

# Effect of Foaming Condition on the Pore Characteristic for Porous Polycaprolactone/Hydroxyapatite (PCL/HA) Composite

Istikamah Subuki, Suffiyana Akhbar, Rahida Wati Sharudin, Muhammad Hussain Ismail

**Abstract:** Porous polycaprolactone/hydroxyapatite (PCL/HA) composite has a great potential as a scaffold materials for bone regeneration. The goal of this study is to investigate the effect of foaming conditions on the pore structure characteristics of porous PCL/HA composite. Foaming process was conducted at different temperatures (35, 40 and 45°C) and pressures (10, 20 and 30 MPa) after four hours of CO<sub>2</sub> dissolution with fast depressurisation rate. The result found that the average pore diameter had increased with the increasing foaming temperature. However, with increasing foaming pressure, the average pore diameter had decreased significantly. The result found that at 45°C and 10 MPa, monomodal pore distribution was produced, with 61.53% of porosity and 116.78±8.94 µm successfully fabricated as high as at 40 wt% of HA. These pore characteristics are beneficial for the growth of bone tissue.

**Index Terms:** Polycaprolactone/hydroxyapatite; foaming; supercritical carbon dioxide; average pore diameter

## I. INTRODUCTION

Nowadays, the combination of a biodegradable polymer with hydroxyapatite (HA) has been extensively studied in bone tissue engineering. Among the commonly used scaffold materials, polycaprolactone/hydroxyapatite (PCL/HA) composite has received considerable attention and is widely studied as a potential material for scaffolds for bone tissue engineering due to its excellent biocompatibility, slow degradability, no toxicity, and ability to promote bone tissue cell growth [1, 2, 3].

Many researchers pay attention on environmentally friendly foaming processes in the development and design of

porous composite scaffold. This foaming process uses supercritical fluids, such as carbon dioxide (CO<sub>2</sub>), as a blowing agent. In this technique, the sample will be saturated with supercritical CO<sub>2</sub> for a certain duration and depressurised rapidly to atmospheric level [4]. The release of pressure results in nucleation and growth of gas bubbles or cells within the sample. This technique has been extensively studied in recent years due to the supercritical carbon dioxide (scCO<sub>2</sub>) being non-toxic, non-flammable, chemically inert, environmentally-safe, and inexpensive [5]. Indeed, the supercritical condition of CO<sub>2</sub> (T<sub>c</sub> = 304.25 K, P<sub>c</sub> = 7.39 MPa) is easily attained.

However, managing composite consisting of semi-crystalline polymer and high content of reinforcement particle is challenging due to the difficulty of supercritical CO<sub>2</sub> in being soluble and diffusible in polymer matrix [5]. Salerno et al (2014), [6] had improved the CO<sub>2</sub>'s diffusivity by using cosolvent ethyl lactate (EL) and ethyl acetate (EA). Other research effort is by using a binary mixture made of scCO<sub>2</sub> and cosolvents, such as ethanol and acetone, to improve the solubility of scCO<sub>2</sub> in PCL composite [7, 8]. Although these approaches are able to produce a more homogenous pore structure, the organic solvents must be completely removed because they may be potentially detrimental to the incorporation of bioactive molecules within these composites, or to the interaction with biological entities, such as in the case of bone tissue engineering scaffold [9]. In other words, organic solvents may leave undesirable residues in the finished products, leading to host reactions due to inflammation or toxicity [9].

Therefore, instead of using cosolvent, this work is to study the effect of foaming condition, which are temperature and pressure, during the foaming process to the pore structure characteristic of porous PCL/HA composite at different HA contents. In this work, porous PCL/HA composite was fabricated using the supercritical CO<sub>2</sub> foaming process without the presence of any organic solvent. The temperature and pressure varied at 35, 40 and 45°C and 10, 20 and 30 MPa, respectively. The success of this green route has a great potential in fabricating porous PCL/HA composite for bone tissue engineering and regeneration.

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## II. METHODOLOGY

### A. Materials

PCL (60,000 g/mol) in pellet form was purchased from Shenzhen Esun Industrial Co., Ltd. Irregular-shaped hydroxyapatite powder was synthesised from the clamshell using the chemical precipitation method [10]. The density of the HA powder was  $3.1991 \pm 0.0189 \text{ g/cm}^3$ . The mean particle size distribution was  $56.01 \pm 4.91 \mu\text{m}$ , where it was analysed using a Malvern Instruments' Mastersizer 2000. Meanwhile, the molar ratio of calcium (Ca) and phosphorus (P), Ca/P, was  $1.59 \pm 0.0419$ , as determined through the Energy-Dispersive X-ray Spectroscopy (EDS).

### B. Extrusion

Before the compounding process, PCL was dried under vacuum at  $38^\circ\text{C}$  for a minimum of 10 hours, while HA powder was dried at  $120^\circ\text{C}$  for 10 hours to avoid moisture-induced degradation reaction. HA loading varied from 10 to 40 wt%. Table 1 shows the designation of the composite blends of PCL and HA. PCL and HA powders were mixed in a shaker before undergoing melt blending in an extruder equipped with an ultrasonic placed at the end of the die. Melt blending was conducted at a temperature profile of 110, 100, 110, 110, and  $100^\circ\text{C}$  from hopper to nozzle with a screw rotation speed of 9 rpm. Ultrasound was used at 100% cycle at 400 watt and 22 Hz. After the extrusion, the strands were cooled in a water bath, and consequently, pelletised. Then, the pelletised PCL/HA composite blend was compressed using a hot press at temperature and pressure of  $110^\circ\text{C}$  and 900 psi, respectively, to produce disc-shaped samples that were 20 mm in diameter and 2 mm thickness.

**Table 1:** PCL/HA designation and composition

Designation	Content of PCL (wt %)	Content of HA (wt %)
PCL	100	0
10S	90	10
20S	80	20
30S	70	30
40S	60	40

### C. Foaming Process

Foaming process was conducted using the 316 stainless steel cylindrical high-pressure vessel (200 ml), where the carbon dioxide ( $\text{CO}_2$ ) contacted the samples in a single pass batch system. The vessel was mounted in a universal oven (XUO32). The desired temperature was achieved by coil-heated oven. The disc-shaped samples of PCL/HA were placed in the vessel that was subsequently heated and filled with  $\text{CO}_2$  up to the desired pressure using a high-pressure pump (brand: SAPAREX). The samples are exposed to high pressure  $\text{CO}_2$  to allow the saturation of  $\text{CO}_2$  in the sample. The vessel was maintained at constant different temperatures (35, 40 and  $45^\circ\text{C}$ ) and constant different pressures (10, 20 and 30 MPa). Thermodynamic instability is then created by rapidly releasing  $\text{CO}_2$  gas from the composite system, followed by nucleation and growth of gas bubbles in the sample. The

holding time was constant for four hours before depressurised to 0 MPa. The depressurised time was less than one minute (0.2–0.5 MPa/s).

### D. Characterization of Foam samples

The morphology of these samples was assessed using a Field Emission Scanning Electron Microscope (FESEM), (model GEMINI: ZEISS SUPRA 55VP) under secondary electron imaging. Prior to the observation by FESEM, the samples were fractured after being immersed in liquid nitrogen and coated with iridium for 45 s. The FESEM images were converted to binary images and then analysed by software Image J to evaluate the pore distribution and the mean pore size of the scaffold. The mean pore size was calculated by image analysis according to the ASTM D3576. At least 100 pores distributed across the micrograph were analysed. Three micrographs were selected for each scaffold formulation.

Porosity is a measure of the total pores spaces in a sample. It is a fraction of the volume of pores over the total volume of sample as percentage unit. The porosity of the foamed composite was determined using the following Equation 1 [11, 12]:

$$\% \text{ porosity} = \left[ 1 - \left( \frac{\rho_s}{\rho_c} \right) \right] \times 100 \quad (1)$$

where,  $\rho_s$  and  $\rho_c$  are the apparent densities of the foamed composite and the initial composite, respectively, determined by using densitometer.

Meanwhile, the pore density is the number of pores per  $\text{cm}^3$  of the foamed sample. The pore density can be estimated using Equation 2 [11, 12]:

$$\text{Pore density, } N_f = \left( \frac{nM^2}{A} \right)^{\frac{1}{2}} \quad (2)$$

where, n, A and M are the number of pores, area of the FESEM micrograph selected for analysis and magnification of FESEM micrograph, respectively.

## III. RESULTS AND DISCUSSION

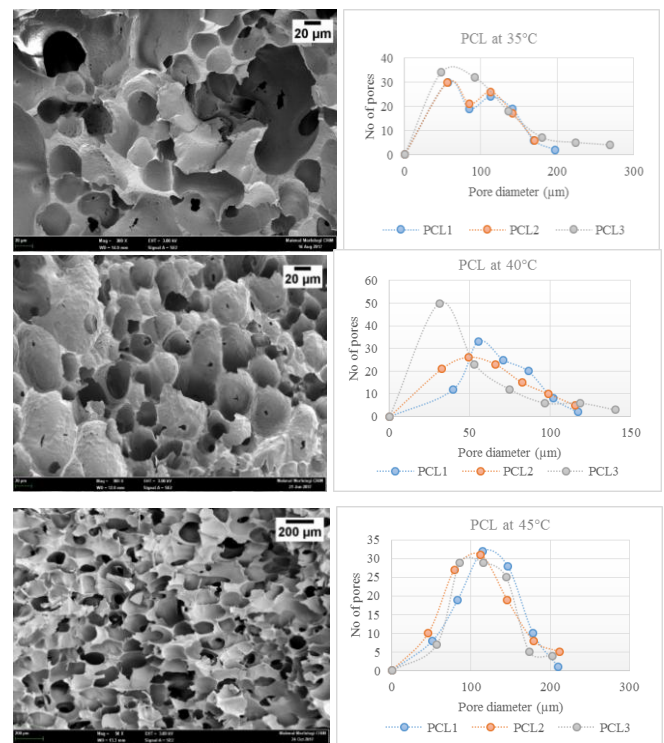
### A. Effect of foaming temperature on the pore characteristic of porous PCL/HA composite

The effect of temperature on the pore morphology of porous PCL and PCL/HA composite was carried out at temperatures 35, 40 and  $45^\circ\text{C}$  with 10 MPa constant pressure at rapid depressurisation. The pore characteristics are tabulated in Table 2. Generally, in PCL, homogeneous nucleation will take place, while in PCL/HA, composite heterogeneous nucleation is more favoured due to the presence of HA as a nucleating agent.

**Table 2:** Pore characteristic of PCL, 10S, 20S, 30S, and 40S at different foaming temperatures

Pore characterisation	PCL	10S	20S	30S	40S
<b>35°C</b>					
Average pore diameter (µm)	117.82±7.25	Incomplete foaming	Incomplete foaming	Incomplete foaming	Incomplete foaming
Number of Pore	586				
Pore Density (pore/cm <sup>3</sup> )	5.54 x 10 <sup>6</sup>				
Porosity (%)	62.19				
Pore Distribution	Bimodal				
<b>40°C</b>					
Average pore diameter (µm)	71.09±5.81	100.79±10.27	125.55±9.09	111.93±8.90	150.14±24.42
Number of Pore	658	808	671	990	689
Pore Density (pore/cm <sup>3</sup> )	8 x 10 <sup>6</sup>	1 x 10 <sup>7</sup>	7.61 x 10 <sup>6</sup>	1.32 x 10 <sup>7</sup>	7.38 x 10 <sup>6</sup>
Porosity (%)	69.44	67.21	67	65.19	63.52
Pore Distribution	Monomodal	Bimodal	Bimodal	Bimodal	Bimodal
<b>45°C</b>					
Average pore diameter (µm)	133.69±5.00	130.12±14.42	174.87±30.89	155.19±14.72	116.78±8.94
Number of Pore	314	358	448	278	357
Pore Density (pore/cm <sup>3</sup> )	2.56 x 10 <sup>6</sup>	3.24 x 10 <sup>6</sup>	4.12 x 10 <sup>6</sup>	1.99 x 10 <sup>6</sup>	2.53 x 10 <sup>6</sup>
Porosity (%)	68.75	69.72	66.69	65.86	61.53
Pore Distribution	Monomodal	Monomodal	Monomodal	Monomodal	Monomodal

For the PCL-CO<sub>2</sub> system, as the temperature increased from 35°C to 40°C, the porosity, pore density and number of pores increased from 62.19% to 69.44%, 5.54 x 10<sup>6</sup> pores/cm<sup>3</sup> to 8.01 x 10<sup>6</sup> pores/cm<sup>3</sup> and 586 to 658, respectively. However, the average pore diameter decreased from 117.82±7.25 µm to 71.09±5.81 µm. At 35°C, the pore distribution is presented as bimodal pore size distribution, while at 40°C, it is presented as monomodal pore size distribution. This is clearly observed from the micrograph FESEM results and pore distribution analysis in Fig. 1. This study found that at 35°C, the gradients of CO<sub>2</sub> concentration present in the sample favoured to non-uniform pore distribution. However, when the temperature increased to 40°C, the diffusivity of CO<sub>2</sub> improved and the concentration of CO<sub>2</sub> was uniformly diffused throughout the whole sample. As a result, the porosity, pore density and number of pores had increased with monomodal pore size distribution. On top of that, the foamed density decreased from 0.4366 kg/m<sup>3</sup> to 0.3529 kg/m<sup>3</sup>. This is expected because as temperature increases, the expansion of cell also increases, thus producing lower density [13]. As the temperature is raised to 45°C, the viscosity of the PCL is reduced and the CO<sub>2</sub> diffusivity had increased [5]. Therefore, it has less resistance for the pore to grow and coalesce, hence, favouring pore growth. As a result, fewer pores with larger size are formed. This is similar with the result of this study, where the average pore diameter increased to 133.69±5.00 µm but the number of pore and pore density decreased to 314 and 2.56 x 10<sup>6</sup>, respectively, at 45°C. Thus, a more uniform pore distribution was observed.



**Fig. 1: FESEM images and pore distribution analysis for PCL at different temperatures of foaming.**

Meanwhile, for the PCL-HA-CO<sub>2</sub> system, the presence of HA contributes to a decrease in diffusivity, where HA particles act as obstructions, hindering the diffusion of CO<sub>2</sub> [14]. The higher the HA content, the lower the diffusivity is expected to be. On top of that, HA particles may also modify the free volume available in the sample and the path of CO<sub>2</sub> molecules diffused [14].



These are also influencing the diffusivity of CO<sub>2</sub> in the PCL-HA-CO<sub>2</sub> system [14]. Besides that, HA may influence the solubility of CO<sub>2</sub> in the polymer, depending on its integration in the polymer matrix. If the HA has a good dispersion in polymer matrix, the polymer ‘wets’ the HA particles and the solubility of CO<sub>2</sub> is decreased. On the other hand, if the HA is not totally wetted by polymer, it may lead to the appearance of air gaps in the structure, which signifies an increased solubility and diffusivity [5, 14 and 15]. As a result, both of these (i.e., presence of HA and contact between HA and polymer matrix) will affect the solubility and diffusivity. From the result in Table 2, at 40°C, the number of pore and pore density of 20S had decreased, compared to that of the 10S. This is because at 20S, the solubility and diffusivity of CO<sub>2</sub> are lower compared to 10S due to the good dispersion of HA at 10S, as reported from previous work [16]. However, at 30S and 40S, poor morphology of HA dispersion was observed, which consequently improved the solubility and diffusivity of CO<sub>2</sub> and the uncontrolled number of pore and pore density produced.

When the temperature is raised to 45°C, the viscosity of PCL/HA had reduced and the CO<sub>2</sub> diffusivity increased. Consequently, uniform pore distribution was observed due the uniform CO<sub>2</sub> diffusion throughout the whole sample. The diffused CO<sub>2</sub> was used for pore growth rather than to nucleate pore. As a result, for each 10S, 20S, 30S, and 40S, the number of pore and pore density decreased with larger average pore diameter, except for 40S.

Besides that, the result found that the higher content of HA resulted in lower porosities of the porous PCL/HAS composite at both temperatures of 40°C and 45°C. Similar result was reported by Xin, Hao-Yang and Lih-Sheng (2017) [17] when the HA content increased from 1, 5 to 10 wt% HA. This is because PCL matrix had decreased, as the HA content increased, which contributed to the lower porosity resulted. However, the porosity is in the standard range of bone scaffold’s porosity (refer to Table 3). Other than that, the pore distribution of porous PCL/HAS changes from bimodal to monomodal when the temperature is increased from 40°C to 45°C.

**Table 3:** Pore characteristic for bone scaffold application

Standard porosity of bone scaffold (%)	Standard average pore diameter of bone scaffold (G.Tripathi and B.Basu, 2012) [20]	
	Pore size (µm)	Biological function
Cancellous bone: 50–90% Cortical bone: <10% (X-Y. Zhang, G. Fang and J. Zhou, 2017) [18]	<1	Protein interaction, responsible for bioactivity.
	1–20	Cell attachment, their orientation of cellular growth (directionally).
Cancellous bone: 75–90% Cortical bone: 5–10% (L. Polo-Corrales, M. Latorre-Esteves and J. E. Ramirez-Vick, 2014) [19]	100–1000	Cellular growth and bone ingrowth.
	>1000	Shape and functionality of implant.

**Table 4:** Pore characteristic of PCL, 10S, 20S, 30S, and 40S at different foaming pressures

Pore characterisation	PCL	10S	20S	30S	40S
<b>10 MPa</b>					
Average pore diameter (µm)	133.69±5.00	130.12±14.42	174.87±30.89	155.19±14.72	116.78±8.94
Number of Pore	314	358	448	278	357
Pore Density (pore/cm <sup>3</sup> )	2.56 x 10 <sup>6</sup>	3.24 x 10 <sup>6</sup>	4.12 x 10 <sup>6</sup>	1.99 x 10 <sup>6</sup>	2.53 x 10 <sup>6</sup>
Porosity (%)	68.75	69.72	66.69	65.86	61.53
Pore Distribution	Monomodal	Monomodal	Monomodal	Monomodal	Monomodal
<b>20 MPa</b>					
Average pore diameter (µm)	104.85±16.99	110.4±13.47	127.12±14.40	128.7±5.51	115.14±12.33
Number of Pore	429	461	492	556	619
Pore Density (pore/cm <sup>3</sup> )	5.95 x 10 <sup>6</sup>	6.65 x 10 <sup>6</sup>	6.74 x 10 <sup>6</sup>	7.09 x 10 <sup>6</sup>	1.07 x 10 <sup>7</sup>
Porosity (%)	78.25	78.42	76	72.87	79.04
Pore Distribution	Monomodal	Bimodal	Bimodal	Bimodal	Bimodal
<b>30 MPa</b>					
Average pore diameter (µm)	48.97±4.72	64.08±6.17	56.69±6.53	76.42±1.44	47.53±7.31
Number of Pore	531	1076	1048	955	950
Pore Density (pore/cm <sup>3</sup> )	6 x 10 <sup>7</sup>	2 x 10 <sup>7</sup>	1.84 x 10 <sup>7</sup>	6.1 x 10 <sup>7</sup>	1.82 x 10 <sup>7</sup>
Porosity (%)	76.09	74.66	73.32	71.82	76.58
Pore Distribution	Monomodal	Bimodal	Bimodal	Bimodal	Bimodal



## B. Effect of foaming pressure on the pore characteristic of porous PCL/HA composite

The effect of pressure on the pore morphology of porous PCL and PCL/HAS composite was carried out at pressures of 10, 20 and 30 MPa, with 45°C constant foaming temperature at rapid depressurisation. The pore structure characteristics are tabulated in Table 4.

For PCL, as the pressure increases, the average pore diameter decreases significantly. As the pressure is increased, the CO<sub>2</sub> gas molecules are forced between the polymer chains, thus increasing their mobility. Increased mobility of the polymer chains allows more CO<sub>2</sub> gas to be absorbed. In other words, the solubility of CO<sub>2</sub> in the sample had increased and there were higher CO<sub>2</sub> uptake in the PCL sample. The high concentration of CO<sub>2</sub> is consumed to nucleate more nuclei. Consequently, the number of pore and pore density produced increased with smaller average pore diameter. However, the porosity increased from 68.75% to 78.25% at 20 MPa, but slightly decreased to 76.09% at 30 MPa.

Meanwhile, for PCL-HA-CO<sub>2</sub> system, similar trend is observed for all formulations (10S, 20S, 30S, and 40S). With an increase in pressure, the average pore diameter decreased significantly with the increased number of pore and pore density.

Overall, for all formulations, this study found that from the Table 4.3, at 10 MPa, the average pore size is greater than 100 µm, with porosity in the range of 60–70% and a uniform pore size distribution produced. Meanwhile, at 20 MPa, the average pore size is also greater than 100 µm, but with higher porosity in 72–79% range and uniform pore size distribution observed. Both conditions (at 10 MPa and 20 MPa) are suitable for bone scaffold application, depending on its application, as stated in Table 3. However, at 30 MPa, the average pore diameter decreases to less than 100 µm but the porosity is in the range of 71–77% for all formulation.

## IV. CONCLUSION

In this work, the monomodal pore distribution of porous PCL/HA composites was successfully fabricated, with 61.53% porosity and 116.78±8.94 µm mean pore diameter as high as at 40 wt% of HA and 10 MPa with 45°C using supercritical carbon dioxide foaming without the presence of any organic solvent. These pore characteristics are beneficial for the growth of bone tissue. This work found that the foaming conditions (e.g., temperature and pressure) and presence of HA significantly affect the pore structure characteristic produced, as well as the pore size distribution.

## V. ACKNOWLEDGEMENT

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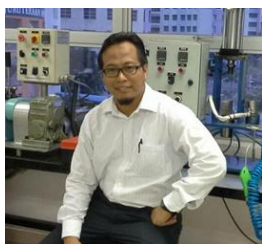
**Istikamah Subuki** received the Chemical Engineering degree and the PhD degree in Mechanical Engineering from the Universiti Teknologi MARA (UiTM) Shah Alam, Malaysia in 2004 and 2010 respectively. From 2007 to 2010, she was the researcher of the Advanced Materials Research Center (AMREC), SIRIM Berhad. She is currently a Senior Lecturer in the Faculty of Chemical Engineering, UiTM Shah Alam. Her current research interests are in advanced materials of synthesize hydroxyapatite powder, injection moulding process, develop new binder system for injection moulding process, plasma spray coating of hydroxyapatite, metal and ceramic composite and polymer composite foam.



**Suffiyana Akhbar** obtained her Master degree in Polymer Technology from Universiti Teknologi Malaysia (UTM), Skudai Malaysia in 2008. Now she is pursuing her Ph.D study in Chemical Engineering major in Polymer Engineering since September 2014. Her study is focusing on the fabrication of polymer composite foam by using supercritical CO<sub>2</sub> for tissue engineering scaffold (TES). One of the main interest in her study is she used a green processing route which is free of organic solvent. The usage of organic solvent in producing TES may leave undesirable residues in the finished products and may thus create host reactions due to inflammation or toxicity. Therefore, the successful of her study will give an alternative method and advantage in TES application. Her main research interest includes polymer composite and polymer composite foam. She is familiar with melt blending assisted by ultrasonic process and supercritical CO<sub>2</sub>. Before furthered study, she is a lecturer in Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM) since 2008. During her service, she managed to secure two FRGS grants and two master degree students graduated under her supervision as co supervisor.



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