Research Article

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Hydrolytic degradation of poly(L-lactic acid)/poly(methyl methacrylate) blends

Naila Boudaoud,[a] Samira Benali,[b] Rosica Mincheva,[b] Hamid Satha,[a*]
Jean-Marie Raquez[b*] and Philippe Dubois[b]

Abstract

The hydrolytic degradation of poly(L-lactic acid)/poly(methyl methacrylate) (PLLA/PMMA) blends was carried out by the immersion of thin films in buffer solutions (pH = 7.24) in a shaking water bath at 60 °C for 38 days. The PLA/PMMA blends (0/100; 30/70; 50/50; 70/30; 100/0) were obtained by melt blending using a Brabender internal mixer and shaped into thin films of about 150 μm in thickness. Considering that PMMA does not undergo hydrolytic degradation, that of PLLA was followed via evolution of PLA molecular weight (recorded by size exclusion chromatography), thermal parameters (differential scanning calorimetry (DSC)) and morphology of the films (scanning transmission electron microscopy). The results reveal a completely different degradation pathway of the blends depending on the polymethacrylate/polyester weight ratio. DSC data suggest that, during hydrolysis at higher PMMA content, the polyester amorphous chains, more sensitive to water, are degraded before being able to crystallize, while at higher PLLA content, the crystallization is favoured leading to a sample more resistant to hydrolysis. In other words, and quite unexpectedly, increasing the content of water-sensitive PLLA in the PLLA/PMMA blends does not mean *de facto* faster hydrolytic degradation of the resulting materials.
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Keywords: PLLA; PMMA; polymer blend; hydrolytic degradation; crystallization

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable and bio-absorbable thermoplastic polyester completely derived from biomass such as wheat, corn, rice and sugar beet,[1–6] and has been investigated in depth in short-term applications. However, long-term high-value applications (e.g. electronics and automobile) are somewhat restricted as durability and resistance to deformation are needed.[7–12] In this regard, blending is usually considered as an economical and practical way of improving heat resistance and mechanical properties of polymers and of controlling their (bio)degradation. Therefore, PLAs were blended with various biodegradable and non-biodegradable polymers such as poly(ε-caprolactone),[13,14] poly(ethylene oxide-*b*-amide-12),[15] poly(butylene succinate),[16,17] poly(butylene adipate-*co*-terephthalate),[18] poly(ether-urethane),[19] poly(ethylene terephthalate),[20] poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate),[21] poly(vinyl acetate),[22] poly(glycolic acid),[23] hyperbranched polymers[24] and rubbers.[25] Amongst all, poly(methyl methacrylate) (PMMA) has been claimed as a promising partner for PLA due to its good physical and chemical properties such as high glass transition temperature, high transparency and long-term stability.[26–32]

Blending poly(L-lactic acid) (PLLA) with PMMA has attracted significant interest; and these blends showed applicability as commodity materials in numerous applications.[33–39] Zhang *et al.*[33] studied the miscibility and phase structure of binary blends of PLA and PMMA. They found that amorphous poly(D,L-lactide) was miscible with PMMA in solution/precipitation, and that the crystallization of PLLA was well restricted by amorphous PMMA in semi-crystalline PLLA/PMMA blends. Samuel *et al.*[34] investigated the miscibility of PLLA/PMMA blends prepared by solvent-casting and extrusion techniques. They reported that chloroform-casted blends remain immiscible, while the PLLA/PMMA blends processed by twin-screw extrusion are miscible afterwards. Very recently, investigations of Bouzouita *et al.*[39] on polylactide-based materials for automotive applications demonstrated that blending PLLA/PMMA with an impact modifier markedly increases ductility and impact resistance of the materials, without altering the PLLA/PMMA thermal properties.

The end of life and the possible negative effects of such promising (bio)degradable plastics, such as fragmentation, raise significant environmental concerns, especially in oceanography, marine biology and freshwater biology.[35] Indeed, with more than 5300 grades of synthetic polymers available commercially, the very young field of (micro)plastics for marine and freshwater research is in demand for studies on their impact on the marine environment before they are put on the market. Therefore, studying the

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* *Correspondence to: H Satha, Laboratory of Silicates, Polymers and Nanocomposites (LSPN), Department of Process Engineering, University of 8Mai 1945, Avenue du 19 mai 1956, BP 401, Guelma, Algeria, E-mail: sathahamid@yahoo.fr; or J-M Raquez, Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Place du Parc 23, 7000-Mons, Belgium. E-mail: jean-marie.raquez@umons.ac.be*

a *Laboratory of Silicates, Polymers and Nanocomposites (LSPN), Department of Process Engineering, University of 8 Mai 1945, Guelma, Algeria*

b *Department of Chemistry, Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Mons, Belgium*

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(bio)degradation of PLA/PMMA blends is of crucial interest prior to any practical applications. Up to now, only one study, published by Shirahase *et al.*,[36] evaluated the hydrolytic degradation of amorphous PLA/PMMA blends prepared using a two-roll mill in alkaline solution ($\mathrm{pH} = 12$). It was found that the hydrolytic degradation rate of the blends is largely controlled by PMMA content, while only PLA was hydrolysed and eluted into solution. However, natural water sources present a pH of approximately 6–9[40,41] and pH values above 9.5 or 10, as studied by Shirahase *et al.*[36] are considered undesirable in aquaculture ponds.

Therefore, and to complement the already available knowledge, the main objective of the work reported here was to study the hydrolytic degradation behaviour of PLLA/PMMA blends in buffer solution of neutral pH (7.24). Deliberately the hydrolytic degradation was conducted at 60 °C, a temperature high enough to range slightly above the glass transition temperature of any commercially available polylactide and allowing the recording of degradation data on an acceptable time scale at least at the laboratory level.[42] The degradation process was followed using size-exclusion chromatography (SEC), DSC and scanning transmission electron microscopy (STEM). It was expected that the investigation would provide additional knowledge on the understanding of hydrolytic degradation of PLLA/PMMA blends used for durable applications like automotive interiors and electronics and would represent a basis for studying the impact of PLLA/PMMA microplastics on seawater or freshwater environments.

EXPERIMENTAL

Materials

Semi-crystalline PLLA was kindly supplied by NatureWorks LLC (grade 4032D, D-isomer <2%, $M_{\mathrm{n(PLLA)}} = 51.400\ \mathrm{g\ mol^{-1}}$, $Đ_M = 2.2$, obtained using SEC calibrated with PMMA standards in $\mathrm{CHCl_3}$ at 25 °C). PMMA was supplied by Evonik (grade 8 N, $M_n = 50\,700\ \mathrm{g\ mol^{-1}}$, $Đ_M = 1.8$, obtained using SEC calibrated with PMMA standards in $\mathrm{CHCl_3}$ at 25 °C). Bis(2,4-di-*t*-butylphenyl)pentaerythritol diphosphite (Ultranox 626A) supplied by GE Specialty Chemicals was selected as thermal stabilizer and used at *ca* 0.3% in all blends during processing.

Sample preparation

Prior to melt blending, both PLLA and PMMA were dried overnight at 60 °C under reduced pressure, and Ultranox 626A was dried overnight at 25 °C, to minimize water content in each component and avoid any excessive degradation upon processing.

PLLA/PMMA blends by melt processing

PLLA/PMMA blends were processed using a Brabender internal mixer equipped with roller-rotors at 210 °C for 7 min at 70 rpm. PLLA/PMMA blends (56 g) were melt-blended at 30 rpm for 3 min hindering any excessive increase of the torque upon melting. Five formulations were prepared (100%PLLA, 70%PLLA/30%PMMA, 50%PLLA/50%PMMA, 30%PLLA/70%PMMA and 100%PMMA) under similar conditions. After collecting and drying all the mixing materials overnight at 60 °C, the different PLLA/PMMA formulations were thermo-compressed with the following procedure: preheating at 210 °C for 4 min, low-pressure cycle for 2 min at 4 bar, high-pressure cycle for 2 min at 9 bar, cooling to 25 °C. The films of approximately 150 μm in thickness were then quenched at ambient temperature.

Hydrolysis tests

Before starting the hydrolysis tests, each film was cut into 1 cm × 1 cm square specimens (from the middle of film roll) by considering three replicates per sample. Each specimen was then dipped in a laboratory vial containing buffer solution at pH 7.24. The flasks were immersed in a shaking water bath at 60 °C. At predetermined periods, the specimens were picked out from the buffered solution and rinsed several times with distilled water. Eventually, the residual water was wiped off from the sample surface before drying by using paper. It was then placed in a desiccator up to 3 days.

Characterization

Molecular weight measurement

Molecular weights of the samples, before and after hydrolysis, were measured using SEC in $\mathrm{CHCl_3}$ at 30 °C with an Agilent liquid chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = $1\ \mathrm{mL\ min^{-1}}$), an Agilent autosampler (loop volume = 200 μL, solution concentration = $2.5\ \mathrm{mg\ mL^{-1}}$), an Agilent-DRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-D 10 μm columns (linear columns for separation of $M_{\mathrm{W(PMMA)}}$ ranging from 500 to $10^6\ \mathrm{g\ mol^{-1}}$). Polystyrene standards were used for calibration.

Differential scanning calorimetry

The thermal properties of dried samples were investigated using DSC with a DSC Q2000 from TA Instruments under nitrogen flow. The samples (weight of about 5–7 mg) were placed in closed aluminium pans within the sample oven, whereas an empty pan was set in the reference oven. The procedure was as follows: a heating scan at $10\ {}^\circ\mathrm{C\ min^{-1}}$ from 0 to 210 °C. The events of interest, that is, the glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature (T_m), as well as their related enthalpies of cold crystallization (ΔH_{cc}) and melting (ΔH_m) were calculated from this first heating scan. The crystallinity (χ_c) of PLLA was calculated using the following equation:

$$\chi_c = \left[\frac{\Delta H_{m(t)} - \Delta H_{c(t)}}{\Delta H_m^0}\right] \times 100 \qquad (1)$$

where $\Delta H_{m(t)}$ and $\Delta H_{c(t)}$ are the melting and cold crystallization enthalpies, respectively, at the time *t* of degradation, and ΔH_m^0 is the melting enthalpy of 100% crystalline PLA ($93\ \mathrm{J\ g^{-1}}$).[43]

Scanning transmission electron microscopy

The morphology of neat PLLA and PLLA/PMMA blends at different degradation times was observed using a STEM instrument (Hitachi SU8020), with field emission gun with landing energy at 3 kV and an SE(UL) detector.

RESULTS AND DISCUSSION

Sample aspect during hydrolysis

Three different PLLA/PMMA blends were studied at PLLA/PMMA weight ratios of 70/30, 50/50 and 30/70 (Table 1). Both neat PLLA and PMMA were also processed for comparison.

As the degradation of any material brings about changes in its visual aspect,[36] this parameter was also followed for the PLLA/PMMA blends and neat polymers. As revealed in Fig. 1, a significant change in the sample opacity was noticed for the neat PLLA and all PLLA/PMMA blends after only 7 days of immersion in

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Table 1. Designation of prepared formulations of PLLA/PMMA

Identification	PLLA content (wt%)	PMMA content (wt%)
Neat PLLA	100	0
PLLA70/PMMA30	70	30
PLLA50/PMMA50	50	50
PLLA30/PMMA70	30	70
Neat PMMA	0	100

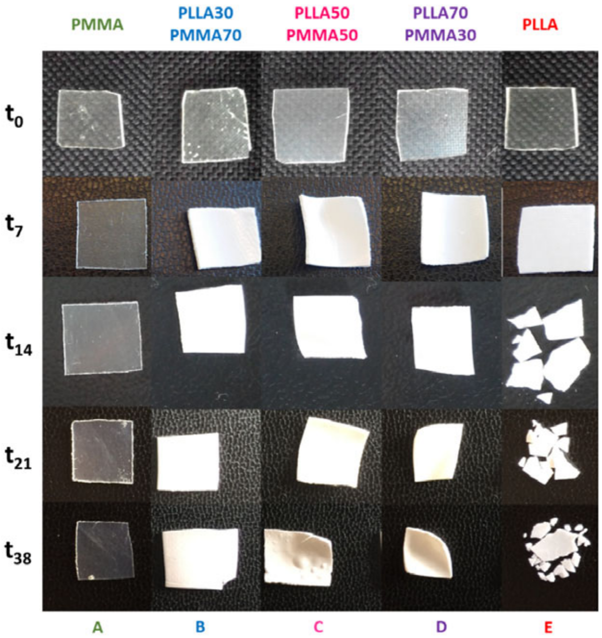

Figure 1. Changes of visual aspect of samples at different times of hydrolysis for neat PMMA, PMMA70/PLLA30, PMMA50/PLLA50, PMMA30/PLLA70 and neat PLLA.

buffered solution. Specifically, neat PLLA and PLLA/PMMA blends became completely white after 7 days regardless the PMMA content. Moreover, the neat PLLA sample became extremely brittle after14 days at 60 °C and pH 7.24; and was recovered in small pieces after the drying step, which followed the removal of the sample from phosphate buffer solution (Fig. 1 at t_{14}, sample E). As far as the PLLA/PMMA blends are concerned, all blends remained relatively intact regardless the PMMA content. However, blends containing 50 wt% of PLLA or more were highly deformed and friable after 21 days (Fig. 1 at t_{21}, samples C and D). Regarding the neat PMMA samples, not only did all specimens keep the same transparent aspect, but each of them remained intact and stable during the entire hydrolytic degradation test, thus confirming the expected stability of PMMA upon hydrolysis.[36]

The opacification of PLLA-based samples has already been discussed in previous papers[44–49] and might be attributed to various phenomena such as (i) degradation products created during hydrolysis, (ii) light scattering of absorbed water, (iii) formation of holes in the bulk of a specimen during degradation,[48,50] (iv) evolution in crystallinity of the polymer matrix[51–55] and (v) phase change of blends.[56] Indeed, it is important to remember that the hydrolytic degradation of a polyester chain first proceeds via random scission of the amorphous phase leading to an accumulation of lower-molar-mass chains of increased mobility, and thus results in an initial increase of the crystallinity.[48,50]

To understand these visual observations, SEC measurements and DSC analyses were further carried out and STEM images obtained.

SEC measurements

SEC measurements were conducted for all blends and neat polymers recovered at predetermined hydrolysis times, i.e. 0, 7, 14, 21 and 38 days, at 60 °C. The elution profile changes are shown in Fig. 2 and the maxima of the various peaks (M_p) are reported in Table 2.

As seen, for neat PMMA (Fig. 2(A)), no change in elution profile and dispersity was recorded during the entire period as expected for a non-degradable polymer. Interestingly, before hydrolysis, the PLLA/PMMA blends presented relatively narrow and monomodal elution curves (Figs 2(B)–(D), green curves), suggesting that under the SEC conditions both PLLA and PMMA presented similar hydrodynamic volumes. However, as hydrolysis time increased, the PLLA30/PMMA70 blend clearly presented a tailing towards higher elution volumes (lower molar masses) with hydrolysis time (Fig. 2(B)). Noteworthy, no change in peak maximum is observed. The tailing became more evident upon increasing PLLA content (Fig. 2(C)) and turned into a multimodal distribution for PLLA70/PMMA30 (Fig. 2(D), Table 2). Additionally, at short hydrolysis times ($7 < t < 14$ days), the first peak maximum shifted towards lower molar masses and dispersity (Đ) values increased. At long hydrolysis times ($t > 14$ days), however, the first peak maximum moved back towards molar mass values closer to that obtained prior degradation (Figs 2(B)–(D)). This shift backwards was accompanied by the clear appearance of second and third elution peaks (Fig. 2(D)) and a 'consumption' of the second peak with respect to the third peak maximum with time. The observations suggest the formation of lower molar mass fractions upon hydrolysis that might reasonably be ascribed to selective (in relation to PMMA) PLLA degradation (in agreement with the literature[43,57,58] and considering that PMMA does not hydrolyse[36]). This hypothesis was supported by the SEC elution curves for neat PLLA during hydrolysis (Fig. 2(E)), where bi- and trimodality as well as a marked shift towards low molar masses were recorded. Indeed, after 38 days, a shift of the first main peak of the neat PLLA from $M_{p1} = 50\,300$ g mol^{-1} at t_0 to $M_{p1} = 3600$ g mol^{-1} at t_{38} was recorded (Table 2). Additionally, upon increasing the amount of PLLA in the blends, the shoulder and/or the second peak seem to appear earlier (Table 2). These observations suggest that the presence of PMMA slows down the hydrolytic degradation of PLLA in PLLA/PMMA blends. As a first assumption, a study of thermal properties using DSC during the hydrolytic degradation could be of help in understanding if these results are related to the weight ratio of PLLA amorphous phase and PLLA crystalline one. However, such a conclusion must be carefully drawn, as the influence of the PLLA loading on its GPC trace might not be negligible.

Thermal characterization of degraded samples

The first heating thermograms of PLLA, PMMA and all blends before and after hydrolytic degradation are shown in Fig. 3 and the main results obtained from DSC measurements are summarized in Table 3. It is to be noted that the degree of crystallinity of PLLA in the blends during degradation studies could not be calculated as an important error in calculation of polyester amount results from the increased brittleness/friability of the samples. Thus, Table 3 proposes a qualitative approach to these DSC measurements.

Before hydrolytic degradation (Fig. 3), all samples exhibited only one T_g value in the range from 57 to 115 °C, located

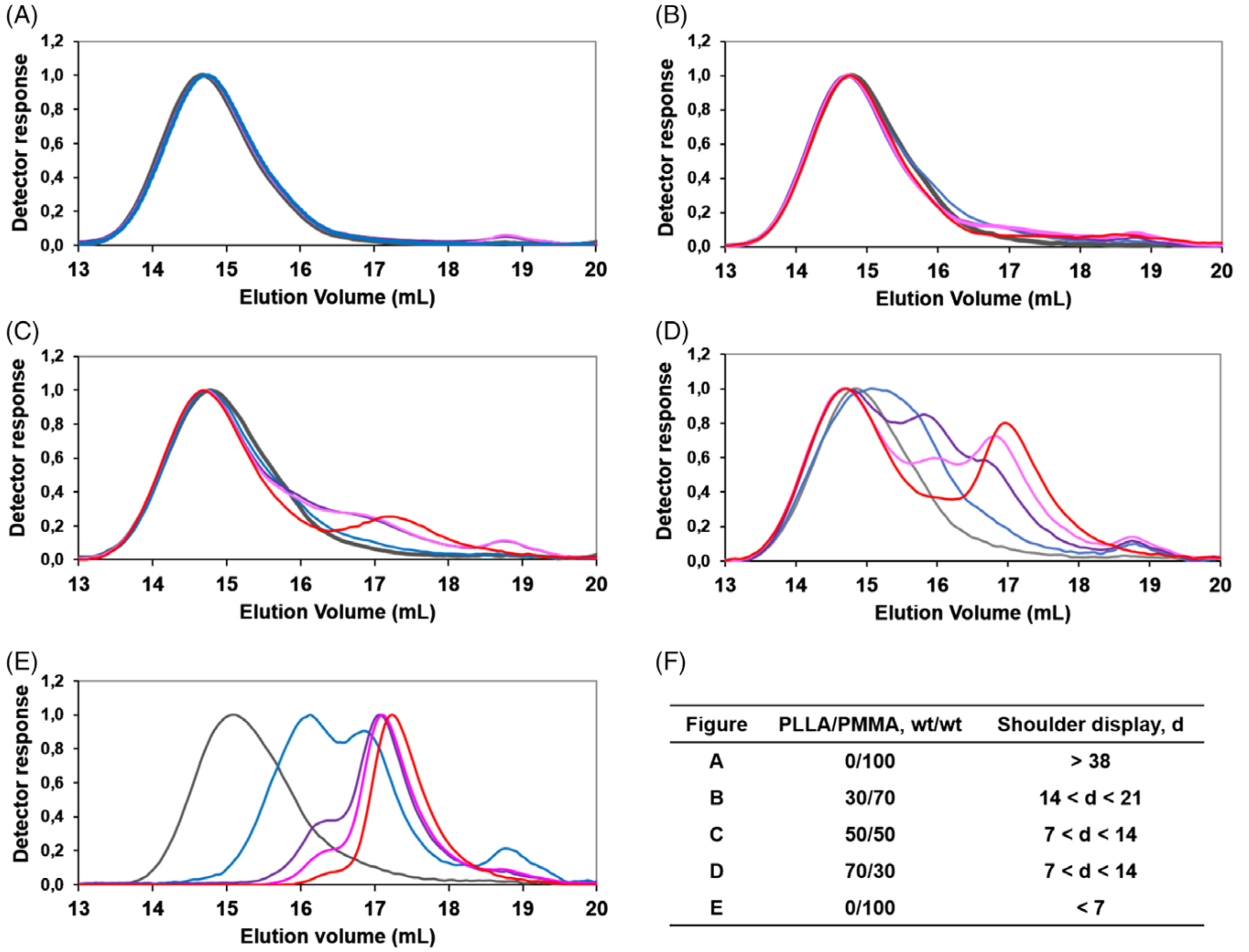

Figure	PLLA/PMMA, wt/wt	Shoulder display, d
A	0/100	> 38
B	30/70	14 < d < 21
C	50/50	7 < d < 14
D	70/30	7 < d < 14
E	0/100	< 7

Figure 2. SEC curves for neat PMMA (A), PLLA30/PMMA70 (B), PLLA50/PMMA50 (C), PLLA70/PMMA30 (D) and neat PLLA (E) during hydrolytic degradation at predetermined time (0 days, green; 7 days, blue; 14 days, violet; 21 days, pink; 38 days, red). (F) Details of shoulder display in days.

between these of neat PLLA (*ca* 60 °C) and neat PMMA (*ca* 115 °C) and shifting towards higher values with PMMA content as reported in the literature.[59] Similar trends were reported by Zhang *et al.*[33] showing that the evolution of a single T_g for miscible amorphous poly(D,L-lactic acid)/PMMA blends obtained by solution/precipitation at different compositions is in a range between the respective T_g of the individual components. The location of T_g of the blend appeared to be more or less proportional to the composition of the blend (following the Fox equation), which is a clear indication for the miscibility of melt-processed PLLA/PMMA blends. Regarding the organization of PLLA chains, before hydrolytic degradation, PLLA70/PMMA30 and neat PLLA exhibited a melting peak at 163 and 167 °C, respectively. Below 70% of PLLA, the presence of amorphous PMMA chains miscible with PLLA chains into the amorphous phase hindered the crystallization organization of PLLA chains.

The thermal behaviour of polymer blends sharply changed during hydrolytic degradation (Fig. 3 and Table 3). As expected for a non-degrading polymer, neat PMMA preserved the same thermal behaviour with a glass transition at 114 °C thus showing that PMMA chain mobility is not affected by hydrolysis. With 30 wt% PLLA, two glass transitions became visible (i.e. 69 and 88 °C, after 38 days). The second T_g was followed by a relaxation signal typical for PLLA. Similar results were obtained for the blends with 50 and 70 wt% PLLA (i.e. T_g of 61 and 97 °C with 50 wt% PLLA and 60 and 102 °C with 70 wt% PLLA). Focusing on PLLA crystalline phase, for PLLA50/PMMA50, the occurrence of a melting peak at 143 °C suggested that the polyester crystalline phase is not completely 'consumed' during hydrolysis. The PLLA70/PMMA30 sample exhibited a cold crystallization peak before degradation, which disappeared after 38 days of hydrolysis. The melting peak remained visible, but shifted to lower temperature (from 163 to 150 °C) suggesting that less stable crystalline phase was formed.

The results are somewhat consistent with observations for neat PLLA, where a slight shift of glass transition from 57 °C, before the degradation, to very slight inflexion at 59 °C after 38 days of hydrolytic degradation occurred. Furthermore, the cold crystallization peak visible at 96 °C before the degradation is absent after 38 days and the melting peak is shifted from 167 to 151 °C. It might be logically supposed that the amorphous fraction of the PLLA phase was firstly 'consumed' upon hydrolysis. Thus, after 38 days no cold crystallization occurs with temperature increase under DSC conditions (10 °C $\min^{-1}$).

A better understanding of the evolution of T_g with the ratio of PLLA to PMMA is provided by Fig. 4. The thermal properties of neat PMMA were preserved during the entire period of hydrolysis with a single T_g occurring around 112 °C. With 30% of PLLA in the blend, T_g decreased from 82 to 75 °C after 14 days of hydrolysis.

Table 2. SEC parameters of PLLA/PMMA blends during hydrolytic degradation

Formulation	Hydrolytic degradation time (days)	Maximum of first peak M_{p1} (g mol^{-1})	Đ	Shape of SEC trace	Maximum of second peak M_{p2} (g mol^{-1})^a
Neat PMMA	0	85 300	1.88	Monomodal	n.c.
	7	84 800		Monomodal	n.c.
	14	83 600		Monomodal	n.c.
	21	83 800		Monomodal	n.c.
	38	83 900		Monomodal	n.c.
PLLA30/PMMA70	0	75 600	2.19	Monomodal	n.c.
	7	78 400		Monomodal with tailing to lower molar masses	18 300
	14	84 400		Bimodal	20 300
	21	83 600		Bimodal	16 600
	38	78 400		Bimodal	n.c.
PLLA50/PMMA50	0	74 800	2.28	Monomodal	n.c.
	7	78 700		Bimodal	22 400
	14	82 900		Bimodal	7 300
	21	84 000		Bimodal	6 100
	38	83 600		Bimodal	3 600
PLLA70/PMMA30	0	69 500	2.22	Monomodal	n.c.
	7	52 500	3.29	Monomodal	n.c.
	14	82 500		Trimodal	6 000
	21	79 800		Trimodal	5 100
	38	81 700		Trimodal	4 900
Neat PLLA	0	50 100	2.22	Monomodal	n.c.
	7	13 500		Trimodal	5 500
	14	10 400		Trimodal	4 400
	21	10 800		Trimodal	4 150
	38	3 600		Multinomodal	n.c.

[a] Not concerned.

Table 3. Thermal properties and crystallinity of PLLA/PMMA blends before hydrolytic degradation[a]

PLLA/PMMA blend	T_g (°C)	T_{g2} (°C)	T_c (°C)	T_m (°C)	Cold crystallization peak	Fusion peak
0/100 before	112	Not visible	n.c.	n.c.	n.c.	n.c.
0/100 after	110	Not visible	n.c.	n.c.	n.c.	n.c.
30/70 before	82	Not visible	n.i.	n.i.	n.i.	n.i.
30/70 after	69	88	n.i.	n.i.	n.i.	n.i.
50/50 before	68	Not visible	n.c.	n.c.	Not visible	Not visible
50/50 after	61	96	n.c.	143	Not visible	Visible
70/30 before	58	Not visible	144	163	Visible	Visible
70/30 after	60	102	n.c.	150	Not visible	Visible
100/0 before	55	Not visible	96	167	Visible	Visible
100/0 after	63	n.d.	n.c.	151	Not visible	Visible

[a] n.c., not concerned; n.i., not identifiable.

After 21 days, two T_g values became apparent at 66 and 105 °C, which can be attributed to PLLA and PMMA amorphous phases, respectively. At the same time, a very small melting enthalpy of the blend was indicated.

At 38 days, the shape of DSC traces did not allow determination of the first-order thermal transition even after changing the heating rate. Data for PLLA50/PMMA50 and PLLA70/PMMA30 blends were in agreement, with the second T_g detected from day 14 and the first T_g remaining relatively constant at around 61 °C. A high PLLA crystallinity is observed in accordance with the opacity of the film.[46]

These results have to be analysed in the light of two parameters, i.e. crystallinity and morphology.[36] Firstly, regarding the crystallinity, for semi-crystalline PLLA, the hydrolytic degradation proceeded preferentially in the amorphous phase, due to the good water permeability in this region. This results in the removal of PLLA chains in amorphous regions, and therefore leads to an increase in crystallinity.[60] Besides, because of improving mobility of PLLA segments due to degradation products and water, recrystallization also results in an increase in crystallinity.[61] On the other hand, for material thicknesses lower than 0.5 mm, PLLA hydrolytic degradation was reported to take place mainly

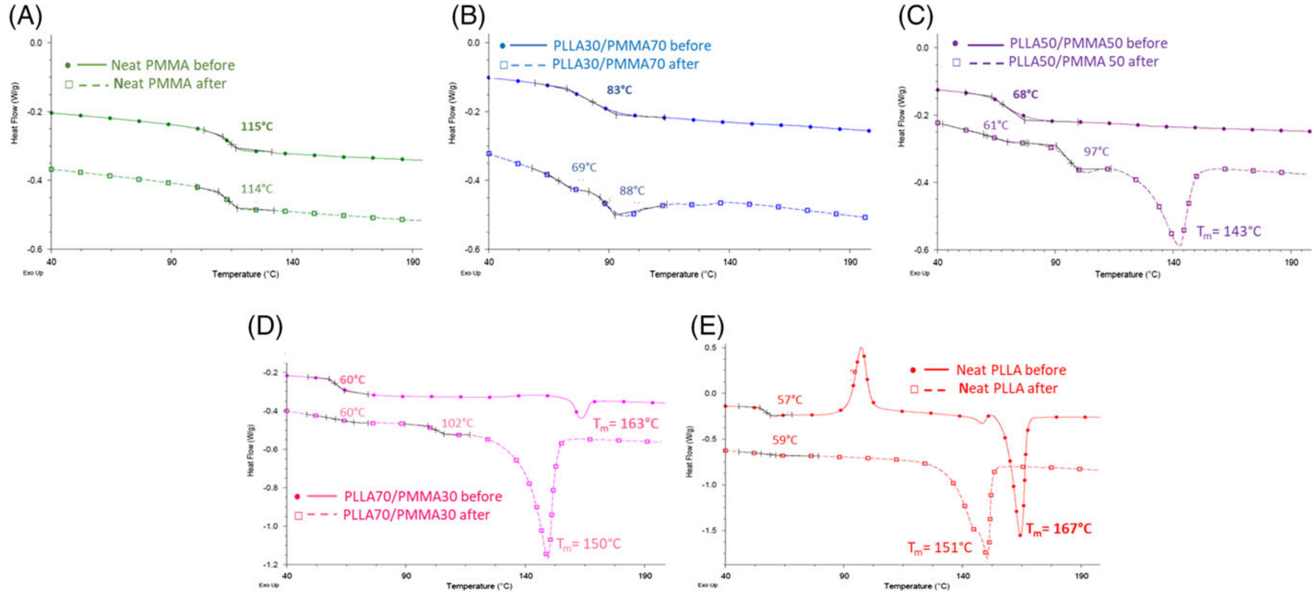

Figure 3. DSC analyses of (A) neat PMMA, (B) PLLA30/PMMA70, (C) PLLA50/PMMA50, (D) PLLA70/PMMA30 and (E) neat PLLA before (solid line) and after (short dash line) hydrolytic degradation (38 days). (First scan: 10 °C min^{-1}.)

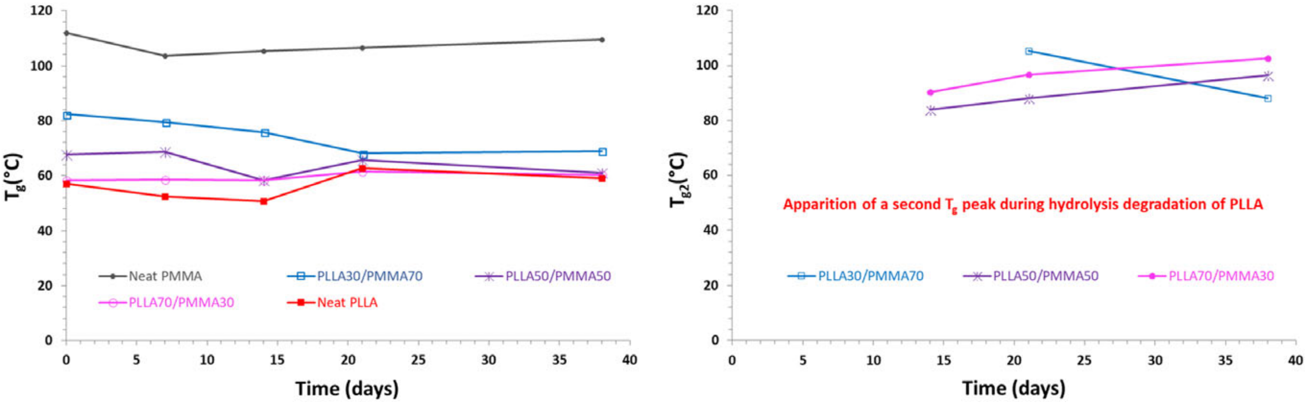

Figure 4. T_g evolution *versus* hydrolysis time for neat PMMA, PLLA30/PMMA70, PLLA50/PMMA50, PLLA70/PMMA30 and neat PLLA. (A) T_g of PLLA/PMMA miscible part. (B) Appearance of second T_g during hydrolytic degradation. (First scan: 10 °C min^{-1}.)

in the bulk of the material rather than on its surface (bulk degradation mechanism).[43] So, T_g observed using DSC at around 60 °C can be reasonably attributed to the amorphous chains of the PLLA phase localized at the surface of samples and not totally degraded. The second T_g attributed to PMMA amorphous chains indicates that a phase separation, between shortened PLLA chains and the PMMA not melt blended,[34] occurs during the hydrolytic degradation of PLLA in the bulk of the material. For a complete understanding, SEM observations were also performed.

Morphology observations

Figure 5 allows a comparison of the morphology of neat PLLA, PLLA70/PMMA30 and PLLA30/PMMA70 before and after hydrolytic degradation. Neat PLLA showed a smooth, homogeneous surface before hydrolysis and the SEM micrographs of PLLA70/PMMA30 and PLLA30/PMMA70 also showed a homogeneous morphology depending on the miscibility obtained within these blends. The observations are in accordance with the results reported by Bouzouita *et al.*[39] After 38 days of hydrolytic degradation, the morphology of neat PLLA was sharply modified. Small, medium and larger holes were seen over the whole sample, and the surface became inhomogeneous. However, the sample is not completely degraded and some PLLA crystals are always present, responsible for the whitening of the sample (Fig. 1(E)). Regarding PLLA70/PMMA30, small holes were also visible, but the sample seemed to contain more polymer than empty volume. So, a part of the PLLA matrix was able to resist the hydrolysis and it is reasonable to conclude that PLLA present after degradation is mostly PLLA in crystalline phase. With a high content of PLLA, the polyester chains organized into crystalline phase leading to white and curved sample (Fig. 1(D)). The PLLA30/PMMA70 morphology analysis highlights a completely different morphology. This blend with increasing PMMA content is again porous but the average size of holes appears greater, and the sample is mainly empty. These holes likely are the indication of the pathway of water molecules in the PLLA matrix. The water molecules penetrate more easily in the amorphous phase. With a majority of PMMA, PLLA is hindered from organizing into crystalline phase, thus known to be more resistant to hydrolysis. So, the white and not

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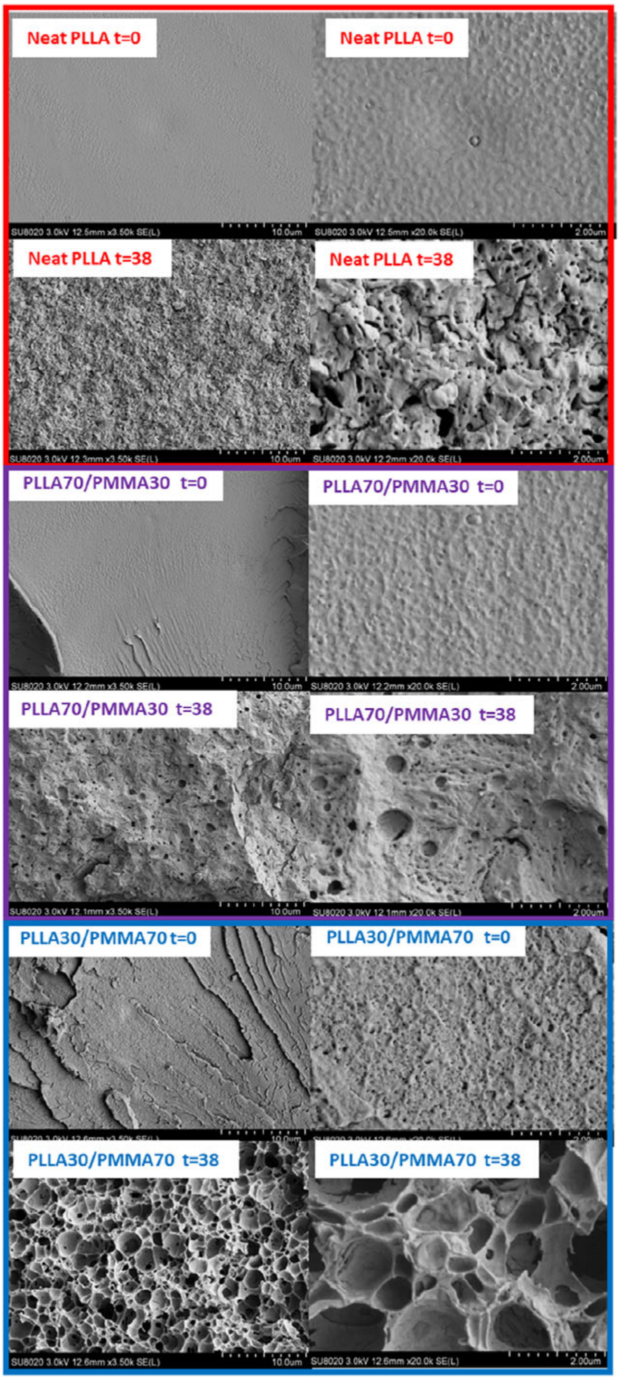

Figure 5. SEM micrographs of neat PLLA, PLLA70/PMMA30, PLLA30/PMMA70 before (top) and after (below) degradation.

deformed sample obtained (Fig. 1(B)) is due to the appearance of holes along the hydrolysis test.

CONCLUSIONS

The study was dedicated to the hydrolytic degradability of PLLA/PMMA blends as produced by melt blending. The hydrolytic degradation was investigated in buffer solution (pH = 7.24) at 60 °C for 38 days. This study confirms that, as with alkaline solution,[36] the hydrolytic degradation rate of a PLLA/PMMA blend can be widely tuned by PMMA content in neutral solution. However, here, morphology studies allow one to specify that the hydrolytic degradation with higher PMMA content leads to porous samples characterized by large holes with little influence on PLLA degradation rate. At lower PMMA contents, PLLA crystallization during the hydrolytic degradation is favoured leading to the slowdown of the hydrolytic degradation of PLLA in the PLLA/PMMA blends. These results offer interesting considerations for future studies of the impact of the biodegradation of PLLA/PMMA blends on the flora and fauna in seawater or freshwater environments.

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