Morphology of polycaprolactone/needle-shaped hydroxyapatite (PCL/HAN) nanocomposite blends using ultrasound assisted melt blending

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Abstract. Polycaprolactone/Hydroxyapatite (PCL/HA) composite is an excellent material for fabricating tissue engineering scaffolds, especially as bone scaffolds. However, polarity differences between the hydrophilic HA and the hydrophobic PCL often leads to poor dispersion during the blending process. This is due to the tendency of the HA particles to agglomerate, and the difficulty to efficiently mix the polymer melt at high loading. The objective of this study is to introduce ultrasound waves during the conventional melt blending to overcome the problem. PCL and needle-shaped hydroxyapatite (HAN) were blended using an ultrasonically assisted extruder. The morphology of the PCL/HAN blend was investigated using field emission scanning electron microscopy (FESEM). This study found that the presence of ultrasound waves during melt blending was helpful in breaking up the HAN agglomerates. Thus, better dispersion of HAN was obtained, although some small agglomerates of HAN were still observed.

1. Introduction
Polycaprolactone (PCL) is a semi crystalline aliphatic polyester with a relatively low melting temperature that ranges between 50 and 60 °C, and a glass transition temperature of approximately -62.15°C [1]. It is employed in various biomedical applications, such as matrices for drug delivery, and tissue engineering scaffolds due to its biocompatibility, non-cytotoxicity, and low degradation rate [1]. Meanwhile, hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂) is a bioactive ceramic that is chemically similar to the inorganic matrix of natural bone. Thus, it has excellent osteoconductive and osteoinductive properties, which makes it commonly used for bone tissue applications. However, in the case of PCL-HA composites, a homogenization and intermixing problem was detected due to the hydrophilic and hydrophobic nature of HA and PCL, respectively. Therefore, this problem needs to be mitigated to utilize the beneficial effects of this composite.

Kim H-W (2007) applied oleic acid, an amphiphilic surfactant, to mediate the interaction between the hydrophilic HA and the hydrophobic PCL [2]. The mixing ratio of the HA/PCL was fixed at 0.3. The results showed that HA was uniformly distributed, which improved the mechanical properties of the composites. Raucci M.G et al. (2010) also utilized a similar approach, whereby an amphiphilic surfactant, Span85, had improved the interaction between PCL and HA, which was shown by the HA’s homogenous dispersion [3]. The actual content of HA was at 34wt%. Meanwhile, Wang Y. et al.
(2010) suggested grafting PCL onto HA to improve the dispersibility of HA in the PCL [4]. Consequently, 20wt% of HA/PCL scaffold had shown better compressive strength (70Pa) and modulus (0.74MPa) compared to none grafted HA/PCL.

Other than that, Choi W.Y et al. (2010) and Rezaei A. and Mohammadi M.R (2013) were proposed another approach, which is in situ HA crystals were synthesized and precipitated with the PCL solution, instead of using a commercial HA [5-6]. However, the size, shape, and amount of HA could not be controlled precisely. Besides, other studies were introduced ultrafine-sized HA (with mean sizes of 0.5 µm, 5 µm, 10 µm, and 200 nm), and ultrasound wave during solution mixing in order to obtain HA well-dispersed [7-10]. However, this approach has one weakness: HA loading is limited due to the different polarity, which could lead to the agglomeration of HA in the PCL/HA composite [10].

All previously discussed approaches had solved the homogenization problem. However, the major drawback of these approaches is the use of large amounts of solvents, which require longer drying. This is the main concern for applications in bone tissue engineering where these solvents must be completely removed to avoid toxicity effect to the human body [11].

Due to this, some studies were introduced plasticized water soluble polymers, namely, polyethylene glycol (PEG) and polyethylene oxide (PEO) in melt blending to improve the intermixing process between PCL and HA at higher content [11-13]. However, PEO and PEG must be leached out prior to application.

This study was interested in introducing another approach, which was the ultrasonic-assisted melt blending process. Ultrasonic wave was expected to improve the homogenization of HA in the PCL blend. The main advantage of this approach is that it is a solvent-free blending method. This study has investigated the effect of ultrasound on the morphology of PCL/HA composite blends, and will be discussed in this paper.

2. Materials and method

2.1. Material

PCL (60,000 g/mol) in pellet form was purchased from Shenzhen Esun Industrial Co., Ltd. Needle-shaped hydroxyapatite powder was purchased from Berkeley. The density of the HA powder was 2.97 g/cm³ and has needle-shaped particles. The mean particle size distribution was 31.06 µm, which was analysed using a Malvern Instruments’ Mastersizer 2000. Meanwhile, the molar ratio of calcium (Ca) and phosphorus (P), Ca/P was 1.64, determined by energy dispersive X-ray spectrometer (EDS). The FESEM micrograph in Figure 1 shows the detail of HAN’s particle surface as received.

![FESEM images for HAN](image1.png)

**Figure 1.** FESEM images for HAN, as received. (a) HAN particles, as received, tend to agglomerate, and have a mean particle size distribution of 31.06 µm, (b) HAN, as received, was presented in the form of agglomerates with many cavities or voids, and shaped like needles.
2.2. Methods

2.2.1. Sample preparations. All PCL-containing materials were dried under vacuum at 38 °C for a minimum of 10 hours, while HAN powder was dried at 120 °C for 10 hours to avoid moisture-induced degradation reactions [12]. HAN loading was varied from 10 to 30wt%. PCL and HAN 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 °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, pelletized. Then, the pelletized PCL/HAN nanocomposite blend was compressed using a hot press at temperature and pressure of 80 °C and 700 psi, respectively, to produce disc-shaped samples that were 20 mm in diameter and 1 mm thick. These discs were fractured using liquid nitrogen for the morphology study.

2.2.2. Morphology of PCL/HAN nanocomposite blends. The morphology of these PCL/HA composite samples were assessed using a field emission scanning electron microscope (FE-SEM). The samples were cross-sectioned, gold–coated, and analyzed using the FE-SEM (model GEMINI: ZEISS SUPRA 55VP) under secondary electron imaging.

3. Results and discussion

3.1. Morphology of PCL/HAN nanocomposite blends
The effectiveness of the ultrasonically assisted melt blending was investigated through the morphology of the PCL/HAN nanocomposite blends, as shown in Figure 2.
Figure 2. (a), (c) and (e) are FESEM images for PCL/HAN nanocomposite blends without ultrasonic for 10, 20 and 30wt% HAN respectively. (b), (d) and (f) are FESEM images for PCL/HAN nanocomposite blends with the presence of ultrasonic for 10, 20 and 30wt% HAN, respectively.

From the micrographs shown in Figure 2, it was clear show the different morphology of PCL/HAN blends due to the influence of ultrasonic wave. In the presence of ultrasonic wave, HAN particles were evenly dispersed in the PCL matrix at 10wt% of HAN. However, some small HAN agglomerates were observed at 20wt% and 30wt% of HAN loadings. Meanwhile, in the absence of ultrasonic, small HAN agglomerates were found at 10wt% HAN and the agglomerates’ size become larger at 20 and 30wt% of HAN.

These results showed that the as-received HAN’s agglomerates could have experienced breakage, and were dispersed in the PCL matrix. According to the mechanism proposed by Zhong J et al. (2016) illustrated in Figure 3, the ultrasonic wave propagation in the cavities of HAN’s agglomerates may have generated oscillatory pressure waves, and induced bubble expansion and contraction, which led to a breakage of the agglomerates [14]. This mechanism was helpful in reducing the size of HAN agglomerates during melt blending, thus leading to better dispersion of HAN particles.

Figure 3. Inside cavitation mechanisms by ultrasonic wave in PCL/HA composite blends [14].

Nonetheless, even though the ultrasonic waves had reduced HAN agglomeration, some small agglomerates were still observed at higher HAN loading (20 and 30wt% HAN). This is because at higher loading, HAN particles have a stronger tendency to agglomerate [5]. Consequently, 400 Watt of ultrasonic waves was still ineffective to completely break HAN agglomeration. However, this method had improved the morphology of PCL/HAN nanocomposite blends compared to conventional melt blending.
4. Conclusion
Ultrasound waves were helpful in the breakage of HAN agglomerates and produced better morphology in PCL/HAN nanocomposites during the melt blending process compared to conventional melt blending (without ultrasonic) which produced many and larger HAN agglomerates. This alternative method can be used to replace solution blending due to its solvent-free usage.

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