


Effect of ultraviolet and moisture action on biodegradable polymers and their blend

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Abstract

In this work, the suitability of polylactic acid (PLA), polybutylene adipate terephthalate (PBAT) and PBAT/PLA blend samples to outdoor applications were investigated in terms of mechanical, morphological and visual properties in presence of ultraviolet action and water, finding that PLA in particular can be actually considered for such applications.

Keywords

Biodegradable polymers, polylactic acid, polybutylene adipate terephthalate, ultraviolet irradiation, humidity

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Introduction

The use of polymers for outdoor applications is strongly dependent on their durability, which is their capability to withstand the degradation phenomena. One of the main degradation phenomena is obviously represented by photooxidation, however it is not usually enough to provide polymer systems with good resistance to photooxidation, but it is also important to link this with the functional needs related to the specific application; furthermore, in some cases (such as, for instance, in cultural heritage conservation) features such as hydrophobicity and transparency should be granted¹.

Among the thermoplastic polymers typically adopted for outdoor applications, it is worth mentioning polyolefins, polyamides, polyesters, fluorinated polymers, acrylic polymers, silanes, and siloxanes^{2–7}. In most of the cited cases, the photooxidation resistance is greatly dependent on the formulation and the presence of antioxidant^{2, 3, 8}.

At the same time, the rising concerns for the reduction of the environmental impacts related to plastics, as well as the search for wiser exploitation of natural resources, are encouraging the investigation of alternative, more environment-friendly polymer systems, such as biodegradable

polymers^{9–12}. However, the issues related to their actual degradation behavior need to be further investigated.

Two of the most interesting biodegradable polymers, which can be considered for outdoor applications, are polylactic acid (PLA), and polybutylene adipate terephthalate (PBAT)¹. In particular, their photodegradation behaviors are available in the literature^{13–20}.

As regards PLA, the main paths are a photolytic mechanism, which leads to the breaking of the C–O bond in the macromolecular chain, and a photooxidative mechanism, which leads to the formation of hydroperoxides, carboxylic acids, and ketones¹³. Furthermore, also the Norrish type II path can occur^{14, 15} even though, under ultraviolet

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(UV) exposure at wavelengths over 300 nm, different chain scission mechanisms were reported¹⁸.

In the case of PBAT, degradation can typically occur via Norrish type I and type II chain scission, and can lead to crosslinking phenomena as well, caused by the free radicals formed during the Norrish type I reaction^{19,20}.

In this work, therefore, we focused on assessing the mechanical properties and the structure and morphology of PLA, PBAT, and a PBAT/PLA blend subjected to UV irradiation and condensation cycles (CC), in order to assess their behavior under typical outdoor conditions (sunlight, dew, and rain), and therefore provide useful information to evaluate the suitability and durability of these materials in actual outdoor applications (also including cultural heritage conservation) and not in limited conditions as it could be if only UV action, or only condensation action, were taken into account.

Materials and methods

Materials

The PLA sample used in this work is a commercially available grade, known as Ingeo 4032D (NatureWorks, USA), with the following main properties: melt flow index (MFI) = 7 g/10 minutes (at 210°C and 2.16 kg); and density = 1.24 g/cm³, $M_n = 1.03 \times 10^5$ g/mol, melting point = 155–170°C. The PBAT sample is commercially available as Ecoflex F C1200 (BASF, Germany), MFI = 2.7–4.9 g/10 minutes, and $M_n = 24400$ g/mol. Finally, a sample of a PBAT/PLA blend commercially available as Ecovio F23B1 (BASF, Germany) was also investigated, consisting of 84% PBAT, 4% of PLA, and 12% of insoluble, inert particles²¹, having MFI = 5–11 g/10 minutes.

Preparation

Compression molded sheets (eight, 10 cm × 10 cm × 0.3–0.5 mm) were thus prepared at $T = 170^\circ\text{C}$ (except for the PLA, 190°C) in a Carver (USA) laboratory bench press (after conditioning in a vacuum oven at 70°C , for 4 hours). Forty specimens (90 mm × 10 mm × 0.3–0.5 mm) were obtained by a manual bench cutter and were thus subjected to accelerated weathering in a Q-UV chamber (Q-Labs Corp., USA) equipped with eight “UVB-313” lamps, at 70°C and up to approximately 128 hours, according to the procedures described elsewhere²². In particular, a comparison was performed between the samples weathered under the previously mentioned conditions, and analogous samples subjected to weathering cycle conditions consisting of 8 hours’ light at $T = 70^\circ\text{C}$ and 4 hours’ condensation at $T = 55^\circ\text{C}$, in order to assess the effect of condensation (i.e., humidity) on the systems, in comparison to the mere UV irradiation.

Mechanical characterization

Mechanical characterization in tensile mode, using an Instron (USA) mod. 3365 universal testing machine, was performed according to ASTM D638, both on weathered and unweathered specimens. The elastic modulus (E), was measured at 1 mm/minute deformation speed up to 10% deformation, then the crosshead speed was raised to 100 mm/minute until breaking. The values of E as well as the ultimate properties (tensile strength (TS) and elongation at break (EB)) were thus calculated as average of 10 tests, with a good reproducibility ($\pm 6\%$). Dimensionless values (deviation: $\pm 5\%$) were also calculated by dividing the values at each irradiation time by those of the same virgin (unirradiated) polymer (available in a previous work¹).

Rheological analysis

The MFI was measured by means of CEAST (Italy) equipment at 170°C under a 2.16 kg load (average of four measurements, data reproducibility: $\pm 5\%$).

Calorimetric analysis

Melting enthalpy was measured by differential scanning calorimetry (DSC), using Shimadzu (Japan) DSC-60 equipment, with $5^\circ\text{C}/\text{minute}$ heating rate from 30 to 200°C in air atmosphere (average of four measurements, data reproducibility: $\pm 6\%$).

Crosslinking degree analysis

The cross-linked fraction was estimated on the basis of the residual gel fraction (GF), obtained after Soxhlet extraction in boiling tetrahydrofuran on triplicates (reproducibility: $\pm 7\%$). The GF was obtained dividing the weight of the gel entrapped in the filters after extraction, by the overall weight of the same sample before of the extraction.

Yellowing

Yellowing index (YI) was calculated on triplicates from UV/Vis spectra according to ASTM E313, using the following equation (1):

$$YI = [(A_{380} - A_{600}) * 0.1] / t \quad (1)$$

where A_{380} is the absorbance at $\lambda = 380$ nm (UV), A_{600} is the absorbance at $\lambda = 600$ nm (visible), and t is the sample thickness (mm) with a $\pm 4\%$ reproducibility. The UV-Vis spectra were obtained on triplicates using a Specord 252 (Analytik Jena, Germany) spectrometer in the 190–1100 nm range.

Table 1. Gel fraction (GF) of the three system (virgin and photooxidized for 128 hours, without and with condensation cycles).

Sample	Weathering conditions	Irradiation time, hours	GF, %
Polybutylene adipate terephthalate (PBAT)	No condensation	0	0
PBAT	No condensation	128	6.8
PBAT	Condensation	128	4.1
Polylactic acid (PLA)	No condensation	0	0
PLA	No condensation	128	0
PLA	Condensation	128	0
PBAT/PLA	No condensation	0	0
PBAT/ PLA	No condensation	128	22.6
PBAT/ PLA	Condensation	128	13.4

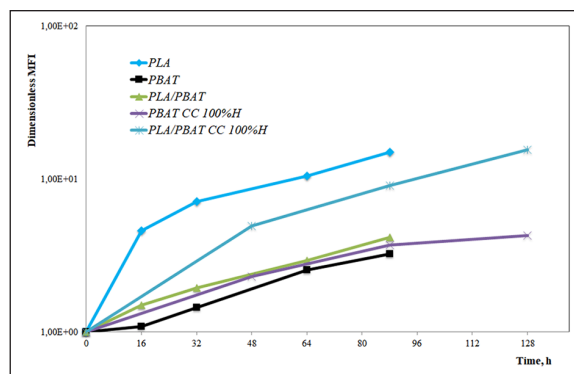
Table 2. Dimensionless melt flow index values of the three systems, in absence of condensation cycles, on increasing the exposure time (hours).

Sample versus irradiation time	0	16	32	64	88
Polybutylene adipate terephthalate (PBAT)	1	0.83	0.15	0.12	0.11
Polylactic acid (PLA)	1	4.45	5.36	9.44	10.36
PBAT/ PLA	1	0.82	0.089	0.27	0.65

Results and discussion

Table 1 reports the values of the measured GF, at 0 and 128 hours' irradiation time (already available in¹), of the three samples, as well those measured for samples irradiated for 128 hours in the presence of CC. Dimensionless MFI (i.e., the ratio between the MFI measured after a given irradiation time and the one measured for the same, unirradiated sample) values are reported in Table 2 in the absence of CC (see¹), and in Figure 1 in the presence of CC (the data reproducibility was +/- 5%).

With regard to the samples not subjected to CC, in agreement with our previous study¹, the photooxidation of PLA leads to an increase of MFI, and therefore to a decrease of the viscosity as a consequence of the decrease of the molecular weight. As the gel content reported in Table 1 is due to the presence of cross-linked structures formed during the photooxidation, no presence of cross-linking is found in the PLA sample. This suggests that the photooxidation of PLA follows a chain scission path without formation of branched structures. The PBAT and the PBAT/PLA blend also shows a decrease of molecular weight but, on the other hand, the formation of cross-linked structures is also observed in both of the systems from the increase of the gel content, especially in the PBAT/PLA blend. The increase of the cross-linking leads,

**Figure 1.** Dimensionless melt flow index of samples subjected to condensation cycles, as a function of the irradiation time. Note: "CC 100%H" refers to samples subjected only to treatment in climatic chamber at 100% relative humidity.

of course, to a reduction of the MFI. This indicates that the cross-linking occurs only in the PBAT phase, and that PLA degradation (which follows a chain scission path) and the related degradation products promote PBAT degradation (which mainly follows a crosslinking path); however, the role of the chain-scission degradation of PLA gains importance on increasing the photooxidation time, leading to a gradual reversal of the trend¹. With regard to the samples subjected to CC, the situation is different, with all of the systems (even PBAT and the PLA/PBAT blend) showing an increase of the MFI; in particular, PLA showed higher MFI increase rates (and thus higher rates of molecular weight reduction). Furthermore, PBAT and the PBAT/PLA blend showed reduced crosslinking fractions in comparison to their previously discussed counterparts (Table 1). This gives a confirmation in the MFI trend, which increases upon the entire investigation range. These results indicate that the presence of humidity, which is known to favor hydrolytic chain scission, accelerates the chain-scission based degradation of the PLA which, in its turn, also promotes the degradation of PBAT and the PBAT/PLA blend¹, but, in this case, increasing the importance of chain scission in comparison to crosslinking. In order to get a further confirmation that this different trend is mainly due to the presence of water rather than to other mechanisms, the same MFI tests were performed on PBAT and PLA/PBAT blend samples subjected only to hydrolytic degradation in a climatic chamber at 70°C and 100% relative humidity (with no UV irradiation). As observable in Figure 1, an increasing trend is found, in close qualitative agreement with the behavior of the same systems subjected to UV irradiation and CC.

The enthalpies of fusion of the three samples, virgin and photooxidized, are reported in Table 3, while DSC thermograms are provided in Figure 2(a–c) for PLA, PBAT, and the PLA/PBAT blend, respectively. Each of Figure 2(a–c) shows the unirradiated sample and the 128-hours' irradiated samples, without and with CC.

Table 3. Melting enthalpy of virgin and photooxidized (128 hours) samples, without and with condensation cycles (CC). For the blend sample, the enthalpies of fusion of the two phases are reported.

Sample	Irradiation time, hours	$\Delta H_m(\text{PLA}), \text{J/g}$	$\Delta H_m(\text{PBAT}), \text{J/g}$
Polylactic acid (PLA)	0	34.4 ± 1.0	–
PLA	128	48.4 ± 1.9	–
PLA	128+CC	51.3 ± 2.1	–
Polybutylene adipate terephthalate (PBAT)	0	–	5.5 ± 0.3
PBAT	128	–	5.6 ± 0.3
PBAT	128+CC	–	12.5 ± 0.6
PLA/ PBAT	0	30 ± 0.9	5.1 ± 0.3
PLA/ PBAT	128	40 ± 1.2	0.7 ± 0.05
PLA/ PBAT	128+CC	42.5 ± 1.1	3.3 ± 0.1

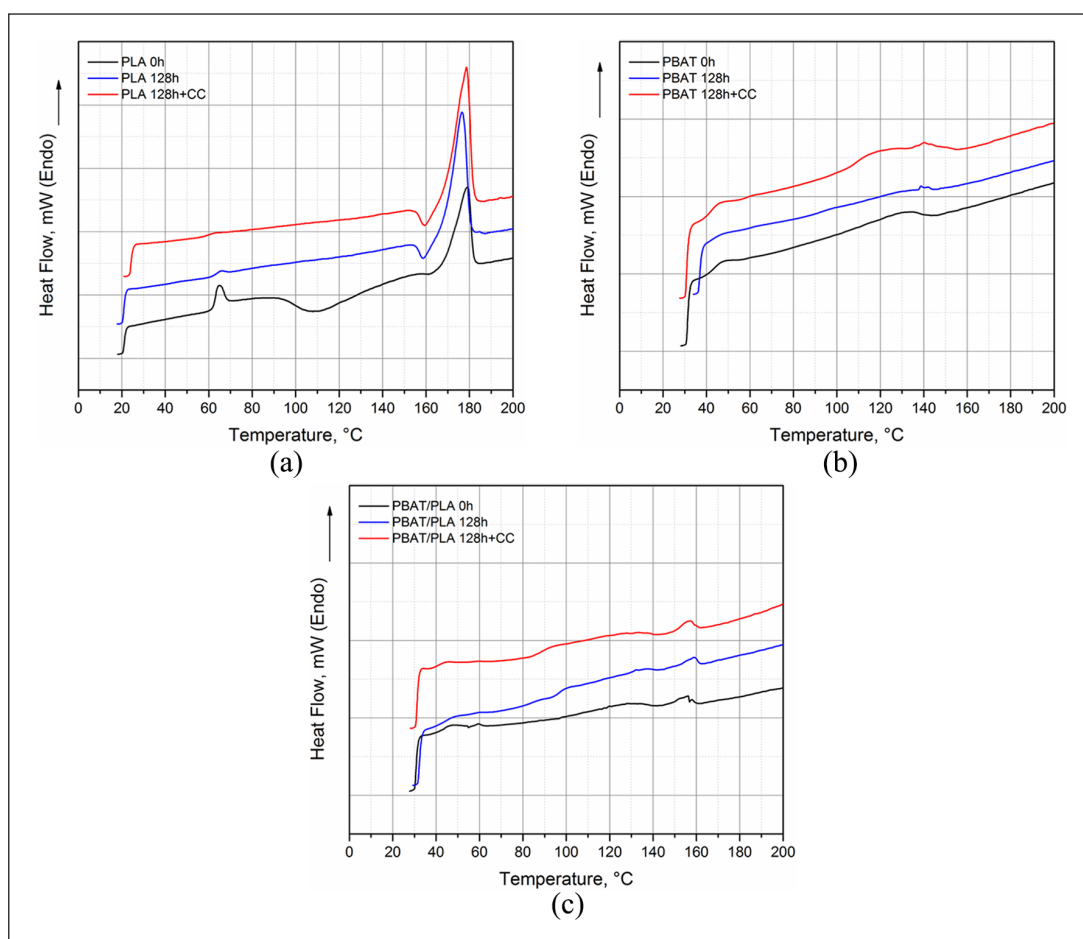


Figure 2. (a) differential scanning calorimetry (DSC) thermograms of virgin and photooxidized (128 hours) polylactic acid (PLA) samples, without and with condensation cycles (CC); (b) DSC thermograms of virgin and photooxidized (128 hours) polybutylene adipate terephthalate (PBAT) samples, without and with CC; and (c) DSC thermograms of virgin and photooxidized (128 hours) PLA/PBAT samples, without and with CC.

The data are in agreement with the above reported findings, particularly with those regarding the GF (i.e., crosslinking): the reduction of molecular weight due to chain scission leads to increased crystallization and decreased crosslinking; more specifically, the presence of

water increases the importance of degradation via chain scission, resulting in decreased crosslinking even in the PBAT sample. Furthermore, it can be observed that the crystallinity of the two components in the PBAT/PLA blend is slightly lower than that in the pure components,

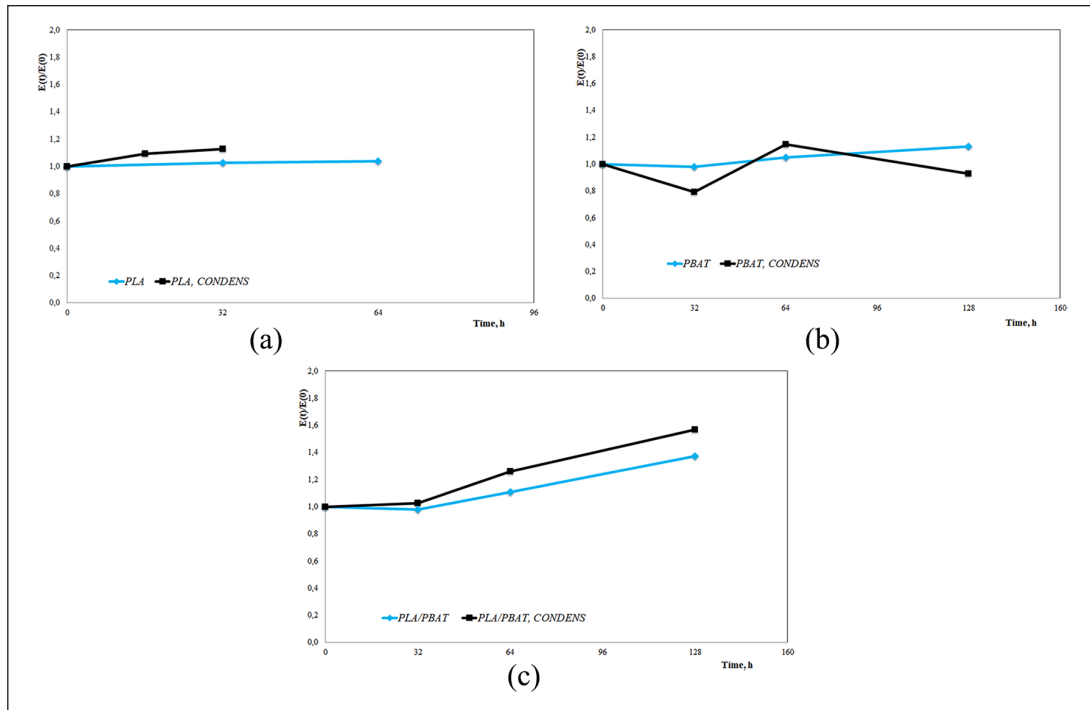


Figure 3. (a) Dimensionless elastic modulus (DEM) of polylactic acid (PLA) as a function of the irradiation time, without and with condensation cycles (CC); (b) DEM of polybutylene adipate terephthalate (PBAT) as a function of the irradiation time, without and with CC; and (c) DEM of PLA/PBAT as a function of the irradiation time, without and with CC.

and that the substantially amorphous nature of PBAT and the PBAT/PLA blend does not change significantly upon exposure.

With regard to the effects of degradation in both conditions (without and with CC) on the mechanical properties of the investigated samples, Figures 3–5(a–c) report the dimensionless values of E , TS , and EB of PLA, PBAT, and the PLA/PBAT blend, respectively. These allow to directly compare the samples, which underwent different degradation paths with reference to the humidity conditions. In some cases, it was not possible to detect the properties at longer irradiation times, due to excessive embrittlement of the sample.

First, it can be observed that the photooxidation (without condensation) dramatically reduces the ductility (EB) of the investigated materials, as could be expected on the basis of the molecular weight reduction and crosslinking. Similarly, the TS decreases, although the reduction is higher in the PBAT rather than in the PLA, probably due to the different embrittlement kinetics of the two materials¹, while this effect was less significant in the PLA/PBAT blend, probably due to the increased crosslinking which partially mitigated the TS loss. For the same reasons (crosslinking and chain scission), there were only small variations of E .

It is even more interesting to observe the effect of CC on the same systems. These do not remarkably affect E (especially in the case of PLA and PBAT samples), and

this can be easily explained admitting that the effects due to the decreased crosslinking are balanced by those depending on the increased crystallinity. For similar reasons, TS is only marginally affected in the PBAT and the PLA/PBAT blend; on the other hand, TS of the PLA significantly decreases in the presence of the CC, due to the increased chain scission phenomena (see also Figure 1). Finally, the ductility (EB) decreased for all of the investigated systems, in agreement with the increased chain scission.

In order to provide further information about the actual suitability of the investigated systems to outdoor applications, visual changes such as yellowing are also important. Therefore, the YI was calculated and is shown in Figure 6.

Obviously, the YI increases on increasing the exposure time, due to the photooxidation of the investigated systems. The comparison between the different samples points out that (considering also the standard deviations already described in the Materials and Methods section) CC lead to high differences in the yellowing only in the PBAT samples. On the other hand, PLA and PBAT/PLA blend do not undergo significant yellowing changes upon being subjected to CC; in other words, it is the UV irradiation which accounts for the yellowing, while the presence of condensed water does not significantly take part in the degradation mechanisms leading to yellowing. Moreover, in both cases (with or without condensed water), the yellowing rate has decreased and levelled soon, since the YI

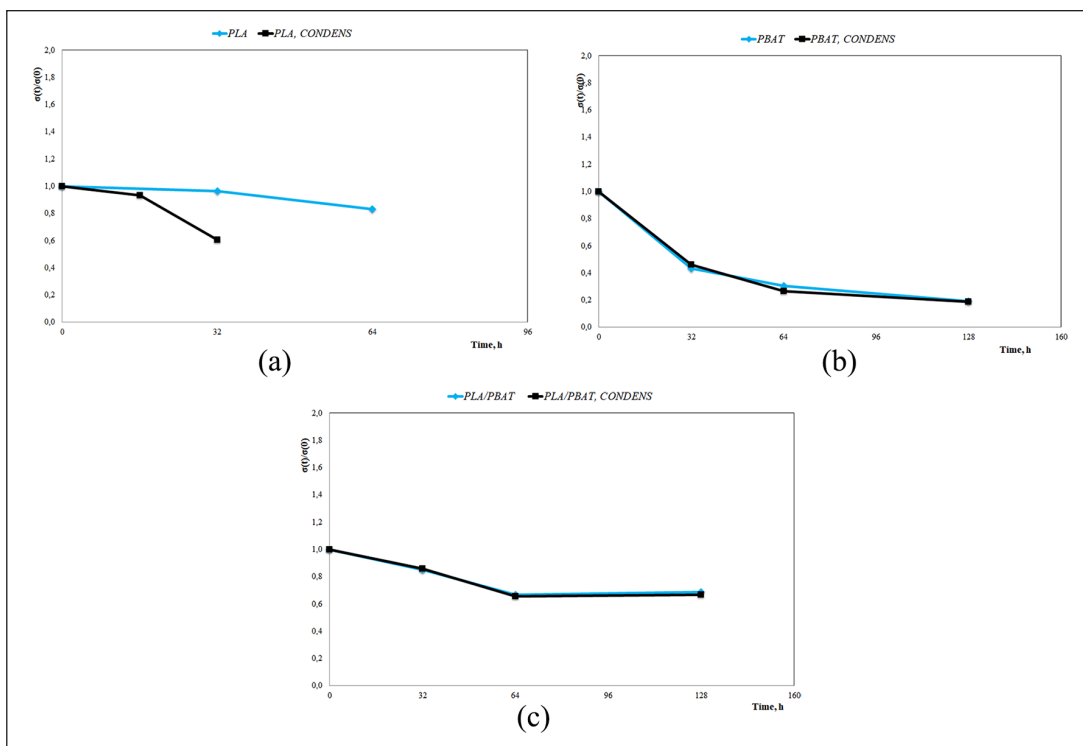


Figure 4. (a) Dimensionless tensile strength (DTS) of polylactic acid (PLA) as a function of the irradiation time, without and with condensation cycles (CC); (b) DTS of polybutylene adipate terephthalate (PBAT) as a function of the irradiation time, without and with CC; and (c) DTS of PLA/PBAT as a function of the irradiation time, without and with CC.

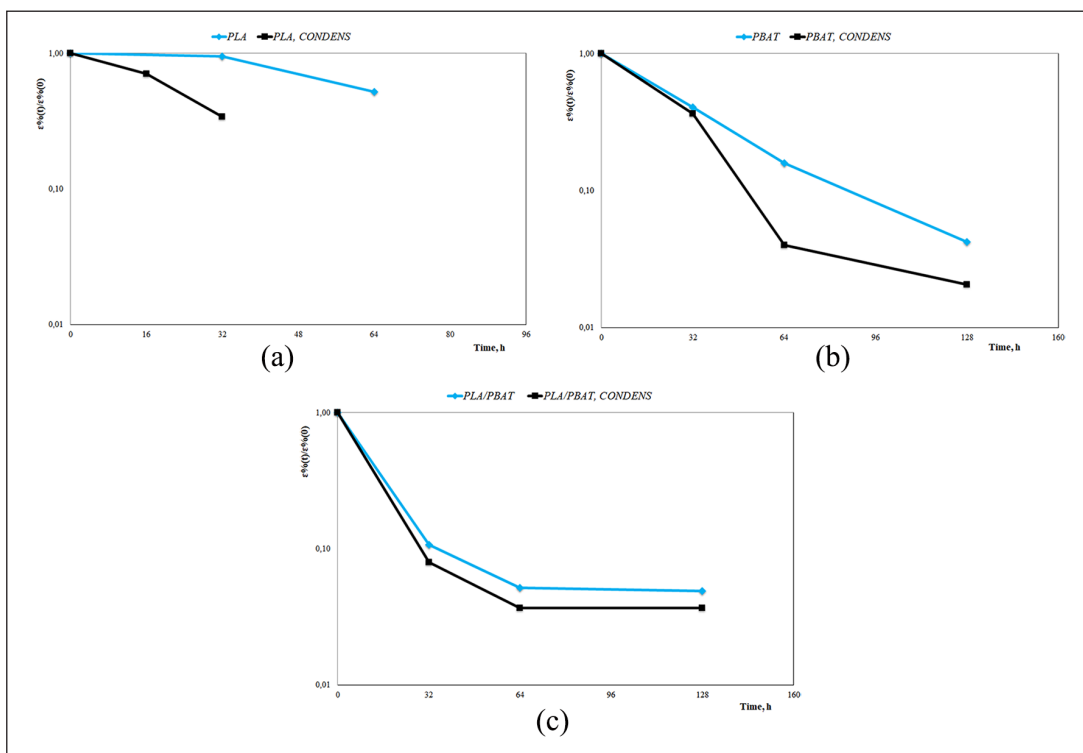


Figure 5. (a) Dimensionless elongation at break (DEB) of polylactic acid (PLA) as a function of the irradiation time, without and with condensation cycles (CC); (b) DEB of polybutylene adipate terephthalate (PBAT) as a function of the irradiation time, without and with condensation CC; and (c) DEB of PLA/PBAT as a function of the irradiation time, without and with CC.

keeps steady after approximately 64 hours' exposure. These results indicate that the mentioned materials (i.e., PLA and the PLA/PBAT blend) can be considered for application in outdoor conditions, since the yellowing rate is moderate and keeps steady after a relatively short exposure time.

In order to provide additional evidence of the moderate changes in terms of visual appearance, high resolution photographs of the samples were taken, at different exposure times (0 and 128 hours) (see Figure 7). It is observed that unweathered PLA has a better visual transparency than the unweathered PLA/PBAT blend (due to the presence of PBAT in the blend, which is intrinsically less transparent). After 128 hours' exposure, the worsening visual

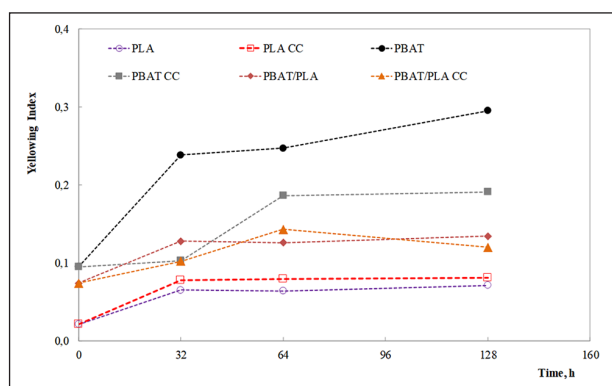


Figure 6. Yellowing index of the investigated systems, without and with condensation cycles as a function of the exposure time.

transparency of the PLA sample is mild, while it is more significant in the PLA/PBAT blend, due to the presence of PBAT and its higher tendency to yellowing, in agreement with the calculated YI. However, this does not contradict the above comments on the applicability of these systems.

Conclusions

In this work, samples of PLA, PBAT, and a PBAT/PLA blend were studied in terms of mechanical performance as well as structural and visual changes, in order to assess their suitability and durability for outdoor applications in the presence of sunlight, dew, and rain. The characterizations were performed before and after exposure to UV irradiation in the presence of CC.

It was found that the photooxidation mechanism involves chain scission of the PLA and crosslinking of the PBAT, with synergistic effects in the PLA/PBAT blend. The UV irradiation worsened the properties of the investigated systems to different extents, with the PLA/PBAT blend experiencing smaller worsening of the main mechanical properties in comparison to the neat PBAT.

The action of CC influenced the degradation phenomena, mainly in terms of higher reduction of the molecular weight due to chain scission phenomena, on the one hand, and reduced crosslinking, on the other hand. However, these two different factors led to small variations of the main mechanical properties in comparison to the same samples not subjected to CC, although differences were much higher in the PBAT/PLA blend as regards E, and in the PLA as regards TS.



Figure 7. Transparency of samples. Upper, from left to right: background support (no polymer sample), polylactic acid (PLA) sample, PLA/polybutylene adipate terephthalate (PBAT) sample; and lower, from left to right: 128-hours' weathered PLA sample, 128-hours' weathered PLA/PBAT sample.

The action of CC did not lead to significant changes in the YI; anyway, the yellowing proved to be slight to moderate in all of the materials (higher in the PBAT).

The obtained results suggest that the biodegradable polymer systems investigated in this work, and in particular the PLA, might be considered for application in actual outdoor conditions. The use of suitable antioxidants, that can strongly improve the photooxidation resistance, will be addressed in following studies, and could make the biodegradable polymer systems investigated more suitable for outdoor applications.

Author Contributions

FPL, MCM, LB, and VT researched the literature and conceived the study. All the authors were involved in protocol development and data analysis. MM, FPL, and MCM wrote the first draft of the manuscript. FPL, MM, and MP reviewed and edited the manuscript. All the authors approved the final version of the manuscript.

Declaration of Conflicting Interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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