A biomaterial for scaffold applications: Thermal properties analysis of a PSZ-TiO$_2$/HDPE system

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Abstract. High-density polyethylene (HDPE) matrices reinforced with titanium dioxide (TiO$_2$) biocomposites are seen as promising biomaterials due to their superior properties. In this work, an attempt was made to study the effects of six biocomposites hybrid Titanium dioxide (TiO$_2$) and yttria-stabilized zirconia (Y-PSZ) samples reinforced with high-density polyethylene (HDPE) matrices, split into two groups, in terms of withstanding the daily activity loads imposed by human bone grafting and repairs. The fabricated composites were investigated using the hot-pressing technique at different compression pressures and compounding temperature. To achieve characterization, thermal analysis of the process using differential scanning calorimetry (DSC) techniques was undertaken. To improve and verify the results, Design Expert 11.0 software and a response surface methodology (RSM) technique were used. For both nanofabricated types, the results showed that an increase in TiO$_2$ ceramic filler from 1% to 10%, caused percentage crystallization to increase by 14.58%. The heat of system fusion for the second fabricated system also decreased by 11%. These results show that this addition reduced the heat of system fusion by 109% compared with previous studies. The glass transition (onset) and end (melting) temperature also increased with increases in the applied compression pressure and hot-pressing temperature when a small value, 1%, of TiO$_2$ ceramic nanoparticle fillers in the HDPE matrix. The temperature values were increased when using higher compression pressure of 60 and 90 MPa, and the onset temperature reached a maximum value of 127 °C. This increase in onset temperature continued when using higher values of TiO$_2$ Nanoceramic filler and the onset temperature reached its maximum value with 10% TiO$_2$ and 2% PSZ Nanoceramic fillers added to the fabricated nanomaterial system. The differential scanning calorimetry (DSC) scanned curves and the 3D atomic force microscopy (AFM) microstructure and granularity distribution images for both fabricated nanocomposite systems clearly showed that the interconnections between the filler’s ceramic nanoparticles within the polymeric matrix offer high surface roughness values due to the excellent nanofiller particle distribution within the polymeric matrix. Keywords: Nano HDPE/ceramic bio-composites, Nano TiO$_2$/PSZ crystallization, Differential scanning calorimetry; Atomic force microscopy, Synthetic bone repair.

1. Introduction
Bone fracture is a common trauma, especially in the lower limbs [1], and The World Health Organization (WHO) predicts that such trauma will be a leading cause of life lost for both developed and developing nations by the year 2020. The femur bone length is about 26% of a person’s height and it is the most proximal bone of the leg, providing capabilities for jumping or walking [2]. Bone strength depends on both geometry and mineralization, which also depend on each other [3]. The femur is both the strongest and the heaviest bone in the human body, as it is responsible for carrying the body weight [4-6]; as many issues can lead to fracture, whether distal or proximal, in the femur, various kinds of the prosthesis are applied according to patient’s age, life activity, and manifested dysfunction to help address issues [7-9].

Nanocomposites are high-performance materials that exhibit unique design possibilities and unusual property combinations for multiple applications, offering business opportunities and new technology for disparate sectors including aerospace, biotechnology, and the automotive and electronics industries [10]. Nanocomposites have gained attention due to their wide variety of useful properties and because the incorporation of low percentages of nano-particles can enhance the mechanical, optical, and thermal
properties of other materials, which is particularly attractive for the medical and food fields [11].

The current state-of-the-art of biocomposites and hybrid biomaterials suitable for biomedical applications nevertheless necessitates further attention to the critical issues and scientific challenges arising, which require further research and development. New hybrid polymeric materials are being continually developed with the addition of fine-tune fillers [12], while for composite materials, polymers are good hosting matrices because they can easily yield a variety of bulk physical properties [13].

Polyethylene (PE) has good biocompatibility and tribological properties. However, polyethylene implants’ lifetimes are limited due to wear complications, and PE released into periprosthetic environment induces osteolysis, followed by implant loosening [14-15].

Bioceramic is the promising class of biomaterials for bone tissue regeneration and replacement due to its distinctive biological and mechanical properties and excellent chemical composition. These are recognized as providing bone-bonding by means of a combination of osteogenic properties, high surface reactivity, and excellent biocompatibility [16]. Ceramics and polymer-matrix composites (PMC) allow physical property tailoring using different types of fillers [17], and TiO2 nanoparticles are inert, nontoxic, and inexpensive with inherent self-cleaning mechanisms [11].

Polymer-based TiO2 composites of varying kinds have been examined in the literature, including polyamide/nano-TiO2 and high-impact polystyrene (HIPS)/nano-TiO2 composites [18]. High-density polyethylene (HDPE), which is composed of carbon and hydrogen atoms, is a biocompatible thermoplastic polymer [12] used for its high strength-to-density ratio. It is converted into ethylene then into polyethylene from methane gas using the application of heat and pressure [19]. It has a wide range of application due to its low cost and good processability, and HDPE can be used in many biomedical applications, including bone repair [20].

The production of bioactive composites for bone replacements by reinforcing high-density polyethylene (HDPE) bioinert matrices with ceramic bioactives was introduced in the early 1980s by Bonfield, Downes, et al., and Tanner et al. [21]. Various forms of bioceramics have since been fabricated based on these applications, including thin-layer coatings on implants, porous networks, and composites with polymer components [22].

Zirconium dioxide (ZrO2) is a crystalline structure that undergoes a phase transformation from monoclinic (stable at room temperature) to tetragonal (at about 1,173 °C) then to cubic (at about 2,370 °C). Yttria (Y2O3) stabilized zirconia (YSZ) undergoes spontaneous phase transformation, even in dry conditions [23], while upon cooling, the martensitic transformation from tetragonal to monoclinic, which is associated with a volume expansion of 4 to 5%, leads to detrimental fracture of pure zirconia ceramics [22, 24-25]. Zirconia (ZrO2) nanoparticles are used in technical and biomedical applications, especially for bone repair and replacement applications due to their excellent chemical and electrical resistance, refractory properties, thermal stability, corrosion and wear resistance, low friction, good mechanical strength, and relatively high thermal expansion coefficients [9, 24, 26].

The effect of different filler types on the thermal properties of polymer matrix has been investigated by several authors [27]. A hot-pressing technique is used in the current work to reduce the effects of thermal deformations and maximum tensile residual stresses produced normal to the crack directions when using traditional polymer fabricated methods. The main aim of this article is thus to study and modify the influence of adding titanium dioxide and partial stabilized zirconia (PSZ) nanoceramic fillers at different volume fractions with different compression pressures and reaction temperatures on the thermal properties of two nanocomposite polymer matrix systems, TiO2/HDPE and Y2O3 partial stabilized zirconia TiO2(Y-PSZ)/HDPE, as produced by hot pressing techniques to create bioactive biomaterials for bone grafting and repair applications.

Nonisothermal differential scanning calorimetry (DSC) analyses were used to characterize the thermal transition properties of HDPE matrices as low melting point (130 °C) material with high melting point Nanoceramic fillers. The surface morphology of the fabricated samples was examined using atomic force microscope (AFM). All experiments were designed using the full factorial method (FFM), with response surface methodology (RSM) and the analysis of variance (ANOVA) technique.
2. Materials and Methods

2.1 Nanocomposite Preparation method
Titanium dioxide (TiO$_2$) of an average particle size of 40 nm with a density of 4.23 g/cm$^3$ and a purity of 99% was supplied by M. K. Nano (Toronto, Canada); the second type of ceramic filler material used in this study was 3 mol% yttria (Y$_2$O$_3$) partially-stabilized zirconia (ZrO$_2$-PSZ), in the form of Y-PSZ Nanopowder with 99.9% purity, a density of 5.91 g/cm$^3$ and an average particle size of 40 nm, also supplied by M.K Nano (Toronto, Canada). High-density polyethylene (HDPE) was used as a biomaterial powder matrix; this had a density of 0.95 g/cm$^3$ and particle size of 5 µm, being supplied by Right Fortune Industrial Limited (Shanghai, China). The prepared powders were first to dry mixed in a ball mill machine for 12 hrs for each of the desired compositions, then hot pressed at 180, 190, and 200 °C, at compounding pressures of 30, 60, and 90 MPa as required. The obtained cylindrical shape test samples had 10 mm diameters and heights of 3 to 5 mm. Figure 1 shows the fabrication hot-press system, which contained the appropriate thermostats and was connected to the digital temperature control system.

![Figure 1. The fabrication hot-press system](image)

2.2 Thermal Analyses
To investigate the effects of nanofillers on thermal stability characteristics and crystallization, the fabricated HDPE matrix composites were tested according to ASTM 3418 using differential scanning calorimetry (DSC) in a Perkin Elmer DSC-8000 thermal analyser system with a liquid nitrogen cooling system of 50 ml/min, as shown in figure 2. Samples of 10 to 12 mg in mass were sealed in aluminum pans and weighed using four separate digital electronic balances before being heated from 30 to 170 °C at a heating rate of 15 °C/min, being maintained at temperature for 5 min to erase any previous morphological history. The samples were then cooled rapidly at 150 °C/min to room temperature to observe crystallinity behaviors. The percentage of crystallinity ($X_c$) for the composite materials was determined using the following formula [27]:

$$X_c \ (% ) = \left( \frac{\Delta H_f}{\Delta H_f^0} \right) \times 10$$

where $\Delta H_f$ and $\Delta H_f^0$ are the enthalpies of fusion of the system and the enthalpy of fusion of perfectly (100%) crystalline PP, respectively. For $\Delta H_f^0$ (PP), a value of 209 J/g is used for 100% crystalline polyethylene (PP).

2.3 Surface Morphology and Nanoparticle Dispersion
To study the surface roughness, surface morphology, and nanoparticle dispersion of the fabricated
samples, the AA3000 Scanning Probe Atomic Force Microscope (AFM) was used with a resolution of 0.26nm lateral and 0.1nm vertical. The XYZ scan scope specifications were 10 micrometers in the Z distance, 2-micrometer image pixels, 128X128, 256X256, 512X512, and 1024X1024 scan angles, 0~360-degree scan rates, and 0.1~100Hz.

Figure 2. Differential Scanning Calorimetry (DSC) used for investigation of the crystallization behavior and thermal characteristics of the fabricated composites

3. Results and Discussion

3.1 Crystallisation and Melting Properties

The measured and calculated data from differential scanning calorimetry (DSC) using a single non-isothermal method for the fabricated nanocomposites systems TiO$_2$/HDPE and TiO$_2$/Y$_2$O$_3$-partially stabilized zirconia (Y-PSZ)/HDPE were obtained. The investigated thermal stability parameters were the glass transition (onset) of melting temperature ($T_o$), the peak of melting temperature ($T_p$), the end of (melting) temperature ($T_c$), and the heat of fusion obtained ($\Delta H_f$).

Thermal parameters were investigated based on the glass transition (onset) temperature of melting ($T_o$), the peak of melting ($T_p$) and heat of fusion obtained from a single non-isothermal DSC scan. The peak melting temperature and extrapolated glass transition (onset) melting temperature was calculated from the peak position and intersection of the extrapolated linear section of the falling peak edge with the baseline extrapolated from temperatures below the peak, while the heat of fusion ($\Delta H$) was calculated by integrating the area under the DSC endothermic peak [29].

The glass transition (onset) of melting temperature ($T_o$), the end of melting temperature ($T_c$) and the heat of fusion ($\Delta H$) values as obtained from different heating and cooling conditions for all fabricated nano biomaterial samples are shown in figures 3 to 9. These figures show that by increasing the heating temperature, the melting peak is shifted to higher values, which may be related to rheological properties changing the viscosity with increases in the heating rates and to the presence of nanofillers, which affect the melting behavior of the composite.

Figure 3 shows the DSC scanned curves at 30 and 90 MPa compression pressures and 200°C for both fabricated nanocomposites systems. All DSC scans show a single endothermic peak for melting [21, 28]; the existence of a single peak in the endothermic and exothermic curves can be attributed to the occurrence of co-crystallisation.

However, some authors have noted that the existence of a single peak is not a reliable way to confirm the occurrence of co-crystallisation. While HDPE, TiO2/HDPE, and Y-PSZ/TiO2 /HDPE samples showed a single melting endotherm, the peak melting temperature and extrapolated onset melting
temperature and heat of fusion were affected by both heating-cooling conditions and nanofiller type and volume fraction. In such cases, basic analysis of the melting and crystallization temperature is inadequate; the other sensitive parameter in such situations is the half-width of the endotherms [28]. A larger half-width is expected if two or more components form separate crystals, despite the melting or crystallization peaks being located in close proximity.

Figure 3. The DSC curves at 30 and 90 MPa compression Pressure and 200°C for both fabricated Nanocomposites systems
Figure 4 shows that the glass transition (onset) temperatures increased with increases in the applied compression pressures and hot-pressing temperatures when using small amounts of 1% TiO$_2$. This temperature value was increased further when using higher compression pressure of between 60 and 90 MPa, where the glass transition (onset) temperature reached its maximum value of 127 °C as shown in figure 4 (a). Figures 4 (a), (c) and (e) show the effects of 1, 5, and 10 % Nano TiO$_2$ ceramic filler on the formation of peak melting temperature, the extrapolated glass transition melting temperature, and heat of fusion, respectively, while figures 4 (b), (d), and (f) show the effects of the same Nano TiO$_2$ ceramic filler percentages with the addition of 2% PSZ. These clearly show that the percentage fraction of nanoceramic fillers significantly affects the resulting glass transition (onset) melting temperature values.
as does filler type. When 2% PSZ of Nano-zirconium ceramics is added to the fabricated nanomaterial system, the glass transition temperature increases at a higher rate, though this increase in temperature is minimized at high compression pressure levels, as shown in figure 4 (b). This increase continues when using higher values of TiO$_2$ Nanoceramic filler, and the glass transition (onset) temperature reaches its maximum value when using 10% TiO$_2$ and 2% PSZ Nanoceramic fillers, as shown in figures 4 (c) to (f).

Figure 5. The relationship between the end (melting) temperature and the applied compression pressure for all fabricated nanosystems.
Figure 5 shows that the end (melting) temperature was increased with increases in the amount of TiO$_2$ and PSZ ceramics nanoparticle fillers in the HDPE matrix. However, the rapid increase in end (melting) temperature was decreased by increasing the proportions of these nanomaterial fillers, which offers greater uniformity and homogeneity to the material after the solidification process, which can reduce the disadvantages of increasing melting temperatures in terms of the crystalline boundaries, reducing structural defects and residual stresses after cooling.

![Graphs showing the relationship between heat of fusion and compression pressure for different nanosystems](image)

**Figure 6.** The relationship between the heat of fusion and the applied compression pressure for all fabricated nanosystems

Figure 6 shows the relationship between the heat of fusion and the compression pressures used. The
heat of fusion required for each unit of mass was reduced by increasing the ratio of TiO$_2$ and PSZ Nano-ceramic fillers in HDPE fabricated matrix systems. Excess heating reduced the durability of the material after solidification, except in the case of 10% TiO$_2$ Nanoceramics, which decreased the amount of heat required at increased compression pressure 60 MPa, as shown in figure 6 (e). This was reduced the heat needed to recrystallize the fabricated nanomaterial. The addition of 2% PSZ Nano-zirconium ceramic filler offered a significant improvement in the balance between the desired melting temperature and complications of the crystallization process, giving high adhesion and a strong structure after material solidification.

The 3D graphs presented in figure 7 show the effects of various input parameters on the heat of system fusion ($\Delta H_{c1}$) for all fabricated TiO$_2$/HDPE and TiO$_2$+ 2% ZrO$_2$/HDPE Nano-bio composite systems. These figures show that the heat of system fusion decreased with increases in the process parameters, including the Nano filler content, the compounding pressure, and the pressing temperature. The heat of system fusion reached its minimum value for the first fabricated system at 88 J/g, a reduction of 2.27%, as shown in figures 7 (a), (b) and (c); adding 2% partially stabilized zirconia (Y-PSZ) caused this value to be further decreased by 11% to 79.3 J/g. This means that the addition of 2% partially stabilized zirconia reduced the heat of system fusion by about five times for the same values of Nanofiller content, which is very important in terms of reducing any defects caused by the heat of the sintering processes, producing better homogeneity of composite materials and the best mechanical and thermal properties for the product. In previous studies, the heat of system fusion values reached 106 and 166 J/g for melting 20% HA/10% Y-PSZ/HDPE and 20% HA/HDPE Nano biocomposites, respectively (Jenan et al., 2016); thus, the current study reduced the heat of system fusion required by 33.76% and 109.33%, respectively.

![Figure 7](image_url)

**Figure 7.** The effects of input parameters on the heat of system fusion ($\Delta H_{c1}$) for all fabricated TiO$_2$/HDPE and TiO$_2$+ 2% ZrO$_2$/HDPE Nano biocomposition systems.
The final prediction equations to determine the heat of system fusion values for both fabricated compositions systems are

\[ \text{Heat of fusion (}\Delta H_c\text{)} (I) = + 86.80497 - 0.288769 \times \text{TiO}_2 \text{Nano ceramic filler content} + 0.008569 \times \text{Compounding pressure (MPa)} + 0.016517 \times \text{Hot pressed temperature (°C)} \]  

(2)

\[ \text{Heat of fusion (}\Delta H_c\text{)} (II) = + 85.99650 - 1.07712 \times \text{TiO}_2+2\% \text{ZrO}_2 + 0.010148 \times \text{Compounding pressure (MPa)} + 0.010444 \times \text{Hot pressed temperature (°C)} \]  

(3)

Figure 8 shows a 3D representation of input parameters in terms of the percentage crystallization values for all fabricated TiO\(_2\)/HDPE and TiO\(_2\)+2%ZrO\(_2\)/HDPE Nano-bio composition systems. The graphs in the figure show that the percentage crystallization values were increased with increases in various process parameters including the Nanoceramic filler content, the compounding pressure, and the hot-press temperature. With the increase in TiO\(_2\) filler ceramic content from 1% to 10%, the value percentage of crystallization increased by 14.58%, as shown in Figures 8 (a), (b) and (c), while using 1% titanium oxide Nanoceramic powder (TiO\(_2\)) with 2% partially stabilized zirconia (Y-PSZ) caused this value to increase with increases in the hot pressing temperature and compounding pressure before decreasing to the lowest percentage of crystallization value of 33% at the highest rate of the added nanofiller and the highest pressing temperature and pressure, as shown in figures 8 (d), (e), and (f).

![Figure 8](image-url)
biomaterials and the compression pressures used during fabrication. By increasing the ratio of TiO$_2$ nanoceramic filler, the pressing temperature and the pressure used, the crystallization percentage was increased, as shown in figures 9 (a), (c) and (e), as the nanoparticles worked as nucleation sites during the crystalline phase.

![Figure 9](image-url)  
**Figure 9.** The relation between the percentage crystallization (%) and the applied compression pressure for the all fabricated Nanosystems

The crystallization was judged via the heat of fusion, $\Delta H$. As the heat of fusion increased, the crystallization also increased in agreement with the literature [21, 29]. However, this was reversed with...
the addition of 2% PSZ nano-ceramic filler when the pressing temperature was increased, as illustrated in figures 9 (d) and (f). Using 1% TiO$_2$, the highest percentage of crystallization increased by up to 48%, especially at lower pressing temperatures. Clearly, a balance can be obtained between the crystallization rate of the fabricated material and the strength and homogeneity of the nanomaterial by using different ratios of TiO$_2$ with the addition of a small proportion of Nano-zirconium filler, which can be adjusted to suit the age of the patient and the

Figure 10. The atomic force microscopy microstructure images and granularity distribution for different Nano compositions
type and strength of the bone to be replaced or supported. Adding Nano Y-PSZ to Nano TiO$_2$/HDPE particles causes a shift in melting peaks to higher values, while the crystallization process is decreased. However, nanoparticles at higher loading restrict the mobility of molecules, and hence decrease crystallinity.

Figure 11. The 2D and 3D AFM images of surface roughness for different nano compositions.
3.2 Surface Morphology and Nanoparticle Dispersion Measurements

The atomic force microscopy (AFM) revealed intricate nano-topographies with an abundance of submicron-sized nano-projections and pits dispersed evenly across the specimen surfaces. The AFM microstructure and granularity distributions for different nano composition samples are shown in figure 10. Figure 10 (a) shows the microstructure for 5% TiO$_2$/HDPE nanocomposite: the sample microstructure indicates a homogeneous distribution of Nano TiO$_2$ particles in the HDPE matrix, and the interconnections between the filler ceramic nanoparticles within the polymeric matrix offer a good explanation for the resultant mechanical properties.

Figure 10 (b) shows that the granularity distribution of the filler agglomerates was on the nano-scale, which explained the enhancement in mechanical properties after 5% TiO$_2$ addition. Figures 10 (c) and (d) show that the TiO$_2$ Nano filler content was increased to 10%, the nanogranular sizes became smaller and the particles produced more interconnections, which reflects the obtained values of mechanical properties. Figures 10 (e) and (f) show that adding 2% 2 PSZ to 10% TiO$_2$ ceramic nanofillers, the nanogranular sizes are slightly increased, with good particle interconnections and excellent mechanical properties.

Figure 11 shows the 2D and 3D AFM images for the surface roughness examinations for the various nano composition specimens. These figures show that the values of surface roughness decreased with increases in the percentage content of ceramic nanoparticles fillers due to excellent nanofiller particle distribution within the polymeric matrix.

4. Conclusions

The following conclusions were deduced from the research results:

- The glass transition (onset) temperature and the end (melting) temperature increased with increases in the applied compression pressures and hot-pressing temperature when using small amounts (1%) of TiO$_2$ ceramic nanoparticle fillers in the HDPE matrix. This temperature value was increased further when using higher compression pressures of between 60 and 90 MPa, reaching its maximum value at 127 °C.
- The increase in the glass transition (onset) temperature continues when using higher values of TiO$_2$ nanoceramic filler, reaching a maximum value for 10% TiO$_2$ and 2% PSZ nanoceramic fillers.
- When 2% of nano-zirconium ceramics (PSZ) were added to the fabricated nanomaterial system, the glass transition (onset) temperature increases at a higher rate, then decreases at high compression pressure levels.
- The results showed that the percentage of crystallization values for all fabricated TiO$_2$/HDPE and TiO$_2$+ 2% ZrO$_2$/HDPE Nanoceramic fillers increased with increases in the process parameter values, while the heat of system fusion values decreased.
- With the increase of the TiO$_2$ filler ceramic from 1% to 10%, the value percentage of crystallisation increased by 14.58%, while when using 1% titanium oxide Nanoceramic powder (TiO$_2$) with 2% partially stabilized zirconia (Y-PSZ), it decreased, reaching its lowest percentage of crystallization value at 33%.
- The heat of system fusion reached its minimum value for the first fabricated system at 88 J/g; adding 2% partially stabilized zirconia (Y-PSZ) further decreased this by 11% to 79.3 J/g. These results suggest that the current study approach reduced the required heat of system fusion by 109.33 %
- All DSC scans showed a single endothermic peak for melting. The DSC scanning curves for both fabricated nanocomposite systems clearly showed that they were significantly affected by both nanofiller type and percentage fraction.
- The atomic force microscopy (AFM) microstructure granularity distribution images for the different nano composition samples showed that the interconnections between the filler ceramic
nanoparticles within the polymeric matrices offered a good explanation for the mechanical properties observed, and that the surface roughness values were decreased with increases in the percentage content of ceramic nanoparticle fillers due to the excellent nanofiller particle distribution within polymeric matrices.

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