

**MECHANICAL AND TRIBOLOGICAL STUDIES OF
EPOXY-BASED COMPOSITES FOR HIP JOINT
APPLICATION**

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MECHANICAL AND TRIBOLOGICAL STUDIES OF EPOXY-BASED COMPOSITES FOR HIP JOINT APPLICATION

by

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CERTIFICATE

This is to certify that the thesis entitled “**Mechanical and Tribological Studies of Epoxy-Based Composites for Hip Joint Application,**” being submitted by **Mr. Jaswant Kumar Hirwani** to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, is a bonafide record of original research work conducted by him under my supervision. The experimental work and the results presented in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any Degree or Diploma.

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ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) is a widely used clinical material for acetabular components in hip joint replacement, but wear debris generation, osteolysis, subsequent loosening, and lower range of motion limit its life. Cross-linked and vitamin E-added UHMWPE have been claimed to solve this problem somewhat. However, the material is still required, which can survive longer for younger and active patients without requiring revision surgery. Epoxy composites have great potential to solve this issue because of their higher mechanical strength, wear resistance, ability to bond with fillers, and ability to be easily modified for a particular application.

In this work, two epoxy systems are selected: one is SU-8-based, and the other is Structuralis-based. UHMWPE filler was added to improve their tribological properties, and hyaluronic acid was added to act as an *in-situ* liquid lubricant during articulation. A novel Prosthetic BiotribometerTM was also designed and manufactured for the wear evaluation of these composites. Complexity in test methodologies, *i.e.*, from unidirectional to multidirectional tests which are required to simulate hip interface movements, were adopted for realistic material performances.

SU-8-based composites were explored first. The SU-8 polymer was mixed with UHMWPE particles in various weight percentages to make these composites. The uniform distribution of filler materials was confirmed by optical microscopy imaging. Cross-sectional SEM analysis showed the formation of the fibrillar structure of UHMWPE, which helped bind UHMWPE particles with the SU-8 matrix. The compressive Young's modulus and strength of the composites were found to decrease with UHMWPE filler addition which was due to the presence of a soft UHMWPE phase. For the initial screening, the composites were tested on a ball-on-disk tribometer using a 12 mm diameter stainless steel (grade SS304) ball under a normal load of 20 N and sliding speed of 32 mm/s. SU-8 with 25 wt% of UHMWPE showed COF of 0.1 and a specific wear-rate of 6.27×10^{-5} mm³/Nm, which were 52% and 61%, respectively, lower in comparison with that of bulk UHMWPE tested on the same machine in an aqueous solution of bovine serum albumin. Further, to improve the tribological performance of UH25, hyaluronic acid was added to the composite, and properties were evaluated using multidirectional sliding conditions. Adding 0.2 wt% and 0.5 wt% of hyaluronic acid (HA) reduced friction and wear. Worn surface morphology revealed that the HA-filled composite has less damage and a smoother appearance than the composite without HA. The phenomenon

of HA lubrication was attributed to the lubricating film formation ability of HA. Also, HA-induced hardness has positively influenced the wear resistance of SU-8 composites. These promising results of SU-8/UHMWPE/HA composites make them potential candidates as future hip implant material. To expedite the process of wear measurements, a novel wear measuring machine hereby named “Prosthetic BiotribometerTM” has been developed. It was designed to produce cross-shear sliding at the pin surface against the counterface disc.

To establish epoxy as a candidate material, another commercially available epoxy, StructalitTM, has been explored. This study evaluated StructalitTM-based composites for their mechanical and bio-tribological properties to find an alternative to UHMWPE. Structalit/UHMWPE composites were successfully developed with excellent filler matrix bonding. Lower friction and wear of the composite (with 24 wt% of UHMWPE) are attributed to the higher bulk mechanical strength and lower interfacial shear strength. Additionally, lubrication was supported by heterogeneity-driven lubricant flow and protein-mediated boundary lubrication mechanism. Burnishing, abrasion, and protuberances were UHMWPE's main surface damage mechanisms, whereas composite had few micro-cracks on its surface when filler loading was less. Further, to impart self-lubricity to the composite, HA was added, and results were compared with S24 composites (Structalit + 24 wt% of UHMWPE) under similar experimental conditions. The coefficient of friction and specific wear rate of Structalit/UHMWPE/HA composites were improved compared to that of the S24 composite. Finally, UH25HA05 and S24HA05 (Structalit + 24 wt% of UHMWPE + 0.5 wt% HA) are proposed for further simulated wear tests for acetabular cup replacement material of the hip joint.

सार

अत्यधिक-उच्च आणविक भार पॉलीथीन (UHMWPE), कूल्हे की जोड़ प्रतिस्थापन में उपयोग होने वाली एसिटाबुलर कप के लिए व्यापक रूप से उपयोग की जाने वाली रोगविषयक सामग्री है, लेकिन टूटे हुए टुकड़े का निर्माण, ऑस्टियोलाइसिस, जोड़ों में ढीलापन और गति की निचली सीमा इसके जीवन को सीमित कर देती है। क्रॉस-लिंकड और विटामिन ई-युक्त UHMWPE से इस समस्या को कुछ हद तक हल करने का दावा किया गया है। हालाँकि, सामग्री की अभी भी आवश्यकता है, जो पुनरीक्षण सर्जरी की आवश्यकता के बिना युवा और सक्रिय रोगियों के लिए लंबे समय तक काम कर सकती है। एपॉक्सी संमिश्रित में उनकी उच्च यांत्रिक शक्ति, टूट फुट क्षमता, फिलर्स के साथ जुड़ने की क्षमता और किसी विशेष एप्लिकेशन के लिए आसानी से संशोधित होने की क्षमता के कारण इस समस्या को हल करने की काफी संभावनाएं हैं।

इस कार्य में, दो एपॉक्सी तंत्र चुने गए हैं: एक SU-8-आधारित है, और दूसरा Strucalite-आधारित है। उनके ट्राइबोलॉजिकल गुणों को बेहतर बनाने के लिए UHMWPE फिलर जोड़ा गया है, और गति के दौरान इन-सीटू तरल स्नेहक के रूप में कार्य करने के लिए हयालूरोनिक एसिड जोड़ा गया है। इन कंपोजिट के घिसाव के मूल्यांकन के लिए एक नया प्रोस्थेटिक बायोट्राइबोमीटर™ भी डिजाइन और निर्मित किया गया है। परीक्षण पद्धतियों में जटिलता, यानी, एक-दिशात्मक से बहु-दिशात्मक स्वरूप, जो कूल्हे की अंतराफलक को अनुकरण करने के लिए आवश्यक हैं, परीक्षण स्थिति में अपनाए गए हैं।

सबसे पहले SU-8-आधारित कंपोजिट की खोज की गई। इन कंपोजिट को बनाने के लिए SU-8 बहुलक को विभिन्न वजन प्रतिशत में UHMWPE कणों के साथ मिलाया गया था। प्रकाशीय सूक्ष्मदर्शी चित्रण द्वारा भराव सामग्री के समान वितरण की पुष्टि की गई। क्रॉस-सेक्शनल SEM विश्लेषण ने UHMWPE की फाइब्रिलर संरचना की पुष्टि की, जिसने UHMWPE कणों को SU-8 मैट्रिक्स के साथ बांधने में मदद की। UHMWPE फिलर जोड़ने के साथ कंपोजिट के कंप्रेसिव यंग मापांक और सामर्थ्य में कमी पाई गई, जो मृदु UHMWPE चरण की उपस्थिति के कारण था। प्रारंभिक जाँच के लिए, कंपोजिट का परीक्षण बॉल-ऑन-डिस्क ट्राइबोमीटर पर 12 मिमी व्यास वाले स्टेनलेस स्टील (ग्रेड एसएस304) बॉल का उपयोग करके 20 N के सामान्य भार और 32 मिमी/सेकेंड की फिसलन गति के तहत किया गया था। 25 wt% UHMWPE के साथ SU-8 ने 0.1 का घर्षण गुणांक और $6.27 \times 10^{-5} \text{ mm}^3/\text{Nm}$ की विशिष्ट घिसाव-दर दिखाई, जो क्रमशः 52% और 61% UHMWPE की तुलना में कम थी। इसके अलावा, UH25 के घर्षण गतिकीय प्रदर्शन को बेहतर बनाने के लिए, हायल्यूरोनिक एसिड को समग्र में जोड़ा गया था, और बहु-दिशात्मक गतिकीय स्थितियों का उपयोग करके गुणों का मूल्यांकन किया गया था। 0.2 wt% और 0.5

wt% हयालूरोनिक एसिड (HA) मिलाने से घर्षण और घिसाव कम हो गया। घिसी हुई सतह की आकृति विज्ञान से पता चला कि HA से भरे कंपोजिट में, HA अनुपस्थित कंपोजिट की तुलना में कम क्षति होती है और यह अधिक चिकनी दिखती है। HA की चिकनाई फिल्म निर्माण क्षमता के लिए HA स्नेहन को श्रेय दिया गया। इसके अलावा, HA-प्रेरित कठोरता ने SU-8 कंपोजिट के घिसाव के प्रतिरोध को सकारात्मक रूप से प्रभावित किया है। SU-8/UHMWPE/HA कंपोजिट के ये आशाजनक परिणाम उन्हें भविष्य के कूल्हे की जोड़ प्रत्यारोपण सामग्री के रूप में संभावित उम्मीदवार बनाते हैं। घिसाव माप की प्रक्रिया में तेजी लाने के लिए, "प्रोस्थेटिक बायोट्राइबोमीटर™" नाम की एक नवीन घिसाव मापने वाली यंत्र विकसित की गई है। इसे काउंटरफेस डिस्क के विरुद्ध पिन सतह पर क्रॉस-शियर फिसलन उत्पन्न करने के लिए निर्मित किया गया है।

एक उम्मीदवार सामग्री के रूप में एपॉक्सी को स्थापित करने के लिए, एक अन्य व्यावसायिक रूप से उपलब्ध एपॉक्सी, Structalit™ की खोज की गई है। इस अध्ययन ने UHMWPE का विकल्प खोजने के लिए उनके यांत्रिक और जैव-घर्षण गतिकीय गुणों के लिए Structalit™-आधारित कंपोजिट का मूल्यांकन किया। उत्कृष्ट फिलर मैट्रिक्स अनुबंध के साथ Structalit/UHMWPE कंपोजिट सफलतापूर्वक विकसित किए गए। कंपोजिट के कम घर्षण और घिसाव (UHMWPE के 24 wt% के साथ), के लिए कंपोजिट के उच्च यांत्रिक शक्ति और कम अंतरसतही कतरनी ताकत को जिम्मेदार ठहराया गया है। इसके अतिरिक्त, स्नेहन को विविधता-संचालित स्नेहक प्रवाह और प्रोटीन-मध्यस्थता सीमा स्नेहन तंत्र द्वारा समर्थित किया गया था। जलन, घर्षण और उभार UHMWPE की मुख्य सतह क्षति तंत्र थे, जबकि फिलर लोडिंग कम होने पर कंपोजिट की सतह पर कुछ सूक्ष्म दरारें थीं। इसके अलावा, कंपोजिट में स्व-चिकनाई प्रदान करने के लिए, HA जोड़ा गया था, और समान प्रयोगात्मक स्थितियों के तहत परिणामों की तुलना S24 कंपोजिट (Structalit + 24 wt% UHMWPE) के साथ की गई थी। S24 कंपोजिट की तुलना में Structalit/UHMWPE/HA कंपोजिट के घर्षण गुणांक और विशिष्ट घिसाव की दर में सुधार हुआ। अंत में, UH25HA05 और S24HA05 (स्ट्रक्चरलिट + UHMWPE का 24 wt% + 0.5 wt% HA) को कूल्हे के जोड़ के एसिटाबुलर कप प्रतिस्थापन सामग्री के लिए आगे के सिमुलेटेड घिसाव के परीक्षणों के लिए प्रस्तावित किया गया है।

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LIST OF NOTATIONS

ASTM: American Society for Testing and Materials

A_r : Real area of contact

CA: Contact Angle

CNT: Carbon nanotube

E: Young's modulus

EDS: Energy Dispersive Spectroscopy

F = Force

FTIR: Fourier Transform Infrared Spectroscopy

H: Hardness

HA: Hyaluronic acid

ISO: International Organization for Standardization

L= Load

MPa: Megapascal

MWCNT: Multi-walled carbon nanotube

PEEK: Polyether ether ketone

PFPE: Perfluoropolyether

PTFE: Polytetrafluoroethylene

R.T.: Room temperature

SEM: Scanning electron microscope

S24: 24 wt% of UHMWPE + balance Structalit

S24HA05: 24 wt% of UHMWPE + 0.5 wt% of hyaluronic acid + balance Structalit

TGA: Thermogravimetric analysis

UHMWPE: Ultra-high molecular weight polyethylene

UH25: 25 wt% of UHMWPE + 7.5 wt% of curing agent + balance SU-8

UH25HA05: 10 wt% of UHMWPE + 0.5 wt% of hyaluronic acid + 7.5 wt% of curing agent
+ balance SU-8

UTM: Universal testing machine

XRD: X-Ray diffraction analysis

μ : Coefficient of friction (COF)

μ_{adh} : Adhesion component of friction

μ_{plow} : Plowing component of friction

$\tau_{interface}$: Interfacial shear strength

ν = Poisson's ratio