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Investigation on Surface Hardness of Organic Nanoparticle Reinforced Polyetheretherketone Implant Material.

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ABSTRACT:

Introduction: The durability of polyetheretherketone (PEEK) composites is reduced by the inadequacies of inorganic reinforcing elements, which include poor bonding and an inadequate interface between the matrix and the reinforcing material. In addition, being effective, PEEK matrix materials used in contemporary composites reinforced with plant-derived organic fibers should have sufficient surface hardness properties. This study aims to evaluate the surface hardness of organic (*Azadirachta indica*) nanoparticle-reinforced polyetheretherketone and its influence on dental implants.

Material and Method: This experiment measured surface hardness for mechanical behavior at the micro and nanoscale to investigate the effects of adding nano-reinforcement materials on performance using the Hysitron Nano Hardness Tester (TI 700 Ubi 1, Florida, USA) and Digital Microhardness Tester (HMV-2000, Shimadzu, Kyoto, Japan). The experiment comprises unreinforced PEEK as the control (NH and MH) and reinforced PEEK at 5, 10, 15, and 20 weight percentages as the experimental groups (NH 5%, 10%, 15%, 20% and MH 5%, 10%, 15%, 20%).

Results: *Azadirachta indica* nanoparticles added with PEEK exhibit an increase in nanohardness ($P = 0.000$) and no change in microhardness ($P = 0.101$). The study's nano hardness values fall between 200 and 330 MPa (megapascals) and the microhardness between 60 to 70 VHN. **A**mong the evaluated organic PEEK-reinforced composites, NH 20% and MH 15% showed the highest nano and microhardness respectively.

Conclusion: The current study observed that the nano hardness is improved by adding 5%, 10%, 15%, and 20% *Azadirachta indica* leaf nanoparticles. The groups' microhardness levels did not appear to differ from one another. In preference to more expensive and environmentally dangerous synthetic nanoparticles, *Azadirachta indica* leaf nanoparticles can be used as an alternative reinforcement material when combined with PEEK.

Introduction:

The materials used in implants at present include ceramics, thermoplastics, metals, and polymers. Carbon-based fibers, graphene oxide, zirconia oxide, zinc oxide, hydroxyapatite, aluminum oxide, silica, and silica oxides, were all used in the development of PEEK nanocomposites.[1,2] Inorganic fillers, such as metals, ceramics, carbon fibers, glass fibers, and carbon fibers, are added to polymers to enhance their physicomechanical properties and wear resistance.[3] Inorganic elements have several shortcomings, including weak bonding and insufficient interface between the matrix and the reinforcing material, which decreases composite durability. Carbon fibers are produced from precursors derived from petroleum and contribute to a carbon footprint and release pollutants. Metallic reinforcing agents are at risk for rusting and corrosion, while inorganic reinforcement materials made of glass and ceramic are stiffer, brittle, heavier, and degrade with time.[4] The use of organic reinforcement elements, such as natural fibers made from sustainable plant sources, lessens these drawbacks.

The interfacial strength of the polymer matrix is strengthened by organic reinforcement materials since these materials are inexpensive, lighter, and bond effectively.[5] Their increased durability results in better composite stiffness and impact resistance. The use of artificial, non-biodegradable reinforcing materials over time raised environmental awareness and ecological concerns. Plant fibers with low density, flexibility, low cost, renewable nature, and biodegradability are gaining consideration as organic fiber reinforcement, which drives researchers to create natural fiber composites.[6] It is noted in the literature that the majority of reinforcement filler materials studied have metallic and inorganic compositions. *Azadirachta indica* (neem) leaf-derived nanoparticles are advantageous for use as reinforcement because of their phytochemicals and flavonoids, which work in concert to produce better effects. The application of *Azadirachta indica* leaf nanoparticles as fillers in the reinforcement of polymer matrix on mechanical behavior is therefore beneficial for investigating. This study aims to investigate and evaluate the micro and nanoscale surface hardness of PEEK-*Azadirachta indica* reinforced implant material with reinforcing filler content varying at 5, 10, 15, and 20 weight percentages.

Materials and Methods:

This experiment assessed surface hardness for mechanical behavior at the micro and nanoscale to investigate the impact of adding nano-reinforcement materials on performance. The mature leaves of *Azadirachta indica* were hand-picked and collected in the springtime from southern India. The leaves were manually crushed and then ground into a powder via a mixer grinder after being shade-dried for 21 days. A Retsch PM 100 centrifugal ball mill (Hann, Germany) was used to ball mill the powdered leaf particles for three hours. The physical ball-milling method was used to create nanoparticles that ranged in size from 50 to 100 nm. At weight percentage ratios of 5, 10, 15, and 20 weight percent, the obtained nanopowder was added to the PEEK powder matrix (Shree Khrishna Polymers, Chennai, Tamil Nadu, India). Magnetic stirring was used for 60 seconds to thoroughly mix PEEK and additional nanoparticles at various ratios to achieve homogeneity. Thermopress 400 (Bredent GmbH & Co., Germany) was used to manufacture the composites through the injection molding process. The equipment works without the need for an external compressed air source. The Unreinforced PEEK and the premixed nano-reinforced PEEK powders were filled in special cartridges and were subjected to polymerize at 390 degrees Celsius with a holding time of 25 minutes to prevent any negative influences. The electric drive injects the materials with a uniform transmission of force. During the entire cooling process, the programmed level of force is maintained so that an optimum fit can be created and porosity prevented. Fifty samples in total (N=10 for each group) were prepared, and the study included samples with perfect dimensions and no porosity (Table 1).

A Hysitron Nano Hardness Tester (TI 700 Ubi 1, Florida, USA) was used to conduct the tests. Utilizing a Berkovich indentation tip, the maximum load of 500 mN and the maximum depth of 200µm were reached at an indentation speed of 100 mN/min. A rigid indenter with a maximum penetration depth of 4000 nm was pressed with a specific force into the material under test, and the indentation's imprint for nanohardness was computed. Each specimen had over thirty indentations made in random locations to produce accurate results. A 400-gm test load is applied downward onto the surface of the test specimen using a digital microhardness tester (HMV-2000, Shimadzu, Kyoto, Japan) having a four-sided standard diamond pyramid with a surface angle of 136° for a 15-second exposure period to determine the Vicker's Hardness Value (VHN). After adjusting the specified load and dwell time, the specimen was

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JCHR (2023) 13(5), 732-738 | ISSN:2251-6727

maintained at the tester's table. The indentation left by the indenter on the specimen's surface was examined under the built-in microscope, and the hardness was computed digitally using the diagonal lengths and measured with a measuring microscope. Three indentations were made at three distinct locations on each specimen, spaced one millimeter apart from the specimen's margins or the previous indentation. The specimen's VHN was determined by averaging the three values obtained, which were then tabulated. The microhardness of the samples was determined by averaging the three hardness readings. (Fig 1).

Table 1: Grouping of Samples

No. Of Samples (n=50)	Nano Hardness (NH)	Micro Hardness (MH)
I.Control Group (Unreinforced PEEK)		
n=10	NH	MH
II.Experimental Groups (Reinforced PEEK)		
n=10	NH 5%	MH 5%
n=10	NH 10%	MH 10%
n=10	NH 15%	MH 15%
n=10	NH 20%	MH 20%

Results:

The software SPSS version 25.0 (SPSS Inc., Chicago, IL, USA) was used to statistically analyze the readings. Data were found to be normally distributed ($P > 0.05$) based on preliminary Shapiro-Wilks test results. Calculations were made for descriptive statistics, such as mean, standard deviation (SD), standard error, maximum, and minimum. One-way ANOVA for differences (95% confidence interval) for the samples' nanohardness (NH) and microhardness (MH) was tested in terms of inferential statistics. The post hoc test ($\alpha=0.05$) was used to compare the groups. P less than 0.05 was taken into account for statistical significance. The control and experimental groups' mean (SD) and one-way ANOVA for nanohardness are shown in Table 2, where there is a statistically significant difference for nanohardness but not for microhardness. Post hoc Tukey's multiple comparison tests (Table 3) revealed no statistical difference for microhardness among the groups of different reinforced percentages, but a statistical difference for nanohardness across all the groups ($P=0.000$).

Table 2: One-way analysis of variance

I. Nano-Hardness (NH) Mpa			
Groups	**Mean ± SD**	**F Value**	**P Value**
NH	292.03 ± 2.80	169.2	0.000
NH 5%	299.04 ± 2.21		
NH 10%	303.89 ± 3.74		
NH 15%	314.81 ± 3.38		
NH 20%	323.21 ± 2.62		
II. Micro-Hardness (MH) vhn			
Groups	**Mean ± SD**	**F Value**	**P Value**
MH	67.17 ± 4.50	2.063	0.101
MH 5%	66.55 ± 2.63		
MH 10%	65.40 ± 3.37		
MH 15%	64.27 ± 3.50		
MH 20%	62.45 ± 2.84		

SD = Standard Deviation

Journal of Chemical Health Risks
www.jchr.org
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Table 3: Post hoc Tukey's test

I. Nano-Hardness (NH) Gpa

Groups	Compared Group	Mean Difference	*P* Value
NH (Control)	NH 5%	-7.012	0.000
	NH 10%	-16.28	0.000
	NH 15%	-22.78	0.000
	NH 20%	-31.18	0.000
NH 5%	NH 10%	-9.263	0.000
	NH 15%	-15.76	0.000
	NH 20%	-24.16	0.000
NH 10%	NH 15%	-6.500	0.000
	NH 20%	-14.90	0.000
NH 15%	NH 20%	-8.400	0.000

II. Micro-Hardness (MH) vhn

Groups	Compared Group	Mean Difference	*P* Value
MH (Control)	MH 5%	2.619	0.539
	MH 10%	1.768	0.833
	MH 15%	2.919	0.431
	MH 20%	4.719	0.057
MH 5%	MH 10%	0.851	0.986
	MH 15%	0.300	0.999
	MH 20%	2.100	0.728
MH 10%	MH 15%	1.151	0.960
	MH 20%	2.951	0.420
MH 15%	MH 20%	1.800	0.824

*. The mean difference is significant at the 0.05 level.

Discussion:

Polyetheretherketone (PEEK) reinforcement is commonly used for implants with chemical resistance, biological compatibility, and a modulus of elasticity comparable to bone, making it an excellent choice for medical and dental applications.[7,8,9] Yet, the scope of prior research on the hardness of organic nanoparticle-reinforced PEEK composite at the nano and microscales is minimal. Chemically produced nanoparticles are toxic, which limits their application in medicine. During the synthesis, injurious, combustible, and non-recyclable chemical substances were used, which is bad for the environment and can have negative effects on medical applications.[10] Biological synthesis was presented as a substitute technique for navigating around this deleterious effect.[11] In a process known as "ball milling," steel balls are mechanically ground into smaller nanoparticles by dropping them into a jar and rotating them horizontally. In the current work, natural physical manufacturing of *Azadirachta indica* leaf nanoparticles by ball milling without the addition of chemicals was used to reduce the toxicity and hard agglomerates of nanoparticles.

Compared to the conventional hardness measurement, which yields a single characteristic value, nanoindentation provides an accurate, depth-dependent evaluation of multiple material-specific properties. This study employed both nanoindentation and microindentation testing techniques, demonstrating variations in the hardness characteristics examined. *Azadirachta indica* nanoparticles added with PEEK exhibit an increase in nanohardness (P = 0.000) and no

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change in microhardness (P = 0.101). The size of the indenter used to measure the hardness is the primary distinction between polymers' microhardness and nanohardness. Micro hardness testing measures the surface hardness of composites using an indenter in the micrometer range. Nano hardness testing, on the other hand, employs an indenter in the nanometer range, such as a sharp diamond tip or Berkovich indenter, to assess the hardness of materials at the nanoscale.[12]

Regarding the hardness of the reinforced composite, Figure 2 indicates a slight decrease in microhardness (P=0.041) with no statistically significant difference and a significant increase in nanohardness (P=0.000). When compared to other studies, an increasing sequence of increases in nanohardness was observed. It's important to keep in mind that composite materials can exhibit complex behavior, and there may not always be a clear correlation between nanohardness and microhardness. In contrast to bulk measurements, the material is indented at very short length scales when measuring nanohardness, where the material behaves differently. Because of nanoscale phenomena like disorientation, grain borders, low glass transition temperatures, surface impacts, and reinforcement position that can add more strengthening mechanisms, the nanoparticle-reinforced PEEK has increased nanohardness while maintaining microhardness.[13,14]

When the reinforcements are properly aligned, they have improved mechanical qualities at the nanoscale. At the microscale, the orientation and distribution of the reinforcements may change, and they might not all align. Lower microhardness values and altered mechanical behavior could arise from this. Microhardness values do not significantly decrease, but a drop in microhardness values could have been caused by an uneven distribution of reinforcement or a poor interfacial connection. This is explained by the formation of soft agglomerates or clusters in the PEEK matrix, which are collections of individual particles bound by physically attractive interactions. This alters the composite's hardness and local microstructure.[15] Soft nanoagglomerates give rise to structural defects like voids or regions of reduced molecular movement, which can impede intermolecular interactions and packing. Because smaller nanoparticles have a higher surface energy, they aggregate more easily and may have changed in orientation, which could have led to a small reduction in microhardness.[16] There may be no statistically significant change in the microhardness of the material as a result of this disruption to its order and crystallinity. Furthermore, several studies showed how the orientation of the reinforced material affected the wear behavior of PEEK composites. It was challenging to identify which direction would most likely increase wear resistance in the composite with non-parallel orientation, despite the composite exhibiting wear resistance.[17,18] Because of this, the uneven distribution of these reinforcements within the matrix may result in localized softening or weaker areas. The study's nano hardness values, which fell between 200 and 400 MPa (megapascals), are normal and in line with other research on PEEK reinforced with carbon fiber.[10,19,20] The results of this study are compared to carbon fiber-reinforced PEEK composites because no research has been done on *Azadiratcha indica* leaf nanoparticle-reinforced PEEK composites. The organic compounds found in *Azadiratcha indica* leaves, such as cellulose, hemicellulose, lignin, and other volatile compounds, undergo combustion and pyrolysis when burned at a temperature of 370 degrees Celsius, and that favors the leaves' conversion into carbon particles. These tiny, black carbon particles are mostly made of elemental carbon.[21]

This investigation is double-blinded. The optimization and weight percentage of *Azadirachta indica* leaf nanoparticles incorporated with PEEK were concealed from the operator and the statistician. The study's limitations include the in vitro environments with their different processing characteristics, reinforcement attributes, and testing protocols for determining microhardness and nanohardness. To better understand the properties of PEEK composites reinforced with *Azadirachta indica* leaves, future research should focus on biological aspects that mimic the oral environment, dynamic loading, and experimental characterization.

Conclusion: The current investigation concluded that increasing the amount of Azadirachta indica leaf nanoparticles by 5%, 10%, 15%, and 20% enhances the nano hardness. There was no apparent statistical difference in microhardness between the groups. Given this, *Azadirachta indica* leaf nanoparticles are potentially considered an alternative reinforcement material with PEEK to replace other high-cost and environmentally hazardous synthetic nanoparticles.

Journal of Chemical Health Risks
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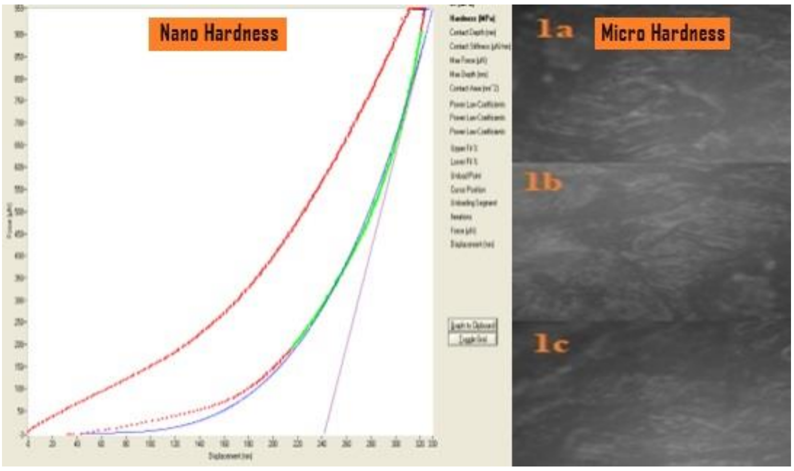

Figure 1: Nano Hardness and Micro Hardness values of an experimental sample

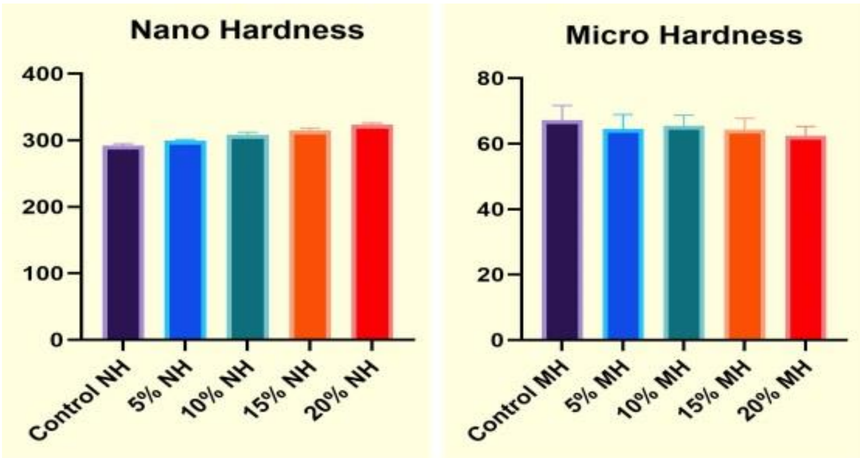

Figure 2: Graphical Comparison of Nano Hardness and Micro Hardness

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