Impact Test and Bioactivity Properties of Polycaprolactone (PCL) by Addition of Nano-Montmorillonite (MMT) and Hydroxyapatite (HA).

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Keywords: Polycaprolactone (PCL), Montmorillonite (MMT), Hydroxyapatite (HA), Nano-single screw extruder, Simulated Body Fluid (SBF), Charpy Impact Test.

Abstract : This report described the Impact Test result and Bioactivity Properties of biodegradable Polycaprolactone (PCL) blend with nano- Montmorillonite (MMT) and Hydroxyapatite (HA). The amount of nano-MMT is varies from 2 to 4 by weight % meanwhile the amount of HA is fixed to 10 by weight percentage (wt%). The addition of nano-MMT and HA filler is to tune and indirectly improve the mechanical and bioactive properties of PCL. The samples for these test are injected from injection molding machine. The Impact test are conducted using Charpy Method. From the analysis it is found that the toughness of PCL are decreased by the addition of these fillers. PCL/MMT composites gives a better result compare to PCL/MMT/HA composites. This is due to the HA characteristic which is brilttle and tends to reduce the ductile properties of the polymer. From the Simulated Body Fluis (SBF) result, formation of apatite layer at the surface of the composites is evidence of excellent bioactivity properties of HA. The enhance of bioactivity has been proved while incorporation of HA into PCL/MMT composite. SEM-EDX image showed the bulk formation of apatite layers on the composite surface with 10 wt% HA after 3 days immersed in SBF solution.

Introduction

Medical practice today has been concern about the existing of implant devices originally created from polymers. According to report by worldwide orthopedic market 2004-2005, the estimated global market for orthopedic devices such as fracture repair, spinal implant and reconstructive devices is in the range of US$25-30 billion [1]. In fact, it leads to stimulate research focuses on producing medical product especially from polymer raw materials. There is a great effort to produce implant material from polymers instead of metal. Since metal has many disadvantage such as the presence of corrosions, fatigue failure of metal alloys and release of metal ions such as Nickel or Chromium which may cause loosening of the implant, polymer are widely choosen to replace metal. One of the biocompatible polymer thats getting a higher demand nowdays is Polycaprolactone (PCL).

Polycaprolactone (PCL) is a bioresorbable polymer with potential applications for bone and cartilage repair. PCL has certain advantages relative to other polymers such as PLA (poly-lacticacid). PCL is more stable in ambient conditions, it is significantly less expensive and is readily available inlarge quantities. Much researcher currently focused on the use of PCL biocomposites and co-polymers of PCL with both natural and synthetic polymers [2, 3]. In the emerging field of tissue engineering, biodegradable polymers are used for realizing polymer scaffolds to assist tissue and cell growth during formation of artificial organs [4]. In such applications, biodegradable polymers have been shown to allow successful cell attachment, proliferation and functioning.

PCL, an aliphatic polyester that has been intensively investigated as a biomedical material [5], demonstrates a low melting point (57 ◦ C) and a low glass-transition temperature (−62 ◦ C). PCL

can be degraded by micro-organisms as well as by a hydrolytic mechanism under physiological conditions [6]. Under certain circumstances, it is possible to enzymatically degrade crosslinked PCL (termed enzymatic surface erosion). Low molecular-weight fragments of PCL are also reportedly absorbed by macrophages intercellularly [7]. The PCL material has a significantly slower biodegradation rate than other BDP materials, making it suitable for design of long- term implantable systems such as apronor, a US FDA- approved contraceptive device [8]. Another interesting property of PCL is its propensity to form compatible blends with a wide variety of polymers. The toxicology of PCL has been extensively studied as part of the evaluation of Capronor [10]; it is currently regarded as non- toxic and tissue compatible.

Methodology

Materials. The biodegradable used in this studies are Polycaprolactone, medical grade of BGH600C in a pellets form supplied by Shenzen BrightChina Industrial Co, China.Type of MMT used in this research is Nanomer I.34TCN (modified montmorillonite) nanoclay in a powder form suppled by Nanocor Inc, America . It is specifically designed for extrusion compounding. The mineral and resin form a near-molecular blend with enhanced mechanical properties, especially in the area of heat distortion. Hydroxyapatite (HA Fluka, 3.16 kg/cm^3) was purchased from Sigma Aldrich. The specific surface area of the powder, measured by N, absorption (according to the Brunnauer-Emmet-Teller) method was found to be 33.05 m^2/g , and the particle size is 57.5 nm.

Table 1: Blend formulation of PCL with MMT and HA.

Designation	PCL (wt%)	HA(wt%)	MMT (wt%)
P100	100	0	0
P9M2	97	0	2
P9M3	97	0	3
P9M4	94	0	4
P8M2HA10	92	10	2
P8M3HA10	90	10	3
P8M4HA10	88	10	4

Sample preparation. The PCL which is in resin form are mix manually with MMT powder and also HA powder. These uniformly dry-mixed batches are melt-blended in a single screw extruder nanomixer (L/D = 30) with a screw speed of 20 rpm. The temperature profile of the extruder is set as 70, 78, 77 and 70 ^{o}C at the fed zone, metering zone and die, respectively. The extruded blends will be cooled in water bath and subsequently, fed to a pelletizer. All the compounded materials were bring to injection section. The tensile and flexural specimens were produced on an injection molding machine with an injection temperature between 40 ^{o}C – 80 ^{o}C. Injection pressure was set to 140 MPa and its varies along with content of HA.

Charpy Impact Test (MS ISO 179). In this research the Charpy Impact test was carried out according to MS ISO 179 on a Wolpert machine. The specimen for this testing is prepared from injection molding machine. The dimension of the specimen was 8 cm x 1 cm x 0.5 cm with the depth of notch was fixed at 0.1 cm.

Simulated Body Fluid. In vitro test was carried out following the Kokubo method [10]. The SBF was prepared by dissolving reagent NaCl, $NaHCO_3$, KCl, $K_2HPO_4.3H_2O$, $MgCl_2.6H_2O$, $CaCl_2.2H_2O$ and Na_2SO_4 into distilled water and buffered with Tris (hydroxyl-methyl-amino-methane, $NH_2C(CH_2OH)_3$) and hydrochloric acid (HCl) to pH 7.4 at 37 ^{0}C. The solution of SBF containing ion similar to human blood plasma. Each specimens was immersed in 200 ml of SBF and the solution was placed in an incubator for 1 and 3 days at temperature of 37 ^{0}C.

Surface analysis. Morphological study of SBF specimen was analyzed by using JOEL JSM-638OLA SEM-EDX microscope. In order to avoid charging during electron irradiation, the composite sample was covered with thin layer of gold in FISON SEM coating system, using a covering time of 120 s at 80 mA.

Result & Discussion.

In Figure 1 below shows the overall result of Impact test carried out on the PCL composites by the addition of MMT and HA. The impact strength of PCL composites are decrease by addition of MMT at all loadings. The reduction in impact strength was due to the presence of partially exfoliated MMT, which restricted the flexibility of the PCL matrix and limits the plastic deformation. Similar observation was reported by other researcher who concluded that impact strength generally decreased with addition of small amounts of MMT (1.5%) relative to the matrix polymer [11]. The embrittlement mechanism in the composites is also because of the large aspect ratio of the nanoclay and its orientation, multiple crazing occurred ahead of the crack tip during fracture may be inhibited, making semicrytalline polymer [12]. In one of the previous studies, it is found that the individual exfoliated clay platelets of very small thickness (~1 nm) of the composites are not effectively prevent the crack from propagating because it is easy to break the exfoliated clay platelets due to their high stiffness [13]. This indicates that the toughness of PCL/MMT composites was decreased where it undergo ductile to brittle transition failure.

It also can be seen that by adding HA into the PCL/MMT even decrease the impact strength of PCL/MMT/HA composites. The reduction in impact strength is expected due to the incorporation of HA which is a brittle and notch sensitive solids, enhanced the composite with a completely brittle behaviour. Incorporation of HA to the polymer matrix also disrupts the continuity of the PCL matrix. The capability of PCL matrix to distribute the impact energy applied was reduced. Thus, the ability of the matrix to stand high stresses is limited and reduced the energy absorbed which consistent with previous studies [14]. Other than that, the characteristic of HA itself which is categorized as ceramics considered to have extremely limited plastic deformation because of its ionic and/or covalent bonding which limits the total energy absorbed [15].

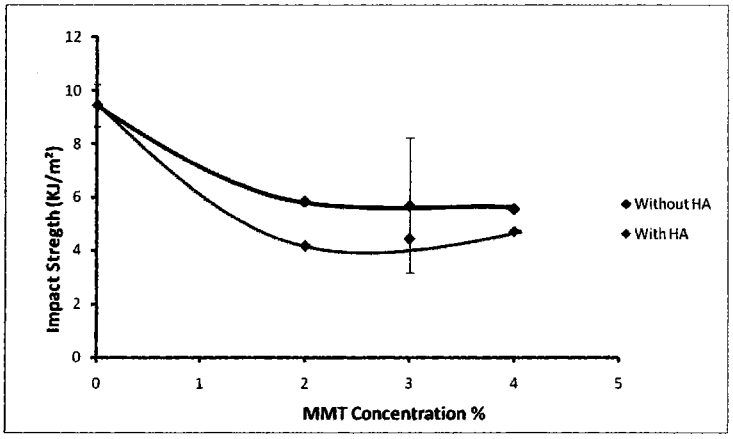

Figure 1 : Impact strength of PCL/MMT/HA and PCL/MMT composite. (n=5).

Morphological study on SBF sample is shown in Figure 2 after 3 day of immersion. It was observed that the bulk formation of apatite layer were result from the ion exchange occurs during immersion. Tree-like shape of apatite layers growth rapidly within 3 days prior to silane-treated hydroxyapatite contains in composite, demonstrating high in vitro bioactivity of the composite. As the time increases, these apatite layers was grew in size and formed a layer to completely cover the entire composite, as apparent from figure 2,3 and 4. Thus, it is suggested that the bone-like apatite

layer may promote the bone bonding with living tissue. Furthermore, EDX analysis of trees-like layer formed on the surface shows the presence of C, Ca, O, and P. It is believed that the carbon (C) demonstrate in the layer maybe the carbonate-containing apatite.This was in aggrement with findings reported by others researchers [16].

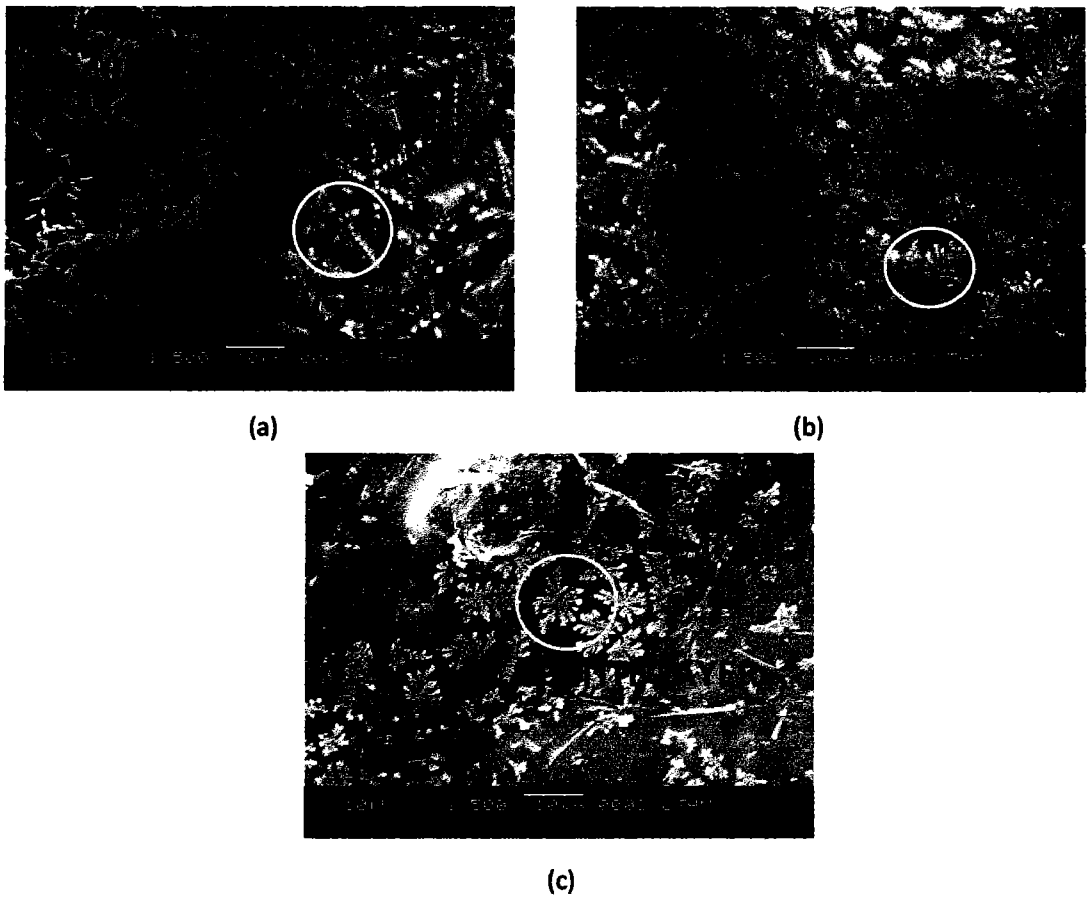

Figure 2 : The SBF result of PCL/MMT/HA composites after 3days.

Conclusion

It can be conclude that by the addition of MMT and HA does actually decreased the impact strength of PCL composites. It is obvious that the impact strenght of PCL/MMT composites gives a better result compare to PCL/MMT/HA as it produce a higher values. But overall it seems the differences are in a minimal range. SEM micrographs reveal the formation of the apatite layer covering the composites surface. The properties of the composites is comparable to the cancellous bone properties and suitable to be used in biomedical applications. It is also emerged from this study that HA particle loadings guarantee the growth of apatite layer as well as needed by the fracture part of bone during healing progression.

Acknowledgement

The authors would like to deliver their greatest acknowledgements to Universiti Tun Hussien Onn (UTHM) and Minister of Higher Education (MOHE) Malaysia for their support and facilities for this research.

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