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ORIGINAL RESEARCH

An investigation on Elastic Modulus of Novel Nanoparticle Enhanced Polyetheretherketone Implant Biocomposite.

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ABSTRACT

Background: Polyetheretherketone (PEEK) shows promise as a biocompatible implant material, but its low elastic modulus necessitates reinforcement. This study explores the potential of *Azadirachta indica* (neem) leaf nanoparticles as eco-friendly reinforcements to enhance polyetheretherketone's (PEEK) elastic modulus for orthopedic and biomedical applications.

Materials and Method: Neem leaves were processed into 100-175 nm *Azadirachta indica* nanoparticles (AINP) via ball-milling. AINP-reinforced polyetheretherketone (PEEK) composites (0, 10, 15, 20 wt%) were prepared using injection molding. Nanoindentation experiments evaluated elastic modulus, with statistical analysis (one-way ANOVA, Tukey test) performed to assess the effects of AINP reinforcement.

Results: Nanoindentation experiments revealed significant enhancements in elastic modulus (E) with *Azadirachta indica* nanoparticle reinforcement. Elastic modulus increased from 1.38 GPa (0% reinforcement) to 2.52 GPa (20% reinforcement), representing an 82.61% increase. ANOVA and Tukey tests confirmed statistically significant differences between unreinforced and reinforced groups (p=0.000), but no significant improvements beyond 20% reinforcement.

Conclusion: The incorporation of *Azadirachta indica* nanoparticles into PEEK enhances and matches the elastic moduli to human bone, rendering it a suitable candidate for replacing traditional metallic implants in orthopedic and dental applications.

Keywords: Nanoindentation, elastic modulus, nanoparticles, implants, polyetheretherketone

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1. INTRODUCTION

Polyetheretherketone (PEEK) potential as an implant material is promising from its biocompatibility and stability. Its low elastic modulus necessitates reinforcement to match cortical bone properties, ensuring effective osseointegration and minimizing stress-shielding in dental applications. Carbon fiber-reinforced PEEK offers optimal durability and stiffness, but has environmental drawbacks and fragility issues.[1,2]

Glass fiber reinforcement compromises chemical resistance and structural integrity, while graphite and PTFE reinforcements limit load-bearing capabilities. Carbon fiber's environmental issues (emissions, recycling challenges) are addressed by organic reinforcement materials from plant sources,

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offering a sustainable solution with a lower carbon footprint, improved bonding, enhanced strength, and biodegradability.[3]

Natural Fiber-Reinforced Polymer Composites (NFPCs) gain traction in automotive and building industries, offering eco-friendly alternatives to traditional PEEK polymers. Natural fibers, with enhanced properties, replace synthetic fibers in various applications.[4] Derived from renewable sources, NFPCs prioritize sustainability and environmental responsibility. Neem (*Azadirachta indica*), native to India and part of the *Meliaceae* family, has garnered attention for its leaf-derived nanoparticles. Neem leaf nanoparticles have garnered significant attention in recent years due to their exceptional medicinal properties, affordability, and widespread availability.

They are abundant in phytochemicals and flavonoids, exhibit enhanced properties when combined, making them a promising reinforcement material. [5,6] These nanoparticles have demonstrated remarkable potential in various fields, including biomedicine, nanotechnology, and environmental science. Notably, the combination of neem leaf nanoparticles with chitosan has been utilized to develop biodegradable composite textile products with enhanced antimicrobial capabilities. [7] Previous studies, explored the preparation of *Azadirachta indica* nanoparticles using solution-based wet processing methods.[8] Researchers developed recyclable epoxy-based composites using neem waste, enhancing impact toughness of 12.32 J/m, along with improved thermal stability.[9] The primary objective of such research has been to create biocompatible nanomaterials that possess medicinal and functional qualities when integrated into textiles. Interestingly, a significant majority of reinforcement filler materials employed in existing studies are metallic and inorganic, primarily due to their superior mechanical characteristics. However, there exists a knowledge gap in the scientific literature regarding the utilization of neem-leaf nanoparticles as reinforcements in polymer matrix composites, particularly with respect to their impact on elastic modulus. This study aims to address this gap by investigating the effects of reinforcing polyetheretherketone with *Azadirachta indica* nanoparticles at varying weight percentages (0wt%, 10wt%, 20wt% and 30wt%). The primary focus of this research is to analyze the Young's elastic modulus (E) of the resulting composites, with the ultimate goal of matching the elastic modulus of human bone. This research has significant implications for the development of advanced biomaterials with tailored mechanical properties for orthopedic and biomedical applications.

2 .MATERIALS AND METHODS

2.1. Specimen Preparation:

Fresh neem leaves collected from Tamil Nadu, India, during the spring season were shade-dried, shredded, grounded and reduced to a size range of 100-175 nm through physical ball-milling, yielding *Azadirachta indica* nanoparticles (AINP). To prepare AINP-reinforced PEEK composite specimens, the dried AINP was added to the PEEK powder matrix as 0wt%, 10wt%, 20wt%, and 30wt%. Homogeneous powders were achieved through premixing using a Mini Cyclomix lab mixer for 60 seconds. The nanoparticles were dispersed uniformly into the matrix to ensure homogeneity.

For specimen preparation, forty-eight samples (n=12) were created for evaluating elastic modulus via nanoindentation experiments. Following ASTM E18 guidelines, cylinder pellets with dimensions of 15 x 2 mm were prepared for both the experimental group (PEEK reinforced with nanoparticles) and the control group (unreinforced PEEK). Type IV hard diestone was used to create molds for injection molding. The homogenous materials were preheated and pressed using the thermopress 400 injection molding system. The aluminum cartridge containing twenty grams of mixed homogenous powder was heated to 398°C and pressed into the mold cavity at 160 MPa for 60 seconds. After holding the temperature for 25 minutes, the injected molds were allowed to cool to room temperature overnight, yielding definitive injection-molded specimens with smooth, non-porous machined surfaces.

2.2 Experiment

Nanoindentation experiments were conducted utilizing a Nano Hardness Tester (Hysitron; TI 700 Ubi 1) equipped with a Berkovich-type indenter tip to evaluate the mechanical properties of the specimens. To ensure reliable results, the specimens were meticulously prepared according to the ISO 14577-4 standard, achieving a surface roughness value of less than 5% of the maximum penetration depth (4000 nm). The nanoindentation process involved applying a predetermined force to the specimens using a rigid indenter with known geometry and hardness. During the test, the Berkovich indentation tip was pressed into the specimen at a rate of 100 mN/min, reaching a maximum load of 500 mN and depth of 200 µm. Following attainment of the maximum force, the indenter was released under controlled conditions, allowing for measurement of the penetration depth during both loading and unloading cycles. The resulting indentation imprint provided valuable insights into the material's behavior, revealing the distinct elastic and plastic components.[10,11]

The permanent deformation caused by the indenter, which did not return to its original depth after unloading, was carefully analyzed to determine the Young's elastic modulus (E) of the tested material. By examining the force-displacement data and indentation dimensions, various parameters, including elastic modulus, were calculated, providing a comprehensive understanding of the material's mechanical properties. This meticulous nanoindentation process enabled the precise evaluation of the specimens' elastic modulus, a critical parameter in assessing the suitability of the AINP-reinforced PEEK composites for orthopedic and biomedical applications, where matching the elastic modulus of human bone is essential.

2.5 Statistical Analysis

To facilitate statistical analysis, the experimental data was collected, organized, and imported into Excel and subsequently into SPSS version 25.0 software. Initial parametric tests using the Kolmogorov-Smirnov (K-S) test revealed non-normal distribution of the data. Consequently, descriptive statistics, including mean, standard deviation, standard error, maximum, and minimum values, were calculated. To examine the differences between groups, inferential statistical analysis was performed using one-way analysis of variance (ANOVA) with a 95% confidence interval. ANOVA was selected to assess the mechanical properties of the reinforced polyetheretherketone due to its ability to compare means among multiple groups, determining whether significant differences existed between various weight percentages.

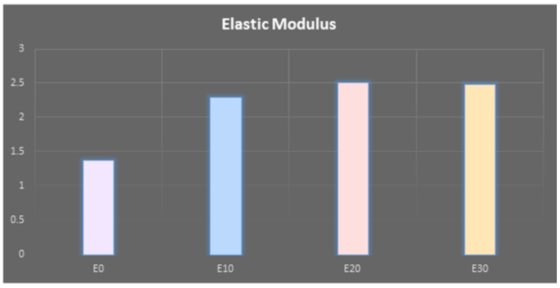
Post hoc Tukey test was conducted to perform pairwise comparisons between groups, providing further insight into the nature of significant differences detected by ANOVA at a significance level of P = 0.05. This comprehensive statistical approach enabled the evaluation of the effects of AINP reinforcement on the mechanical properties of PEEK composites.

3. RESULTS

The tables present an analysis of the elastic modulus (E) of a material with varying percentages of reinforcement (0wt%, 10wt%, 20wt%, and 30wt%). Table 1 displays a one-way ANOVA analysis for the elastic modulus (E) in GPa. It shows that the elastic modulus increases as the percentage of reinforcement increases from 0wt% to 30wt%. The mean elastic modulus for the 0wt% group is 1.38 ± 0.34 GPa, which increases to 2.30 ± 0.51 GPa for the 10wt% group, 2.52 ± 0.38 GPa for the 20wt% group, and 2.49 ± 0.36 GPa for the 30wt% group. The ANOVA reveals a statistically significant difference between these groups (F value = 17.019, p = 0.000), suggesting that the reinforcement percentage significantly affects the elastic modulus.

Groups	Mean ± SD	Maximum	Minimum	*F* Value	*P* Value
E 0%	1.38 ± 0.34	1.92	1.01	17.019	**0.000***
E 10%	2.30 ± 0.51	3.11	1.72		
E 20%	2.52 ± 0.38	3.04	1.99		
E 30%	2.49 ± 0.36	1.97	2.96		

Table 1: One-way Analysis of Variance (ANOVA) on Elastic Modulus (E) of Azadirachta indica nanoparticles reinforced polyetheretherketone with various weight percentages (E0, E10, E20, and E30).



Graph 1: Mean Values of Elastic Modulus of E0, E10, E20, and E30 Groups

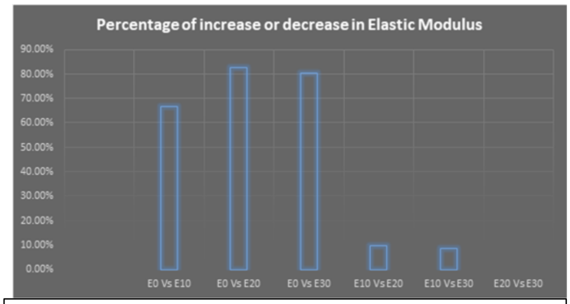
Table 2 presents the post hoc Tukey test for multiple comparisons. It indicates that there are significant differences between the elastic modulus of the 0wt% group and all other groups (10wt%, 20wt%, and 30wt%) with a p-value of 0.000. However, when comparing the groups with 10wt%, 20wt%, and 30wt% reinforcement, no statistically significant differences are observed (p-values = 1.000), implying that increasing the reinforcement beyond 10wt% does not lead to a further significant change in the elastic modulus. Table 3 shows the percentage increase or decrease in the elastic modulus between different reinforcement groups. A notable increase in elastic modulus is observed when moving from 0wt% to 10wt% (66.67%) and further increases up to 20wt% reinforcement (82.61%). The change from 10wt% to 20wt% is minimal (9.57%), and there is even a slight decrease of -1.19% between the 20wt% and 30wt% groups. This suggests that while initial reinforcement significantly boosts the elastic modulus, further additions beyond 20wt% may not be beneficial and could slightly decrease the modulus.

Groups	Compared Group	Mean Difference	*P* Value
E 0%	E 10%	0.918	**0.000***
	E 20%	1.136	**0.000***
	E 30%	1.111	**0.000***
E 10%	E 20%	0.218	1.000
	E 30%	0.193	1.000
E 20%	E 30%	0.025	1.000

Table 2: Multiple Comparison on Elastic Modulus (E) of *Azadirachta indica* nanoparticles reinforced polyetheretherketone with various weight percentages (E0, E10, E20, and E30).

Elastic Modulus (E) Gpa	Percentage of increase or decrease
0% Vs 10%	66.67%
0% Vs 20%	82.61%
0% Vs 30%	80.43%
10% Vs 20%	09.57%
10% Vs 30%	08.26%
20% Vs 30%	**-1.19%***

Table 3: Percentage Increase/Decrease in Elastic Modulus (E) between *Azadirachta indica* nanoparticles reinforced polyetheretherketone with various weight percentages (E0, E10, E20, and E30).



Graph 2: Percentage of increase or decrease among the groups (E0, E10, E20, and E30)

4. DISCUSSION

PEEK composites typically use inorganic nanoparticles, but toxicity concerns led to exploring naturally synthesized *Azadirachta indica* nanoparticles (AINP). Nanoindentation analysis; a precise measurement technique demonstrated significant elastic modulus variations with neem nanoparticle incorporation, highlighting AINP's potential as a biocompatible substitute for therapeutic applications.[12,13]

The elastic modulus, a critical property influencing a material's load-bearing capacity and shape retention, is affected by temperature and crystallinity in carbon-reinforced PEEK. Notably, higher crystallinity enhances elastic modulus, and incorporating AINP transforms virgin PEEK's semi-crystalline structure into a uniform crystalline phase. Unreinforced PEEK's elastic modulus can be significantly enhanced through fiber mass fractions and reinforcements, as demonstrated in this study. Notably, the incorporation of *Azadirachta indica* nanoparticles (AINP) into PEEK composites, a previously unexplored area of research, yields result consistent with existing studies on carbon nanoparticle-reinforced PEEK composites, particularly considering AINP's conversion to carbonaceous material during manufacturing. Significant improvements in elastic modulus were observed with 10wt%, 20wt%, and 30wt% AINP reinforcements. The data in Tables 1-3 reveal a substantial improvement in the elastic modulus (E) of AINP-reinforced PEEK as the reinforcement increases to 20wt%. However, beyond this threshold, the marginal difference between 20wt% and 30wt% reinforcement suggests that additional nanoparticles do not provide further enhancement and may even slightly decrease the modulus. This phenomenon is consistent with the established behavior of carbon nanoparticles in polymer matrices, where reinforcement effectiveness plateaus due to factors like nanoparticle dispersion, agglomeration, and matrix-nanoparticle interactions, ultimately reaching a saturation point.

To ensure optimal dental implant performance, the elasticity modulus of the implant material should closely match that of surrounding bone tissue, preventing stress concentrations at the implant-bone interface. [1,14] This compatibility is crucial for minimizing stress-shielding effects, which can weaken the bone and lead to implant failure. Research by Geetha et al. highlights that implant failure often results from mismatches between the implant material's elasticity modulus and that of human bone. [15] The elastic modulus increase, particularly up to 20wt% AINP, is due to nanoparticles' high aspect ratio, exceptional mechanical properties, and strong interfacial interactions with PEEK. Nanoscale effects enhance stress transfer, making AINP an effective reinforcement phase in PEEK composites.[16,17]

Effective mechanical interlocking and bonding between carbon nanoparticles and the PEEK matrix significantly boost the elastic modulus. Optimal dispersion and strong interfacial adhesion are crucial, but higher loadings can lead to nanoparticle clustering, diminishing the reinforcing effect. This is evident in the modest or negative change in modulus between 20wt% and 30wt% loadings.[18] This study reveals that AINP-reinforced PEEK composites achieve optimal elastic modulus at 10wt% and 20wt% loadings, with a value of approximately 2.52 GPa, before decreasing by 1.2% at 30wt%. Notably, 20wt% and 30wt% AINP reinforcements yield significant elastic modulus enhancements of 82% and 80%, respectively (Tables 2 and 4). The remarkable improvements are attributed to the uniform dispersion of nanoparticles, synergistic interactions between reinforcement and matrix, and efficient stress transfer. Furthermore, the high surface area and potential for percolating network formation within the polymer enable nanoparticles to provide exceptional mechanical property enhancements.[19,20]

The elastic modulus plateaus and slightly declines beyond 20wt% AINP reinforcement due to challenges in achieving uniform nanoparticle dispersion, leading to agglomeration and impaired stress transfer. This aligns with existing literature, suggesting an optimal reinforcement percentage exists within a narrow range for maximizing mechanical properties. Furthermore, increasing the weight percentage of reinforcement can lead to volatile gas formation and void creation, introducing stress concentration points and weakening the material's resistance to deformation and are consistent with hardness of other study.[21,22] As a result, the optimal reinforcement percentage is critical to balance mechanical property enhancements and minimize potential drawbacks, highlighting the importance of precise composition control in AINP-reinforced PEEK composites.[23] Also, during material injection into the mold, the matrix pressure falls below atmospheric pressure, becoming supersaturated. This enables gas molecules generated by AINP to diffuse into the polymer matrix, forming microvoids. As noted by Matsuzaki et al., the void space fluctuates due to void migration into the matrix, driven by pressure changes at the void-matrix interface. The injection pressure and pressure gradient significantly influence this process. 24,25

This study highlights the critical role of optimized AINP nanoparticle loading in PEEK composites for enhanced mechanical performance in dental and medical implants. Identifying the ideal 20wt% reinforcement threshold can lead to improved implant longevity, reduced failure rates, and enhanced patient outcomes. However, further reinforcement up to 30wt% offers no additional benefits and may decrease modulus. The addition of *Azadirachta indica* nanoparticles to PEEK achieves biomimetic elastic properties, closely matching those of human bone, thereby emerging as a viable, biocompatible replacement for metal implants in orthopedic and dental surgeries.

Despite limitations related to processing conditions, material characteristics, and testing protocols, the incorporation of AINP reinforcement improves PEEK's properties, making it a promising material for dental implants. Further research is crucial to translate these findings into clinical practice, particularly dynamic loading studies to simulate oral environment conditions, thermal properties, material aging, biological characteristic and long-term properties evaluation to ensure durability and resistance to degradation. Additionally, it is necessary to investigate the long-term biocompatibility, cytotoxicity, biological stability, and degradation behavior of AINP-reinforced PEEK composites in vivo, including their effects on bone-implant interface and osseointegration. In conclusion, *Azadirachta indica* (neem) leaf nanoparticles effectively reinforced polyetheretherketone (PEEK), significantly enhancing its elastic modulus by 82.61% with 20% reinforcement. This eco-friendly approach demonstrates promising potential for developing biocompatible implants with improved mechanical properties, suitable for orthopedic and biomedical applications. The optimal 20% reinforcement threshold ensures compatibility with human bone, paving the way for future clinical applications and replacing traditional metallic implants.

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