Exp. Theo. NANOTECHNOLOGY 9 (2025) 405-414 https://doi.org/10.56053/9.S.405

Employment of poly ether ether Ketone/Zirconia composite in dental industry

Sadeer M. Majeed[1,*], *Jaafar M.Mousa*[2]

[1]Department of Applied Science, University of Technology, Baghdad, Iraq
[2] Applied Science Department, Dental Collage, University of Baghdad, Baghdad, Iraq
[*]) Email: Sadeer.m.majeed@uotechnology.edu.iq

Received 11/2/2025, *Received in revised form* 21/3/2025, *Accepted* 19/4/2025, *Published* 15/5/2025

Polyether ether ketone (PEEK) is a very common thermoplastic polymer because of its mechanical characteristics; it has a very high durability under the conditions of high temperature. Through comparing the composites to unfilled PEEK, the degree of crystallinity related to PEEK resin with the addition of NPs is investigated via XRD. The composites are polycrystalline with peaks (110), (111), (220), and (213). Varieties of the modifications are carried out in the PEEK matrix through the incorporation of a variety of the nanoparticles of zirconia powders (100 nm), which added four percentages (1, 3, 5, and 7) % wt. to the polymer matrix. This project summarizes the effect of zirconia nanoparticles on green (0.9-1.7 g/cm^3) bulk and (1.2-1.5 g/cm^3) theoretical densities, apparent porosity (82%-84%), and Shore hardness (55-80), which are shown to improve with an increase in powder percentage.

Keywords: PEEK; Nano composites; Sintering; Nano zirconia particles.

1. INTRODUCTION

Incorporating Nano-additive particles into polyether ether ketone (PEEK) can significantly enhance its physical, thermal, and mechanical properties. These enhancements make PEEK more suitable for advanced applications in aerospace, biomedical, and industrial sectors. 1. Mechanical Properties Enhancement Nano-additives, such as ZnO, TiO_2, or SiO_2, improve the stiffness, hardness, and wear resistance of PEEK. They act as reinforcement agents, increasing the tensile strength and impact resistance while maintaining the polymer's lightweight nature. 2. Thermal Stability Improvement Nanoparticles enhance the thermal conductivity and heat resistance of PEEK, making it more suitable

for high-temperature applications. Some Nano-additives also act as nucleating agents, promoting better crystallization, which improves dimensional stability at elevated temperatures 3. Tribological Performance The addition of Nano-fillers reduces friction and wear in PEEK-based composites, making them ideal for applications in bearings, gears, and other high-friction environments. ZnO nanoparticles, in particular, enhance wear resistance due to their self-lubricating properties. 4. Electrical and Barrier Properties Certain Nano-additives, such as carbon nanotubes or grapheme, improve the electrical conductivity of PEEK, making it suitable for electronic and conductive applications. Additionally, Nano-fillers enhance the polymer's barrier properties against gases and moisture, improving its durability. 5. Antimicrobial and UV Resistance ZnO and TiO_2 nanoparticles provide antimicrobial properties, making Nano-enhanced PEEK beneficial for medical implants and healthcare applications. Furthermore, UV-resistant Nano-additives protect PEEK from degradation in outdoor environments. Overall, the incorporation of Nano-additive particles into PEEK leads to a multifunctional material with improved mechanical strength, thermal resistance, wear performance, and specialized properties, expanding its potential applications in high-performance industries [1-3].

There is high importance in noting that the incorporation of micron-sized particulates into polymers commonly necessitates a high filler content (no less than 20 vol.%), which can negatively impact a few critical matrix polymer features like appearance, processability, aging performance, and density. It is thus highly desirable to have composites with low particle concentrations and enhanced performance. The recently created nano composites, which are metals or polymers reinforced via nanoscale fillers, could become competitive candidates in light of this worry [4]. The polyether ether ketone (PEEK) can be defined as a linear, semi-crystalline, aromatic, polycyclic, thermoplastic polymer. PEEK has an excellent electrical and mechanical resistance because of its hydrolysis resistance and high temperature [5].

The polyether ether ketone that is reinforced with the Ceramic is progressively turning into one of the primary replacement candidates for the metallic implants because of the fact that it has adjustable mechanical characteristics that are similar to the characteristics of the human cortical bone [6]. Osseo integration, where the implants undergo the integration with surrounding bones, is highly necessary for the success of the re-generation of the bone as well as the healing in the orthopedic and/or dental applications. Even though considerably enhanced biological characteristics are attained by using PEEK-based ZrO_2, Nano-hydroxyapatite (n-HAp) and calcium silicate [7-8], the binary composites through the blending modification, those simple reinforcements typically result in impairing mechanical characteristics of PEEK (such as the work-to-failure limit and tensile strength) [9]. One of the latest studies in this area have highlighted the significance of the ternary composites in the compensation for weaknesses of the traditional binary composites; the ternary composites promote advanced mechanical characteristics as well as bio-compatibility of the materials for mimicking the natural bone's structure and constituents [9-13].

Goyal et al. discovered that the stiffness and micro hardness regarding PEEK-Al_2O_3 composites increase as Al_2O_3 content increases. In comparison to unfilled PEEK, a greater friction coefficient has been obtained. Over 3.5 vol% of Al_2O_3, wear resistance decreases [14]. PEEK implants had the lowest results when Koch et al. examined the bone-implant contact values regarding titanium, zirconium, and PEEK implants. This is attributed to the fact that PEEK is made of a bioinert material, hence there is not enough bone apposition potential. [15]. The Nanoparticles like TiO2, HAF, and Hap can be combined with PEEK to develop bioactive Nano composite [16]. Kartzer et al. mentioned that there is no evidence of either mutagenicity or cytotoxicity with PEEK on the human organs and this shows that PEEK has good biocompatibility properties [17].

2. EXPERIMENTAL

2.1 Poly ether ether keton Matrix Material

The material that has been utilized in the present work as matrix has been polyether ether ether keton, containing Nano powders of ZrO_2 (100) nm which added in 3 percentages (1, 3, 5and 7) % wt. to polymer matrix.

2.2 Forming green stage and sintering

The first stage is mixing the PEEK powder as a matrix with ZrO_2 NPs in three different weight percentages (1, 3, 5, and 7) % wt. to disperse the ZrO_2 NPs with PEEK. This has been done through the incorporation of (2 g) of the filler particles, which are placed in (20 ml) of ethanol and subsequently placed in a round-bottomed flask and stirred for (10 min) while being scanned with an agitating tool for (10 min) to help disperse the mixture. After that, an ultrasonic device will be used to check for specimen images with thickness. Thereafter, the mixture is dried in an oven for 15 minutes at 50°C, and then the resulting powders are typically pressed damp in metal dies. The powder contains a binder (~3% of the composite) and has been formed through uniaxial pressing at 4 tons of pressure in cylindrical metal dies for the formation of the 20mm diameter pellets. The sintering procedure of the samples has been carried out in a programmable furnace at a temperature of 340°C for 35 min. The cooling and heating rate has been 15°C/min.

3. CHARACTERIZATIONS

3.1 X-ray Diffraction

Shimadzu- 6000 X-ray Diffract meter, equipped with the graphite monochromatic and a copper source with the use of the Kα as radiation is used. X-ray tube has been operated at 40 kV and current 30mA at a 0.154nm wavelength. The range of the scanning as 20- 70 deg with the use of step size of 0.02º and 0.10 sec/step. Phase quantification and crystallite size carried out with the use of Eva Software (pro8) IBM PC/AT compatible with Windows XP.

3.2 Physical & Mechanical testes

3.2.1 Density and Porosity

The green and bulk density (B.D) as well as apparent porosity (A.P) regarding sintered materials have been evaluated with the use of Archimedes approach of drainage. The test has been applied based upon the ASTM (C373 – 08).
The green density: Which represents ratio between mass to volume of the sample before sintering after pressing.

$$p = M / V \quad (1)$$

p: The green density (gm/cm^3), M: the mass of green sample (g), V: the volume of green sample (cm^3).

Bulk density (BD): which represents ratio between weight to total volume (i.e. the volume of the material grain + open and close porosity volume). That is calculated from the follow's relationship:

$$(B.D) = \frac{W_d}{W_s - W_n} . D \quad (2)$$

where Wd represents the dry sample weight. Wn represents the weight of the sample that is being immersed in the water. Ws represents the weight of the sample that is infiltrated with the water. D: represents the water density (1g/cm^3).

The apparent porosity (A.P) of those samples has been assessed with the use of the conventional Archimedes rule. Briefly, the dry sample with (W_d) weight has been boiled in the water for a 5 min duration for the purpose of removing air that is trapped within pores. After that, it has been cooled down to the ambient temperature, and weighed in order to have sample weights that are being immersed in water (W_n) and the ones that are being infiltrated with the water (W_s). A.P. has been estimated with the use of the equation:

$$(A.P)\% = \frac{W_s - W_d}{W_s - W_n}.100 \quad (3)$$

where W_d represents the dry sample weight, Wn represents the weight of the sample that is being immersed in the water, W_s represents the weight of the sample that is being infiltrated with the water. ASTM (C373 – 08).

3.2.2 The Linear shrinkage (L.S)

The variation of the specimen lengths prior to and post sintering has been measured by vernier calliper and linear contraction has been tested.

$$(L.Sh)\% = \frac{Lo - L}{Lo}.100 \quad (4)$$

where L.S represents samples' liner shrinkage, L_0 represents length of samples prior to sintering process, L represents length of samples post sintering process.

3.2.3 Shore D hardness

Shore D hardness is a scale used to measure the hardness of harder plastics and rigid elastomers. It is determined by using a device called a durometer-a specialized tester that presses an indenter against the material with a precisely defined force.The indenter, usually made from hardened steel with a pointed or conical tip creates a small indentation in the surface. The depth of that indentation, which is inversely related to the material's hardness, is then read off a scale from 0 to 100, with higher numbers meaning a harder material. ASTM D2240 standards are used for measuring the hardness of rubber and similar materials using a durometer.

4. RESULT AND DISCUSSION

4.1 X-Ray diffraction

A phase analysis of the various samples has been performed with the use of XRD, utilizing Cu Kα radiation with a 0.154 nm wavelength. Relative phase composition of the samples, as shown in Figure 1, has been calculated from measurements of the peak height of respective peaks. The crystalline phases have been characterized through the comparison with the PDF2/PDF4 reference data from the International Centre for Diffraction Data (ICDD). XRD is used to examine the impact of filler content on d-spacing regarding the crystalline PEEK in order to gain a better understanding of the potential chemical interaction between the NPs and the PEEK matrix. Figure 1 illustrates that when zirconia NPs (7 wt.%) are added, no additional peak is produced or vanishes in comparison to those of pure PEEK. The ZrO_2 diffractions in Figure 1 cannot be resolved because they are extremely low. There doesn't seem to be any interaction present that may cause considerable new interfacial phases. The smaller PEEK crystallites, in conjunction with a lower PEEK weight fraction, are the primary causes of the reduced diffraction intensity in composites containing a high number of NPs. A lower degree of crystallization may occasionally take place for composites containing a significant fraction of NPs (7%), due to the fact that the abundant ZrO_2 present in the PEEK matrix could reduce the mobility regarding the polymer chain segments throughout crystallization. [10,19]. As shown in Figure 2, which represents the XRD of zirconia nanoparticles, the powder before sintering contained tetragonal as well as monoclinic phases [19].

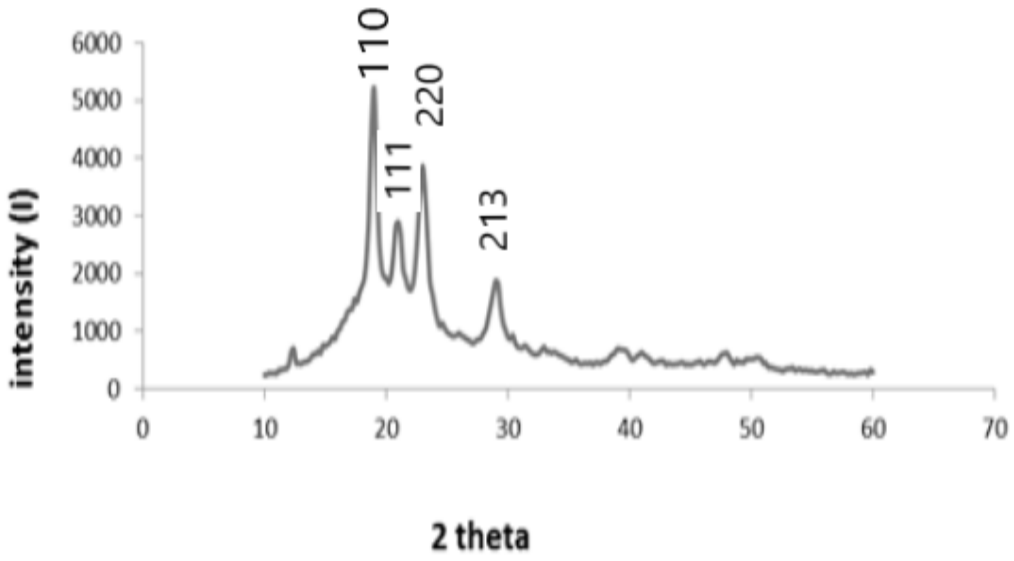

Figure 1 XRD Pattern of PEEK- 7% ZrO_2 nanocomposites.

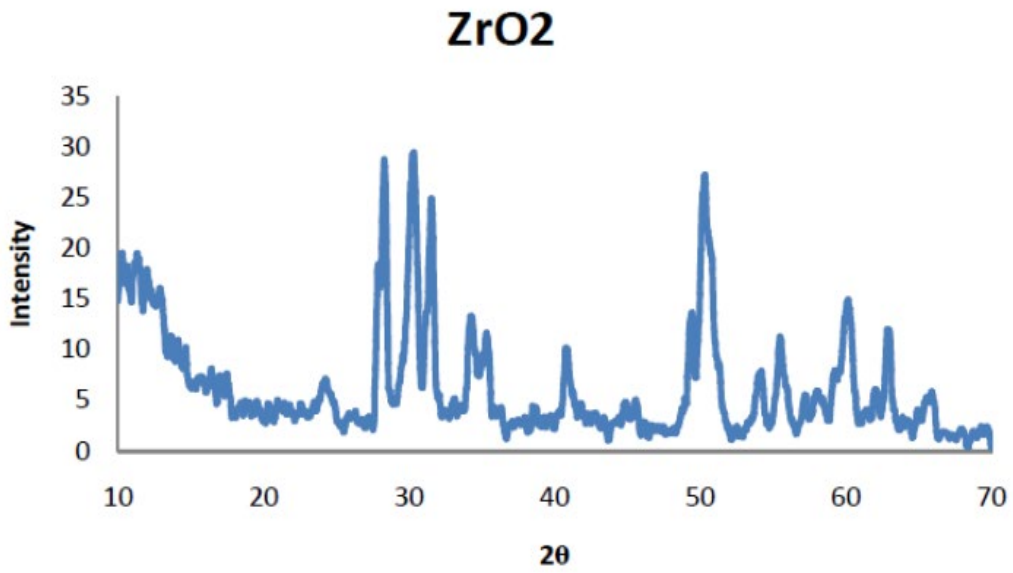

Figure 2 XRD Pattern regarding ZrO_2 NP.

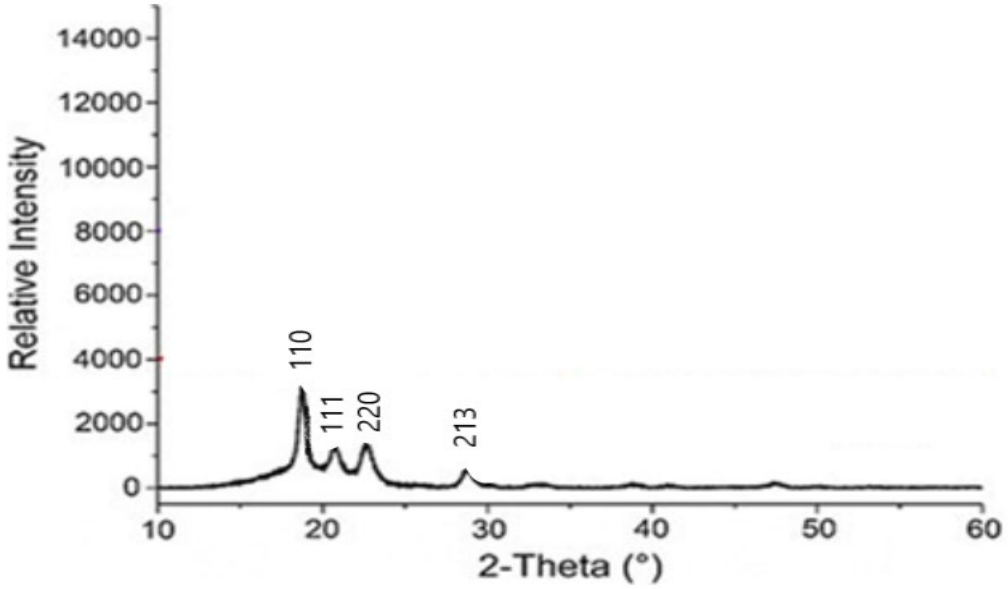

Figure 3 XRD Pattern regarding pure PEEK.

4.2 Density and porosity

The figures below illustrate the values of densities, porosity, and liner shrinkage for all samples. Figure 4 shows that the green density of all samples increases in a gradual manner with ZrO_2 NP content because ZrO_2 NP theoretical density (6.020 g/cm³) is higher than the density of PEEK (1.32 g/cm³). The agglomerate nature affects pore size in the green body. The densification becomes high in the case where a powder that consists of the soft agglomerates has been compacted [20]; un-calcined powders can't be sintered into a dense body that follows a single-stage process of sintering due to the volume expansion that is related to sample formation [20].

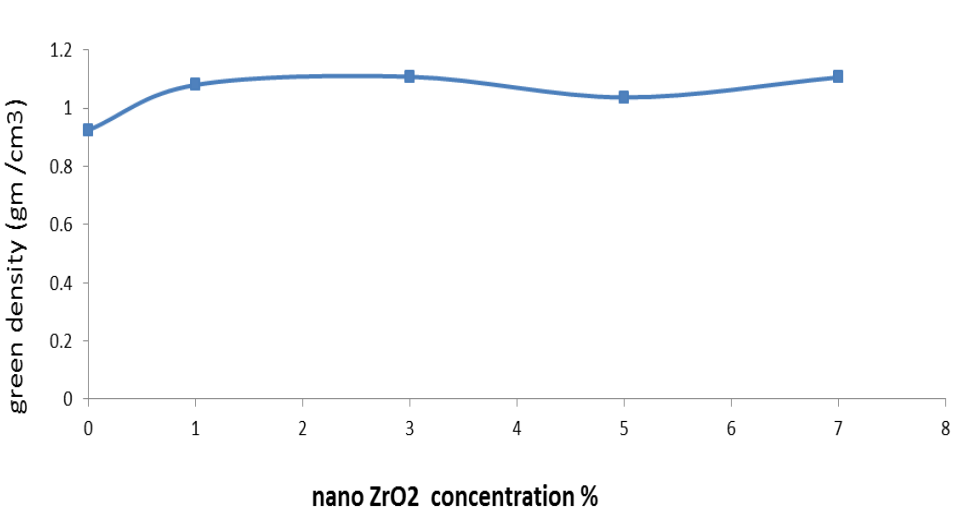

Figure 4 Variation of green density (GD) with ZrO_2NP percentage.

As can be seen in Figure 5 in the sample regarding PEEK-ZrO_2 NP composites, the maximal bulk density values may not be at (7% ZrO_2 NP); the increase in the density could be a result of incorporating heavier ZrO_2 NP into PEEK compared to it from the densification.

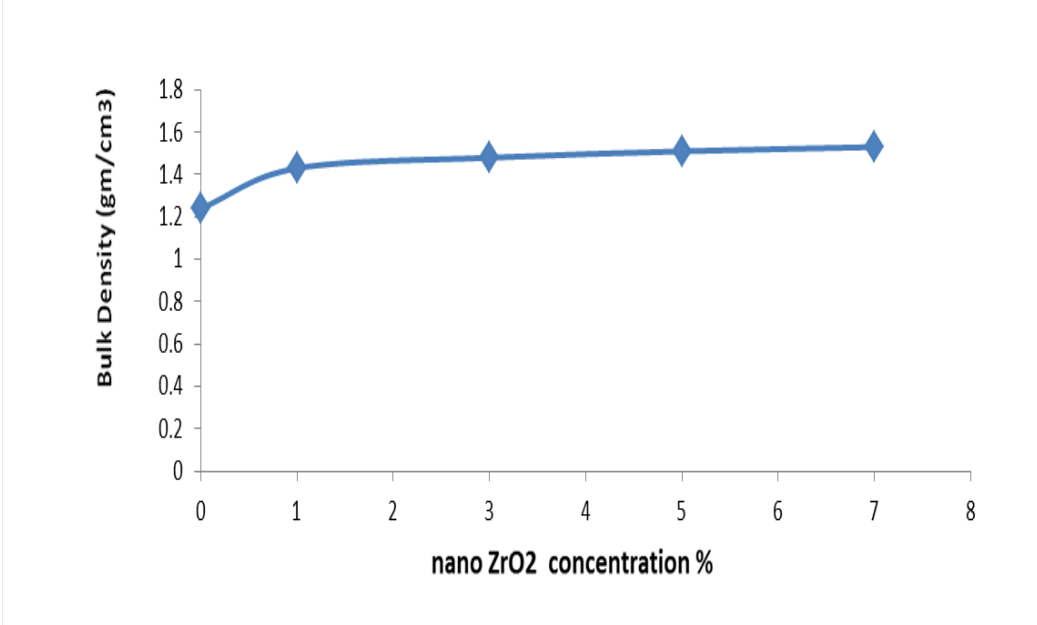

Figure 5 Variation of bulk density with ZrO_2 NP percentage.

Thus, the pores will be eliminated from the surface, which enhances the densification of PEEK-7 % wt. ZrO_2 NP at the rising temperature of sintering, as shown in Figure 6. [21]

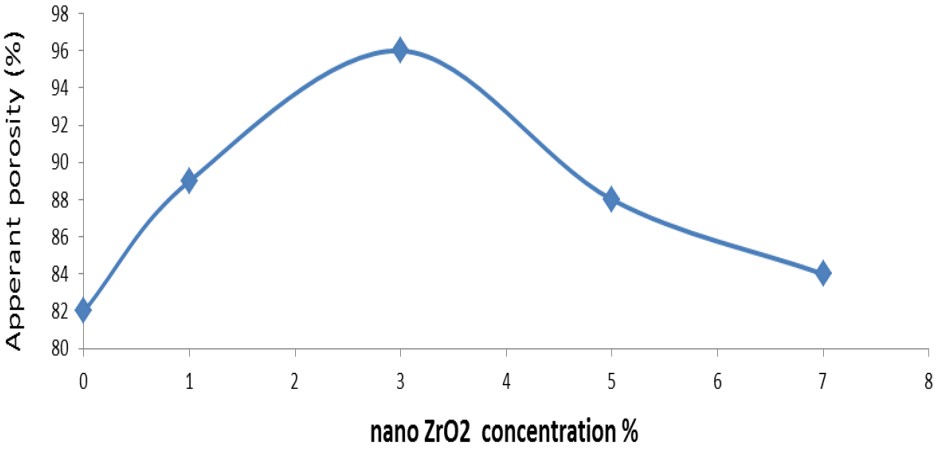

Figure 6 Variation of apparent porosity with ZrO_2NP percentage.

Further, an additional potential reason for improving the sintering capability of PEEK in the presence of ZrO_2 NP is that the ZrO_2 NP has been known to result in the accelerated diffusion of oxygen ions; thus, the materials' sintering capability, the same mechanism, could be applicable in this type of system as well. All PEEK-ZrO_2 NP composites have shown the apparent values of porosity nearly approximate to zero in the case where they are sintered at the temperature of 340°C for 35 min, so the behavior of the apparent porosity is in the density's opposite direction [20, 21, 22], as shown in Figure 6. Figure 7 gives the linear shrinkage values, which are lower with filler addition increase for various composites, substantiating information that is obtained from their values of bulk density. Zirconium filler led to an increase in density and hardness because it filled all the vacancies between ions in the composite matrix.

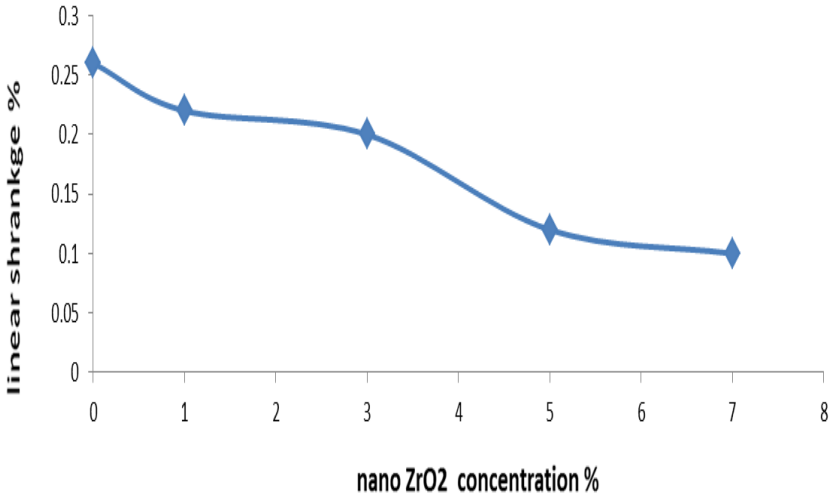

Figure 7 Variation of linear shrinkage with ZrO_2NP percentage

4.3 Shore D hardness

Durometer hardness of the PEEK/ZrO_2 NP composites as filler loading function can be seen from Figure 8. The composite hardness is increased from 54.8 Shore D to 77.8 Shore D for PEEK-ZiO_2 NP Nano composites. This variation is an indication of the fact that nanocomposites' load-carrying capacity is enhanced with the increase of the filler loading; the even distribution of NPs in the PEEK matrix could lead to an increase in the resistance to the PEEK matrix indentation [23, 24]. Yet, as filler loading increases, inter-particle distance decreases, which could help the PEEK matrix, resist local plastic deformation more effectively [23,25].

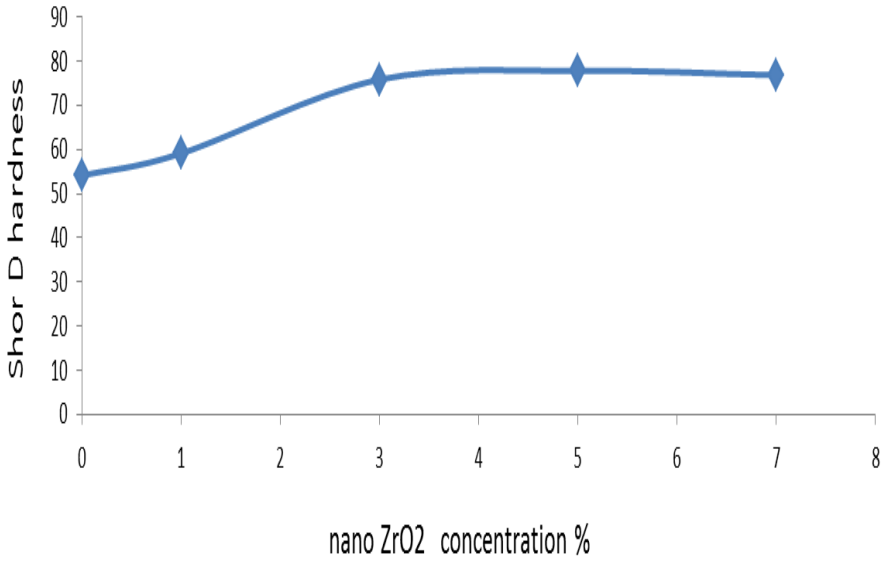

Figure 8 Variation of shore D with ZrO_2NP percentage.

5. CONCLUSIONS

1. The green density of all samples increases in a gradual manner with ZrO_2 NP content.
2. A sample of PEEK-ZrO_2 NP composites has maximal bulk density values that may be noted at 7% ZrO_2 NP; the increase in the density could have resulted from incorporating heavier ZrO_2NP into PEEK than from densification.
3. All PEEK-ZrO_2 NP composites showed values of apparent porosity that were nearly zero; also, the linear shrinkage values that are lower with filler addition increased for various samples of PEEK-ZrO_2 nanocomposites.
4. The Shore D hardness of composites is increased from 54.8 Shore D to 77.8 Shore D for PEEK-ZiO_2 nanocomposites with increasing the addition of nanoparticles of zirconia.
5. In comparison to those of pure PEEK, neither an additional peak nor one that has disappeared has been formed.

References

[1] C. Feng, J. Cen, T. Wu, T. Hou, K. Chen, X. Li, D. Zhang, ACS Appl. Polym. Mater. 4 (2022) 8869
[2] A.M. Díez-Pascual, C. Xu, R. Luque, J. Mater. Chem. B 2 (2014) 3065
[3] L. Hao, Y. Hu, Y. Zhang, W. Wei, X. Hou, Y. Guo, X. Hu, D. Jiang, RSC Adv. 8 (2018) 27304
[4] L.M. Wenz, K. Merritt, S.A. Brown, et al., J. Biomed. Mater. Res. 24 (1990) 207
[5] V. Arrighi, I.J. McEwen, H. Qian, M.B. Serrano Prieto, Polymer 44 (2003) 6259
[6] P. Zoidis, I. Papathanasiou, G. Polyzois, J. Prosthet. Dent. 25 (2015) 580
[7] J. Shijun, C. Sun, J. Zhao, H. Yu, J. Comput. Theor. Nanosci. 12 (2015) 2969
[8] L. Hallmann, A. Mehl, N. Sereno, C.H. Hämmerle, Appl. Surf. Sci. 258 (2012) 7213
[9] E.S. Bechir, A. Bechir, C. Gioga, R. Manu, A. Burcea, I.T. Dascalu, Mater. Plast. 53 (2016) 394
[10] A.A. Mohammed, J.K. Oleiwi, E.S. Al-Hassani, Eng. Technol. J. 38 (2020) 1126

[11] M.E. AL-Samaray, A.A. Fatalla, J. Compos. Mater. 57 (2023) 2955
[12] G.H. Jani, A.A. Fatalla, Res. J. Pharm. Technol. 15 (2022) 3034
[13] A.S. Kadhum, A.F. Alhuwaizi, J. Baghdad Coll. Dent. 33 (2021) 1
[14] J. G. Kim, P. Tan, Exp. Theo. NANOTECHNOLOGY 8 (2024) 17
[15] R.K. Goyal, Y.S. Negi, A.N. Tiwari, U.P. Mulik, J. Appl. Polym. Sci. 104 (2007) 568
[16] F. Koch, D. Weng, S. Krämer, S. Biesterfeld, A. Jahn-Eimermacher, W. Wagner, Clin. Oral Implants Res. 21 (2010) 350
[17] S. Najeeb, Z. Kurshid, S. Zohaib, M.S. Zafer, J. Oral Implantol. 42 (2016) 512
[18] A. Kartzer, H. Marquardt, J. Westendorf, J.V. Wenning, D.V. Forster, Biomaterials 23 (2002) 1749
[19] S. Najeeb, M.S. Zafar, Z. Khurshid, F. Siddiqui, J. Prosthodont. Res. 60 (2016) 12
[20] S.M. Majeed, Eng. Technol. J. 33 (2015).
[21] M. Tadres, Exp. Theo. NANOTECHNOLOGY 8 (2024) 11
[22] S. M.M. Ahmed, D.S. Ahmed, J. Phys. Conf. Ser. 2114 (2021) 012064
[23] B. Stawarczyk, N. Bähr, F. Beuer, T. Wimmer, M. Eichberger, W. Gernet, D. Jahn, P.R. Schmidlin, J. Eng. Technol. 28 (2010) 5165
[24] Kejie Qin, Dejin Zang, Yongge Wei, Chinese Chemical Letters 34 (2023) 107999
[25] H.S. Ahmed, S.M. Majeed, D.S. Ahmed, A.A. Taha, Exp. Theor. Nanotechnol. 9 (2025) 147