

The influence of Silane Coupling Agent and porogen ratio on 3D scaffold PCL/HA

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Abstract

The design of scaffold based on polycaprolactone (PCL) and hydroxyapatite (HA) has attracted attention as a solution for bone tissue regeneration. However, the main challenge in its development is the difficulty in achieving an optimal balance between porosity and mechanical strength. Suboptimal porosity limits the scaffold ability to support cell proliferation, and weak mechanical properties result in the scaffold being less than optimal as a load-bearing implant material during the bone cell regeneration process. This study aims to address these issues by evaluating the effects of the silane coupling agent 3-aminopropyltriethoxysilane (APTES) and the porogen ratio (NaCl) on the mechanical properties, morphology, and biodegradation of PCL-HA-based 3D scaffold. The scaffold were synthesized using the solvent casting/particulate leaching (SCPL) method with varying APTES concentrations (1%, 3%, and 5%) and porogen ratios. (4:1, 6:1, and 8:1). The results of characterization show that the addition of 1% APTES increases compressive strength by 283% and tensile strength by 138% compared to scaffold without APTES. A higher porogen ratio (8:1) results in the highest porosity of 78.16%, but reduces mechanical strength by 84%. The optimal combination was found in scaffold with 1% APTES and a porogen ratio of 4:1, which have optimal mechanical strength, porosity of 69.65%, and a biodegradation time of up to 380 days. This research offers a comprehensive solution to enhance the properties of PCL-HA based 3D scaffold, making a significant contribution to the development of materials for bone tissue engineering applications.

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INTRODUCTION

Bone is one of the most important tissues in the human body because it serves as a support for the body and as a protector of vital organs [1][2]. However, various conditions such as degenerative diseases, trauma, and infections can cause significant fractures or bone damage. Bone fractures occur when the pressure received by the bone exceeds its elasticity limit, resulting in cracks to breaks [3, 4, 5].

Bone tissue engineering offers innovative solutions for the treatment of complex fractures.

The main focus in this field is the development of three-dimensional (3D) scaffold-based implant structures that can support the bone regeneration process [6][7]. These scaffold are designed to support the adhesion and proliferation of osteogenic cells, facilitate the differentiation of cells into osteoblasts, support the transport of nutrients and waste disposal through structured pores, and provide a physical framework that can be gradually degraded and replaced by new bone tissue [3][8].

To fulfill these functions, scaffold must possess appropriate properties, including biocompatibility, osteoconductivity, bioactivity, biodegradability, and adequate mechanical strength. Research shows that the optimal porosity for cancellous bone is in the range of 60–90%, while pore sizes between 200–350 μm are most ideal for bone tissue regeneration [9].

Poly(ϵ -caprolactone) (PCL) and Hydroxyapatite (HA) are materials widely used in the development of 3D scaffold for bone tissue engineering. The combination polymers (PCL) and HA provide unique advantages. PCL is a synthetic polymer with high biodegradability, mechanical flexibility, and good thermal and chemical stability [9, 10, 11, 12]. However, PCL has low hydrophilic properties, which can directly affect cell adhesion. Whereas HA is a bioactive ceramic with a chemical composition similar to natural bone minerals. HA provides excellent osteoconductivity and bioactivity, supporting cell adhesion and differentiation. However, the brittle mechanical properties of HA pose a challenge, so the combination of PCL and HA offers an optimal solution, namely the flexibility and mechanical strength of PCL along with the bioactivity of HA [3].

Fabrication techniques play a crucial role in determining the morphology, porosity, and mechanical performance of scaffold. One of the most popular techniques is solvent casting/particulate leaching (SCPL), where porogens such as salt are used to create a porous structure. The advantages of SCPL include a simple process, good control over pore size and porosity, and the ability to produce interconnected pores essential for nutrient transport and cell proliferation [13, 14, 15].

Previous studies have shown that the porogen-to-composite material ratio significantly affects the structure and mechanical properties of scaffold. The higher the porogen ratio, the greater the porosity, but the mechanical strength tends to decrease [16, 17, 18]. Therefore, optimizing the porogen ratio becomes a critical aspect in the design of scaffold that meet clinical needs.

To enhance the interaction between the PCL matrix and HA particles, the use of silane coupling agents such as 3-aminopropyltriethoxysilane (APTES) has become the subject of research. APTES can enhance the chemical bonds between organic and inorganic components through the formation of siloxane bonds [17]. Studies show that the addition of APTES can enhance the tensile and compressive strength of scaffold, strengthen the material interface, thereby reducing the biodegradation rate, and supporting long-term morphological

stability [19][20]. However, an excessively high number of APTES can cause uneven reactions, resulting in a decrease in mechanical strength and material stability. Therefore, further research is needed to determine the optimal APTES concentration.

Although developments in this field have been significant, several challenges still need to be addressed, such as optimizing the combination of porosity and mechanical strength to meet specific clinical needs, enhancing the bioactivity of PCL without compromising its mechanical properties, and determining the porogen ratio and APTES concentration that yield the best morphology and performance. Until now, many studies have focused on the influence of only one parameter, such as morphology or bioactivity. The combination of parameters, including porogen ratio, APTES concentration, and fabrication techniques, has not yet been comprehensively explored [6][21].

This research aims to evaluate the influence of variations in porogen ratio and APTES concentration on the morphology, mechanical properties, and biodegradation capability of PCL/HA-based scaffold fabricated using the SCPL method. This study combines experimental and theoretical analyses to determine the optimal combination of porogen ratio and APTES concentration to produce 3D scaffold with appropriate mechanical strength and porosity.

The results of this research are expected to not only expand knowledge in the field of tissue engineering, particularly bone, but also provide practical references for the development of bone implants based on 3D scaffold in the future.

METHOD

The HA modification process was carried out by dissolving it with APTES according to its variations (1%, 3%, and 5% relative to the weight of HA) using 90% ethanol and 10% deionized water for 15 minutes at a speed of 500 rpm at room temperature. Then adjusted with NaOH to pH 10 and stirred for 2 hours at 40°C. Finally, filtered and heated at 50°C for 24 hours to obtain the modified HA/APTES powder.

Figure 1 illustrates the schematic procedure of the research flow, while Table 1 presents the sample variation codes used in this study. 3D scaffold fabrication was carried out using the solvent casting/particulate leaching technique (SCPL). 1gram of PCL is dissolved in 10ml of

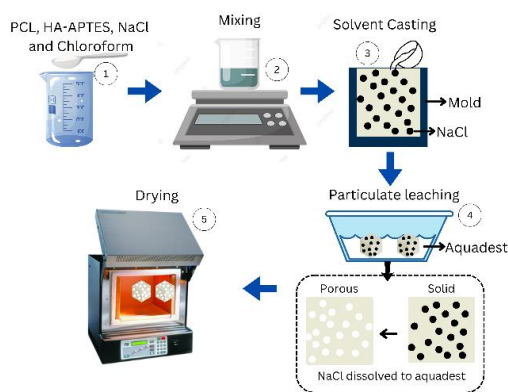


Figure 1 Schematic of the research procedure

Table 1. Sample Variation Code

Specimen	Variation	
	APTES (%)	Ratio Porogen (NaCl : PCL-HA)
A0N4	0	4:1
A1N4	1	4:1
A3N4	3	4:1
A5N4	5	4:1
A3N6	3	6:1
A3N8	3	8:1

chloroform, then 0.25 grams of HA modified with APTES according to its variations (1%, 3%, and 5%) are added. Next, NaCl with a ratio to the composite (PCL/HA) of 4:1, 6:1, and 8:1 was added and stirred at a speed of 1000 rpm for 30 minutes. Then the solution is dried in silicone molds. After the solid composite is formed, it is soaked for 2 days using deionized water, which is replaced every 12 hours to remove the NaCl porogen. After that, the samples were dried at a temperature of 50°C for 48 hours. The schematic procedure of the research flow is presented in Figure 1 and Table 1 show the sample variation code uses.

MATERIAL

PCL CAPA-6800 (Mw = 80,000, density = 1.14 g/cm³) from petroshop, Hydroxyapatite (HA) with particle size 10×200 nm from sigma-aldrich, Sodium chloride from Merck, and 3-aminopropyltriethoxysilane (APTES) from Guangzhou Double Peach Fine Chemical Co., Ltd.

FTIR test was performed using the Thermo Scientific Nicolet IS10 instrument with a wavelength of 400-4000 cm⁻¹. Digital microscope performed using MIK USB U500X LED with magnification 50-500x.

Tensile and compressive test using the Universal Testing Machine Hung ta HT 2402 Seri 4035 with the speed 2 mm/min. Tensile test is conducted using the ASTM D638 type 1 standard.

Compressive test conducted using ASTM D5024-95 standard (height:diameter equals 2:1).

To determine the 3D scaffold biodegradation rate, an in vitro Hydrolysis Biodegradation test was conducted. It was performed by immersing the specimen in Phosphate Buffer Solution (PBS) with the same temperature as the body (37°C). The samples were weighed before immersion and 5, 10, and 15 days after. Finally, the following (1) is used to measure weight loss:

$$W = \left(\frac{mb - ma}{mb} \right) \times 100 \% \quad (1)$$

where *ma* and *mb* are the measured mass after and before immersion, respectively. After the weight loss value is obtained, the lifetime of the sample is predicted using the linear regression method, and the test specimen is in the form of a cube with side length 1 cm.

RESULTS AND DISCUSSION

Figure 2 shows the results of the FTIR test on the HA/APTES modification, where several peaks belonging to the functional groups of HA and APTES are observed. There are 3 waves with strong intensities, namely at 1025.68 cm⁻¹, 599.53 cm⁻¹, and 561.74 cm⁻¹, which indicate the presence of P-O asymmetrical stretching and P-O symmetrical stretching bonds in the phosphate ion (PO₄³⁻). The peak at 1419.49 cm⁻¹ shows the C=O asymmetrical stretching bond in the carbonate ion. (CO₃²⁻). The FTIR characterization results can confirm that hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] is present, although there are no OH bonds because the OH bonds are presumed to have formed siloxane bonds.

At the wave peak of 470.62 cm⁻¹, there is a Si-O-Si bending siloxane bond, at 1654.594 cm⁻¹ and 1510.053 cm⁻¹, there are N-H deformation and bending bonds, at 790.7048 cm⁻¹, there is a Si-O bending bond, and at 873.04 cm⁻¹, there is a Si-N bond indicating that silanol forms a siloxane bond with the NH₂ group located on the surface of hydroxyapatite. Additionally, there is a possibility of overlap between the phosphate functional group and siloxane in the 1130-1000 cm⁻¹ region due to the strong intensity of the phosphate group in that region [22][23]. The results of this test indicate that APTES successfully bonded with hydroxyapatite, as evidenced by the presence of the NH₂ group that can bond with PCL which is also consistent with research conducted by Biggeman et al. [24]. Figures 3 and 4 present the results obtained from the SEM analysis.

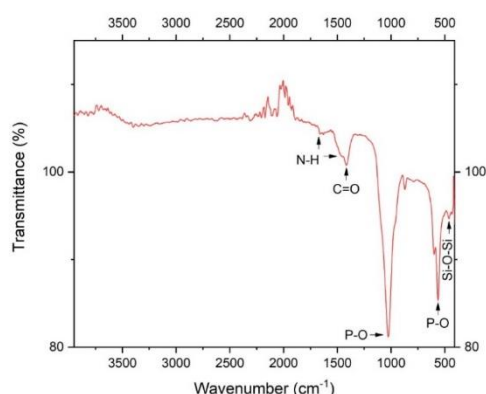


Figure 2. Fourier transforms infrared spectroscopy (FTIR) spectra of HA/APTES

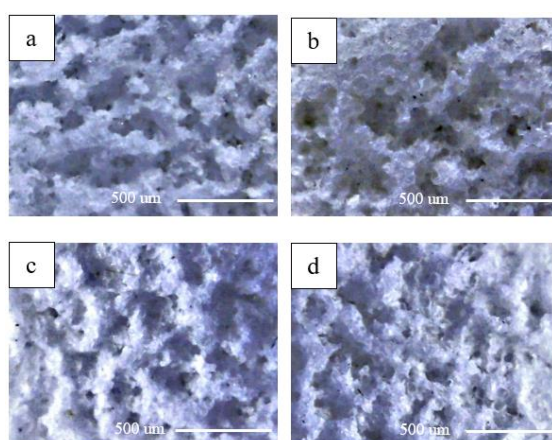


Figure 3. Result of digital microscope on samples (a) A0N4, (b) A1N4, (c) A3N4, and (d) A5N4

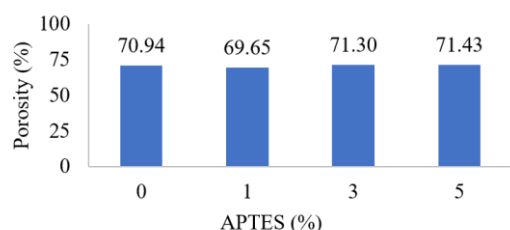


Figure 4. Effect of APTES on porosity

From Figure 3, it can be seen that the morphology of all samples has evenly distributed pores, and the addition of the silane coupling agent (APTES) up to 5% does not cause significant differences. Figure 4 shows the results of the porosity percentage analysis using ImageJ software, which indicates that the addition of APTES has relatively the same porosity values across all APTES variations, with a change range only 1.78%. Therefore, it can be concluded that the addition of the APTES binding agent does not have a significant effect on the morphology of porosity [25].

In Figure 5, the morphology of all samples shows a uniform distribution of porosity, indicating that the method used has appropriate parameters to produce a homogeneous 3D scaffold. Figure 6 shows the analysis results using ImageJ, indicating that with the addition of a 4:1 ratio of NaCl to the composite (PCL/HA) up to 6:1 and 8:1, the porosity increased to 74.53% and 78.16%, respectively. From these results, it can be concluded that the higher the amount of porogen used, the greater the increase in porosity. This occurs because the NaCl used as a porogen dissolves and acts as a space holder, so the more NaCl used, the more the space holder, which then becomes porosity (pores), will increase [26].

The standard application of 3D scaffold for bone implants has a porosity value of 50-90%. Therefore, based on these test results, all samples have met the minimum requirements as 3D scaffold implants [9].

Figure 7 shows the tensile test results on APTES variations, indicating that the addition of APTES increases tensile strength with the highest values occurring in sample A1N4 using 1% APTES, showing a tensile strength increase of 138%. However, adding more than 1% results in a decrease of up to 25% in the 5% APTES variation. Based on this, it can be concluded that APTES can enhance tensile strength by strengthening the interface bonds in the composite. However, excessive APTES addition will cause some APTES to not form good bonds due to incomplete hydrolysis reactions. A surplus of APTES will be distributed within the composite as free molecules. These free molecules cause a decrease in the mechanical properties of the 3D PCL/HA composite scaffold [27][28].

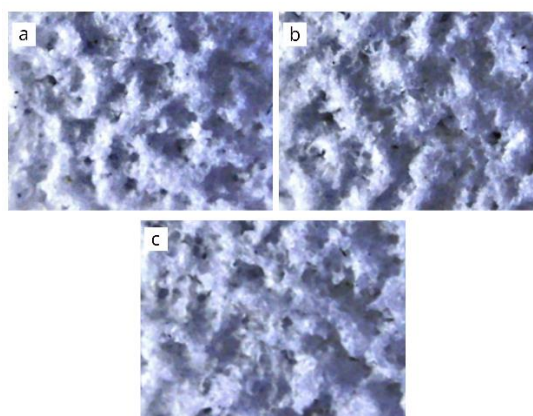


Figure 5. Result of digital microscope on samples (a) A3N4, (b) A3N6, and (c) A3N8

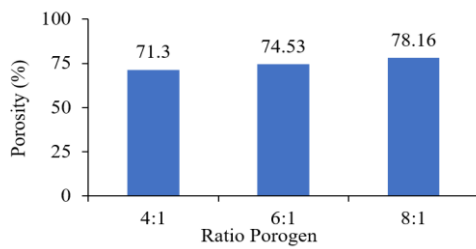


Figure 6. Effect ratio porogen on Porosity

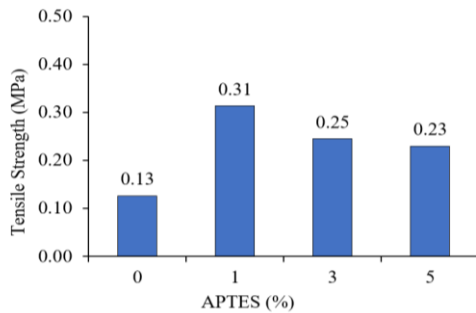


Figure 7. Effect APTES on Tensile Strength

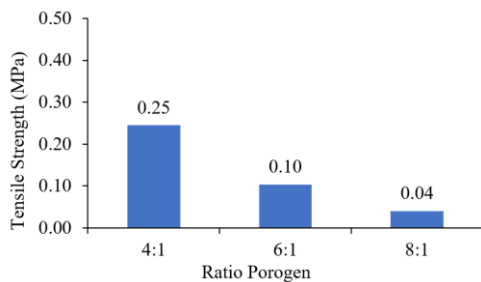


Figure 8. Effect Ratio Porogen on Tensile Strength

Figure 8 shows the tensile test results at various porogen ratios, indicating that as the porogen ratio increases, the tensile strength values decrease. The highest decrease occurs at a ratio of 8:1 between the porogen (NaCl) and the composite (PCL/HA), which is 84%. This occurs because NaCl, as the space holder agent used, dissolves during the leaching process and causes the formation of pores. Thus, with the increasing use of NaCl, the porosity of the PCL/HA 3D scaffold will increase [29].

Figure 9 shows the results of the compressive test on the APTES variations, indicating that the highest compressive strength occurred in sample A1N4, which used 1% APTES, with a compressive strength increase of 283%. However, the addition of more than 1% resulted in a compressive strength decrease of up to 59% in the 5% APTES. The compressive strength behavior of the scaffolds is presented in Figures 9 and 10.

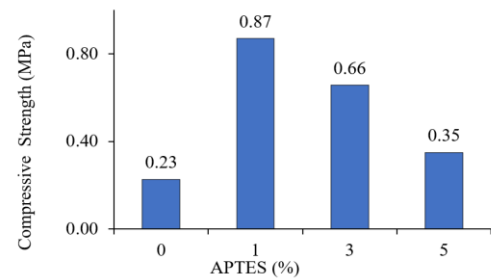


Figure 9. Effect APTES on Compressive Strength

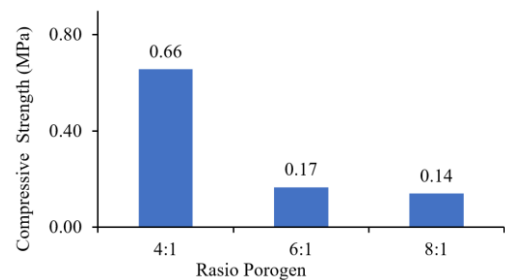


Figure 10. Effect Ratio Porogen on Compressive Strength

It can be concluded that APTES can increase compressive strength by strengthening the interface bond in the composite. However, excessive addition of APTES will cause some APTES to not form good bonds due to incomplete hydrolysis reactions. A surplus number of APTES will be distributed within the composite as free molecules. These free molecules cause a reduction in the mechanical properties of the 3D PCL/HA composite scaffold [27].

Figure 10 shows the effect of the porogen ratio on compressive strength, indicating that as the porogen ratio increases, the compressive strength value decreases. The highest decrease occurs at a ratio of 8:1 between the porogen (NaCl) and the composite (PCL/HA), which is 78%. This occurs because NaCl, as the space holder agent used, dissolves during the leaching process and causes the formation of pores. Thus, with the increasing use of NaCl, the porosity of the PCL/HA 3D scaffold will increase [16].

Figure 11 (a) shows the results of the weight loss test evaluated over 15 days with evaluations every 5 days. From the image, it can be seen that the addition of APTES tends to reduce weight loss. With the addition of 1% APTES, there is a 32% reduction in the biodegradation rate. However, after adding more than 1%, there is an increase of up to 49% in the 5% APTES variation.

Based on the weight loss test results, APTES can reduce the biodegradation rate by increasing the strength of the interface bonding in the composite. With stronger bonds, the

composite becomes more resistant to biodegradation, resulting in a decrease in weight loss [28][30]. Meanwhile, the addition of the porogen ratio increases the weight loss rate by up to 34% in the A3N8 sample with an 8:1 ratio.

In Figure 11 (b), the effect of the porogen ratio on weight loss is shown. From the figure, it can be seen that with the addition of the porogen ratio, the weight loss value increases. The highest increase occurs in the sample with an 8:1 ratio between the porogen and the composite, which is 34%. This occurs because the higher the porogen ratio, the greater the porosity, and with increased porosity, the surface area exposed to the environment (PBS) also increases, leading to a higher weight loss value [31].

The predicted lifetime of the composite can be observed from the amount of weight loss over a certain period. When the weight loss reaches 100%, it can be said that the material has been substituted with human bone tissue. The lifetime of the samples with APTES addition can be seen in Table 2.

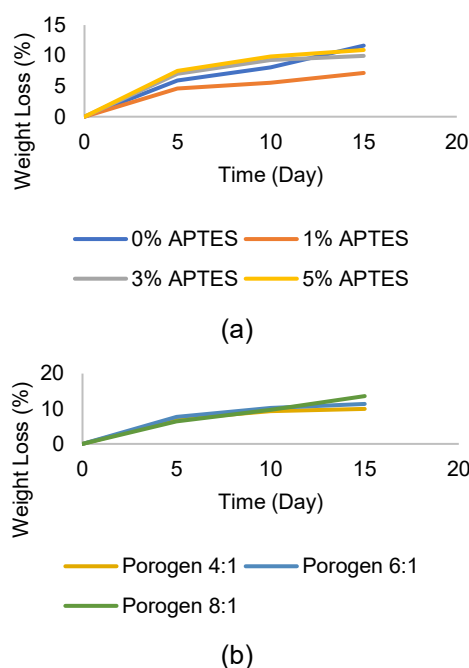


Figure 11. Effect of (a) APTES and (b) Porogen Ratio on Rate of Weight Loss

Table 2. The Effect of APTES on Lifetime

Sample	Lifetime (day)
A0N4	170
A1N4	380
A3N4	320
A5N4	274

From the table, it is evident that the addition of APTES can increase the lifetime by 120% at the 1% APTES variation.

However, with the addition of more than 1%, there is a decrease in lifetime by 27% at the 5% APTES variation. This occurs because the addition of APTES can enhance the bond strength at the composite interface, thereby increasing the lifetime. On the other hand, with the addition of more than 1%, there is APTES that does not bond well due to incomplete hydrolysis reactions. Causing the interface strength to be uneven, thus the lifetime will decrease [24].

Table 3 shows the estimated lifetime at various porogen ratios. It can be seen that as the porogen ratio increases, the lifetime will decrease. The highest decrease occurs at a ratio of 8:1 between the porogen and the composite, which is 58%. This occurs because as the porogen ratio increases, the porosity will also increase. With the increase in porosity, the surface area exposed to the environment (PBS) will also increase, resulting in a larger weight loss value. A large weight loss value leads to a decrease in lifetime [21].

The standard application of 3D scaffold for bone implants has a porosity value of 50-90%. Therefore, based on these test results, all samples have met the minimum requirements as 3D scaffold implants [9].

Meanwhile, the standard tensile strength value for cancellous bone is 1.5 – 38 MPa and compressive strength is 5-10 MPa. Based on the results of the mechanical tests conducted, the sample with the highest strength value is the A1N4 variation with a tensile strength of 0.31 MPa and a compressive strength of 0.87 MPa. However, this variation still does not meet the standard, so to improve the mechanical strength of the PCL/HA composite, more advanced fabrication techniques such as freeze drying and 3D printing can be employed [32][33].

The standard application for bone implants is to have a lifetime of 3-24 months. Therefore, based on the results of this weight loss test, all samples can be candidates for bone replacement, with the longest duration being sample A1N4, which is 380 days (12 Months) [34].

Table 3. The Effect of Porogen Ratio on Lifetime

Sample	Lifetime (day)
A3N4	320
A3N6	253
A3N8	134

CONCLUSION

This study shows that the addition of 1% APTES significantly increases tensile strength up

to 138% and compressive strength up to 283% in PCL/HA composites, due to the reinforcement of the matrix and HA particle interface. However, APTES concentrations above 1% reduce mechanical strength due to incomplete hydrolysis reactions. A higher porogen ratio (4:1 to 8:1) increases porosity up to 78.16%, but decreases tensile strength by 84% and compressive strength by 78% due to the dominance of the porous structure. In terms of biodegradation, 1% APTES extends the scaffold's lifetime to 380 days (12 months), while a higher porogen ratio accelerates biodegradation.

The best sample, A1N4 (APTES 1%, porogen ratio 4:1), shows an optimal balance between mechanical properties, porosity, and biodegradation, although it has not yet met the clinical standards for cancellous bone. The development of advanced fabrication techniques is recommended to enhance the performance of this scaffold as a potential candidate for bone regeneration.

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