POLYLACTIC ACID / POLYHYDROXYALKANOATE /EGGSHELL BASED HYDROXYAPATITE BIOCOMPOSITES FOR BONE TISSUE APPLICATIONS

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Dedicated to my beloved Ammi and Abbo, my Husband, and my daughters Hareem & Hamnah

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ABSTRACT

Orthopedic issues related to bone repair and regeneration are common and difficult. Biodegradable polymer composites containing hydroxyapatite can solve this issue by mimicking the composition and structure of genuine mineralized bone tissue. Eggshell waste precursor was chemically precipitated to generate HAP powder. Melt-blended polylactic acid (PLA) and polyhydroxyalkanoate(PHA) were optimized using the statistical design of the experiment, the Taguchi technique. PLA/PHA/HAP biocomposite was made by melting and injection moulding. HAP powder, PLA/PHA melt blend, and PLA/PHA/HAP samples were characterized by X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), Melt flow index (MFI), Universal testing machine (UTM), Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and Scanning electron microscopy (SEM). From XRD and FTIR results, the optimal eggshell $CaCO_3$ conversion calcination temperature was 900°C. EDX reported Ca/P ratio of 1.64 for HAP synthesized by chemical precipitation. Uncalcined HAP was found to have the Ca/P closest to the original HAP value of 1.67. PLA and PHA were melt blended to improve their mechanical properties as well as to reduce the cost, as PHA is a very expensive polymer. The PLA and PHA MFIs were 6.3 and 13.2 g/10 minutes. As PHA content rose, melt blend MFI rose. According to UTM analysis, 75PLA/25PHA improves tensile strength by 84%, impact strength by 80%, and elongation by 30%. According to TGA, PHA starts degrading at 295°C and PLA at 363°C. PLA improves PLA/PHA melt blend stability. Taguchi method optimized PLA/PHA melt mixing at 190°C, 60 rpm, and 6 minutes. 2% Maleic anhydride, as a compatibilizer, improved interfacial adhesion. The PLA/PHA/HAP biocomposite results showed that 10% uncalcined HAP loading to optimum blend exhibited superior mechanical properties. Greater loading of HAP decreases composites' tensile strength due to poor interfacial adhesion and agglomeration of HAP particles. The biocompatibility of biocomposite was tested using simulated body fluid. SEM showed the growth of apatite layers on biocomposite surfaces, making them viable for bone implants.

ABSTRAK

Isu ortopedik yang berkaitan dengan pembaikan dan penjanaan semula tulang adalah perkara biasa dan sukar. Komposit polimer terbiodegradasi yang mengandungi hidroksiapatit boleh menyelesaikan masalah ini dengan meniru komposisi dan struktur tisu tulang bermineral tulen. Prekursor sisa kulit telur dimendakkan secara kimia untuk menghasilkan serbuk HAP. Asid polilaktik (PLA) campuran cair dan polihidroksialkanoat (PHA) telah dioptimumkan menggunakan reka bentuk statistik eksperimen, teknik Taguchi. Komposit polimer PLA/PHA/HAP dihasilkan secara peleburan dan acuan suntikan. Serbuk HAP, campuran cair PLA/PHA dan sampel PLA/PHA/HAP dicirikan oleh pembelauan sinar-X (XRD), spektroskopi sinar-X serakan tenaga (EDX), indeks aliran lebur (MFI), mesin ujian Universal (UTM). analisis termogravimetrik (TGA), Fourier transformasian infra merah (FTIR) dan microscope elektron imbasan (SEM). Daripada keputusan XRD dan FTIR, suhu pengkalsinan penukaran $CaCO_3$ kulit telur yang optimum ialah 900°C. EDX mencatatkan nisbah Ca/P 1.64 untuk HAP yang disintesis oleh pemendakan kimia. HAP yang tidak dikalsin mempunyai Ca/P yang paling hampir dengan nilai HAP asal iaitu 1.67. PLA dan PHA diadun lebur untuk memperbaiki sifat mekanikalnya serta mengurangkan kos kerana PHA adalah polimer yang sangat mahal. PLA dan PHA MFI ialah 6.3 dan 13.2 g/10 minit. Apabila kandungan PHA meningkat, campuran cair MFI meningkat. hasil analisis UTM, 75PLA/25PHA meningkatkan kekuatan tegangan sebanyak 84%, kekuatan hentaman sebanyak 80%, dan pemanjangan sebanyak 30 hasil TGA, PHA mula merosot pada 295°C dan PLA pada 363°C. PLA meningkatkan kestabilan campuran leburan PLA/PHA. Kaedah Taguchi mengoptimumkan pencampuran lebur PLA/PHA pada 190°C, 60 rpm dan 6 minit. 2% Maleik anhidrida (MAH), sebagai penyerasi meningkatkan lekatan antara muka. Keputusan komposit polimer PLA/PHA/HAP menunjukkan 10% pemuatan HAP tidak terkalsin kepada adunan optimum menunjukkan sifat mekanikal yang unggul. Pemuatan HAP yang lebih besar mengurangkan kekuatan tegangan komposit disebabkan oleh lekatan antara muka yang lemah dan penggumpalan zarah HAP. Biokompatibiliti komposit polimer

telah diuji menggunakan simulated body fluid. SEM menunjukkan pertumbuhan lapisan apatit pada permukaan komposit polimer menjadikannya berdaya maju untuk implan tulang.

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LIST OF SYMBOLS AND ABBREVIATIONS

cm	-	Centimeter
cm^2	-	Centimeter Square
cm^3	-	Centimeter Cubic
°C/min	-	Degree Celsius per Minute
D	-	Diameter
d	-	Interspacing between Diffraction Lattice Plane
ΔT	-	Change in Temperature
ΔHm	-	Change in Melt Enthalpy
F	-	Force (N)
GPa	-	Giga Pascal
h	-	Hour
Kg	-	Kilogram
kt	-	Metric kilo tons
L	-	Length (cm)
λ	-	Wavelength
µm	-	Micrometer
µ	-	Micron
mm	-	Millimeter
mg	-	Milligram
MPa	-	Mega Pascal
nm	-	Nanometer
Pa	-	Pascal
%	-	Percentage
P	-	Pressure
Q3	-	Cumulative Distribution by Volume or Mass
q_3	-	Density Distribution by Volume or Mass
ρ	-	Density, g/cm3

η	-	Lattice Strain
θ	-	Diffraction Angle
Tm	-	Melting Temperature
Tc	-	Crystallization Temperature
Tcc	-	Cold Crystallization Temperature
Tg	-	Transition Temperature
T	-	Temperature (°C)
W	-	Width (mm)
wt%	-	Weight Percentage
Xc	-	Crystallinity
ATR	-	Attenuated Total Reflectance
ASTM	-	American Society for Testing and Materials
Al_2O_3	-	Aluminum Oxide
α –*TCP*	-	Alpha Tri Calcium Phosphate
β –*TCP*	-	Beta Tri Calcium Phosphate
Cl	-	Chlorine
CaO	-	Calcium Oxide
$CaCO_3$	-	Calcium Carbonate
d-HAP	-	Ca-Deficient HAP
DMA	-	Dynamic Mechanical Calorimetry
DNA	-	Deoxyribonucleic Acid
DCP	-	Dicumyl Peroxide
DMA	-	Dynamic Mechanical Analysis
DSC	-	Differential Scanning Calorimetry
EDX	-	Energy-dispersive X-Ray
ESW	-	Eggshell waste
FDA	-	Food and Drug Administration
FTIR	-	Fourier-Transform Infrared Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
FWHM	-	Full Width at Half Maximum
hMSCs	-	Human Mesenchymal Stem Cells
HAP	-	Hydroxyapatite
ICDD	-	International Centre for Diffraction Data

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