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"EFFECTS OF CONTACT ANGLE ON PHYTO-BASED NANOPARTICLE-REINFORCED POLYETHERETHERKETONE FOR IMPLANT APPLICATIONS"

Dr. Vidhyasankari N[1*], Dr. Reena Rachel John[2], Dr. Senthilmurugan R[3], Dr. Vijayalakshmi V[4],

[1*]MDS, Professor, Department of prosthodontics and crown & bridge, KSR Institute of Dental Science and Research, Tiruchengode, Tamilnadu, India, and Ph.D. Scholar, Vinayaka Mission's Research Foundation - DU, Salem, Tamilnadu, India. E-mail: drvidhyasankari@ksridsr.edu.in, vidhya_3010@yahoo.com
[2]MDS, Ph.D., FIBOMS, Associate Dean – Research, Professor, Department of Oral and Maxillofacial Surgery, Vinayaka Mission's Sankarachariyar Dental College, Vinayaka Mission's Research Foundation - DU, Salem, Tamilnadu, India, E-mail: drreenaracheljohn@vmsdc.edu.in
[3]BE, ME, Ph.D., Associate Professor, Department of Mechatronics Engineering, K.S.Rangasamy College of Technology, Tiruchengode, Tamilnadu, India, E-mail: prsmuruga@gmail.com
[4]Post-Graduate, Department of Prosthodontics and Crown & Bridge, KSR Institute of Dental Science and Research, Tiruchengode, Tamilnadu, India, E-mail: vijilakshitha14@gmail.com

***Corresponding Author:** Dr. Vidhyasankari N
*MDS, Ph.D Scholar, Professor, Department of prosthodontics and crown & bridge, KSR Institute of Dental Science and Research, Tiruchengode, Tamilnadu, India. Ph.D Scholar, Vinayaka Mission's Research Foundation - DU, Salem, Tamilnadu, India. E-mail: drvidhyasankari@ksridsr.edu.in, vidhya_3010@yahoo.com

ABSTRACT:
Composites made of polyetheretherketone (PEEK) are biocompatible materials that solve the aesthetic and allergy issues with titanium dental implants. PEEK matrix materials utilized in modern composites reinforced with plant-based organic fibers should not only be highly performant but also have good surface wettability and adhesion qualities. This work describes the wetting behavior and adhesion characteristics of PEEK augmented with phyto-based nanoparticles. The study used a phyto-based nanoparticle at various weight percentages (Group 1- 10% Filled PEEK, Group 2-20% Filled PEEK, and Group 3-30% Filled PEEK) to assess the contact angle value and its impact on the wettability and adhesion of various reinforced PEEK specimens. Group 1 showed the greatest advancing (74.86) and average (68.74) values, while Group 3 indicated the lowest advancing (67.47) and receding (49.83) contact angle values. A statistically significant difference in contact angle was found between the reinforced PEEK groups. The reinforced PEEK used in this work has enhanced wettability, allowing for further investigation into its mechanical and biological qualities for usage as a substitute for metallic implants without compromising its favorable bulk features. It has been found that the hydrophobic properties of the pure PEEK matrix can be altered with the addition of the phyto-based nanoparticle.

Keywords: PEEK polymer, wettability, dental implants, phyto-based nanoparticles, contact angle
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INTRODUCTION:

PEEK is promising as a material for dental implants due to its qualities. Since the early 1990s, polyetheretherketone (PEEK) biomaterial has been utilized extensively in fabricating orthopedic and dental implants. Due to its outstanding biocompatibility, ease of modeling, superior mechanical qualities, and lower cost when compared to analogues constructed of titanium or platinum alloys, it is being employed growing rate these days.[1,2] It is common knowledge that most polymers benefit from the addition of fillers, frequently as fibers, to further enhance their mechanical characteristics. Biocompatible and non-hazardous polymers must be employed in medical applications. The low surface energy of PEEK, however, makes it extremely difficult for an implant or prosthesis to integrate with the surrounding tissues. Thus, the degree of adhesion influences how well the polymer is biocompatible with the human body and helps to prevent side effects including infections, allergies, and implant rejection.[3,4] Among the many inorganic fibers, carbon fibers have the maximum strength, density, and modulus resulting in fiber reinforcement in a wide range of applications.[5] The chance of carbon fiber composite materials scarcity as a result of the rising demand for carbon fibers has recently been converted from glass fiber composites to carbon fiber composites for greater performance and less weight. In order to address the rising demand and declining supply of carbon fibers, lightweight, higher-performance fiber alternatives are being sought. Due to their superior mechanical and physical qualities, organic fibers have drawn interest and can be employed as reinforcement in composite materials for high-impact applications. It should be noted that organic fibers have distinct advantages as they do not experience metallic corrosion.[6]

In the disciplines of the science of materials, concepts like contact angle and adhesion are crucial for knowing the way liquids bond to solid surfaces. The angle created at the point where a liquid interface contacts and spreads on a solid surface is known as the contact angle. They are frequently used to describe whether a material's surface is hydrophilic (water-attracting) or hydrophobic (water-repellent). Adhesion is the term used to describe the attraction forces that exist between molecules of different materials that cause them to adhere together at their contact. Understanding contact angle and adhesion play a crucial role in implant osseointegration as they impact the uniform spread of blood and fluids and the formation of biofilm around the endosseous implant. Also, in designing applications like implant coatings and microfluidic devices controlling wetting behavior is essential. Good adhesion reveals an intense attraction between the liquid and solid surfaces, while poor adhesion suggests weaker interactions. A modest contact angle of around 0 degrees denotes a strong bond between the liquid and the solid surface. This indicates that the liquid evenly and thoroughly wets the surface. A liquid that forms a bead or droplet on the surface indicates poor adherence when the contact angle is almost 180 degrees. The ideal hydrophilic-hydrophobic nature and surface free energy values of the biomaterial's surface play a significant part in osseointegration and cell adherence to artificial materials.[7] The current experiment was conducted for the purpose of investigating specific wetting and adhesion characteristics of phyto-based nanoparticle-reinforced polyetheretherketone composites for intended implant applications.

MATERIAL AND METHODS:

Phyto-based nanoparticles were prepared from neem which was collected from the western part of Tamil Nadu, India during the spring season. The aerial-fresh matured hand-plucked leaf part was used in the current study. Standard preparation of nanoparticles by ball milling including cleaning, drying, and milling into fine powder was performed. Polyetheretherketone (Aldrich Sigma, Merck Group) powder was mixed with the prepared nanoparticles in 10%. 20%, and 30% using vacuum rotators. Fifteen experimental discs, 10 mm in diameter and 2.5 mm in thickness were fabricated through compression melting resulting in 3 different groups namely Group 1- 10% Filled PEEK, Group 2-20% Filled PEEK, and Group 3-30% Filled PEEK, with 5 discs per group.

Measuring the contact angle: To measure the advancing contact angles, a 6L regulated volume of distilled water droplets was applied using a tiny syringe to the experimental disc's surface. The drop's receding contact angle was then measured when 2L of the liquid was drawn back. Images were taken with a micro video system (DGD ADR model with GBX S.A.R.L.) at 5 and 45 seconds after each droplet was deposited in order to measure the advanced and retreating contact angles, respectively. The measurement chamber's temperature, humidity, and tilt were constant throughout the process. Furthermore, the inert nitrogen gas was added and injected into the chamber to lessen the impact of airborne moisture. The WinDrop++ program was used to analyze the captured photos. Each sample yielded sixteen contact angle measurements, one per second. All the procedures for all the groups were performed by the double-blinded, trained single operator.

Statistical analysis: Statistical Package for Social Sciences (SPSS, Version 25, SPSS Inc, Chicago, IL) was used to collect, tabulate, and statistically analyze the data. Means and standard deviations were used to define advancing, receding, and average mean contact angle values. Shapiro-Wilk tests were employed to examine the data for normality. One-way ANOVA was used to compare the three groups, followed by the Bonferroni post hoc test for comparisons among pairs. A P-value of 0.05 or less was recognized as statistically significant.

RESULTS:

The contact angle of Group 1 showed the highest advancing (74.86) and average (68.74) contact angle values, while Group 3 revealed the lowest advancing (67.47) and receding (49.83) contact angle values (Table 1). For contact angles, a statistically significant difference was found among the reinforced PEEK groups (Tables 3 and 4).

TABLE 1: Mean Contact Angle Values

Contact Angle	Group 1	Group 2	Group 3
Advancing	74.86	72.53	67.47
Receding	62.67	53.44	49.83
Average	68.74	62.98	58.65

TABLE 2: Groupwise comparison of average contact value using one-way ANOVA

ANOVA	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	512.392	2	256.196	164.331	.000
Within Groups	42.094	27	1.559		
Total	554.485	29			

TABLE 3: Pairwise comparison of average contact value using Bonferroni post hoc test.

	Mean Difference	Std Deviation	*p* Value
Group 1 vs. Group 2	05.75	0.56	0.00
Group 1 vs. Group 3	10.09	0.59	0.00
Group 2 vs. Group 3	04.33	0.55	0.00

DISCUSSION:

In association with dental implant applications, material surface characteristics including topography and wettability have drawn much interest in recent years.[8] Theoretically, the surface energy should rise to increase wettability to improve biocompatibility and facilitate interactions between an implant's surface and the biological environment.[9] PEEK has been criticized for being hydrophobic or having a poor wettability by aqueous solutions due to the presence of extremely non-polar carbon-fluorine and carbon-hydrogen bonds. PEEK is resistant to water and aqueous solutions because of its low wettability, which causes high contact angles of more than 90 degrees. PEEK surfaces frequently require surface alterations or treatments to improve adhesion to other materials or to encourage wetting by particular liquids in order to achieve acceptable wettability. The biological effects of hydrophilicity have led to an essential alteration in implant surface wettability. Initial contacts between an implant surface and host interface involve interactions with water and ions through conditioning by the creation of protein-rich films, up to the level of cellular connections.[10]

The equilibrium of the intermolecular interactions governs wettability, the capacity of a liquid to retain contact with a solid surface. However, contaminants, poor bonding, detachments, cracks, voids, or any other undesirable intermetallic compound may significantly degrade the final performance.[11] Among the factors that have a significant impact on wettability are chemical structure, roughness, heat and pressure conditions, environmental composition, and the chemistry of the surface.[12,13,14] The current study evaluates the advancing, receding, and average contact angle values to identify their influence on the wettability of reinforced PEEK materials with phyto-based reinforcement nanomaterial for future use in the fabrication of dental implants and its components. The findings of this study showed a positive aspect of a decrease in the ascending, receding, and average contact angle values for an increase in 10 to 30 percent of nanomaterials reinforcement in the matrix [Table 1]. One-way variance of analysis resulted in the existence of differences in wettability property based on the contact angle values within the groups [Table 2]. This could be because interparticle interactions have produced van der Waals affinity when particle sizes reduce at the nanoscale, resulting in large surface areas. Surface tension and the energy at the interface between solids and liquids are reduced by this increase in particle energy. The result is in agreement with the study results of Czwartos et al.[15]

Though the high degree of wetting and strong interfacial adhesion for the phyto-based organic fibers into the polymer matrix has been problematic compared to inorganic fibers, the steady decrease of advancing and receding contact angle values among the three groups of this study ensures better wettability of the reinforced materials. The distribution of the polymeric matrix on the fiber, which is influenced by viscosity and contact angle, may be one of the causes. Reinforcing particle distribution is improved by mechanical agitation and stirring, which also speeds up interfacial reactions and decreases porosities and trapped gases in solid-liquid interfacial zones. Two processes, namely spreading of the polymeric matrix on the fiber surface and penetration of the polymeric matrix into the fiber surface cavities, can be used to characterize the wetting behavior of a reinforced fiber surface by a polymer resin matrix. The wettability of reinforced groups appears to have risen in this study, as a result of the intense shearing force used to separate clusters and deagglomerate smaller-sized particles. A key statistic for defining how the reinforced material interacts is viscosity. The faster a liquid drop spreads across solid surfaces and the quicker it takes to attain the equilibrium of liquid-solid interaction, the less viscous the matrix. This is the additional cause of the present experimental materials' reduced contact angle values as wettability increases.

Multiple comparisons for contact angle show a significant difference among the groups. Typically, the contact angle for water on an untreated PEEK surface falls within the range of 80 to 100 degrees or more. The values of advancing contact angles measured on the untreated PEEK surfaces were estimated in the range of 75◦–95◦ obtained by other authors and are compared for the experimental groups of the present study.[16,17,18] Untreated PEEK has high contact angle values, which means water bead up does not rapidly saturate the surface and is of typical hydrophobic material. The lowered contact angle for PEEK reinforced with 10%, 20%, and 30% nanoparticles is shown in Table 2. Wettability has an impact on the material's biocompatibility in medical applications, particularly for implants manufactured of ex-situ PEEK. In order to establish osseointegration, this will aid in drawing certain plasma proteins, electrolytes, and growth factors. Its wettability has an impact on the material's capacity to prevent biofouling, or the buildup of biological substances, and promote tissue integration. These PEEK reinforcements are a highly promising replacement for metallic implants and other PEEK materials reinforced with inorganic particles. In summary, the improved wettability of reinforced PEEK in this study enables more research on the mechanical, and biological properties to use as an alternative for metallic implants without sacrificing its desirable bulk properties. It has been shown that the advancing, receding, and average contact angle increases with the increase in the percentage of reinforcing material to the PEEK matrix. These results show that the addition of the phyto-based nanoparticle can alter the hydrophobic character of the pure PEEK matrix.

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