

Preliminary Evaluation of Packaging-Content Interactions: Mechanical and Physicochemical Characterization of Polylactide Bottles

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ABSTRACT: Biodegradable materials as polylactide (PLA) are very interesting for cosmetic packaging application. However, these polymers, under environmental conditions or/and chemical treatments, can undergo “aging,” compromising their performances such as container. The aim of this study was the evaluation of mechanical, physicochemical, and organoleptic properties of PLA bottles present in the cosmetic market. In particular, mechanical tests and thermal analyses were applied to study the PLA container degradation under stressed physicochemical conditions. Calorimetric and morphological analyses were applied to evaluate differences between internal and external surface of containers. Results highlighted that the heating process together with chemical treatment determined a significant modification on polymer, leading to a more resistant and fragile material, whereas the only physical or chemical treatment alone showed a plasticizing effect. In conclusion, this study represents a start point to evaluate content–packaging interactions to optimize the choice of PLA polymer as cosmetic packaging. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40067.

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INTRODUCTION

The packaging plays a very important role in the quality of cosmetic products. It must carry the correct information and identification of the product and it must protect the formulation against all adverse external influences, e.g., moisture, light, oxygen, and temperature variations, that could alter its properties.

It also must protect the content against biological contamination and physical damage. The complexity of packaging materials and the highly technological nature of cosmetic products is such that manufacturers have to deal with significant problems. The stability of the product and its compatibility with the containing material are distinct concepts, separate and complementary, that must be evaluated before that the product is commercialized. In fact, polymeric packaging can interact heavily with all components such as active ingredients, excipients, and solvents, used in a variety of cosmetic formula, and it is not said that protective layers, present onto contact area, are really efficient.

In some cases, this interaction determines color and thickness alteration of the cosmetic formula. In other cases, substance present into formulation could be absorbed or could be attacked from substances migrated from packaging (Figure 1).¹

For this reason, it is very important to reveal these effects by setting up of protocols and specific tests.

Testing about migration of material additives into cosmetic products is a crucial point of safety assessment of packaging material. However, New Regulation 1223/2009 establishes clearly that packaging–product interactions must be studied but it does not explicate them in details.² In fact, unlike the food and pharmaceutical products, in cosmetic field there are not yet specific guidelines concerning packaging/content interaction studies. At the present moment, the environmental problem from the waste of plastic packaging increases every year due to its light weight, easy process, and good properties for various application. However, these packaging, obtained from petrochemical-based polymers, such as polyethylene (PE), polypropylene, and polystyrene, are not biodegradable and can lie around for 500–1000 years without degrading. To solve this problem, the biobased polymers, made from renewable natural resources, biodegradable in 0.5–2 years, such as polylactide (PLA), polyhydroxyalkanoates, and polycaprolactone, are selected as packaging material.³ Replacing the use of petrochemical plastic with bioplastic with comparable properties can reduce the use of fossil fuel such as crude oil, gas, and coal, which increase the CO₂ level in the air.⁴

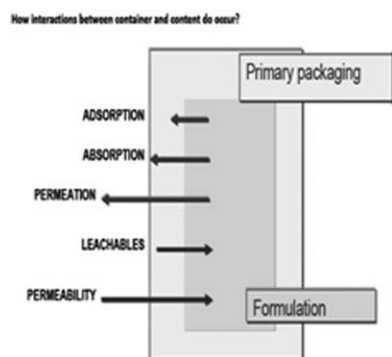


Figure 1. Scheme of possible interactions between packaging and contents.¹

In particular, among bioplastic materials, PLA attracts both industries and research institutions. PLA is a member of the polyester family and it plays a predominant role as sustainable alternative to petrochemical-derived products. PLA is the linear thermoplastic aliphatic polyester produced by either ring-opening polymerization of lactide or condensation polymerization of lactic acid monomers that are produced from renewable resources such as corn by a fermentation process.^{5–7}

The production of PLA presents numerous advantages: it can be obtained from a renewable agricultural source (corn); its production consumes small quantities of carbon dioxide; it provides significant energy savings; it is recyclable and compostable; its physical and mechanical properties can be manipulated by polymer architecture.⁶ PLA exhibits good properties such as biodegradability, heat resistance, transparency, good mechanical properties, and processability, leading it to be used in many packaging applications.^{8–10} The important requirement for packaging materials is high tensile strength, ductility, flexibility, transparency, and good barrier properties. However, PLA is still limited for its application because of its price, brittleness, rigidity, and low crystallization rate.^{11–13} Due to its higher cost, the initial use of PLA as a packaging material has been in high value films, rigid thermoforms, food, and beverage containers and coated papers. In the last 5 years, the use of PLA as a packaging material has increased all across Europe, Japan, and the United States, mainly in the area of fresh products where PLA is being used as a food packaging polymer for short shelf life products. Currently available, PLA is used in compostable yard bags to encourage recycling and composting programs.

The main objective of this study was to investigate product–polymeric packaging relationship into cosmetic field, because low information have been found in this field. In fact, even more and more information are present in the literature relatively to characteristics and properties of polyethylene terephthalate and PE, a very few studies are related to PLA behavior used as packaging. In fact, about PLA, it is known from literature that degradation of this kind of polymer, when processed as plates or blends, is mainly due to intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide.^{14–16}

It has been found that PLA degradation is dependent on a range of factors, such as molecular weight, crystallinity, purity,

temperature, pH, presence of terminal carboxyl or hydroxyl groups, water permeability, and additives acting catalytically that may include enzymes, bacteria, or inorganic fillers.^{3,17,18} Polymer degradation determines changes in the properties—tensile strength, color, shape, etc., of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light, or chemicals.¹⁹ In our knowledge, only one paper reports the degradation of PLA commercial film as finished cosmetic packaging.²⁰ For this reason in this work, PLA commercial bottles were studied and characterized. PLA bottles, both empties and filled with monophasic standard solution of pH 2, were studied under stressed conditions (ultraviolet [UV]–vis exposition and temperature/humidity treatment) to evaluate the possible degradation both of packaging and contained formulation. These conditions are meant to simulate what will happen to the product during its life cycle and they were selected for the degradation experiment according to the recommendations of stability tests for cosmetic products.²¹ In the case of PLA, the contact with cosmetic formulation can have an influence on crystallinity, leading to thermal and barrier property changes. Mechanical and thermal analyses techniques were employed to characterize physicochemical properties of containers. In particular, in this study, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier Transform Infrared Spectroscopy (FT-IR) were successfully applied to monitor and control the degradation of packaging due to photo-oxidation and/or environmental conditions by analyzing both internal and external surfaces of bottles. Finally, the ultimate goal of this work was to identify and understand the possible degradation phenomena that the PLA container may sustained during the life of the cosmetic product, to choose the best use of this polymer as cosmetic packaging depending on the type of product that must be marketed. In according to literature, parameters such as humidity, temperature, pH, salinity, presence or absence of oxygen have important effects onto degradation process.³ For these reasons, in this work, PLA containers, in climatic room stored and UV–vis photoexposed were tested. Furthermore, it was very important to study simultaneously the internal and the external sides of the container to better understand what is the main factor that influences packaging stability and content–container interactions.

EXPERIMENTAL

Materials

Packaging materials, object of this study, were commercial bottles of 150 mL made of the resin Ingeo biopolymer produced by Nature Works, Minnetonka. The resin is a PLA biopolymer, PLA7001D, semicrystalline material, specific gravity 1.24, glass transition temperature 55–60°C, and crystalline melting temperature 145–160°C.

Degradation Testing Procedures

PLA bottles were numbered, weighted, and washed according to a washing procedure described below. Afterward, bottles filled with standard solution of pH 2 and empty bottles were subjected to different degradation tests:

- photostability test by simulating UV–visible ray irradiation using SUNTEST XLS +II (Atlas®) for 24 and 96 h;
- accelerated stability test by incubation into climatic room (ClimaCell 111 MMM) at 40°C with 75% RH for 30 days.

SUN TEST instrument was set up according to standard European procedures²² and precisely to the following parameters:

- Time: 4 h corresponding to 192 h solar light
- Irradiation control: 300–800 nm
- Irradiation (W/m^2): 750
- Room temperature: 35°C
- Black standard temperature: 45°C.

In particular, solar ID65 filter has been used. This type of filter simulated solar radiation behind 6 mm window glass; it meets CIEID65 according to ICH Guideline.

Photostability test was performed according to Colipa guidelines about cosmetic products.²¹

Accelerated stability test was performed according to EMA: test parameters (duration, temperature, and humidity values) were set up by considering accelerated stability testing relative to pharmaceuticals products.^{22,23}

The washing procedure, used at the beginning of the study and at the end of all treatments, was the following: all bottles were washed for three times with 1% bicarbonate solution and then for another three times with distilled water to remove bicarbonate residuals. The bicarbonate solution was considered appropriate to immediately buffer a possible release of additional acidic monomers from the polymeric chain, subsequent to treatment. The subsequent washing with water served, in turn, to remove any possible residual bicarbonate.

Finally, for all samples, several specimens were obtained to carry out mechanical, physicochemical, and morphological analyses.

Evaluation of Organoleptic Properties and pH Values of Contained Solutions

Organoleptic control of pH 2 standard solution, at the end of described treatments, was examined. In particular, color alterations, unpleasant odor, and particulate precipitation in aqueous solution were considered. Finally, pH of buffer solution was controlled after each treatments to verify a possible degradation of PLA. Values were compared with pH ones obtained considering PLA containers filled with distilled water and treated in the same conditions of photostability test after 24 and 96 h.

Mechanical Testing

The investigation of the mechanical properties of the bottles was performed using a tensile machine, AGS 500ND (Shimadzu corporation, Kyoto-Japan) equipped with a 500-N load cell; the test was performed using a strain rate of 2.0 mm/min. Five “bone-shape” specimens were obtained from each bottles sample; the feature of the specimens followed the principles of the European Standard EN ISO 527,²⁴ suitably modified for bottle containers. Samples were kept under constant temperature (23°C) and humidity (52% RH) for a week until tension test started. It has been retained opportune to maintain a temperature of 23°C and a relative humidity of 52% also during

mechanical characterization at tensile tester. This procedure permitted to obtain a stress versus strain curve. From each set of results was possible to estimate the tendency of materials to oppose to deformation, to evaluate the curve profile in elasticity regime, the elongation percentage in elasticity regime and the absolute elongation elasticity.

Colorimetric Analysis

The instrumental assessment of packaging color was performed with Cutometer MPA580 (CK electronic GmbH, Germany) equipped with the Colorimeter CL400 probe. Technical data of probe are length: 126 mm, illumination: \varnothing 24 mm, measuring area: \varnothing 8 mm, weight: 85 g, illuminated area approx. 17 mm \varnothing ; units: xyz , and RGB, $L \times a \times b$; light: 8 white LEDs arranged circularly, range of emitted wavelengths: 440–670 nm; and accuracy: $\pm 5\%$.

The color acquisition is done by specifying the three tristimulus values X , Y , and Z , of a color in according to the CIE system, where X is a tristimulus value of red, Y to a green value, and Z to a blue value. Results are expressed by using the chromatic coordinates, which are set with x , y , and z , not to be confused with the functions X , Y , and Z ; only two of these “chromatic coordinates” are independent, because the third is determined by the relationship: $x + y + z = 1$. So, since the chromatic characteristics of a color, such is the tone and the saturation, are easy specified by two coordinates, it is possible to use a planar representation of simple construction and easy to understand.

Differential Scanning Calorimetry

Temperature and enthalpy values were measured with a Mettler STARE system (Mettler Toledo, Novate Milanese, MI, Italy) equipped with a DSC821^e Module and an Intracooler device for subambient temperature analysis (Julabo FT 900) on 6–7 mg (Mettler M3 Microbalance) samples in sealed aluminum pans with pierced lid. Each sample was cut in a flat piece of suitable size to completely cover the bottom surface of the crucible. The piece was placed in the crucible in such a way that its internal or external side was in closely contact with the bottom to evaluate possible differences in the polymer glass transition temperature due to the acid solution and/or the UV irradiation effect, respectively. To better characterize the solid state of PLA, thermal cycling, i.e., heating from 0 to 75°C, cooling to 0°C and reheating to 200°C [$\beta = 10 \text{ K min}^{-1}$, nitrogen air atmosphere flux (50 mL min^{-1})], were performed. The instrument was preventively calibrated with Indium as standard reference. Measurements were carried out at least in triplicate.

Simultaneous Thermogravimetric Analysis (TG/DSC1)

Mass losses were recorded with a Mettler STARE system (Mettler Toledo) TG simultaneously DSC (TG/DSC1) on 6–8 mg samples in open alumina crucibles [$\beta = 10 \text{ K min}^{-1}$, nitrogen air atmosphere (flux 60 mL min^{-1}), and 30–500°C temperature range]. The instrument was preventively calibrated with Indium as standard reference. Measurements were carried out at least in triplicate.

Fourier Transform Infrared Spectroscopy

Mid-IR (650–4000 cm^{-1}) spectra were recorded on samples using a Spectrum One Perkin-Elmer FT-IR spectrophotometer

(resolution 4 cm^{-1} , 16 scans; Perkin Elmer, Wellesley, MA) equipped with a MIRacle™ ATR device (Pike Technologies, Madison, WI). Internal and external surfaces were considered. To confirm physicochemical analyses and to evaluate differences between internal and external surfaces, bottles were macroscopically examined also by visual evaluation during the degradation tests. Morphological characterization of both bottles surface was performed by scanning electron microscopy (SEM, Zeiss EVO MA10, Germany). Samples were immobilized on aluminum stubs and gold sputtered.

RESULTS AND DISCUSSION

Evaluation of Organoleptic Properties, pH, and Color

Buffer solutions were opportunely characterized to identify possible organoleptic alterations as a consequence of thermal and UV-vis treatments. Buffer solutions did not show color alterations and precipitate was not observed into bulk. Similarly, alterations of container shape and color of surface packaging were evaluated. Figure 2 shows results about colorimetric analyses carried out on PLA bottles before and after stability tests. In detail, color of PLA container as change in the chromatic coordinates x , y , and z , was observed. At the beginning of the study,

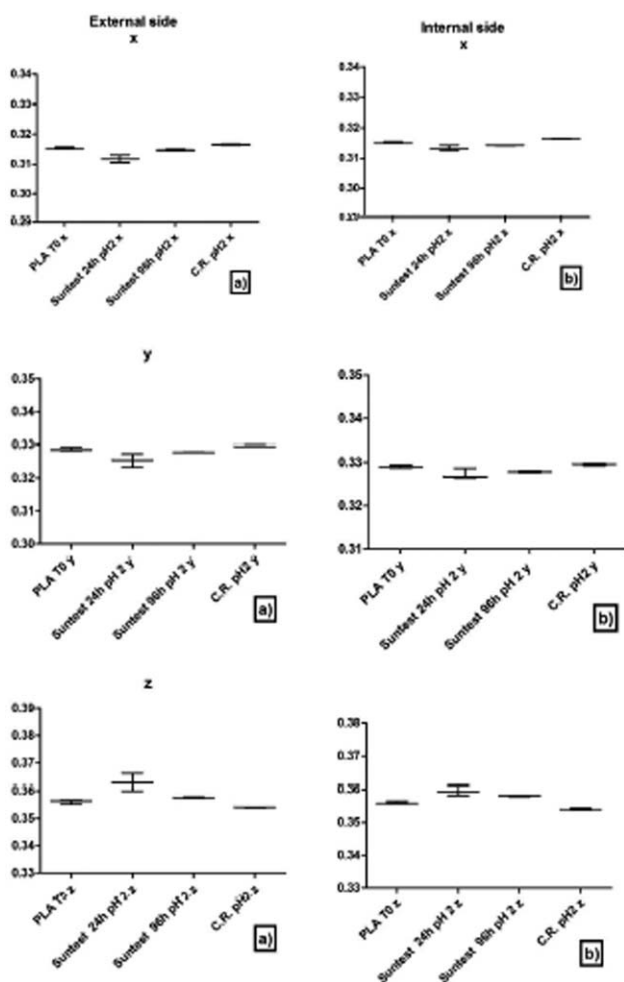


Figure 2. Chromatic coordinates x , y , and z values measured on PLA bottles during stability tests.

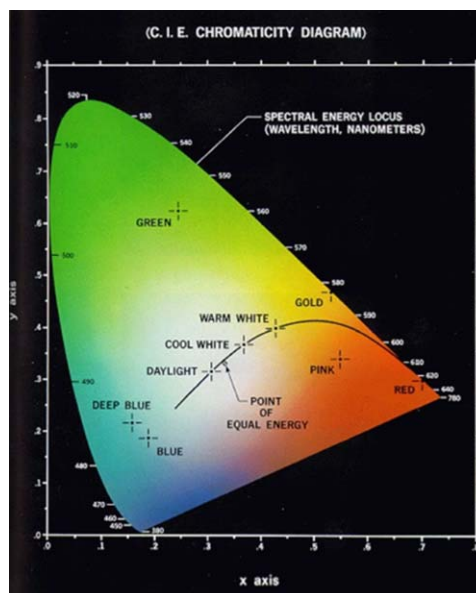


Figure 3. C.I.E. chromaticity diagram.²⁶ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containers showed the same color both in the external and in the internal sides with coordinates values in the white color gradation of the CIE chromaticity diagram (Figure 3).²⁵ However, irradiated containers lost this gradation and seem clear.

This alteration was confirmed also from colorimeter analysis. In fact, after 24 h in suntest, all coordinates were different from the standard, both in the external and in the internal side (Figure 2). Instead, visible color changes were not revealed for containers maintained at room temperature and into climatic room. Table I shows the pH decrease percentage of buffer solution and distilled water, after photo and heat treatment. A significant pH reduction was observed after 24 h in suntest and after 30 days in climatic room both for buffer and for water. However, after 96 h UV-vis exposition, a considerable pH reduction was not noticed. We explain these results considering that, according to the literature, PLA degrades more quickly if subjected to high humidity percentage and high temperature and that degradation involves high molecular weight polyester chains that could hydrolyze into oligomers of lower molecular weight. In this way, lactic acids residuals could be released into solution determining a possible pH reducing and supporting an hydrolytic process. It is known that hydrolysis can be accelerated from acids and basis or simply from water, and affected by temperature and moisture levels.^{26,27} Thus, we claim that pH reductions after 24 h of UV-vis irradiation and after 30 days in the climatic room could be due to respectively a release of some acid interchain monomers release and a surface erosion mechanism with consequent scission of acid lactic monomers. On the contrary, after 96 h of photoirradiation, the buffer effect of standard solution justified the insignificant difference of the pH value in respect to the initial one. In the samples containing water was not possible to speak about buffer effect. Indeed, the pH decrease was bigger than the one of samples containing buffer solution. In conclusion, results reported in Table I show that the solar radiation has a degradative effect greater, in terms

Table I. Percentage of pH Reduction in Respect to the Initial pH Value During Stability Test

Sample	pH decrease (%)
PLA suntest (24 h) H ₂ O	27 ± 1.2
PLA suntest (96 h) H ₂ O	8.2 ± 0.1
PLA suntest (24 h) pH 2	23 ± 0.17
PLA suntest (96 h) pH 2	1 ± 0.09
PLA climatic room (30 days) pH 2	15 ± 0.3

of pH, compared to the combined effect of humidity and temperature, characteristic of the climatic chamber. The lowering of pH, characteristic of buffer and water, resulted more evident when the samples have been treated in suntest for 24 h. It has been observed a drop of almost double compared to the value recorded in a climatic chamber at 30 days. However, the data recorded for irradiated samples at 96 h go against this trend and appear to be characterized by a lower degradation. An explanation for this phenomenon could be correlated to a possible tendency of the system to achieve a balance polymer–water/buffer more or less stable, depending on the ionic

strength. In this sense, one could explain the greater lowering of pH immediately after 96 h in the case of polymer–buffer system, compared to the polymer–water system: the higher ionic strength of buffer system determines a bigger competitions between charges and this slows down the achievement of a balance.

Mechanical Properties

Starting from the principles of the European Standard EN ISO 527 concerning the evaluation of tensile properties of plastic materials,²¹ in a previous not yet published work, Capra et al. set up an experimental protocol to obtain reproducible and standardized measurement of mechanical properties of commercial bottles thanks to a specimen realization with a suitable geometry. The same protocol was used to obtain mechanical results reported in this study. Figure 4 shows some stress/strain curves obtained in this work. From these curves, it is possible to calculate, for all samples, angular coefficients, as representative values of Young's modulus, % elongation in elasticity regimen and % absolute elongation.

Table II reports these parameters for the analyzed samples. It is possible to observe a correspondence between empty and filled

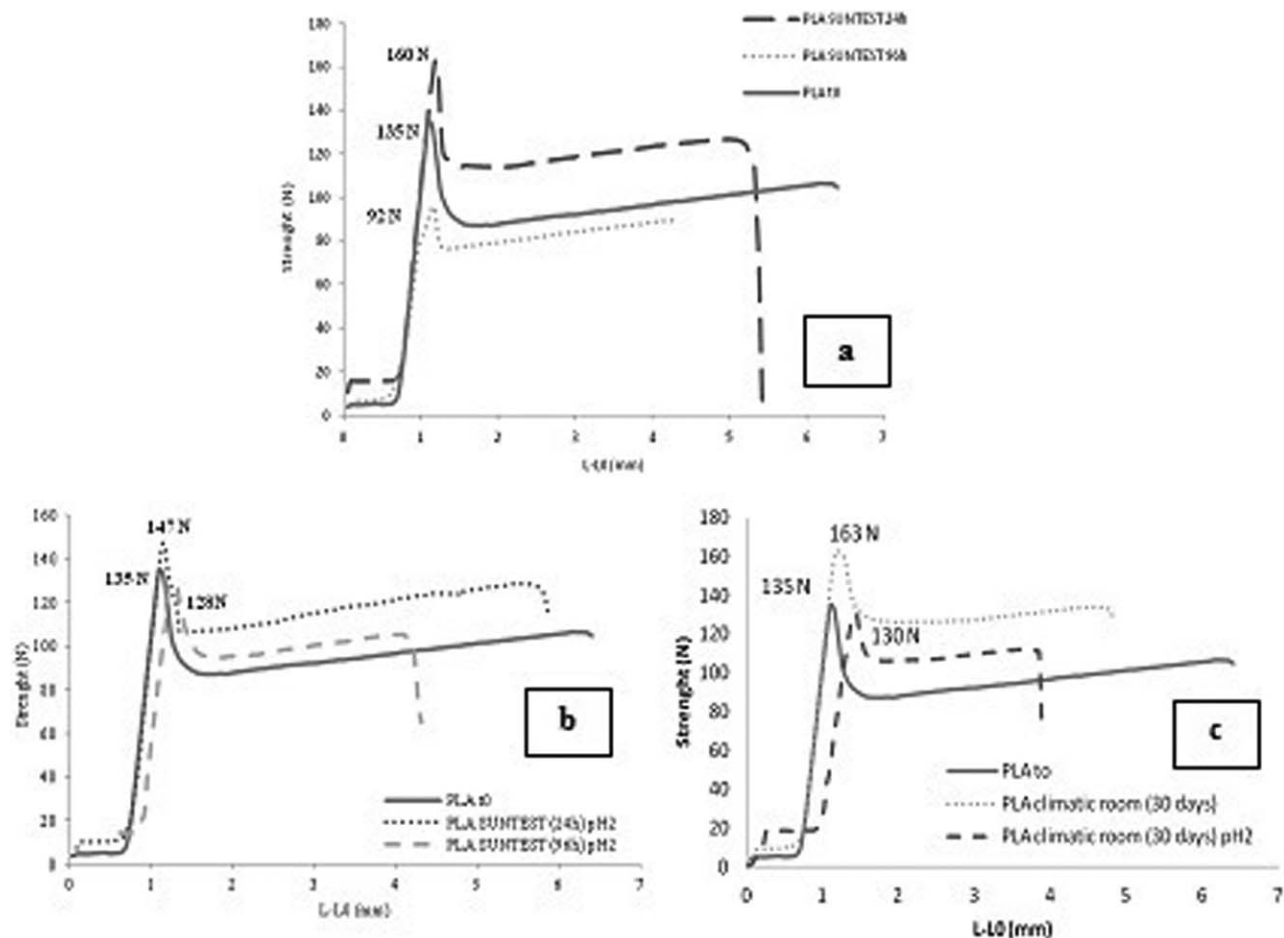


Figure 4. Stress–strain profiles of: (a) empty PLA bottles after photostability test; (b) PLA filled bottles (pH2) after photostability test; and (c) PLA filled bottles (pH2) after accelerated test, compared with the standard.

Table II. Mechanical Parameters of PLA Bottles, Treated With Standard Solution at pH 2 and to Different Simulated Environmental Conditions

Sample	Angular coefficient ^a	Elongation in elasticity regime (%)	Absolute elongation (%)
PLA0 (standard)	317.81 ± 7.1	6.4	79.4
PLA suntest (24 h)	321.28 ± 5.7	7	23.6
PLA suntest (96 h)	286.53 ± 3.2	6.9	25.5
PLA suntest (24 h) pH 2	330.32 ± 8.2	6.6	32.9
PLA suntest (96 h) pH 2	252.40 ± 1.3	7.1	23.8
PLA climatic room (30 days) pH 2	269.02 ± 3.2	8.1	21.2
PLA climatic room (30 days)	361.32 ± 3.3	7.1	26.4

^a Angular coefficient represents the tendency of material to oppose to deformation in the portion of elastic regime.

irradiated samples: after 24 h of exposition, elasticity profiles increase compared to the standard sample (PLA t_0). However, after 96 h of treatment an opposite tendency was observed: the angular coefficient decreases relative to standard. Comparing values of angular coefficient and elongation in elasticity regime with graphs reported in Figure 4(a,b), it is evident that PLA t_0 and PLA irradiated 24 h do not show significant differences in elasticity regime, because curve profiles are overlapped. However, strength at necking of irradiated sample (24 h) is higher than standard sample and this phenomenon can be explained with polymer plasticization during photoirradiation, but also, in the case of filled samples [Figure 4(b)], with plasticizing effect due to water contact. Otherwise, prolonged UV-vis exposition led to a significant reduction of strength at necking. These results highlight that, with exacerbate expositions, PLA degrades by polymeric chain break down. In particular, samples filled with acid solution show lower values: in this case, degradation must be attributed to the association irradiation pH 2. Moreover, water content could have to also hydrolytic effect by inducing depolymerization of PLA chains. Also where results obtained by photoirradiation are compared to those from samples stored in climatic room for 30 days [Figure 4(c)], it is worthwhile to speak about degradation process due to humidity, heat and buffer contact. In particular, from Table II, it is evident as filled sample is more fragile, with an higher tendency to break. This result can be explained by the fact that packaging material, in stressed environmental conditions of climatic room, become more permeable because of polymeric chain mobility and consequently more susceptible to structure degradation. Finally, in all treated samples, percentage of absolute elongation was obviously lower than that of standard containers. Consequently, environmental and chemical factors made polymer more fragile and more easily subjected to fracture.

Physicochemical and Morphological Characterization

Thermal analysis techniques were applied to control the degradation effects on the PLA packaging, as such or containing pH 2 solution, caused by UV-vis irradiation, temperature and humidity. Every PLA packaging was cut in pieces weighing approximately 6–7 mg and analyzed both on internal and external side.

In DSC thermal cycling, the first heating up to 75°C had the aim to eliminate the thermal history of the sample. The second

heating, for all samples, revealed similar thermal events, in particular the glass transition, the cold crystallization and the melting processes. In Figure 5 is shown, for example, the thermal cycling of internal (Curve a) and external (Curve b) sides of empty PLA packaging at room temperature. In the first heating, an endothermic effect, due to the structural relaxation, superimposed to the glass-transition temperature (T_g) is observed at 65.7 ± 0.6 and $66.6 \pm 0.3^\circ\text{C}$ for internal and external side, respectively. As expected, during the second heating, the enthalpy relaxation disappeared, and the T_g was precisely measured as the temperature at the inflection point of the effect, $T_{\text{midpoint}} = 60.5 \pm 0.2$ and $62.3 \pm 0.1^\circ\text{C}$ for internal and external sides, respectively. The difference in the T_g between the two sides can be correlated to a non homogeneity of the starting sample as confirmed by SEM measurements. Indeed, as evident in the microphotograph of Figure 6, internal and external surfaces are different: the first one [Figure 6(b)] is smooth while the second one shows high surface roughness [Figure 6(a)].

After the T_g , the polymer chains acquire some translation mobility which allow the sample to freely crystallize at $86 \pm 3^\circ\text{C}$ with an exothermic effect, in both cases. The following endothermic peak is due to melting process and is characterized by thermal and calorimetric parameters very similar for internal

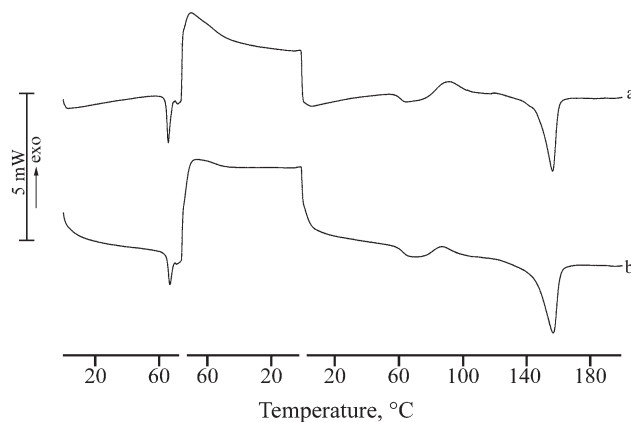


Figure 5. DSC cycling of internal (Curve a) and external (Curve b) side of empty PLA packaging.

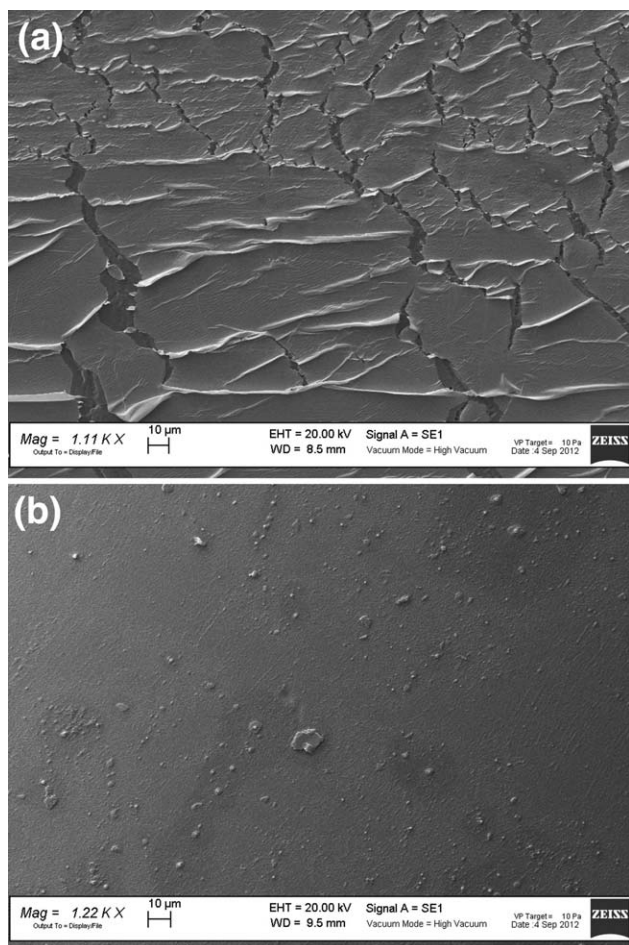


Figure 6. External (a) and internal surface (b) PLA filled bottles, at zero time.

and external sides ($T_m = 156 \pm 1^\circ\text{C}$; $H_m = 27 \pm 2 \text{ J g}^{-1}$). In Table III and IV are listed the DSC parameters (second heating) of all samples, recorded for internal and external sides, respectively.

The absence of significant differences in the thermal data of the internal side of all PLA packaging suggested that the polymer solid state of this side is not influenced by the different storage conditions. The presence of a shoulder at around 147°C in the melting endotherm of the original PLA crystallites, recorded after UV irradiation for 96 h and storage in controlled climatic conditions, is probably due to a rearrangement of chains during crystallization,

as reported in the literature.²⁸ This effect is probably correlated to the formation of a more fragile crystalline packaging, confirming the different mechanical behavior of these samples described above. For the external side, the thermal cycling performed on empty PLA shows a progressive decrease in T_g with the increasing of the irradiation time ($T_{g,t=0} = 62.3 \pm 0.1$, $T_{g,t=24\text{ h}} = 61.7 \pm 0.5$ e $T_{g,t=96\text{ h}} = 59.4 \pm 0.7$, respectively) probably due to polymer plasticization. The same effect on T_g is observed also for the samples stored in controlled climatic conditions probably as a consequence of the combined action of temperature and humidity. The same behavior recorded for internal side of empty PLA, is recorded also for the internal side of PLA packaging containing pH 2 solution to confirm that for this side the storage conditions not influenced the polymer solid state. In the external side of PLA containing pH 2 solution the T_g decreasing, after UV irradiation and storage in controlled climatic conditions, is concomitant with the increasing of the cold crystallization and melting temperatures. The presence of acid solution together with storage conditions cause a lower chain mobility in the amorphous region responsible also for the advance breaking recorded in mechanical analysis. For all samples, the melting enthalpy of original samples is unchanged after treatment ($H_m = 27 \pm 2 \text{ J g}^{-1}$). It is not possible to calculate the crystallinity degree of samples because of the difficulty in assessing the enthalpy of the cold crystallization effect due to low data reproducibility.

All the samples were also characterized by TGA to evaluate the thermal decomposition after melting. In all cases, the thermal weight loss (around 97–98%) takes place in a single step. The corresponding decomposition onset, peak and endset temperatures (T_{onset} , T_{peak} , and T_{endset} , respectively) are extrapolated by the first derivate of the TGA curves (DTG) as shown in Figure 7 for empty PLA at the beginning (Curve a) and after UV irradiation for 24 and 96 h (Curves b and c). All decomposition temperatures recorded are listed in Table V.

For the empty PLA after suntest, the decomposition temperatures progressively increase with the irradiation time. These results suggest modifications in the chains arrangement of the polymer; in particular the hydrolytic reactions caused by UV irradiation can generate smaller chains able to reorganize causing a higher resistance to thermal decomposition.¹⁵ A similar behavior is observed for empty PLA stored for 30 days in controlled climatic conditions. In the PLA packaging containing pH 2 solution, an increasing of the thermal decomposition temperatures is observed, higher after 24 h in suntest, probably as a

Table III. Temperatures Recorded in the DSC Second Heating for Internal and External Sides of Empty PLA (Standard Deviation in Parentheses)

	Internal side				External side			
	t_0	24 h suntest	96 h suntest	30 days C.R.	t_0	24 h suntest	96 h suntest	30 days C.R.
$T_{\text{midpoint}} (^\circ\text{C})$	60.5 (2)	61.3 (1)	60.2 (1)	60.2 (6)	62.3 (1)	61.7 (5)	59.4 (7)	61.1 (2)
$T_{\text{exo}} (^\circ\text{C})$	86 (3)	86.6 (1)	86.5 (1)	86.0 (9)	86 (3)	86 (1)	87 (1)	87 (1)
$T_m (^\circ\text{C})$	156 (1)	155 (1)	156 (1) ^a	157 (1) ^a	156 (1)	156 (1)	157 (1)	157 (1)

C.R. = climatic room.

^a Presence of a shoulder at $147 (2)^\circ\text{C}$.

Table IV. Temperatures Recorded in the DSC Second Heating for Internal and External Sides of PLA Packaging Containing pH 2 Solution (Standard Deviation in Parentheses)

PLA pH 2	Internal side				External side			
	t_0	24 h suntest	96 h suntest	30 days C.R.	t_0	24 h suntest	96 h suntest	30 days C.R.
T_{midpoint} (°C)	60.5 (2)	59.3 (9)	60.3 (4)	59.8 (9)	62.3 (1)	61.6 (6)	60.5 (1)	60.8 (9)
T_{exo} (°C)	86 (3)	86 (2)	86 (1)	89 (2)	86 (3)	86 (1)	88 (1)	92 (1)
T_{m} (°C)	156 (1)	156 (1)	155 (1)	157 (1)	156 (1)	156 (1)	158 (1)	159 (1)

C.R. = climatic room.

consequence of the initial hydrolytic decomposition effect of the acid solution. The following buffer solution effect determine an increasing of decomposition temperatures, lower than that recorded at 24 h in suntest, probably associated with the different chains mobility in the amorphous region, correlated to the higher cold crystallization and melting temperatures described above in the DSC. To better characterize PLA solid state, all the samples were analyzed by FT-IR spectroscopy, on internal and external sides. In Figure 8, the FT-IR spectra recorded on the internal side at $t = 0$ and after 24 and 96 h of UV irradiation of empty PLA and on PLA containing pH 2 solution after 24 h at room temperature are compared (the same results were obtained for external side). UV irradiation causes the appearance of two peaks at 1638 and 1546 cm^{-1} which become more intense with increasing the time of irradiation and in the presence of the acid solution just after 24 h. These vibrational effects are due to the —C=O carboxyl stretching generated by hydrolytic reactions, confirming the thermal decomposition results obtained by thermal analysis. The unchanged —C=O carbonyl stretching band at 1744 cm^{-1} indicates that no phase

transitions occurs in the crystalline region of these samples. The effect of the acid solution is confirmed by SEM and from the evaluation of shape container. In particular, Figure 9 shows the external and internal surfaces of a sample of PLA bottle treated with acid solution and irradiated for 24 h; it is evident that the external side [Figure 9(a)] shows a surface homogeneous and more resistant to high vacuum treatment, during picture collection. However, onto internal side, the effect of irradiation in addition to acidic solution make the surface more susceptible to high vacuum effect, emphasized by the breakage [Figure 9(b)] and this confirms the brittleness of irradiated sample with pH2 solution. Finally, visual evaluation of container shape showed a swelling of the bottom of the 24 h irradiated bottles treated with acid solution (Figure 10), confirming, one more time, degradation process due to contact with low pH.

CONCLUSIONS

In conclusion, the research presented in this study investigated the effects of acid buffer solution onto mechanical,

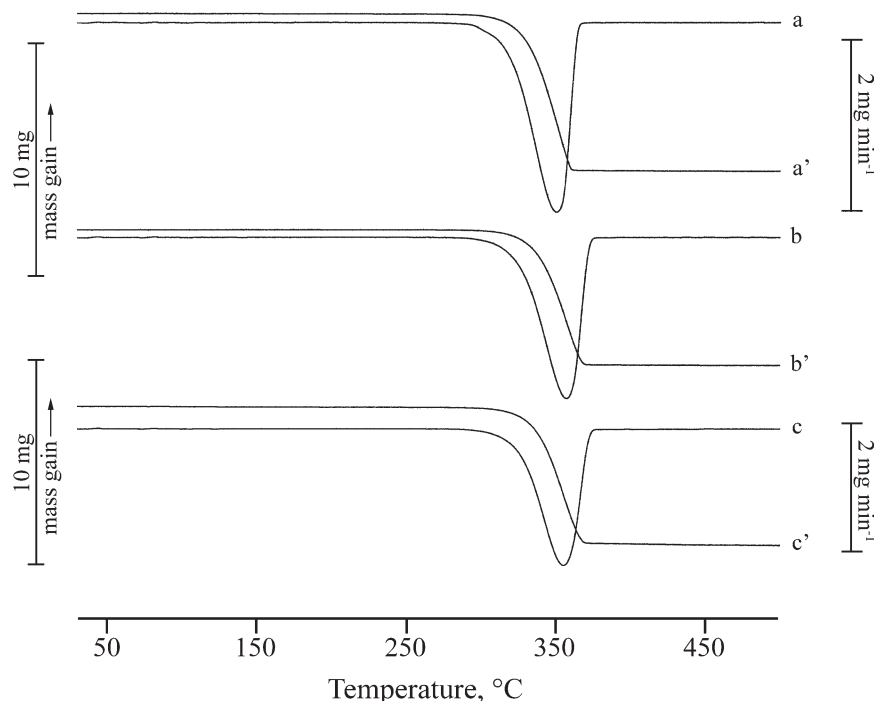


Figure 7. TGA and DTG curves of empty PLA as such (Curve a), after UV irradiation for 24 h (Curve b), and 96 h (Curve c).

Table V. Decomposition Temperatures From DTG Curves (Standard Deviation in Parentheses)

	t_0	24 h suntest	96 h suntest	30 days C.R.
Empty PLA				
T_{onset} (°C)	324.6 (1)	329.4 (9)	331.3 (3)	330.6 (9)
T_{peak} (°C)	356.8 (2)	359.9 (8)	360.6 (9)	359.3 (9)
T_{endset} (°C)	371.7 (2)	374.9 (8)	377.1 (9)	373.6 (8)
PLA pH 2				
T_{onset} (°C)	324.6 (1)	330.2 (9)	328.3 (5)	329.2 (9)
T_{peak} (°C)	356.8 (2)	361.2 (1)	358.4 (9)	360.1 (9)
T_{endset} (°C)	371.7 (2)	377.9 (3)	374.2 (9)	375.9 (4)

C.R. = climatic room.

physicochemical, and morphological properties of PLA bottles exposed to stressing environmental conditions (heat, humidity, and UV-vis irradiation). The experimental techniques put into evidence that UV-vis irradiation and acid medium can affect stability of PLA used as packaging in cosmetic products. Furthermore, internal and external surfaces can be influenced very differently depending on the type of the stress. In particular, thanks to this study, it was possible to set up a protocol to

study packaging-content interaction sustained during the life of the cosmetic product to choose the best use of the PLA polymer as packaging depending on the type of product that must be marketed.

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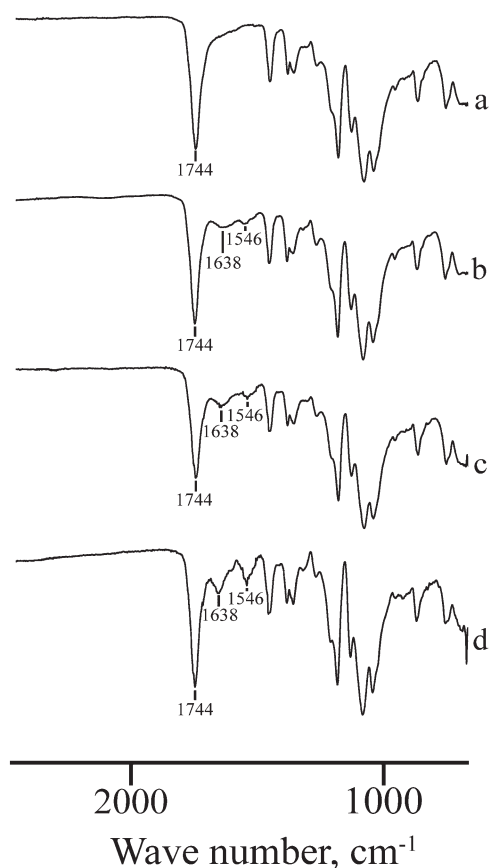


Figure 8. FT-IR spectra of empty PLA internal side as such (Spectrum a) after 24 h (Spectrum b), and 96 h (Spectrum c) of UV irradiation, and of PLA containing pH 2 solution after 24 h at ambient temperature (Spectrum d).

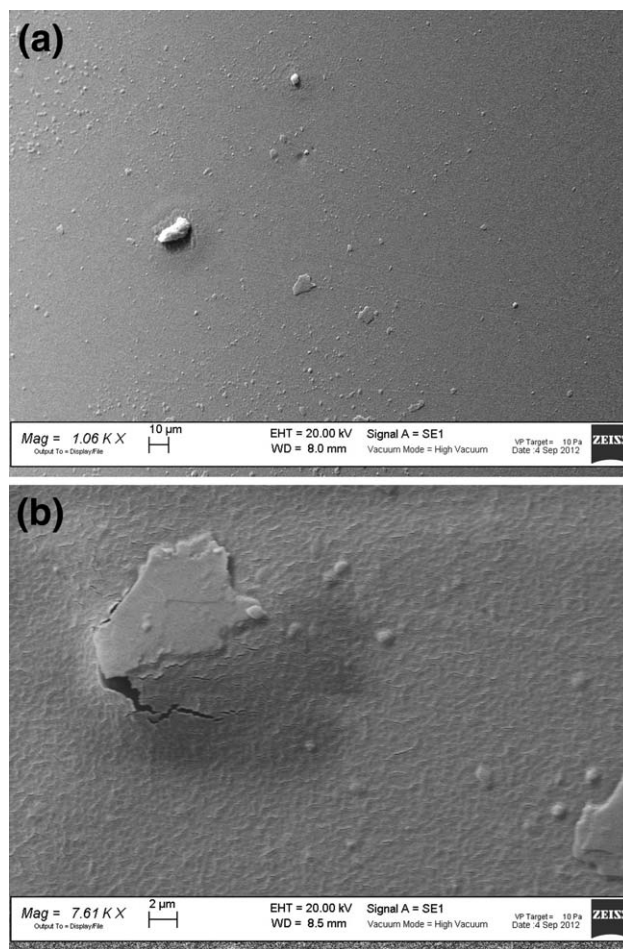


Figure 9. External (a) and internal (b) surface of PLA samples containing buffer solution (pH 2), after UV-vis irradiation for 24 h.

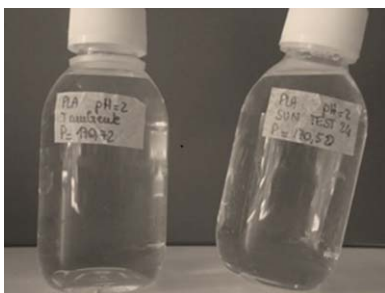


Figure 10. Digital photograph of container alteration after UV-vis irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

- Newsham, M. D. Product/package interaction. Ph D. Thesis School of Packaging, Michigan State University, East Lansing MI, **1998**.
- Regulation (EC) No. 1223/2009 of the European Parliament and of the council, November 30, 2009.
- Nampoothiri, K. M.; Nair, N. R.; John, R. P. *Bioresour. Technol.* **2010**, *101*, 8493.
- Mangmeemak, J.; Tangboniboonrat, P.; Rattanasom, N.; Somwangthanaroj, A. Toughening of poly(lactic acid) film blended by natural rubber. In: Paccon 2011—Pure and Applied Chemistry International Conference, Thailand, January 5–7, **2011**.
- Henton, D. E.; Gruber, P.; Lunt, J.; Randall, J. Polycationic acid technology. In: Natural Fibers, Biopolymers and Biocomposites, A. K. Mohanty, L. T. Drzal; M. Misra Eds. CRC press, **2005**; p 527.
- Auras, R.; Harte, B.; Selke, S., *Macromol. Biosci.* **2004**, *4*, 835.
- Jamshidian, M.; Tehrani, E. A.; Imran, M.; Jacquot, M.; Desobry, S. *Compr. Rev. Food Sci. Food Saf.* **2010**, *9*, 552.
- Ljungberg, N.; Wesslen, B. *Polymer* **2003**, *44*, 7679.
- Matsumoto, T.; Shinnomate, H.; Kumazawa, S.; Kimura, M., US patent 7,632,897B2, December 15, 2009.
- Lemmouchi, Y.; Murariu, M.; Santos, A. M. D.; Amass, A. J.; Schacht, E.; Dubois, P. *Eur. Polym. J.* **2009**, *45*, 2839.
- Huneault, M. A.; Li, H. *Polymer* **2007**, 270.
- Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2010**, *35*, 338.
- Li, T. N.; Turng, L. S.; Gong, S. Q.; Erlacher, K. *Polym. Eng. Sci.* **2006**, *46*, 1419.
- Santonja-Blasco, L.; Moriana, R.; Badía, J. D.; Ribes-Greus, A. *Polym. Degrad. Stabil.* **2010**, *95*, 2185.
- Badía, J. D.; Santonja-Blasco, L.; Moriana, R.; Ribes-Greus, A. *Polym. Degrad. Stabil.* **2010**, *95*, 2192.
- Abdelwahab, M. A.; Flynn, A.; Chiou, B. S.; Imam, S.; Orts, W.; Chiellini, E. *Polym. Degrad. Stabil.* **2012**, *97*, 1822.
- Park, K. I.; Xanthos, M. A. *Polym. Degrad. Stabil.* **2009**, *94*, 834.
- Zhang, X.; Espiritu, M.; Bilyk, A.; Kurniawan, L. *Polym. Degrad. Stabil.* **2008**, *93*, 1964.
- Bismarck, A.; Aranberri-Askargorta, I.; Springer, J.; Lampke, T.; Wielage, B.; Stamboulis, A.; Shenderovich, I.; Limbach, H. H. *Polym. Compos.* **2002**, *23*, 872.
- Rydz, J.; Adamus, G.; Wolna-Stypka, K.; Marcinkowski, A.; Misiurska-Marczak, M.; Kowalczyk, M. M. *Polym. Degrad. Stabil.* **2013**, *98*, 316.
- Guidelines on stability testing of cosmetics product. Colipa guidelines, March 2004.
- Photostability testing of new active substances and medicinal products—ICH topic Q1B. EMEA, European medicines agency. CPMP/ICH279/95, January 1998.
- Stability Testing of new Drug Substances and Products—ICH Topic Q1A (R2). EMEA, European medicines agency. CPMP/ICH/2736/99, August 2003.
- Plastics—determination of tensile properties. European Standard EN ISO 527, 1993.
- CIE Commission internationale de l'Eclairage proceedings, 1931. Cambridge University Press: Cambridge, **1932**.
- Höglund, A.; Odelius, K.; Albertsson, A. C. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2788e93.
- De Jong, S. J.; Arias, E. R.; Rijkers, D. T. S.; Van Nostrum, C. F.; Kettenes-van den Bosch, J. J.; Hennink, W. E. *Polymer* **2001**, *42*, 2795e802.
- Martin, O.; Avérous, L. *Polymer* **2001**, *42*, 6209.