



Degradation of polylactide in paraffin and selected protic media

Joanna Rydz^{a,*}, Grażyna Adamus^a, Katarzyna Wolna-Stypka^a, Andrzej Marcinkowski^a,
Marlena Misiurska-Marczak^b, Marek M. Kowalczyk^a

^a Polish Academy of Sciences, Centre of Polymer and Carbon Materials, 34 M. Curie-Skłodowska St., 41-800 Zabrze, Poland

^b Dr Irena Eris Sp. z o.o., Centre for Science and Research, 12 Armii Krajowej St., 05-500 Piaseczno, Poland

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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

Poly lactide (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

* Corresponding author. Tel.: +48 322716077; fax: +48 322712969.
E-mail address: jrydz@cmpw-pan.edu.pl (J. Rydz).

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 \times 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 cm³ 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 Multi-Mode with a NanoScope III D controller, Veeco (USA) equipped with a piezoelectric scanner with a scan range of 10 μm \times 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 ¹H and ¹³C 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. ¹H NMR spectra were obtained with 64 scans, a 11 μs pulse width, and a 2.65 s acquisition time, and ¹³C 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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