Investigation on Strain Rate Sensitivity of 3D Printed sPEEK-HAP/rGO Composites

Sagar Mahalingappa Baligidad (✉ smbaling@gmail.com)  
CMR Institute of Technology  https://orcid.org/0000-0003-2602-736X

Chethan Kumar Gangadhara  
CMR Institute of Technology

Maharudresh Aralikatte Chandrashekar  
CMR Institute of Technology

Research Article

Keywords: Polyetheretherketone (PEEK), Hydroxyapatite, Graphene Oxide, Mechanical testing, strain rate sensitivity,

Posted Date: December 8th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1125996/v1

License: ☕ This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

Nanofillers can be added to polymers to improve their mechanical behavior. However, the yield behaviour of most polymer composites is influenced by strain rate. The majority of the research focused on the behaviour of polymer composites at high strain rates. This work aims to investigate how hydroxyapatite (HAP) and reduced Graphene Oxide (rGO) nanofillers affect the mechanical properties of sulphonated polyetheretherketone (sPEEK) at low (tensile and compression behaviour) and high strain rates (compression behaviour). The thermal, mechanical, and energy absorption responses of sPEEK filled with HAP and varying mass fraction ($M_f$) of rGO (0.5%, 1%, and 1.5%) at different strain are studied in detail. The strong strain rate effect was seen in HAp and rGO loaded sPEEK composites. The strain rate sensitivity factor of sPEEK-HAP/rGO improved as the strain rate increased, but decreased when the $M_f$ of rGO increased. Under low strain rate compression, HAp and rGO loaded sPEEK absorbed more energy at $M_f$ about 4%. SEM micrography was used to study the microstructures of the fractured interfaces of the components, revealing that the HAp and sPEEK materials formed a good compatibility in presence of rGO.

1. Introduction

Growing cases of road crashes, sports injuries and increased bone-related risks among the elderly population has resulted in a rising need for orthopaedic equipment. Orthopedic implant therapy has been introduced on a regular basis and has proven to be quite successful in repairing irreversible bone deterioration [1]. PEEK is a commonly used biopolymer with good biocompatibility and mechanical compatibility [2]. Due to its unique architecture, PEEK exhibits enticing properties identical to human bone. Because of its features, PEEK has been widely used for the preparing of products like knee joint, artificial spine and skull [3, 4]. Owing to its outstanding efficiency, it exhibits poor bioactivity and limited bone binding ability and heat and friction performance of the premeditated higher specifications can still not be met [5, 6].

At present, there are primarily two strategies that have been reviewed in this paper, including composite preparation and surface alteration to increase the bioactivity property of PEEK. Therefore, PEEK and its products filled with fibre have since become a trend. The fillers such as SiO$_2$, Al$_2$O$_3$, ZrO$_2$, Si$_3$N$_4$, and; carbon fiber [7, 8]. Ceramic fillers, such as HA, bioglass, TCP and calcium silicate (CS), are favoured as bioactive materials and, because of their ability to naturally bind to living bones, are preferred as bone replacements [9]. Hydroxyapatite (HAP) is a biocompatible bioceramic material. Due to its brittleness and complicated processing, the use of HAP alone as a bone scaffold is limited [10]. As a scaffold material, the composite of biopolymer and bioceramic may manifest their respective advantages while avoiding their drawbacks [11]. Zhang et al. (2009) [12] investigated the morphology and cell attachment nature of HA/PEEK composites fabricated via SLS. They concluded that, relative to PVC and TMXX, higher levels of HA composite demonstrated strong cell growth and osteoblast formation. R. Ma et al. (2014) [13] employed In-situ process to develop HA/PEEK composite. The composite demonstrated excellent bonding and improved mechanical properties between HA and PEEK. Cao et al. (2019) [14] developed
multi-layered carbon nontubes/PEEK/BG ternary composite via injection moulding. Unfortunately, relative to human cortical bone, these bioactive materials demonstrate poorer fracturing resistance and greater elastic modulus [15]. HAP has trouble distributing homogeneously in the PEEK substrate because of variances in physical and chemical characteristics, and the overall performance of their composite suffers as a result [16, 17]. Hence, the use of an interface media is suggested as an effective means to enhance compatibility between the PEEK and HAp phases.

GO has recently become the subject of concern in both experimental research and functional application studies due to its distinctive form and extraordinary properties. However, only a few studies have employed GO as an interface phase medium, despite the fact that it possesses excellent mechanical and thermal behaviour of PEEK [18]. Lynch-Branzoi et al. [19] used in-situ shear exfoliation to develop a graphene filled PEEK composite with a 400% improvement in tensile modulus. Song et al. [20] employed a GO nanosheets filler with PEEK. Because of tiny size of GO sheet and its thin structure increases the wear resistance of PEEK. The behaviour of PEEK/GO composite is heavily influenced by dispersion of graphene particle within the PEEK matrix and interfacial compatibility between them. However, graphene tends to cluster in the PEEK medium and is difficult to distribute evenly due to the higher melting point and melt viscosity of PEEK [21]. Coating GO particles on PEEK improves its compatibility with the material.

Yang et al. [22] attempted to increase interfacial adhesion between PEEK and GO by treating GO nanosheets with polyethersulfone (PES). They found a homogeneous distribution of GO nanosheets within the PEEK medium, as well as improved mechanical characteristics and compatibility between them. Song et al. [23] employed γ-aminopropyl trimethoxysilane silane agent to modify the surface of GO. The modified GO was distributed uniformly in PEEK, resulting in better friction and anti-wear properties than uncoated GO and MWNTs. Physical modifications to the graphene surface or using non-covalent coating processes have no effect on the binding force between GO and PEEK. Furthermore, GO has huge quantities of oxygen functional groups on its surface and edges, makes it strongly negatively charged. The negatively charged GO surface can attract calcium atoms in the HAP crystal plane, which are positively charged [24]. The scientific and technical society is increasingly valuing additive manufacturing (AM), which offers several benefits such as customizable geometry, cost effectiveness, and time savings [25]. The most extensively used AM technology is fused deposition modelling (FDM), which involves extruding molten filament via a nozzle and depositing it layer by layer on a builtplate [26]. Although the availability of simple polymeric material for FDM process has grown in recent years, the need for functional parts necessitates additional advancements in filler and fibre additive inclusion technologies.

Considering these issues, GO was firstly treated and form rGO, then mixed with HAP. HAP-GO mixture was then used to prepare PEEK/HAP-rGO composites by melt blending method. The PEEK/HAP-rGO parts were fabricated via FDM process. The mechanical behaviour of HAP-rGO loaded with varying volume fractions of rGO were studied. In this work, parts were carefully evaluated for compressive and tensile behaviours at low strain rates, as well as compressive behaviours at high strain rates. The phase
composition and fractured surface morphologies were analysed by using SEM images. Thermal behaviour of PEEK and its composited were evaluated via thermogravimetric analysis (TGA).

2. Experimental Method

2.1 Materials

For this investigation, PEEK granules of grade PE10 with a melt flow of 24 g/10 min and a molecular weight of 98,200 g/mol was used. To surface treat the PEEK, sulfuric acid with a concentration of 95-98% and a molecular weight of 98.079 g/mol, as well as ethanol and NaOH were procured from Sigma Aldrich. Hydroxyapatite (HAP) powder with the 10mm particle size and graphene oxide (GO) powder with 1.2 nm particle size were procured from Sigma Aldrich.

2.2 Methods

2.2.1 Surface treatment

PEEK pellets were submerged in concentrated H$_2$SO$_4$ for a regulated period of time before being immersed in water for 20 sec to eliminate any leftover H$_2$SO$_4$ to form sulphonated surface on PEEK (sPEEK).

A hydrothermal reduction process was used to treat the surface of GO in order to produce reduced graphene oxide (rGO), which involved adding 100 ml of ethanol to 1 gramme of GO powder and stirring for 30 minutes with magnetic stirring. The solution was then moved to Teflon autoclave and heated for 9 hours at about 210°C in an oven. The solution then soaked in distilled water before being dried at 70°C for 6 hours. The solid precipitate was then dissolved in chloroform (100 mL), sonicated for 30 minutes, then centrifuged at 4000 rpm for 5 minutes.

2.2.2 Extrusion process

HAP and rGO were thoroughly mixed by using the Brabender. The HAP-rGO compound was then combined with sPEEK pellets and put into the hopper of a single screw extruder. To produce a 1.75 mm diameter filament, an extruder temperature profile of 300$^0$, 350$^0$, 350$^0$, and 380$^0$ C were maintained from hopper to die, with a screw speed of 18 rpm. During extrusion, the screw speed and mix temperature settings were chosen to preserve and ensnare the air holes in the filament. sPEEK/HAP-rGO composite filaments were produced with varying volume fractions of rGO such as 2%, 4%, 6%. Newly produced sPEEK/HAP-rGO filaments were used to 3D print test specimens by using an Ultimaker IMKI 3D printer. Because of the presence of HAPs in the PEEK matrix, the 3D printer used a 0.6 mm diameter hot end nozzle to avoid printing blockage. To ensure no porosity between the layers, all parts were printed at 100% density, 0.2 mm layer thickness, and a print speed of 50 mm/sec, with the exception of porosity inside the filament.

2.3 Experimentation
2.3.1 Density measurement

The tensile test specimen is used to calculate the densities of the syntactic foam matrix and it is computed using ASTM D792-13. The sample's weight was divided by its volume, and the average of five values was used in the computation. The theoretical densities were derived by Eq. (1):

\[ \rho_{\text{theor}} = \rho_{\text{HGM}} \cdot W_f + \rho_p \cdot (1 - W_f) \]  

(1)

where \( \rho_{\text{theor}} \) is the theoretical density of the matrix. \( \rho_{\text{HGM}} \) and \( \rho_p \) are the densities of the HGM and PEEK respectively and \( W_f \) - weight fraction of HGM.

2.3.2 Low strain rates testing

The compression and tensile test samples were 3D printed using a commercial 3D printer and prepared according to ASTM D695 and ASTM D638 standards, respectively. The dimensions of the tensile and compression test samples are shown in Fig 1. The tests were run using a Vector Pro MT universal tester at a low strain rate. Tensile tests were carried by using an extensometer with a gauge length of 25mm. Both tests were performed at strain rates of 0.001, 0.01, and 0.1 s-1, which were calculated by dividing the cross-head stroke rate of the machine by the gauge length of the specimen.

2.3.3 High strain rates testing

The compression test at high strain rates of 800 s-1 and 1000 s-1 were carried by using a SHPB. The strain signal obtained from the incident and transmitter bars may be used to determine basic data such as stress and strain rates using Eqns (2) to (4) and the required basic data such as stress and strain. In the bars, 1-D elastic wave propagation is considered.

\[ \varepsilon_s(t) = -\frac{2S_0}{l_0} \int_0^t \varepsilon_R \, dt \]  

(2)

\[ \sigma_s = E \cdot \frac{A}{A_s} \cdot \varepsilon_r \]  

(3)

\[ \varepsilon = -\frac{2S_0}{l_0} \cdot \varepsilon_r \]  

(4)

where, \( S_0 \) = sound wave velocity (bar), \( e_R \) = Reflect strain, \( l_0 \) = Initial specimen length, \( E \) = Modulus, \( A \) = C/s area of bar, \( A_s \) = C/s area of specimen, and \( \varepsilon_r \) = Transmit strain.

The dynamic equilibrium factor has been identified as a significant feature in evaluating the dependability of the SHPB approach. The sum of the stresses imposed by the incident and reflection waves may be used to calculate the stress applied at the sample's front end. The stress imposed by the transmitted wave is applied to the sample's back end. The stresses acting at the front and back ends of the specimen during the procedure are shown in Fig 2. As can be observed, force equilibrium has been established to a great extent, implying that the SHPB data is reliable.
2.3.4 Thermal analysis

Universal TGA 2950 TA instrument was used to inspect the thermal degradation characteristics of PEEK/HAP-rGO composites under an inert atmosphere. During the process, all samples were heated at a constant rate of 10°C from 350 °C to 900 °C. The composites were also thermally analysed in the air using a TA Instruments Q500 TGA. The thermogram curve was plotted by residual weight% vs temperature to examine the degradation temperatures at the maximum weight loss. Differential scanning calorimetry (DSC) of 3 STARe System was used to derive the Tg of the composites.

2.3.5 Morphology study

SEM micrography investigation was carried out by using a Carl Zeiss AxioVertA1 Low-Vacuum in order to evaluate microstructure of the fractured surfaces. All of the broken tensile test parts were coated with conductive material before to SEM evaluation, and the analysis was performed at a 20-kW acceleration voltage.

3. Results And Discussion

3.1 MFI and Rheology of sPEEK/HAP-rGO

The flowability of PEEK and its composite is determined using melt flow index (MFI), which was measured at 400°C, in context of filament manufacture by extrusion and subsequent 3D printing of parts. It is observed from Table 1, MFI decreases as rGO concentration rises due to filler resistance to polymer flow [27]. PEEK has the highest MFI (5.204% g/10 min) when compared to its composites, and MFI decreases as rGO increases, which might cause printing concerns. MFI was decreased by 24.1%, 28.3%, and 33.1% when compared to neat PEEK at 2%, 4%, and 6%, respectively [28]. Reduced MFI must be studied carefully and accounted for by raising the printing temperature, particularly for composite with a higher rGO%. To reduce warpage, the bed temperature is maintained constant, and the multiplier factor was modified to account for the greater rGO%. The MFI of polymer rises as the filler infusion increases, as seen throughout the frequency sweep [29]. PEEK has a shear-thinning area at higher frequencies. The limitation of polymer chain motions by different concentration of rGo (2%, 4% and 6%) causes PEEK/HAP to behave similarly, with a little increase in \( \eta' \).

Table 1. MFI comparison
| Composition           | MFI (g/10 min) Mean value | Standard Deviation |
|-----------------------|---------------------------|--------------------|
| sPEEK                 | 5.2                       | 0.4                |
| sPEEK-HAP             | 3.4                       | 0.3                |
| sPEEK-HAP/rGO(0.5)    | 2.7                       | 0.2                |
| sPEEK-HAP/rGO(1)      | 1.9                       | 0.2                |
| sPEEK-HAP/rGO(1.5)    | 3.1                       | 0.2                |

### 3.2 Compression properties

Figure 3a shows the compressive strength of sPEEK, sPEEK/HAP and sPEEK/HAP-rGO composites containing different $M_f$ of rGO at low strain rates. The compressive strength has been found to be strain rate sensitive, increasing as the strain rate increases. As the strain rate increased, the compression strength of the PEEK/HAP composite reduced by 10% compared to the sPEEK sample. PEEK material used is brittle, became amorphous after sulphonation, with a yield point processed by the formation of a neck. Adding HAP to the sPEEK matrix reduces the volume fraction of composite, weakening the overall strength of the material because composite is the principal stressed component. The addition of rGO to the sPEEK/HAP composite boosts compression strength even further. The compression strength of sPEEK/HAP-rGO composites improves as the $M_f$ of rGO increases, compared to sPEEK and sPEEK/HAP composites. With a rise in rGO concentration from 0.5–1.5%, compression strength increases by 3.4%, 5.2%, and 3.8% for 0.001, 0.01, and 0.1 s$^{-1}$ strain rates, respectively. The maximum compressive strength was observed for 1.5% concentration at 0.1 s$^{-1}$ strain rate, which is identical to sPEEK but 1.3% less. The reason for this is because GO possesses a hexagonal carbon network with hydroxyl and epoxide functional groups, which improves compression strength by establishing strong interfacial bonding between PEEK and HAP, as well as increasing the composite's mechanical properties.

Figure 3b shows the compressive strength of sPEEK, sPEEK/HAP and sPEEK/HAP-rGO composites containing different $M_f$ of rGO at high strain rates such as 800 and 1000 s$^{-1}$. It was found that sPEEK and its composites had stronger compression strength at higher strain rates than they do at lower strain rates. As strain rate increased, the compression strength of the PEEK/HAP composite decreased by 15% compared to the sPEEK sample. At high strain rates, however, the material's molecular structure does not have enough time to absorb the deformation, resulting in a decreased fracture rate. When rGO is added to the PEEK/HAP composite, its compression strength improves. The maximum compressive strength was found at a concentration of 1.5% rGO at 800 s$^{-1}$ strain rate.

This idea also applies to the increase in the density of composites as shown in Fig. 4. It shows that $M_f$ and $\rho$ have a linear relation. This shows that the composites' strength is proportionate to their densities. When comparing identical HAP and rGO filled composites under similar strain rate loading, this
occurrence allows for the examination of HAP and rGO filled polymer strength considering specimen density as one factor.

### 3.3 Strain rate effect

Compression test stress-strain curves of sPEEK and sPEEK/HAP samples at 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates are shown in Fig. 5. The sPEEK exhibits abrupt and linear elastic behaviour until it reaches the apex, after which it yields and the fracture propagates linearly until it reaches fracture failure (Fig. 5a). For all strain rates, the curve had a same pattern. The results reveal that sPEEK exhibits positive strain rate sensitivity with increase in strain rate and the fracture strain increases, from 0.01 to 0.3 for strain rates of 0.001 s\(^{-1}\) to 0.1 s\(^{-1}\). A loss of ductility was observed with increasing strain rates. The inclusion of HAP makes the sPEEK composite amorphous, and the elastic behaviour of the composites decreases as the strain rates increase. sPEEK/HAP composite also showed a sharp and linear until it reaches the peak. The curve gradually declines from the top, resulting in increased energy loss, and continues to fall until it reaches fracture failure (Fig. 5b).

Fig. 6(a-c) stress-strain curve of compressive test specimens of sPEEK/HAP-rGO with different M\(_f\) of rGO carried under different low strain rates. The curve is sharp and linear until it reaches the peak. After yielding, the curve drops down for a short period and continued to be linear till to the failure. The compressive strength of sPEEK/HAP-rGO composites are enhanced by the carbon content of rGo, which rises with increasing rGo concentration. rGo exhibits good interfacial bonding between HAP and sPEEK.

The specimens are subjected to hydrostatic pressure and shear stress during low strain rate loading, causing localised damage. Dispersibility and compatibility can be used to measure the improvement in interfacial bonding strength. Fig. 7 shows the SEM micrographs of sPEEK-HAP/rGO samples with varying rGO concentrations, with sPEEK-HAP sample serving as a control. For the sPEEK-HAP samples, HAP particles were disseminated and agglomerated in a non-uniform manner in the PEEK matrix (Fig. 7a). Similar findings on the biopolymer-bioceramic composites were found to indicate poor compatibility due to differences in chemical and physical characteristics [30]. The degree of agglomeration in the sPEEK-HAP/rGO samples reduced as the rGO concentration increases (Fig. 7b–d). In the fracture surface of sPEEK-HAP/rGO samples with 1.5% rGO, rGO was uniformly distributed in the matrix, which minimises the HAP particle crushing and resulting in lower stress concentration. This helps to avoid local damage within the specimen which enhances the mechanical properties of the composites.

Compressive tests for sPEEK, sPEEK/HAP, and sPEEK/HAP-rGO composites were also performed at high strain rates (800 and 1000 s\(^{-1}\)) to validate the strain rate sensitivity properties of sPEEK and its composites for the defined objectives. The stress–strain curve's distinctive form is not the same at both rates. The sPEEK/HAP displays much higher post-yield softening than that of sPEEK (Fig. 5b). The softening effect of sPEEK/HAP composite increases as the strain rate increases, and it is linked to non-isothermal tests. Thermal softening of polymers occurs as a result of insufficient heat transfer out of the material, resulting in increased plastic straining.
The composite's rate sensitivity determines the rate sensitivity of the HAP and rGO loaded sPEEK polymer. At high strain rate, the fracture is induced to propagate through the HAP. Energy is squandered during crack growth, which may be regarded as one factor impacting the energy absorption capacity of HAP loaded polymer. To put it another way, a rapid strain rate allows the fracture to spend less time exploring low-resistance routes, resulting in less energy use. In contrast, with low strain rate loading, the fracture prefers to avoid passing through HAP particles, resulting in HAP particle debonding, as seen in Fig. 7e.

The stress-strain curves of PEEK/HAP-rGO(0.5), PEEK/HAP-rGO(1), and PEEK/HAP-rGO(1.5) specimens conducted at high strain rates are comparable to those made at low strain rates; the curve is broken into two halves here (Fig. 6a-c). The steep and linear elastic curve till to the apex and sudden drop from the apex for a short period and continued to be linear till to fracture. The PEEK/HAP composite's compression strength was found to be lower than that of sPEEK and to increases with increasing rGO concentration. The PEEK/HAP composite, on the other hand, shows a weaker trend than neat sPEEK specimen. Meanwhile, the compressive strength increases as the M\(_f\) of rGO increase at the same strain rate. rGo exhibits good interfacial bonding between HAP and sPEEK. The stress-strain curves have similar structure for both strain rates, and the fracture strain is lower at 1000 than at 800 s\(^{-1}\), as expected.

### 3.4 Tensile testing

The stiffness of the curve was calculated by fitting the first linear segment with a linear curve. Fig. 8 shows the tensile strength of sPEEK, sPEEK/HAP and sPEEK/HAP composites containing different M\(_f\) of rGO at low strain rates. The tensile strength has been found to be strain rate sensitive, increasing as the strain rate increases. In comparison to PEEK, the tensile strength of sPEEK/HAP decreased with increasing strain rates. The tensile strength of sPEEK/HAP declined by an average of 11% as strain rates increased, indicating that the addition of HAP significantly reduces the material's tensile strength. The rate sensitivity of sPEEK/HAP composite has been shown to be influenced by its viscoelastic behaviour, which tends to reduce absolute strength due to microscopic local damage. However, the rGO filler, may have little influence on the overall sensitivity of PEEK/HAP composites. The tensile strength of sPEEK/HAP-rGO composites increases as rGO M\(_f\) increases as compared to sPEEK and sPEEK/HAP. An average of 3%, 2.5% and 3% increase in tensile strength was observed for 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates respectively, with in increased concentration of rGO from 0.5–1.5%. The oxygen groups and negative ions on the surface of rGO particles are thought to be able to interact efficiently with sPEEK/HAP via H-bonding and electrostatic force. The strong interfacial bonding between PEEK and HAP particles resulting in dramatically improved mechanical characteristics of PEEK composite and also, it improves the dispersion of HAP particles in the sPEEK matrix.

### 3.5 Strain rate sensitivity

The properties of the elements must be studied in order to comprehend the failure causes of a composite material. Fig. 9 shows the tensile stress-strain curves of sPEEK and sPEEK/HAP samples obtained at
strain rates of 0.001, 0.01 and 0.1 s\(^{-1}\). The strain distributions of the gauge section for tensile testing of sPEEK samples at various low strain rates are shown in Fig. 9(a). The curve is separated into two parts, the first of which demonstrates the elastic behaviour of the composites by observing a linear relationship till an apex. After yielding, necking initiated and propagated. For the strain rates of 0.001 and 0.01 s\(^{-1}\), necking progressed slowly to the next section and continued to be linear until the maximum strain reached 110.4%, resulting in final crush failure. At a 0.1 s\(^{-1}\) strain rate, however, necking is focused rather than broadly dispersed, leading in a substantially faster specimen fracture at strain level of 0.2. These findings highlight to PEEK's high sensitivity to strain rate, which is consistent with these reference [31, 32], which reveals that when the strain rate crossed 0.001 s\(^{-1}\), the yield stress of PEEK increased fast due to the greater crystallite perfection.

Figure 9(b) shows strain distribution for tensile strength for sPEEK/HAP samples under different low strain rates. The curve initially shows progressive elastic behaviour till to the apex. After yielding, the curve drops linearly, which adds to energy loss and continued to be drop to attain eventual crush failure for 0.001 and 0.01 s\(^{-1}\) strain rates. At 0.1 s\(^{-1}\) strain rate, the curve drops sharply after the yield point at the strain levels of 0.03, 0.025 and 0.02 for 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates respectively. As the temperature rises, the addition of HAP lowers the crystallinity of PEEK, and a higher strain rate generates more heating inside the specimen. While comparing the stress-wave propagation rates for 0.001, 0.01 and 0.1 s\(^{-1}\), the latter case's rate is substantially lower than the loading rate, limiting necking propagation and resulting in an early fracture.

Figure 10(a,b&c) shows the tensile test stress-strain curves of sPEEK-HAP/rGO(0.5%), sPEEK-HAP/rGO(1%) and sPEEK-HAP/rGO(1.5%) under different low strain rates. All these composites showed similar stress-staring curve nature. The curves showed progressive elastic behaviour till to the apex. Necking was prolonged for a short time after yielding and then dropped linearly at the strain levels of 0.04, 0.055 and 0.06 for 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates respectively for sPEEK-HAP/rGO(0.5%) composite (Fig. 9a), 0.035, 0.05 and 0.065 for 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates respectively for sPEEK-HAP/rGO(1%) composite (Fig. 9b) and 0.045, 0.065 and 0.08 for 0.001, 0.01 and 0.1 s\(^{-1}\) strain rates respectively for sPEEK-HAP/rGO(1.5%) composite (Fig. 9c). These results demonstrated that maximum tensile stresses are sensitive to low strain rate loading for all composites.

3.6 Thermal analysis

The thermal properties of sPEEK loaded with HAP and rGO with variable concentrations were evaluated using the TGA method. Samples of sPEEK, sPEEK/HAP, and sPEEK/HAP-rGO composites were analysed in an inert environment, and the average results of the triplicate tests are given in Fig. 11(a), revealing that the incorporation of HAP affected the thermal degrading behaviour of sPEEK significantly. PEEK and its composites deteriorate in two stages, with sPEEK decomposing at roughly 550°C, which is much higher than the temperature at which most polymers decompose. In first stage, decomposition occurs around 580°C and is related to arbitrary chain scission of the ether and ketone bonds [33]. After 600°C, the
second stage of breakdown starts, which is attributed to the development of residue as a result of crosslink breaking and dehydrogenation, resulting in a thermally stable carbonaceous char. Within 30°C of time, sPEEK loses 30% of its weight in the initial stage, and continues to drop 10% of its weight between 580 and 600°C. As a result, the first stage resulted in a total weight decrease of 40%. There is no foreign substance in the sPEEKs media that is associated with a 40% weight reduction. In the second step, just 10% of the weight is lost up to 800°C, resulting in a 50% yield. Beyond 800°C, there is minimal further loss, and the material appears to be stable at 850°C. A 40% weight loss shows that formation of aromatic molecules as products, presumably in the form of phenol, a significant sPEEK breakdown product [34].

sPEEK/HAP-rGO samples had a slightly higher beginning temperature than sPEEK and sPEEK/HAP sample. The initial stage of decomposition of sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples is comparable, with weight loss of roughly 28% and 27%, respectively. At 580°C, the decomposition process begins, and both materials progress to the second stage of decomposition. Further, after 750°C, small loses in weight occurs and the final remaining weight of the materials for sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples is 65% and 68% respectively. For sPEEK/HAP-rGO(1.5) sample, the initial decomposition begins at 600°C, with the weight loss of 21% and continuing to decompose at a faster rate than sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples. After 800°C, the weight of the sPEEK/HAP-rGO(1.5) sample decreased significantly, and the final residual weight was 71%, slightly higher than others, as well as the char fraction.

Similarly, the thermal properties of sPEEK loaded with HAP and rGO with variable concentrations were evaluated in an oxidative environment as shown in Fig. 11(b). Thermal oxidative degradation begins between 510°C and 530°C for sPEEK/HAP, sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples. The temperature at which thermal oxidative decomposition begins in sPEEK/HAP-rGO(1.5) sample is somewhat greater, at around 560°C. sPEEK/HAP loses 35% of its weight in the first stage, with 30% of the weight loss occurring within a 30°C time frame, which correlates to thermal disintegration under inert atmosphere, suggesting that scission of ether and ketone bonds does not enhance by an oxidative environment. The rest of the sPEEK/HAP weight is lost during the second stage, which involves thermally oxidising the whole material at 720°C. sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples lose weight at a slower pace than sPEEK/HAP, although having a same commencement of thermal oxidative decomposition temperature. The first decomposition stage is responsible for a 3% weight loss difference between sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples at roughly 580°C, with weight losses of 25% and 22%, respectively. In the second stage, sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples continue to lose 35% and 32% weight, respectively, at a comparable pace as sPEEK/HAP and there is no further decomposition of materials. For sPEEK/HAP-rGO(1.5) samples, the initial decomposition begins at 600°C, with the weight loss of 20% and continuing to decompose at a faster rate than sPEEK/HAP-rGO(0.5) and sPEEK/HAP-rGO(1) samples. After 700°C there in no further decomposition. The addition of microspheres enhances the thermal stability of sPEEK/HAP-rGO(0.5), sPEEK/HAP-rGO(1) and sPEEK/HAP-rGO(1.5) samples in an inert environment, with sPEEK/HAP-rGO(1.5) samples being the most thermally stable.
The glass transition (Tg) temperatures from DSC analysis of sPEEK loaded with HAP and rGO with different concentrations of rGO samples are shown in Table 2. The DSC analysis reveals that the Tg of the neat sPEEK/HAP, sPEEK/HAP-rGO(0.5), and sPEEK/HAP-rGO(1) samples are not considerably different. When the Tg values of sPEEK/HAP-rGO(1.5) samples and sPEEK/HAP are compared, the Tg values of sPEEK/HAP-rGO(1.5) samples is greater. This reveals that while 1.5% Mf of rGo increase the physical interactions between the HAP and sPEEK, improving the mechanical characteristics of the composites, they have no effect on the composite’s Tg.

**Conclusion**

In this work, extrusion process was used to prepare sPEEK-HAP/rGO composites with three different concentrations of rGO, and test samples were fabricated using 3D printing technology for usage in weight-sensitive contexts. Filament and 3D printed components are mechanically characterised to assess their flexibility and practicality for 3D applications. HAP filled sPEEK polymer absorbs more energy at both low strain rate compression. When compared to sPEEK, the tensile strength improves significantly. The strain rate sensitivity of HAP filled sPEEK is high, and the strain rate sensitivity factor decreases as the mass fraction of rGO increases. The sPEEK filled with 1.5% Mf of rGo showed good intact within the sPEEK-HAP matrix, because they endure the melt processing better than other two concentrations of rGO. Increased rGO density resulted in lower sPEEK-HAP composite density and better mechanical characteristics, even at low strain rates. MFI decreases as rGo concentration increases, which might resolve printing issues. The increased compatibility between sPEEK-HAP and rGO particles was demonstrated by SEM images. The addition of rGO to sPEEK-HAP improves the thermal stability of the composite. sPEEK-HAP/rGo(1.5) is extremely heat resistant, with decomposition below 550 °C.

**Declarations**

**Funding** - Not applicable

**Conflicts of interest** - The authors declare that they have no competing interests

**Data transparency** – Not applicable

**Code availability** – Not applicable

**Ethics approval** – Not applicable

**Consent to participate** - Not applicable

**Consent for publication**- Not applicable

**Authors' contributions**

Conceptualization: [SAGAR BALIGIDAD];

Methodology: [SAGAR BALIGIDAD], [CHETHAN KUMAR G];
Formal analysis and investigation: [MAHARUDRESH A C], [CHETHAN KUMAR G];

Writing - original draft preparation: [SAGAR BALIGIDAD], [MAHARUDRESH A C];

Writing - review and editing: [SAGAR BALIGIDAD], [MAHARUDRESH A C];

Resources: [SAGAR BALIGIDAD], [CHETHAN KUMAR G];

Supervision: [SAGAR BALIGIDAD];

References

1. M. Alexandru, M. Cazacu, S. Vlad, and F. Iacomi, “Polydimethylsiloxane-silica composites. Influence of the silica on the morphology and the surface, thermal, mechanical properties,” High Perform. Polym., vol. 21, no. 4, pp. 379–392, 2009, doi: 10.1177/0954008308094327.

2. S. M. Kurtz and J. N. Devine, “PEEK biomaterials in trauma, orthopedic, and spinal implants,” Biomaterials, vol. 28, no. 32, pp. 4845–4869, 2007, doi: 10.1016/j.biomaterials.2007.07.013.

3. M. He et al., “Super tough graphene oxide reinforced polyetheretherketone for potential hard tissue repair applications,” Compos. Sci. Technol., vol. 174, pp. 194–201, 2019, doi: 10.1016/j.compotech.2019.02.028.

4. K. T. Kang, Y. G. Koh, J. Son, J. S. Yeom, J. H. Park, and H. J. Kim, “Biomechanical evaluation of pedicle screw fixation system in spinal adjacent levels using polyetheretherketone, carbon-fiber-reinforced polyetheretherketone, and traditional titanium as rod materials,” Compos. Part B Eng., vol. 130, pp. 248–256, 2017, doi: 10.1016/j.compositesb.2017.07.052.

5. Elschner C. et al.. In vitro response of human mesenchymal stromal cells to titanium coated peekfilms and their suitability for magnetic resonance imaging. J. Mater. Sci. Technol. 31, 427–436(2015).

6. Lee J. H. et al.. In vitro and in vivo evaluation of the bioactivity of hydroxyapatite-coatedpolyetheretherketone biocomposites created by cold spray technology. Acta. Biomater. 9, 6177–6187 (2013).

7. M. Sattari, A. Molazemhosseini, M. R. Naimi-Jamal, and A. Khavandi, “Nonisothermal crystallization behavior and mechanical properties of PEEK/SCF/nano-SiO2 composites,” Mater. Chem. Phys., vol. 147, no. 3, pp. 942–953, 2014, doi: 10.1016/j.matchemphys.2014.06.041.

8. J. Song, Y. Liu, Z. Liao, S. Wang, R. Tyagi, and W. Liu, “Wear studies on ZrO2-filled PEEK as coating bearing materials for artificial cervical discs of Ti6Al4V,” Mater. Sci. Eng. C, vol. 69, pp. 985–994, 2016, doi: 10.1016/j.msec.2016.08.007.

9. T. Kokubo, H. M. Kim, and M. Kawashita, “Novel bioactive materials with different mechanical properties,” Biomaterials, vol. 24, no. 13, pp. 2161–2175, 2003, doi: 10.1016/S0142-9612(03)00444-9.
10. [10] Wang M. C. et al. Crystalline size, microstructure and biocompatibility of hydroxyapatite nanopowders by hydrolysis of calcium hydrogen phosphate dehydrate (DCPD). Ceram. Int. 41, 2999–3008 (2015).

11. [11] Gentile P., Chiono V., Carmagnola I. & Hatton P. V. An overview of poly (lactic-co-glycolic) acid (PLGA)-based biomaterials for bone tissue engineering. Int. J. Mol. Sci. 15, 3640–3659 (2014).

12. Y. Zhang, L. Hao, M. M. Savalani, R. A. Harris, L. Di Silvio, and K. E. Tanner, “In vitro biocompatibility of hydroxyapatite-reinforced polymeric composites manufactured by selective laser sintering,” J. Biomed. Mater. Res. - Part A, vol. 91, no. 4, pp. 1018–1027, 2009, doi: 10.1002/jbm.a.32298.

13. R. Ma et al., “Mechanical performance and in vivo bioactivity of functionally graded PEEK-HA biocomposite materials,” J. Sol-Gel Sci. Technol., vol. 70, no. 3, pp. 339–345, 2014, doi: 10.1007/s10971-014-3287-7.

14. J. Cao, Y. Lu, H. Chen, L. Zhang, and C. Xiong, “Preparation, properties and in vitro cellular response of multi-walled carbon nanotubes/bioactive glass/poly(etheretherketone) biocomposite for bone tissue engineering,” Int. J. Polym. Mater. Polym. Biomater., vol. 68, no. 8, pp. 433–441, 2019, doi: 10.1080/00914037.2018.1455679.

15. R. K. Roeder, G. L. Converse, R. J. Kane, and W. Yue, “Hydroxyapatite-reinforced polymer biocomposites for synthetic bone substitutes,” Jom, vol. 60, no. 3, pp. 38–45, 2008, doi: 10.1007/s11837-008-0030-2.

16. Nikpour M. R., Rabiee S. M. & Jahanshahi M. Synthesis and characterization of hydroxyapatite/chitosan nanocomposite materials for medical engineering applications. Compos Part. B Eng. 43, 1881–1886 (2012).

17. Coldea A., Swain M. V. & Thiel N. Mechanical properties of polymer-infiltrated-ceramic-network materials. Dent. Mater. 29, 419–426 (2013).

18. Ma, Ruixue; Zhu, Bo; Zeng, Qianqian; Wang, Pan; Wang, Yaming; Liu, Chuntai; Shen, Changyu (2019). Melt-Processed Poly(Ether Ether Ketone)/Carbon Nanotubes/Montmorillonite Nanocomposites with Enhanced Mechanical and Thermomechanical Properties. Materials, 12(3), 525–. doi:10.3390/ma12030525

19. Lynch-Branzoi, J. K., Ashraf, A., Tewatia, A., Taghon, M., Wooding, J., Hendrix, J., Kear, B. H., & Nosker, T. J. (2020). Shear exfoliation of graphite into graphene nanoflakes directly within polyetheretherketone and a spectroscopic study of this high modulus, lightweight nanocomposite. Composites Part B: Engineering, 188, [107842]. https://doi.org/10.1016/j.compositesb.2020.107842

20. Song, HJ., Li, N., Yang, J. et al. Preparation and tribological behaviors of poly (ether ether ketone) nanocomposite films containing graphene oxide nanosheets. J Nanopart Res 15, 1433 (2013). https://doi.org/10.1007/s11051-013-1433-8

21. Tewatia, Arya; Hendrix, Justin; Dong, Zhizhong; Taghon, Meredith; Tse, Stephen; Chiu, Gordon; Mayo, William E.; Kear, Bernard; Nosker, Thomas; Lynch, Jennifer (2016). Characterization of melt-blended graphene – poly(ether ether ketone) nanocomposite. Materials Science and Engineering: B, () S092151071630054X–. doi:10.1016/j.mseb.2016.05.009
22. Yang, Lilong; Zhang, Shuling; Chen, Zheng; Guo, Yunliang; Luan, Jiashuang; Geng, Zhi; Wang, Guibin (2014). Design and preparation of graphene/poly(ether ether ketone) composites with excellent electrical conductivity. Journal of Materials Science, 49(5), 2372–2382. doi:10.1007/s10853-013-7940-2

23. Song, HaoJie; Li, Na; Li, Yanjie; Min, Chunying; Wang, Zhen (2012). Preparation and tribological properties of graphene/poly(ether ether ketone) nanocomposites. Journal of Materials Science, 47(17), 6436–6443. doi:10.1007/s10853-012-6574-0

24. Goto, T., Kim, I. Y., Kikuta, K. & Ohtsuki, C. Hydroxyapatite formation by solvothermal treatment of α-tricalcium phosphate with water-ethanol solution. Ceram. Int. 38, 1003–1010 (2012).

25. Huang, S.H., Liu, P., Mokasdar, A. et al. Additive manufacturing and its societal impact: a literature review. Int J Adv Manuf Technol 67, 1191–1203 (2013). https://doi.org/10.1007/s00170-012-4558-5

26. Bettina Wendel; Dominik Rietzel; Florian Kühnlein; Robert Feulner; Gerrit Hülder; Ernst Schmachtenberg (2008). Additive Processing of Polymers., 293(10), 799–809. doi:10.1002/mame.20080121

27. Escócio, V. A.; Pacheco, E. B. A. V.; da Silva, A. L. N.; Cavalcante, A. d. P.; Visconte, L. L. Y. Rheological Behavior of Renewable Polyethylene (HDPE) Composites and Sponge Gourd (Luffa cylindrica) Residue. Int. J. Polym. Sci. 2015, 2015, 1−7.

28. Mohanty, S.; Nayak, S. K. Short Bamboo Fiber-reinforced HDPE Composites: Influence of Fiber Content and Modification on Strength of the Composite. J. Reinf. Plast. Compos. 2010, 29, 2199–2210.

29. Shaikh, H.; Anis, A.; Pouluse, A. M.; Alam, M.; A-Otaibi, M. N.; Alam, M. A.; Al-Zahrani, S. M. Studies on High Density Polyethylene Reinforced with Phosphate Ore Particles: Thermal, Rheological, Mechanical and Morphological Properties. Polym.-Plast. Technol. Eng. 2016, 55, 1831–1841.

30. Ramesh, S., Ramesh, K. & Arof, A. K. Fumed silica-doped poly (vinyl chloride)-poly (ethylene oxide) (PVC/PEO)-based polymer electrolyte for lithium-ion battery. Int. J. Electrochem. Sc. 8, 8348–8355 (2013).

31. Hamdan S, Swallowe GM. Crystallinity in PEEK and PEK after mechanical testing and its dependence on strain rate and temperature. J Polym Sci B 1996;34:699–705.

32. Swallowe GM, Fernandez JO, Hamdan S. Crystallinity increases in semi crystalline polymers during high-rate testing. J Phys IV Fr 1997;7:453–8.

33. Patel, P., Hull, T. R., McCabe, R. W., Flath, D., Grasmeder, J., and Percy, M., (2010), Mechanism of Thermal Decomposition of Poly (Ether Ether Ketone) (PEEK) From a Review of Decomposition Studies. Polymer Degradation and Stability. 95(5), pages 709-718.

34. Tsai, C. J., Perng, L. H., and Ling, Y. C., (1997), “A Study of Thermal Degradation of Poly (Aryl-Ether-Ether-Ketone) using Stepwise Pyrolysis/Gas Chromatography/Mass Spectrometry”, Rapid Communications in Mass Spectrometry, 11, 1987-1995.
Figure 3

Compressive strength of sPEEK, sPEEK/HAP and sPEEK/HAP-rGO composites under (a) low strain rate, and (b) high strain rate

Figure 4

Complex viscosity
Figure 5

Compression test stress-strain curves of (a) sPEEK and (b) sPEEK-HAP, at strain rates of 0.001, 0.01, 0.1, 800 and 1000 s⁻¹
Figure 11

TGA curves for neat sPEEK, sPEEK-HAP, and sPEEK-HAP/rGO composites carried under (a) Inert environment, and (b) oxidative environment