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Effect of particle size, shape, and weight percentage of hydroxyapatite (HA) on rheological behaviour of polycaprolactone/hydroxyapatite (PCL/HA) composites

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Abstract

The aim of this study is to investigate the influence of hydroxyapatite's (HA) particle size, shape, and variation of HA weight percentage on the rheological behaviour of polycaprolactone/hydroxyapatite (PCL/HA) composite. The composite was produced by melt blending process using a single screw extruder assisted with an ultrasonic wave with varied HA weight content (0 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.%). Two types of HA were used, which are needle shape (HAN) and irregular shape (HAS). The rheological behaviour of the PCL/HA composite was investigated through the melt flow index (MFI) test at a varied temperature of 100, 110, and 120 °C. The result indicated that an increase of HA content decreases the MFI values of the PCL/HA composite. At similar content of HA, PCL/HAN composite has higher activation energy with lower MFI values compared to PCL/HAS composite. In conclusion, this study concluded that the particle size, shape, and weight percentage of HA significantly affect the rheological behaviour of PCL/HA composites.

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1.0 Introduction

Combination of polymer and ceramic shows a good feature of both constituents in which the toughness of polymer and the stiffness of ceramic over composite compare of either only polymer or ceramic (Sangeeta & Shubhajit, 2021). The benefits of this approach have been extensively investigated in bone tissue engineering applications. Particularly, polycaprolactone (PCL) and hydroxyapatite (HA) based composites have attracted much attention due to the complementary properties of PCL and HA (Jiao et al., 2019).

HA is essential for bone that is made up of natural mineral constituents. It has been widely used in medicine as an implant material, owing to its good biocompatibility and bioactivity with high osteoconductive properties (Kim et al., 2017). Hence, HA is incorporated in PCL to improve the osteoconductive property of PCL. Meanwhile, the strength of PCL helps to improve the brittleness problem of HA and overcome that dense HA is not easily absorbed. In recent work, several types of ceramic, such as hydroxyapatite (HA), tri-calcium phosphate (TCP), nukbone (NKB), halloysite, and nano-aluminium oxide have been used to produce composites with polycaprolactone (Huang et al., 2018; Xiao et al., 2009; Gómez-Lizárraga et al., 2017; Jing et al., 2017; Chern et al., 2013). Huang et al. (2018) and Poletto (2018) reported that an increment of HA content in polycaprolactone produced composite with lower mechanical properties. Like other general fillers, the presence of HA increases the composite viscosity. Research conducted by Huang & Bártolo (2018) reported that viscosity of polycaprolactone increased with increasing in HA loading as HA hindered the polymer flow. Another study assessed the rheological properties on the effect of HA in PCL/chitosan (Ghorbani et al., 2016; Kim et al., 2015). A finding reported that the HA particle reduces the polymer chain mobility and decrease the viscous dissipation.

On the other hand, the rheological behaviour of a material is important for further process. For example, in foaming process to produce porous polymer ceramic composite for bone tissue engineering application. The foaming behaviour of a polymer ceramic composite has straggly affected by its viscosity and may result in rheological effects. It has been reported that the increase of material's viscosity restricted the pore growth and pore coalescence, which results in an increment of pore size and pore density (Jing et al., 2017). Therefore, it is important to study the rheology behaviour of polymer ceramic composite before further process. This study aims to investigate the effect of HA particle size and shape at different HA weight percentages on the rheological behaviour of PCL/HA composite by conducting melt flow index (MFI) test. Thus, the effect of temperature on viscosity and activation energy of PCL/HA composites are further discussed.

2.0 Methodology

2.1 Material

Polycaprolactone (PCL) (60,000 g/mol), a semi-crystalline polyester, was purchased in pellet from Shenzhen ESUN Industrial Co. Ltd., China, and needle-shaped HAN was purchased from Berkeley Advanced Biomaterials, United States of America. Meanwhile, irregular shaped HAS powder was synthesized from clamshell using a chemical precipitation method (Goloshchapov et al., 2013). The mean particle size distribution of HAN and HAS been 30.90 ± 0.28 μm and 56.01 ± 4.91μm, respectively and was determined using particle analyser (Malvern Mastersizer 2000, UK). Meanwhile, the density of PCL, HAN, and HAS particles is 1.1548 g/cm^3, 2.9657 g/cm^3 and 3.1991 g/cm^3, respectively.

2.2 Sample preparation

PCL/HA composite blends with different concentrations of HA were prepared using a single screw extruder assisted with ultrasonic waves. The composition of the PCL/HA composites is shown in Table 1. The melt blending process 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 (Akhbar et al., 2018). After the extrusion, all samples were pelletized using a pelletizer.

Table 1: Composition of the PCL/HA composite blends

Samples Designation	Compositions	
	PCL (wt.%)	**HA (wt.%)**
PCL	100	0
10S	90	10
20S	80	20
30S	70	30
40S	60	40
10N	90	10
20N	80	20
30N	70	30

2.3 Methods

2.3.1 Melt flow index (MFI)

The melt flow index (MFI) is measured by following ASTM D1238 using a Tinius–Olsen MP600 extrusion plastometer. MFI indicates the flowability of polymer materials where it correlates with the viscoelastic behaviour of PCL/HA composites (Shojaeiarani et al., 2019). All the samples were tested at temperatures varied at 100, 110, and 120 °C based on the extrusion process with the dead load of 2.16 kg. The molten material flowered through the orifice of 2.1 mm diameter and length of 8.0 mm for 10 minutes, and the values of MFI were in g/10 minutes.

2.3.2 Activation energy, E_a

The activation energy, E_a, was determined using the Arrhenius Equation in Eq. (1) (Patel et al., 2014):

$$MFI = Be^{E_a/RT} \quad (1)$$

where E_a can be calculated from the slope of ln MFI versus 1/T plot, where B is a constant, R is the universal gas constant 8.314 J mol^{-1}·K^{-1} and T is the temperature in Kelvin (K).

3.0 Results and discussion

3.1 Melt flow index (MFI)

MFI is a physical parameter used to evaluate the ability of a polymer to flow when melted, and it is only reflecting the rheological properties of PCL/HA composites at a low shear rate (Anpilogova et al., 2017; Saw et al., 2014). Fig. 1 illustrates MFI values of PCL/HA composites with two different types of HA shapes used at different temperatures. It was found that PCL had a higher MFI value which indicates the lowest melt viscosity of all samples. However, the addition of HA content in the PCL decreased the MFI value of all samples. This shows that the incorporation of HA particles in the PCL matrix restricted the PCL to flow. Besides, an increase in HA content resulted in the increment of melt viscosity. According to Escócio et al. (2015), the hydroxyl (–OH) group on the HA surface would create hydrogen bonding interactions between PCL and HA, increasing the polymer composite melt viscosity. Besides, as HA content increased, the frictional interaction among the HA particles also increased due to agglomeration phenomena. This hinders the flowability of the PCL/HA composite.

On the other hand, the MFI value of 10N, 20N and 30N is lower compared to 10S, 20S, 30S and 40S at similar content of HA, as indicated in Fig. 1. This may be due to HAN has smaller particle size, which is 30.90 ± 0.28 μm, compared to HAS particle size, which is 56.01 ± 4.91 μm. The smaller particle size of HAN has high surface area, which encourages better interaction between PCL and HAN during melt blending. Consequently, more hydrogen bondings are expected between PCL and HAN compared to PCL and HAS particles.

Meanwhile, the effect of temperature on the viscosity of materials, either polymers or composites, is an important parameter since these materials undergo considerable temperature changes during processing (Poletto et al., 2018). Fig. 2 shows the influence of temperatures on the MFI for PCL/HAN and PCL/HAS composites at varied HA content. As expected, the results show that the viscosity decreased with the increase of temperature from 100 to 110 °C and 120 °C. A similar observation was reported by Huang & Bártolo, (2018) for polymer ceramic composite. From Fig. 2, the MFI values of the composites increased linearly with increasing temperatures from 100 to 110 °C and 120 °C for all samples. However, the MFI values of 10N, 20N and 30N are lower at all temperatures compared to 10S, 20S, 30S and 40S at similar HA loading as observed in Fig. 2. As the temperature increased, the free volume was also increased and accelerated the molecular motion (Poletto et al., 2018). Thus, the entanglement density was decreased, the intermolecular interactions became weaker and enhanced the viscosity of polymer composite (Hsissou et al., 2020; Salmah et al., 2012). On the other hand, the flow activation energy (E_a) values were determined from the angular coefficient obtained from the straight-line fit illustrated in Fig. 3. E_a was determined from the slope of ln MFI versus 1/T straight line graph in Fig. 3.

Meanwhile, Fig. 4(a) and Fig. 4(b) show the activation energy, E_a for PCL/HAS composite and PCL/HAN composite, respectively. PCL has lower activation energy compared to all samples of PCL/HA composites. This indicates that melt viscosity of the composite is affected significantly by the addition of HA particles. The presence of HA restricted the material's movement, and more energy is required for

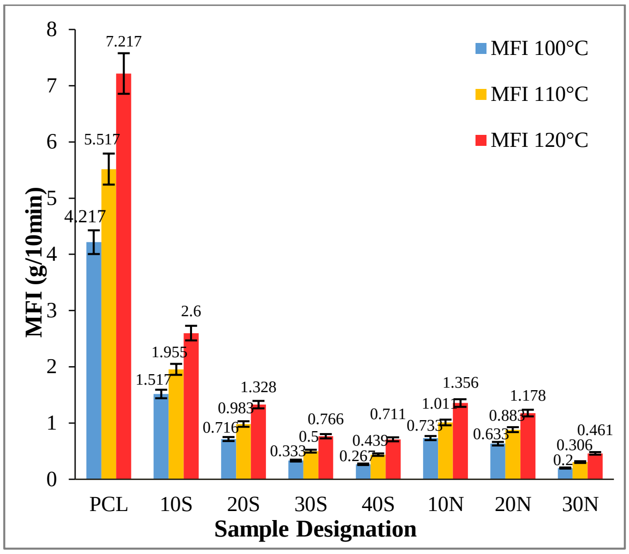


Fig. 1: MFI of PCL/HA composites at varied HA content

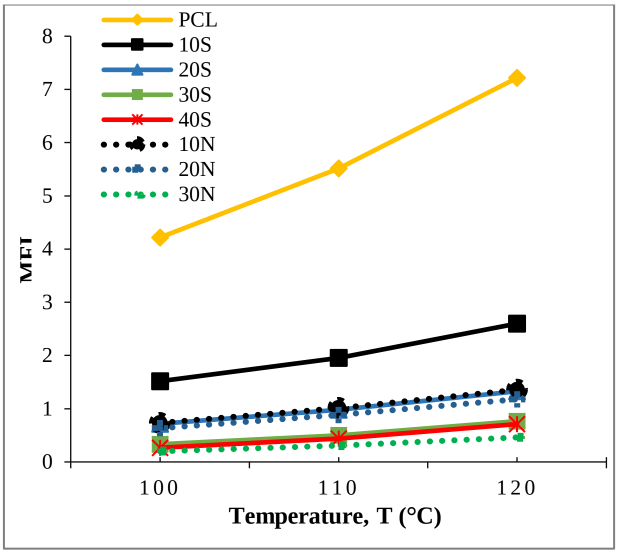


Fig. 2: The effect of temperature on MFI of PCL/HAN and PCL/HAS composites at different HA loading

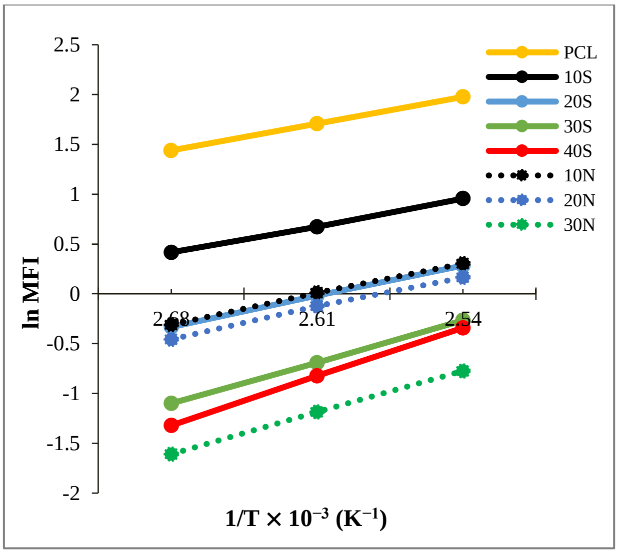
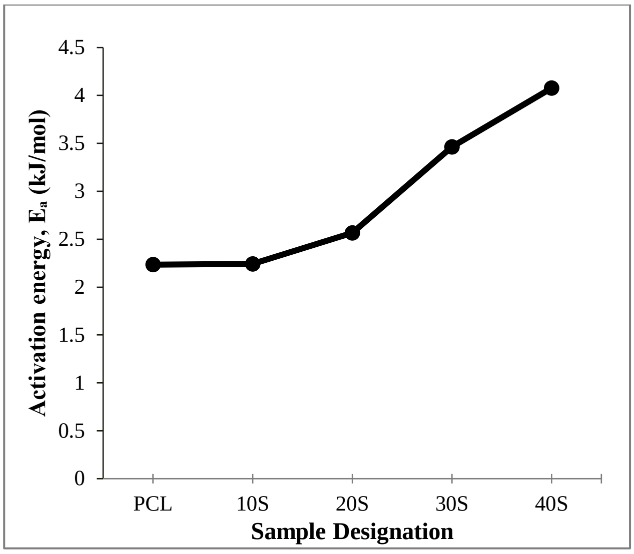
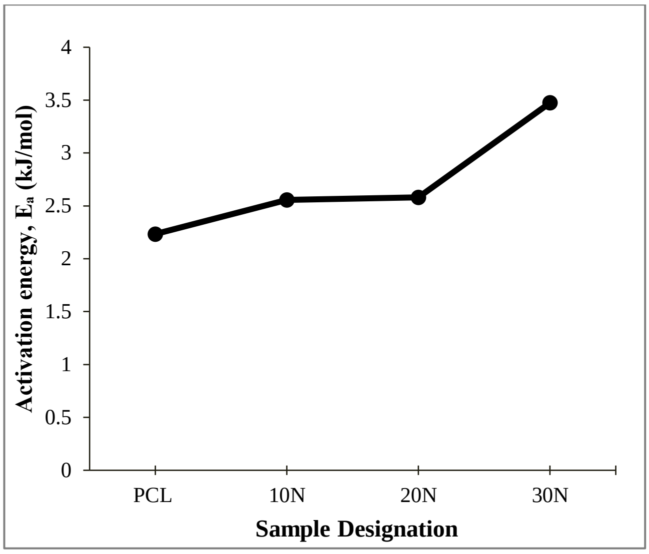


Fig. 3: Graph of ln MFI versus 1/T for PCL/HA composites



(a)



(b)

Fig. 4: The activation energy of (a) PCL/HAS composites and (b) PCL/HAN composites

that composite to flow through the matrix, resulting in an increase in the E_a values. Both PCL/HAS and PCL/HAN composite show a similar trend in which E_a increased as HA content increased, as observed from Fig. 4(a) and Fig. 4(b), respectively.

Furthermore, Table 2 shows the values of E_a of PCL/HA composites at varied HA loading. The linear correlation coefficients, R^2, were more than 0.99, which indicates that ln MFI and (1/T) had a strong positive linear correlation. The activation energy, E_a of the material provides important information on the sensitivity of the material towards the change in temperature. The higher the activation energy indicated more temperature sensitivity of the composites (Salmah et al., 2012).

As a result, the addition of HA into PCL increased the activation energy of the composites. Besides, the results showed that 10N, 20N, and 30N samples have a higher activation energy of the composites compared to 10S, 20S, 30S and 40S at similar content of HA. Again, the reason is that HAN has a smaller particle size (30.90 ± 0.28 μm) which provide a larger surface area which leads to better interfacial interaction between the PCL and HAN.

Table 2: Activation energy (E_a) of PCL/HA composites

Samples	Activation Energy, E_a (kJ/mol)	R^2
PCL	2.2340	1.0000
10S	2.2406	0.9989
20S	2.5649	0.9998
30S	3.4644	0.9998
40S	4.0764	0.9999
10N	2.5566	0.9993
20N	2.5807	0.9982
30N	3.4744	0.9999

4.0 Conclusions

In conclusion, the addition of HA in the PCL/HA composite decreased the MFI values. The increase of HA content in the PCL increased the melt viscosity. Besides, temperature significantly affected the MFI values, which is as the temperature increased from 100°C to 110°C and 120°C, the MFI values of the composites increased with a decrement of viscosity. The results also concluded that the PCL/HAN composite has higher activation energy but lower MFI values than the PCL/HAS composite due to smaller particle size.

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