Biodegradability Assessment of 3D Printed Polycaprolactone (PCL) for Coronary Stent Applications

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Abstract. Coronary artery stents, such as bare metal stents and drug-eluting stents, have limitations due to their permanent nature, potentially leading to late stent failure. Bioresorbable stents (BRS), made from materials like polycaprolactone (PCL), offer a solution by degrading completely over time. This study investigates how 3D printing parameters affect the degradation rate of PCL stents. Samples were immersed in simulated body fluid (SBF) for 33 days, and degradation was measured by stent weight and dimensions. The results show significant weight loss and varying degradation rates depending on nozzle temperature (T_N), flow rate percentage (P_{FR}), and printing speed (S_P). These findings highlight the impact of 3D printing parameters on PCL stent degradation, providing valuable insights for optimizing BRS fabrication for coronary applications.

Keywords: Coronary artery stents, bioresorbable stents, polycaprolactone (PCL), 3D printing, degradation rate.

1 Introduction

Industry 4.0 includes additive manufacturing, notably 3D printing, which is widely used in prototyping and manufacturing, especially for medical devices. Fused Deposition Modeling (FDM) is the most common method, being simple, solvent-free, and costeffective [1]. Coronary artery disease, often treated with Percutaneous Coronary Intervention, involves using stents to improve blood flow in blocked arteries. These

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stents can be made from PCL, a biodegradable, biocompatible polyester ideal for controlled drug release [2]. The degradation rate of PCL, influenced by molecular weight and crystallinity, is crucial for biomedical stents. It is assessed through weight loss, swelling, temperature behavior, molecular weight changes, and mechanical properties [3, 4]. As known, the 3D printing parameter will affect the degradation of the stent [5, 6]. Therefore, this study aims to: (1) examine how 3D printing parameters (T_N, P_{FR}, and S_P) affect the degradation rate of PCL stents, and (2) identify optimal 3D printing parameters for desired degradation characteristics. By investigating these factors, the research seeks to improve the understanding and performance of PCL stents in biomedical applications.

2 Material and Method

2.1 Experimental Work

This research methodology is divided into three phases: experimental, characterization, and analysis. In the experimental phase, PCL samples with a 1.75 mm diameter were printed using an Artillery Genius PRO FDM 3D printer. The stent design, created in SOLIDWORKS (**Fig. 1**), had a stent length (L_S) of 16.47 mm, strut thickness (T_S) of 1.0 mm, and strut width (W_S) of 0.5 mm. Printing parameters were set using the One Factor at a Time method (**Table 1**). During characterization, the L_S, T_S, and W_S were measured, and degradation was assessed after the immersion of SBF. In the final analysis phase, degradation metrics such as weight, degradation speed, location, and dimensional changes were examined, and critical 3D printing parameters were analyzed to achieve the desired outcomes, with trends plotted based on the findings.

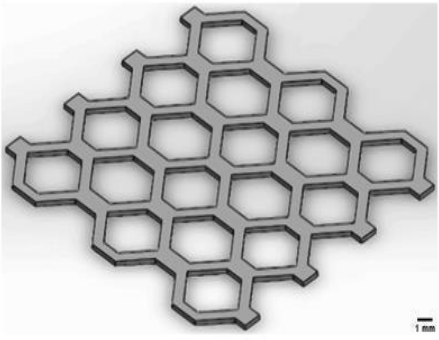


Fig. 1. Stent design.

Table 1. Design of Experiment by using OFAT method.

Run	T_N	S_P	P_{FR}	Run	T_N	S_P	P_{FR}	Run	T_N	S_P	P_{FR}
1	70	100	60	10	100	80	60	19	100	100	70
2	80	100	60	11	100	90	60	20	100	100	80
3	90	100	60	12	100	100	60	21	100	100	90
4	100	100	60	13	100	110	60	22	100	100	100
5	110	100	60	14	100	120	60	23	100	100	110
6	120	100	60	15	100	130	60	24	100	100	120
7	130	100	60	16	100	140	60	25	100	100	130
8	140	100	60	17	100	150	60	26	100	100	140
9	100	70	60	18	100	100	60	27	100	100	150

2.2 Preparation of SBF

SBF solutions are prepared by dissolving the following reagent grade chemicals based on the sequence given in Table 2. These solutions are prepared based on Kokubo method [7].

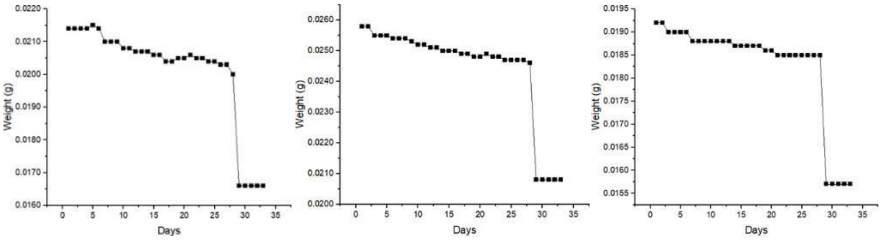
Table 2. Reagent grade chemicals for SBF solution.

Sequence	Reagent	Amount
1	Sodium chloride (NaCl)	8.035g
2	Sodium hydrogen carbonate (NaHCO3)	0.355g
3	Potassium chloride (KCl)	0.225g
4	Di-potassium hydrogen phosphate trihydrate (K2HPO43H2O)	0.231g
5	Magnesium chloride hexahydrate (MgCl2.6H2O)	0.311g
6	Calcium chloride (CaCl2)	0.292g
7	Sodium sulfate (Na2SO4)	0.072g
8	Tris-hydroxymethyl aminomethane ((HOCH2)3CNH2)	6.118g

3 Result and Discussion

3.1 Weight and Dimension of Sample After Experiment

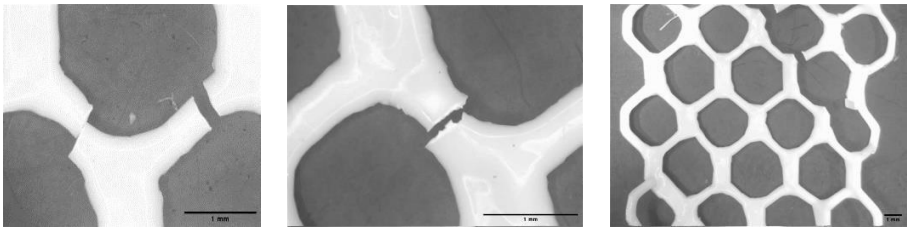
As PCL undergoes hydrolysis, ester bonds are cleaved, leading to degradation byproducts and a reduction in the stent's molecular weight and weight. In this experiment, stent weight was measured daily for 33 days. The consistent sample size throughout the period suggests the stent's potential to effectively support blood vessels. Notably, **Fig. 2** shows a significant weight decrease on the 29th day for samples 14, 17, and 21, indicating a critical stage in the polymer's breakdown. This sudden weight drop suggests a marked shift in degradation behavior due to the decreasing molecular weight. As PCL degrades, its mechanical strength and integrity diminish, increasing the risk of stent fracture if degradation exceeds its structural capacity.



(a) (b) (c)

Fig. 2. The weight of sample vs the day of the experiment (a) sample 14, (b) sample 17, and (c) sample 21.

During the degradation of a PCL stent, dimensional changes occur due to the reduction in molecular weight and polymer chain length, causing the stent to shrink. **Fig. 3** shows fractures in the strut of samples 14, 17, and 21 after 33 days, likely due to hydrolysis or enzymatic breakdown, which weaken the stent structure. External factors such as mechanical stresses and environmental conditions may also have contributed to these fractures.



(a) (b) (c)

Fig. 3. Structure of (a) sample 14, (b) sample 17, and (c) sample 21 after 33-days immersed.

3.2 Simulated Body Fluid (SBF) pH Change

During the PCL degradation, the pH of SBF can change as the polymer degrades and releases acidic substances, leading to a gradual decrease. Thus, in this study, pH measurements were recorded using pH meters to measure the degradation reaction of PCL stent. **Fig. 4** shows the pH values of the SBF during the immersion period. Initially, the pH of the SBF solution was 7.42, which was within the expected range. After one week, the pH slightly increased to 7.45, which might be due to hydroxyapatite neutralizing the acidic by-products of PCL degradation. However, starting in the second week, the pH began to decrease, reaching 7.37 and continuing to decline until the fifth week. This gradual decrease was attributed to the hydrolysis of PCL, which released acidic compounds that exceeded the solution's buffering capacity.

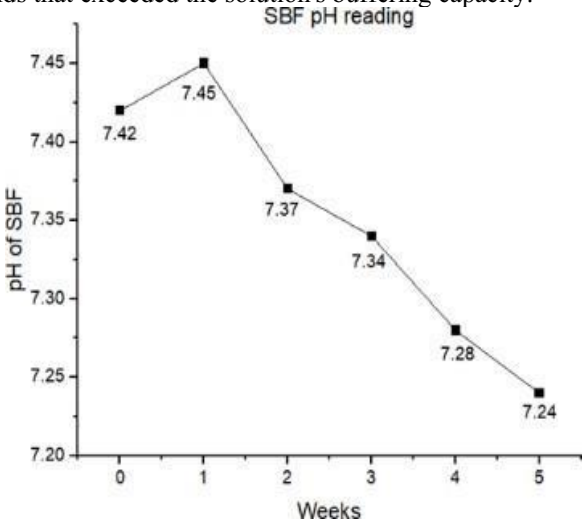


Fig. 4. The pH of the SBF solution

3.3 Rate of Degradation

The degradation rate, which measures how quickly a material breaks down over time, is typically expressed in units such as mass loss or molecular weight reduction per unit time. To evaluate weight loss and dimensional changes, samples were maintained at a constant temperature of 25 ℃ throughout the experiment. Initially, the samples underwent three consecutive weighing sessions to establish a baseline weight (W_0) before immersion in the SBF. After a 33-day immersion period, the samples were retrieved and weighed again, with the final weight (W_r). This final weight measurement allowed for the calculation of the weight loss percentage (W_L%) experienced by the samples during the degradation period, using Equation (1).

$$W_L\% = ((W_0 - W_r) / W_0) \times 100\% \quad (1)$$

Fig. 5 presents a comparative analysis of the degradation rates among various samples, with each sample represented by a distinct data point on the graph. Notably,

samples 14, 17, and 21 exhibit higher degradation rates, indicating a more rapid degradation process over the 33-day immersion period. In contrast, sample 11 demonstrates the lowest degradation rate, suggesting greater stability and resistance to degradation under the experimental conditions. Meanwhile, the data presented in Fig. 6 (a, b, and c) indicate that the slow degradation rate of PCL material is best achieved with specific parameter values: a T_N of 140 °C, a P_{FR} of 90%, and a S_P of 150 mm/s. These settings demonstrated optimal degradation rates compared to other parameter values, balancing degradation and structural integrity. Consequently, PCL stents printed with these parameters exhibited a controlled and gradual degradation process, making them suitable for their intended application.

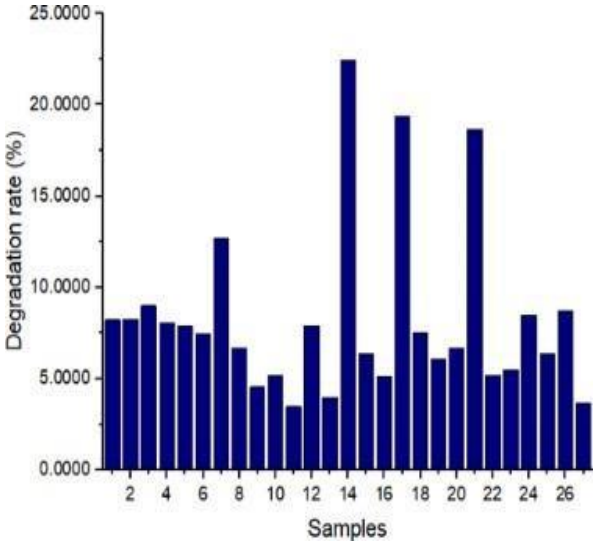
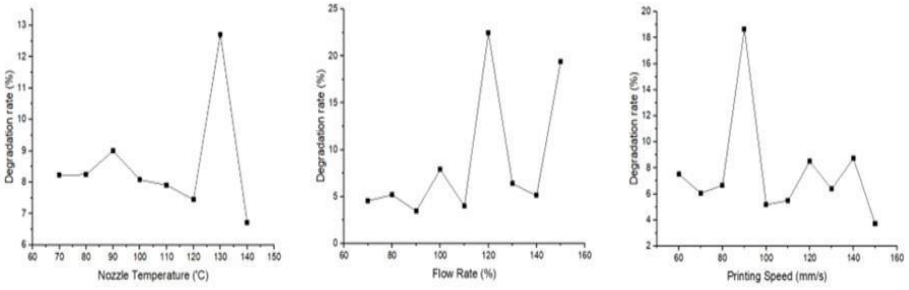


Fig. 5. The degradation rate of each sample immersed in SBF



(a) (b) (c)

Fig. 6. (a) The degradation rate vs TN, (b) The degradation rate vs PFR, and (c) The degradation rate vs SP.

4 Conclusion

This study examined how 3D printing parameters (T_N, S_P, P_{FR}) influence the degradation rate of PCL stents for coronary applications. The findings highlight the significant impact of specific printing parameters on stent degradation. The results revealed that a P_{FR} of 130% resulted in a higher degradation rate, whereas 90% led to the lowest rate.

Besides, a T_N of 130 ℃ showed higher degradation compared to 140 ℃, and a higher S_P of 150 mm/s correlated with lower degradation. Optimizing these parameters—specifically, a T_N of 140 ℃, a P_{FR} of 90%, and a S_P of 150 mm/s—achieved the desired degradation characteristics of BRS. However, these optimal parameters are specific to the conditions and 3D printing system used in this study. Future research should include longer-term degradation studies beyond 33 days to understand long-term performance. Additionally, studying the biodegradation of 3D-printed stents in vitro or using an incubator shaker can provide further insights, helping to optimize the design of biodegradable stents for improved clinical outcomes.

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