

DECLARATION OF JUNE ANN MUNFORD

1. My name is June Ann Munford. I am over the age of 18, have personal knowledge of the facts set forth herein, and am competent to testify to the same.
2. I earned a Master of Library and Information Science (MLIS) from the University of Wisconsin-Milwaukee in 2009. I have over ten years of experience in the library/information science field. Beginning in 2004, I have served in various positions in the public library sector including Assistant Librarian, Youth Services Librarian and Library Director. I have attached my Curriculum Vitae as Appendix CV.
3. During my career in the library profession, I have been responsible for materials acquisition for multiple libraries. In that position, I have cataloged, purchased and processed incoming library works. That includes purchasing materials directly from vendors, recording publishing data from the material in question, creating detailed material records for library catalogs and physically preparing that material for circulation. In addition to my experience in acquisitions, I was also responsible for analyzing large collections of library materials, tailoring library records for optimal catalog

search performance and creating lending agreements between libraries during my time as a Library Director.

4. I am fully familiar with the catalog record creation process in the library sector. In preparing a material for public availability, a library catalog record describing that material would be created. These records are typically written in Machine Readable Catalog (herein referred to as “MARC”) code and contain information such as a physical description of the material, metadata from the material’s publisher, and date of library acquisition. In particular, the 008 field of the MARC record is reserved for denoting the date of creation of the library record itself. As this typically occurs during the process of preparing materials for public access, it is my experience that an item’s MARC record indicates the date of an item’s public availability.
5. Typically, in creating a MARC record, a librarian would gather various bits of metadata such as book title, publisher and subject headings among others and assign each value to a relevant numerical field. For example, a book’s physical description is tracked in field 300 while title/attribution is tracked in field 245. The 008 field of the MARC record is reserved for denoting the creation of the library record itself. As this is the only date reflecting the inclusion of said materials within the library’s collection, it is my experience

that an item's 008 field accurately indicates the date of an item's public availability.

6. I am familiar with the Internet Archive, a digital library accessible to the general public. Among other services that the Internet Archive makes available to the general public is the Wayback Machine, an online archive of the web. The Internet Archive's Wayback Machine service archives webpages as of a certain capture date to track changes in the web over time. The Internet Archive has been in operation as a nonprofit library since 1996 and has hosted the Wayback Machine service since its inception in 2001. During my time as a librarian, I frequently used the Internet Archive's Wayback Machine for research and instruction purposes. This includes teaching instructional classes on using the Wayback Machine to library patrons and using the Wayback Machine to research reference inquiries that require hard-to-find online resources. I consider the Internet Archive's recordskeeping to be as rigorous and detailed as other formal library recordskeeping practices such as MARC records, OCLC records and Dublin Core.

7. I have reviewed Exhibit EX1039, "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites" by Cheng Liu, et al as published in Materials April 2021.
8. Attached hereto as Appendix LIU01 is a true and correct copy of the MARC record for Materials as held by the Penn State University Library. I secured this record myself from the library's public catalog. The MARC record contained within Appendix LIU01 accurately describes the title, publisher and ISSN number of Materials. The Showing Results field present on page 4 of this record indicates the library's collection includes the April 2021 issue of Materials containing "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites".
9. Attached hereto as Appendix LIU02 is a true and correct copy of "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites" as published in Materials as held by the Penn State University Library. These scans were secured from the library's collection. In comparing Exhibit EX1039 to Appendix LIU02, it is my determination that Exhibit EX1039 is a true and correct copy of "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites" by Cheng Liu, et al as published in Materials.

10. The 008 field of the MARC record in Appendix LIU01 indicates the date of record creation. The 008 field of Appendix LIU01 indicates the Penn State University Library first acquired Materials as of June 3, 2009 and held the journal in perpetuity until the publication of "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites". Considering this information, it is my determination that Materials April 2021 and therefore "Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites" was made available to the public shortly after its initial publication in April 2021.

11. I have reviewed Exhibit EX1040, "Modified Epoxy Coatings on Mild Steel: Tribology and Surface Energy" by Witold Brostow, et al as published in European Polymer Journal November 2010.

12. Attached hereto as Appendix BROSTOW01 is a true and correct copy of the MARC record for European Polymer Journal as held by the Penn State University Library. I secured this record myself from the library's public catalog. The MARC record contained within Appendix BROSTOW01 accurately describes the title, publisher and ISSN number of European Polymer Journal. The Showing Results field present on page 3 of this record

indicates the library's collection includes the November 2010 issue of European Polymer Journal containing "Modified Epoxy Coatings on Mild Steel: Tribology and Surface Energy".

13. Attached hereto as Appendix BROSTOW02 is a true and correct copy of "Modified Epoxy Coatings on Mild Steel: Tribology and Surface Energy" as published in European Polymer Journal as held by the Penn State University Library. These scans were secured from the library's collection. In comparing Exhibit EX1040 to Appendix BROSTOW02, it is my determination that Exhibit EX1040 is a true and correct copy of "Modified Epoxy Coatings on Mild Steel: Tribology and Surface Energy" by Witold Brostow, et al as published in European Polymer Journal.

14. The 008 field of the MARC record in Appendix BROSTOW01 indicates the date of record creation. The 008 field of Appendix BROSTOW01 indicates the Penn State University Library first acquired European Polymer Journal as of April 14, 1998 and held the journal in perpetuity until the publication of "Modified Epoxy Coatings on Mild Steel: Tribology and Surface Energy". Considering this information, it is my determination that European Polymer Journal November 2010 and therefore "Modified Epoxy Coatings

on Mild Steel: Tribology and Surface Energy" was made available to the public shortly after its initial publication in November 2010.

15. I have reviewed Exhibit EX1041, "Tribological Studies of Epoxy Composites with Solid and Liquid Fillers" by Vikram Kumar, et al as published in Tribology International September 2016.
16. Attached hereto as Appendix KUMAR01 is a true and correct copy of the MARC record for Tribology International as held by the Penn State University Library. I secured this record myself from the library's public catalog. The MARC record contained within Appendix KUMAR01 accurately describes the title, publisher and ISSN number of Tribology International. The Showing Results field present on page 5 of this record indicates the library's collection includes the September 2016 issue of Tribology International containing "Tribological Studies of Epoxy Composites with Solid and Liquid Fillers".
17. Attached hereto as Appendix KUMAR02 is a true and correct copy of Tribological Studies of Epoxy Composites with Solid and Liquid Fillers" by Vikram Kumar, et al as published in Tribology International as held by the Penn State University Library. These scans were secured from the library's

collection. In comparing Exhibit EX1041 to Appendix KUMAR02, it is my determination that Exhibit EX1041 is a true and correct copy of "Tribological Studies of Epoxy Composites with Solid and Liquid Fillers" by Vikram Kumar, et al as published in Tribology International.

18. The 008 field of the MARC record in Appendix KUMAR01 indicates the date of record creation. The 008 field of Appendix KUMAR01 indicates the Penn State University Library first acquired Tribology International as of June 4, 1998 and held the journal in perpetuity until the publication of "Tribological Studies of Epoxy Composites with Solid and Liquid Fillers". Considering this information, it is my determination that Tribology International September 2016 and therefore "Tribological Studies of Epoxy Composites with Solid and Liquid Fillers" was made available to the public shortly after its initial publication in September 2016.

19. I have been retained on behalf of the Petitioner to provide assistance in the above-illustrated matter in establishing the authenticity and public availability of the documents discussed in this declaration. I am being compensated for my services in this matter at the rate of \$200.00 per hour plus reasonable expenses. My statements are objective, and my compensation does not depend on the outcome of this matter.

20. I declare under penalty of perjury that the foregoing is true and correct. I

hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Dated: 5/12/2025

A handwritten signature in black ink, appearing to read 'June Ann Munford', with a stylized flourish at the end.

June Ann Munford

APPENDIX CV

June A. Munford
Curriculum Vitae

Education

University of Wisconsin-Milwaukee - MS, Library & Information Science, 2009
Milwaukee, WI

- Coursework included cataloging, metadata, data analysis, library systems, management strategies and collection development.
- Specialized in library advocacy, cataloging and public administration.

Grand Valley State University - BA, English Language & Literature, 2008
Allendale, MI

- Coursework included linguistics, documentation and literary analysis.
- Minor in political science with a focus in local-level economics and government.

Professional Experience

Researcher / Expert Witness, October 2017 – present
Freelance ● Pittsburgh, Pennsylvania & Grand Rapids, Michigan

- Material authentication and public accessibility determination. Declarations of authenticity and/or public accessibility provided upon research completion. Experienced with appeals and deposition process.
- Research provided on topics of public library operations, material publication history, digital database services and legacy web resources.
- Past clients include Alston & Bird, Arnold & Porter, Baker Botts, Fish & Richardson, Erise IP, Irell & Manella, O'Melveny & Myers, Perkins-Coie, Pillsbury Winthrop Shaw Pittman and Slayden Grubert Beard.

Library Director, February 2013 - March 2015
Dowagiac District Library ● Dowagiac, Michigan

- Executive administrator of the Dowagiac District Library. Located in Southwest Michigan, this library has a service area of 13,000, an annual operating budget of over \$400,000 and total assets of approximately \$1,300,000.

- Developed careful budgeting guidelines to produce a 15% surplus during the 2013-2014 & 2014-2015 fiscal years while being audited.
- Using this budget surplus, oversaw significant library investments including the purchase of property for a future building site, demolition of existing buildings and building renovation projects on the current facility.
- Led the organization and digitization of the library's archival records.
- Served as the public representative for the library, developing business relationships with local school, museum and tribal government entities.
- Developed an objective-based analysis system for measuring library services - including a full collection analysis of the library's 50,000+ circulating items and their records.

November 2010 - January 2013

Librarian & Branch Manager, Anchorage Public Library ● Anchorage, Alaska

- Headed the 2013 Anchorage Reads community reading campaign including event planning, staging public performances and creating marketing materials for mass distribution.
- Co-led the social media department of the library's marketing team, drafting social media guidelines, creating original content and instituting long-term planning via content calendars.
- Developed business relationships with The Boys & Girls Club, Anchorage School District and the US Army to establish summer reading programs for children.

June 2004 - September 2005, September 2006 - October 2013

Library Assistant, Hart Area Public Library

Hart, MI

- Responsible for verifying imported MARC records and original MARC cataloging for the local-level collection as well as the Michigan Electronic Library.
- Handled OCLC Worldcat interlibrary loan requests & fulfillment via ongoing communication with lending libraries.

Professional Involvement

Alaska Library Association - Anchorage Chapter

- Treasurer, 2012

Library Of Michigan

- Level VII Certification, 2008
- Level II Certification, 2013

Michigan Library Association Annual Conference 2014

- New Directors Conference Panel Member

Southwest Michigan Library Cooperative

- Represented the Dowagiac District Library, 2013-2015

Professional Development

Library Of Michigan Beginning Workshop, May 2008

Petoskey, MI

- Received training in cataloging, local history, collection management, children's literacy and reference service.

Public Library Association Intensive Library Management Training, October 2011

Nashville, TN

- Attended a five-day workshop focused on strategic planning, staff management, statistical analysis, collections and cataloging theory.

Alaska Library Association Annual Conference 2012 - Fairbanks, February 2012

Fairbanks, AK

- Attended seminars on EBSCO advanced search methods, budgeting, cataloging, database usage and marketing.

Depositions

2019 ● Fish & Richardson

Apple v. Qualcomm (Case No. IPR2018-001281, 39521-00421IP, IPR2018-01282 and 39521-00421IP2)

2019 ● Erise IP

Implicit, LLC v. Netscout Systems, Inc (Case No. 2:18-cv-53-JRG)

2019 ● Perkins-Coie

Adobe Inc. v. RAH Color Technologies LLC (Case No. IPR2019-00627, IPR2019-00628, IPR2019-00629 and IPR2019-00646)

2020 • O'Melveny & Myers

Maxell, Ltd. v. Apple Inc. (Case No. 5:19-cv-00036-RWS)

2021 • Pillsbury Winthrop Shaw Pittman LLP

Intel v. SRC (Case No. IPR2020-1449)

2022 • Perkins-Coie

Realtek v. Future Link (Case No. IPR2021-01182)

2023 • Fish & Richardson

Neuroderm Ltd. v. Abbvie, Inc (Case No. PGR2022-00040)

2023 • Fish & Richardson

Nearmap US Inc. v. Pictometry International Corp. (Case No. IPR2022-00735)

2023 • Fish & Richardson

Samsung Electronics v. MemoryWeb LLC (Case No. 39843-0136PS1)

2023 • Pillsbury Winthrop Shaw Whitman LLP

Gravel Rating Systems v. Costco Wholesale Corp. (Case No. 4:21-cv-149-ALM)

2024 • Willkie-Farr

Netflix, Inc. v. VideoLabs. Inc. (Case No. IPR2023-00628)

2024 • Quinn Emanuel Urquhart & Sullivan

Purdue University v. Wolfspeed (Case No. 1:21-CV-840)

2024 • Fish & Richardson

Dish Network v. Entropic Communications (Case No. IPR2024-00393)

2025 • Perkins Coie

Amazon.com, Inc. v. Nokia Technologies Oy (Case No. IPR2024-00572)

2025 • Fish & Richardson

Dish Network v. Entropic Communications (Case No. IPR2024-00373)

Limited Case and Clientele History

Alston & Bird

- Ericsson

v. Collision Communications (Case No. IPR2022-01233)

- Nokia

v. Neptune Subsea, Xtera (Case No. 1:17-cv-01876)

- Universal Electronics Inc

v. Roku Inc (Case No. IPR2022-00818)

Alavi & Anaipakos PLLC

- Stingray Group Inc. and Stingray Music USA, Inc.

v. Edwin A. Hernandez-Mondragon and Egla Corp. (Case No. 1:24-cv-21226-RAR)

Arnold & Porter

- Ivantis

v. Glaukos (Case No. 8:18-cv-00620)

- Samsung

v. Jawbone (Case No. 2:21-cv-00186)

Benesch Friedlander Coplan & Aronoff

- Voyis
v. Cathx (Case No. 5:21-cv-00077-RWS)

Buchanan, Ingersoll & Rooney PC

- Google LLC, AT&T Service Inc., T Mobile USA Inc., Cellco Partnership, Ericsson Inc. & Nokia of America Corp.
v. KT Corp & Pegasus Wireless Innovation LLC (Case No. IPR2025-00293)

Deschert LLP

- Smaxtec Animal Care
v. ST Reproductive Technologies, LLC (Case No. IPR2024-00885)

Duane Morris

- Kangxi Communication Technologies
v. Skyworks Solutions Inc. (Case No. IPR2025-00373)
- Microsoft
v. Edge Networking Systems LLC (Case No. 1:24-cv-00215)

Erise I.P.

- Apple
v. Ericsson Inc. (Case No. IPR2022-00715)
v. Future Link Systems (Case No. IPRs 6317804, 6622108, 6807505, and 7917680)
v. INVT (Case No. 20-1881)
v. Navblazer LLC (Case No. IPR2020-01253)
v. Qualcomm (Case No. IPR2018-001281, 39521-00421IP, IPR2018-01282, 39521-00421IP2)

- v. Quest Nettech Corp (Case No. 2:19-cv-00118-JRG)
- v. Telefonaktiebolaget LM Ericsson (Case No. IPR2022-00275)
- v. Theta IP, LLC (Case No. IPR2024-00818)
- v. THL Holding Company LLC (Case No. 1:23-cv-00548)

- Fanduel

- v. CGT (Case No. 19-1393)

- Garmin

- v. Phillips North America LLC (Case No. 2:19-cv-6301-AB-KS)

- Netscout

- v. Longhorn HD LLC (Case No. 2:20-cv-00349)
 - v. Implicit, LLC (Case No. 2:18-cv-53-JRG)

- Sony Interactive Entertainment LLC

- v. Bot M8 LLC (Case No. IPR2020-01288)
 - v. Infernal Technology LLC (Case No. 2:19-CV-00248-JRG)

- Tesla

- v. Charge Fusion Technologies LLC (Case No. IPR2025-00032)

- Unified Patents

- v. GE Video Compression (Case No. 2:19-cv-248)

Fish & Richardson

- Apple

- v. AliveCor (Case No. 3:21-cv-03958)
 - v. LBS Innovations (Case No. 2:19-cv-00119-JRG-RSP)
 - v. Koss Corporation (Case No. IPR2021-00305)

- v. Masimo (Case No. IPR 50095-0012IP1, 50095-0012IP2, 50095-0013IP1, 50095-0013IP2, 50095-0006IP1, 50095-0135IP1)
- v. Neonode (Case No. 21-cv-08872-EMC)
- v. Qualcomm (Case No. IPR2018-001281, 39521-00421IP, IPR2018-01282, 39521-00421IP2)
- v. Resonant Sys. (Case No. 7:23-cv-00077-ADA)
- AsusTek Computer Inc.
 - v. Videolabs, Inc. (Case No. 22-CV-00720-ADA)
- Dell
 - v. Neo Wireless (Case No. IPR2022-00616)
- Dish Network
 - v. Entropic Communications, LLC (Case No. 2:2023-CV-01043)
 - v. Entropic Communications LLC (Case No. IPR2024-00393)
 - v. Realtime Adaptive Streaming (Case No. 1:17-CV-02097-RBJ)
 - v. TQ Delta LLC (Case No. 18-1798)
- Evapco Dry Cooling
 - v. SPG Dry Cooling (Case No. IPR2021-00688)
- Genetec
 - v. Sensormatic Electronics (Case No. 1:20-CV-00760)
- Huawei
 - v. Bell Northern Research LLC (Case No. IPR2019-01174)
- Kianxis
 - v. Blue Yonder (Case No. 3:20-cv-03636)

- LG Electronics
 - v. Bell Northern Research LLC (Case No. 3:18-cv-2864-CAB-BLM)
- MediaTek
 - v. MOSAID (Case No. IPR2024-00718)
- Metaswitch
 - v. Sonus Networks (Case No. IPR2018-01719)
- Microsoft
 - v. Throughputer Inc (Case No. IPR2022-00757)
- Mom Enterprises
 - v. Ddrops Company (Case No. 1:22-cv-00332)
- MLC Intellectual Property
 - v. MicronTech (Case No. 3:14-cv-03657-SI)
- Nearmap Inc
 - v. EagleView Technologies (Case No. IPR2022-01009)
- Neuroderm Ltd.
 - v. Abbvie, Inc (Case No. PGR2022-00040)
- Posco Co Ltd.
 - v. Pascal Drillet et al. (Case No. IPR2025-00370)
- Realtek Semiconductor
 - v. Future Link (Case No. IPR2021-01182)

- Quectel

- v. Koninklijke Philips (Case No. 1:20-cv-01710)

- Samsung

- v. Aire Technology (Case No. IPR2022-00877)

- v. Bell Northern Research (Case No. 2:19-cv-00286-JRG)

- v. Communication Technologies Inc (Case No. IPR2022-01221)

- v. Jawbone Innovations (Case No. IPR2022-00865)

- v. MemoryWeb LLC (Case No. IPR2022-00885)

- v. Dodots Licensing Solutions (Case No. IPR2023-00701)

- v. Telefonaktiebolaget LM Ericsson (Case No. IPR2021-00615)

- Texas Instruments

- v. Vantage Micro LLC (Case No. IPR2020-01261)

- Xilinx

- v. Sentient Sensors LCC (Case No. 1:22-cv-00173)

Goodwin Proctor

- Intel

- v. Proxense, LLC (Case No. 6:24-cv-00283)

- Samsung Electronics

- v. Mobile Data Technologies (Case No. 2:24-cv-00435)

- Taiwan Semiconductor Manufacturing Company Ltd.

- v. Advanced Integrated Circuit Process LLC (Case No. 2:24-cv-00623)

Groombridge Wu

- Nearmap

v. Eagle View Technologies Inc. and Pictometry International Corp. (Case No. 2:21-cv-00283-TS-DAO)

Irell & Manella

- Curium

Latham & Watkins LLP

- Apple

v. Advanced Coding Research LLC

Leydig, Voit & Mayer, Ltd.

- Public Availability Consultancy

O'Melveny & Myers

- Apple

v. Maxell (Case No. 5:19-cv-00036-RWS)

- Disney Media & Entertainment Distribution LLC

v. Digital Media Technology Holdings, LLC (Case No. 2:22-cv-01642)

- Micron Technology Inc.

v. Besang Inc (Case No. IPR2023-00900)

- Samsung

v. Daedalus Prime LLC (1335 Investigation)

Perkins-Coie

- Amazon
 - v. Nokia (Case No. IPR2024-00847 and IPR2024-00848)
 - v. Nokia Technologies Oy (Case No. IPR2024-00572)
- Heru Industries
 - v. The UAB Research Foundation (Case No. IPR2022-01148)
- Intel Corporation
 - v. BeSang Inc. (Case No. IPR2023-00991)
 - v. BitMICRO (Case No. 5:23-cv-00625)
 - v. Telefonaktiebolaget L M Ericsson (Case No. IPR2024-00610)
- Realtek Semiconductor
 - v. Future Link (Case No. IPR2021-01182)
- r-pac
 - v. Adasa, Inc. (Case No. 1:2024cv06102)
- Twitter Inc
 - v. VOIP-Pal.com (Case No. 3:20-cv-02397-JD)
- TCL Industries
 - v. Koninklijke Philips NV (Case No. IPR2021-00495, IPR2021-00496 and IPR2021-00497)
- VusionGroup
 - v. Hanshow (Case No. IPR2024-00857)

Pillsbury Winthrop Shaw Pittman

- Intel

v. FG SRC LLC (Case No. 6:20-cv-00315)

- Gravel Rating Systems

v. Costco (Case No. 4:21-cv-149)

v. Lowe's Home Centers (Case No. 4:21-cv-150)

v. T-Mobile USA (Case No. 4:21-cv-152)

v. Kohl's Inc. (Case No. 4:21-cv-258)

v. Under Armor (Case No. 4:21-cv-356)

Quinn Emanuel

- Exact Sciences Corporation

v. Geneoscopy, Inc. (Case No. IPR2024-00459 and IPR2024-1330)

- ServiceNow, Inc.

v. InQuisient, Inc. (Case No. 22-900-CJB)

- Wolfsped

v. The Trustees of Purdue University (Case No. 1:2021-cv-00840)

Sheppard, Mullin, Richter & Hampton LLP

- Advanced Micro Devices, Inc and Pensando Systems, Inc.

v. Concurrent Ventures LLC and Xtreamedge, Inc. (Case No. IPR2025-00478)

- Cadence Design Systems Inc.

v. Semiconductor Design Technologies (Case No. 3:23-cv-01001)

Shook, Hardy & Bacon LLP

- HP Inc.

v. Universal Connectivity Technologies (Case No. 1:23-cv-01177)

Stern, Kessler, Goldstein & Fox

- Preliminary Research

Wilmer, Cutler, Pickering, Hale and Dorr

- Apple

v. Shunock (Case No. 1:23-cv-08598)

- Quest Diagnostics Inc., Haystack Oncology Inc. and Haystack Oncology GmbH

v. Natera, Inc. (Case No. 1:23-cv-08598)

- Roche Diabetes, Inc.

v. Trividia Health, Inc. (Case No. 1:24-cv-00668)

Willkie, Farr & Gallagher LLP

- Lenovo, Dell, HP

v. Universal Connectivity Technologies Inc. (Case No. 2:2023cv00449)

- Neurent

v. The Foundry, LLC (Case No. IPR2024-00669)

- Netflix, Inc.

v. VideoLabs, Inc. (Case No. IPR2023-00628)

APPENDIX LIU01



Keyword



Search...

Search

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MARC View

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003 SIRSI

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010 a| 2011252120

016 7 a| 101555929 2| DNLN

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016 7 a| 2487261-1 2| DE-600

019 a| DO NOT EDIT this 360 MARC RECORD

022 a| 1996-1944 I| 1996-1944

024 8 a| eb66487068

030 a| MATEG9

035 a| (WaSeSS)ssj0000331829

040 a| WaSeSS b| eng c| QE2 d| OCLCQ d| CUD d| UX0 d| UV0 d| WAU d| AU@ d| DEBBG d| GWDNB d| CUS d| OCLCQ d| GBVCP d| OCLCF d| OCLCO d| OCLCQ d| NLM d| OCLCO d| CASUM d| OCLCA d| OCLCQ d| GUA d| OCLCQ d| AUD d| WaSeSS

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050 1 4 a| TA401

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130 0 a| Materials (Basel, Switzerland)

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210 1 a| Materials b| (Basel)

222 0 a| Materials b| (Basel)

245 1 0 a| Materials h| [electronic resource].

260 a| Basel, Switzerland : b| Molecular Diversity Preservation International, c| 2008-2010.

260 3 3| May 2010- : a| Basel, Switzerland : b| MDPI

310 a| Monthly, b| 2010-

321 a| Quarterly, b| 2009

362 1 a| Began with vol. 1, issue 1 (Dec. 2008).

515 a| Volume 1 complete in one issue.

515 a| Numbering from table of contents page.

538 a| Mode of access: World Wide Web.

580 a| Has companion journal: Electronic materials (Basel, Switzerland).

588 a| Description based on: Vol. 1, issue 1 (Dec. 2008); title from article PDF (publisher's Web site, viewed Jan. 7, 2011).

588 a| Latest issue consulted: Vol. 10, issue 2 (Feb. 2017) (viewed Feb. 21, 2017).

650 0 a| Materials science v| Periodicals.

650 0 a| Materials v| Periodicals.

650 1 2 a| Biomedical and Dental Materials.

650 1 2 a| Biomimetic Materials.

655 0 a| Electronic journals.

655 2 a| Periodical.

710 2 a| Molecular Diversity Preservation International.

710 2 a| Multidisciplinary Digital Publishing Institute.

787 1 t| Electronic materials (Basel, Switzerland) x| 2673-3978 w| (DLC) 2022239685 w| (OCoLC)1239678781

856 4 0 u| http://SK8E54MC2L.search.serialssolutions.com/?V=1.0&L=SK8E54MC2L&S=JCs&C=TC0000331829&T=marc

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Keyword

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Search

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Materials [electronic resource].

Uniform Title	Materials (Basel, Switzerland)
Additional Titles	Materials (Basel)
Published	Basel, Switzerland : Molecular Diversity Preservation International, 2008-2010. May 2010- : Basel, Switzerland : MDPI
Additional Creators	Molecular Diversity Preservation International and Multidisciplinary Digital Publishing Institute

ASK
A LIBRARIAN

Access Online

[serialssolutions.com](#)

Dates of Publication and/or Sequential Designation

Began with vol. 1, issue 1 (Dec. 2008).

Subject(s)

[Materials science—Periodicals](#)
[Materials—Periodicals](#)
[Biomedical and Dental Materials](#)
[Biomimetic Materials](#)

Genre(s)

[Electronic journals](#)

ISSN

1996-1944

Publication Frequency

Monthly, 2010-
Quarterly, 2009

Special Numbering

Volume 1 complete in one issue.
Numbering from table of contents page.

Technical Details

Mode of access: World Wide Web.

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APPENDIX LIU02



Article

Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites

Cheng Liu, Meijuan Li, Qiang Shen and Haikun Chen



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Article

Preparation and Tribological Properties of Modified MoS₂/SiC/Epoxy Composites

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Abstract: In order to improve the tribological properties of epoxy (EP), EP composites were prepared by filling different proportions of silicon carbide (SiC) particles and molybdenum disulfide (MoS₂) powder. SiC and MoS₂ particle surfaces were modified by the silane coupling agent KH560 to improve dispersion and avoid agglomeration of the inorganic particles in the EP resin matrix. The effect of different proportions of modified MoS₂ content on the tribological properties of SiC/EP composites, and the wear mechanism of the worn surface, were investigated when the filler content was fixed at 55 wt.%. The results indicate that the friction and wear properties of modified MoS₂/SiC/EP composites are better than SiC/EP composites without modified MoS₂. When the modified MoS₂ content is 4 wt.%, the average friction coefficient and volume wear rate of the modified MoS₂/SiC/EP composite are 0.447 and $14.39 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$, respectively, which is reduced by 10.06% and 52.13% in comparison with that of the 55 wt.% SiC/EP composite. Furthermore, the average friction coefficient of a composite containing 4 wt.% MoS₂ is 16.14% lower, and the volume wear rate is 92.84% lower than that of pure EP.

Keywords: molybdenum disulfide; silicon carbide; surface modification; epoxy matrix composite; tribological properties

1. Introduction

Epoxy (EP) is one of the most commonly used industrial materials. Owing to its excellent properties, such as high adhesive capacity, excellent chemical stability, and good solvent resistance, it is a very widely used thermosetting resin [1,2]. It has been widely reported that the addition of inorganic powders, such as silicon carbide (SiC), SiO₂, graphite, etc., can significantly improve the mechanical properties, heat resistance and wear resistance of EP [3–5]. However, due to its three-dimensional network structure and poor surface properties, EP cannot be directly used as a wear-resistant material [6]. In order to strengthen and improve the tribological properties of EP, adding different fillers into the EP matrix has become an important and valid approach for solving these problems [7,8]. Most notably, the composite filling of hard particles and solid lubricants is very effective at improving the properties of EP composites, because the complementary properties of these different fillers, and the synergistic effect between fillers, make the tribological properties of EP composites more effective. For example, graphite/glass-EP composites reinforced by SiC particles can obtain better wear resistance [9], and an EP composite with TiO₂ and graphite fillers together has a lower friction coefficient and better wear resistance than a single filled EP, under all loads and speed conditions [10].

SiC has many excellent properties, such as high hardness, high wear resistance, high mechanical strength, and so on. It can be used to enhance the mechanical properties and

tribological properties of polymer composites [11–13]. Molybdenum disulfide (MoS_2) has a special layered structure, similar to graphite, which can enhance the various properties of polymer composites. They can not only improve the mechanical and electrical properties but can also act as a solid lubricant [14–17]. The layered structure is connected by a weak van der Waals force between the layers, which has good lubricity, making it possible to form a lubricating film on the surface of the polymer and, therefore, improving the friction and wear performance of the polymer composite [18,19].

There is much research on the friction and wear of epoxy resin filled with SiC or MoS_2 [20–24], but, so far, there are few reports on the synergistic filling of SiC and MoS_2 . In this paper, EP composites with different proportions of SiC and MoS_2 were prepared. Due to the significant differences in chemical structure and physical form, and a lack of affinity between inorganic fillers and EP resin, surface modification of fillers is essential to make them combine better with polymer and have good dispersion, especially when the filler content is higher, which cannot be well dispersed in the polymer, even through mechanical stirring [25,26]. Therefore, an important silane coupling agent, KH560 (c-glycidoxypropyltrimethoxysilane), is used to form a layer of single molecule membrane on the surface of fillers and improve their wettability and dispersion. There are many reports that focus on the effects of KH560-modified SiC [27,28], but the research on KH560-modified MoS_2 in relation to the tribological properties of reinforced composites is scarce. In our work, the effect of surface modification by KH560 on MoS_2 powder was studied in detail. At the same time, KH560- MoS_2 was added into an EP composite reinforced with a high content of silane coupling agent, KH560-modified SiC powder. The effect of SiC and MoS_2 on the friction and wear properties of EP composites was studied, and the worn surface morphology of EP composites was analyzed. On this basis, the wear mechanism of SiC and MoS_2 synergistically reinforced EP composites was discussed, which provided a reference for the high wear resistance design and application of EP composites.

2. Materials and Methods

2.1. Materials

The experimental reagents mainly included MoS_2 powder (particle size $\leq 2 \mu\text{m}$, 99.8% grad, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), SiC powder ($D_{50} = 0.9 \mu\text{m}$, 99.5% grad, Shanghai Yaotian New Material Technology Co., Ltd., Shanghai, China), epoxy E51 (Hangzhou wuhuigang adhesive Co., Ltd., Hangzhou, China), curing agent polyethylene polyamine (Aladdin, Shanghai, China), silane coupling agent, KH560, acetone, ethanol, and acetic acid (all purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

2.2. Preparation of KH560- MoS_2

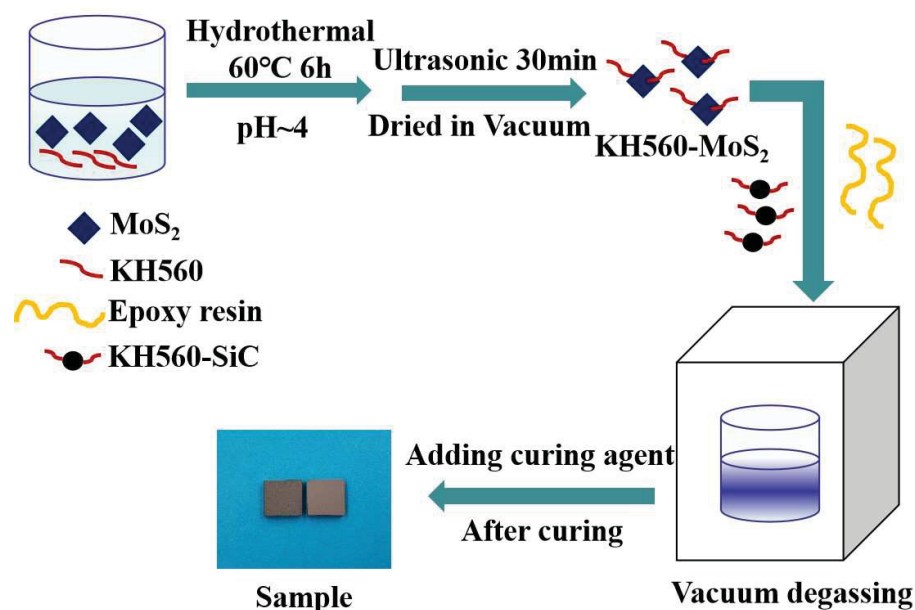
Firstly, MoS_2 and KH560 were mixed in an ethanol and water solvent with proper prescription ($\text{pH} \sim 4$) in a reactor. Then, the mixture reacted for 6 h, with stirring at 60°C and ultrasonic dispersion for 30 min. After cooling to room temperature, the modified MoS_2 was centrifugally washed 3 times using ethanol, and, finally, it was dried in a vacuum for 8 h to remove the solvent at 120°C .

2.3. Composites Preparation

The as-prepared KH560- MoS_2 was added into the preheated EP and stirred for 1 h. Then, the KH560-SiC and a little acetone was added into the mixture, stirred, and defoamed at 70°C under a vacuum for 2 h. After that, the polyethylene polyamine was added into the mixture by slowly stirring. Then, the suspension was poured into the preheated mold and cured in the blast air oven. The selected curing process was $40^\circ\text{C}/12 \text{ h} + 60^\circ\text{C}/2 \text{ h} + 100^\circ\text{C}/4 \text{ h}$. Finally, the EP composites were obtained after demoulding. The ingredients of EP composites are listed in Table 1, and the entire synthetic approach of modified MoS_2 /SiC/EP composites is shown in Figure 1.

Table 1. Ingredients of epoxy composites.

Sample	Fillers (wt.%)		EP (wt.%)
	SiC	MoS ₂	
EP	0	0	100
SE	50	0	50
S0	55	0	45
S1	54	1	45
S2	53	2	45
S3	52	3	45
S4	51	4	45
S5	50	5	45

**Figure 1.** Diagrammatic representation of modified MoS₂/SiC/EP composites' preparation.

2.4. Measurement and Characterization

A thermal-gravimetric analyzer (TGA) measurement was performed on an STA449F3 instrument (Netzsch instruments, Selb, Germany). About 3.5 mg of sample was put in an alumina crucible and the heating rate was set as 10 °C/min, with the test range from room temperature to 800 °C at argon atmosphere. A Raman laser spectroscopy measurement was performed using a confocal laser, Raman evolution (LabRam HR Evolution, Paris, France), with excitation provided in back-scattering geometry by a 532 nm laser line in an air-ambient environment. An X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, Waltham, MA, USA) was used to characterize the surface chemical composition and elemental content of the sample.

A Vickers hardness of samples was obtained by a digital microhardness tester system (Wilson Tukon 1202, Norwood, MA, USA). The maximum indentation load was 0.1 kg, while the holding time at maximum depth was 15 s. In order to reduce the tolerance, the experiments were conducted at five indents for each sample. A field emission scanning electron microscope (FESEM, FEI, Quanta + FEG250, Hillsboro, OR, USA) was used to observe the fracture morphology and dispersion of the samples. The friction and wear tests were tested by an MFT-4000 multifunctional material surface performance instrument (MFT-4000, Lanzhou Huahui Instrument Technology Co., Ltd., Lanzhou, China), with GCr15 steel balls 5 mm in diameter, as the upper specimens at room temperature. The single reciprocating stroke was 10 mm. The speed was 180 mm/min and the time lasted

for 30 min. The friction coefficient was recorded by the tester, and the volume wear rate K ($\text{mm}^3/\text{N}\cdot\text{m}$) was calculated according to the Formula (1):

$$K = \frac{\Delta V}{F \times L} \quad (1)$$

where ΔV is the wear volume (mm^3), F is the test load (N), and L is the total reciprocating stroke (m).

A three-dimensional optical profilometer (Nanovea ST400, Irvine, CA, USA) was used to observe the three-dimensional contour map of wear track, and a field emission ultra-high resolution scanning electron microscope (SEM, Zeiss sigma500, Oberkochen, Germany) was used to analyze the worn surface morphology of samples.

3. Results and Discussion

3.1. Characterization on The Modification of MoS_2 Powder by KH560

The TGA thermal analysis curves of MoS_2 and KH560- MoS_2 were shown in Figure 2a. It was seen from the figure that when the temperature started to rise to about 124°C , the weight loss trend of the two kinds of powders was the same. However, the thermal weight loss of KH560- MoS_2 was obviously more stable than that of unmodified MoS_2 in the temperature range of 124°C – 230°C , which indicated that KH560 successfully modified MoS_2 and improved the thermal stability of MoS_2 . Overall, the weight loss of modified MoS_2 was higher than that of unmodified MoS_2 from room temperature to 800°C , which was attributed to the decomposition of KH560. A Raman spectroscopy was carried out to garner more structural information, as shown in Figure 2b. Pure MoS_2 had two dominant peaks, at 379.4 cm^{-1} and 403.4 cm^{-1} , which were, respectively, the in-plane E_{2g}^1 and out-of-plane A_g^1 vibrational modes [29]. It was observed that the E_{2g}^1 and A_g^1 vibrational modes had different degrees of shift to higher frequencies, and that the shift of E_{2g}^1 was larger than that of A_g^1 , suggesting that the KH560 molecule used for surface modification was combined with MoS_2 and introduced tensile strain into MoS_2 layers [30].

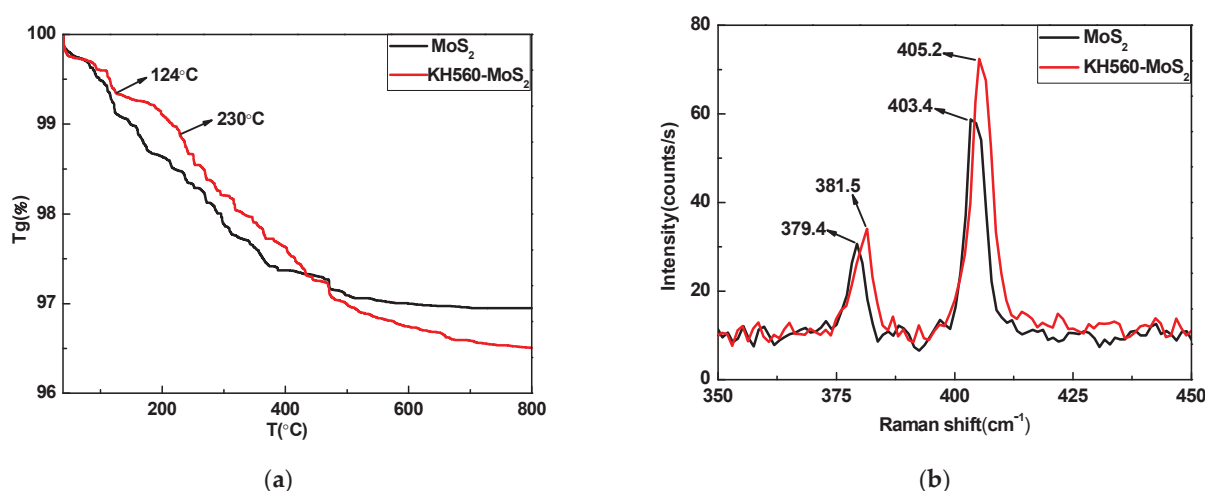


Figure 2. TGA curves (a) and Raman Spectroscopy (b) of MoS_2 and KH560- MoS_2 .

XPS was used to confirm the chemical composition of MoS_2 and KH560- MoS_2 , as shown in Figure 3. From the full spectrum in Figure 3a, it was found that the peak intensity of C and O elements of the modified MoS_2 was higher than that of the unmodified MoS_2 , and that the characteristic peaks of silicon (3.76%) appeared in KH560- MoS_2 , indicating that KH560 was grafted onto the MoS_2 surface successfully. The high-resolution C1s and O1s spectra were to estimate the function groups for KH560- MoS_2 in Figure 3b,c. The functional groups of C1s peak included C-O, C-C, and Si-C, at 286.22 eV, 284.78 eV, and

283.79 eV, respectively [31,32], and the C-O and Si-O of O1s peaked at 532.68 eV and 531.89 eV, respectively [33,34]. These functional groups were related to KH560 grafted on the surface of MoS₂. In addition, the high-resolution of Mo3d and S2p for KH560-MoS₂ and MoS₂ were studied. Mo3d_{3/2}, Mo3d_{5/2}, S2p_{1/2}, and S2p_{3/2} peaks of KH560-MoS₂ were located at 232.36 eV, 229.23 eV, 163.30 eV, and 162.08 eV, respectively, and Mo3d_{3/2}, Mo3d_{5/2}, S2p_{1/2}, and S2p_{3/2} peaks of MoS₂ were located at 232.90 eV, 229.77 eV, 163.80 eV, and 162.58 eV, respectively. It was found that the binding energy of Mo3d and S2p of KH560-MoS₂ all shifted to lower energy. This could be explained by the electrostatic interaction between MoS₂ and KH560 [35].

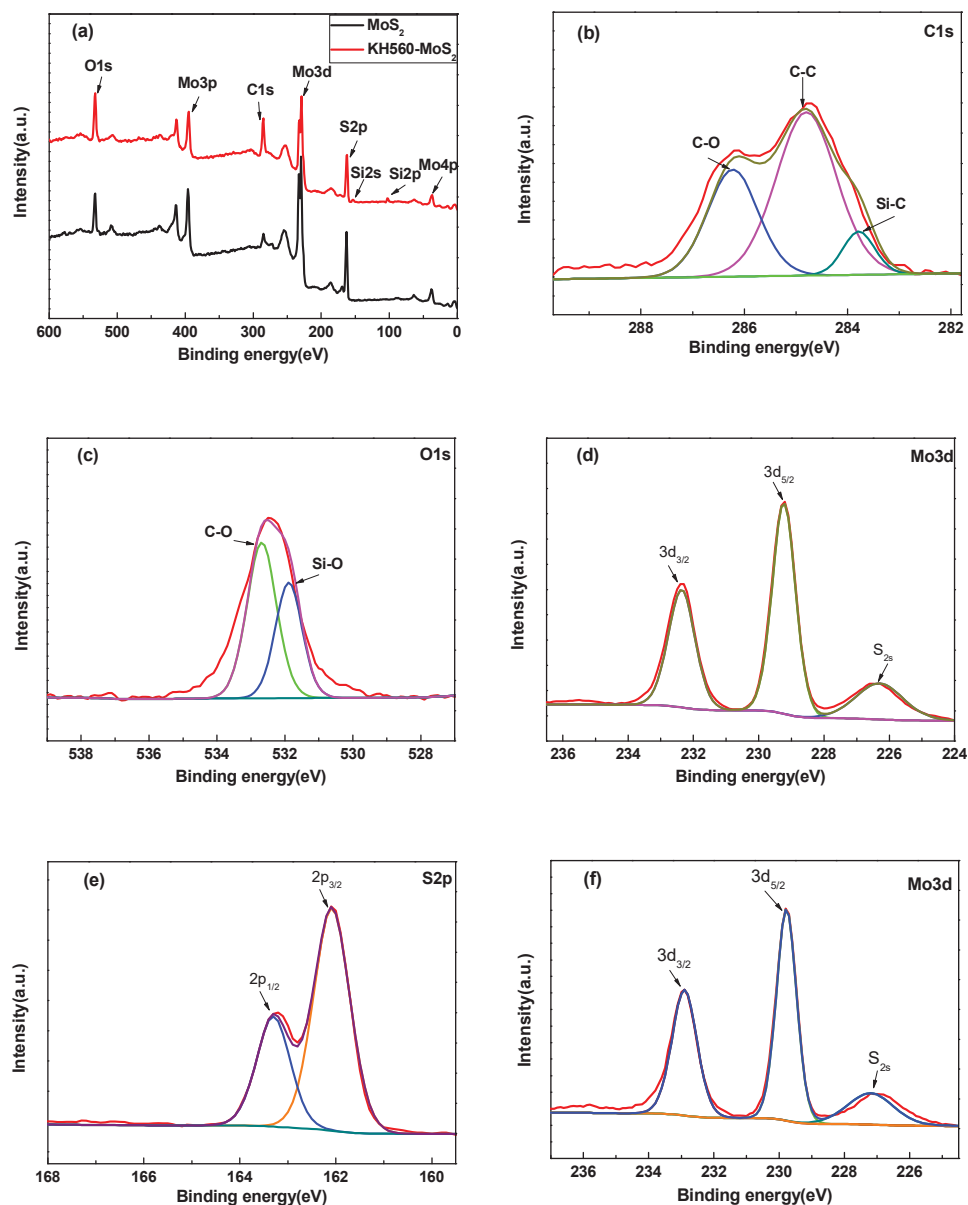


Figure 3. Cont.

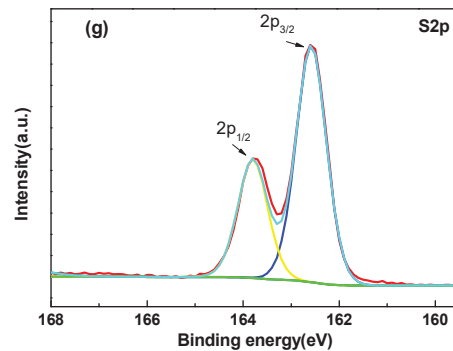


Figure 3. XPS spectra of MoS₂ and KH560-MoS₂ (a), high-resolution XPS spectra of C1s (b); O1s (c); Mo3d (d); S2p (e) for KH560-MoS₂, and Mo3d (f); S2p (g) for MoS₂.

3.2. Dispersion of High Content of Modified MoS₂/SiC in Epoxy Matrix

The dispersion uniformity of fillers in the epoxy resin matrix directly affects the performance of the EP composites. Most notably, this effect will be more significant when the filler is added in a large proportion [36]. As shown in Figure 4, SEM fracture scanning combined with EDS analysis was used to study the dispersion of high-content-modified SiC/MoS₂ in EP composites. When the content of KH560-SiC was as high as 55 wt.% (sample S0), it was still evenly distributed in the EP with good dispersibility, and was well combined with the epoxy resin matrix (Figure 4a–c). The total content of inorganic fillers was fixed at 55 wt.%, and KH560-MoS₂ partially replaced the same mass fraction of KH560-SiC particles; the highest proportion of KH560-MoS₂ was 5 wt.% (sample S5). SEM and EDS analysis (Figure 4d–g) showed that the modified MoS₂ with lamellar structure was closely embedded in the modified SiC/EP composites, with uniform distribution and good dispersion. The KH560-MoS₂ powder size was less than or equal to 2 μm, without agglomeration phenomenon in EP composites, which proved that the MoS₂ lamellar powder modified by KH560 could also be well dispersed and combined in the epoxy resin matrix.

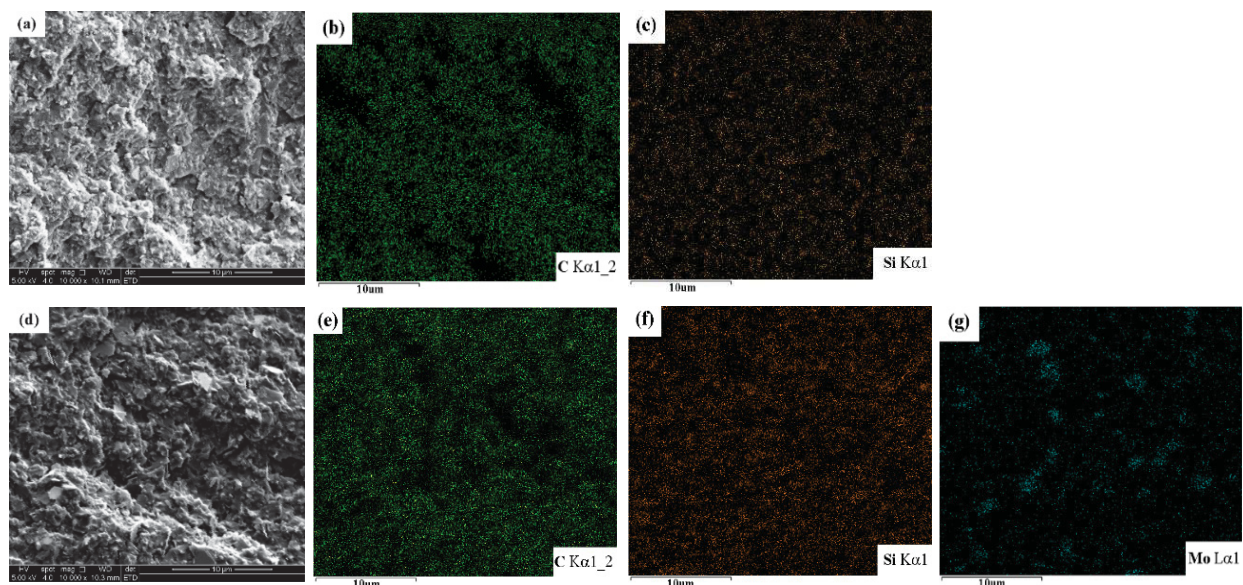


Figure 4. Fracture morphology of S0 (a) and EDS results of C (b); Si (c), and Fracture morphology of S5 (d) and EDS results of C (e); Si (f); Mo (g).

3.3. Tribological Properties of Composites

The real-time friction coefficient (COF) for the EP and other EP composites, and the resulting variation in the average COF and volume wear rate of composites at 60 N, are shown in Figure 5. It was obvious that all samples had experienced two stages of running-in period and stable period from the friction test curve (Figure 5a,c). In the early stage of the running-in period, the friction coefficients of all samples increased rapidly with the progress of friction. Compared with pure EP, the friction coefficient of EP composites with SiC and MoS₂ added had relatively small fluctuations in the stable period. In addition, the friction coefficient of pure EP still fluctuated greatly after the stable period. The reason was that, compared with the EP composites, the hardness of pure EP was the lowest, which was 19.0 HV (Figure 6, Vickers hardness of EP and EP composites). The plastic deformation of the EP worn surface was more serious during the friction process, which resulted in serious fatigue wear and which led to a large fluctuation of friction coefficient after the stable period [37]. It was found that when the content of modified SiC increased to 50 and 55 wt.%, the friction coefficient of SE and S0 was lower and tended to be stable [38,39], as shown in Figure 5a. This indicated that the modified SiC particles could be well combined with the epoxy resin matrix, and the matrix stress could be better transmitted to endure higher normal loads when the content of SiC particles was higher. At the same time, a large amount of SiC particles distributed on the friction interface could reduce the tearing of the EP composite surface and the formation of furrows, thereby reducing the friction coefficient [40].

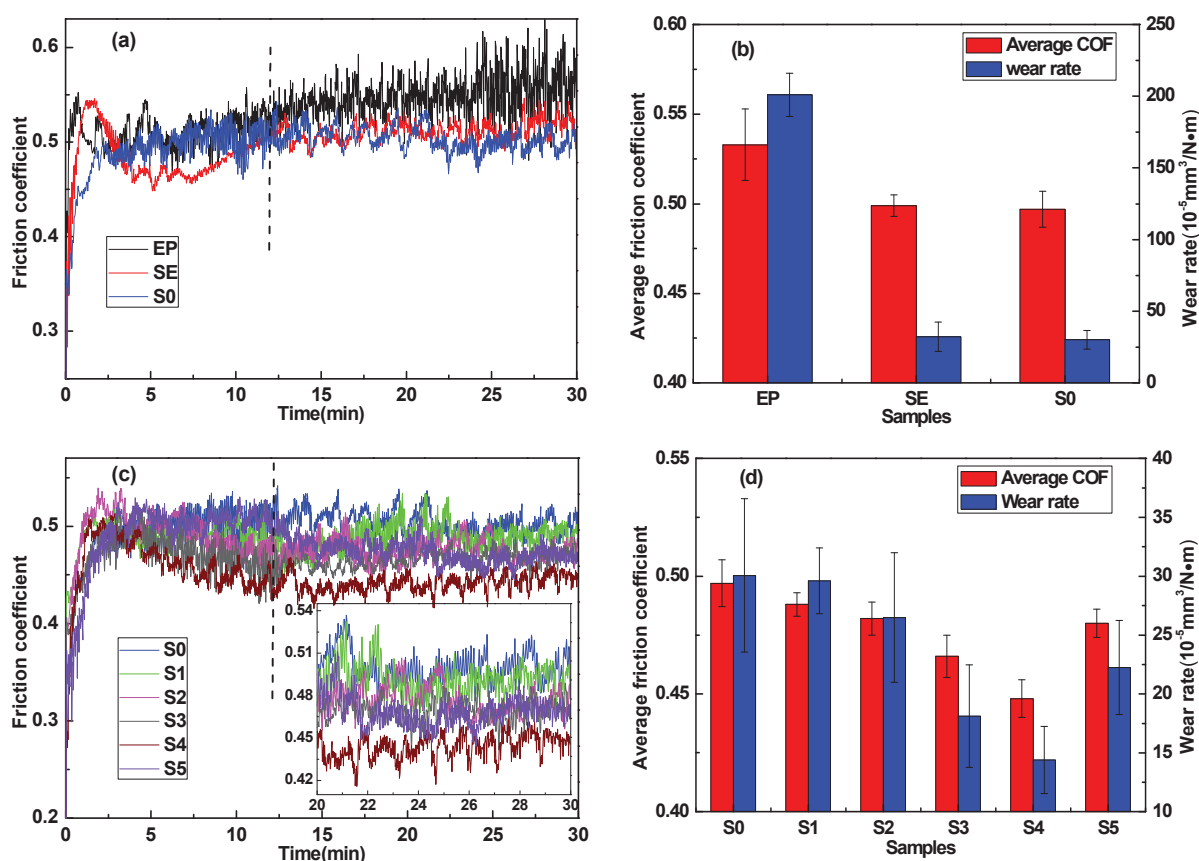


Figure 5. Development of friction coefficient over testing time for EP composites (a,c), and average COF and wear rate for EP composites at 60 N (b,d).

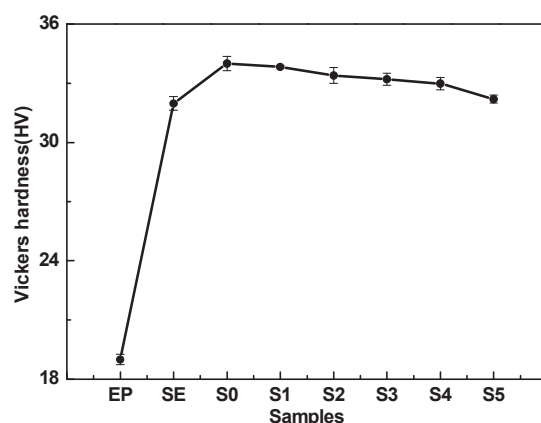


Figure 6. Vickers hardness of EP composites.

Figure 5b depicts that the average COF of the EP composite adding 55 wt.% SiC particles was 0.497, and the volume wear rate was $30.06 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$. Compared with pure EP, the average COF was reduced by 6.75% from 0.533, and the volume wear rate was reduced by 85.04% from $200.98 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$. If the addition of SiC particles was reduced to 50 wt.% (sample SE), the average COF and volume wear rate had no obvious change compared to sample S0. Therefore, the fixed total content of fillers added in EP was 55 wt.% in the composite material with modified MoS₂ powder. As shown in the inset of Figure 5c, the friction coefficient of the EP composites with modified MoS₂ powder in the stable period was lower than that of S0, which proved that the addition of MoS₂ improved the friction-reducing performance of EP composites better [41]. When the content of modified MoS₂ was increased to 4 wt.% (Figure 5d, sample S4), the measured lowest average COF was 0.447, which was reduced by 10.06% compared to 0.497 of S0, and was reduced by 16.14% compared to 0.533 of EP. At the same time, the measured lowest volume wear rate was $14.39 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ of S4, which was reduced by 52.13% compared to $30.06 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ of S0, and was reduced by 92.84% compared to $200.98 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ of EP. When the content of modified MoS₂ continued to increase, the average COF and volume wear rate of the modified MoS₂/SiC/EP composites increased; but they were still lower than those of S0. With reference to Figure 6, as the content of modified MoS₂ increased, the hardness of the EP composites decreased. When the content of modified MoS₂ was 5 wt.% (S5), the hardness of modified MoS₂/SiC/EP composite was the lowest, which was 32.2HV. Although the modified SiC and MoS₂ could be well dispersed in the resin matrix, the composite hardness would be reduced when MoS₂ replaced the same amount of SiC. This is because the hardness of SiC particles is higher than that of MoS₂, and some MoS₂ particles had larger particle size, smaller specific surface area, and lower surface energy, which made the bonding strength between MoS₂ and epoxy resin weak. In this case, the contact area of the friction pair on the surface of the composites increased, and more hard abrasive SiC particles were produced in the early stage of the running-in period, which resulted in slight abrasive wear during the friction process and led to the increase of the friction coefficient and the volume wear rate.

Figure 7 showed the effect of applied load on the friction coefficient and wear rate of modified MoS₂/SiC reinforced EP composites, and the test sample was S4. As shown in Figure 7a, when the applied load was only 10–20 N, the friction curve of the stable period tends to be flat and straight, indicating that the friction process was proceeding on its surface. The wear rate was very small, and a small number of particles adhered to the dual surface. When the applied load was gradually increased to 40–60 N, the MoS₂ particles with weak bonding interface, bonded by van der Waals force between the layers, would extrude and penetrate into the matrix, resulting in the formation of lubricating film at the friction interface, which reduced the friction resistance and decreased the friction coefficient gradually. However, with the applied load increasing to 80 N, the lubricating

film produced by MoS_2 particles could reduce the friction coefficient in the middle stage of friction. The friction coefficient began to fluctuate greatly in the late stage after 20 min (shown in the inset of Figure 7a), resulting in the damage of the lubricating film on the friction interface and severe fatigue wear, which led to the obvious increase of the friction coefficient and volume wear rate (Figure 7b) [42].

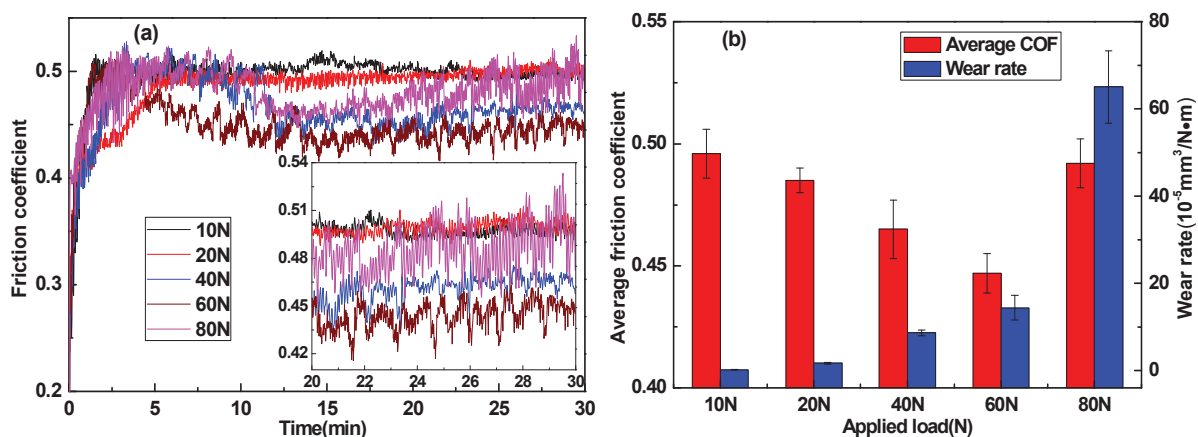


Figure 7. Development of friction coefficient over testing time for S4 (a), and average COF and wear rate for S4 at different applied loads (b).

3.4. Wear Mechanism Analysis of Composites

Comparing the three-dimensional profile of S0 and S4 samples after the friction test at 60 N (shown in Figure 8), and combining it with the hardness test results (shown in Figure 6), it can be seen that when the additional amount of modified MoS_2 is 4 wt.%, the depth of the wear scar is relatively shallow and the depth distribution of the wear scar is relatively consistent; although, the hardness of EP composites is lower than that of 55 wt.% SiC/EP composites without modified MoS_2 . This illustrates that the soft phase addition of MoS_2 can reduce the hardness of the composites, and the addition of properly modified MoS_2 can not only improve the composite's ability to withstand applied loads, but, also, spread on the friction surface, thereby effectively reducing the actual friction area and playing a better role in wear resistance [43].

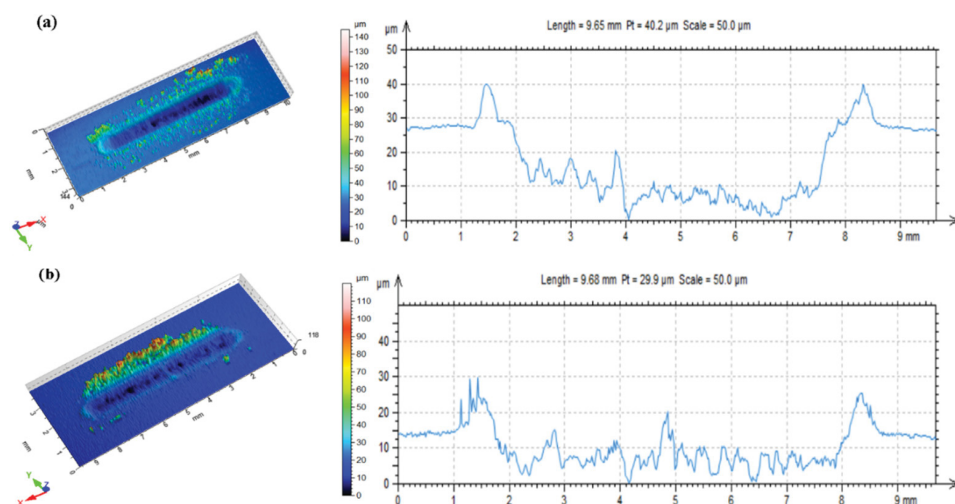


Figure 8. Three-dimensional contour map of wear track of S0 (a) and S5 (b) at 60 N.

In order to investigate the wear mechanism for filled and unfilled composites, the corresponding low and high magnification SEM images of the worn surfaces are demonstrated in Figure 9. The worn surface of EP (Figure 9a) appears rough and more microcracked. This indicates that part of the EP is detached and the friction damage to the material is more serious, showing typical fatigue wear characteristics. For the composite with 55 wt.% modified SiC, the worn surface is relatively smooth, and some hard abrasive SiC particles are produced (Figure 9b). In addition, the hard abrasive SiC particles can be seen protruding on the worn surface at higher SEM magnification (Figure 9i), which shows the abrasive wear mechanism. After adding appropriately modified MoS₂, which lends solid lubricant properties, the MoS₂ particles evenly dispersed in the composites gradually migrate to the worn surface during the friction process, and provide a lubrication effect, thus, making the worn surface smoother (Figure 9c–f). In addition, it seems that the transfer film has a compact and smooth structure; this can be seen clearly in a high SEM magnification (Figure 9j). When the content of modified MoS₂ increases to 5 wt.% (Figure 9g), some hard abrasive SiC particles exist on the worn surface, resulting in slight abrasive wear, which increases the friction coefficient and volume wear rate. Nevertheless, with the normal load increases exceeding the capacity of the modified MoS₂/SiC/EP composite, the lubricant film will be partially destroyed, and more microcracks appear on the worn surface, as shown in Figure 9h. At this moment, the main wear mechanism is fatigue wear, which greatly increases volume wear rate.

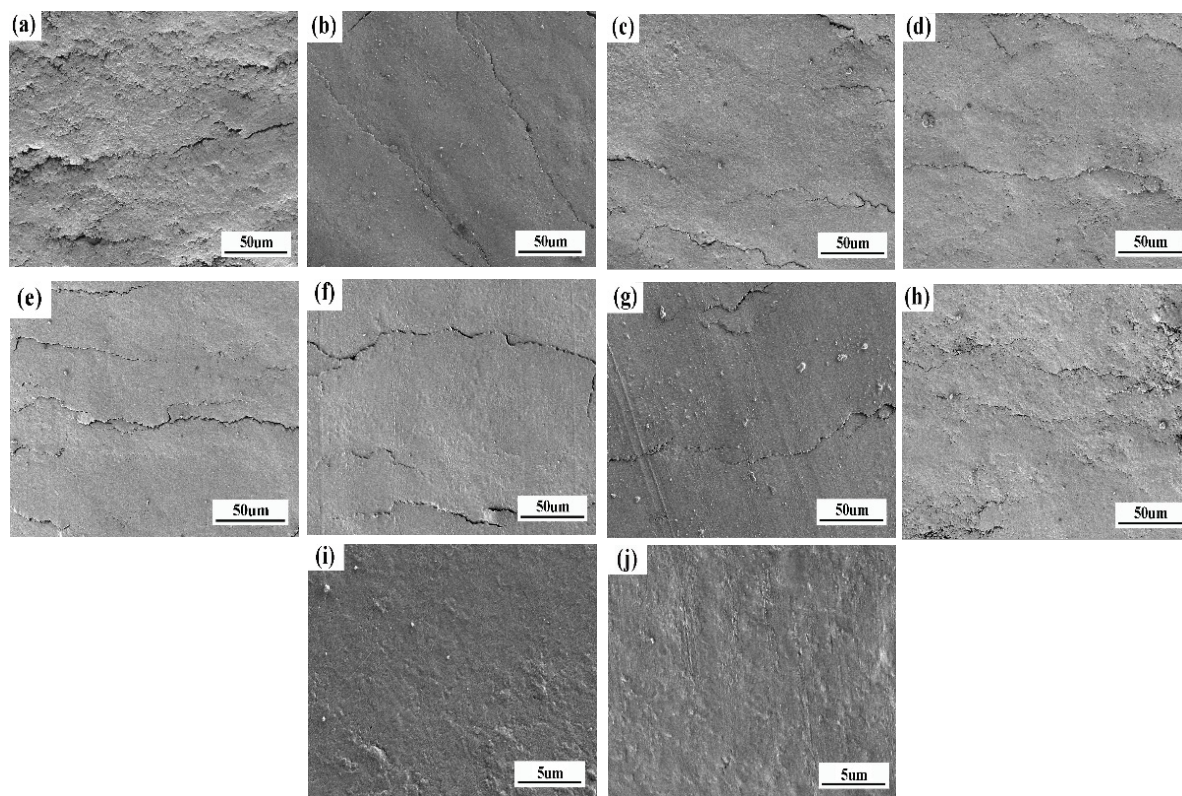


Figure 9. SEM images of wear track on the composites EP (a); S0 (b,i); S1 (c); S2 (d); S3 (e); S4 (f,h,j); S5 (g). The load of S4 (h) is 80 N, while the others are 60 N.

4. Conclusions

The surface of MoS₂ particles was successfully modified by silane coupling agent KH560 to improve its dispersion in EP composites. An MFT-4000 multifunctional material surface performance tester was used to evaluate the friction and wear properties of the

composites filled with modified MoS₂, instead of SiC, with the same mass fraction when the fixed filler content was 55 wt.%. The wear mechanism was discussed by analyzing the worn surface. Our main conclusions could be drawn as follows:

- (1) The results of TGA, Raman and XPS showed that the surface of MoS₂ particles was successfully modified by KH560.
- (2) It is found that the friction and wear properties of SiC/EP composites with MoS₂ are better than those without MoS₂. When the adding fraction of modified MoS₂ is 4 wt.%, the friction coefficient and volume wear rate of EP composites are lowest. Compared with 55 wt.% SiC/EP composite, the friction coefficient and volume wear rate of the SiC/EP composite containing 4 wt.% MoS₂ are reduced by 10.06% and 52.13%, respectively. Furthermore, the composite friction coefficient is decreased by about 16.14%, from 0.533 to 0.447, and the volume wear rate is reduced by 92.84%, from $200.98 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ to $14.39 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$, in comparison with those of pure EP, proving the significant improvement of wear resistance of EP composites.
- (3) When the appropriate content of MoS₂ with lubricating properties is added, the MoS₂ homogenously dispersed in the material gradually migrates to the surface during the friction process to form the lubricating film, so as to make the worn surface smoother. However, when the weak-bonded MoS₂ content increased to 5 wt.%, some hard abrasive SiC particles existed on the wear surface, resulting in slight abrasive wear, which increased the friction coefficient and volume wear rate. In addition, if the load increases and exceeds the capacity of the modified MoS₂/SiC/EP composite, the lubricant film is partially destroyed, and the main wear mechanism is fatigue wear.

Author Contributions: Conceptualization, C.L. and M.L.; methodology, C.L. and M.L.; validation, C.L. and H.C.; formal analysis, C.L. and Q.S.; investigation, C.L., M.L. and Q.S.; resources, H.C.; writing—original draft preparation, C.L.; writing—review and editing, M.L.; supervision, Q.S. and H.C.; funding acquisition, M.L. and H.C. All authors have read and agreed to the published version of the manuscript.

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APPENDIX BROSTOW02



Modified epoxy coatings on mild steel: Tribology and surface energy

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ABSTRACT

A commercial epoxy diglycidylether of bisphenol-A (DGEBA) was modified by adding fluorinated poly(aryl ether ketone) fluoropolymer and in turn metal micro powders (Ni, Al, Zn, and Ag) and coated on mild steel. Two curing agents were used; triethylenetetramine (a low temperature curing agent) and hexamethylenediamine (a high temperature curing agent) for understanding the curing temperature effect on the properties. Variations in tribological properties (dynamic friction and wear) and surface energies with varying amounts of metal powders and curing agents were evaluated. When cured at 30 °C, dynamic friction and wear decrease significantly due to phase separation reaction being favored between the fluoropolymer and the epoxy. However, when cured at 80 °C, friction and wear increase; this can be explained in terms of a crosslinking reaction favored at that temperature. There is a significant decrease in surface energies with the addition of modifiers.

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1. Introduction

Epoxyes are noted for their versatility, high resistance to chemicals, outstanding adhesion to a variety of substrates, toughness, high electrical resistance, durability at high and low temperatures, low shrinkage upon cure, flexibility, and the ease with which they can be poured or cast without forming bubbles [1–5]. These properties make them eligible for use in various applications such as protective coatings (for appliance, automotive primers, pipes) [6], encapsulation of electrical and electronic devices, adhesives, bonding materials for dental uses, replacement of welding and riveting in aircraft and automobiles, composites materials in space industry, printed circuitry, pressure vessels and pipes,

and construction uses such as flooring, paving, and airport runway repair [1,7].

One of the ways of improving the performance of polymers is by introducing a metallic dispersed phase. Metallic materials have useful properties and characteristics that are crucial for many applications; among them high electric conductivity, paramagnetism, high thermal conductivity as well as good mechanical properties. Combination of polymers with metals results in materials with electrical and magnetic properties comparable to neat metals and with a significant improvement in thermal properties of polymers. Also, the processability is the same as for neat polymers – a significant advantage for speed of production and processing costs.

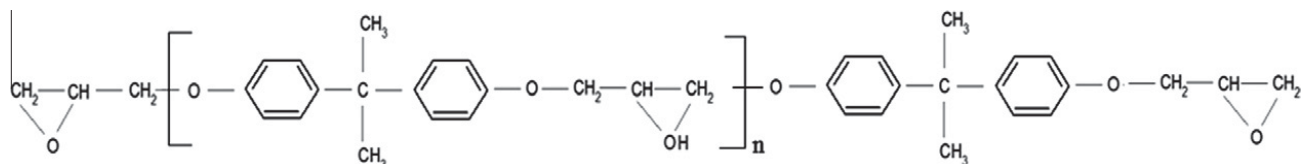
Al particles added to poly(ethylene oxide) affect electric conductivity as reported by Muszynska and her colleagues [8]. Mamunya et al. used Cu and Ni powders as fillers in an epoxy resin and in poly(vinyl chloride) and studied the concentration dependence of electric and thermal conductivity [9]. Kim and coworkers added a soft Al + Fe + Si magnetic powder to a polymeric matrix to

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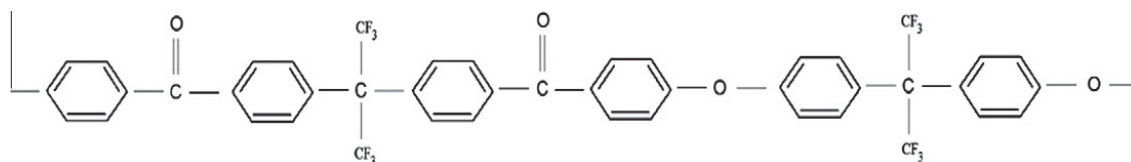
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produce magnetic films to be used for shielding of electromagnetic waves [10]. Metal powders have been distributed in low density polyethylene (LDPE) without agglomeration [11], resulting in improvement of tribological properties [12,13]. Brito and Sanchez [14] used Zn, Cu, and Al as fillers in thermoset polymer systems composed by epoxy and amino resins at several concentrations up to 30 wt.%; they studied mechanical properties as well as thermal decomposition. They observed that the temperature of decomposition decreases when metal



is added to epoxy + amine resins, this for all metals and all epoxy:amine ratios.

Modification of epoxies for achieving a wide range of properties including the above mentioned ones can be effective. Fluoropolymer modified epoxy provides better scratch resistance, low surface tension, better overall tribological properties and hydrophobicity [15–18]. Ku-



mar, Alagar and Mohan developed siliconized epoxy interpenetrating coatings over mild steel wherein Zn powder was used for achieving good corrosion resistance [19]. Bazyliak, Bratychak, and one of us proposed the use of oligomers containing peroxy groups as epoxy modifiers in order to improve adhesion [20–22]. Polymer composites including carbon nanotubes (CNTs) are used for a variety of applications [23]; epoxies as corrosion protection coatings on steels have been reported [24]. Epoxy powder coatings modified using nano-CaCO₃, resulting in tensile and corrosion resistant properties were described by Yu and coworkers [25]. There has also been work reported on blends of thermoplastics like polysulfones and poly(methyl methacrylate) with epoxies for achieving toughness [26,27]. Kumar, Balakrishnan, Alagar and Denchev used silicone and phosphorus for modifying an epoxy to achieve anticorrosion, antifouling and flame retardant properties [28]. Fibers can also be used to alter the properties of the material [29].

In this work, modification of pure epoxy had been carried using a fluoropolymer and metal powders to achieve an advantageous combination of tribological and hydrophobic properties.

2. Experimental

2.1. Materials

Epon™ Resin 828, an undiluted clear difunctional bisphenol-A/epichlorohydrin derived liquid epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), from Hexion Speciality Chemical Inc., was used as the base epoxy. The glass transition temperature T_g of the epoxy is 92 °C [16]. The epoxide equivalent weight of the epoxy is 185–192 g/eq. Its chemical formula is:

Fluorinated poly(aryl ether ketone) (FPEK) fluoropolymer was used as one of the modifiers due to its low surface energy nature which could provide hydrophobicity to the material and for its scratch resistance [19]. FPEK was synthesized in the Department of Chemistry, Texas State University, San Marcos according to a procedure reported in [30,31]. The T_g of the FPEK is 180 °C. Its chemical formula is:

The other modifier used was a metal powder. Four types of metal powders of size 1–5 µm were used: Ni, Al, Ag, and Zn. These metals powders were obtained from Atlantic Equipment Engineers (a division of Micron Metals Inc.). The Ni particles were used in flakes form whereas the Al particles were atomized particles. The shape of Ag was irregular, whereas the Zn particles were a combination of irregular and spherical particles.

Two types of curing agents were used in this work. One of them is triethylenetetramine (TETA) – a room temperature curing agent (from Hexion Speciality Chemical Inc.) and the other is hexamethylenediamine (HMDA) – a high temperature curing agent (from Sigma Aldrich). It has been reported in literature that curing temperature has a significant effect on a variety of properties – especially mechanical ones, friction, tensile bond strength, electrical resistivity, etc. of cured epoxies [16,32,33].

2.2. Epoxy modification, coating, and curing

Amount of FPEK used was 10 wt.% of the total system. Amount of curing agent used was 13 g TETA/100 g epoxy; 15 g HMDA/100 g epoxy. 25 wt.% metal powder/100 g epoxy was used.

Calculated amount of FPEK was dissolved in chloroform (20 ml chloroform/1 g FPEK) and then the epoxy resin was added. Then calculated amounts of metal powders were in turn added. This mixture was subjected to vacuum to remove chloroform and any trapped air. The curing agents were then added accordingly. These epoxy mixtures were coated onto ASTM A366 steel substrates (1" × 2") using a brush. Thus, two different types of systems were synthesized using TETA and HMDA. Each system consisted of six compositions:

Unmodified epoxy; epoxy + FPEK; epoxy + FPEK + Ni; epoxy + FPEK + Al; epoxy + FPEK + Ag; epoxy + FPEK + Zn.

Samples with TETA were cured at 30 °C (24 h), whereas samples with HMDA were cured at 30 °C (5 h) and then

post-cured at 80 °C (24 h) to allow formation of a smooth and even coating. After curing all the samples were stored at room temperature.

2.3. Friction determination

Nanovea pin-on-disc tribometer from Micro Photonics, Inc., was used for determining dynamic friction. A SS 302 grade stainless steel ball with diameter 3.20 mm was used as the pin. The pin was loaded onto the test sample with a known weight 5.0 N. A highly stiff elastic arm insures a nearly fixed contact point and thus a stable position in the friction track. Dynamic friction is determined during the test by measuring the deflection of the elastic arm by

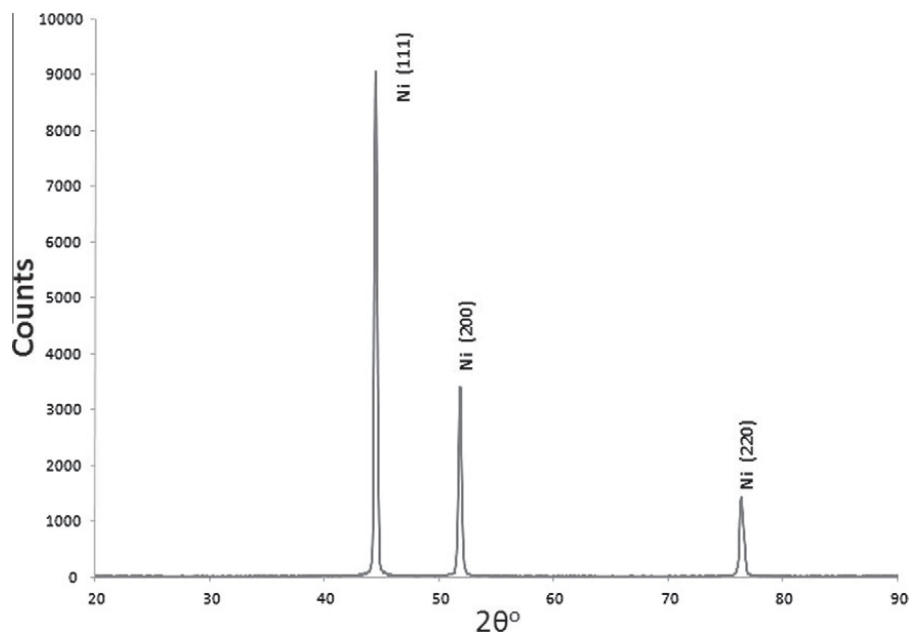


Fig. 1a. Diffraction pattern of Ni powder.

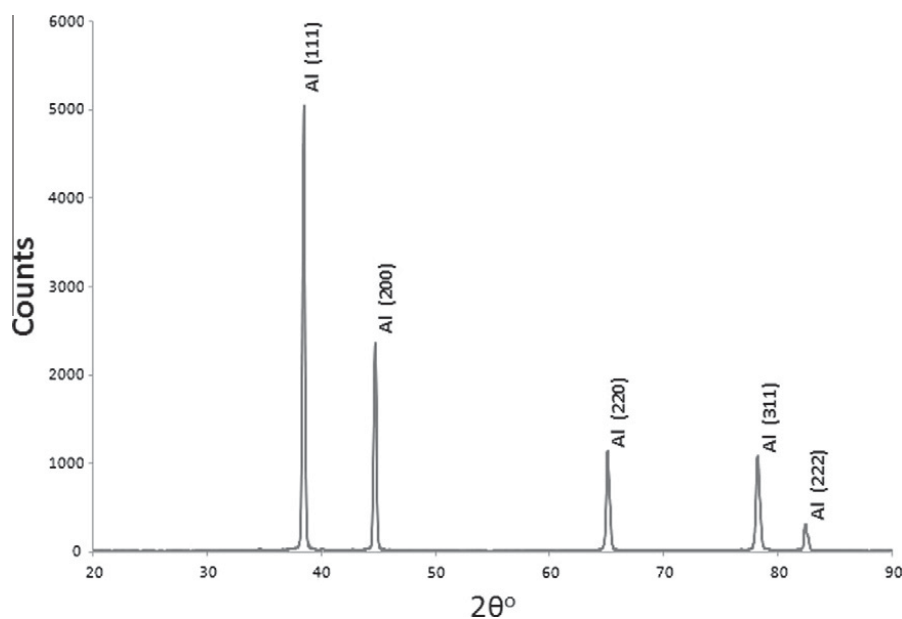


Fig. 1b. Diffraction pattern of Al powder.

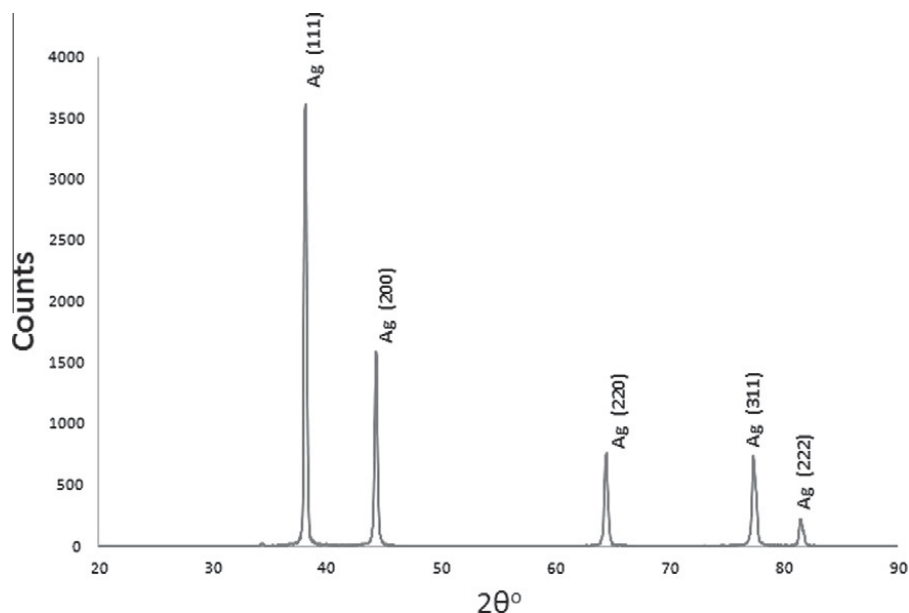


Fig. 1c. Diffraction pattern of Ag powder.

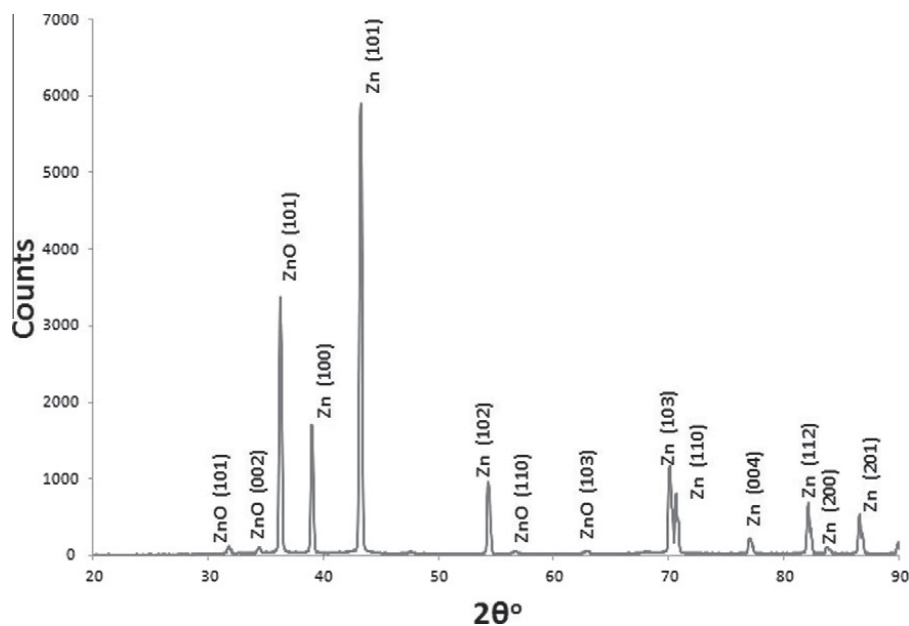


Fig. 1d. Diffraction pattern of Zn powder.

direct measurement of the change in torque. The rotation speed of the disc was 100 rpm and the radius of wear track was 2.0 mm. The test was performed for 500 and 5000 revolutions under room temperature conditions. The results reported are averages from three runs.

2.4. Wear rate determination

Wear was determined by studying the wear track resulted due to the pin-on-disc friction test after 5000 revolutions. FEI Quanta 200 SEM was used for analysing the

wear track and determining the wear track width. The accelerating voltage was 20.0 kV. Ten values of wear track width were measured at different locations on each sample and averaged for the purpose of accuracy. The volume loss due to wear V_m was then calculated using the following formula according to ASTM G99-05:

$$V_m = 2\pi R[r^2 \sin^{-1}(d/2r) - (d/4)(4r^2 - d^2)^{1/2}] \quad (1)$$

where R is the wear track depth radius in mm (2.0 mm in this case), d is the wear track width in mm, and r is the pin end radius in mm (1.6 mm in this case).

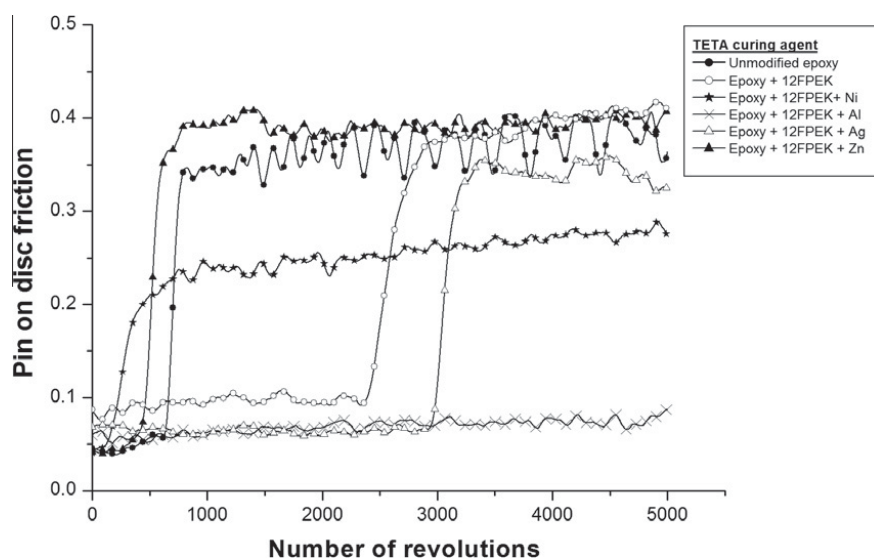


Fig. 2. Pin-on-disc friction vs. number of revolutions of samples cured with TETA.

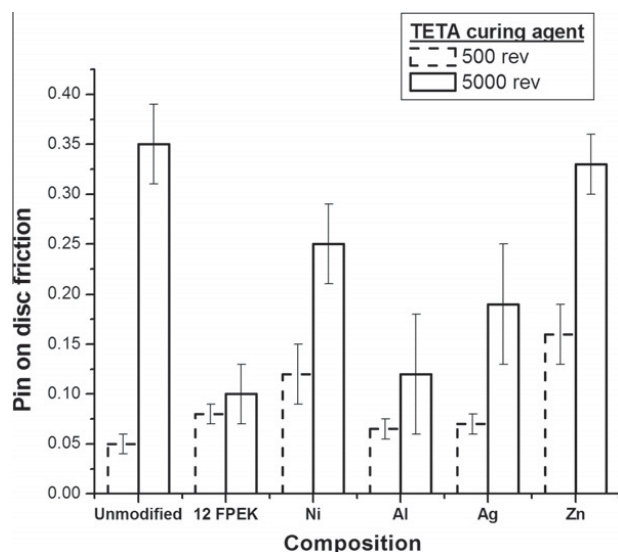


Fig. 3. Pin-on-disc friction after 500 and 5000 revolutions of samples with TETA.

Wear rate (Z) was then calculated using:

$$Z = V_m / WX \quad (2)$$

where W is load in N and X is the sliding distance in m .

2.5. Determination of contact angle and surface energy

In order to determine the surface energies of the samples, first contact angles were determined using sessile drop technique. A Ramé–Hart Instrument Co. goniometer was used for this purpose. A polar liquid (water) and an apolar liquid (diiodomethane) were used as testing liquids [18]. Surface tension values at 20 °C of water and diiodomethane are 72.80 mN/m and 50.80 mN/m respectively. The mean of five contact angles for each sample was calculated.

The Ramé–Hart goniometer which was used for calculating contact angles was used for determining surface energies of the coatings as well. The surface energy values were calculated from the contact angles using the harmonic-mean method [34]:

$$(1 + \cos \theta_1) \gamma_1 = 4 \{ [(\gamma_1^d \gamma_s^d) / (\gamma_1^d + \gamma_s^d)] + [(\gamma_1^p \gamma_s^p) / (\gamma_1^p + \gamma_s^p)] \} \quad (3)$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \{ [(\gamma_2^d \gamma_s^d) / (\gamma_2^d + \gamma_s^d)] + [(\gamma_2^p \gamma_s^p) / (\gamma_2^p + \gamma_s^p)] \} \quad (4)$$

where θ_1 and θ_2 are contact angles made by liquids 1 and 2 on the solid respectively, γ_1 and γ_2 are surface tensions, γ_1^d and γ_2^d are dispersion components of surface tensions of liquids, γ_s^d are dispersion components of surface energy of solid, γ_1^p and γ_2^p are polar components of surface tension while γ_s^p is the polar component of surface energy of solid.

2.6. Surface analysis of coating

Surface composition of the coatings was determined using a Nicolet 6700 Spectrometer with Smart Horizontal ATR micro-sampling accessory from Thermo Electron with 4 cm^{-1} resolution. ATR spectra were collected in the range 800–4000 cm^{-1} . The area of the sample to be measured was selected visually and the spring-loaded ATR element was lowered to make contact with the surface of the sample.

2.7. Metal powder analysis

In order to determine the existence of any secondary phases in the metal powders (as they were used in their pure form) XRD was carried out for all the four metal powders (Ni, Al, Ag, and Zn). This was done using a Rigaku Ultima III High-Resolution XRD. Cu $K\alpha$ radiation of wavelength 0.154 nm was used. Additional acquisition parameters were: 2θ range = 20° – 90° and scan rate = 2° -

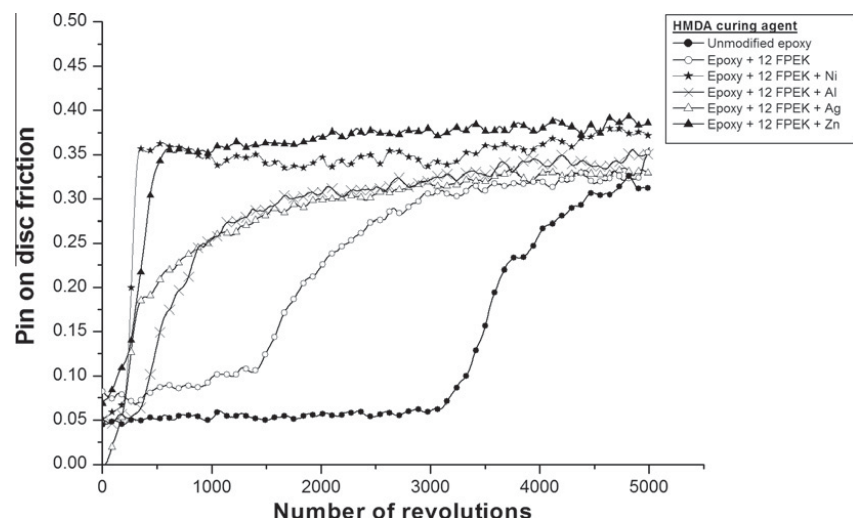


Fig. 4. Pin-on-disc friction vs. number of revolutions of samples cured at 80 °C.

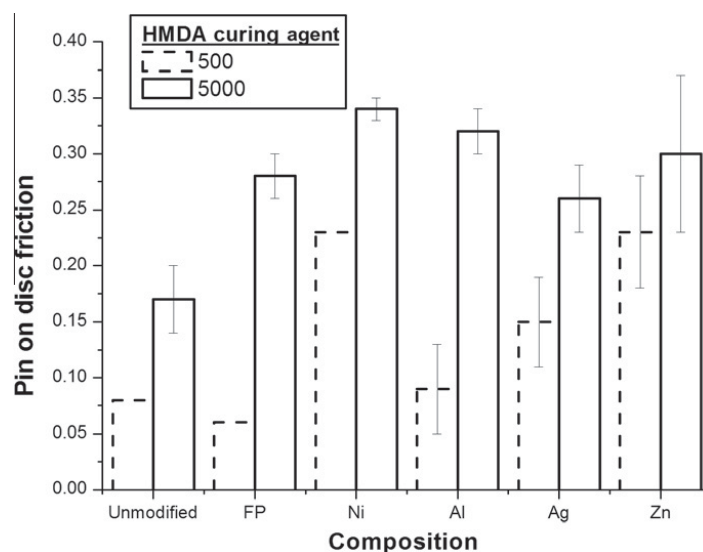


Fig. 5. Pin-on-disc friction after 500 and 5000 revolutions of samples cured at 80 °C.

min^{-1} . Diffraction patterns were referenced against the JCPDS database for sample identification.

3. Results and discussion

3.1. Metal powder characterization

3.1.1. Composition

Since the coatings were prepared in laboratory atmosphere, there was a chance of formation of a new secondary phase within the metal powders like a metal oxide phase which would affect the tribological properties of the final coating. Hence it was pertinent to analyze the composition of the metal powders to determine the existing phases. Diffraction patterns of Ni, Al, and Ag powders did not show traces of any secondary phases but the diffraction pattern of Zn powder shows some peaks related to ZnO phase (Figs. 1a–1d).

3.2. Pin-on-disc friction

Friction increased as the number of revolutions increased from 500 to 5000 irrespective of the curing temperature. To explain this, let us consider the set of samples with TETA curing agent cured at 30 °C. The friction of most of the coatings (except for the epoxy + FPEK + Ni sample) cured at 30 °C was constant up to 500 revolutions. After 500 revolutions the coating on the testing surface got worn out completely and the pin touched the steel substrate; at this point there occurs a sharp increase in friction (Fig. 2) resulting in an increase in friction – continuing up to 5000 revolutions. However, the epoxy + FPEK + Al sample did not get worn even after 5000 revolutions (Fig. 3). Also, friction decreased with the addition of FPEK to the epoxy; during slow curing the FPEK migrates to the free surface since the surface energy of the fluoropolymer is lower than that of pure epoxy [16]. The second set consists

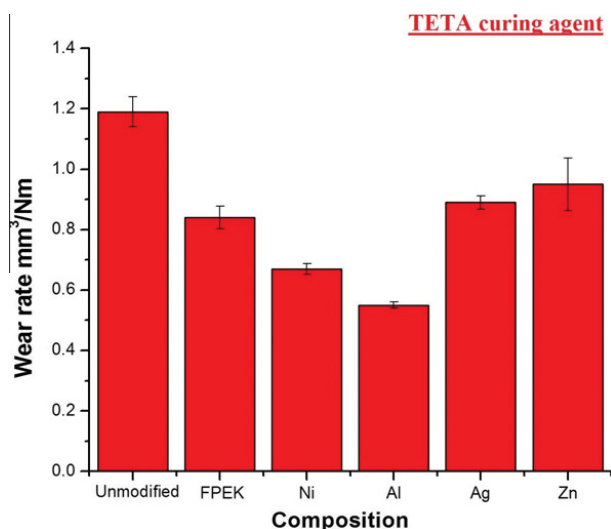


Fig. 6. Z of samples with TETA cured at 30 °C.

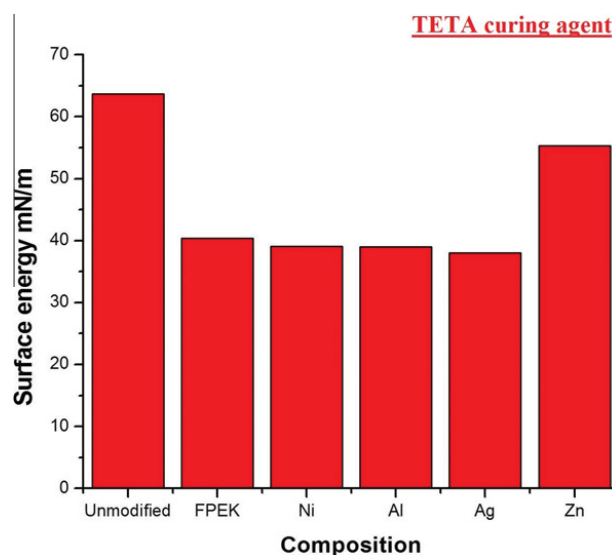


Fig. 8. Surface energies of samples with TETA cured at 30 °C.

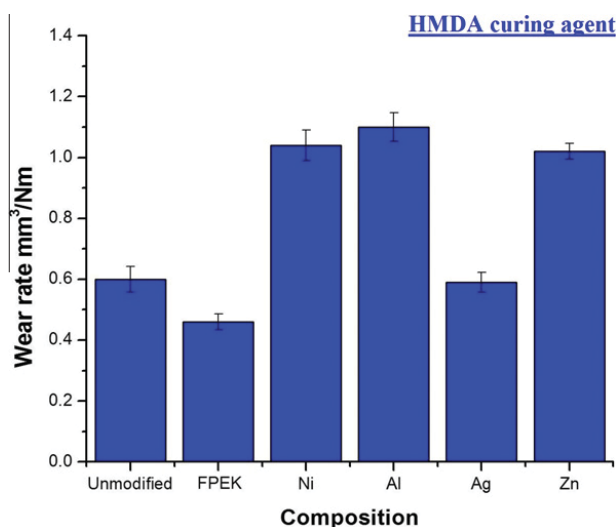


Fig. 7. Z of the samples with HMDA cured at 80 °C.

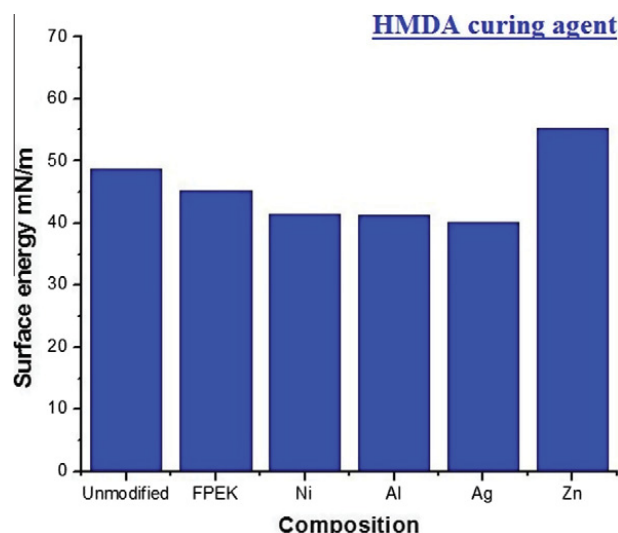


Fig. 9. Surface energies of samples with HMDA cured at 80 °C.

of samples with HMDA post-cured at 80 °C. In this case only the unmodified epoxy sample and the epoxy + FPEK sample got worn out after 500 revolutions. All other samples got worn out before 500 revolutions – the reason for lower friction of the unmodified epoxy sample and the epoxy + FPEK sample compared to other materials (Figs. 4 and 5). This can be explained by the following hypothesis: at high temperatures the crosslinking reaction competes with phase separation and is favored over the latter – resulting in a mixture of epoxy and FPEK phases at the free surface. Samples containing Zn show high friction in both cases – clearly because of the presence of ZnO phase along with Zn phase. Also the morphology of the Zn and ZnO particles is responsible for high friction. Samples containing Al show the least friction when compared to other metal powder containing nanocomposites. This can be explained by spherical morphology of Al particles which results in rolling friction.

3.3. Wear

Wear results are presented in Figs. 6 and 7, respectively for TETA and HMDA curing agents.

For the samples with TETA we find that Z decreases with the addition of FPEK and metal powders. We note that epoxy and FPEK are softer phases while each metallic phase is relatively harder. Samples containing Ni, Ag, and Zn show higher Z values than Al-containing nanohybrids because of the already mentioned spherical morphology of Al. In the materials containing the remaining metal powders, there exists stresses at the interfaces of the particles because of irregular morphologies and hence higher Z values. We recall a discussion by Kopczynska and Ehrenstein of the importance of interfaces for composite properties [35]. We also note that connections between various tribological properties can be pursued [36] while the popular

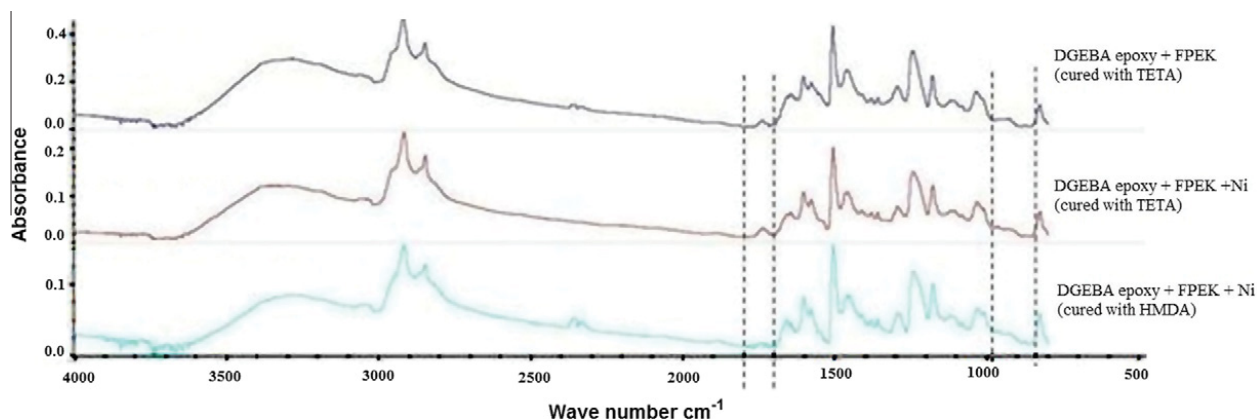


Fig. 10. ATR graph of three samples with epoxy + FPEK + Ni cured at different curing temperatures compared with the epoxy + FPEK sample.

assumption “higher friction means more wear” is by no means generally valid.

In the case of samples with HMDA, since the crosslinking reaction is favored, these systems tend to show higher *Z* values upon addition of the metal powders. The high *Z* of sample containing Zn can be related to the same fact of existence of ZnO phase. Samples containing Ni and Al show high *Z* values when cured at 80 °C. The test surface of the coating gets worn out as early as ≈ 250 revolutions in the case of the sample containing Ni and before 1000 revolutions in the case of sample containing Al (Fig. 4).

3.4. Surface energy

Fluorine-containing polymers have low surface free energy, low tendency for water uptake, and high water repellence [15,18,34,37,38]. Therefore, the addition of FPEK to the epoxy should decrease the surface energy significantly. We find that the expected trend is followed; see Figs. 8 and 9. The decrease in surface energy is smaller at the higher curing temperature. The reason is the same as discussed above: as the curing temperature increases, the phase separation process is less pronounced. Therefore, in the case of curing at 30 °C, the FPEK phase is present at the entire free surface. Hence a steep decrease in surface energy. When curing at 80 °C, less fluoropolymer reaches the surface since more of it is trapped by the crosslinking on its way to the surface. In both the cases, the sample containing Zn shows high surface energy consistent with its high friction.

3.5. FTIR-ATR measurements

Three samples: epoxy + FPEK (cured at 30 °C) and epoxy + FPEK + Ni (cured at 30 and 80 °C) were tested for surface composition using FTIR-ATR to analyze the phases present at the surface when cured at different temperatures. The results are presented in Fig. 10. Since characteristic absorbance literature for FPEK was not available, it was pertinent to obtain the ATR for the FPEK sample and then compare the results of the rest of the samples with the FPEK sample to detect what phases were present at the surface of the samples after curing.

There are few new bands which appear when the curing temperature increases. The band at $\sim 1750\text{ cm}^{-1}$ refers to carbonyl group [39] and such a group is present only in FPEK among the materials used. Thus, this band represents the FPEK phase. The band slowly disappears as the temperature increases – what means that the fluoropolymer phase amount is slowly decreasing at the surface as the temperature increases. At the same time, there are new characteristic bands forming between 820 and 980 cm^{-1} as the curing temperature increases; they correspond to the DGEBA epoxy [40]. Apparently, as the temperature increases, there is a mixture of FPEK and epoxy phases that coexist at the free surface. This supports the increasing trend of surface energy and friction with increasing curing temperature. The bands at 3300 and $2900\text{--}3050\text{ cm}^{-1}$ correspond to the hydroxyl and C–H groups of DGEBA. There is no change in these peaks in all the four systems corresponding to the presence of DGEBA present near the surface [41].

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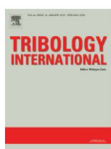
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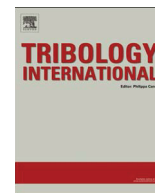
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APPENDIX KUMAR02



Tribological studies of epoxy composites with solid and liquid fillers



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ABSTRACT

Epoxy-based composites are promising tribological coatings. The tribological properties of epoxy composites with filler materials such as graphene, graphite, and liquid lubricants (base-oil SN150 and perfluoropolyether) are studied. The composite coatings were applied on cylindrical steel surface and a steel ball was used as the counterface. Tests were conducted at 10 N normal load and 0.63 m/s linear sliding speed. Among all coatings, epoxy filled with graphene and SN150 lubricant provided the lowest coefficient of friction of 0.09 with wear cycles exceeding 200,000 and specific wear rate of $5.4 \times 10^{-7} \text{ mm}^3/\text{N-m}$. Speed effects on friction were also evaluated.

1. Introduction

Presently, there is a trend towards using lubricants without any additives (such as friction modifiers) that are harmful to the environment. Metals, such as steel, wear heavily if only base lubricant oil is used specially in boundary lubrication regime. Polymer-based coatings have been applied on steel surfaces which work well in both dry and base oil lubricated conditions [1]. Machine components can be protected by such tribological coatings. A suitable polymer coating provides low coefficient of friction (CoF), low wear and very good adhesion properties with many substrates [2]. There are many polymers such as epoxy, SU-8 (an epoxy-based polymer), PEEK, UHMWPE, PTFE, etc. which have been used as coatings to improve the tribological performances of solid surfaces [2–4]. They can work like an effective boundary lubricant, thus protecting the steel surfaces.

Epoxy resin is a thermoset polymer having a number of well-known advantages including high toughness and strength, adhesion, durability at low and high temperatures and thermal stability, high chemical resistance, low shrinkage and ease of fabrication [5–8]. Epoxy resins are widely used in applications ranging from electric and electronic systems to automotive parts, aircraft components, biocompatible implants, protective coatings, and adhesives [5]. Normally, epoxy is a poor tribological material. However, addition of suitable fillers such as graphene and liquid lubricants (such as base oil SN150) can enhance its performance with low coefficient of friction and high wear life [1]. Such kind of tribological bearing materials (with liquid fillers) successfully operates in the boundary to mixed lubrication regimes. Hence, a literature review on this type of lubrication and associated analysis are presented below.

Different micro/nano-filler have been added in epoxy and other polymers for tribological performance enhancement. Microencapsulated lubricant (70SN) was incorporated in epoxy by Guo et al. [9]. The results showed that at 10 wt% of the microcapsules the coefficient of friction was reduced from 0.56 to 0.14 and there was a reduction in the specific wear rate by two orders of magnitude. However, mechanically, the composite was weaker (flexural strength) by half at 10 wt% of the filler compared with the base polymer and also there was a tendency for the coefficient of friction and wear to increase beyond the optimum 10 wt% filler content. Similar work has also been reported by Khun et al. [10]. Sarvanan et al. [11] have used perfluoropolyether (PFPE) lubricant in the form of micro/nano sized droplets in SU-8 matrix reducing the steady-state coefficients of friction by ~6 times, and increasing the wear life by more than 10^4 times. It was shown that liquid lubricant-filled SU-8 provides lubrication by the mechanism of physical boundary layer. The friction and wear performances are largely unaffected by load, however, there is a limiting maximum speed beyond which physical boundary layer may become ineffective.

Surface modification by developing polymer brushes of alkyl methacrylates with hexyl, octadecyl and dodecyl side chain on silica and iron surfaces were carried out by Bielecki et al. [12]. The Stribeck curves were plotted for hexadecane, toluene and ethanol as lubricants between the polymer brushes which showed very low friction coefficient (~0.01) at low speed (0.1 m/s) which increased with speed. The study concluded that the increase in viscosity causes gradual increment of shear stress at the interface.

Sophie et al. have found that for monolayers of additives and friction modifiers, the coefficient of friction increases with velocity

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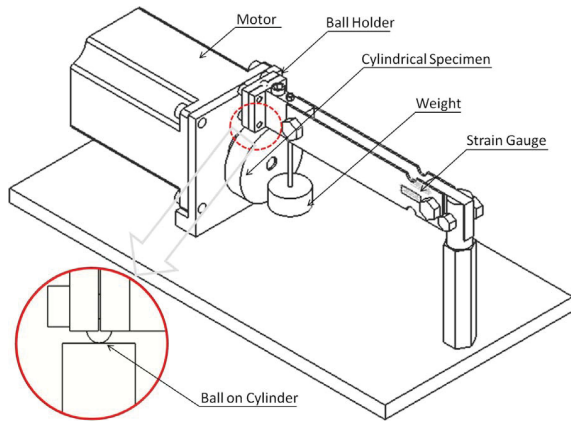
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Table 1

Tensile properties and Vicker's hardness data for pure epoxy and its composites. All fillers, graphene, graphite, SN150 and PFPE were in concentration of 10 wt% in each case.

Material	Epoxy			Epoxy/Graphene		Epoxy/Graphite	
Liquid filler material	none	PFPE	SN150	PFPE	SN150	PFPE	SN150
Young modulus GPa	0.815	0.687	0.716	0.832	0.848	0.755	0.838
Tensile strength MPa	40	40.571	41.53	38.331	43.96	28.903	32.64
Hardness MPa	215	134.1	132.3	204.3	157.4	144.6	141.8

**Fig. 1.** Schematic diagram of the ball-on-cylinder tribometer.

under boundary lubrication regime [13]. They observed that the saturated friction modifiers (such as stearic acid), which are adsorbed on the surface in orderly closed-packed configuration, show low friction whereas the unsaturated friction modifiers (such as oleic acid and elaidic acid) exhibit high friction due to not closely-packed monolayer.

The frictional behavior of automotive transmission fluids for wet clutch in which regimes of boundary lubrication occur over the complete sliding velocity range, was studied by Ingram et al. [14]. Friction modifiers and additives (such as 12-hydroxystearic acid, C18-acid and C18-amine) provide low friction at low velocities (less than 0.01 m/s), and friction increases with speed. They also reported that the functional polar groups such as –OH and –COOH displayed a trend of a rapid increase in friction with increasing speed and at high speeds there is certain fall due to insufficient time to return to their original state of bonding between friction modifiers and the pad surface.

The frictional behavior of silica surfaces with and without adsorbed brush like copolymer of poly (L-lysine)-*graft*-poly (ethylene glycol) (PLL-*g*-PEG) and poly (L-lysine)-*graft*-dextran (PLL-*g*-dextran) in aqueous solution were studied as a function of shear viscosity by Prathima et al. [15] with the help of colloidal-probe lateral force microscopy. Nano-scale Stribeck curves were obtained for bare silica in selected solvents which described the effect of solvent viscosity on measured frictional force. Under the boundary lubrication regime, the adsorbed hydrated ions acted as a surface-solvating thin film, preventing direct physical contact. It was also found that polymer brushes reduce the friction for a specific solvent mixture. Further, solvated polymer brushes shift the hydrodynamic lubrication regime to the left towards smaller values of the product, sliding speed $\times$ viscosity ($U\eta$).

In the boundary lubrication regime (i.e. low value of Sommerfeld number), the lubricant film thickness is lower than the surface roughness, and the coefficient of friction lies between 0.08 and 0.12. The coefficient of friction was found to be independent of normal load [16]. The lubrication regime of ball bearings and gears were found to be in the elasto-hydrodynamic lubrication regime only at high and moderate speeds and fluid film thickness gives a trend with $(U\eta)^{0.7}$. In this regime of lubrication, the coefficient of friction lies between 0.02 and

0.10, and it is independent of viscosity and depends upon molecular structure of the lubricant [17].

Earlier study has shown that in the *in situ* lubrication case, there is strong dependence of coefficient of friction on the sliding speed but there is minimum effect of the normal load within a range [18]. The *in situ* lubrication is indeed a case of mixed lubrication for which two analyses have been provided. Albertson [16] proposed that for the lubricants with additives, the boundary film formation is a diffusion controlled phenomenon (based on Eyring's rate of diffusion [19]) and hence the coefficient of friction will depend upon the sliding speed.

It was presented by Sophie et al. [13] that in the boundary and mixed lubrication regimes the interfacial shear stress is a function of the sliding speed. The analysis uses the Eyring [19] equation for activated slip model. It is based on the principle that when one layer of molecules slips over another, there is an activation energy needed for this slip to overcome the energy barrier. The values are different in forward and backward directions. The rates of slip depend upon the applied shear stress and the thermal fluctuations. Using this approach they have shown that the net velocity for slip is an exponential function of the shear stress. Thus, upon taking logarithm on both sides, the following relation is obtained [13,18],

$$\tau = (kT/\phi) \ln \left(\frac{v}{v_0} \right) + \frac{1}{\phi} (E + P\Omega) \quad (1)$$

where τ is the shear stress, v is the relative velocity, v_0 is a reference velocity, ϕ is the shear activated volume, Ω is the pressure activation volume, T is the absolute temperature, k is the Boltzmann constant, E is the activation energy and P is the hydrostatic pressure. The full derivation of Eq. (1) is given in Ref. [13].

Thus, the relation between v and τ can be given as follows;

$$\tau = \tau_1 + \theta \ln(v) \quad (2)$$

where,

$$\tau_1 = \frac{1}{\phi} (E + P\Omega - kT \ln(v_0)); \quad \theta = \frac{kT}{\phi};$$

where τ_1 and θ are constants for the given boundary layer. The coefficient of friction is very much influenced by interfacial shear strength [18]. Eq. (2) was also derived by Briscoe and Evans [20] which also described the experimental data for monolayers very well. If it is assume that for a fixed applied load, the contact area and thus the pressure is constant, Eq. (2) can be re-written for the boundary friction as,

$$\mu_b = a + a_1 \ln v \quad (3)$$

where a and a_1 are constants for a set of load and temperature.

For the boundary lubrication by mono and multilayers of carboxylic acid, Briscoe and Evans [20] also proposed the relations for shear stress as functions of constant pressure, P , and temperature, T , which are given as;

$$\tau = \tau_2 + \alpha P \quad (\text{At constant temperature and velocity}) \quad (4)$$

$$\tau = \tau_3 - \beta T \quad (\text{At constant pressure and velocity}) \quad (5)$$

where α , β , τ_2 , τ_3 are constants for a given lubricant.

The wear and lubrication mechanisms of SU-8 filled with PFPE (Z-

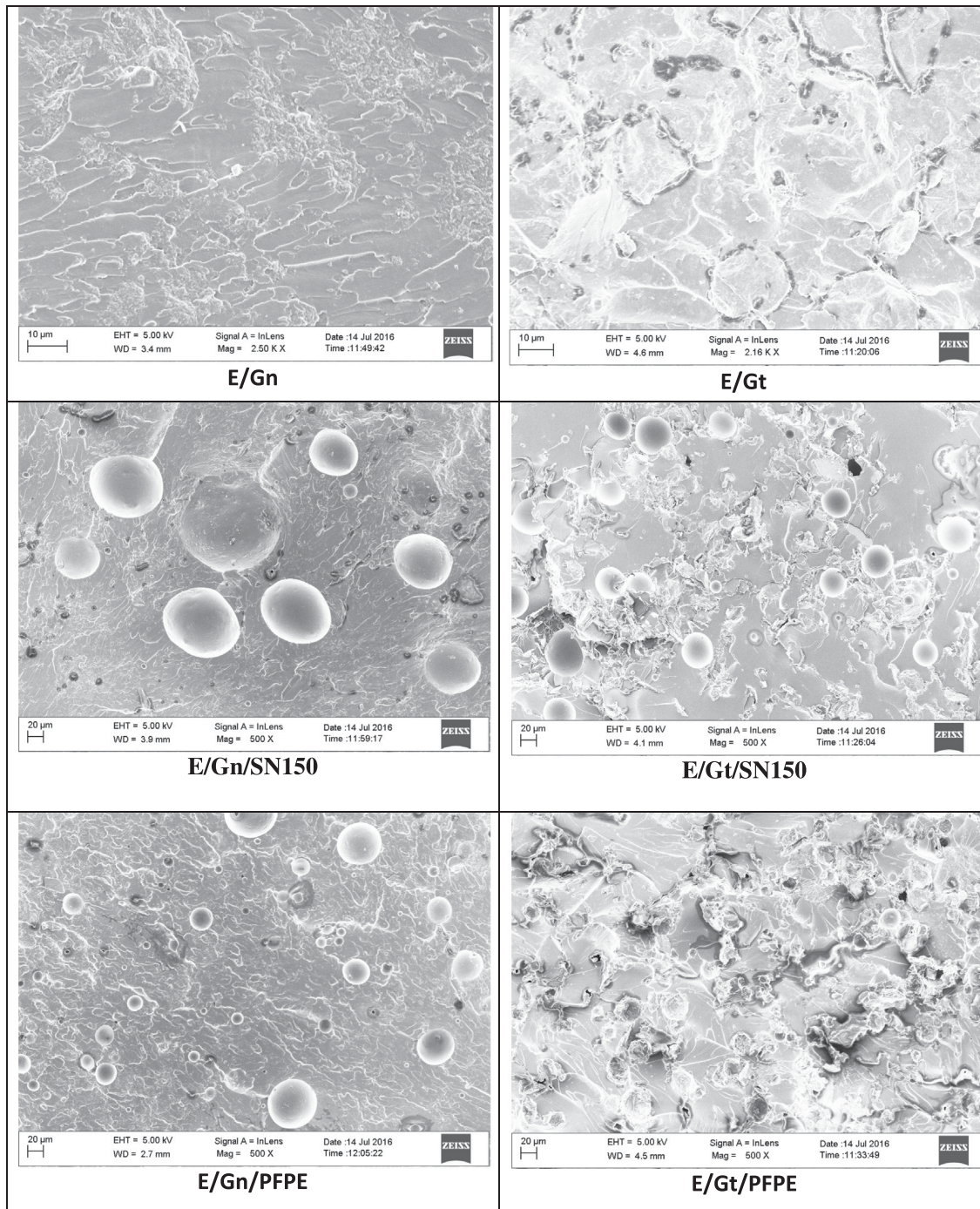


Fig. 2. FESEM images of the cross-sections of the coatings.

dol) droplet were investigated by Saravanan et al. [18] under different regimes of lubrication. The lubrication mechanism was explained by studying the variation of coefficient of friction with the sliding velocity trends by dividing it in three zones.

From the above literature survey, it can be concluded that there is a strong dependence of the CoF on the speed, whereas CoF is mostly independent of normal load. The mixed lubrication is a possible mechanism of lubrication for liquid-filled polymer coatings where lubrication is continuously provided *in situ*. In the present study, we will compare the CoF with respect to speed and normal load for the epoxy composites filled with two solids (graphene and graphite) and two liquid (SN150 and PFPE) lubricants.

2. Experimental procedure

2.1. Materials

Epoxy and its composites filled with liquid lubricants (SN150 or PFPE) and graphene or graphite particles were coated onto D2 tool steel cylindrical shaft (diameter = 40 mm). The thickness of the coating was in the range of 50–60 μm. Base-oil SN150 (Indian Oil Corporation Limited Faridabad India) of Group-I with viscosity 24.25 cP (at 40 °C) and PFPE (commercial name Fomblin Y, supplied by Sigma Aldrich, India) with viscosity of 43.38 cP (at 40 °C) were used. Graphene with particle sizes < 100 nm was supplied by Reinste Nano Ventures Pvt

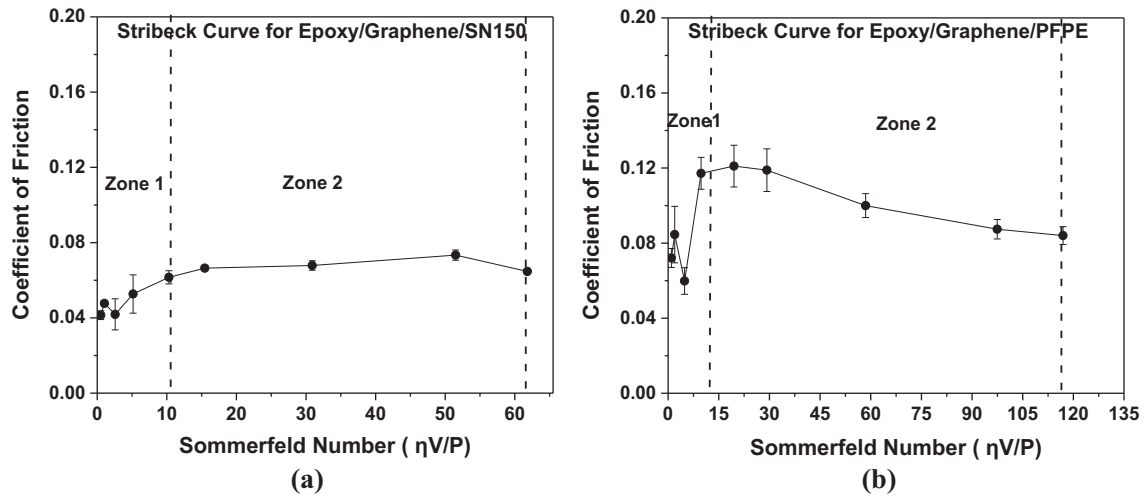


Fig. 3. Stribeck curve for (a) epoxy/10 wt% graphene/10 wt% SN150 and (b) epoxy/10 wt% graphene/10 wt% PFPE composite tested at a normal load of 10 N for a fixed 5000 sliding cycles. Zone 1 and Zone 2 are two regimes with different frictional behaviors. Zone 1: CoF increases steeply with Sommerfeld number (a) 0–11 and (b) 0–19. Zone 2: CoF increases marginally for (a) 11–52 and decreases marginally for (b) 19–119.

Ltd, India, and graphite with particle sizes < 20 μm was purchased from Sigma Aldrich, India. The epoxy used was Araldite AY 103 with hardener HY 951, supplied by Huntsman Advanced Material Pvt. Ltd. Steel ball (SAE 52100 with hardness of 58 HRC) of 4 mm diameter and roughness 50 nm was used as counterface for all tribological tests.

2.2. Sample preparation

D2 tool steel cylindrical specimen of diameter ~40 mm and width ~12 mm was prepared by turning and then grinding the surface till the roughness of $R_a \sim 0.40 \mu\text{m}$. The surface was cleaned with acetone, air-dried and treated with air plasma [1]. Air plasma cleaning was carried out on steel surface to remove any organic impurity and to generate hydroxyl groups on the substrate which increase the adhesion of the coating to the substrate. The filler materials were added into liquid monomer epoxy and stirred thoroughly using ultrasonication. After this, the hardener was mixed and the air bubbles were removed by exposing the mixture to vacuum. Four different types of composites were prepared:

- Epoxy/graphene (10 wt%)/SN150 (10 wt%) (named as E/Gn/SN150).
- Epoxy/graphene (10 wt%)/PFPE (10 wt%) (named as E/Gn/PFPE).
- Epoxy/graphite (10 wt%)/SN150 (10 wt%) (named as E/Gt/SN150).
- Epoxy/graphite (10 wt%)/PFPE (10 wt%) (named as E/Gt/PFPE).

The steel surfaces were coated with epoxy composites by a lab-fabricated 'dip and rotate' coating machine and then by rotating the coated shaft at 100 rpm for 4 h in order to distribute the epoxy composite uniformly over the shaft while it air-cured. The coatings were cured initially at room temperature for 16 h followed by thermal curing at 80 $^{\circ}\text{C}$ for 4 h. The final coating thickness varied between ~50 and 60 μm . The samples were then stored in a desiccator before any further use.

2.3. Material characterization of epoxy composites

Mechanical properties such as tensile strength and modulus of elasticity of the polymer composites were measured using tensile tests and the hardness was measured by Vickers hardness tester.

2.3.1. Tensile strength and modulus of elasticity

ASTM standard D638 test samples were prepared by casting in a mould of dimensions 3 mm $\times$ 3.9 mm cross-section with a gauge length of 10 mm [1]. The curing process followed was same as explained for the coating on the steel shaft. Tensile tests of composites were performed using a universal testing machine with a cross-head speed of 0.1 mm/min. The moduli of elasticity and tensile strengths of epoxy composites filled with liquid lubricants and graphene or graphite particles are given in Table 1. Each datum represents an average of three repeated tests. These observations show that there is some decrement in the tensile strength on adding graphite with liquid filler whereas with graphene there is an increment by ~10%. The modulus of elasticity is increased for both graphene and graphite additions. However, this increase in the elastic modulus is more for graphene than for graphite. In general, graphene is more effective in improving the mechanical properties of epoxy which indicates better bonding between the two because of smaller size of the graphene particles.

2.3.2. Hardness

Hardness of the composites was evaluated by Vickers hardness tester [1]. The hardness values of different composites are also presented in Table 1. The data reported are averages of ten measured values on at least two different specimens.

2.4. Tribological test

Friction and wear tests were performed using lab-fabricated ball-on-cylinder tribometer setup (Fig. 1). Photo of the experimental set-up was shown in our earlier publication [1]. The polymeric coatings were coated on the cylinder outer surface. The ball used was bearing steel (SAE 52100) of diameter 4 mm. The tests were conducted at the normal load of 10 N and at different rotational speeds of 10, 20, 50, 100, 200, 300, 600, 1000 and 1200 rpm. The linear sliding speed range was varied from 0.021 m/s to 2.5 m/s. In order to understand the load effect, the tests were also performed at a speed of 0.63 m/s and three different normal loads (3, 6 and 10 N). All tests were conducted at room temperature (25 ± 2 $^{\circ}\text{C}$) and relative humidity of $45 \pm 5\%$. The steady-state coefficient of friction (CoF) was estimated by taking average of the last 1000 values before coating failed. Sommerfeld

number ($\eta V/P$) was also calculated in order to plot the Stribeck curve for two composites which are epoxy/graphene/SN150 and epoxy/graphene/PFPE. In order to calculate the volumetric wear rate, the wear track width and depth profiles were measured by using 3D optical profiler (Contour GTK, Bruker, USA). Images of worn surfaces on the cylindrical and ball surfaces were taken by optical microscope.

2.5. Surface characterization of epoxy composites

2.5.1. Optical and scanning electron microscopy

The worn surfaces of specimen sample and ball were observed by Digital Microscope (Dino-lite, Kontrelek Instruments, India) to analyze the wear behavior of each sample. This is a portable type microscope with 270–480 X magnification. The images of tested ball were also analyzed by Confocal Microscope. Field Emission Scanning Electron Microscopy (FESEM) was carried out on EIGMA, Zeiss, USA FESEM machine. The samples were gold coated using a sputter coater (SC7620-CF, Quorum Laughton Lewes) prior to FESEM imaging. SEM images of the cross-sections of the four composites E/Gn/SN150, E/Gn/PFPE, E/Gt/SN150 and E/Gt/SN150 are shown in Fig. 2. It is seen in these images that the volume of SN150 is much larger than that of PFPE. Also, between graphene and graphite based composites, the lubricant droplets are larger and more in volume in the case of graphene than in the case of graphite presence. These differences will be discussed in later sections.

2.5.2. 3D optical profiler analysis

3D optical profiler (Contour GTK, Bruker, USA) was used for wear track profile measurements. The cross-sectional area of the wear track was calculated by integrating the width and depth profiles which was then multiplied by the total track length to obtain the wear volume. The specific wear rate (W_{sp}) was calculated using the following relation [8],

$$W_{sp} = \frac{V}{LD} \text{ mm}^3/\text{N m}, \quad (6)$$

where V is the wear volume, L is the normal load and D is the total sliding distance.

2.5.3. Atomic force microscopy

Atomic force microscope (XE7, Park System, South Korea) was used for the surface topography of the epoxy composites. The AFM imaging of the specimen surfaces and the wear tracks was carried out to understand material surface topography before and after the wear process.

3. Results and discussion

3.1. Friction results and stribeck curve

Fig. 3 presents the steady-state coefficient of friction (CoF) values versus Sommerfeld number for the epoxy/graphene composites with (a) 10 wt% SN150 and (b) 10 wt% PFPE. The Sommerfeld number was calculated as $\eta v/P$, where η is the viscosity of the liquid filler, v is the sliding speed in m/s and P is the normal load (10 N). The coefficient of friction was inspected for a fixed 5000 sliding cycles for different Sommerfeld numbers. The plot is divided into two different zones based on their frictional behavior with respect to the Sommerfeld number, Zone 1 and Zone 2, which represent an abrupt change in the coefficient of friction as the Sommerfeld number increases. In Zone 1, the coefficient of friction increased very steeply from 0.04 to 0.06, while in zone 2, it was nearly constant (0.06–0.07) for SN150. In the case of PFPE, the CoF in Zone 1 increases from 0.06 to 0.12 and in Zone 2 decreases from 0.12 to 0.10. The mechanisms responsible for frictional

behavior in Zone 1 and 2 are explained in the next section.

Table 2 presents optical images of coating worn surfaces and the ball surfaces. These images show less amount of lubricant transfer onto the ball in Zone 1. In Zone 2, there is less lubricant on the ball and the composite surface ($v=0.63$ m/s). However, at $v=2.51$ m/s the amount of lubricant increases at the interface. This somewhat correlates with the CoF which stabilizes at higher sliding speed or reduces marginally.

3.1.1. Zone 1 mechanism

In Zone 1, the coefficient of friction rises sharply as the Sommerfeld number is increased. This rise is in contrast to the typical Stribeck curve in which the CoF decreases in value as Sommerfeld number is increased.

A schematic of the coating cross-section with the bonded and mobile lubricant is shown in Fig. 4. There is presence of lubricant liquid droplets in the bulk and at the sliding surface; there is mobile lubricant presence due to the opening up of those droplets. In the beginning of the sliding process, the bonded and mobile lubricant molecules present on the surface provide sufficient lubrication [12,15], keeping the CoF in the range of 0.042. The trapped droplets of the lubricant are quickly released in the beginning of the sliding process which maintains low shear stress at the interface. The low CoF condition is maintained for 5000 cycles and above because of the *in-situ* supply of lubricant.

It is seen that with increase of sliding velocity, lubricant displacement increases from contact point. At low sliding speed, a balance is maintained between the displacements of lubricant from the wear track and re-flow. But at higher speed, the displaced lubricant is not quickly available on the wear track due to insufficient time leading to lubricant starvation [16]. The repeated movement of lubricant from wear track causes asperity contact, and the coefficient of friction increases, which leads to wear. The images of the counterface ball after wear test and the worn surfaces also support the proposed mechanism for displaced lubricant as given in Table 2. The images of the counterface ball show the presence of lubricant on their surfaces which initially increases with increase of speed and also some amount of wear debris is present on the ball surface.

3.1.2. Zone 2 mechanism

Zone 2 shows a mechanism where lubricant is mixed with the wear debris in the form of slurry. The slurry effectively provides lubrication. The CoF is maintained at constant value of approximately 0.07–0.08 for SN150 filled composites. The CoF decreases from 0.12 to 0.09 for the PFPE-filled composites as the Sommerfeld number is increased from 15 to 120.

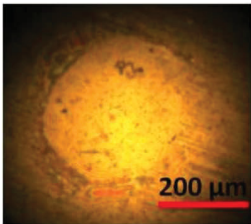
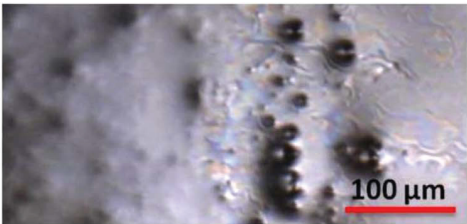
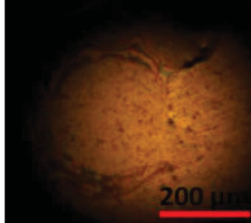
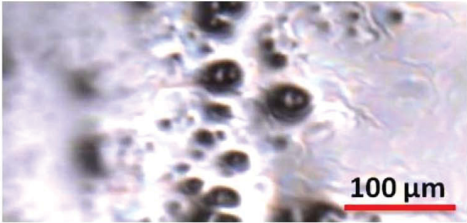
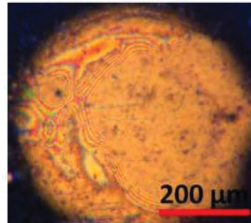
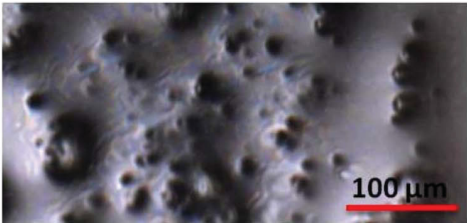
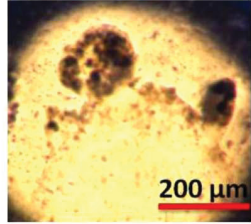
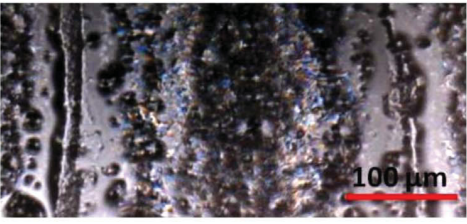
These observations clearly show that there is strong influence of the *in-situ* lubricant present in the matrix of epoxy. The lubrication regime is that of mixed lubrication type where both liquid and solid interactions play their parts. It is seen that for liquid-filled composites, the slurry of lubricant and initial wear debris also play an important role in maintaining low CoF at high speed. In fact CoF decreases for epoxy/graphene/PFPE when the Sommerfeld Number is increased (Fig. 3(b)).

3.2. Effects of speed on the coefficient of friction

As the liquid filler (SN150 and PFPE) is added in epoxy composites (epoxy/graphene and epoxy/graphite) the coefficient of friction goes down drastically and load bearing capacity also increases. Fig. 5(a) and (b) presents the coefficient of friction versus sliding velocity for epoxy/graphene composite with the liquid fillers SN150 and PFPE, respectively, for three different loads. From Fig. 5(a) it is observed that the variation of coefficient of friction with sliding velocity is nearly same at the loads of 3 N, 10 N and 12 N. At lower speed, the coefficient of friction is low (0.04–0.06) and increases steeply with velocity up to

Table 2

Optical images of the ball contact surface and the corresponding wear tracks for epoxy/graphene (10 wt%)/SN150 (10 wt%) composite coating at the steady-state of the sliding process. They are typical examples of the interfaces in Zone 1 and Zone 2 regimes. Scales are provided in each image.

Speed (m/s)	CoF	Ball Images	Worn Surfaces
Zone 1 0.02	0.042		
	0.062		
Zone 2			
0.63	.066		
2.51	0.065		

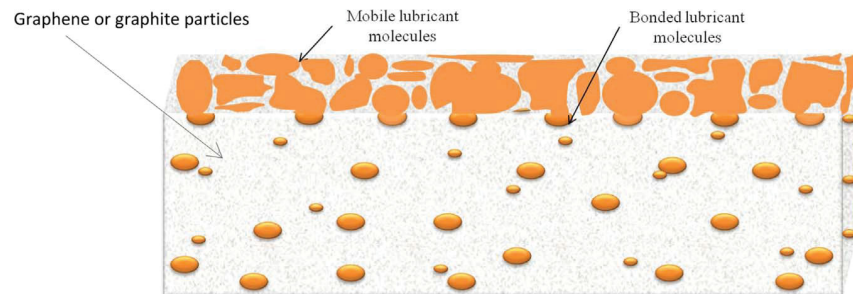


Fig. 4. Possible sequence of lubrication mechanisms at the ball-surface interface during tribological test and lubricant distribution in composite.

0.42 m/s and then becomes nearly constant ($\text{CoF} \sim .09$) in the velocity range of 0.42 m/s–2.51 m/s for all composites. The epoxy composites filled with SN150 shows lower coefficients of friction (0.04–0.1) as compared to those for PFPE (CoF 0.06–0.17). In Fig. 5(b), the variation of the coefficient of friction at different loads (3 N, 10 N

and 12 N) shows same behavior with velocity but has very different coefficients of friction. At 10 N normal load, the coefficient of friction for epoxy/graphene/PFPE shows the lowest value (0.06–0.11) whereas at other loads the values are much higher. For PFPE, in general for all loads, slight reduction in the CoF at high speeds is observed. However,

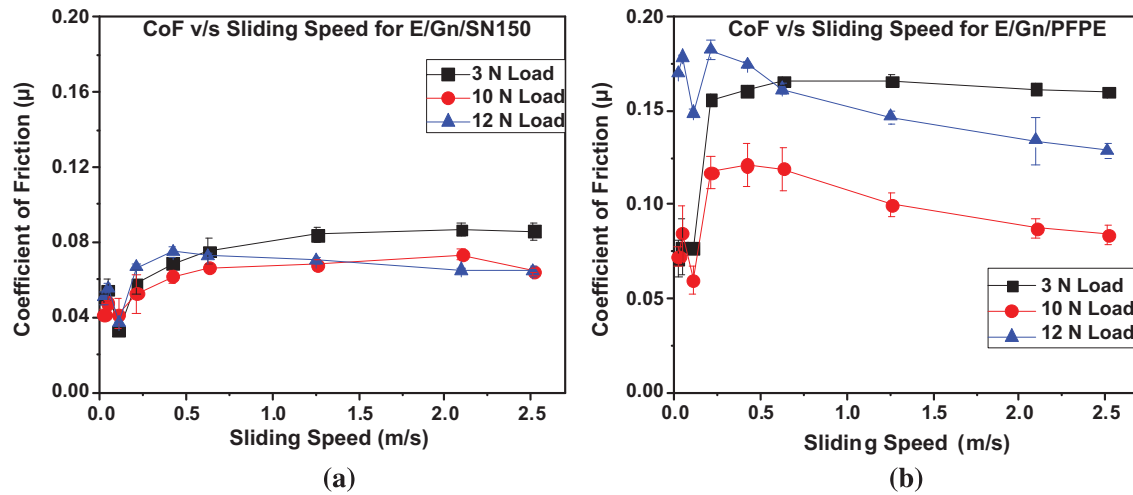


Fig. 5. Variation of coefficient of friction with sliding velocity of epoxy/graphene composites with liquid lubricant coated on cylindrical surface of steel for three different loads (a) epoxy/graphene/SN150, (b) epoxy/graphene/PFPE. Each filler concentration was 10 wt%.

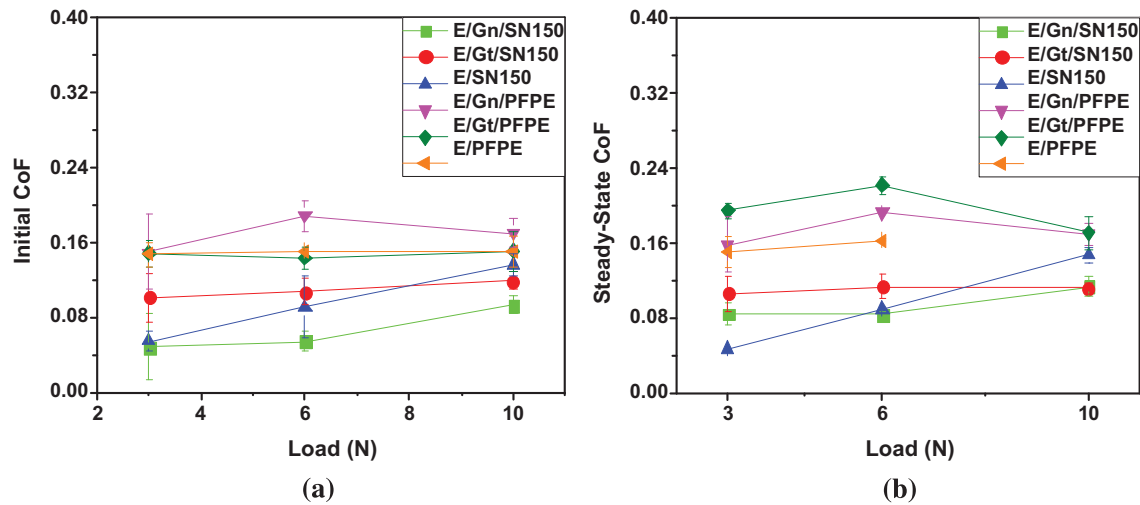


Fig. 6. The effect of load on coefficient of friction for epoxy composite with liquid lubricant coated on steel cylinder and tested on ball. Each filler concentration was 10 wt%.

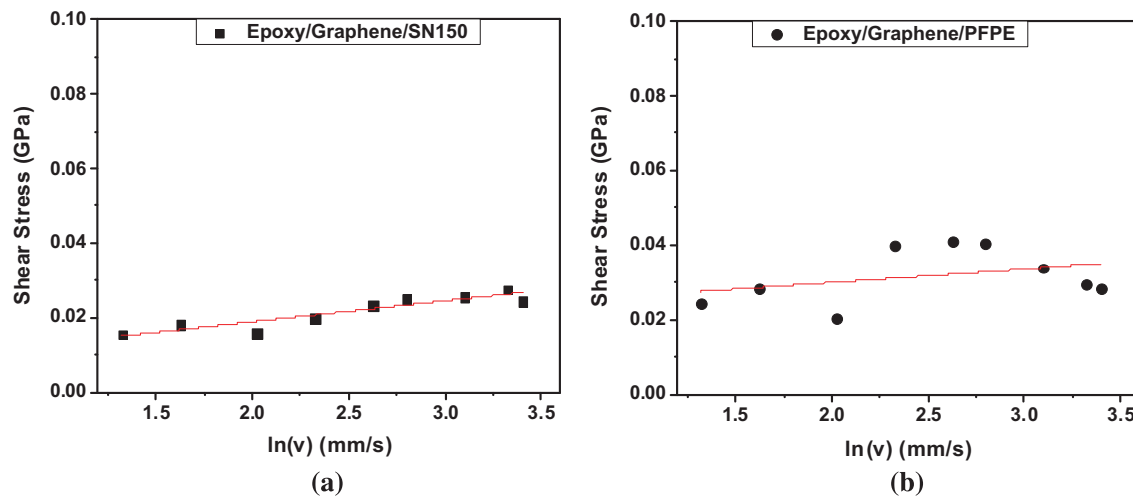


Fig. 7. Shear stress (τ) versus $\ln(v)$ plot for (a) epoxy/graphene/SN150 and (b) epoxy/graphene/PFPE composites, tested at 10 N load with various sliding speed for 5000 no. of cycles. The curve was fitted to Eq. (3) and the values of τ_1 and θ were calculated from the intercept and slope, respectively. Each filler concentration was 10 wt%.

the CoF values for PFPE composites are higher in comparison to those for SN150 composites. It appears to be the effect of the volume of the lubricants in the composites. SN150 is less dense (density=840 kg/m³)

in comparison to PFPE (density=1810 kg/m³) and hence, the volume of SN150 is nearly double in the composite for the same wt%. Hence, more volume of SN150 liquid lubricant is present at the interface. With

lower viscosity of SN150, it is able to form much more lubricating slurry at the interface at higher sliding speeds. Hence, SN150 is able to provide lower CoF in comparison to that of PFPE at all sliding speeds.

3.3. Effects of load on the coefficient of friction

Fig. 6(a) and (b) present the initial and steady-state coefficients of friction of the coatings at different applied normal loads for the same linear speed of 0.63 m/s (300 rpm). For all composites, as the load increases, the initial coefficient of friction also increases. For epoxy/graphene/SN150 the initial coefficient of friction is 0.04 at 3 N load and 0.08 at 10 N load, which are the lowest values amongst all epoxy composites with liquid fillers. It is found that the initial and steady-state coefficients of friction for PFPE are higher than those of SN150 in their composite forms. As explained before, the volume of SN150 was nearly twice that of PFPE because of density difference. This can result in large volume of SN150 lubricant present at the interface and hence low CoF. Another reason could be because of viscosity difference. PFPE has viscosity of 43.38 cP in comparison to 24.25 cP for SN150. Low viscosity fluid can provide low coefficient of friction. The steady-state coefficient of friction for Epoxy/graphene/SN150 composite is minimum (0.08) at lower loads (3 N and 6 N) and increases to 0.10 at 10 N load. Both for SN150 and PFPE cases, it is found that composites with graphene have lower CoF in comparison with that for the composite with graphite particle. Observing Fig. 2, it can be seen that the lubricant droplets are more in number in the case of graphene-based composite than in the case of graphite-based composite. In order to see the difference in the interaction between liquid lubricants and the filler particles, oil droplet contact angle was measured for each powder using the lubricants as the droplets. The contact angle of SN150 on graphene was measured as 47° in comparison to 28° on graphite. The contact angle of PFPE was measured as 73° on graphene in comparison to 27° on graphite. The experimental errors for all measurements were within $\pm 1^\circ$. These data indicate that, in general, graphene is oliophobic than graphite. This property of graphene renders graphene-based composite with higher amount of free or mobile lubricant which helps in reducing friction. Graphite is oliophilic leading to physical absorption of the lubricant molecules much faster. Hence, in relative terms, graphene-based composite show low coefficient of friction for both the lubricants in epoxy. It will be shown in latter section that epoxy/Gn/SN150 has the lowest wear rate at all loads when compared to all other composites. At 10 N load, all composite coatings survive 200,000 no. of cycles except epoxy/PFPE.

3.4. Shear stress

Fig. 7(a) and (b) present the shear stress (τ) as a function of $\ln(v)$ plots for epoxy/graphene/SN150 and epoxy/graphene/PFPE composites, respectively, tested at the normal load of 10 N and at different sliding speeds for 5000 no. of cycles. The shear stress is calculated by assuming the contact area to be the Hertzian contact and the shear stress of interface is CoF times the pressure applied (Supplementary information, S1, provides the details). The data are fitted to Eq. (3) which is given as follows-

$$\tau = \tau_1 + \theta \ln v$$

The values of τ_1 and θ are calculated for epoxy/graphene/SN150 as 0.00758 GPa and 0.00565, respectively, and for epoxy/graphene/PFPE as 0.02279 GPa and 0.00358, respectively. There is an excellent fit of the data to this equation proving that the lubrication mechanism is in the mixed lubrication regime as proposed by Spikes [17]. The data also validate the relation given earlier by Briscoe and Evans [20] for monolayers of carboxylic acids and their soaps. In an earlier work [18], this equation was found to fit the experimental data for a SU-8 (epoxy type molecule) polymer matrix and functionalized PFPE (Z-dol) liquid filler composite. However, the curve fitting parameters were found to be different for different regimes. Hence, such differences are possible for different combinations of matrix and the liquid fillers.

3.5. Wear analysis

Wear performances of the coatings were evaluated by conducting the sliding tests at the maximum normal load of 10 N for all composites. After this, the wear rate was calculated by measuring the wear track profiles on 3D Optical Profilometer. Wear life was also observed in terms of the number of cycles for which the CoF remained at a low steady-state value. Failure of the coating was defined as the point when the CoF rose sharply (above 0.3) or became fluctuating. Fig. 8(a) presents plots of coefficient of friction as a function of the number of cycle at 10 N load and 0.63 m/s linear sliding speed for epoxy composites with liquid fillers. From this figure it can be observed that epoxy/PFPE and epoxy/graphite/PFPE fails very early as compared to other composites. It is clear from these data that epoxy/PFPE coating is much poorer in wear life compared with the other composites at different loads and sliding velocities tested. At 3 N and 6 N normal loads, wear lives of all the composites with liquid filler are more than 200,000 no. of cycle. Further, epoxy/graphite/PFPE coating gives poor wear-life at 10 N load and 0.63 m/s speed due to delamination of the coating. Based on the failure definition ($\mu \geq 0.3$), epoxy composites filled

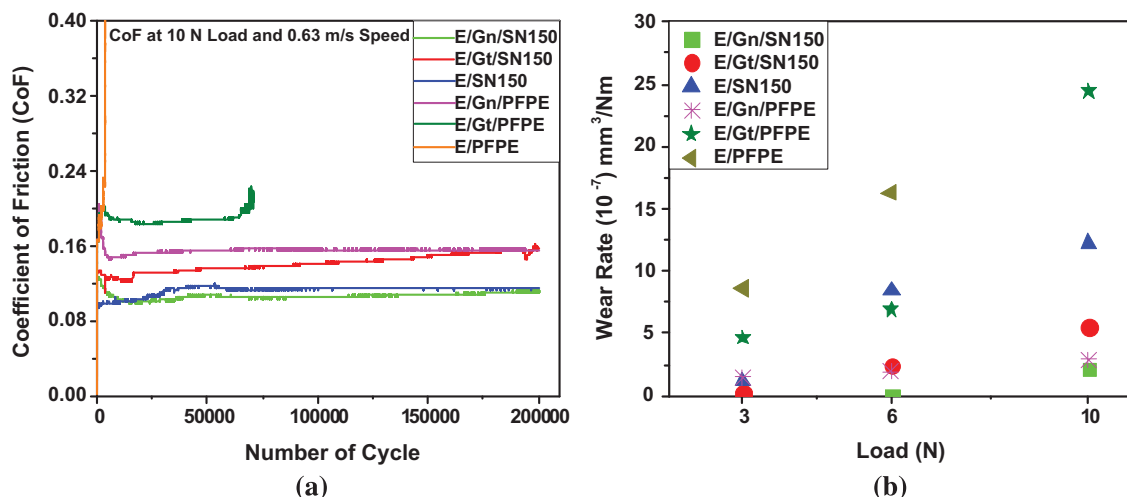


Fig. 8. (a) Wear life as a function of number of cycle for sliding speed of 0.63 m/s (300 rpm) and 10 N load (b) Specific wear rate variation with load at 0.63 m/s (300 rpm) speed, for composites with liquid lubricant in dry test condition. Each filler concentration was 10 wt%.

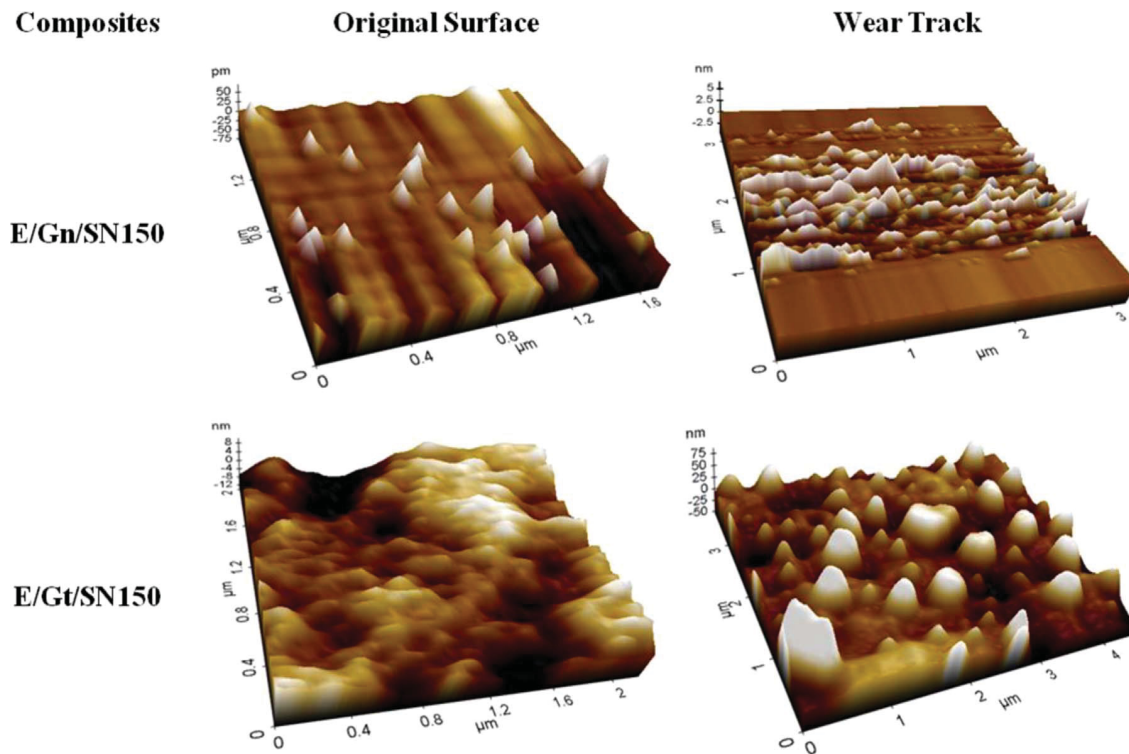


Fig. 9. AFM images of original and worn surfaces of epoxy/graphene/SN150 (E/Gn/SN150) and epoxy/graphite/SN150 (E/Gt/SN150) composites. These composites showed the least steady-state coefficients of friction and minimum wear rates.

with SN150 do not fail till 200,000 no. of cycle. The experiments were stopped at 200,000 cycles due to long test duration. At 0.63 m/s (300 rpm) sliding velocity and 10 N load, all samples survived except epoxy/PFPE which failed very early within few 100 s of cycles and epoxy/graphite/PFPE coating which failed at nearly 70,000 no. of cycle.

In Fig. 8(b) specific wear rates ($\text{mm}^3/\text{N}\cdot\text{m}$) are plotted as a function of normal load for 0.63 m/s (300 rpm) sliding speed. It is found that epoxy/graphite/PFPE coating shows the highest wear rate at 10 N load. The wear rate of epoxy/PFPE coating is much higher ($311.95 \times 10^{-7} \text{ mm}^3/\text{N}\cdot\text{m}$) than those of composite coatings of epoxy/graphite and epoxy/graphene combined with liquid lubricant filler. Hence, the datum for epoxy/PFPE is not included for 10 N normal load. Wear rates for the epoxy/graphene/SN150 composites remain nearly zero at low loads (3 N and 6 N) and gives lowest value than all other composites at the maximum load of 10 N. Epoxy/graphite/SN150 also shows very low wear rate even at the highest load of 10 N. For all composites, the rate of change of wear rate follows different trend below 6 N normal load and above, except for Epoxy/SN150 composite, in which case there is sharp increase in the wear rate beyond 6 N load. The composites with graphene nano particles and liquid filler have the best wear resistance. Fig. 9 provides AFM images of the unworn (original) and worn surfaces for two composites Epoxy/graphene/SN150 and Epoxy/graphite/SN150. Whereas the original surface is very smooth, the worn surfaces show many pillars which tend to reduce the contact area which may also contribute to their excellent tribological performance in addition to the other effects mentioned earlier.

4. Conclusions

Coated samples of epoxy composites (with 10 wt% of graphene or graphite particles) with liquid lubricant fillers (10 wt% of SN150 or PFPE) were tested for tribological performance under dry sliding condition. The counterface was 4 mm diameter steel (SAE 52100) ball.

The sliding velocity and normal load were varied during the tribological tests. The conclusions drawn are as follows:

1. The composites filled with liquid lubricant coated on D2 steel act as self-lubricating layer with drastically reduced coefficient of friction (2 times reduction over the sample without liquid filler) and low wear rate.
2. The coefficient of friction increases with increase of sliding velocity initially, and after a speed of 0.42 m/s becomes nearly constant for the case of SN150. There is a decreasing trend for CoF of the composite with PFPE beyond a critical sliding speed.
3. Among all composites, the epoxy/SN150 gives lowest CoF (0.045) but at high load epoxy/graphene/SN150 shows the lowest coefficient of friction.
4. The wear rate for epoxy/graphene/SN150 is very low ($2.5 \times 10^{-7} \text{ mm}^3/\text{N}\cdot\text{m}$) at 10 N load and nearly zero at low load of 3 N. This performance is followed by epoxy/graphite/SN150 which gives wear rate of $5.4 \times 10^{-7} \text{ mm}^3/\text{N}\cdot\text{m}$ at 10 N load.

Overall, liquid-filled epoxy-based composites are very suitable as tribological coatings for load bearing applications in journal bearings, engine piston rings etc.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.triboint.2016.09.010>.

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