UNIVERSITI TEKNOLOGI MARA

DEVELOPMENT AND CHARACTERIZATION OF POROUS POLYCAPROLACTONE/ HYDROXYAPATITE (PCL/HA) COMPOSITE USING SUPERCRITICAL CARBON DIOXIDE FOAMING PROCESS

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of the requirements for the degree of
Doctor of Philosophy
(Chemical Engineering)

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The usage of solvent in preparing porous polymer ceramic composite using solution techniques is a main limitation in bone tissue engineering application. The solvent may act as a host to produce toxicity and harmful to cell and tissue if incompletely removed. On the other hand, the free solvent technique such as gas foaming process, the stiff ceramic particle (such as hydroxyapatite (HA)) become obstacle for the gas to diffuse efficiently. Moreover, HA tends to agglomerate and unevenly distribute at high content. Therefore, to fabricate porous polymer ceramic composite that mimic to the HA content composition in natural bone is a challenging. The aim of this study is to prepare porous polycaprolactone/hydroxyapatite (PCL/HA) composite mimic to the HA content composition in natural bone without using any solvent. Two (2) type of HA was used which is needle shape (HAn) and irregular shape (HAs). The PCL and HA were blended using melt processing via single-screw extruder assisted with ultrasonic wave. It was then moulded into 20 mm diameter of disc-shaped mould with 2 mm thickness. The porous structure was then foamed using supercritical carbon dioxide ($ScCO_2$) foaming process. The characteristics of PCL/HA composites were examined through flow and thermal analysis via rheological test, and DSC/TGA test respectively; composite blend's morphology via FESEM test and; phase and chemical bonding of composite analysis via XRD and FTIR test respectively. Quantitative analysis was done on the average pore size; pore distribution and; pore density using ImageJ Software. Also, the pores interconnectivity was quantitatively analysed using Skyscan^{TM} CT-analyser. The present of ultrasonic wave during the melt processing improved the morphology of PCL/HA composites by reducing the HA's agglomerations size and quantity. However, uneven HA's distribution significantly promotes bimodal pore size distribution. The effect can be minimised by increasing the foaming pressure from 10 MPa up to 30 MPa and introducing slow depressurization rate. Hence, uniform pore size distribution was achieved. It has been observed that, increasing the foaming pressure from 10 MPa to 20 MPa and 30 MPa resulted in better pores interconnectivity despite significant reduction in average pore size. The results also showed that the average pore size can be further improved by increasing the foaming temperature and slowing the depressurization rate. Mathematical models representing the average pore size and porosity were established using ANOVA. The models accuracy were validated using Average Absolute Relative Deviation of which both models; (i) Average pore size model and (ii) Porosity model denoted the average value of 5.95% and 5.74% respectively. This study indicated that the combination of melt processing and gas foaming process in fabricating of PCL/HA composite without the existence of solvent is possible up to 20 wt% of HAn and 30 wt% of HAs of porous scaffold with homogenous pore size distribution.

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