AN IN VITRO STUDY ON THE MECHANICAL BEHAVIOR OF POLYETHERETHERKETONE IMPLANT MATERIAL INCORPORATED WITH HERBAL NANOPARTICLES.

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Abstract:

Background - Polyetheretherketone is a semi-crystalline, thermoplastic, polyaromatic ketone. There are disadvantages to the addition of inorganic fillers as reinforcement. Nanoparticles derived from Neem (*Azadirachta indica*) leaves are organic sources to use as reinforcement of polyetheretherketone. Hence, it was investigated to evaluate the surface hardness, stiffness, and modulus of elasticity of PEEK-*Azadirachta indica* reinforced polyetheretherketone at varying weight percentages. **Materials and Method -** This experiment is intended to evaluate the surface hardness for mechanical behavior at micro and nano levels. A total of 96 samples (N=12 for each group) where 48 samples underwent the nanoindentation test and the remaining 48 samples for the microhardness test. The unreinforced PEEK specimens and nanoparticle-reinforced specimens were prepared by injection molding. The tests were carried out using a Nano Hardness Tester which shows elastic and plastic values (hardness, indentation modulus, and elastic modulus) of the tested material. A digital microhardness tester was used to observe the indentation made by the indenter on the surface of the specimen to calculate the hardness value. **Results -** One-way ANOVA of control and experimental groups showed a p-value for nano hardness-NH (P=0.000), microhardness-MH (P=0.041), reduced elastic modulus-ER (P=0.000), and contact stiffness-S (P=0.000). **Conclusion –** The addition of 10%, 20%, and 30% *Azadirachta indica* leaves nanoparticles as a reinforcement material does improve the nano hardness. A minimal decrease in microhardness was noted among 10%, 20%, and 30% PEEK-*Azadirachta indica* leaves nanocomposite. 30% PEEK-*Azadirachta indica* leaves nanocomposite had the highest reduced elastic modulus and contact stiffness followed by 20% and 10% PEEK-*Azadirachta indica* leaves nanocomposite.

Keywords – Implant material, Polyetheretherketone, Herbal nanoparticles, Nanoindentation, Elastic modulus.

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1. Introduction:

PEEK is a semi-crystalline thermoplastic polyaromatic ketone responsible for the structure's tensile strength, stiffness, and flexibility. Current implant materials include metals, ceramics, polymers, and thermoplastics. There are few biomechanical limitations for ceramics due to their brittleness and high elastic modulus. PEEK nanocomposites have been recently developed containing graphene oxide, carbon-based fibers, silica, silica oxides, zirconia oxide, aluminum oxide, hydroxyapatite, and Zinc oxide. [1-4] The addition of inorganic fillers like glass fibers, carbon fibers, metals, and ceramics to a polymer is to improve physicomechanical qualities and wear resistance.[5] The several disadvantages of inorganic elements are poor bonds and inadequate interface link between the reinforcing substance and the matrix, reducing the durability of composite. Carbon fibers are made from petroleum-based precursors, have a carbon footprint, and release pollutants.[6,7] Glass and ceramic inorganic reinforcement materials are stiffer, brittle, add weight, and degrade over time whereas metal reinforcing agents are prone to rusting and corrosion.[8] These disadvantages are reduced by the addition of organic reinforcement materials, like natural fibers derived from plant renewable sources.

Organic reinforcement materials are lighter in weight, bond well, adhere to the polymer matrix, and are less expensive improving the interfacial strength of the polymer matrix.[9] They are more ductile leading to improved composite stiffness and durability against impacts. Over the years, the use of synthetic non-biodegradable reinforcement materials generated ecological concerns and environmental awareness influencing researchers to develop natural fiber composites. Plant fibers of low density, flexibility, low cost, renewable, and biodegradable are getting attention as organic fiber reinforcement.[10] Nanoparticles derived from Neem (*Azadirachta indica*) leaves are beneficial to use as reinforcement due to their phytochemicals, flavonoids, and better effects through the synergism of their constituents.[11] Recent studies have investigated the potential of neem leaves nanoparticles as a reinforcing agent in polyvinyl alcohol (PVA) to improve the mechanical characteristics and water resistance of the polymer. Neem leaves nanoparticles are added to chitosan to create a biodegradable composite material with enhanced antimicrobial qualities.[12] In the literature, it is observed that most of the reinforcement filler materials focussed on are metallic and inorganic in nature. Owing to this, it is worthwhile on exploring the applicability of Neem (*Azadirachta indica*) leaf nanoparticles as fillers in the reinforcement of polymer matrix on mechanical behavior. The purpose of this investigation is to investigate and evaluate the surface hardness, stiffness, and modulus of elasticity of PEEK-*Azadirachta indica* reinforced (Filler content varying at 10%, 20%, and 30%) implant material both in micro and nanoscale.

2. Material and Methods:

This experiment is intended to evaluate the surface hardness for mechanical behavior at micro and nano levels to study the effect on performance due to the addition of nano reinforcement materials.

2.1. Preparation of Neem (*Azadirachta indica*) nanoparticles:

Matured *Azadirachta indica* leaves were freshly hand plucked and collected during the spring season from the campus of KSR educational institutions, Tiruchengode, Tamil Nadu, India. The leaves were shade dried for twenty-one days, manually crushed, and powdered using a mixer grinder. The powdered leave particles were then ball milled using a Retsch PM 100 centrifugal ball mill (Hann, Germany) for 3 hrs. Nano herbal particles of 50 – 100 nm in size were prepared by the physical ball-milling method (Fig 1).

2.2. Preparation of PEEK- Neem (*Azadirachta indica*) homogenous powder:

Dried nanopowder of *Azadirachta indica* leaves was added to the PEEK powder matrix (Shree Khrishna Polymers, Chennai, Tamil Nadu, India) at 10 wt%, 20 wt%, and 30 wt% ratios. Both PEEK and added nanoparticles at different ratios were premixed for 60 seconds through magnetic stirring for homogeneity.

2.3. Sample Preparation: A total of 96 samples (N=12 for each group) where 48 samples underwent the nanoindentation test and the remaining 48 samples for the microhardness test (Table 1). The unreinforced PEEK specimens and nanoparticle-reinforced specimens were prepared according to ASTM E18 (15mm cylindrical pellets) for nanohardness and ISO 6507-1:2005 for microhardness tests, by injection molding (Super Master Injection Molding Machine, Model No.: Sm-250ts) at a speed of 150 rpm for 5 minutes and melt blended. Samples of perfect dimension without any porosities were included in the study.

2.4. Experiment:

2.4.1. Nanoindentation Test:

The tests were carried out using a Nano Hardness Tester (Hysitron; TI 700 Ubi 1, Florida, USA). A Berkovich indentation tip was used at an indentation speed of 100 mN/min at a maximum load of 500mN and a maximum depth of 200µm. All measurements were carried out according to standard ISO 14577-4. A rigid indenter of maximum penetration depth of 4000 nm is pressed into the tested material with a given force, and the imprint of the indentation was calculated. The penetration test shows both elastic and plastic values for the determination of the micromechanical properties (hardness, indentation modulus, and elastic modulus) of the tested material. In order to obtain reliable results, more than 30 indentations were made on each specimen in random locations (Fig 2).

2.4.2. Vickers Hardness Test:

A digital microhardness tester (HMV-2000, Shimadzu, Kyoto, Japan) with a regular four-sided diamond pyramid and surface angle of 136° is pressed vertically into the polished surface of the test specimen with 400 gm test load for 15 seconds exposure time. The specimen was kept at the table of the tester, and the specified load and dwell time were adjusted. The built-in microscope was used to observe the indentation made by the indenter on the surface of the specimen, and the hardness was calculated digitally based on the lengths of the diagonals. Then the two diagonals (d1 and d2) of the indentation on the test samples were measured with a measuring microscope. For each specimen, three indentations were made at 3 points with a 1mm distance from the previous indentation or the margins of the specimen. The mean of the three values obtained was considered as VHN for that specimen and was tabulated. The average of the three hardness readings was reported as the microhardness of the samples (Fig 3).

2.5. Statistical Analysis:

The readings were subjected to statistical analysis in SPSS version 25.0 (SPSS Inc., Chicago, IL, USA) software. Preliminary results of the Shapiro–Wilks test indicated the data were normally distributed ($P > 0.05$). Descriptive statistics, including mean, standard deviation (SD), standard error, maximum, and minimum were calculated. Concerning Inferential statistics, one-way ANOVA for differences (95% confidence interval) for nanohardness (NH) and microhardness (MH), reduced elastic modulus (ER), and contact stiffness (CS) of the samples were tested. To compare the groups, the post hoc Bonferroni test ($\alpha=0.05$) was performed. A value of $P < 0.05$ was considered for statistical significance.

Table 1: Grouping of samples

No. Of Samples (*N*=96)	**Nano Hardness (NH)**	**Micro Hardness (MH)**	**Reduced Elastic Modulus (ER)**	**Contact Stiffness (CS)**
I.Control Groups: Virgin PEEK				
N=12	P-NH	P-MH	P-ER	P-CS
II.Experimental groups: Reinforced PEEK				
N=12	PA-NH 10%	PA-MH 10%	PA-ER 10%	PA-CS 10%
N=12	PA-NH 20%	PA-MH 20%	PA-ER 20%	PA-CS 20%
N=12	PA-NH 30%	PA-MH 30%	PA-ER 30%	PA-CS 30%

P-NH (PEEK- Nano Hardness)	PA-NH (PEEK *Azadirachta indica* – Nano Hardness)
P-MH (PEEK- Micro Hardness)	PA-MH (PEEK *Azadirachta indica* – Micro Hardness)
P-ER (PEEK- Reduced Elastic Modulus)	PA-ER (PEEK *Azadirachta indica* – Reduced Elastic Modulus)
P-CS (PEEK- Contact Stiffness)	PA-CS (PEEK *Azadirachta indica* – Contact Stiffness)

3. Results:

Table 2 presents the mean (SD) and one-way ANOVA of control and experimental groups for nano hardness-NH (P=0.000), microhardness-MH (P=0.041), reduced elastic modulus-ER (P=0.000), and contact stiffness-S (P=0.000). Bonferroni multiple comparison tests (Table 3) showed a statistically zero difference between all the groups for nano hardness (P=1.000). There is no statistical difference among the groups for microhardness except between P-MH 0% and PA-MH 30% (p=0.038). Reduced elastic modulus showed statistical differences among all the reinforced samples compared with the control group. Finally, concerning contact stiffness values, PA-CS10% compared with P-CS control samples (p=0.975) and PA-CS10% compared to PA-CS20% (p=0.265) showed no differences while the other groups showed statistical differences when compared among them.

Table 2: One-way analysis of variance

I. Nano-Hardness (NH) Mpa

Groups	Mean ± SD	*F* Value	*P* Value
P-NH (Control)	291.35 ± 2.32	927.86	**0.000***
PA-NH10%	306.96 ± 1.63		
PA-NH20%	324.89 ± 2.23		
PA-NH30%	337.03 ± 2.77		

II. Micro-Hardness (MH) vhn

Groups	Mean ± SD	*F* Value	*P* Value
P-MH (Control)	66.58 ± 4.78	2.990	**0.041***
PA-MH10%	64.64 ± 4.95		
PA-MH20%	63.12 ± 4.38		
PA-MH30%	61.47 ± 3.08		

III. Reduced Elastic Modulus (ER) Gpa

Groups	Mean ± SD	*F* Value	*P* Value
P-ER (Control)	2.68 ± 0.43	43.224	**0.000***
PA-ER10%	3.35 ± 0.43		
PA-ER20%	3.97 ± 0.56		
PA-ER30%	4.83 ± 0.47		

IV. Contact Stiffness (CS) Micro Newton/nm

Groups	Mean ± SD	*F* Value	*P* Value
P-CS (Control)	3.88 ± 0.51	15.004	**0.000***
PA-CS10%	4.21 ± 0.54		
PA-CS20%	4.69 ± 0.51		
PA-CS30%	5.33 ± 0.54		

SD = Standard Deviation

Table 3: *Post hoc* Bonferroni test

I. Nano-Hardness (NH) Gpa

Groups	Compared Group	Mean Difference	Sig. *P* Value
P-NH (Control)	PA-NH10%	15.613	**0.000***
	PA-NH20%	33.537	**0.000***
	PA-NH30%	45.680	**0.000***
PA-NH10%	PA-NH20%	17.924	**0.000***
	PA-NH30%	30.067	**0.000***
PA-NH20%	PA-NH30%	12.143	**0.000***

II. Micro-Hardness (MH) vhn

Groups	Compared Group	Mean Difference	Sig. *P* Value
P-MH (Control)	PA-MH10%	1.942	1.000
	PA-MH20%	3.460	0.350
	PA-MH30%	5.119	**0.038***
PA-MH10%	PA-MH20%	1.517	1.000
	PA-MH30%	3.166	0.494
PA-MH20%	PA-MH30%	1.649	1.000

III. Reduced Elastic Modulus (ER) Gpa

Groups	Compared Group	Mean Difference	Sig. *P* Value
P-ER (Control)	PA-ER10%	0.675	**0.008***
	PA-ER20%	1.294	**0.000***
	PA-ER30%	2.152	**0.000***
PA-ER10%	PA-ER20%	0.618	**0.018***
	PA-ER30%	1.476	**0.000***
PA-ER20%	PA-ER30%	0.858	**0.000***

IV. Contact Stiffness (CS) Micro Newton/nm

Groups	Compared Group	Mean Difference	Sig. *P*
Value			
P-S (Control)	PA-S10%	0.327	**0.975**
	PA-S20%		0.805
0.007*			
	PA-S30%		1.453
0.000*			
PA-S10%	PA-S20%	0.477	**0.265**
	PA-S30%		1.125
0.000*			
PA-S20%		PA-S30%	0.648
0.044*			

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

4. Discussion:

Polyetheretherketone (PEEK) reinforcement is frequently used for implants to match the elastic moduli of human bones. According to research, PEEK has chemical resistance, biological compatibility, and a modulus of elasticity that is comparable to bone and is a good option for medical and dental purposes.[13-15] However, previous studies are negligible about the mechanical qualities of herbal nanoparticle reinforcement to PEEK on nano hardness (NH), microhardness (MH), reduced elastic modulus (ER), and contact stiffness (CS). Nano hardness testing is one of the most accurate methods for determining a material's microstructure and assessing microstructure-related behaviors, including stiffness, plasticity, fatigue life, toughness, adhesion, and wear behavior at short-length scales.[16] Nanoindentation offers an accurate, depth-dependent assessment of several material-specific properties, as opposed to the traditional hardness measurement, which identifies a single characteristic value. Both nanoindentation and micro indentation testing methods were used in this investigation and showed differences among the mechanical properties experimented on. The addition of *Azadirachta indica* nanoparticles with PEEK shows a significant difference with increased nano hardness (*P* = 0.000), reduced elastic modulus (*P* = 0.000), contact stiffness (*P* = 0.000), and decreased microhardness (*P* = 0.041). The toxicity of chemically produced nanoparticles restricts their use in medicinal implementation. The synthesis involved the usage of harsh, flammable, and non-biodegradable chemicals that are harmful to the environment leading to adverse effects in medical applications.[17] To overcome this, biological synthesis was introduced as an alternative method.[18] Ball milling is a type of physical synthesis that involves the mechanical milling of particles by dropping steel balls into a container and rotating it horizontally, which produces smaller nanoparticles. To reduce the toxicity and hard agglomerates of nanoparticles, a pure physical synthesis of *Azadirachta indica* leaf nanoparticles by ball milling without the inclusion of chemicals was used in the current work. The main difference between the microhardness and nano hardness of polymers lies in the size of the indenter used to measure the hardness. Micro hardness testing uses an indenter in the range of micrometers (10^-6 meters) to measure the surface hardness of composites. In contrast, nano hardness testing uses an indenter in the range of nanometers (10^-9 meters), such as a sharp diamond tip or Berkovich indenter to evaluate the elastic and plastic deformation of materials at the nanoscale.[19]

Concerning the hardness of the reinforced composite, there is a significant increase in nanohardness (P=0.000) and a mild decrease in microhardness (P=0.041). Nanohardness of PA-

NH, PA-NH10%, PA-NH20%, and PA-NH30% are 291.35, 306.96, 324.89, and 337.03, and microhardness of PA-MH, PA-MH10%, PA-MH20%, and PA-MH30% are 66.58, 64.64, 63.12, and 61.47 respectively (Fig 4). An ascending series of increases in nanohardness as compared with other studies was seen. It's crucial to remember that the behavior of composite materials can be intricate, and the correlation between nanohardness and microhardness might not always be apparent. When measuring nanohardness, the material is indented at very short length scales where the material behaves differently as opposed to bulk measurements. The increase in nanohardness and decrease in microhardness of *Azadirachta indica* leaves reinforced PEEK can be attributed to nanoscale phenomena like dislocation generation, grain boundaries, low glass transition temperatures, surface effects, and reinforcement alignment that can add more strengthening mechanisms.[20-22] Improved mechanical qualities at the nanoscale arise from the ability of the reinforcement when they are properly aligned. The distribution and orientation of the reinforcements may alter at the microscale, where they may not all be aligned. This might result in different mechanical behavior and lower microhardness values. A drop in the microhardness values may result from the reinforcement not being evenly distributed or from the interfacial connection being poor. This can be attributed to forming clusters or soft agglomerates in the PEEK matrix, changing the local microstructure and hardness of the composite. Soft agglomerates are collections of separate particles joined together by physically attractive interactions like van der Waals or hydrogen bridge forces.[23] Localized softening or weaker areas can emerge from the uneven distribution of these reinforcements within the matrix. The existence of soft nanoagglomerates results in structural flaws such as voids or areas with decreased molecular mobility, which can impair packing and intermolecular interactions. This disruption may influence the material's crystallinity and order that results in lowered microhardness Additionally, various investigations demonstrated the impact of reinforced material orientation on PEEK composite wear behavior. The composite with non-parallel orientation exhibited wear resistance and it was difficult to determine which direction may increase wear resistance the most.[24,25] Smaller nanoparticles possess higher surface energy, which results in particle aggregation which could have altered the orientation of the nanoparticles resulting in a slight decrease in microhardness.[26]

Generally, the nano hardness of PEEK falls within the range of 200 to 400 MPa (megapascals). The values obtained in this study were in the range of 290.72 to 337.03 Mpa which is within the normal range and is consistent with previous studies conducted on carbon fiber-reinforced PEEK.[17,22,27] As no study conducted on *Azadiratcha indica* leaves nanoparticles reinforced PEEK composites, the outcome of the current study is compared to carbon fiber-reinforced PEEK composites due to the forthcoming reason. When *Azadiratcha indica* leaves were burned at a temperature of 370 degrees Celsius in the injection molding technique, the organic compounds such as cellulose, hemicellulose, lignin, and various volatile compounds present in the leaves undergo combustion and pyrolysis that favors turning into carbon particles. These carbon particles are fine black particles composed primarily of elemental carbon.[28]

The phrase "reduced elastic modulus" abbreviated as Er refers to the elastic modulus, stiffness, or rigidity to assess a material's capacity to resist deformation subjected to localized stress brought on by the nanoindentation.[29,30] The reduced modulus considers the characteristics of both the fibers and the matrix to give an idea of the PEEK composite reaction to various loading. Ideally, synthetic load-bearing implants should mimic living bone tissues in the mechanical and osteogenic potential to facilitate bone repair. In terms of biomechanical compatibility, the elasticity modulus of the implant's material must be matched to that of the bone tissue to enable ideal load transmission and prevent concentrated stress at the implant-bone interface.[31.32] This is to provide a suitable balance of strength and flexibility, allowing for better osseointegration with tissue around and minimizing stress-shielding effects. A mismatch in stiffness occurs if the implant's reduced elastic modulus is much higher than the bone resulting in implant strain. Stress shielding has the potential to weaken the bone, promote bone resorption, and result in implant failure.[24] On the other side, inadequate load transmission and decreased implant stability may ensue if the implant's reduced elastic modulus is much lesser than bone. Therefore, it's crucial for implant placement to comprehend that the reduced elastic modulus of the material used should match both cancellous and cortical bone. According to Geetha et al., and Sumner et al., avoiding implant loosening and extending the life of the device can be accomplished by matching the implant's modulus to the host bone tissue.[33.34] Human cortical bone normally has a reduced elastic modulus of 8 to 25 gigapascals (GPa), whereas cancellous bone has a reduced elastic modulus of 0.1 to 8 GPa. Cancellous bone found inside the bone having a more porous and lattice-like architecture is less rigid than cortical bone. For an upsurge in the weight percentage of reinforced nanoparticles incorporated, the reduced elastic modulus findings of PEEK composites in the current study reveal an ascending enhancement in values of 2.68 to 4.83 Gpa (approximately an 80% increase) (Fig 5). The values noted for all three reinforced PEEK composite matches the ideal reduced elastic modulus of human bone to achieve an appropriate balance between load transfer and bone stimulation to prevent stress shielding. The current finding is consistent with that of Godara et al., who found that reduced elastic modulus increased from 4.42 GPa to 10.73 GPa (143% increase) by the inclusion of carbon fibers into the polymer matrix.[35] Contact stiffness, as used in this study, is the stiffness or resistance to deformation felt at the place where two objects come into contact, in this case, the interface that connects the PEEK matrix and reinforced material. The increase in contact stiffness of the experimental groups compared to the control group shows the addition of reinforcement agents formed a better orientation with the matrix PEEK particles. This in turn had enhanced the need for improved stiffness of implant materials positively. This research is a triple-blinded study. The author, the operator, and the statistician were blinded by concealing the optimization and weight percentage of *Azadirachta indica* leaves nanoparticles incorporated with PEEK to avoid expectation bias that might creep into the result. This is the only study to evaluate the hardness and elastic properties of PEEK- *Azadirachta indica* leaves nanocomposite. The focus is not just on nano hardness and elastic qualities pertaining to PEEK implants, but also on other aspects including biocompatibility, resistance to wear, and fatigue properties. The limitations of the study are the processing settings, reinforcement qualities, and characteristics, as well as the testing procedures used to assess nanohardness and microhardness. Further investigations on experimental characterization, cyclic masticatory load stresses, thermal analysis, and biological qualities simulating the oral environment need to be focused on future experiments to understand the characteristics of *Azadirachta indica* leaves-reinforced PEEK composites.

5. Conclusion:

The conclusions of this study were as follows:

(1) Addition of 10%, 20%, and 30% *Azadirachta indica* leaves nanoparticles as a reinforcement material does improve the nano hardness.
(2) A minimal decrease in microhardness was noted among 10%, 20%, and 30% PEEK-*Azadirachta indica* leaves nanocomposite.
(3) 30% PEEK-*Azadirachta indica* leaves nanocomposite had the highest reduced elastic modulus and contact stiffness followed by 20% and 10% PEEK-*Azadirachta indica* leaves nanocomposite.

Hence, *Azadirachta indica* leaves nanoparticles can be thought to be a novel reinforcement material with PEEK to substitute the other environmental hazard and high-cost nanoparticles to be utilized as an implant material.

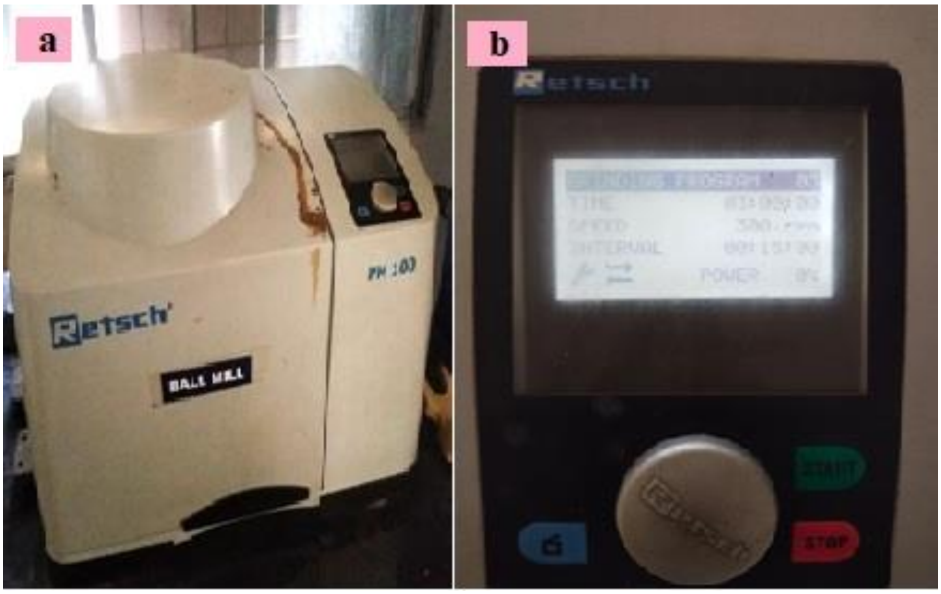

Figure 1: a) - Ball Milling Machine and b) - Program Chart

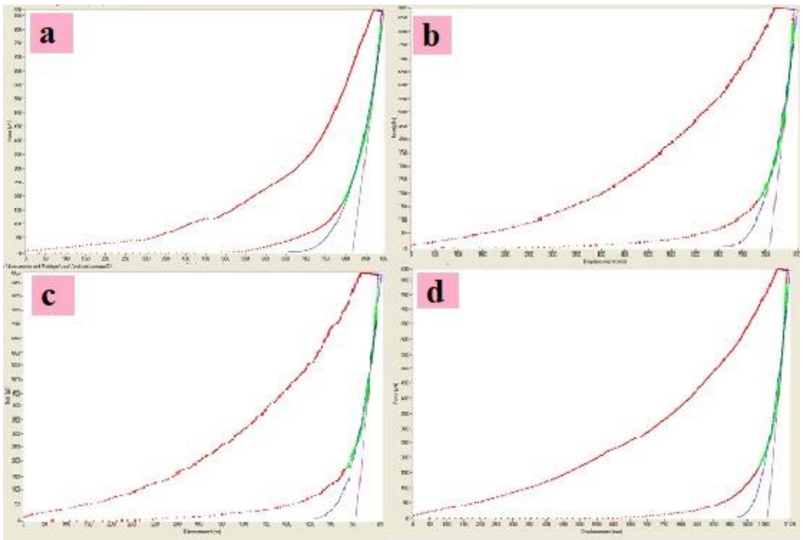

Figure 2: a) - Nanoindentation of control samples b) - Nanoindentation of 10% experimental samples c) - Nanoindentation of 20% experimental samples d) - Nanoindentation of 30% experimental samples

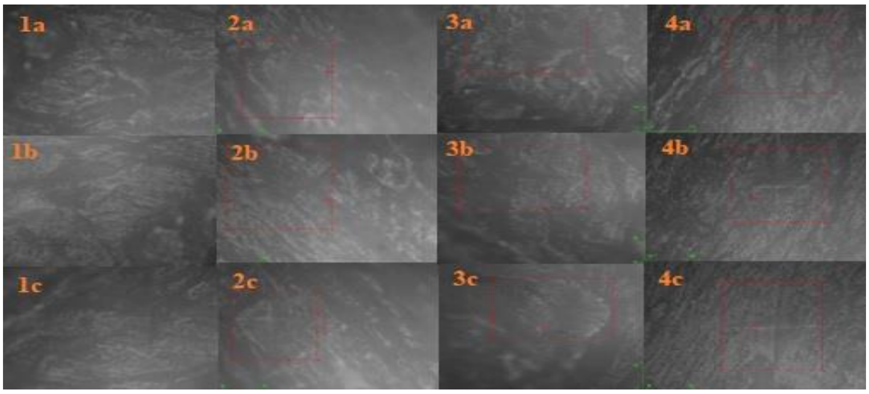

Figure 3:1a,1b,1c) - Microhardness of the control group at 3 points
2a,2b,2c) - Microhardness of the 10% experimental group at 3 points
3a,3b,3c) - Microhardness of the 20% experimental group at 3 points
4a,4b,4c) - Microhardness of the 30% experimental group at 3 points

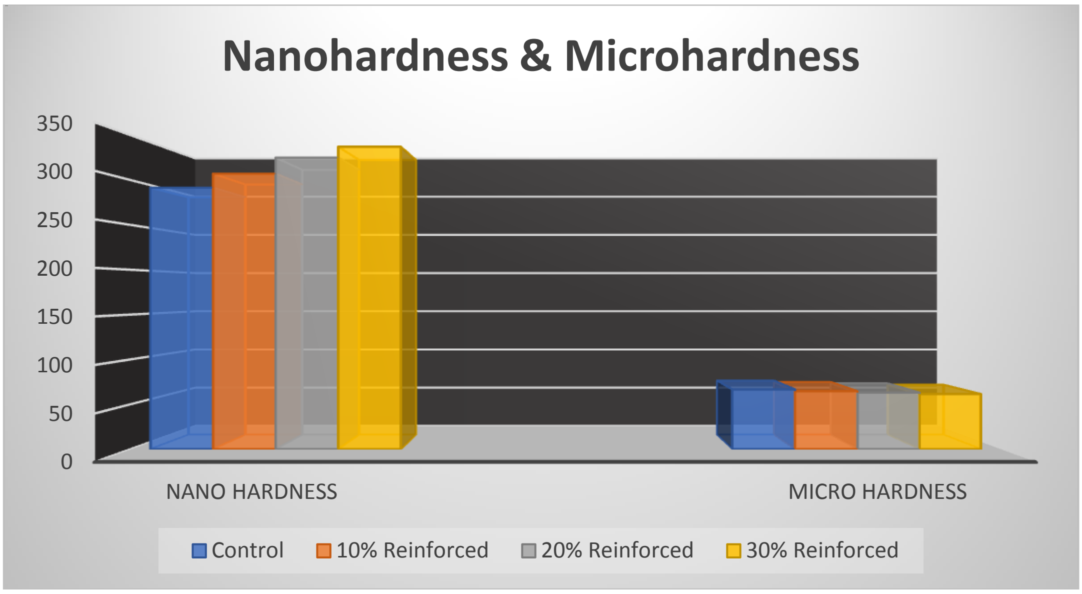

Figure 4: Graphical Comparison of Nanohardness and Microhardness

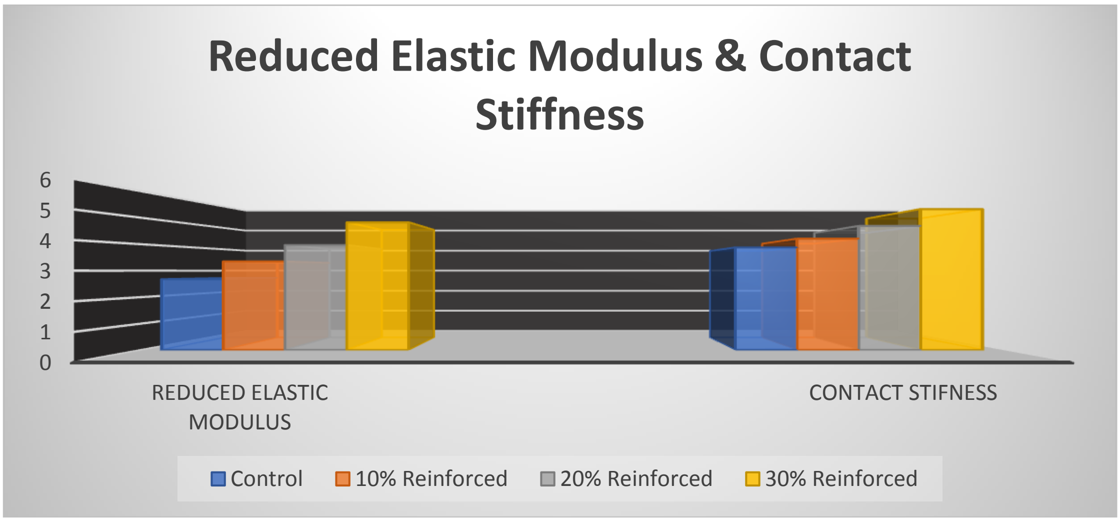

Figure 5: Graphical Comparison of Reduced Elastic Modulus and Contact Stiffness

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