

POLYETHERETHERKETONE/HYDROXYAPATITE BIOCOMPOSITES COMPOUNDED VIA NANO- MIXER SINGLE SCREW EXTRUDER: THERMAL AND CHARACTERIZATION

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Graphical abstract



Abstract

The aim of this study is to produce polyetheretherketone/hydroxyapatite (PEEK/HA) biocomposite using a nano-mixer single screw extruder. The use of a special design compounding machine, nano-mixer single screw extruder as a processing route could probably induce PEEK/HA composite with uniform compounding. Thermal testing and characterization were conducted to obtain information concerning the effects of single screw on the thermal properties and compounding characteristic. From this study, TGA analysis showed a minimal loss of weight for all composite samples up to 500°C and above this temperature, the decomposition occurred for PEEK/HA composite. Significant change in crystallinity was observed from DSC study of this composite where the increase in HA content was proportional to the crystalline structure in the composite. Apart from that, XRD measurement showed that HA was successfully embodied into PEEK matrix as the peak of intensity increased proportionally with the increase in HA content.

Keywords: Polyetheretherketone (PEEK), Hydroxyapatite (HA), Nano-mixer single screw extruder

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1.0 INTRODUCTION

The compatibility of polymer for implantation in human body leaves a significant effect on bone healing. Currently, many medical devices which made of polymer are gaining popularity than that of metal. One of the most renowned biomaterial used in medical device is Polyetheretherketone (PEEK). In

1990, PEEK had emerged as the leading high-performance thermoplastic candidate for replacing metal implant components, especially in orthopedics and trauma [1]. The ability of PEEK to maintain its properties at high temperature are well-proven, besides exposure to chemical solution and fatigue environments. It also has a very good thermal stability. PEEK is an excellent material for a large array of thermal plastic applications where combustion,

thermal, and chemical performance is critical. PEEK exhibits a high ability to retain flexural and tensile properties at very high temperatures, 250 °C (482 °F) or more within steam, or high water pressure environments. PEEK is inert to all common organic and inorganic liquids and regular solvents. Researchers have generally chosen 450 G as the PEEK resin for their composites research.

Over the past decade, there has been interest in further tailoring the polymer to stimulate bone apposition for load bearing orthopedic applications [2-4]. Bioactive PEEK composites are created by compounding the PEEK with calcium phosphate biomaterials, such as beta-tricalcium phosphate (b-TCP) and hydroxyapatite (HA). The incorporation of bioactive filler in polymer becomes interest to further enhance bioactivity of implant material. At present, the hydroxyapatite is widely used as fillers in polymer matrix. Hydroxyapatite with chemical formula $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is a synthetic analog of the calcified tissues of vertebrates. It has often been considered as fillers in load bearing applications due to direct bonding between HA to bone and this promotes the new formation of bone that is necessary for implant osseointegration [5]. The manufacturing of composite with desirable mechanical properties close to human bone is getting attention recently. The selection of processing method is important to understand the direct thermal effect on composite. To the best of authors' knowledge, there have been few studies on the evaluation of PEEK/HA composite produced via nano-mixer single screw extruder with special design at metering section of screw. The aim of this study is to evaluate the effect of HA loadings and processing route on the crystallinity content of PEEK/HA composites.

2.0 METHODOLOGY

2.1 Materials.

PEEK used in this study is a standard viscosity PEEK (VICTREX 450G) in granule form supplied by Victrex Plc., United Kingdom. Whilst HA (Fluka) used in this study was purchased from Sigma Aldrich with density of 3.16 kg/cm³.

2.2 Compounding and Injection Molding.

The manufacturing of PEEK/HA composite was done by compounding the materials using nano-mixer single screw extruder (NANO TECHRUDER, 2010 machine, Malaysia) as shown in Figure 1. HA with up to 40 wt% loading was successfully extruded at temperature between 350°C – 380°C. Constant screw speed of 30 rpm was applied during compounding. Length/Depth (L/D) ratio for this machine is 26. Further, PEEK and its composite samples were produced by injection molding JSW

(Model NIOOB II, Japan) with parameters of barrel temperature of 340–390°C, nozzle temperature of 395°C, mold temperature of 50°C, injection pressure of 14 MPa, follow-up pressure of 8–12 MPa, and screw speed of 30 rpm. Pure thermoplastic sample was coded as PEEK, and PEEK composites were designated as PEEK/XHA where X is 10, 20, 30, and 40 wt% of HA loaded to PEEK matrix.

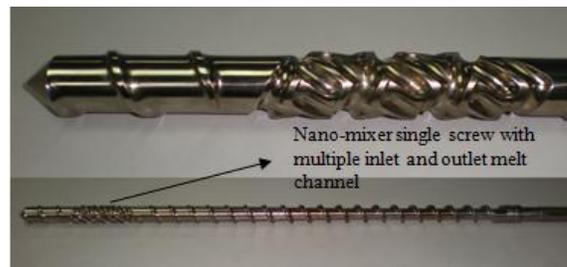


Figure 1 Single screw with special design nano-mixer (U.S. Patern no. 6497508)

2.3 Thermal Analysis and Characterization.

A differential scanning calorimetry (DSC, Perkin-Elmer, USA) was used to examine the crystallinity of the polymer matrix after processing. Approximately, 5–20 mg of pure PEEK and composite samples were heated from 30 to 380 °C in nitrogen atmosphere at a heating rate of 10 °C/min, and the degree of crystallinity was determined as follows:

$$X_c (\%) = \frac{\Delta H_f}{w_i \Delta H_f^o} \times 100$$

where ΔH_f^o to be 130 Jg⁻¹.

TGA is a technique used to quantify the filler content of a polymer composite. In this study, the loss of HA particle with various content of filler were determined. The rationale behind this analysis is to ensure that the applied processing temperature will not degrade the HA. The ashing of composites was carried out by using a Perkin Elmer TGA 7, USA. About 20 g of sample was heated up to 850°C in nitrogen atmosphere at a scan rate of 20°C/min. Characterizations were performed using a Siemens X-ray diffractometer on Izod bars, with a voltage of 40 kV and an intensity of 40mA, using Cu K α (k = 0.15418 nm) radiation, with an aperture of 0.6 mm. Diffractograms were recorded at room temperature in the angular region $2\theta = 5-60^\circ$, at a scan speed of 0.2⁻¹ s and 0.02° angular increment.

3.0 RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimetry (DSC)

DSC was applied to estimate the effect of the HA fillers on the crystallization behaviour of the PEEK molecules. Consequently, the crystallization temperature (T_c), melting temperature (T_m), rate of crystallinity (X_c) and heat (ΔH_m) for both PEEK and HA reinforced PEEK composited could be determined. Table 1 shows the thermal data that was influenced by HA weight loadings on the crystallinity of PEEK/HA composite. As shown in Table 1, the melting temperature (T_m) of the HA filled PEEK composites are nearly similar, varies slightly than that of the neat PEEK by about 1-3 °C. Furthermore, all the crystallization temperatures (T_c) of the composites were noticed to be lower than that of pure PEEK. It seemed that at

higher filler contents, the T_c of the composites will be reduced proportionally. These could be attributed to the HA filler in the PEEK matrix where it may hinder the movement of the polymer chain segment during crystallization. It is noteworthy that the crystallinity of the composite increased with the increase in HA content. The incorporation of particles in polymer matrix could have influenced its crystallization behaviour with two undermining effects [6]. One of the effects is that the particles act as nuclei to encourage nucleation on particle surfaces, hence might resulting in increasing the crystallization temperature and crystallinity of composite [7-8]. Another effect is that HA particles can hinder the motion of polymer chain during crystallization. Accordingly, this has resulted in a lower crystallinity fraction and crystallization temperature [9].

Table 1 Thermal properties of PEEK and PEEK/HA composites

Composition	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%) PEEK
PEEK	168	349	47.5	36.5
10HA	167	346	44.1	37.7
20HA	166	349	46.7	44.8
30HA	165	348	51.3	56.4
40HA	165	349	48.5	62.2

3.2 Thermal Gravimetric Calorimetry (TGA)

TGA thermograms for the different samples of PEEK and PEEK/HA composites are shown in Figure 2 The degradation temperature (T_{10}) was set at 10 wt% loss as tabulated in Table 2. It can be seen that the temperature of neat PEEK at 10 wt% weight loss was found to be higher than composite with HA content of 10wt%. However, the decomposition temperature of 40wt% HA is lower than others probably due to the removal of adsorbed water in the HA crystal lattice at temperature ranges from 80 – 120°C and dehydroxylation of the HA material up to 700°C [10]. It can be observed from Figure 2 that there is no significant loss of weight at temperature range until 500°C for PEEK and all composites except for 30 wt% HA content. It should be noted that the residue after degradation of PEEK increases gradually with the composition of HA. This may be due to the strong physical bonding between the HA filler and PEEK matrix. The solid residue at temperature of 700°C for the composite increased as expected as HA is extremely stable at this temperature. This is consistent

with the findings from Meenan *et al.* [11] who reported the similar thermal stability of PEEK/HA composite, i.e, when HA content increased, the total solid residue also increased.

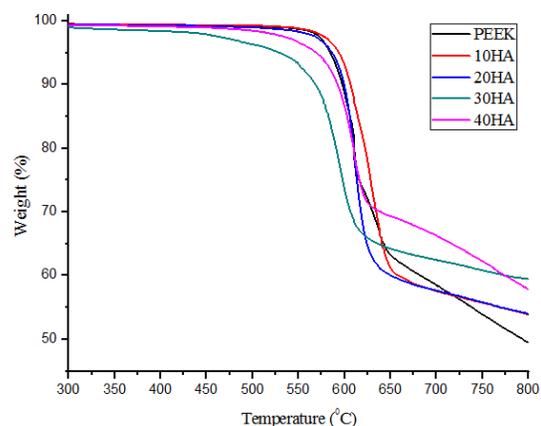


Figure 2 TGA thermograms of the PEEK and various PEEK/HA compositions

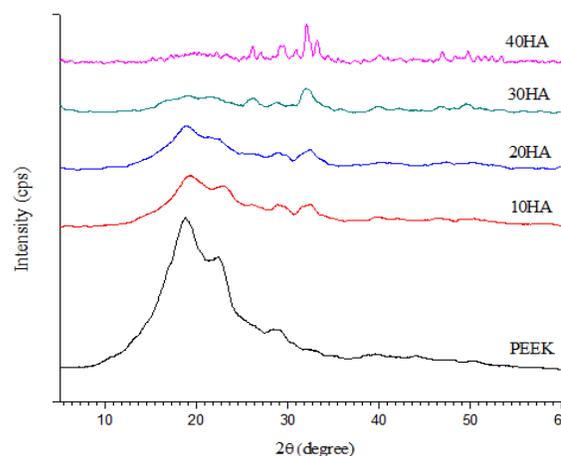
Table 2 TGA results of PEEK and PEEK/HA composites

Composition	HA content (wt %)	T ₁₀ (°C)	% Solid residue at 700 °C
PEEK	0	597	58.5
10HA	10	606	57.5
20HA	20	598	57.6
30HA	30	598	60.3
40HA	40	592	66.2

3.3 Characterization By XRD

It is known that X-ray diffraction method can be applied to discover the microstructure, interfacial interaction, and degree of crystallization of the polymer composite. The XRD patterns of the pure PEEK and HA composite are shown in Figure 3. It shows that the orthorhombic phase diffraction peaks for PEEK are mainly in the range of 15°-25° whilst the HA phase exists in the range of 30-45°. There are no extra peaks with the addition of HA filler, suggesting that no considerable new interfacial phase formed. It is important to note that the XRD patterns showed some HA wide reflections, indicating a poor crystalline phase formation. Moreover, it can be seen that the broad pattern at 17° to 24° were related to the characteristic peaks of PEEK verified that PEEK possessed semi-crystalline structure. As can be seen from Table 3, the inter planer spacing (*d*-spacing) for the pure PEEK was the highest. However, a noteworthy decrease in *d*-spacing was observed from 4.72Å to 2.79Å as the HA content increased which could be attributed to perfection of crystals. Similar results were reported by Goyal *et al.* [13] where the addition of Al₂O₃ had decreased the inter planer spacing in all directions perpendicular to plane *d*_{hkl} (110) and (111). Due to the decreasing value of *d*-spacing, the proportion of crystalline units was also decreased, thus improving the crystallinity of composite. It is interesting to note that the XRD peaks of phase of PEEK disappear with the introduction of

40 wt% HA which proved that the addition of HA alters the structure of the crystalline phase. This disappearance suggests that the accumulation of HA disturbs the perfect arrangement of hydrogen bonded sheets of the crystalline phase [12]. In another study by Lee *et al.* [14] discovered that the intensities of all peaks for HA in poly (propylene fumarate) (PPF) composite had no significant changes because simple blending of preformed HA with amorphous matrix did not influence the crystalline structure of HA.

**Figure 3** XRD pattern of pure PEEK and the variation PEEK/HA composite**Table 3** The 2θ angle and *d*-spacing of PEEK and PEEK/HA

Composition	PEEK (wt %)	HA (wt %)	2θ	<i>d</i> -spacing (Å)
PEEK	100	0	18.78	4.72
10HA	90	10	19.01	4.66
20HA	80	20	18.78	4.72
30HA	70	30	31.97	2.79
40HA	60	40	31.97	2.79

4.0 CONCLUSION

Thermal properties and characterization of PEEK/HA composite has been discussed throughout this study. The TGA result has demonstrated that the ceramic HA plays a role to reduce the onset temperature of PEEK degradation up to 7°C as the HA content is increased. Moreover, the use of DSC to analyze thermal characteristic of this composite allows the value of crystallinity of PEEK (X_c), crystallization temperature (T_c) and melting temperature (T_m) to be decided. Measurement on existing HA phase in PEEK matrix using XRD revealed that the HA particles was successfully blended using the nano-mixer single screw extruder.

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