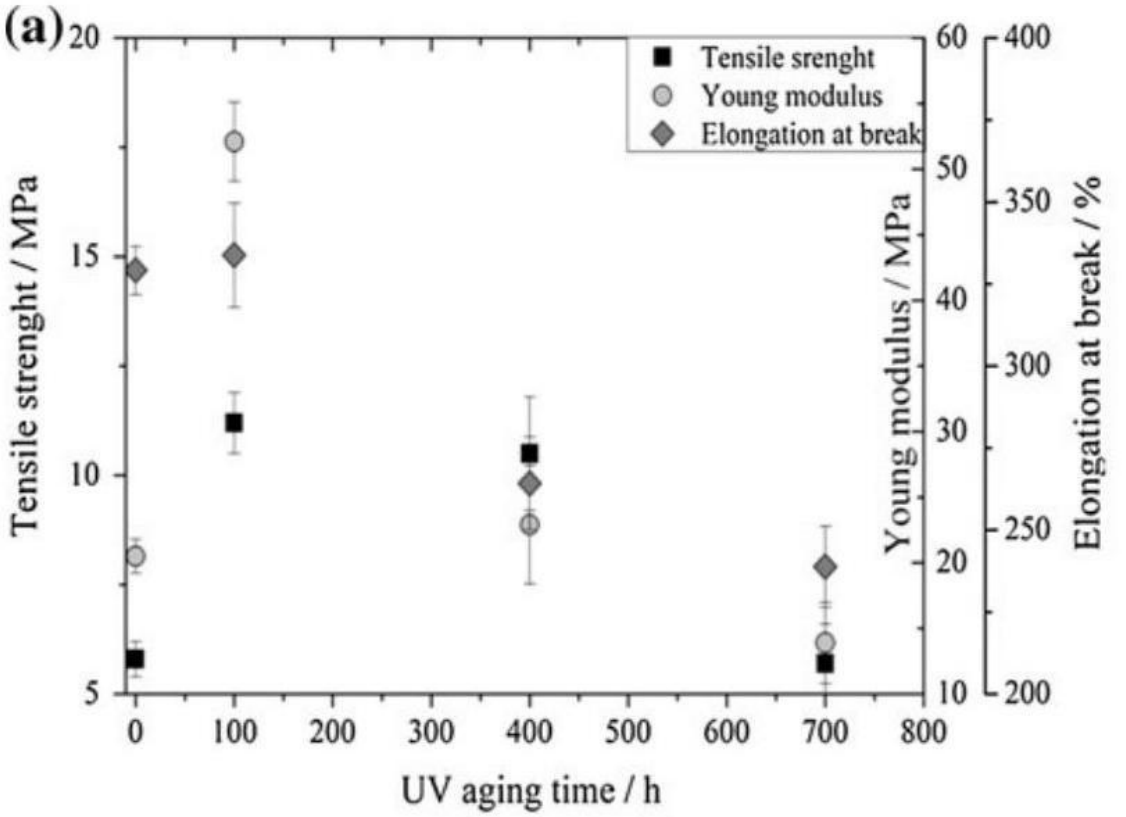

(b)
EVA
PLA
Embritllement point
Embritllement point
Xc (%)
50
40
30
20
0
100
200
300
400
500
600
700
800
UV aging time / h

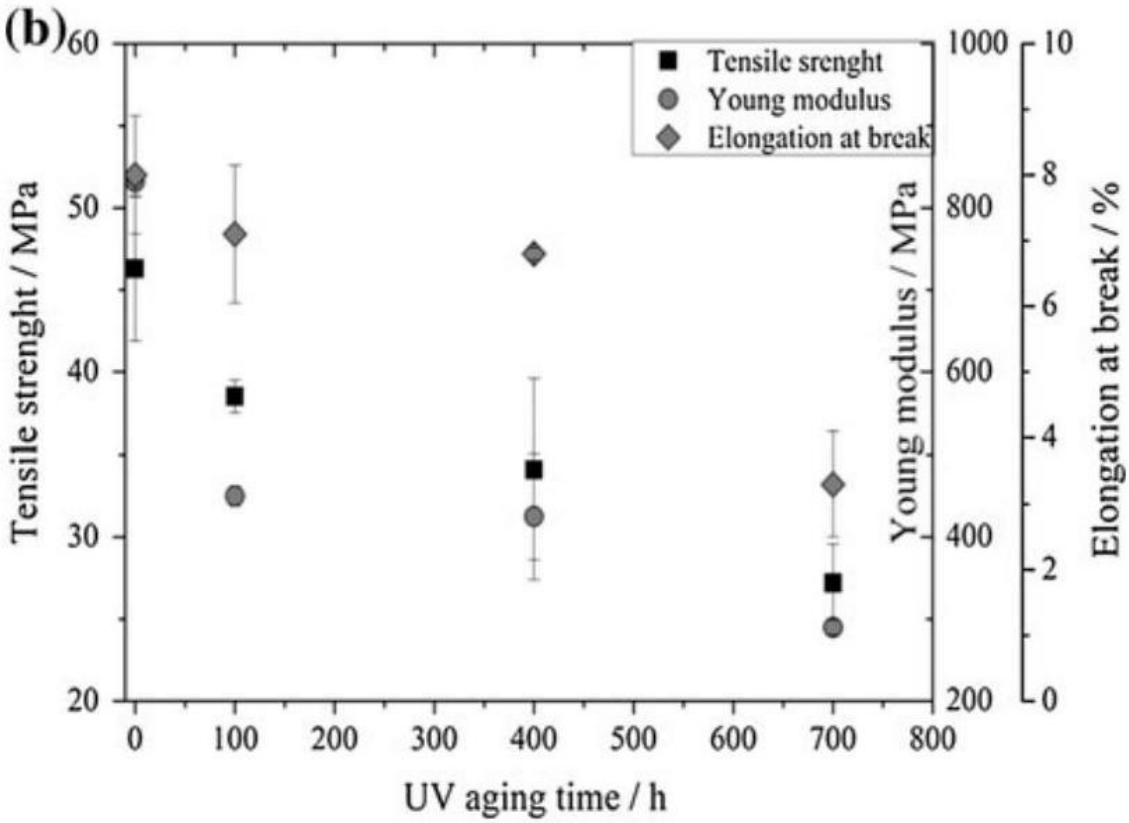
Fig. 8 Crystallinity degree as function of exposure time a EVA and PLA, and b EVA and PLA of EVAPLA1.9 sample

polymers, EVA shows the lowest degree of biodegradability and PLA the highest. Blending PLA with EVA increases slightly the biodegradability of the latter, but it increases more as the amount of grafted copolymer in the sample increases. According to literature, grafting reactions favour the formation of branched/crosslinked structures, promoting the increase of the amorphous zones concentration in the polymer [33]. Since the increase in the concentration of amorphous regions increases the biodegradability, it would be expected that the sample with

Table 3 Melting temperature (Tm) and degree of crystallinity (Xc) of prepared samples

Time (h)	Tm (°C)/Xc (%) (EVA)				Tm (°C)/Xc (%) (PLA)			
	0	100	400	700	0	100	400	700
EVAPLA0	86/20	87/26	87/27	88/28	153/25	153/26	150/27	147/28
EVAPLA0.9	89/18	88/31	90/40	92/42	155/24	151/25	149/26	147/27
EVAPLA1.9	88/17	89/28	89/36	92/48	152/22	150/25	148/26	141/27


(a)
Tensile srenght
Young modulus
Elongation at break
Tensile strenght / MPa
Young modulus / MPa
Elongation at break / %
UV aging time / h


(b)
Tensile srenght
Young modulus
Elongation at break
Tensile strenght / MPa
Young modulus / MPa
Elongation at break / %
UV aging time / h

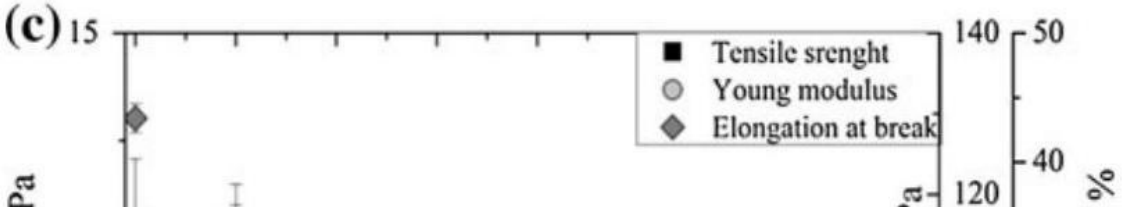

(c)
Tensile srenght
Young modulus
Elongation at break

Fig. 9 Mechanical properties of **a** EVA, **b** PLA and **c** EVAPLA1. 9 along exposure time lower crystallinity would have higher biodegradability or lower durability.

Conclusions

In this work, the combination of several characterization techniques allowed to evaluate the durability of EVA, PLA

Table 4 Percentage of biodegradation

Sample	Biodegradation (%)
EVA	8.9
PLA	52.9
EVAPLA0	10.7
EVAPLA0.9	12.4
EVAPLA1.9	24.2

and EVA/PLA blends with different compositions under UV radiation and microorganism's action. Results obtained from FTIR, DSC and rheological properties of the collected samples indicate that chain scission is the main reaction.

From FTIR, the enlargement absorption corresponding to the carbonyl stretching and the increase in hydroxyl bands demonstrate that the EVAPLA1.9 sample, containing the higher amount of copolymer, undergoes higher structural modifications during UV exposure. The embrittlement point of EVAPLA1.9 was lower than for the other materials. Rheological and tensile properties confirm that this sample undergoes major changes along UV exposure.

The present work confirmed that EVAPLA1.9 sample presents lower durability when exposure to UV radiation or microorganisms. This is a central feature for materials with short lifetime since it would be important to have a short durability, when disposed. Therefore, samples synthesized from a biodegradable polymer and a synthetic non-biodegradable polymer can be very interesting for environment, namely in applications where they are used for a short period of time before becoming waste.

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References

1. Vogel C, Wessel E, Siesler HF (2008) Biomacromolecules 9:523
2. Tsuji H, Echizen Y, Nishimura Y (2006) Polym Degrad Stab 91:1128

3. Luckachan G, Pillai C (2011) J Polym Environ 19:637
4. Drumright RE, Gruber PR, Henton DE (2000) Adv Mater 12:1841
5. Ray S (2012) Acc Chem Res 45: 1710
6. Auras R, Harte B, Selk S (2004) Macromol Biosci 4:835
7. Rabek JF (1995) Polymer photodegradation: mechanism and experimental methods. Chapman and Hall, London
8. Tsuji H, Saeki T, Tsukegi T, Daimon H, Fujie K (2008) Polym Degrad Stab 93:1956
9. Gardette M, Thérias S, Gardette JL, Murariu M, Dubois P (2011) Polym Degrad Stab 9:616
10. Bocchini S, Fukushima K, Di Blasio A (2010) Biomacromolecules 11:2919
11. Saha N, Zatloukal M, Saha P (2003) Polym Advan Technol 14:854
12. Jin J, Chen S, Zhang J (2010) Polym Degrad Stab 95:725
13. Morlat-Therias S, Fanton E, Gardette JL, Peeterbroeck S, Alexandre M, Dubois P (2007) Polym Degrad Stab 92:1873
14. Chen SJ, Zhang J, Su J (2009) J Appl Polym Sci 112:1166
15. Moura I, Machado AV, Nogueira R, Bounor-Legare V (2011) React Funct Polym 71:694
16. Moura I, Machado AV, Nogueira R, Bounor-Legare V (2012) Mater Chem Phys 134:103
17. Duarte FM, Botelho G, Machado AV (2006) Polym Test 25: 91
18. Larché JF, Bussiére PO, Gardette JL (2011) Polym Degrad Stab 96:1530
19. Santos RM, Botelho G, Machado AV (2010) J Appl Polym Sci 116:2005
20. ISO 4892-2 Plastics: methods of exposure to laboratory light sources: part 2: Xenon-Arc Lamps 2006
21. Moura I, Machado AV, Duarte FM, Nogueira R (2011) Biodegradability assessment of aliphatic polyesters-based blends using standard methods. J Appl Polym Sci 119:3338-3346
22. Allen NS, Edge M, Mohammadian M, Jones K (1994) Polym Degrad Stab 43:229
23. Copuroglu M, Sen M (2005) Polym Advan Technol 16:61
24. Copuroglu M, Sen M (2004) Polym Advan Technol 15:393
25. Skowronski T, Rabek JF, Ranby B (1984) Polym Eng Sci 24:278
26. Dalai S, Wenxiu C (2002) J Appl Polym Sci 86:1296
27. Fasce L, Chiaverano G, Lach R, Frontini P (2007) Macromol Sym 247:271
28. Ali ZL (2007) J Appl Polym Sci 104:2886
29. Dalai S, Wenxiu C (2002) J Appl Polym Sci 86:553
30. Belbachir S, Zaïri F, Ayoub G, Maschke U, Naït-Abdelaziz M, Gloaguen JM, Benguediab J, Lefebvre JM (2010) J Mech Phys Solids 58:241
31. Liu M, Horrocks AR, Hall ME (1995) Polym Degrad Stab 49:151

32. Copinet A, Bertrand C, Govindin S, Coma V, Couturier Y (2004) Chemosphere 55:763
33. Jand WY, Shin BY, Lee TJ, Narayan R (2007) Thermal properties and morphology of biodegradable PLA/starch compatibilized blends. J Ind Eng Chem 13:457-464