Contents lists available at ScienceDirect

### **Polymer Testing**

journal homepage: www.elsevier.com/locate/polytest

# Effect of exposure of phosphate buffered saline solution on creep behavior of polylactic acid: *in-situ* testing and modeling

Soo-Hyun Woo<sup>a</sup>, Min-Gyu Jo<sup>a</sup>, Byeong-Heon Park<sup>b</sup>, Jung-Wook Wee<sup>c,\*</sup>

<sup>a</sup> Department of Mechanical Engineering, Kumoh National Institute of Technology, 61 Daehak- Ro, Gumi, Gyeongbuk, 39177, Republic of Korea
 <sup>b</sup> School of Mechanical System Engineering, Kumoh National Institute of Technology, 61 Daehak- Ro, Gumi, Gyeongbuk, 39177, Republic of Korea

<sup>c</sup> School of Mechanical Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, 41566, Republic of Korea

#### ARTICLE INFO

Keywords: Polylactic acid Creep testing Failure mechanism map Phosphate buffered saline solution Larson-miller parameter

#### ABSTRACT

In this study, a custom immersion creep tester was developed to investigate the *in-situ* creep behavior of polylactic acid (PLA) in contact with phosphate buffered saline (PBS) solution at various temperatures. Hydrolysis in PBS accelerated creep strain and shortened the lifespan compared to air. The elevated temperatures further facilitate molecular mobility and hydrolysis, leading to faster degradation in PBS environments. The failure mechanisms varied depending on the media, with brittle failure predominating in air and surface hydrolysis accelerating the failure in PBS. The Larson-Miller parameter (LMP) effectively predicted the long-term creep behavior of PLA by incorporating the time-temperature-environment correlation and showed high accuracy. These results highlight the important role of environmental factors in determining the structural integrity and mechanical properties of PLA and emphasize the need to carefully consider environmental conditions when designing PLA-based materials for applications such as biomedical implants or packaging.

#### 1. Introduction

Polylactic Acid (PLA) is an amorphous biodegradable polymer synthesized by polymerizing lactic acid derived from renewable natural resources such as corn [1,2]. As an aliphatic polyester, PLA is widely recognized for its eco-friendliness compared to conventional fossil fuel-based polymers and its mechanical strength comparable to petroleum-based plastics, making it a promising alternative material for various applications [3–8]. Unlike traditional petroleum-based plastics that often take hundreds to thousands of years to degrade [9], the PLA can decompose within several years through microbial activity and hydrolysis [10,11]. This property positions PLA as a sustainable solution to the growing environmental concerns associated with plastic waste.

In biomedical applications, an excellent biocompatibility of the PLA materials allows it to metabolize into water and carbon dioxide within the human body, enabling its use in load-bearing applications such as medical implants, tissue engineering scaffolds, and cardiovascular stents [12–18]. Also, the PLA-based nano composites have been developed and characterized to adjust their physical properties including conductivity and viscosity, and so on [19–21].

Because PLA is mainly used as biomedical implants to ensure the initial healing process, early degradation causes challenges to achieve treatment period that rely on biodegradable polymers. On the other hand, an excessively long lifetime can also cause interference, e.g., inflammation or adverse effects. To prevent such issues, it is crucial to predict both the timing of PLA degradation and changes in its durability under *in vivo* conditions. Additionally, the degradation process of PLA can alter the local pH environment due to the release of amorphous fragments, accelerating further degradation and affecting mechanical stability [22,23].

To understand the degradation behavior of PLA materials in human body, numerous studies have been conducted using *in vitro* tests in phosphate-buffered saline (PBS) at 37 °C [1,24–28]. A study evaluated the hydrolysis properties of commercial PLA and laboratory-synthesized PLLA and found that the prepared PLLA hydrolyzed faster than commercial PLA, with a more pronounced decrease in molar mass, especially during the first 28 days [29]. However, PLA retained its physical properties longer than PLLA, and crystallinity had a significant effect on the hydrolysis rate. Kim et al. [28] developed a tunneling-based conductivity model and systematically characterized the hydrolytic degradation behavior of PLA-based nanocomposites in PBS solution. Polidar et al. [30] research has demonstrated that specific phosphate additives have the capacity to regulate and expedite the hydrolysis rate of PLA. The aforementioned effects manifested more distinctly at elevated

https://doi.org/10.1016/j.polymertesting.2025.108877

Received 11 February 2025; Received in revised form 1 May 2025; Accepted 29 May 2025 Available online 29 May 2025

0142-9418/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).







<sup>\*</sup> Corresponding author. *E-mail address:* jwwee@knu.ac.kr (J.-W. Wee).



Fig. 1. Preparation procedures for creep specimens. (a) Polylactic acid (PLA) resins, (b) preparation of mold assembly, (c) heating-press machine, (d) fabricated PLA plate, (e) machining of creep specimens, and (d) manufactured creep test specimens.

temperatures; however, even at 37 °C, progressive degradation was observed over time. In the context of biomedical applications, the incubation of medical PLA/hydroxyapatite (HAp) composites in phosphate-buffered saline (PBS, pH 7.4) at 37  $^\circ C$  for a period of 10 weeks has been observed to result in a decline in the degradation rate, with the rate of degradation exhibiting an inverse correlation to the HAp content, indicating that the HAp contributes to the enhancement of the structural stability of PLA [31]. Furthermore, experiments conducted in a phosphate-buffered saline (PBS) solution (pH 7.4) at 37 °C demonstrated that the rate of hydrolysis of PLA-based drug delivery systems can vary depending on pH and environmental conditions. Specifically, a decline in molar mass and alterations in structure over time were observed [32]. Both in vivo and in vitro experiments, the primary degradation mechanism of PLA was identified as hydrolysis of ester bonds, which was stable at neutral pH. Furthermore, experimental conditions maintained at 37 °C in a phosphate-buffered saline (PBS) solution resulted in a progressive degradation of PLA [17]. The exposure of PLA to the PBS solution resulted in chain cleavage and surface damage, which in turn led to physical changes due to hydrolysis. It was further observed that these effects were more pronounced at higher temperatures [33].

Previous studies examining PLA hydrolysis in PBS solution at elevated temperatures (50, 60, and 70 °C) have reported the loss of molecular weight and chain cleavage, leading to progressively diminished tensile strength and elongation [34]. The surface degradation-induced tensile stresses on the polymer surface and surface cracking were identified as the primary damage mechanisms. It was also investigated that, when PLA was exposed to PBS at 37 °C, its elastic modulus was initially maintained, but mechanical properties gradually weakened due to degradation. Additionally, a high-pH environment accelerated this degradation, leading to a significant decrease in impact resistance [35]. Furthermore, the degradation of PLLA fibers in a PBS solution results in the development of microcracks on the surface and a decrease in mechanical strength with a decrease in molecular weight. The fracture surface analysis revealed microcracks and low plastic deformation, which are characteristic of brittle fracture [36,37].

For *in vivo* medical implants, mechanical stresses are also applied during the service period in the human body. For example, stents implanted in blood vessels, such as coronary arteries, for the purpose of vascular dilation are subjected to external surface pressure exerted by the surrounding vessel. In the case of sutures used in the human body, they are subjected to the tensile stress throughout their biodegradation process. Moreover, bone and joint implants are subjected to even more complex stress conditions. Thus, it is important to evaluate long-term properties such as creep and fatigue rather than short-term properties. Tábi et al. [38] found that the  $\alpha$  crystalline in PLA significantly reduces creep deformation, suggesting that crystallization improves the mechanical stability of PLA and provides better performance under thermal and long-term loading conditions. Ezeh et al. [39] evaluated the fatigue strength of PLA fabricated by FDM and found that the Lester angle and average stress had a significant impact on fatigue life. In particular, the fatigue strength decreases at certain fabrication orientations, suggesting that manufacturing process variables and design conditions play an important role in the fatigue behavior of PLA.

When biodegradable polymers are implanted in the body, however, hydrolytic degradation and mechanical loading, including fatigue and creep, do not occur independently but rather it undergoes mechanochemical degradation simultaneously. Hence, the *in-situ* testing that examine the fatigue or creep behavior of PLA in a simulated physiological environment, while simultaneously accounting for mechanical stress and chemical hydrolysis, are required. However, to the best of the author's knowledge, no research has yet examined the long-term creep behavior of PLA materials in saline solutions at various temperatures. To achieve this, creep or fatigue tests must be performed in an environment where the PLA material is in contact with fluids that mimics bodily conditions, e.g., saline solution at body temperature.

In this study, to elucidate the long-term mechanical behavior of PLA in the human body, an in-situ four-stage creep testing apparatus enabling contact with phosphate-buffered saline (PBS) solution was designed and constructed. A dual-bath system was employed to maintain stable temperature levels and prevent heater corrosion, as well as the frame was designed to ensure that no creep load was transmitted to the baths. To apply both creep stress and solution exposure simultaneously, the grip parts were first attached to the creep specimen and then connected to main frame with a pin connection. During testing, the creep deformation was continuously measured using the displacement sensors. Through this apparatus, the creep deformation and rupture behavior of PLA under various temperatures and stresses in a PBS environment were analyzed, and a stress-lifetime diagram was established for different temperature levels, i.e., 37, 45, and 50 °C. A comparison with creep behavior performed in air under the same conditions enabled a quantitative evaluation of PBS solution exposure, revealing a significant reduction in creep durability. Additionally, failure modes were categorized based on the testing environment, temperature, and stress level, and a failure mechanism map (FMM) was suggested. By introducing the Larson-Miller parameter, a creep lifetime prediction model was



Fig. 2. Design and actual implementation of various experimental devices. (a) Isometric view of a fluid environment creep tester designed as a 3D model. (b) Constructed fluid environment creep tester. (c) Schematics of dual-bath design with load transferring and sensor system.

constructed in both PBS and air environments. This comprehensive analysis of the combined effects of stress and hydrolysis for *in vivo* applications of PLA is expected to aid in estimating the long-term durability and reliability of PLA in body condition under arbitrary mechanical stress levels. Therefore, this study uniquely quantifies the temperature dependent creep behavior of PLA in PBS, comparing with air environment, and presents FMM that clarifies the coupled influence of long-term hydrolytic degradation and mechanical stress, offering guidance for designing load-bearing biodegradable scaffolds.

#### 2. Materials and methods

#### 2.1. Creep specimens manufacturing methods

Polylactic acid (PLA) resin (4032D, NatureWorks LLC) as shown in Fig. 1a was compression molded into plates using a heating press machine, QM900M (QMESYS, Korea). Initially, a release film was positioned between the rectangular bottom plate and the middle plate in steel, with a dimension of  $250 \times 250 \times 2$  mm. The middle plate contains

a rectangular opening with a dimension of  $180 \times 180 \times 2$  mm, and the resin was evenly distributed on the film. Another release film was then placed over the resin, followed by the upper steel plate (see Fig. 1b). The entire assembly was subsequently placed into the heating press for compression molding as illustrated in Fig. 1c. The resin was first preheated at 190 °C under a pressure of 2 MPa for 15 min, followed by a main heating process at the same temperature and 15 MPa for an additional 10 min. The heated plates were then quenched in water at 20 °C for 1 min and molded PLA plate with a dimension of  $180 \times 180 \times 2$  mm was obtained (see Fig. 1d). Compression molding eliminates interlayer adhesion defects that occur in additive manufacturing (FDM) and provides uniform crystallinity, allowing for analysis of pure material properties. The tensile specimens following ASTM D 638 Type 5 with a thickness of 2 mm were machined through CNC and used for the creep tests (see Fig. 1e and f).

#### 2.2. Design and construction of fluid-environment creep tester

In this study, a special creep testing machine was designed to analyze



Fig. 3. Air-environment creep tester: (a) modeling and grip design, and (b) schematics of load transferring and sensor system.



Fig. 4. The maintenance of temperature during air and phosphate buffered saline (PBS) creep test. The actual measured temperature through thermocouple sensor during the creep test are shown at (a) 37, (b) 45, and (c) 50 °C, respectively.

the *in-situ* creep behavior of PLA under physiological environmental conditions, as shown in Fig. 2a–b, for 3D modeling and actual system, respectively. Unlike conventional creep testers for polymers, which are usually designed to operate in air or at a constant temperature, this apparatus was specifically designed to evaluate the degradation and creep behavior of PLA in an environment such as PBS solution. In addition, a simple air-based creep test apparatus was also used (Fig. 3a), and the creep properties of PLA were evaluated using the two creep testers.

Creep tests were conducted using a PBS solution due to its physiological relevance, its pH of 7.4, the inclusion of sodium chloride (NaCl) and potassium chloride (KCl), and its excellent buffering capacity, which make it suitable for *in vitro* testing [1,34,36,40,41]. The experiments were performed at three temperatures commonly applied *in vitro* degradation studies: 37 °C (body temperature), 45 °C, and 50 °C. Additionally, the test specimens were aged for at least 1 h at each test temperature and environment before testing. These conditions enabled a comparative analysis of PLA creep behavior under varying thermal environments. Real-time creep strain data provided quantitative insights into PLA long-term mechanical stability and degradation behavior in contact with the PBS solution. The apparatus was developed by integrating corrosion-resistant materials, precise load application mechanisms, and real-time monitoring systems. This apparatus successfully simulates *in vitro* environments for evaluating PLA creep properties under realistic conditions while adhering to international standards for mechanical testing.

#### 2.2.1. Creep tester frame and bath design

In the creep tester for liquid environment, the main and side frames were installed on an optical table for vibration damping (Fig. 2a-b). This configuration provides structural stability and allows simultaneous testing of multiple specimens under different conditions without mutual interference. Each frame incorporates a corrosion-resistant load transfer mechanism, ensuring durability and reliability in submerged environments. The apparatus adopts a dual-bath structure to create an optimized liquid testing environment. The outer tank, made of stainless steel and filled with distilled water, while the inner tank, glass baths, contains the PBS solution where the specimens are submerged (see Fig. 2c). The outer tank includes a titanium heater that indirectly heats the PBS solution by regulating the temperature of the distilled water, preventing corrosion of the heater. The PBS solution was prepared using HPBS-2010-74 (Forbio Korea, Korea) and maintained at a physiological pH of 7.4  $\pm$  0.2 with a salinity of 1.0  $\pm$  0.1 % by replacing the solution every three days [34]. The temperature of PBS solution was maintained within  $\pm 1$  °C using thermocouples to monitor fluctuations, ensuring consistent experimental conditions (Fig. 4a-c). Additionally, a Teflon



Fig. 5. Grip jig design for creep testing in liquid and high temperature environments: (a) modelling and (b) actual photograph of the grip jig for the liquid environment creep tester, (c) actual photograph of the grip cross-section, and (d) grip pattern.



**Fig. 6.** Creep behavior under different conditions: (a) creep strain as a function of time at 50 °C in PBS at 5 MPa, (b) creep strain rate as a function of time at 50 °C in PBS at 2 MPa, (c) creep strain rate as a function of time at 37 °C in air at 18 MPa.

cover was placed over the double tank to prevent evaporation of the solution. This dual-bath design not only ensures precise temperature control but also minimizes contamination risks and enhances experimental reliability by simulating *in vitro* degradation conditions effectively.

The constructed testing system is shown in Fig. 2b. In case of creep tester for air environment, the temperature was maintained by the dry oven equipped with the frame (Fig. 3a). Also, the temperature inside the dry oven measured by thermocouples in the vicinity of the specimens was maintained in  $\pm 1$  °C as shown in Fig. 4a–c.

#### 2.2.2. Creep loading and sensor system

Fig. 2c reveals a schematic diagram of the creep loading and sensor

system. It is designed to apply a constant tensile load to the specimen immersed in PBS solution. The system uses sprockets, chains and weights to ensure that the applied load remains within  $\pm 1$  % accuracy throughout the test process. To mitigate the possibility of errors due to vibration or shock, the device is mounted on an optical table, and each jig is individually installed to ensure stable and precise test conditions. To ensure the accuracy of displacement measurement, a linear variable differential transformer (LVDT) sensor (KPF-100, MIRAN, China) was used to monitor the deformation of the upper grip due to the specimen deformation. This approach allows for accurate tracking of the creep deformation by measuring the displacement of the upper grip rather than the weight displacement. The LVDT sensor with a measuring range of 100 mm was adopted to measure the deformation of specimens during



Fig. 7. Graphs showing the creep strain over time under different conditions: (a) 37 °C in PBS solution, (b) 37 °C in air, (c) 45 °C in PBS solution, (d) 45 °C in air, (e) 50 °C in PBS solution, and (f) 50 °C in air.

the creep test. A precision sensor with an error range of  $\pm 1$  % in displacement measurement was used, and the sensor was driven by a 20 V transformer and provided real-time data on the displacement of the upper grip. As shown in Fig. 3a, in case of air environment test, the upper grips were fixed to the frame, and the displacement of the lower grip was measured by the LVDT sensor (see Fig. 3b).

To capture the detailed creep behavior, data was recorded using a data logger at 0.02 s intervals for 1 h of testing and then at 1 min intervals thereafter. This configuration allowed for uninterrupted observation and evaluation of specimen deformation over time, ensuring reliable creep displacement measurements under controlled

environmental conditions. By measuring the displacement of upper grip rather than that of weights, the system provided accurate measurement of deformation of specimens over long-term creep testing.

#### 2.2.3. Creep tester grips and fixture design

Fig. 5 shows the jig design and actual grips of the creep testers. The upper and lower grips were designed non-slip patterns on the inner surface as shown in Fig. 5c–d. These patterns were designed to prevent slippage under long-term tensile loading while maintaining consistent alignment throughout the test. To facilitate specimen setup, the grips were designed to be removable from the frame. In addition, to prevent



Fig. 8. Steady state creep strain rate of PLA in (a) PBS solution and (b) air at various temperatures.



Fig. 9. Creep stress ( $\sigma$ ) against failure time ( $t_f$ ) curves for PBS solution and air. (a) 37, (b) 45, and (c) 50 °C at different mediums. (d)  $\sigma$ - $t_f$  plots with different temperatures in air environment and (e) PBS solution.

eccentricity of the specimen, the grips are attached to the specimen as shown in Fig. 5c and then fixed to the main frame using pins so that fluid contact and creep loading are initiated simultaneously (see Fig. 5b). To ensure durability during extended exposure to the PBS solution, the immersion frames and grips were fabricated from 316L stainless steel, known for its corrosion resistance, and further coated with chrome to enhance durability.

#### 2.2.4. Characterization of creep behavior in PBS solution and air

The failure of polymeric materials is closely related to the accumulation of plastic deformation under applied loads. Creep testing is essential for predicting and evaluating the long-term behavior of materials, as it provides important insights into the time-dependent deformation mechanism of polymers. Fig. 6a shows the creep strain as a function of time in case of 5 MPa of creep stress at 50 °C in PBS solution, for examples. The example creep curve for 18 MPa in air environment at 37 °C is also shown in Fig. 6c. In some cases, the specimens underwent severe creep.

To analyze the creep strain, numerical differentiation was applied to calculate the instantaneous creep strain rate ( $\dot{e}$ ) from the relationship between strain ( $\varepsilon$ ) and time (t) [42]. The numerical differentiation used a finite difference method that utilizes neighboring data points to estimate the rate of change:

$$\dot{\varepsilon}(t) = \frac{\varepsilon(t_{i+1}) - \varepsilon(t_i)}{t_{i+1} - t_i},\tag{1}$$

where the  $\dot{\epsilon}$  (t) represents the instantaneous strain rate at time  $t_i$ . In order to reduce noise and obtain a smooth curve, the strain rate obtained from numerical differentiation was further processed using a moving average smoothing technique. It has been well known that the secondary stage of the creep curve can be identified based on the creep curves, and the steady-state creep strain rate could be determined [43]. This stage is critical for comprehending long-term material deformation, as it signifies a stable phase where the creep rate remains constant. The identification of the secondary stage and the calculation of the steady-state creep strain rate have been established as standard practices in creep analysis [43,44]. In this study, the steady-state creep strain rate ( $\dot{\varepsilon}_{ss}$ ) was defined by the minimum value of  $\dot{\varepsilon}$  (t), as shown in Fig. 6b-d. The smallest value is used to conservatively estimate the steady-state creep strain rate, especially since experimental data can be noisy or variable. If the strain rate is not completely constant in the secondary creep regime, the minimum value represents the theoretically most stable state.

#### 2.3. Surface observation for morphological damages

After the creep testing in air and PBS environments, the surface of the



**III. Semi-brittle Fracture** 

III. Ductile failure with craze opening

Fig. 10. (a) Failure modes in air-based creep test: semi-brittle fracture, ductile failure, and mixed mode. (b) Schematics of crazing behavior in semi-brittle fracture and ductile failure. In semi-brittle fracture, the generated crazes propagate, and final fracture occurs with limited plastic deformation. In some cases of ductile failure, the crazes are opened without additional growth.

specimens was closely observed through optical microscopy (OM) and scanning electron microscopy (SEM). The PLA specimen surfaces were examined using a DIMIS M5 optical microscope (DIMIS, Korea) with a magnification of 50. For some specimens, MAIA 3 LM (TESCAN, Czech) was applied for the scanning electron microscope (SEM) observations, to investigate a more detailed analysis of the surface damage morphology. Prior to SEM observation, the samples were platinum-coated, and imaging was conducted at an accelerating voltage of 5 kV.

#### 3. Results and discussions

#### 3.1. Creep strain with elapsed time in PBS solution and air

Fig. 7a–f exhibit the creep strain curves against the elapsed time for creep tests conducted in PBS solution and in air, at the different temperature levels, 37, 45, and 50 °C, respectively. In general, the increased temperature or applied stress accelerates the creep deformation of PLA specimens and shortens the creep lifetime, in both mediums. Despite the same temperature conditions, the lifespan when testing at 15 MPa stress in PBS at 37 °C compared to air shows a significant difference: the lifespan in PBS is 15 h, while in air it is 220 h, revealing a difference of over 13 times.



Fig. 11. (a) Failure modes of creep behavior in PBS solution. Semi-brittle fracture, ductile failure, and mixed mode. In PBS solution, the specimens with ductile failure are whitened and lose their transparency at a relatively low stress level. (b) Schematics of creep deformation with hydrolysis degradation in PBS solution, initiation of micro pits, growth of pitting, and degradation surface.

In the PBS medium, the diffusion of the solution in the PLA specimen could lubricate between the adjacent molecules, facilitating the mobility of chain molecules and ease of disentanglement [45]. Furthermore, the mechanical stress accelerates the fluid diffusion into the polymers by enlarging the vacant in the medium [46]. Thus, the plasticization-assisted creep deformation accelerates the creep rupture of PLA specimens. Also, PLA materials could undergo hydrolysis degradation in aqueous environments such as the PBS solution. When moisture is present, the ester bonds in PLA are randomly cleaved, leading to faster degradation and a reduction in mechanical properties over time [34,47,48]. The increased temperature accelerates the diffusion and hydrolysis mechanisms; thus, the high temperature clearly shortened the rupture time in the PBS solution [49,50]. Generally, PLA in air, which is not an aqueous environment, undergoes oxidative degradation, which is known to occur more slowly than hydrolytic reactions. Although oxidation can occur quickly at high temperatures, it does not damage the material as rapidly as hydrolysis in a moist environment [47].

Fig. 8 shows the changes in creep rate with stress for PLA under steady-state creep at various temperatures and media. The creep rate at steady state increases from low to high temperatures, as well as with increasing applied stress [51]. This is due to the increased molecular mobility at higher temperatures, which facilitates deformation under stress. As the temperature rises, the activation energy required for molecular motion decreases, accelerating the creep process, particularly as it approaches the glass transition temperature. Additionally, the creep rate follows a power law relationship with stress, indicating that higher

stress leads to increased deformation rates. The results from tests conducted in PBS show a significantly higher steady-state creep strain rate at the same temperature compared to tests in air. This indicates that the creep process is considerably accelerated in a liquid environment. The PBS solution promotes hydrolytic reactions and weakens the interactions within the polymer matrix, making it easier to deform under sustained stress. It can be observed that the steady-state creep rate increases progressively and nonlinearly with increasing stress and temperature.

#### 3.2. Creep stress-lifetime plots in PBS solution and air

Fig. 9a, b, and 9c illustrate the creep rupture times as a function of applied stress at each temperature, 37, 45, and 50 °C, respectively. At 37 °C, the difference in lifespan increases as stress decreases, while at 45 °C and 50 °C, there is a knee point in stress-lifetime plots. Notably, at 45 °C in PBS, the failure time decreases nonlinearly and sharply starting from 12 MPa, and at 50 °C, there is a knee point of the lifespan at 6 MPa in PBS and 8 MPa in air. Fig. 9d–e exhibit the effect of temperature levels in different mediums, air and PBS solution, respectively. It is evident that the stress–lifetime diagram shifts downward with increasing temperature. In the air environment, the knee point was observed only at 50 °C, whereas in the PBS environment, knee points emerged at both 45 °C and 50 °C. It has been known that such knee points in creep or fatigue testing are closely related to the transition of failure modes, e.g., ductile-brittle transition.

According to the literature, PLA has been reported to have lower



Fig. 12. Failure mode map (FMM) in air-environment creep testing with regard to applied stress level and temperature.

creep resistance at high temperatures and under high loads compared to other polymers [50]. In amorphous polymers, the increase in applied stress may exhibit a quasi-asymptotic relationship between failure time, suggesting that the lifespan of the material decreases exponentially as stress increases [52]. This indicates that once a certain stress level is exceeded, the failure time decreases sharply. The relatively low glass transition temperature of PLA material compared to other petroleum-based polymers may lead to increased molecular mobility at the testing temperatures, resulting in a sharp drop in deformation resistance and consequently a significant reduction in lifespan at lower loads. The increased mobility of the polymer chains, combined with hydrolytic reactions in PBS, may compromise the structural integrity of PLA, leading to faster failure at lower stress levels [53]. To investigate the knee points observed in the creep lifetime diagram, the next chapter will examine the failure mechanisms in detail and determine whether transitions in failure mode are associated with these knee points.

## 3.3. Creep failure modes and failure mechanisms map in PBS solution and air

To understand the knee points of the creep lifetime plots in both mediums, the failure mechanisms were closely investigated. In the creep test in air environment, three failure modes were observed for PLA depending on the temperature and stress level, namely semi-brittle, ductile, and mixed modes, which are shown in Fig. 10a. The semibrittle mode corresponds to creep failure characterized by minimal plastic deformation, whereas the ductile failure involves extensive plastic deformation and large amount of drawing. The intermediate failure mode, i.e., mixed mode, was also observed. In the scanning electron microscopy (SEM) observation, the semi-brittle fracture arises from the initiation of micro-crazes and growth, and final brittle fracture. In some specimens with ductile failures, micro-crazes were observed at the surface; however, these crazes did not grow extensively but rather exhibited a craze opening.

For PLA creep test failure mechanism in PBS solution, similar to the air-based creep, three failure mechanisms are observed: semi-brittle, ductile, and mixed modes as shown in Fig. 11a. However, at higher temperatures and relatively lower stress levels, distinct surface whitening was observed in the ductile mode in Fig. 11a. It has been observed that the whitening in PLA material, when exposed to moisture, indicates hydrolytic degradation [34]. Correspondingly, clusters of micro-pits were also observed in the microscopic analysis of these whitened specimens. Thus, it can be thought that the elevated temperature and sufficient exposure duration at lower creep stresses not only induce creep damage but also accelerate hydrolytic degradation of PLA.

Based on this definition of the failure modes, a failure mechanisms map (FMM) for the air environment testing was suggested with the SEM observations, depending on the stress level and temperature (Fig. 12). Within the semi-brittle region (37 °C, 30 MPa), the SEM images show rapid crack growth with microscopic crazes. This reflects clear brittle behavior, where the material is characterized by local absorption of energy while maintaining fracture resistance. In the brittle-ductile mixed mode region (37 °C, 20 MPa), the coexistence of brittle and ductile behavior is clear, the material gradually begins to transfer to ductile failure, but brittle elements remain. This is evidenced by the micro-crazes and slight necking observed in the SEM images. The ductile region (45 °C, 14 MPa) is characterized by significant creep deformation and clear necking at the high temperature and low stress conditions,



Fig. 13. Failure mode map (FMM) in creep testing immersed in PBS solution, with regard to applied stress level and temperature.

demonstrating the material's significant deformability and energy absorption capacity before fracture [54]. At temperatures above 50 °C, the ductile failure without micro-crazes occurred, above the 8 MPa. However, the micro-craze initiation and opening become a dominant phenomenon at low stress conditions, as shown in SEM images for 7 and 8 MPa at 50 °C [55]. It is worth noting that the knee point at the air-environment condition at 50 °C in Fig. 9 is closely related to the existence of micro-crazing at the ductile failure. That is, even when the ductile failure mode appears macroscopically identical, the occurrence of additional micro-crazing at the microscopic level results in a rapid reduction in creep lifetime, as exhibited by the knee point observed in the air creep test at 50 °C.

The dominant fracture mechanism in the PBS solution exhibits a behavior that varies with temperature and stress (Fig. 13). In the semibrittle region (37 °C, 30 MPa), the SEM images show brittle fracture accompanied by crazes. This is attributed to the interaction of hydrolysis in the PBS solution and stress concentration. A combination of brittle and ductile behavior is observed in the brittle-ductile mixed mode (37 °C, 20 MPa), where SEM images show craze with slight necking. In the ductile region, severe creep deformation and necking are observed. At relatively high stress levels in the ductile region, micro-damage, e.g., micro-crazing, was not observed (45 °C, 14 MPa). Unlike the behavior seen in the air environment, specimens exposed to PBS solution under very low stress levels in the ductile failure region, e.g., 45 °C, 3 MPa and 50 °C, 3 MPa did not exhibit mechanical damage such as micro-crazing. Instead, localized hydrolysis pits were observed on the surface, indicating the hydrolysis-induced chain scission and shrinkage [33,34,48]. SEM images show irregular erosion marks and rough surfaces, indicating chemical degradation rather than creep-induced damage. This is because the material surface becomes weaker over time due to hydrolysis, leading to a gradual degradation of performance [56].

The abovementioned FMMs for creep behavior of PLA show that there are marked differences in the fracture behavior between air and PBS solution environments due to environmental influences. In air, the failure mechanism is dominated by mechanical factors, transitioning from semi-brittle behavior at high stress levels (e.g., 37 °C, 30 MPa) to ductile behavior at intermediate stress and high temperature (e.g., 45 °C, 14 MPa), whereas crazes occur at low stress and high temperature. Conversely, hydrolysis in PBS solutions significantly impacts material performance, resulting in surface degradation under low stress and high temperature conditions (e.g., 45  $^\circ C$  and 50  $^\circ C$  at 3 MPa). SEM images illustrate these differences, showing sharp crazes and localized deformation in air, whereas hydrolysis in PBS produces porous and rough surfaces. These results reinforce the conclusion that PBS solution accelerates crack initiation, propagation, and overall material weakening compared to air environment. This result should be concerned for the PLA-based biomedical applications in the human body, requiring careful design considerations to ensure durability.

#### 3.4. Creep lifetime modeling in PBS solution and air

Based on the creep properties obtained in previous chapters, the Larson-Miller Parameter (LMP) was applied to predict the long-term behavior of PLA by considering time, temperature, and environmental conditions (PBS solution and air). The LMP is a parametric approach commonly used to extrapolate short-term creep behavior to predict long-term performance [57,58]. The LMP is defined by the following equation [59]:

$$LMP = \frac{T}{1000} (C + \log t_f).$$
<sup>(2)</sup>

In the above equation, T represents the absolute temperature (K),  $t_f$  is



Fig. 14. Larson-Miller parameter (LMP) modeling of creep rupture time in (a) PBS solution and (b) air-environment. The LMP plots for PBS solution and air mediums are compared in (c). (d) The normalized discrepancy of LMP for PBS solution and air environment against stress level. (e) and (f) compare the LMP-based prediction (dotted curves) with test data (symbols) in PBS and air environments, respectively.

the creep rupture time (h), and C is a coefficient determined empirically. To construct a single master curve, experimental data obtained under various temperature and stress conditions were superimposed by adjusting the value of C [60]. In case of the PBS solution, the stress-lifetime plots in different temperatures in Fig. 9e collapsed in one master curve at C of 70 in Eq. (2), as shown in Fig. 14a. The creep lifetime in the air environment, the parameter C of 93 construct the stress-LMP master curve as shown in Fig. 14b. That is, the resulting master curves represent the relationship between stress and the LMP, integrating time-temperature correlations depending on the creep

medium.

Based on the collapsed curves for stress-LMP, fitting was performed using an allometric quadratic equation for each environment, i.e.,

$$\sigma = a + b \cdot LMP^n \tag{3}$$

Here, the  $\sigma$  represents creep stress, and *a*, *b*, and *n* are the fitting parameters. For the air environment, the fitting parameters were determined as a = 41.95,  $b = -5.040 \times 10^{-15}$ , and n = 10.67. The fitted result is denoted by dotted curve in Fig. 14a, where the coefficient of determination (R-squared) was obtained by 0.9226. For the PBS

solution condition, the parameters were fitted by a = 53.79,  $b = -3.075 \times 10^{-13}$ , and n = 10.48, where the fitting curve is shown in Fig. 14b. The R-squared was determined by 0.9510. Through this fitting equations, one can estimate the LMP under the arbitrary creep stress at the air and PBS solution environments, by Eq. (3). Subsequently, the rupture time  $t_f$  could be also predicted through Eq. (2).

Fig. 14c illustrates that exposure to PBS solution significantly reduces the LMP value at a given stress level, reflecting the markedly shorter creep rupture time under identical temperature and stress conditions due to the diffusion-induced plasticization or hydrolysis degradation. To investigate the effect of PBS solution corresponding to the LMP modeling, the ratio of LMP differences according to stress ( $\sigma$ ) is shown in Fig. 14d. The normalized difference in the LMP depending on the medium, defined as  $(LMP_{Air} - LMP_{PBS})/LMP_{Air}$ , shows a decreasing tendency with increasing stress. It indicates that the difference in degradation rate between the two environments decreases rapidly in the high-load region. At the lower stress, on the other hand, the contacting time with the PBS solution during the creep testing becomes increased significantly, thus the magnified effect of the PBS solution in the lower stress region is manifested by the increased value of the LMP difference in Fig. 14d. That is, while the LMP-based model is suitable for predicting PLA creep life under various conditions, its performance may vary depending on environmental factors and stress levels. The creep test results of PLA according to temperature and medium were modeled using Larson-Miller Parameter (LMP). Figs. 14e-f compare the failure time experimental data and LMP-based prediction curves under various stress conditions in PBS solution and air. Through this, it was confirmed that the LMP model accurately predicts the creep lifetime of PLA.

#### 4. Conclusions

This study is the first to systematically investigate the creep behavior of PLA in PBS solution. By designing a water-environment creep tester, we were able to observe both the hydrolysis reaction of PLA and its failure mode in real time. Furthermore, the comparative creep tests in PBS solution and air reveal how environmental conditions significantly affect the long-term performance of PLA. In PBS solution, hydrolysis accelerated creep deformation and shortened the lifespan, for example, at 37  $^\circ\mathrm{C}$  and 10 MPa stress conditions, the lifespan was 15 h in PBS and 220 h in air. In both media, creep strain increased with increasing temperature and stress, but this effect was more pronounced in PBS due to hydrolysis. In addition, high temperature accelerated molecular mobility and hydrolysis reaction, which accelerated the degradation in PBS solution, which significantly shortened the lifespan compared to the oxidative degradation in air. The fracture mechanism analysis results showed that brittle failure mainly occurred at high load and low temperature in air, but it changed to ductile behavior at low load or high temperature. In contrast, in PBS solution, hydrolysis accelerated the failure due to surface degradation and water infiltration into the cracks formed during the creep.

This study also developed a predictive model using the Larson-Miller Parameter (LMP) integrated with a Failure Mechanism Map (FMM) to quantify PLA long-term reliability under various stress and temperature conditions, addressing actual service conditions of PLA implants by combining mechanical stress and exposure to body fluid. The LMP-FMM model provides a quantitative framework for predicting PLA structural stability in physiological environments, which offers design guidelines for biodegradable implants subjected to combined stress-hydrolysis interactions.

#### CRediT authorship contribution statement

**Soo-Hyun Woo:** Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Min-Gyu Jo:** Visualization, Investigation, Formal analysis. **Byeong-Heon Park:** Methodology, Data curation. **Jung-Wook Wee:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2022R1F1A1064397).

#### Data availability

Data will be made available on request.

#### References

- [1] M.C. Araque-Monrós, A. Vidaurre, L. Gil-Santos, S. Gironés Bernabé, M. Monleón-Pradas, J. Más-Estellés, Study of the degradation of a new PLA braided biomaterial in buffer phosphate saline, basic and acid media, intended for the regeneration of tendons and ligaments, Polym. Degrad. Stabil. 98 (2013) 1563–1570.
- [2] T.A. Hottle, M.M. Bilec, A.E. Landis, Sustainability assessments of bio-based polymers, Polym. Degrad. Stabil. 98 (2013) 1898–1907.
- [3] C.L. Jun, Reactive blending of biodegradable polymers: PLA and starch, J. Polym. Environ. 8 (2000) 33–37.
- [4] D. Garlotta, A literature review of poly(lactic acid), J. Polym. Environ. 9 (2001) 63–84.
- [5] C.-C. Chen, J.-Y. Chueh, H. Tseng, H.-M. Huang, S.-Y. Lee, Preparation and characterization of biodegradable PLA polymeric blends, Biomaterials 24 (2003) 1167–1173.
- [6] S. Farah, D.G. Anderson, R. Langer, Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review, Adv. Drug Deliv. Rev. 107 (2016) 367–392.
- [7] S. Mangaraj, A. Yadav, L.M. Bal, S.K. Dash, N.K. Mahanti, Application of biodegradable polymers in food packaging industry: a comprehensive review, J. Packag. Technol. Res 3 (2019) 77–96.
- [8] K.J. Jem, B. Tan, The development and challenges of poly (lactic acid) and poly (glycolic acid), Adv. Ind. Eng. Polym. Res. 3 (2020) 60–70.
- [9] R. Mori, Replacing all petroleum-based chemical products with natural biomassbased chemical products: a tutorial review, RSC Sustain. 1 (2023) 179–212.
- [10] I. Vroman, L. Tighzert, Biodegradable polymers, Materials (Basel) (2009) 307–344.
  [11] A. Samir, F.H. Ashour, A.A.A. Hakim, M. Bassyouni, Recent advances in
- biodegradable polymers for sustainable applications, npj Mater. Degrad. 6 (2022) 68.
- [12] P.B. Maurus, C.C. Kaeding, Bioabsorbable implant material review, Operat. Tech. Sports Med. 12 (2004) 158–160.
- [13] I. Armentano, N. Bitinis, E. Fortunati, S. Mattioli, N. Rescignano, R. Verdejo, M. A. Lopez-Manchado, J.M. Kenny, Multifunctional nanostructured PLA materials for packaging and tissue engineering, Prog. Polym. Sci. 38 (2013) 1720–1747.
- [14] K.L. Ong, B.M. Yun, J.B. White, New biomaterials for orthopedic implants, Orthop. Res. Rev. 7 (2015) 107–130.
- [15] J.S. Bergström, D. Hayman, An overview of mechanical properties and material modeling of polylactide (PLA) for medical applications, Ann. Biomed. Eng. 44 (2016) 330–340.
- [16] B. Tyler, D. Gullotti, A. Mangraviti, T. Utsuki, H. Brem, Polylactic acid (PLA) controlled delivery carriers for biomedical applications, Adv. Drug Deliv. Rev. 107 (2016) 163–175.
- [17] D. da Silva, M. Kaduri, M. Poley, O. Adir, N. Krinsky, J. Shainsky-Roitman, A. Schroeder, Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems, Chemical Engineering Journal 340 (2018) 9–14.
- [18] V. DeStefano, S. Khan, A. Tabada, Applications of PLA in modern medicine, Eng. Regen. 1 (2020) 76–87.
- [19] Y. Zare, K.Y. Rhee, Effects of interphase regions and filler networks on the viscosity of PLA/PEO/carbon nanotubes biosensor, Polym. Compos. 40 (2019) 4135–4141.
- [20] Y. Zare, S. Rhim, H. Garmabi, K.Y. Rhee, A simple model for constant storage modulus of poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites at low frequencies assuming the properties of interphase regions and networks. J. Mech. Behav. Biomed. Mater. 80 (2018) 164–170.
- [21] Y. Zare, K.Y. Rhee, Modeling of viscosity and complex modulus for poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites assuming yield stress and network breaking time, Compos. B Eng. 156 (2019) 100–107.
- [22] M. Vert, S. Li, H. Garreau, More about the degradation of LA/GA-derived matrices in aqueous media, J. Contr. Release 16 (1991) 15–26.

#### S.-H. Woo et al.

- [23] A. Göpferich, Mechanisms of polymer degradation and erosion, in: D.F. Williams (Ed.), The Biomaterials: Silver Jubilee Compendium, Elsevier Science, Oxford, 1996, pp. 117–128.
- [24] H. Tsuji, Y. Ikada, Properties and morphology of poly(l-lactide) 4. Effects of structural parameters on long-term hydrolysis of poly(l-lactide) in phosphatebuffered solution, Polym. Degrad. Stabil. 67 (2000) 179–189.
- [25] X. Niu, Q. Feng, M. Wang, X. Guo, Q. Zheng, In vitro degradation and release behavior of porous poly(lactic acid) scaffolds containing chitosan microspheres as a carrier for BMP-2-derived synthetic peptide, Polym. Degrad. Stabil. 94 (2009) 176–182.
- [26] R.M. Felfel, K.M.Z. Hossain, A.J. Parsons, C.D. Rudd, I. Ahmed, Accelerated in vitro degradation properties of polylactic acid/phosphate glass fibre composites, J. Mater. Sci. 50 (2015) 3942–3955.
- [27] A. Leonés, L. Peponi, M. Lieblich, R. Benavente, S. Fiori, In vitro degradation of plasticized PLA electrospun fiber mats: morphological, thermal and crystalline evolution, Polymers (Basel) 14 (2020) 2975.
- [28] S. Kim, Y. Zare, H. Garmabi, K.Y. Rhee, Variations of tunneling properties in poly (lactic acid) (PLA)/poly (ethylene oxide) (PEO)/carbon nanotubes (CNT) nanocomposites during hydrolytic degradation, Sensor Actuator Phys. 274 (2018) 28–36.
- [29] A. Höglund, K. Odelius, A.-C. Albertsson, Crucial differences in the hydrolytic degradation between industrial polylactide and laboratory-scale poly(L-lactide), ACS Appl. Mater. Interfaces 4 (2012) 2788–2793.
- [30] M. Polidar, E. Metzsch-Zilligen, R. Pfaendner, Controlled and accelerated hydrolysis of polylactide (PLA) through pentaerythritol phosphites with acid scavengers, Polymers (Basel) 14 (2022) 4237.
- [31] L. Bauer, A. Rogina, M. Ivanković, H. Ivanković, Medical-grade poly(lactic acid)/ hydroxyapatite composite films: thermal and in vitro degradation properties, Polymers (Basel) 15 (2023) 1512.
- [32] F. Ng, V. Nicoulin, C. Peloso, S. Curia, J. Richard, A. Lopez-Noriega, In vitro and in vivo hydrolytic degradation behaviors of a drug-delivery system based on the blend of PEG and PLA copolymers, ACS Appl. Mater. Interfaces 15 (2023) 55495–55509.
- [33] S. Lee, J.-W. Wee, Effect of temperature and relative humidity on hydrolytic degradation of additively manufactured PLA: characterization and artificial neural network modeling, Polym. Degrad. Stabil. 230 (2024) 111055.
- [34] S.-H. Woo, J.-W. Wee, Characterization of accelerated hydrolysis degradation of poly (lactic acid) in phosphate buffered saline solution, Polym. Degrad. Stabil. 223 (2024) 110726.
- [35] A.F. Balogová, M. Trebuňová, D. Bačenková, M. Kohan, R. Hudák, T. Tóth, M. Schnitzer, J. Živčák, Impact of in vitro degradation on the properties of samples produced by additive production from PLA/PHB-based material and ceramics, Polymers (Basel) 14 (2022) 5441.
- [36] X. Yuan, A.F.T. Mak, K. Yao, In vitro degradation of poly(L- lactic acid) fibers in phosphate buffered saline, J. Appl. Polym. Sci. 85 (2002) 936–943.
- [37] X. Yuan, A.F.T. Mak, K. Yao, Comparative observation of accelerated degradation of poly(l-lactic acid) fibres in phosphate buffered saline and a dilute alkaline solution, Polym. Degrad. Stabil. 75 (2002) 45–53.
- [38] T. Tábi, S. Hajba, J.G. Kovács, Effect of crystalline forms (α' and α) of poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties, Eur. Polym. J. 82 (2016) 232–243.
- [39] O.H. Ezeh, L. Susmel, Fatigue strength of additively manufactured polylactide (PLA): effect of raster angle and non-zero mean stresses, Int. J. Fatig. 126 (2019) 319–326.
- [40] Y. Zare, K.Y. Rhee, S.-J. Park, Simple model for hydrolytic degradation of poly (lactic acid)/poly(ethylene oxide)/carbon nanotubes nanobiosensor in neutral phosphate-buffered saline solution, J. Biomed. Mater. Res. 107 (2019) 2706–2717.

- [41] H. Deplaine, V.A. Acosta-Santamaría, A. Vidaurre, J.L. Gómez Ribelles, M. Doblaré, I. Ochoa, G. Gallego Ferrer, Evolution of the properties of a poly(l-lactic acid) scaffold with double porosity during in vitro degradation in a phosphate-buffered saline solution, J. Appl. Polym. Sci. 131 (2014).
- [42] S. Moon, J.-M. Kim, J.-Y. Kwon, B.-S. Lee, K.-J. Choi, M.-C. Kim, Creep strain modeling for alloy 690 SG tube material based on modified theta projection method, Nucl. Eng. Technol. 54 (2022) 1570–1578.
- [43] R. Sandström, Basic Analytical Modeling of Creep Strain Curves, Materials, 2023.[44] M.E. Kassner, Taylor hardening in five-power-law creep of metals and Class M
- alloys, Acta Mater. 52 (2004) 1-9. [45] J.-W. Wee, Y. Zhao, B.-H. Choi, Observation and modeling of environmental stress
- cracking behaviors of high crystalline polypropylene due to scent oils, Polym. Test. 48 (2015) 206–214.
- [46] A.A. Fahmy, J.C. Hurt, Stress dependence of water diffusion in epoxy resin, Polym. Compos. 1 (1980) 77–80.
- [47] D. Rasselet, A. Ruellan, A. Guinault, G. Miquelard-Garnier, C. Sollogoub, B. Fayolle, Oxidative degradation of polylactide (PLA) and its effects on physical and mechanical properties, Eur. Polym. J. 50 (2014) 109–116.
- [48] W. Limsukon, M. Rubino, M. Rabnawaz, L.-T. Lim, R. Auras, Hydrolytic degradation of poly(lactic acid): unraveling correlations between temperature and the three phase structures, Polym. Degrad. Stabil. 217 (2023) 110537.
- [49] S. Tolga, S. Kabasci, M. Duhme, Progress of disintegration of polylactide (PLA)/ Poly(Butylene succinate) (PBS) blends containing talc and chalk inorganic fillers under industrial composting conditions, Polymers (Basel) 13 (2021) 10.
- [50] O. Dogan, Short-term creep behaviour of different polymers used in additive manufacturing under different thermal and loading conditions, Strojniški vestnik -J. Mech. Eng. 68 (2022) 451–460.
- [51] Y.-S. Jhao, H. Ouyang, F. Yang, S. Lee, Thermo-mechanical and creep behaviour of polylactic acid/thermoplastic polyurethane blends, Polymers (Basel) 14 (2022) 5276.
- [52] T.H. Smit, T.A.P. Engels, S.H.M. Söntjens, L.E. Govaert, Time-dependent failure in load-bearing polymers: a potential hazard in structural applications of polylactides, J. Mater. Sci. Mater. Med. 21 (2010) 871–878.
- [53] J. Esmaeilzadeh, S. Hesaraki, N.H. Ebrahimzadeh, G.H. Asghari, A.R. Kachooei, Creep behavior of biodegradable triple-component nanocomposites based on PLA/ PCL/bioactive glass for ACL interference screws, Arch Bone Jt Surg 7 (2019) 531–537.
- [54] N. Tan, P.Y. Ben Jar, Deformation transitions of ethylene-hexene copolymers under creep loading, Polymer 208 (2020) 122905.
- [55] Y. Sasaki, Y. Nishizawa, T. Watanabe, T. Kureha, K. Uenishi, K. Nakazono, T. Takata, D. Suzuki, Nanoparticle-based tough polymers with crack-propagation resistance, Langmuir 39 (2023) 9262–9272.
- [56] E. Linde, N.H. Giron, M.C. Celina, Diffusion-limited hydrolysis in polymeric materials, Polym. Degrad. Stabil. 204 (2022) 110095.
- [57] X. Duan, H. Yuan, W. Tang, J. He, X. Guan, A phenomenological primary-secondary-tertiary creep model for polymer-bonded composite materials, Polymers (Basel) 13 (2021) 2353.
- [58] D. Gibhardt, A.E. Krauklis, A. Doblies, A. Gagani, A. Sabalina, O. Starkova, B. Fiedler, Time, temperature and water aging failure envelope of thermoset polymers, Polym. Test. 118 (2023) 107901.
- [59] M. Amjadi, A. Fatemi, Creep behavior and modeling of high-density polyethylene (HDPE), Polym. Test. 94 (2021) 107031.
- [60] O. Starkova, A.I. Gagani, C.W. Karl, I.B.C.M. Rocha, J. Burlakovs, A.E. Krauklis, Modelling of environmental ageing of polymers and polymer composites—durability prediction methods, Polymers (Basel) 14 (2022) 907.