Technical Physics Letters, 2025, Vol. 51, No. 12

Study of the Water Absorption Process by Aliphatic Polyesters

© *A.G. Dunaev*[1], *S.A. Minaeva*[1], *A.V. Mironov*[1], *V.K. Popov*[1], *E.M. Trifanova*[1,2], *N.V. Minaev*[1]

[1] Institute of Photonics Technology, Kurchatov Complex of Crystallography and Photonics,
National Research Center „Kurchatov Institute,“ Moscow, Russia
[2] Petrovsky National Research Centre of Surgery, Moscow, Russia
E-mail: dunaewan@gmail.com

Received May 5, 2025
Revised July 9, 2025
Accepted July 9, 2025

This study focuses on investigating the kinetics of water sorption at the early stages of the hydrolytic degradation of aliphatic polyesters (D,L-polylactides) using optical detection methods. An original experimental technique has been developed, enabling real-time analysis of the spatial and temporal distribution of water concentration within the samples. It was found that moisture penetration occurs predominantly from the surface layers of the material, gradually spreading inward. A direct correlation was demonstrated between the increase in water content and the formation of microstructural defects — pores arising as a result of polymer chain degradation.

Keywords: polylactic acid, polymer resorption, water diffusion, IR radiation.

DOI: 10.61011/TPL.2025.12.62795.8051

The issues of hydrolytic stability and chemical and structural degradation of polymers of the homologous series of aliphatic polyesters (polylactides, polyglycolides, polycaprolactones, and their copolymers) in biological environments are presently in the focus of research attention [1]. Such materials are resorbed in a living organism at a controllable rate in the process of their hydrolytic or enzymatic hydrolysis [2]. To predict changes in the properties of these biomedical products in biological systems, one needs to determine the main factors and parameters influencing the processes of resorption and degradation of materials from which they are fabricated. Model environments with aqueous media are perfectly suitable for such studies [3].

To estimate the rate of degradation of samples in water, one may analyze the initial section of the temporal dependence of sample weight change within which the processes of their hydrolysis are insignificant [4]. However, small weight changes of a sample are often hard to measure due to problems with its thorough drying. The disadvantages of this gravimetric method also include the fact that it does not allow for analysis of the spatial distribution of water concentration within the bulk of the studied sample.

An alternative approach to examining the spatiotemporal distribution of water concentration in polymers may be based on measuring the absorption of infrared (IR) radiation at 1.5, 1.9, and 3 μm (i.e., in the regions where water has intense absorption bands). In our view, laser radiation with a wavelength of 1960 nm, at which the approximate absorption coefficient of water is 115 cm^{-1} [5], is fit for this purpose. Thus, with a sample thickness of just 1 mm and a water saturation level of 10 mass%, the measured value of IR radiation absorption should change approximately by 11 %. This is quite sufficient for quantitative measurements of water concentration in the polymer under study with a relative error of 2–5 %.

The aim of the present study is to examine experimentally the process of water sorption at the initial stage of hydrolysis of aliphatic polyester (15 days) using an original technique that was proposed and developed by our research team and is based on real-time optical detection of the spatial distribution of water concentration in the bulk of D,L-polylactide.

The changes in surface morphology and internal structure of the studied samples were analyzed using a Bresser Advance ICD (Germany) optical microscope and a Phenom ProX (Netherlands) scanning electron microscope (SEM).

The initial granules of Purasorb PDL-05 (Corbion Purac, Netherlands) D,L-polylactide (hereinafter referred to as PDL-05) 1–3 mm in size were ground in a rotary mill, and the fraction with a particle size of 100–200 μm was separated with a set of sieves. Monolithic samples were produced by injection molding [6] from 477 mg of polymer powder in a mold with a 25 × 30 mm rectangular cross section at a temperature of 67 °C and a pressure of 15 MPa within 50 min. The prepared monolithic plate was cut into samples $5 \times 2 \times 0.7$ mm in size with a scalpel.

These samples were introduced into a cell made of three standard 1-mm-thick microscope slides 76 × 26 mm in size that were positioned with their wide faces adjacent to each other, forming a stack. A hole in the form of an elongated ellipse with semi-axes of 5 and 10 mm was made in one plate. Another plate was glued to it, and the sample was glued to the bottom of the formed recess. The third plate with two round holes was glued to the top of the sample and the glass surface. Pipes with silicone tubes attached to them were glued into these holes, and water circulation was initiated in these pipes using a gear pump. Thus, water contacted the surface of the sample only at its ends. Water was heated to a temperature of 36–38 °C in a flask 1 l in volume. The flow cell with the sample was mounted on a copper heater, which maintained its temperature at $40 \pm 1\,^{\circ}$C. The sample was placed above a round hole with a diameter of 12 mm in the heater. A laser power meter was positioned behind this hole (Fig. 1).

All elements of this system were positioned so that the laser probe beam passed through the sample and hit the power meter sensor (Fig. 1).

Radiation of a thulium fiber laser with a wavelength of 1960 nm (TLM-3, IRE-Polyus, Russia) was used to probe the sample in the IR region. The probing radiation power was 100 mW. Such radiation did not induce any changes in structure of the sample during the experiment. The laser beam was focused on the sample surface in a spot $\sim 280\,\mu$m in diameter by a galvano-scanning system (LScan-H, Ateko-TM, Russia) with an F-theta lens (SL-2000-100-160, Ronar-Smith, Singapore). The length of the laser beam waist at the focus was 5.5 mm, which exceeded the thickness of the sample. A Coherent LM-10 (United States) measuring head with a sensitive region 18 mm in diameter was positioned behind the sample. The laser radiation power data were recorded using a LabMax-TOP meter (Coherent, United States). The beam was scanned across the sample at a rate of 0.1 mm/s. Five tracks spaced $400\,\mu$m apart were scanned in each measurement.

A He–Ne laser with a wavelength of 632.8 nm (SIOS Messtechnik GMBH, Germany) was used to determine the scattering coefficient of the sample. Laser radiation was directed onto the sample by two mirrors through a lens with a focal length of 11.2 cm. Radiation was then passed through the filter to the measuring head (LM-2 VIS Semiconductor Power Sensor, Coherent, United States) of the power meter. The power of laser radiation passing through the sample was recorded in the experiment.

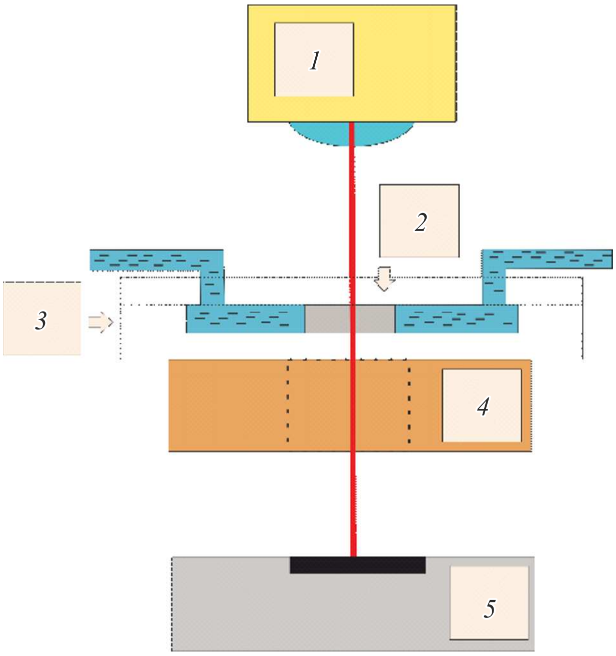

Figure 1. Schematic sectional view of the experimental setup. *1* — Laser radiation source, *2* — sample, *3* — flow cell, *4* — copper plate with a hole, and *5* — laser radiation power sensor.

The sample was kept under experimental conditions for 15 days to examine the changes in absorption of radiation from the thulium fiber laser. The experiment was terminated when the intensity of laser radiation passing through the sample dropped almost to zero. Figure 2 presents the photograph of the sample made after the measurements were completed.

Changes in sample morphology in the process of degradation were studied using the SEM (Fig. 3) alongside with the above measurements. The photographs confirm the results of observations made with the optical microscope: pores started to appear on the second day of the experiment. They formed predominantly near the surface of the sample in contact with water; however, on the 12th day of the experiment, the number of pores evened out across the entire sample section, and the size of near-surface pores increased.

Optical experiments with the thulium laser confirm that pores formed first at the edges of the sample, but the overall transmittance in the middle of the sample decreased by 10 % within the first day.

Figure 4, *a* presents the dependence of the thulium laser radiation power transmitted through the sample on time elapsed from the start of the experiment. The obtained data demonstrate that although the samples were in contact with water only at the edges, pores were already forming in the middle of the sample within the first 26 h of the experiment. Therefore, hydrolysis was not confined just to the edges of the sample as well. It is important that this fact be taken into account in both *in vivo* and *in vitro* experiments.

As the morphology of the sample changed due to the diffusion of water into it, the scattering of laser radiation intensified and, consequently, the recorded power of transmitted radiation of the He–Ne laser decreased (Fig. 4, *b*). This process was also initiated at the edges, but the reduction recorded within the first day was not as significant as the one in the experiment with the thulium laser. This may be indicative of penetration of water into the sample.

We have confirmed that the change in transmittance coefficients of the sample is correlated with the emergence of pores inside it.

Although water came into contact with the sample only at its ends, the optical density in its central part decreased significantly even within the first 24 hours. This is indicative of a high rate of water diffusion in the bulk of the sample. Thus, moisture diffusion proceeds faster than visible morphological changes, which is consistent with previously published data on water diffusion in aliphatic polyesters [3].

The proposed method is suitable for quantitative analysis of water content in aliphatic polyesters and modeling of their degradation processes. It allows one to perform continuous monitoring of water sorption dynamics with high temporal and spatial resolution without destruction of the examined sample.

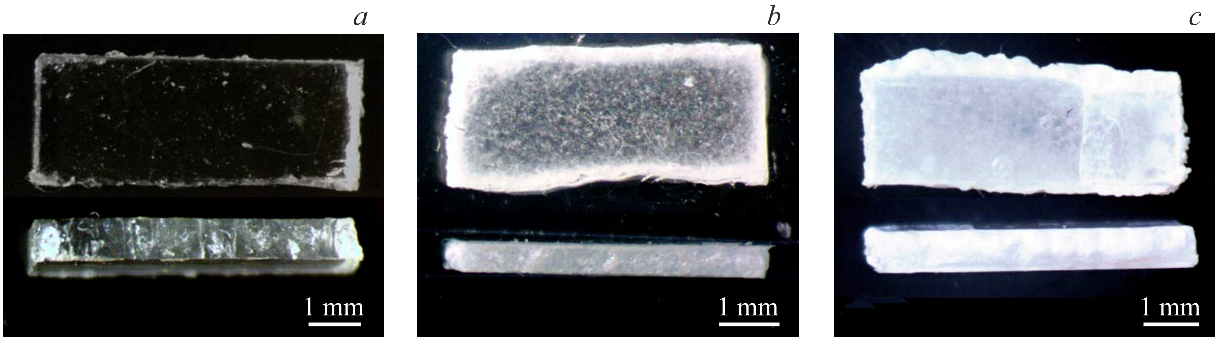

Figure 2. Optical photographs of the sample at different stages of resorption: *a* — initial state, *b* — two days of resorption, *c* — 15 days of resorption.

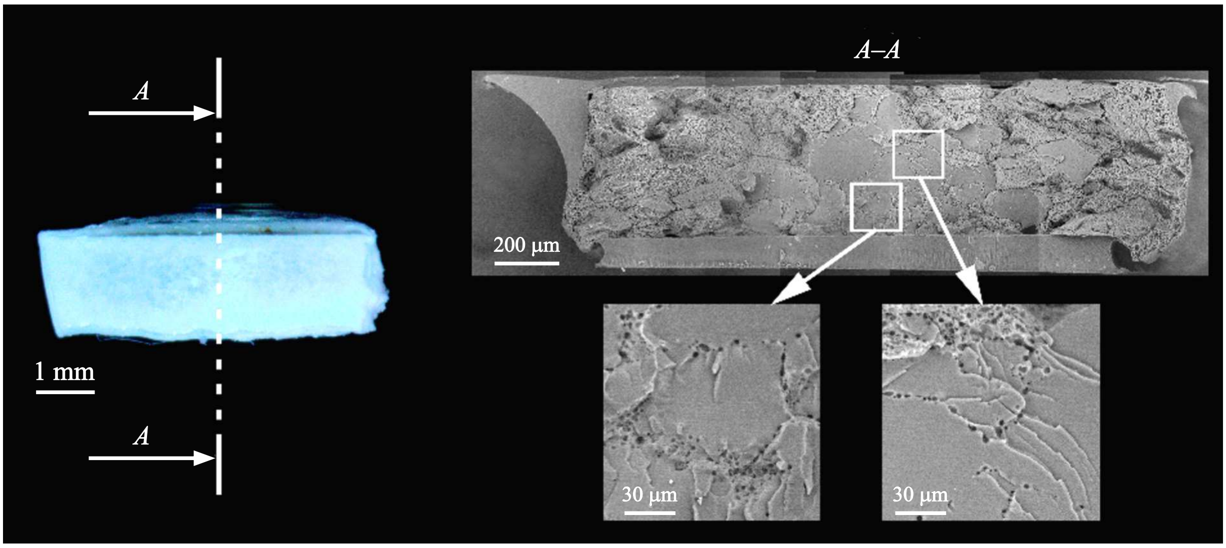

Figure 3. Optical photograph and SEM image of a section of the sample on the ninth day of resorption.

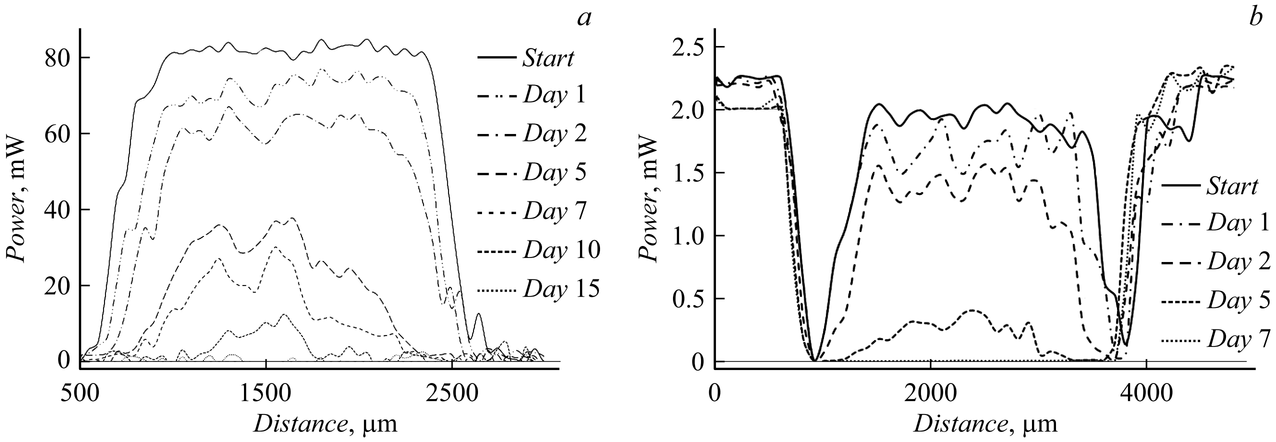

Figure 4. Dependence of the laser radiation power transmitted through the sample on time elapsed from the start of the experiment. *a* — Thulium laser; *b* — He–Ne laser.

The obtained data will be used to construct a mathematical model of water diffusion into a polymer sample.

Funding

This study was carried out under the state assignment of the National Research Center „Kurchatov Institute.“

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y. Xu, C. Kim, D.M. Saylor, D. Koo, J. Biomed. Mater. Res. B, **105** (6), 1692 (2017). DOI: 10.1002/jbm.b.33648
[2] Y. Wang, M.A. Murcia Valderrama, R.-J. van Putten, C.J.E. Davey, A. Tietema, J.R. Parsons, B. Wang, G.-J.M. Gruter, Polymers, **14** (1), 15 (2021). DOI: 10.3390/polym14010015
[3] P.I. Borovikov, A.P. Sviridov, E.N. Antonov, A.G. Dunaev, L.I. Krotova, T.K. Fatkhudinov, V.K. Popov, Polym. Degrad. Stab., **159**, 70 (2019). DOI: 10.1016/j.polymdegradstab.2018.11.017
[4] Z.A.M. Ishak, J.P. Berry, J. Appl. Polym. Sci., **51** (13), 2145 (1994). DOI: 10.1002/app.1994.070511306
[5] L. Kou, D. Labrie, P. Chylek, Appl. Opt., **32** (19), 3531 (1993). DOI: 10.1364/AO.32.003531
[6] I.V. Arutyunyan, A.G. Dunaev, E.M. Trifanova, M.A. Khvorostina, A.V. El'chaninov, A.G. Soboleva, T.Kh. Fatkhudinov, V.K. Popov, Perspekt. Mater., № 5, 22 (2023). DOI: 10.30791/1028-978X-2023-5-22-34

Translated by D.Safin