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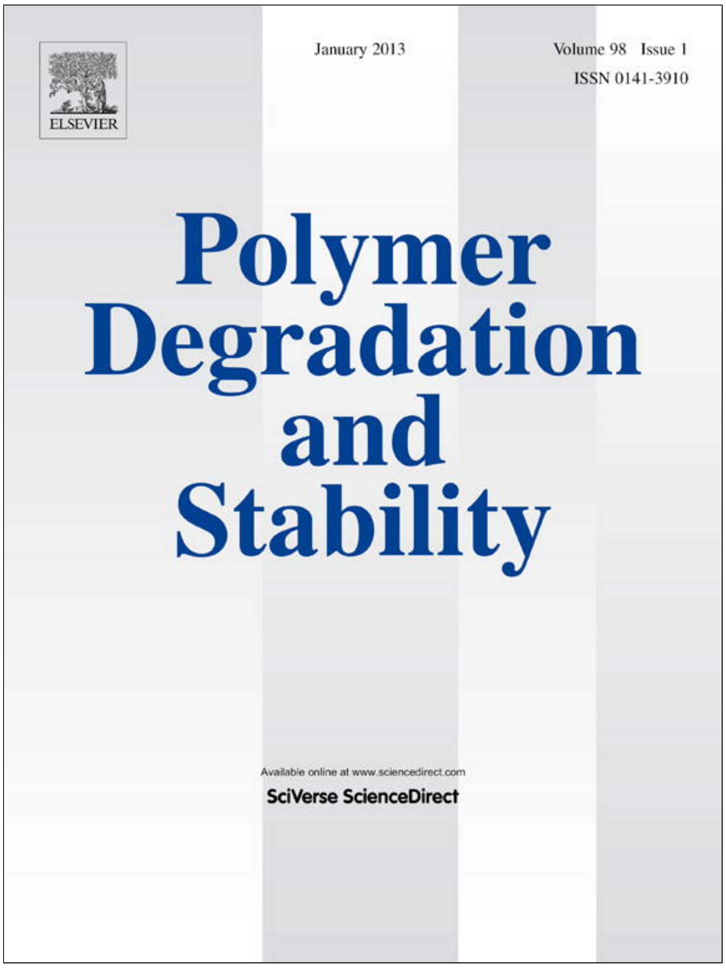

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Degradation of polylactide in paraffin and selected protic media

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ABSTRACT

The degradation of polylactide commercial films caused by selected ingredients used in the preparation of cosmetics is reported. Despite the wide application of polylactide as a food packing material, its limitation for applications in the packaging of cosmetics is observed. Gel Permeation Chromatography (GPC), Atomic Force Microscope (AFM), Electrospray Mass Spectrometry (ESI-MS) and Nuclear Magnetic Resonance (NMR) reveal that polylactide degradation occurs not only in the presence of polar solvents (ethyl alcohol, glycerine, propylene glycol) but also in the presence of paraffin. We report the applicability of this green polymeric material for cosmetic packages based on the studies of both the eroded polymer and its degradation products.

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1. Introduction

Polylactide (PLA), a thermoplastic polymer derived from the lactic acid obtained in the fermentation of renewable natural resources such as starch, sugar or cellulose, has attracted great attention due to its excellent material properties that permit a wide variety of potential applications in various areas (e.g., medical devices, textiles, food packages). PLA can be processed at a large-scale to produce materials with good mechanical strength, especially for packaging applications [1].

The use of environmentally friendly polymers as packaging materials for long shelf-life applications as cosmetic packages is the new trend for production. Thus, the development of this research area is particularly needed.

Cosmetics represent a large group of products applied to the human body, designed to improve the health, cleanliness and physical appearance of the human exterior and to protect a body part against damage from the environment without affecting the body's structure or functions [2]. Materials intended for use as components of cosmetic products perform specific functions. They must also meet acceptable standards of safety during use and exhibit chemical and physical stability during storage or shipment. Manufacturers of cosmetics must be careful not only to guard against microbial but also chemical contamination. Chemical contamination arising from overheating or other decomposition reactions during processing or from improper storage of incoming supplies must also be avoided. For these reasons, adherence to documented production processes and periodic reassessment of stored supplies are required. The interaction between cosmetic and package components that produce new chemical entities or decomposition products is unacceptable [3]. Therefore, it is important to identify the interactions between green polymer containers and the cosmetic formulation that they contain. In this case, the complete replacement of conventional plastics with environmentally friendly packaging is impossible to achieve without recognising and assessing the possible risk.

One of the requirements for plastic packaging during storage is to avoid migration of any low molecular weight components, such as residues and additives, into a cosmetic formulation [4]. In the case of biodegradable packaging material, environmental conditions leading to biodegradation must be avoided during the storage period of the product, especially for liquid-state products, because low molecular weight degradation products of polymer containers could also be released into the cosmetic products, as in the case of food products [5]. The amount of any component that migrates into a formulation depends on the concentration and its solubility as well as the temperature, mechanical stresses and contact time. In addition, the transfer of compounds originating from cosmetic formulations such as lipids or aroma compounds can interact with the biopolymer container, causing modification and deterioration

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of their gas and aroma barrier properties. In the case of polylactide, contact with cosmetic formulation can have an influence on crystallinity, which can lead to thermal and barrier property changes [6]. It is extremely difficult to directly measure the migration into the final cosmetic formulation. The migration behaviour of the plastic material should be easily measured by simulant tests in media such as ethanol, distilled water, acetic acid or heptanes [5,7]. The correct selection of simulants for a product-package system degradation experiment depends on several factors including the tested material and the cosmetic products with which the material will be in contact. Paraffin, glycerine, propylene glycol, ethyl alcohol and water play an important role in cosmetology and are ingredients commonly found in cosmetic formulations [8]. These ingredients were selected for the cosmetic formulation simulant tests.

The degradation process of aliphatic polyesters in various types of environments such as deionised water [9], distilled water [10], buffers [11,12], high humidity [13], seawater [14–17], river [17,18] and lake [17] water, soil [19,20], household compost heaps [12], industrial composting pile [10,21], compost pile with activated sludge [15,16], anaerobic sludge [22] as well as in buffer [11] or mineral medium [23] in the presence of microorganisms has been thoroughly investigated, however, to the best of our knowledge, there has been no report on their degradation in selected simulants as ingredients used for the preparation of cosmetics. In this paper, the degradation of PLA commercial film in selected simulants is investigated. Analysis of PLA surface erosion was followed by an investigation using the AFM technique. Polymer molecular weight changes were evaluated using GPC and the resulting degradation products were characterised using ESI-MS and NMR analysis. Furthermore, the effects of the interaction between the polymer and cosmetic ingredients monitored during a degradation experiment are reported.

2. Experimental

2.1. Materials

Poly(L-lactide) 40 μm thick film used in this study was commercial product from Nature Works LLC, USA and was kindly provided by Pakmar® (NatureWorks® PLA). According to DSC and POM analysis the polylactide film used in this study was oriented with 1% of the saturated hydrocarbon modifier (according to NMR analysis). The D-lactide contents were equal to 6.5% as estimated according to previously described method [24]. Additional material properties: $M_w = 224{,}000$ g/mol, $M_w/M_n = 1.9$, $T_g = 53.3$ °C, $T_m = 147.4$ °C, $w_c = 32.9\%$.

The following simulants were used for the degradation experiments: distilled water (used as reference), liquid paraffin (99.98%, water content: 0.016% by Karl Fischer method) from Pharmaceutical Laboratory COEL, Poland, anhydrous glycerine (99.5%, water content: 0.11% by Karl Fischer method), propylene glycol (99.5%, water content: 0.05% by Karl Fischer method), buffer solution of pH 4.00 ± 0.05 and pH 10.00 ± 0.05 as well as ethyl alcohol 96% (water content: 5.7% by Karl Fischer method) and anhydrous 99.8% ethyl alcohol (water content: 0.035% by Karl Fischer method) all from POCH SA, Poland were used without further purification.

2.2. Degradation experiments

For the degradation experiments PLA samples (6 cm × 1 cm strips) with an average weight of 0.05 g were dried under vacuum at room temperature to a constant weight to eliminate ultimate water content and then were incubated at 70 °C and 37 °C (±0.5 °C) in screw-capped vials with air-tight PTFE/Silicone septum, containing 25 cm^3 of simulants. After a predetermined degradation time, the samples were separated from the degradation medium. For the distilled water, ethyl alcohol and buffer solutions, the samples were washed with distilled water and dried under vacuum at room temperature to a constant weight. For the viscous simulants such as liquid paraffin, glycerine and propylene glycol, the samples were drained on a filter paper. The dried films were weighed on an analytical electronic balance (Radwag WAS 160/X, repeatability 0.1 mg) to calculate the mass changes. The degradation experiment was conducted over 3 years or until complete disintegration (fragmentation and loss of visibility) of the sample was observed. After a specified period ranging from 1 day to 3 years surface erosion, the sample mass changes, molecular weight, and molecular-weight dispersity, as well as the resulting degradation products of the polymeric material were determined. Mass loss, molecular weight loss and pH changes were performed with triplicates measurements. The molecular weight loss was calculated using the following equation:

$$\%\ \text{Molecular weight} = \frac{M_{w0} - M_{wx}}{M_{w0}} \times 100\%$$

where M_{w0} is the initial average molecular weight and M_{wx} is the consecutive or final average molecular weight.

2.3. Measurements

The morphology of the PLA surfaces was investigated using an atomic force microscope. AFM images were obtained using MultiMode with a NanoScope III D controller, Veeco (USA) equipped with a piezoelectric scanner with a scan range of 10 μm × 10 μm. Imaging of the samples was conducted in TappingMode under ambient air conditions at a scan rate of 1 Hz using etched silicon probes (TESP, VEECO) of nominal spring constant 20–80 N/m and operating at a resonant frequency of 280–320 kHz.

The molecular weights and molecular-weight dispersity of the samples were determined using gel permeation chromatography conducted in $CHCl_3$ (GPC Solvent, stabilised with amylene, purity 99.8%, Fischer Chemical) at 35 °C with an eluent flow rate of 1 mL/min, using a set of two PLgel 5 μm MIXED-C ultrahigh efficiency columns (Polymer Laboratories) with a mixed bed and linear range of M_w 200–2,000,000. An isocratic pump (Spectra Physics 8800) as the solvent delivery system, differential refractive index detector stabilised to a temperature of 35 °C (Shodex SE 61) was applied. 10 μL of 3% w/v sample solution in $CHCl_3$ was injected. Polystyrene standards (Calibration Kit S-M-10, Polymer Laboratories) with a narrow molecular-weight dispersity were used to generate a universal calibration curve. The samples were measured using OmniSEC 4.1 (Viscotek) software.

Nuclear magnetic resonance ^{1}H and ^{13}C spectra were recorded using a Bruker-Advance spectrometer operating at 600 MHz with Bruker TOPSPIN 2.0 software using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. ^{1}H NMR spectra were obtained with 64 scans, a 11 μs pulse width, and a 2.65 s acquisition time, and ^{13}C NMR spectra were obtained with 76,800 scans, a 9.40 μs pulse width, and a 0.9088 s acquisition time.

The pH measurements of the degradation liquid were performed at $T = 23.0 \pm 2.0$ °C using a Mettler Toledo SevenMulti S40 pH-meter (resolution: ±0.1 mV, ±0.001 pH units) equipped with an InLab Science Pro 3-in-1 electrode with reference system ARGENTHAL™ and an Ag^+ trap and 3 mol/L KCl reference inner electrolyte (Metrohm, Switzerland). Calibration of the electrode was performed using buffers (Mettler Toledo, Switzerland) of pH 4.01 ± 0.02, pH 7.00 and pH 9.21 ± 0.02 at $T = 23.0 \pm 2.0$ °C.

The electrospray mass spectrometry analysis of low molecular weight degradation products was performed for the PLA

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degradation products remaining after 7, 10 and 52 weeks of degradation in ethyl alcohol, distilled water and paraffin, respectively as well as for low molecular weight remaining PLA films after 10 and 52 weeks of degradation in distilled water and paraffin, respectively. The analysis was performed using a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). The samples of the low-molecular-weight degradation products and remaining PLA films were dissolved in the water/methanol system (1:1 v/v), and the solutions were introduced to the ESI source by continuous infusion using the instrument syringe pump at a rate of 3 μL/min. The LCQ ESI source was operated at 4.5 kV, and the capillary heater was set to 200 °C. Nitrogen was used as the nebulising gas. The analyses were performed in the positive- and negative-ion mode.

3. Results and discussion

The hydrolytic degradation of PLA occurs by uptake of water followed by hydrolysis of ester bonds. Despite the differences between hydrolytic degradation of industrial origin films and films casted from laboratory-scale synthesised PLA the important factor affecting the hydrolysis process is the acidity or basicity of the degradation media [25,26]. Therefore, it is important to determine the influence of pH because cosmetic formulations vary from pH 2 (e.g., for anti-ageing creams) to pH 10 (e.g., for shaving creams).

The stability of cosmetic products also depends on temperature and UV radiation. The stability test for cosmetic products requires the placement of samples under different environmental conditions for a specified period. These conditions are meant to simulate what will happen to the product during its lifecycle and should always correspond to the most severe (worst foreseeable) conditions of contact between the plastic material or article and the food product and to any labelling information on the maximum temperature for use. The high temperature testing is used as a predictor of long-term stability. In this work, temperatures of 70 °C and 37 °C were selected for the degradation experiment according to the recommendations of stability tests for cosmetic products [27] and according to the ISO standard [28].

3.1. Visual examination

The plain polymer film before degradation test was transparent with a smooth surface. A decrease in transparency of the studied PLA sample surfaces (assumed to be an effect of molecular reorganization [29] or as increase in irregularity, which might result from accelerated new spherulite formation) [30] was observed for PLA films in the studied simulants during the first 4 weeks of degradation at 70 °C. At 37 °C, a relatively slower decrease in transparency was observed starting from week 15 of the sample degradation in the pH 10.00 buffer solution.

Macroscopic visual evaluation of the PLA film during the degradation process at 70 °C indicated erosion as disintegration of the strips starting from the 1st week of incubation for degradation in distilled water (used as reference) as well as in the buffer solutions. For the degradation process in paraffin, disintegration began at week 24 of degradation (Fig. 1). After 17 weeks of sample degradation in distilled water and the pH 10.00 buffer solution as well as after 32 weeks of sample degradation in the pH 4.00 buffer solution, complete disintegration of the material was observed. Finally, after 1 year in ethyl alcohol and after 2 years of sample degradation in liquid paraffin, a high degree of disintegration of the material was observed. Only for the sample degradation in glycerine was slight disintegration of the material observed after 3 years of degradation.

The degradation process at 37 °C after 52 weeks revealed erosion in the fragility of the strips. Only degradation in buffer solutions led to erosion, as evidenced by the disintegration of the strips after 1 year. For sample degradation in glycerine, erosion of the material was not observed. In the case of semicrystalline PLA at low temperature (37 °C), hollow structures such as holes and cavities due to the crystallisation of degradation products and their low solubility in degradation media were not observed [31].

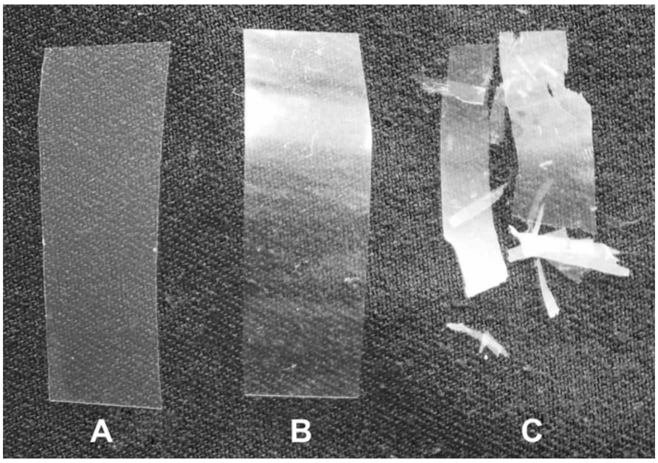

Fig. 1. Visual evaluation of the PLA film before degradation (A), after 16 weeks (B) and after 24 weeks (C) of degradation in paraffin at 70 °C.

3.2. Surface morphology

The PLA plain film had a fairly smooth surface. The dissolution of degradation products in polar simulants and erosion create cracks and pores. Small cracks, formed by water absorption or polymer erosion, grow as contact with water leads to hydrolysis, and the locally produced acids catalyse the degradation and cause polymer dissolution inside the pores, leading to subsequent erosion. Water absorption was faster at higher pH and slower at lower pH due to the degree of dissociation of the polymer terminal carboxyl acids, which cause an increase of roughness with an increase of pH [32]. During degradation, the surface becomes more rough from the beginning of the degradation process in all the studied simulants in both ageing temperatures, at 70 °C and 37 °C, however, the difference in surface roughness was on the nanometre scale, as observed by AFM (Fig. 2). The pores in the surface of the PLA plain films had a depth up to 12 nm. After 2 weeks of degradation at 70 °C in buffer solutions of pH 4.00 and pH 10.00, the pores had depths up to 140 nm and 400 nm, respectively. The largest pores, observed to have a depth up to 470 nm, were formed on the surface after degradation in distilled water.

In an environment such as paraffin, propylene glycol, and glycerine, the surface erodes much slower but also from the beginning of the degradation process (Fig. 2). At the beginning of degradation, the surface erosion depended on the solubility of the low molecular weight degradation products in the studied simulants. After 2 weeks, the largest pores were observed to have a depth up to 162 nm and were formed on the surface after degradation in propylene glycol. This result is in agreement with the molecular-weight dispersity, which remains constant only for propylene glycol because the low molecular weight products diffused into the degradation medium (Fig. 6). After 1 year of degradation in glycerine, where macroscopic erosion of the material was not observed, pores with a depth of 330 nm were observed.

After 52 weeks of degradation in paraffin, propylene glycol and glycerine at 37 °C, the pores had a depth comparable to the pores of the PLA plain film (up to 12 nm), however, their number increased

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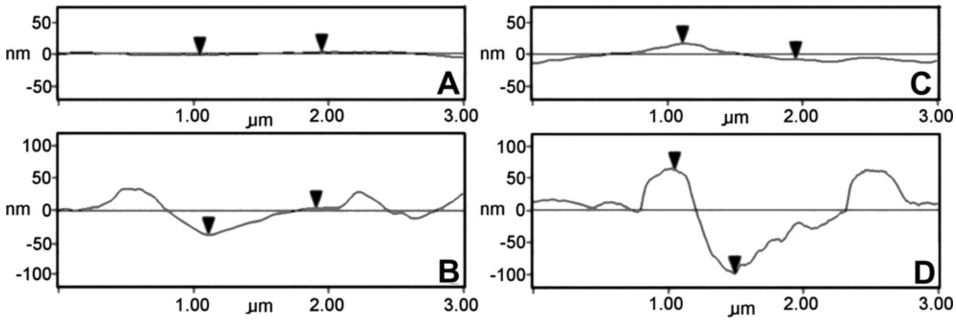

Fig. 2. Line profile data of selected PLA film surface erosion before (A) and after 2 weeks of the degradation process in paraffin (B), glycerine (C) and propylene glycol (D) at 70 °C.

as observed in the microscopic AFM images (Fig. 3). The largest pores were found to have a depth up to 1.4 μm and were formed on the surface after degradation in distilled water (the data do not reveal this result because of the disintegration of sample during AFM experiment). In buffer solutions of pH 10.00 and pH 4.00 as well as ethyl alcohol, the pores had depths up to 845 nm, 150 nm and 118 nm, respectively.

3.3. *Mass changes*

The mass of samples in the polar simulants decreased continuously from the beginning of the experiment for both ageing temperatures, at 70 °C and 37 °C. The rate of degradation greatly increased at temperatures above the glass transition of polylactide, therefore, the degradation rate at 37 °C was considerably slower [29,33].

Monitoring of sample mass changes during the degradation process in 70 °C indicated that mass loss of the PLA strips occurred rapidly from the beginning of sample degradation in distilled water, ethyl alcohol, and the buffer solutions of pH 4.00 and pH 10.00 (Fig. 4). Higher degradation rates in alkaline medium compared with acidic conditions correlate with the surface morphology and literature data [29,30].

It has been reported that the hydrolysis reaction can be acid-catalysed or alkali-catalysed. Hydrolysis and alcoholysis may share the same mechanisms but different acyl acceptors (water or alcohol) [34]. Polyesters can be cleaved at the ester linkages within the polymer backbone using an alcohol, preferably a C1-C12 monohydric or dihydric alcohol such as methanol, ethanol, iso-propanol, *t*-butyl alcohol, ethylene glycol, or propylene glycol [35]. Alcoholysis of polyesters can also occur without catalyst. The small amount of lactic acid can promote this reaction [36].

During degradation in ethyl alcohol, the mass decreases continuously during the first 2 weeks up to approximately 33%, after which the degradation rate decreased (Fig. 4). This phenomenon can be explained by the fact that the rate constants for alcoholysis decrease with increasing total hydroxyl group concentration [37]. For glycerine and propylene glycol, a decrease of the sample mass was observed mainly at the beginning (data not presented). The main problem with the viscous simulants (particularly for paraffin) was related with difficulties in the cleaning process, especially after disintegration of the sample.

Monitoring of sample mass changes during the degradation process in 37 °C indicated only a slight decrease (up to approximately 14% of the initial mass of the sample incubated in the buffer solution of pH 10.00) after the 52nd week of incubation (Fig. 4).

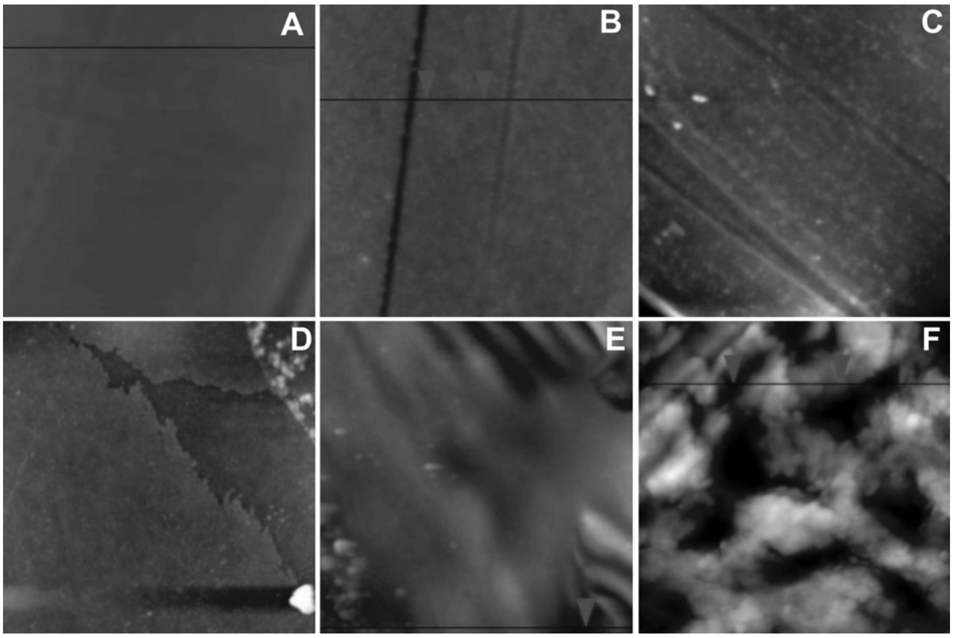

Fig. 3. Selected 3 × 3 μm AFM images of PLA film surface erosion before (A) and after 52 weeks of degradation process in paraffin (B), glycerine (C), propylene glycol (D), buffer solution of pH 4.00 (E) and ethyl alcohol (F) at 37 °C.

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Despite total degradation in distilled water and buffer solutions of pH 4.00 and pH 10.00, approximately 1% of the residue was observed to be a nondegradable part of the PLA film. This 1% of the residue was identified (NMR data not presented) as the saturated hydrocarbon modifier added to commercial polylactide materials to increase the elongation at break and to reduce the crystallisation temperature of the film [38]. Such an additive is also used as an external lubricant, a material that controls the fluxing (melting) point in the extruder/moulder to achieve the best processing characteristics and physical properties [39].

3.4. Molecular weight changes

The degradation process in the studied simulants resulted in a continuous decrease of the PLA film molecular weight from the beginning of the experiment for both ageing temperatures (70 °C and 37 °C).

During the first step (1st week) of degradation at 70 °C in distilled water, ethyl alcohol, and the buffer solutions of pH 4.00 and pH 10.00, the molecular weight of PLA decreased rapidly with a slight mass loss (Figs. 4,5), which is typical for the hydrolytic degradation mechanism. The degradation of polylactide in an aqueous environment occurs through the hydrolysis of ester bonds autocatalysed by carboxylic acid end-groups, and the hydrolysis rate increases with degradation time. The molecular-weight dispersity increased in the first step when the molecular weight of polylactide decreased rapidly. In the next step, when the molecular weight loss slowed down, the molecular-weight dispersity decreased because low molecular weight compounds were removed from the polymer matrix, and the catalytic effect of the carboxylic acid groups was reduced [40]. Subsequently, the molecular weight loss slowed down with increasing mass loss. For distilled water and the buffer solutions of pH 4.00 and pH 10.00, 99% mass loss and nearly 100% molecular weight loss were noted. For ethyl alcohol, 93% molecular weight loss was noted after 1 year of the degradation process with 60% mass loss.

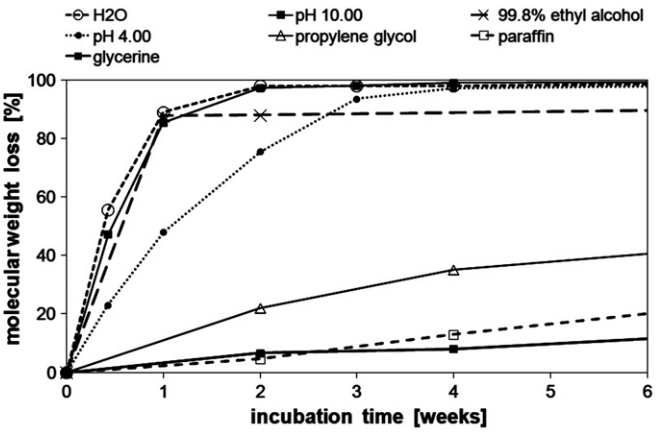

Fig. 5. Molecular weight loss of PLA samples as a function of incubation time during the first 6 weeks of the degradation process in distilled water, ethyl alcohol, and the buffer solution of pH 4.00 and pH 10.00 as well as in paraffin, propylene glycol and glycerine at 70 °C. The molecular weight loss is given as a percentage of the original M_w.

In paraffin, propylene glycol and glycerine, the degradation process was also observed (Fig. 5). After 36 weeks of degradation, the molecular weight loss of the PLA film was 99%. Paraffin is a non-polar, unreactive medium. Thus, the explanation for this unexpected phenomenon could be the hydrophobicity of paraffin which can generate the autocatalytic effect. Grizzi et al. reported that submillimetre films degraded homogeneously and more slowly (erosion is restricted at the surface) than large-sized devices [41]. Faster internal degradation of PLA polymers is regarded as a general phenomenon. The hydrolytic chain cleavage causes an increase in the concentration of carboxylic acid end-groups with degradation time, which accelerates the internal degradation (autocatalytic effect) and enhances the surface/interior differentiation [42,43]. Paraffin is considered one of the most hydrophobic water-repellent agents [44]. The residual content of water in paraffin (0.016%, see Experimental Section) could be absorbed by the dry PLA film. Water diffused into the sample at the beginning to penetrate the polymer matrix, and the process of autocatalytic hydrolysis began [42]. Due to limited migration, low-molecular-weight products, insoluble in paraffin, remain in the hydrophilic environment (PLA sample), and molecular-weight dispersity increases rapidly as well as the bimodal GPC curves after 44 weeks of degradation in paraffin was observed (Fig. 6). Therefore, the results of this study demonstrate, that the autocatalytic effect is observed not only in water medium as described by Vert but also in the case of aprotic solvents (i.e. paraffin) even for thin sample films. Vert explained the bimodal GPC chromatogramme as the result of the autocatalytic mechanism and due to the presence of two populations of macromolecules degrading at different rates from surface/interior parts which is in agreement with our results [31,45]. The bimodal GPC curves could be explained also as the

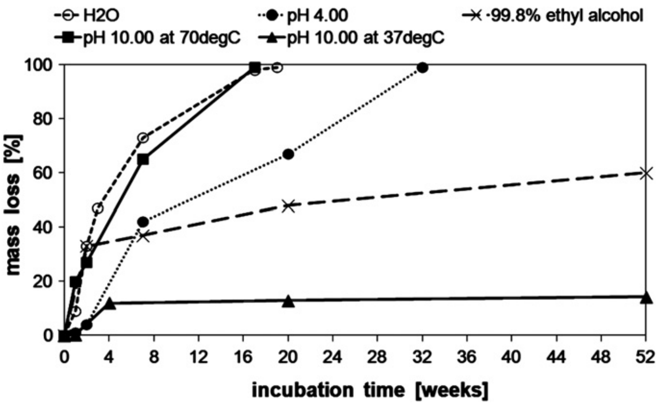

Fig. 4. Mass loss of selected PLA samples as a function of incubation time during the degradation process in distilled water, ethyl alcohol, and buffer solutions of pH 4.00 and pH 10.00 at 70 °C as well as in a buffer solution of pH 10.00 at 37 °C, where the weight loss was largest.

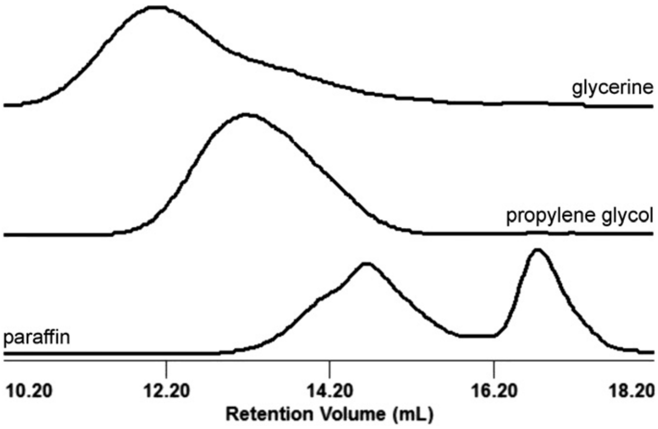

Fig. 6. Changes in GPC chromatogramme of PLA samples after 44 weeks of degradation in glycerine, propylene glycol and paraffin at 70 °C.

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results of the crystallisation of degradation by-products in the initially amorphous but crystallisable polymers [46]. From DSC measurements (data not presented) degree of crystallinity increases more rapidly during degradation in propylene glycol however for this stimulant bimodal GPC curves of PLA film was not observed as well as the molecular-weight dispersity remains constant due to diffusion of the low molecular weight products into the degradation medium (Fig. 6).

Glycerin and propylene glycol act as humectants, and the hygroscopic substances hold water molecules from the surrounding environment [8]. The small content of water from the environment was absorbed by the hydrophilic medium (glycerine or propylene glycol), and the degradation process of the PLA film was consequently slow. For propylene glycol, which is used in chemical recycling as a reagent in the depolymerisation methods of polyesters, the degradation proceeded more rapidly [35].

During the degradation process at 37 °C in distilled water, ethyl alcohol, and the buffer solutions of pH 4.00 and pH 10.00, the molecular weight of PLA decreased rapidly with a slight mass loss. Up to 14% mass loss and 90% molecular weight loss for the buffer solution of pH 10.00 were noted (Figs. 4,7). The explanation for this phenomenon could be the low solubility of the degradation products in the studied simulants at 37 °C and the fact that the low molecular weight degradation products do not migrate into the incubating medium due to their crystallisation in the case of semicrystalline PLA [26], which also correlated with the slight decrease of the pH of the incubating media (data not presented). However, the internal (core) part of the polymer matrix can degrade faster than the outer part. During the degradation process, dominated by autocatalysed bulk degradation, the hydrolysed products were entrapped in the polymer matrix and did not diffuse out of the matrix. Consequently, the pH remained at the same level [47]. Moreover, the high water repellent property of the saturated hydrocarbon, a film additive, led to much slower water penetration into the PLA matrix, which may contribute to the degradation process [48]. The degradation rate for paraffin and propylene glycol was considerably slower. For the glycerine simulant, no molecular weight loss of the PLA film was observed.

3.5. Degradation products

The structure of the PLA film samples after the degradation experiment and of the products released to the selected cosmetic simulants after a specified period of incubation were determined using ESI mass spectrometry which is a typical method to analyse the polyester degradation products [49]. Fig. 8 plots the negative ESI-mass spectra of the remaining PLA film and the low molecular weight compounds that migrated from this film to the distilled water after 10 weeks of hydrolysis (Fig. 8b).

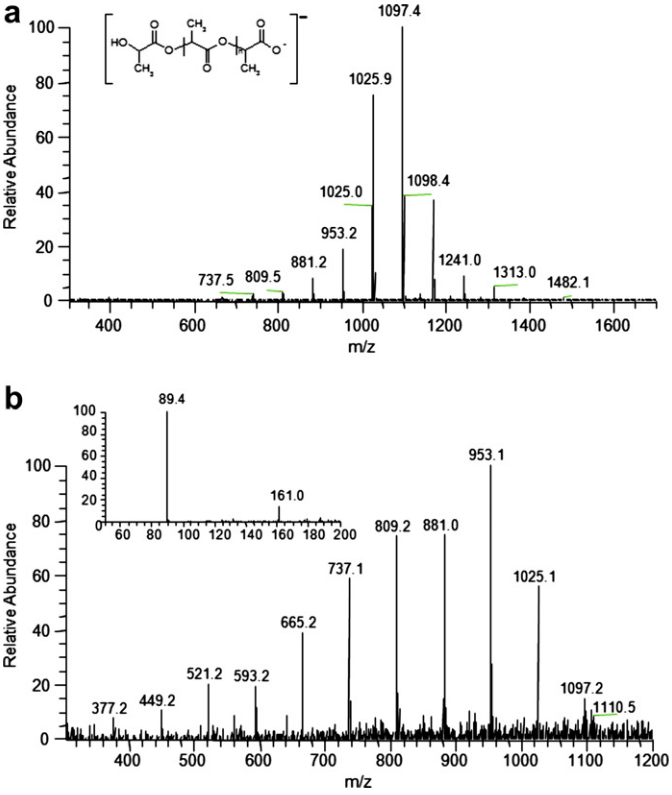

Fig. 8. The ESI-mass spectra (negative ion-mode) of the remaining PLA film (a) and of the degradation products released to the distilled water after 10 weeks of hydrolytic degradation of the PLA film at 70 °C (b).

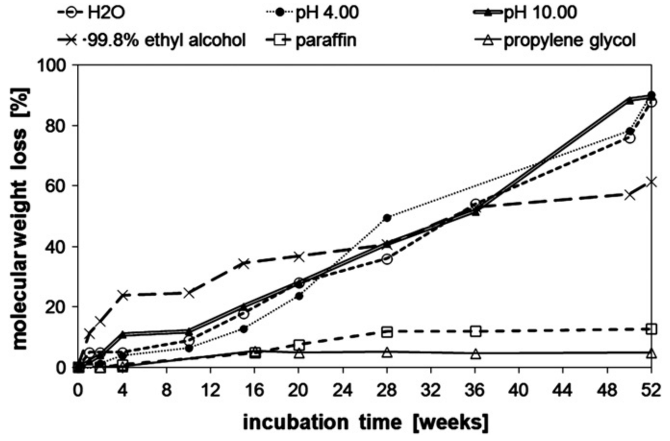

Fig. 7. Molecular weight loss of PLA samples as a function of incubation time during the degradation process in distilled water, ethyl alcohol, and buffer solutions of pH 4.00 and pH 10.00 as well as in paraffin and propylene glycol at 37 °C. The molecular weight loss is given as a percentage of the original M_w.

ESI-MS analysis of the PLA film remaining after 10 weeks of degradation in distilled water confirmed a drastic reduction in molecular weight caused by the statistical breaking of the ester bonds in the studied polyester. The one set of singly charged anions with a peak-to-peak mass increment of 72 Da, which is equal to the molecular weight of the lactic acid repeating unit, is observed in the spectrum (Fig. 8a). For the MS spectra of PLA, the repeat unit structure should exhibit a mass increment of 144 Da [50]. Indeed, this result was recently reported by Blakey et al. for the MALDI-TOF-MS of PLA obtained by controlled polymerisation of lactide, performed in the presence of organocatalysts in supercritical CO_2 [51]. However, when transesterification or hydrolysis occurs, a peak-to-peak mass increment of 72 Da is observed [52,53].

The signals observed in the mass spectrum in Fig. 8a correspond to PLA macromolecules containing from 10 (*m*/*z* 737) up to 18 (*m*/*z* 1313) lactic acid repeating units terminated by carboxyl and hydroxyl end-groups. For comparison, Fig. 8b plots the mass spectrum obtained for the solution of water in which the PLA film was incubated for 10 weeks. The signals observed in this mass spectrum are located in the lower mass region and correspond to water-soluble lactic acid oligomers containing up to 15 (*m*/*z* 1097) repeating units terminated by carboxyl and hydroxyl end-groups (Fig. 8b). Moreover, the lactic acid and its dimer (signal at *m*/*z* 89 and at *m*/*z* 161 expanded region of Fig. 8b) were identified as water-soluble degradation products.

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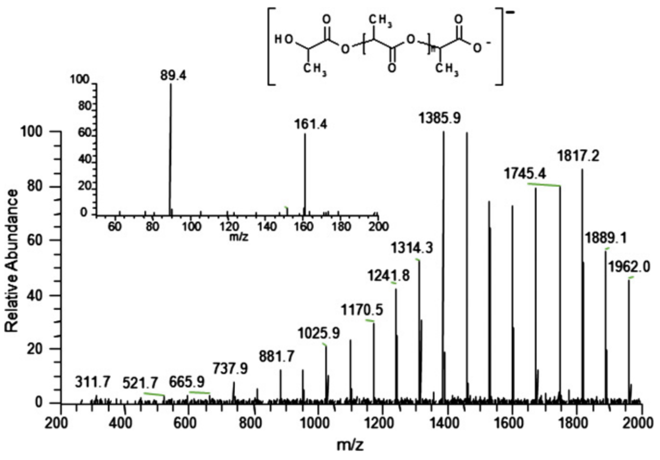

Fig. 9. The ESI-mass spectrum (negative ion-mode) of the remaining PLA film after 1 year incubation in paraffin at 70 °C.

When applying the ESI-MS technique for the analysis of mixtures containing hydroxyacids and their oligomers, the intensities of the signals corresponding to the acids are lower than the intensities of the signals of their respective oligomers. To estimate oligomer and hydroxyacid content quantitatively, separated calibration for the acid and respective oligomers is required. However, the mass spectrometry analysis confirmed that both lactic acid as well as their respective oligomers terminated by hydroxyl and carboxyl end-groups are formed during hydrolytic degradation of PLA film.

The results of this study indicate that even a small amount of water present in the ingredients of cosmetics can initiate a process of hydrolytic degradation of the PLA film. For example, Fig. 9 plots the ESI-mass spectrum of the remaining PLA film after 1 year of incubation in paraffin that contained 0.016% water.

The presence in this spectrum of low molecular weight PLA oligomers containing hydroxyl and carboxyl end-groups indicates a significant reduction in the molecular weight of the PLA film due to the statistical hydrolysis of ester bonds. In addition, the low value of *m*/*z* of the spectrum signals corresponds to the detection of the lactic acid molecule and its dimer (signal at *m*/*z* 89 and at *m*/*z* 161 expanded region, respectively, of Fig. 8b). The presence of lactic acid inside the PLA film confirms that the degradation process occurs on the sample surface and, due to limited migration, is also associated with acid-catalysed internal degradation in the depths of the sample.

In the case of PLA films incubated in ethanol, it was expected that the low molecular weight products that migrate into ethyl alcohol should be composed mainly of the ethyl esters of lactic acid and its oligomers. Indeed, in the positive ESI-MS spectrum of the degradation products formed after 7 weeks of degradation of the PLA sample in absolute alcohol (water content 0.035%) a unimodal series of molecular ions of ethyl ester oligomers between *m*/*z* 521 to *m*/*z* 1961 was observed (data not presented).

However, for 96% ethyl alcohol (water content 5.7%), due to the expected presence of oligomers with ester and carboxylic end-groups, the ESI-MS analysis was performed in both the positive- and negative-ion mode. Fig. 10 plots the mass spectrum of 96% ethyl alcohol, in which a PLA film was incubated for 7 weeks. The negative ESI-MS spectrum presented in Fig. 10a reveals one set of singly charged anions corresponding to the PLA oligomers terminated by hydroxyl and carboxyl end-groups. In the low mass range, signals at *m*/*z* 89 and 161 matching the lactic acid molecule and its dimer, respectively, were also detected. The formation of oligomers with hydroxyl and carboxyl end-groups is related to the presence of some amount of water in the ethanol, which hydrolyses the ester bonds in the PLA sample. However, the real distribution of low molecular weight compounds that had migrated from this film to

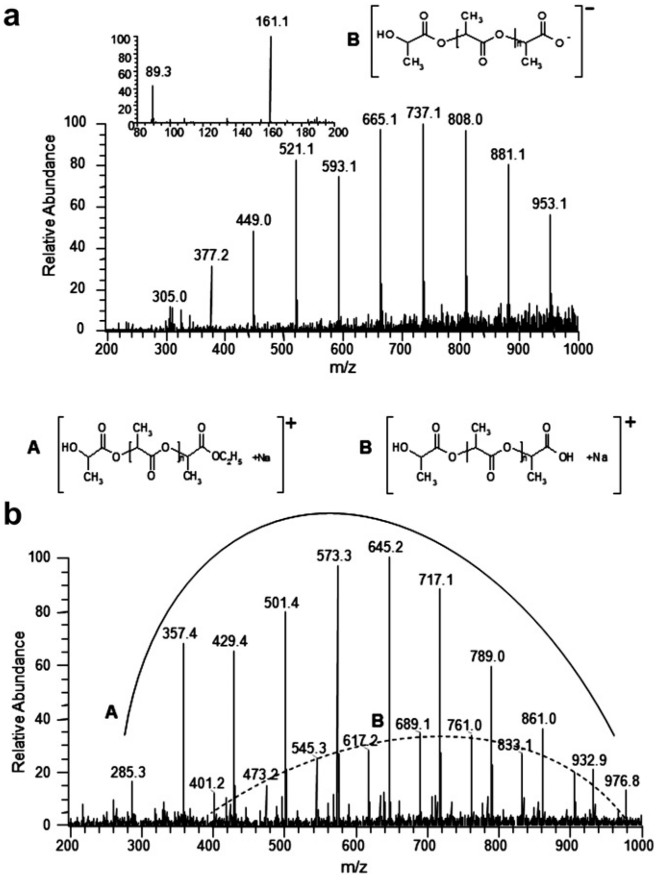

Fig. 10. ESI-mass spectrum (negative-ion mode) (a) and ESI-mass spectrum (positive-ion mode) (b) of the products that migrated into ethanol after 7 weeks of incubation of the PLA film at 70 °C.

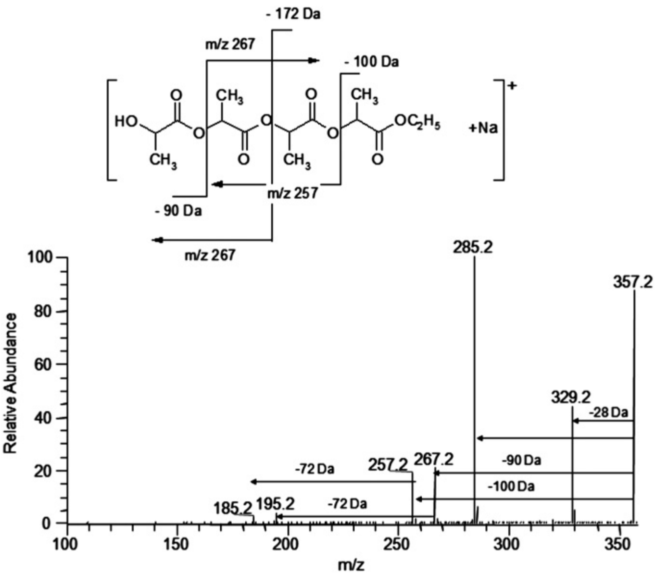

Fig. 11. ESI-MS/MS fragmentation experiments of the molecular ions belonging to series A (Fig. 10).

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the ethanol after 7 weeks of incubation is presented in the positive ESI-MS spectrum (Fig. 10b). The main series of signals labelled as (A) corresponds to the sodiated PLA oligomers terminated by hydroxyl and ethyl ester end-groups. They are formed because of the transesterification of the ester groups in the PLA chains by ethanol. The second series of ions labelled as (B) (with much lower intensities) corresponds to the sodiated PLA oligomers with hydroxyl and carboxyl end-groups.

The structural assignment of the molecular ion belonging to series (A) was confirmed by the ESI-MS/MS experiment, which was performed for the selected molecular ion at m/z 357 (Fig. 11).

The fragmentation experiment confirmed that the main products that can migrate from the PLA film to ethanol are the low molecular weight PLA oligomers terminated by hydroxyl and ethyl ester end-groups.

The ^{1}H NMR spectroscopy results (data not presented) correlate with the ESI-MS analysis and confirms the migration of low-molecular-weight lactic acid degradation products into the investigated simulants.

4. Conclusions

The most important requirement for plastic cosmetic packages is to avoid degradation and the migration of any low molecular weight components into a cosmetic formulation during storage. Thus, a comprehensive PLA material characterisation using AFM, GPC, ESI-MS and NMR analyses was performed to describe the degradation process of a commercial PLA film at temperatures of 70 °C and 37 °C in selected simulants used as ingredients in the preparation of cosmetics.

As expected, during hydrolytic degradation (in distilled water and buffer solutions), a rapid decrease of the mass and molecular weight of the samples occurred at 70 °C. It was accompanied by the release of low molecular weight degradation products. Macroscopic and microscopic evaluation of the surface of the PLA samples after the specified degradation times indicated erosion of the surface of the materials starting between the 1st and 3rd week of the degradation process, depending on the tested degradation medium. The total mass loss of the PLA matrix during hydrolytic degradation was observed after 32nd week.

It was originally observed that in an environment with a residual moisture content such as paraffin, the degradation process also occurs. Degradation in paraffin was significantly faster than in glycerine. Substantial disintegration of PLA film in paraffin was observed after week 24 of degradation.

The results of the present study demonstrate that selected simulants damage the PLA film during degradation, which can affect the future application of polylactide as a packaging material in long shelf-life applications. It may be concluded that polylactide is an imperfect alternative for classical polymers, and its decomposition strongly depends on the degradation environment. Further studies on more resistant biodegradable candidates for plastic cosmetic packages are currently under way at our laboratories.

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