Performance of Polycaprolactone/Hydroxyapatite (PCL/HA) Composite Blended by Ultrasound Assisted Melt Blending

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ABSTRACT

Conventional melt blending is limited in producing of biocomposite material implants with high loading of hydroxyapatite (HA) content for orthopaedic application and bone tissue engineering. The objective of this study is to produce polycaprolactone/hydroxyapatite (PCL/HA) composite blend with high loading of HA by assist conventional melt blending with ultrasonic wave. Rheological behaviour, morphology, thermal behaviour and chemical characteristics of PCL/HA composite blends were investigated. This study found that 400 Watt of ultrasonic wave provided sufficient process ability of PCL/HA composite blend up to 30 wt% of HA based on rheological behaviour. Meanwhile field emission scanning electron microscopy (FESEM) micrograph showed that the size of as-received HA was reduced during extrusion and better dispersion of HA was obtained although some agglomerates of HA were observed. Melting temperature and crystallization temperature of PCL/HA composite blends were almost similar and did not change significantly regardless to HA content. However, crystallinity of PCL/HA composite blends were increased as HA content increased from 10 to 30 wt%. The thermogravimetric analysis (TGA) indicated that 10.0 wt%, 20.8 wt%, 30.1wt% and 40.8 wt% of HA were well incorporated in 10 wt%,

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20 wt%, 30 wt% and 40 wt% of PCL/HA composites respectively. This was concurrently to X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FTIR) results. As a conclusion this study found that present of ultrasonic wave during melt blending extrusion aided in blended of PCL with high loading of HA.

Keywords: *PCL/HA composite blend, ultrasonic wave, rheological, morphological*

Introduction

Bone is a composite comprising a polymer matrix reinforced with ceramic particles. The polymer is the protein with 22 wt% and the balances are 8 wt% water and 70 wt% mineral [1]. HA accounts for about 65 wt% of bone which provides most of its strength and stiffness [2]. Among the polymeric materials used for bone tissue engineering fabrication, polycaprolactone (PCL) is more preferable due to its highly biocompatibility, flexibility, moldability and slow degradation properties [3].

PCL is a biodegradable polymer that has been recognized as a bone tissue compatible material without producing toxic response [4]. Besides, it is easy to process owing to low melting temperature which is in the range of 59-64 °C [5]. Thus, PCL is a hydrophobic and semi crystalline biodegradable polymer with a glass transition temperature (Tg) of -60°C. However, PCL implanted alone into bone defect remains as foreign body and does not adhere to bone due to absent of bioactivity and osteoconductivity (ability to promote bone cell/tissue growth). Therefore, it needs the present of hydroxyapatite (HA) in order to promote an osteogenic response. Hydroxyapatite (HA) is an inorganic ceramic with chemical formula $Ca_{10}(PO_4)_6(OH)_2$. HA is a reinforcement particle that has a chemical composition that mimics the natural mineral phase of bone tissue and has osteoconductive properties. However, HA is inherently a brittle material to stand alone and hard to shape [6].

Owing to this, [7, 8] discovered that blending both materials (PCL and HA) is promising a biodegradable polymer composite with improve of bioactivity, osteoconductive enhancement and balance of mechanical strength. The higher HA content in the blend the higher osteoconductive property. Nevertheless, homogenous PCL/HA composite blend with high content of HA (up to 65 wt% of HA, which similar to bone composition) is a great challenge to be achieved. Many studies have used different blending methods in achieving high content of HA loading in PCL/HA composite blend. The methods are either by conventional melt blending [6, 7, 9, 10, 11] or by solution mixing which involve organic solvent [3, 8, 12, 13, 14, 15, 16].

Both blending methods have their own advantage and disadvantage. In conventional melt blending process, the critical issues are to maintain sufficient fluidity for the PCL/HA blend and to obtain good dispersion of HA in polymer matrix at high loading of HA [17].This limit the application of conventional melt blending technique. In previous studies by [18, 19, 20], they were utilized ultrasonic to improve the processability of propylene, linear low density polyethylene (LLDPE), polypropylene (PP), high density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE) with filler during extrusion. Meanwhile [21] found that both higher ultrasonic intensity and lower rotation speed contribute to the larger reduction of die pressure, thus increasing the output of extruded. However, the great advantage of this technique is no organic solvent is involved during blending. In medical application, usage of organic solvent should be avoided owing to potential toxic in human body.

On the other hand [12, 14] were preferred solution techniques for higher loading of HA content even though requires organic solvent during mixing. Nevertheless, [12] found that sonification that applied in solution mixing facilitated better dispersion of HA in PCL matrix and reduced the amount of agglomerated HA particles. This was agreed by [14], who proved that sonicator technique is a simple and versatile technique for particle dispersion. However, this solution technique is suitable for small production. Some innovative improvement the system has yet to be studied for mass production.

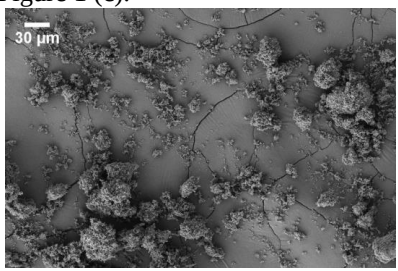
Therefore this study is applying ultrasonic wave in conventional melt blending method in order to blend PCL with high loading of HA with free of organic solvent. To the best of our knowledge, blending of HA in PCL matrix with the aided of ultrasonic wave is rarely in open discussion. This ultrasonic wave is expected to improve the processability and give sufficient flowbility of PCL/HA composite blends at high loading of HA [18, 19, 20]. On top of that, achieving a greater effective breakup of the particle agglomerates in the absence of solvents or chemical is also an advantage. The effect of ultrasonic wave on rheological, morphological and characterization of PCL/HA composite blends are analysed and discussed in detail.

Methodology

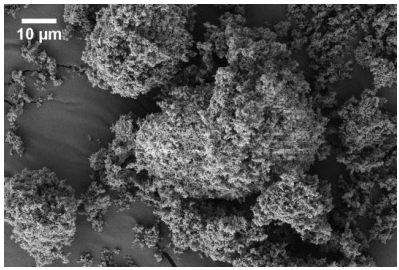
Material

PCL (Mw = 60,000 g/mol) in pellet form was purchased from Shenzhen ESUN Industrial Co., Ltd. Hydroxyapatite powder was synthesized from clamshell by using chemical precipitation method [22, 23]. The density of synthesized HA powder is 3.20±0.02g/cm^3, having irregular shape and have an average particle size of 56.01±4.91 µm analysed by particle analyser. Meanwhile, molar ratio of calcium (Ca) and phosphorus (P); Ca/P is 1.59±0.04. The FESEM micrograph in Figure 1 indicates the present of

agglomerate's HA as received. This as-received HA's agglomerate present in the form of porous agglomerates with many cavities or voids as shown in Figure 1 (c).



(a)



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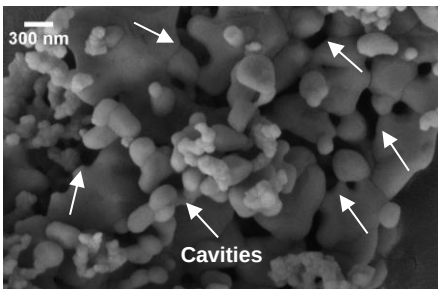


(c)

Figure 1: FESEM image for HA, as received; (a) and (b), HA particles, as received, tend to agglomerate and have a mean particle size distribution of 56.01±4.91µm, (c) HA particle, as received, was in irregular shape and presented in the form of agglomerates with many cavities or voids indicated by white arrows.

Sample preparation

All PCL containing material was dried under vacuum at 38 °C for at least 10 hours while HA powder was dried at 120 °C for 10 hours to avoid moisture induced degradation reactions [6]. HA was varied from 10 to 40 wt%. PCL and HA were mixed in a shake container before melt blending in extruder equipped with ultrasonic placed at end of die. Melt blending was conducted at temperature profile of 110, 100, 110, 110, and 100 °C from hopper to nozzle with screw rotation speed of 9 rpm. Ultrasonic was used at 100% cycle at 400 watt and 22 Hz. After extrusion, the strands was cooled in water bath and pelletized. Finally pelletized PCL/HA composite blend was compressed by hot press at temperature and pressure of 80 °C and 700 psi respectively, to produce disc shape samples with 20 mm diameter and 1 mm thickness.

Rheology of PCL/HA composite blends

The melt behaviour of the PCL/HA composite blends were studied via oscillating disc rheometer (ODR). The samples were standardized in disc shape samples with 20 mm diameter and 1 mm thickness. The gap size was constant in the range of 1.0 to 0.8mm. Viscosity versus shear rate graphs were obtained and analysed.

Morphology of PCL/HA composite blends

The morphology of PCL/HA composite blend samples were assessed by field emission scanning electron microscopy (FESEM). The samples were cross sectioned, gold coated and analysed by FE-SEM (GEMINI: ZEISS SUPRA 55VP) under secondary electron imaging.

DSC Analysis

The thermal behaviour and crystallization of the PCL/HA composite blends were analysed by differential scanning calorimetry (Mettler Toledo TGA/DSC SDTA851). The PCL/HA composite blend samples were heated up to 110 °C at a heating rate of 5°C/min in a flowing nitrogen atmosphere and then cooled to room temperature. The melting temperature (T_m) and crystallization temperature (T_c) were determined. The crystallinity (X_c) was also calculated by considering the following equation 1 [14].

$$C(\%) = \frac{\Delta H_m}{\Delta H_o \times X_{PCL}} \times 100 \quad (1)$$

Where ΔH_m is the melting enthalpy for the PCL/HA composite blend sample, ΔH_o (136 J/g) is the melting enthalpy for 100% crystalline PCL polymer [14] and X_{PCL} is the weight percentage of the PCL in the PCL/HA composite blend samples.

TGA Analysis

The final content of HA in the samples were investigated by thermogravimetric analysis (Mettler Toledo TGA/DSC SDTA851). The samples were heated up to 800 °C at a heating rate of 10 °C/min in a flowing nitrogen atmosphere.

FTIR and XRD Analysis

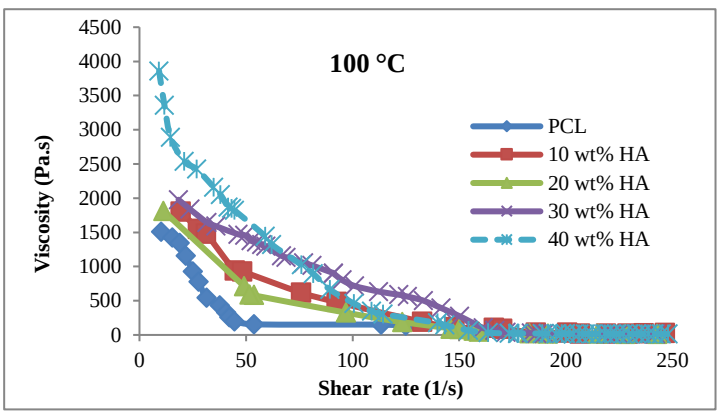
X-ray diffraction analysis was performed by X-ray diffractometer (XRD, Rigaku Model Ultima IV) equipped with Cu Kα radiation (λ= 1.54059Å) at 40 kV and 30 mA setting. Scanning rate of 1°/minute and 2θ step size of 0.02° were used in the range of 10°-70° diffraction angle. Identification of phases was performed by comparing the experimental XRD patterns to standards compiled by the International Centre for Diffraction Data (ICDD) called Powder Diffraction File (PDF) using the card number of (01-074-

0565). Meanwhile fourier transform infrared spectroscopy (FTIR) analysis was carried out at 515 cm^{-1} to 4000 cm^{-1} wavelength using FTIR spectroscopy (Perkin Elmer).

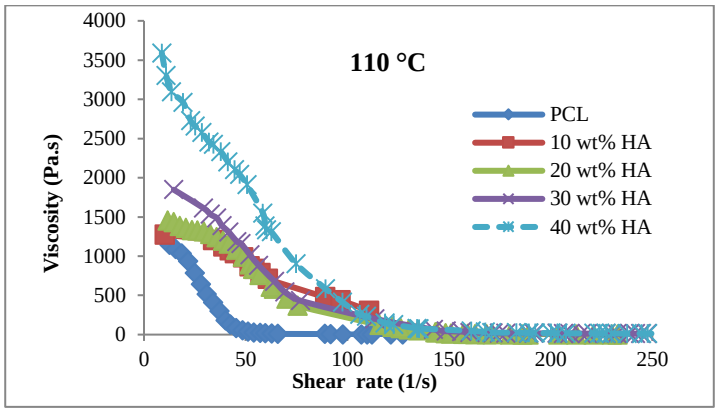
Results and discussions

Rheological behaviour of PCL/HA composite blends

Rheological oscillating disc testing have been performed at different temperatures (100 °C and 110 °C) in order to study the melt behaviour of the PCL/HA composite blends. These temperatures were selected based on operating temperature during melt blending. At both temperatures as shown in Figure 2, the PCL/HA composite blends show a notable difference in viscosity at low shear rate, while at high shear rate the PCL/HA composite blends viscosity is almost the same. The viscosity of all blend decreased with the increase of shear rate, indicating pseudoplastic behaviour. Thus, all blends exhibit the non-Newtonian and shear thinning behaviours.



(a)



(b)

Figure 2: Rheology of PCL/HA composite blends at different temperatures; (a) 100 °C; (b) 110 °C

Besides, it is also clearly observed that incorporation of HA increased the viscosity of neat PCL. This was expected due to present of hydrogen bonding interactions as a consequence of higher amount of –OH on the surface of HA which are able to interact with the PCL matrix [24, 25]. The neat PCL has the lowest viscosity and decreased sharply as the shear rate increasing. However, for the PCL/HA composite blends, the viscosity decrease slowly as the shear rate increasing, indicating that the interaction between HA and PCL matrix are so strong that the shear stress nearly cannot destroy the interaction between the polymer chains and HA [25].

Meanwhile at 10 to 30wt% of HA, it was observed that the viscosity value is low and closer to each other at both temperatures. However, at 40wt% of HA, the viscosity was significantly boost and large difference compared to others composite blends. Consequently this interrupted the processability and followability of PCL/HA composite blend during melt blending where the extruded strands produced were not smooth and discontinuous. Therefore this study found that 30 wt% HA incorporated in PCL was considered as the maximum loading to maintain the followability of the PCL/HA composite blend at 400 watt ultrasonic.

Morphology of PCL/HA composite blends

The morphology of PCL/HA composite blends was investigated in order to study the effectiveness of ultrasonic aided in HA's dispersion in the PCL matrix. From the FESEM micrograph shown in Figure 3, the as-received of HA's agglomerates seem to be breakage and dispersed in PCL matrix. The breakage of the as-received HA's agglomerate was probably due to the combination effect of screw rotation and ultrasonic during mixing [19, 26].

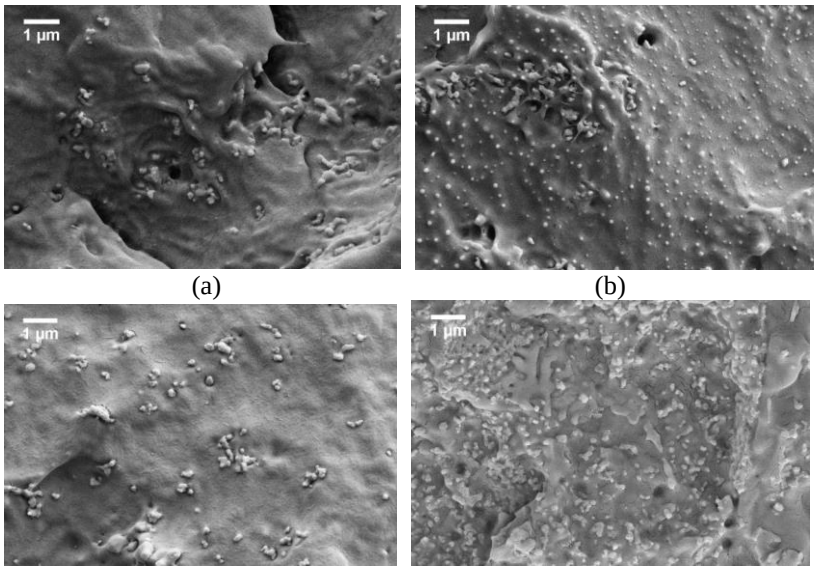


Figure 3: FESEM images for (a) 10 wt% HA, (b) 20 wt% HA, (c) 30 wt% HA and (d) 40 wt% HA

According to mechanism proposed by [27] illustrated in Figure 4, the as-received of HA's agglomerates had inside bubble cavitation in the system.

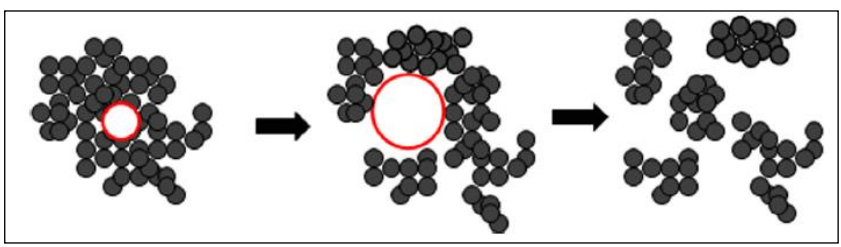
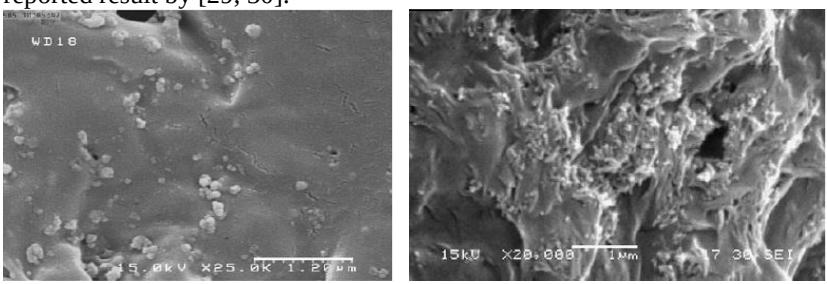


Figure 4: Inside cavitation mechanisms by ultrasonic wave in PCL/HA composite blends [27]

Therefore the ultrasonic wave propagation in the composite blend generates oscillatory pressure waves and induces the bubble expansion and contraction leading to a breakage of the agglomerates. Thus, reduce the size of the agglomerates of HA particles and dispersed them evenly in the PCL matrix. Similar mechanism happens to the as-received HA during melt blending process which reduces HA agglomeration. From the morphological point of view, at 20 wt% HA, the HA was better dispersed compared to other

composite blends. In fact, when compared with previous works in Figure 5, the 20 wt% of HA in this work exhibited better distribution compared to reported result by [29, 30].



(a) (b)

Figure 5: FESEM micrograph of HA/PCL by previous reported studies; (a) FESEM micrograph of HA/PCL (20/80 wt%) prepared by in situ sol-gel process [29], (b) SEM micrograph of the fracture surface of HAP (20wt%)/PCL scaffold produced by thermally induced phase separation [30].

DSC Analysis

Thermal behaviour and crystallization of PCL/HA composite blend were characterized by using DSC. The result which including melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (H_m) and crystallinity (X_c) are summarized in Table 1. From Table 1, it shows that melting temperature and crystallization temperature of all samples are almost similar comparable at all composition. The melting temperature is in the range of 61-63 °C. Meanwhile crystallization temperature is in the range of 27- 34 °C.

Table 1: Result summary of DSC analysis for various content of HA

PCL Content (wt %)	HA Content (wt%)	T_m (°C)	T_c (°C)	H_m (J/g)	X_c (%)
100	0	62.78	27.59	69.95	51.4
90	10	61.89	32.79	67.53	55.2
80	20	61.91	32.16	70.06	64.4
70	30	62.01	31.99	51.35	65.3
60	40	62.39	33.52	50.54	61.9

On the other hand, the crystallinity of PCL was increased as HA content increased from 10 to 30 wt%. This is due to the fact that HA particles act as a nucleating agent, promoting the formation of PCL's crystallites [33]. However, at higher HA content of 40 wt%, the crystallinity was decreased. This is because present of HA at high loading produced PCL/HA composite blend with high viscosity (refer Figure 2) and thus reduce the mobility of

polymer chains. In turn, the restricted mobility of the polymer chains leads to a decrease of crystallinity [20]. Similar trend result reported by [14, 30].

TGA Analysis

The actual content of HA particles in PCL/HA composite blend was determined by TGA analyses. The result is illustrated in Figure 6. The actual content of HA was 10.0 wt%, 20.8 wt%, 30.1 wt% and 40.8 wt% for HA content of 10, 20, 30 and 40 wt% respectively. This finding suggests that HA particles were effectively incorporated in PCL/HA composite blend during melt blending assisted with ultrasonic.

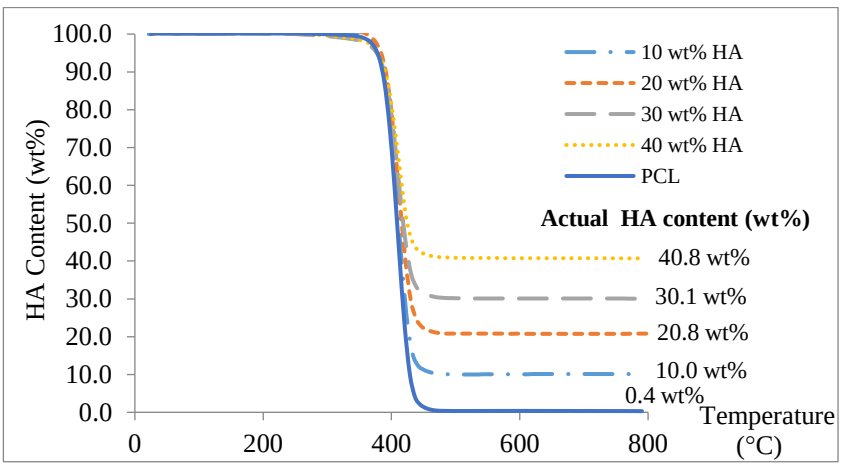


Figure 6: Graph of TGA analysis for PCL and various HA content from 10 to 40 wt%.

FTIR and XRD Analysis

The incorporation of various content of HA particle in PCL/HA composite blend was evaluated by FTIR and XRD analyses. The FTIR spectrum was shown in Figure 7. Figure 7 (a) and 7 (f) show peaks that correspond to crystalline PCL and HA phases, respectively. Meanwhile Figure 7 (b), (c), (d) and (e) show the spectrum of PCL/HA composite blends.

From the FTIR spectrum, corresponding bands of PCL and HA confirms the formation of both compound in the PCL/HA composite blends. The C=O, C-O and C=H bands were attributed to PCL and P-O and O-H bands were related to HA. For HA, a notable peak at 1032 cm^{-1} and 963 cm^{-1} represent symmetric and asymmetric P-O bond stretching from ester carbonyl group (PO_4^{-3}). Moreover peak at 3572 cm^{-1} belongs to O-H of hydroxyl group. Meanwhile for PCL, a clear/sharp peak at 1721 cm^{-1} assigned to C=O ester carbonyl group stretching. The peaks at 2865 cm^{-1} and 2944 cm^{-1}

correspond to the symmetric and asymmetric CH_2 stretching respectively. Other than that, peaks at 1160 cm^{-1} and 1239 cm^{-1} belong to symmetric and asymmetric C-O-C band stretching respectively. Beside peak at 1294 cm^{-1} attributed to the C-O and C-C stretching. Meanwhile for all PCL/HA blends all peaks represented PCL and HA were notables.

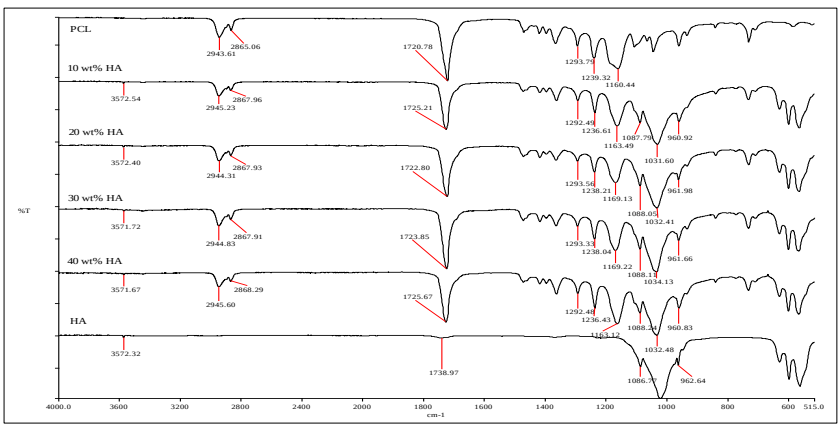


Figure 7: FTIR spectrum pattern of PCL (a), HA (f) and PCL/HA composite blend with various HA contents of (b) 10 wt%, (c) 20 wt%, (d) 30 wt% and (e) 40 wt%.

Meanwhile from the XRD analysis in Figure 8, similar XRD pattern for PCL, HA and PCL/HA blends were reported by [14, 29, 34]. Generally, all PCL/HA blends showed similar XRD patterns regardless of the HA content. XRD pattern clearly shows the increasing of relative intensities of peaks that attributed to crystalline HA phase. The relative intensities of peaks that attributed to crystalline HA phase was increased as HA content increased. Meanwhile the relative intensities of peaks that attributed to crystalline PCL phase were decreased as HA content increased.

Present of PCL peaks can be detected by 2 specific peaks at 2Θ = 21.38° and 23.66° which labelled as triangle mark. These two strong diffraction peaks attributed to the (110) and (200) crystallographic planes of semi crystalline PCL [35]. Meanwhile peaks that corresponding to HA at 2Θ = 31.74 was identified by the standard database made by the International Centre for Diffraction Data (ICDD) called Powder Diffraction File (PDF) using the card number of (01-074-0565). The HA peaks were labelled as circle mark.

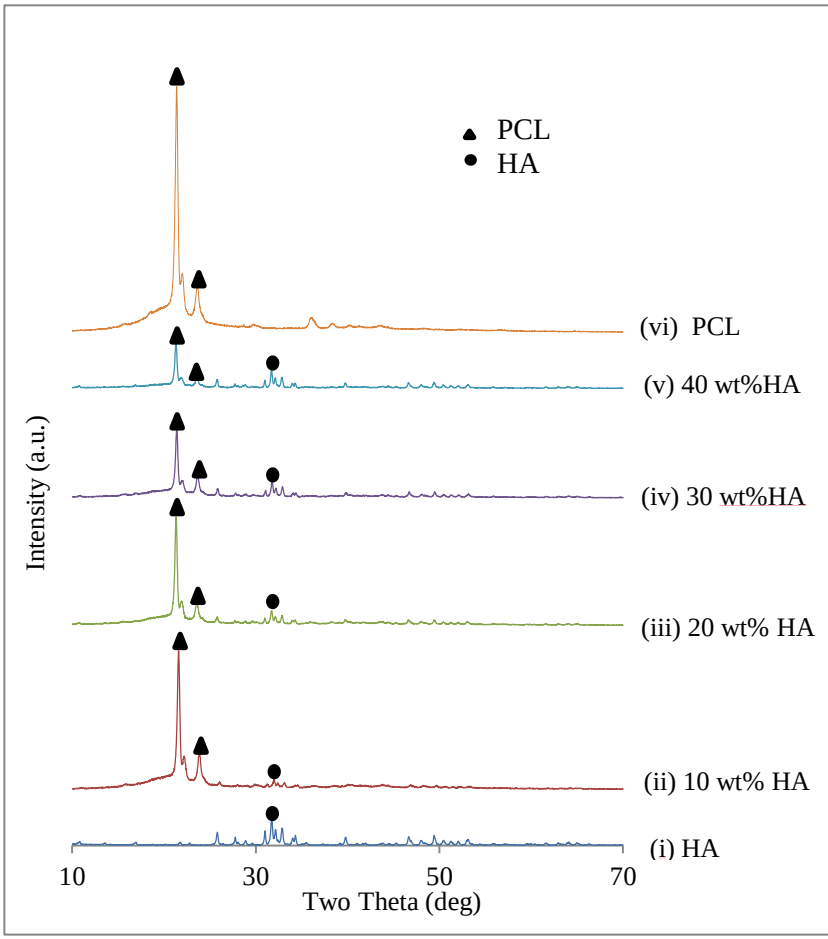


Figure 8: XRD pattern of (i) HA, (vi) PCL, and PCL/HA blends with various HA contents of (ii) 10 wt%, (iii) 20 wt%, (iv) 30 wt% and (v) 40 wt%.

Conclusion

This paper reports on the performance of PCL/HA composite blends in high loading content of HA. It was found that the incorporation of ultrasonic wave during extrusion process aided in providing sufficient processability and flowbility of PCL/HA blends up to 30 wt% of HA based on rheological behaviour. Thus, helping breakage of agglomerate's HA and improving HA dispersion in PCL matrix at 20 wt% HA. This ultrasound assisted extrusion process has a potential to replace the solution mixing technique.

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