

**TRIBOLOGICAL EVALUATION OF POLYETHER ETHER
KETONE (PEEK) NANOCOMPOSITE COATINGS
REINFORCED WITH CERIA**

BY
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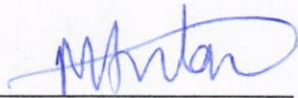
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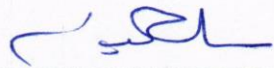
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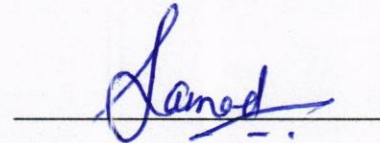
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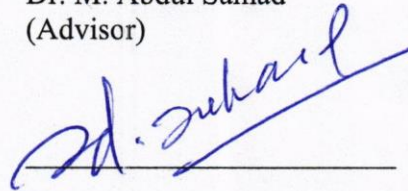
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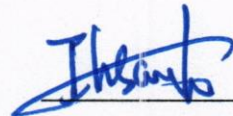
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|I dedicate this thesis wholeheartedly to my mother, father, sister, and entire family,
whose steadfast support has been my pillar through every circumstance.|

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TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES.....	ix
LIST OF TABLES.....	xvii
ABSTRACT.....	xviii
ملخص الرسالة.....	xxi
CHAPTER 1 INTRODUCTION.....	1
1.1 Background.....	1
1.2 Motivation and Justification.....	2
1.3 Objectives	4
1.4 Project Phases	4
1.5 Organization of the Thesis.....	9
CHAPTER 2 LITERATURE REVIEW.....	10
2.1 Introduction to Tribology.....	10
2.2 Significance of polymer and polymer-based nanocomposite coatings in tribological applications.....	11
2.3 Limitations of these polymers	12
2.4 Polyether Ether Ketone (PEEK)	12
2.4.1 Applications of PEEK	14
2.4.2 Limitations of PEEK	15
2.4.3How to overcome these limitations.....	15
2.5 Cerium dioxide/Ceria (CeO ₂)	16
2.6 Existing gaps in the literature and addressing the existing gaps.....	18
2.7 PEEK coatings	20

2.7.1 PEEK nanocomposite coatings	22
2.7.2 Significance of roughness parameters of the substrate on the tribological properties of PEEK coatings.....	23
2.7.3 Various reinforcements used to fabricate the composite /hybrid PEEK coatings.....	28
2.7.4 Dispersion techniques of the reinforcements within the PEEK matrix.....	29
2.7.5 Tribology of PEEK nanocomposite coatings	33
2.8 Summary	48
CHAPTER 3 EXPERIMENTAL WORK	50
3.1 Materials	50
3.1.1 PEEK powder	50
3.1.2 Cerium dioxide (CeO ₂)	51
3.2 Characterization techniques	51
3.2.1 X-ray diffraction (XRD)	51
3.2.2 Fourier transform infrared (FTIR) spectroscopy	52
3.2.3 Dispersion analysis.....	52
3.2.4 Thickness measurements.....	52
3.2.5 Hardness measurements	52
3.2.6 Tribological testing	53
3.2.7 Evaluation of wear morphology.....	54
3.2.8 Water contact angle (WCA) measurements.....	55
3.2.9 Ultraviolet (UV) radiation tests.....	55
3.2.10 Scratch testing	55

CHAPTER 4 RESULTS AND DISCUSSION.....	56
4.1 Phase 1 - Evaluating the effect of surface texturing on the tribological properties of pristine PEEK coatings deposited on mild steel substrates.....	56
4.1.1 Evaluation of coating thickness.....	57
4.1.2 Evaluation of the tribological performance of PEEK coatings deposited on the polished and ground substrates	57
4.1.3 Discussion.....	65
4.1.4 Effect of height parameters on the tribological performance of the PEEK coatings	66
4.1.5 Effect of spatial parameters on the tribological performance of the PEEK coatings	67
4.1.6 Effect of statistical roughness parameters on the tribological performance of the PEEK coating.....	68
4.1.7 Summary	69
4.2 Phase 2 – Selection of a mixing technique to uniformly disperse the ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties	71
4.2.1 PEEK/1.5 wt% ceria composite powder preparation	72
4.2.2 Quality assessment of the coatings formed by the powders using ball milling and sonication methods	73
4.2.3 X-ray diffraction (XRD) characterization of the nanocomposite powders	75
4.2.4 FTIR analysis of the nanocomposite powders	77
4.2.5 TGA analysis of the nanocomposite powders	81
4.2.6 Tribological characterization of the nanocomposite coatings	82
4.2.7 Summary	86
4.3 Optimized parameters for substrate, dispersion, and coating preparations	87

4.3.1 Preparation of nanocomposite powders for coating	87
4.3.2 Substrate preparation before coating.....	88
4.3.3 Ultrasonic cleaning and drying	89
4.3.4 Coating procedure.....	90
4.4 Phase 3 - Optimizing the composition of ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties of the nanocomposite coatings	91
4.4.1 XRD analysis of pristine and developed nanocomposite powders	91
4.4.2 FTIR analysis of pristine and developed nanocomposite coatings.....	93
4.4.3 Analysis of microhardness of the pristine and developed nanocomposite coatings.....	95
4.4.4 Analysis of the thickness measurements and dispersion of nanofillers in the polymer matrix	96
4.4.5 TGA analysis of the developed coatings	99
4.4.6 Tribological performance of the pristine and developed nanocomposite coatings.....	100
4.4.7 Summary	122
4.5 Phase 4 – Optimizing the composition of ceria nanoparticles in the PEEK matrix, which would result in the best scratch resistance behavior of the nanocomposite coatings.....	123
4.5.1 Change in water contact angles of the developed coatings reinforced with different loadings of ceria.....	123
4.5.2 Scratch test results of the developed coatings reinforced with different loadings of ceria	125
4.5.3 Summary	128
4.6 Phase – 5 Evaluating the effect of counterface material on the wear resistance of the optimized nanocomposite coating from Phase - 3 and Phase - 4.....	130

4.6.1 Summary	133
4.7 Phase 6 – Evaluating the effect of UV exposure on the wear and scratch resistance characterization of the optimized nano composite coating from Phase-3 and Phase-4.....	134
4.7.1 Analysis of the water contact angle measurements on UV exposed samples.....	134
4.7.2 FTIR analysis of PEEK and optimized PEEK/ceria nano composite coatings exposed to UV radiation.....	136
4.7.3 Effect of UV-radiation on the tribological performance of pristine PEEK and PEEK/1.5 wt% ceria nanocomposite coatings.....	138
4.7.4 Effect of UV-radiation on the scratch test results of pristine PEEK and PEEK/1.5 wt% ceria nanocomposite coating.....	141
4.7.5 Summary	145
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS	146
5.1 Conclusions	146
5.2 Achievements.....	154
5.3 Recommendations.....	155
REFERENCES.....	156
VITAE.....	175

LIST OF FIGURES

Figure 1.1 Research Methodology followed in the present study.....	8
Figure 2.1 Polymer pyramid, listing PEEK with other thermoplastic polymers with regard to performance and formability	14
Figure 2.2 Schematic of Surface Roughness 2D profile showing the Rp, Rv, and Rz measurements.....	26
Figure 2.3 Representation of (a) skewness and (b) kurtosis	27
Figure 2.4 COF graph for PEEK and PEEK/BG coatings (sintered at 400 ° C) [73]	34
Figure 2.5 (a) The friction coefficients and (b) wear rates of the different coatings vs the different applied loads.....	37
Figure 2.6 Coefficient of friction vs sliding distance for baseline and oxygenhardened Ti-6Al-4V alloy and TiN/PEEK708 coated oxygen-hardened alloy	40
Figure 2.7 The scratch test results (friction force, penetration depth and residual depth signals) of (a) PEEK coating, and (b) graphite/PEEK coating, and (c) friction coefficient of the coatings vs. diamond stylus in a scratch test at 0.25 N constant load.....	41
Figure 2.8 The friction coefficient of the uncoated and PTFE/PEEK 708 coated Ti-6Al-4V alloy during dry friction with an Al ₂ O ₃ ball at RT, 150, and 260 ° C	45
Figure 2.9 (a) Friction coefficient vs. wear rate of seven polymeric coatings under both unidirectional and oscillatory testing and (b) zoom-in of only oscillatory testing result	47
Figure 3.1 SEM image of PEEK powder	50
Figure 3.2 SEM image of ceria	51
Figure 4.1 A flowchart illustrating the research methodology adopted in this study	56
Figure 4.2 Cross-sectional FE-SEM images of the thickness of PEEK coatings on (a) polished and (b) rough samples respectively	57
Figure 4.3 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph.....	58

Figure 4.4 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph.....	59
Figure 4.5 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph.....	60
Figure 4.6 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph.....	60
Figure 4.7 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph.....	62
Figure 4.8 (a-b) The before and after test ball images, (c) the coefficient of friction graph, and (d) peeled-off coating at 50 N load, 0.2 m/s.	63
Figure 4.9 Comparison of the specific wear rate of the coatings at different normal loads at a sliding velocity of 0.2 m/s.....	64
Figure 4.10 Comparison of average wear life of pristine PEEK at normal loads of 30 N, 40 N, and 50 N at a linear sliding speed of 0.2 m/s for 10,000 cycles ...	64
Figure 4.11 A 3-D optical profilometry image depicting the height parameter distinction between (a) polished and (b) rough sample	67
Figure 4.12 A graphical representation of the peak density of the surface profiles of (a) polished and (b) rough samples.	68
Figure 4.13 An illustration of the (a) coated sample with (b) corresponding cross-sectional SEM image of the PEEK/1.5 wt% Ceria powder prepared from probe sonication.....	74
Figure 4.14 An illustration of the coated sample (a) after the pre and post- heat treatment, and (b) unmelted ball-milled powder after the post-heat treatment	75
Figure 4.15 XRD patterns of pristine PEEK, ceria, and PEEK reinforced with ceria powders prepared through sonication and ball milling	76
Figure 4.16 The FTIR spectra of PEEK and Ceria	78

Figure 4.17 (a) The FTIR spectra of PEEK, ceria, and the nanocomposite powders prepared from sonication and ball milling and (b) the graph highlighting the signature peak of ceria among the nanocomposite powders	80
Figure 4.18 TGA thermograms of pristine PEEK and PEEK nanocomposite powders ..	82
Figure 4.19 An illustration of the (a) coated sample with (b) corresponding cross-sectional SEM image of the PEEK+1.5 wt% Ceria powder prepared from ball milling after 90 minutes of post-heat treatment.....	83
Figure 4.20 The (a) frictional graph of PEEK+1.5 wt% ceria nanocomposite coating prepared from probe sonication along with the (b) wear track photograph, (c) the 2D wear track depth, (d) the EDS scan, and (e) the counter face ball images before the test (BT) and (f) after the test (AT) at a normal load of 70 N for 10,000 cycles at 0.1 m/s.....	84
Figure 4.21 The (a) frictional graph of PEEK+1.5 wt% ceria nanocomposite coating prepared from ball milling technique along with the (b) wear track photograph, (c) the 2D wear track depth, (d) the EDS scan, and (e) the counter face ball images before the test (BT) and (f) after the test (AT) at a normal load of 70 N for 10,000 cycles at 0.1 m/s	85
Figure 4.22 Nanocomposite powder preparation setup (a) Probe sonication of filler material (b) Mixing of filler and polymer matrix by magnetic stirring (c) Drying of nanocomposite powder	88
Figure 4.23 Grinding machine	89
Figure 4.24 Ultrasonic cleaner	89
Figure 4.25 Electrostatic spray gun.....	90
Figure 4.26 XRD patterns of pristine PEEK and PEEK reinforced with ceria at different loading conditions.....	93
Figure 4.27 FTIR spectra of PEEK, ceria, and nanocomposite powders prepared from different wt% of ceria nanoparticles.....	94
Figure 4.28 Comparison of the hardness values of PEEK nanocomposite coatings at different loadings of ceria.....	95
Figure 4.29 Cross-sectional SEM images of the coatings	97
Figure 4.30 SEM images PEEK matrix reinforced with (a) 0.5wt%, (b) 1.5wt% and (c) 3wt% ceria loadings along with EDS maps for Cerium (Ce).....	98
Figure 4.31 TGA thermograms of pristine PEEK and PEEK nanocomposite powders ..	99

Figure 4.32	Comparison of the (a, i, q) frictional graph of pristine PEEK coatings along with (b, j, r) wear track photographs and (c, k, s) SEM images of the wear track with corresponding (d, l, t) EDS scans, the (e, m, u) counter face ball images before the test and (f, n, v) after the test, the (g, o, w) 2D wear track depth, and (g, p, x) 3D profile images at varying normal loads for 10,000 cycles at 0.1 m/s	101
Figure 4.33	Pristine PEEK coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM image of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track.....	103
Figure 4.34	Pristine PEEK coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning	104
Figure 4.35	Comparative wear life of pristine PEEK coatings at a normal load of 70 N for 10,000 cycles at different sliding velocities.....	105
Figure 4.36	PEEK/0.5 wt% ceria coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM image of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track	106
Figure 4.37	PEEK/0.5 wt% ceria coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning	107
Figure 4.38	Comparative wear life study of PEEK/0.5 wt% Ceria coatings at a normal load of 70 N for 10,000 cycles at different sliding velocities.....	108
Figure 4.39	(a, g) Frictional graphs of PEEK/1.5 wt% Ceria coatings along with (b, c & h, i) SEM images of the wear track with corresponding (d, j) EDS scans, (e, k) 3D profile and (f, l) wear track depth images at varying sliding velocities for 10,000 cycles at 70 N.....	110
Figure 4.40	PEEK/3 wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM images of the wear track at along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track	111
Figure 4.41	PEEK/1.5wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph (b) – (c) SEM images of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track for 50,000 cycles.....	112

Figure 4.42 PEEK/3wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning	113
Figure 4.43 Comparative wear life study of nanocomposite coatings at a normal load of 70 N for 50,000 cycles at a sliding velocity of 0.5 m/s	114
Figure 4.44 (a, g) Frictional graphs of PEEK/1.5 wt% Ceria coatings along with (b, c & h, i) SEM images of the wear track with corresponding (d, j) EDS scan, (e, k) the 3D profile and (f, l) the wear track depth images at varying normal load for 10,000 cycles at 0.4 m/s	116
Figure 4.45 PEEK/1.5wt% Ceria coating at a sliding velocity of 0.4 m/s presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning	117
Figure 4.46 Comparative wear life study of PEEK/1.5 wt% Ceria coatings at a sliding velocity of 0.4 m/s for 10,000 cycles at different normal loads	117
Figure 4.47 PEEK/1.5wt% Ceria coating at a normal load of 90 N presenting (a) frictional graph (b) – (d) SEM images of the wear track along with (e) corresponding EDS scan (f) 3D optical scan of the wear track and (g) 2D optical scan of the wear track for 50,000 cycles.....	118
Figure 4.48 WCA measurements of 0, 0.5, 1.5, and 3wt% ceria nanoparticle reinforced PEEK nanocomposite coatings	124
Figure 4.49 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK coating	125
Figure 4.50 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on PEEK/0.5 wt% ceria nanocomposite coating	126
Figure 4.51 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on PEEK/1.5 wt% ceria nanocomposite coating	127
Figure 4.52 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on PEEK/3 wt% ceria nanocomposite coating	128
Figure 4.53 Critical loads of failure of the coatings	128

Figure 4.54 Comparison of the (a, f, k) frictional graph of PEEK+1.5 wt% ceria nanocomposite coatings along with (b, g, l) wear track photographs and (c, h, m) SEM images of the wear track with corresponding (d, i, n) 3D wear track depth images and (e, j, o) 2D profile images at normal load of 90 N at 0.4 m/s for 10,000 cycles	132
Figure 4.55 WCA measurements of PEEK and PEEK/1.5 wt% ceria nanocomposite coating obtained before and after 500 hours of UV exposure	135
Figure 4.56 FTIR spectra of the UV unexposed and exposed (a) PEEK and (b) PEEK /1.5 wt% ceria coatings.....	137
Figure 4.57 Comparison of the (a, g) frictional graph of PEEK coatings along with (b, h) before test ball and (c, i) after test ball images with (d, j) SEM images of the wear track with corresponding (e, k) 2D profile and (f, l) 3D profile wear track depth images at normal load of 50 N at 0.1 m/s for 10,000 cycles	139
Figure 4.58 Comparison of the (a, g) frictional graph of PEEK/1.5 wt% ceria coatings along with (b, h) before test ball and (c, i) after test ball images with (d, j) SEM images of the wear track with corresponding (e, k) 2D profile and (f, l) 3D profile wear track depth images at normal load of 50 N at 0.1 m/s for 10,000 cycles.....	140
Figure 4.59 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on pristine PEEK coating before exposure to UV radiation.....	142
Figure 4.60 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on pristine PEEK coating after exposure to UV radiation.....	143
Figure 4.61 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK/1.5 wt% ceria coating before exposure to UV radiation....	144
Figure 4.62 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK/1.5 wt% ceria coating after exposure to UV radiation	144

LIST OF TABLES

Table 2.1 Structural, mechanical, and thermal properties of PEEK	13
Table 2.2 Effect of post-deposition treatment on coating characteristics	21
Table 2.3 Classification and characteristics of reinforcements used in PEEK composite/hybrid coatings.....	28
Table 2.4 Dispersion parameters used for wet mixing of powders	31
Table 2.5 Tribological evaluations of the coatings performed under linear sliding conditions	47
Table 4.1 The various surface parameters of the polished and rough samples	65
Table 4.2 Ball milling process parameters	73
Table 4.3 Comparison of results obtained in this study to past work	121
Table 4.4 Measurements of the roughness & water contact angles of the counterfaces	131

ABSTRACT

Full Name : Amal Ameen Seenath

Thesis Title : Tribological Evaluation of Polyether Ether Ketone (PEEK) nanocomposite Coatings Reinforced with Ceria

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Metal-to-metal contact in moving parts increases friction and wear, which alter the mechanical and thermal properties of the contacting surfaces. This results in faster deterioration of the materials/machine components, reducing the life of products. Surface coating is one of the most reliable techniques among the various approaches adopted by researchers to protect material surfaces. Composite coating systems are generally recommended by specifying engineers of various organizations for applications demanding protection from a range of corrosive media. Within this field, there is a constant search for novel coatings that can endure severe tribological conditions without compromising their mechanical integrity or longevity. Tribological analyses are essential for assessing the effectiveness of these coatings since they provide information on their wear, lubrication, and friction characteristics. As a result, polymer and polymer composite coatings are widely employed to protect metallic components against wear under various conditions.

Polyether Ether Ketone (PEEK) is one such semi-crystalline, high-performance thermoplastic engineering material that provides a distinctive combination of properties including excellent thermal stability, good chemical resistance, exceptional mechanical strength, and reasonably good tribological properties. Moreover, PEEK, like many

polymers, faces degradation issues when exposed to ultraviolet (UV) radiation over time. The exposure can lead to photodegradation, affecting its surface properties and mechanical integrity. Ceria nanoparticles, a rare earth metal compound that exhibits exceptional mechanical strength, thermal stability, and resistance to UV radiation, make it highly desirable for use in demanding industrial environments and are added to improve the load-bearing capacity of the coating and to improve the mechanical properties and resistance against UV exposure. Hence the main objective of this work is to develop a nanocomposite coating of PEEK reinforced with cerium dioxide/ceria (CeO_2) for bearing applications under dry lubricated conditions.

In the initial phase of our work, the ideal surface roughness required to achieve the optimum adhesion level of the deposited pristine PEEK coatings on mild steel substrates was studied. Later, based on the literature survey conducted, experimental investigations were performed to determine the ideal dispersion technique, namely ball milling, and probe sonication, required to develop homogenous PEEK/ceria nanocomposite powder. In the next phases of our study, PEEK coatings reinforced with different loadings (0.5, 1.5, and 3 wt%) of cerium dioxide/ceria (CeO_2) nanofillers were developed and deposited using an electrostatic spraying technique on mild steel substrates with optimized roughness parameters and their mechanical and tribological properties are evaluated under significantly higher loads (50, 60 and 70 N) and higher sliding speeds (0.1, 0.2, 0.3 m/s). In addition to it, the scratch resistance properties of the different loadings (0.5, 1.5, and 3 wt%) were also evaluated to obtain the bonding strength and degree of adhesion of the developed coatings. The optimized nanocomposite coating was then tested against different counterface materials (Alumina, Tungsten Carbide, Silicon nitride, and 440C

Hardened Steel) to obtain the tribological effect of various counterparts on the developed coatings. Furthermore, the optimized coatings were then subjected to ultraviolet (UV) exposure to study the wear performance and scratch resistance.

Ball-on-disk configuration wear tests were conducted with an alumina ball as a counter face. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), microhardness tests, scanning electron microscopy (SEM), and optical profilometry techniques were conducted to characterize the chemical and mechanical properties of the coatings in terms of dispersion of the nanofillers, morphology, and wear mechanisms, respectively. Results show that the PEEK coating reinforced with 1.5 wt% of ceria nanoparticles did not fail even until ~50,000 cycles at a normal load of 90 N and a linear speed of 0.4 m/s and at a normal load of 70 N and a linear speed of 0.5 m/s showing a significant improvement in wear resistance as compared to PEEK reinforced with 0.5 and 3 wt% ceria loadings. The UV resistance and the scratch tests conducted also highlighted the exceptional performance of the 1.5 wt% loaded ceria nanocomposite coatings.

ملخص الرسالة

الاسم الكامل: أمل أمين سيناث

عنوان الرسالة: التقييم التآكلي لطلاءات نانوية مركبة من بولي إيثر إيثر كيتون معززة بجسيمات ثاني أكسيد السيريوم

التخصص: الهندسة الميكانيكية

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٤

يزيد التلامس المعدني بين الأجزاء المتحركة من الاحتكاك والتآكل، مما يؤدي إلى تغيير الخصائص الميكانيكية والحرارية للأسطح المتلامسة. يؤدي ذلك إلى تدهور أسرع للمواد ومكونات الآلات، مما يقلل من عمر المنتجات. تُعد الطلاءات السطحية واحدة من أكثر التقنيات موثوقية بين الأساليب المختلفة التي يعتمد عليها الباحثون لحماية الأسطح. المهندسون في مختلف المنظمات باستخدام أنظمة الطلاء المركبة للتطبيقات التي تتطلب الحماية من مجموعة من الأوساط المسببة للتآكل. في هذا المجال، هناك بحث مستمر عن طلاءات جديدة يمكنها تحمل الظروف التآكلية القاسية دون المساس بسلامتها الميكانيكية أو عمرها الافتراضي. لتقييم فعالية هذه الطلاءات لأنها توفر معلومات عن خصائص التآكل، والتشحيم، والاحتكاك.

نتيجة لذلك، تُستخدم الطلاءات البوليمرية والبوليمرية المركبة على نطاق واسع لحماية المكونات المعدنية من التآكل تحت ظروف مختلفة. يُعتبر إيثر كيتون أحد هذه البوليمرات شبه البلورية ذات الأداء العالي، حيث يتميز بمزيج فريد من الخصائص، بما في ذلك الاستقرار الحراري الممتاز، والمقاومة الكيميائية الجيدة، والقوة الميكانيكية الاستثنائية، وخصائص تآكلية جيدة نسبياً. علاوة على ذلك، يواجه إيثر كيتون، مثل العديد من البوليمرات، مشاكل التحلل عند التعرض للأشعة فوق البنفسجية بمرور الوقت، مما قد يؤدي إلى تدهور خصائصه السطحية وسلامته الميكانيكية.

تُعتبر جسيمات ثاني أكسيد السيريوم، وهي مركب معدني نادر، مادة تتمتع بقوة ميكانيكية استثنائية، واستقرار حراري، ومقاومة للأشعة فوق البنفسجية، مما يجعلها مرغوبة للاستخدام في البيئات الصناعية القاسية. تُضاف هذه الجسيمات لتحسين قدرة الطلاء على تحمل الأحمال وتحسين الخصائص الميكانيكية ومقاومة الأشعة فوق البنفسجية.

لذلك، كان الهدف الرئيسي من هذا العمل هو تطوير طلاء نانوي مركب من إيثر كيتون معزز بجسيمات ثاني أكسيد السيريوم لاستخدامه في تطبيقات المحامل تحت ظروف التشحيم الجاف. في المرحلة الأولى من العمل، تمت دراسة خشونة السطحية المثالية لتحقيق أفضل مستوى التصاق للطلاءات المترسبة من إيثر كيتون النقي على ركائز من الصلب الطري. بعد ذلك، وبناءً على أجريت تجارب لتحديد التقنية المثلى لتشيتت الجسيمات، مثل الطحن الكروي والموجات فوق الصوتية، لتطوير مسحوق نانوي متجانس من إيثر كيتون وثاني أكسيد السيريوم.

في المراحل اللاحقة، تم تطوير طلاءات من إيثر كيتون معززة بنسب مختلفة من جسيمات ثاني أكسيد السيريوم (٠.٥، ١.٥، ٣ بالمائة بالوزن)، وتم ترسيبها باستخدام تقنية الرش الكهروستاتيكي على ركائز صلب طري ذات خشونة محسنة. تم تقييم الخصائص الميكانيكية والتآكلية لهذه الطلاءات تحت أحمال عالية (٥٠، ٦٠، ٧٠ نيوتن) وسرعات انزلاق عالية (٠.١، ٠.٢، ٠.٣ متر لكل ثانية). بالإضافة إلى ذلك، تم تقييم خصائص مقاومة الخدش لنسب ٠.٥، ١.٥، ٣ بالمائة لاختبار قوة الالتصاق ودرجة التصاق الطلاءات.

تم اختبار الطلاء النانوي الأمثل ضد مواد تلامس مختلفة (ألومينا، كربيد التنجستن، نيتريد السيليكون، وفولاذ مقوى من النوع ٤٤٠ سي) لدراسة التأثير التآكلي لمواد التلامس المختلفة. علاوة على ذلك، تم تعريض الطلاءات المثلى للأشعة فوق البنفسجية لدراسة أداء التآكل ومقاومة الخدش.

أُجريت اختبارات التآكل باستخدام تقنية الكرة على القرص، حيث تم استخدام كرة من الألومينا كوجه ملامس. تم استخدام حيود الأشعة السينية، وتحليل الطيف بالأشعة تحت الحمراء، والتحليل الحراري الوزني، واختبارات الصلادة الدقيقة، والمجهر الإلكتروني الماسح، وتقنية قياس تضاريس السطح الضوئية لتوصيف الخصائص الكيميائية والميكانيكية للطلاءات من حيث توزيع الجسيمات النانوية، والتضاريس السطحية، وآليات التآكل.

أظهرت النتائج أن طلاء البولي إيثر إيثر كيتون المعزز بنسبة ١.٥ بالمائة من جسيمات ثاني أكسيد السيريوم لم يفشل حتى بعد ٥٠٠٠٠ دورة تحت حمل ٩٠ نيوتن وبسرعة خطية قدرها ٠.٤ متر لكل ثانية، وأيضًا تحت حمل ٧٠ نيوتن

وبسرعة ٠.٥ متر لكل ثانية، مما يدل على تحسن كبير في مقاومة التآكل مقارنةً بالطلاءات ذات نسب ٠.٥ و ٣ بالمائة من جسيمات ثاني أكسيد السيريوم. كما أظهرت اختبارات مقاومة الأشعة فوق البنفسجية والخدش الأداء الاستثنائي للطلاء المعزز بنسبة ١.٥ بالمائة.

CHAPTER 1

INTRODUCTION

1.1 Background

Friction and wear are major concerns in practically all tribological applications. At present, about one-third of energy resources are being wasted due to the involvement of friction directly or indirectly [1]. Therefore, it is significantly important to consider the causes of friction and wear to develop a strategy that can minimize the losses due to friction and wear.

Polymeric coatings, with their inherent adaptability, affordability, and excellent properties, have emerged as potential alternatives among the wide range of materials investigated for tribological applications. As a result, polymer and polymer composite coatings are widely employed to protect metallic components against wear under various conditions. Nevertheless, the application of these polymer coatings has been limited by factors including low strength, low load-bearing capacity, low-temperature stability, and problems with water absorption.

The incorporation of nanoparticles into polymeric matrices is a revolutionary development in surface engineering, providing a flexible method for strengthening materials against tribological deterioration. The mechanical, thermal, and tribological characteristics of the resultant nanocomposites may be tailored by carefully choosing and distributing the nanoparticles inside the polymer matrix.

1.2 Motivation and Justification

However, there is still a lot of scope to further improve the properties of these polymer nanocomposite coatings so that they can be used in varying environments.

Polymeric coatings are essential due to their ability to provide a protective barrier that enhances the surface properties of underlying substrates. They offer advantages such as reduced friction, increased wear resistance, and corrosion protection, which are critical for extending the life and reliability of mechanical components in a variety of applications. However, these coatings are often subjected to a range of environmental conditions that can challenge their performance, including high temperatures, fluctuating humidity, exposure to UV radiation, corrosive chemicals, and mechanical stress. The polymer nanocomposite coatings can be exposed to different environments during their operational life.

As a result, we were motivated by the necessity of finding a suitable filler that addresses the limitations inherent in unmodified polymeric coatings, which may not withstand prolonged exposure to severe environmental stressors. A well-chosen filler can enhance properties such as hardness, wear resistance, and thermal stability, enabling the coating to maintain its structural integrity and functionality under harsh conditions. This ensures that the coatings not only protect the substrate but also contribute to the overall durability and performance of the system. The search for an effective filler is driven by the need to develop coatings that are capable of performing reliably in applications where exposure to high friction, varying temperatures, UV radiation, and chemical agents is common.

Hence based on this concept, we set about selecting the best polymer matrix and the nanofillers which would help in developing a polymer coating that would protect the

sliding components under extreme environmental conditions. For this purpose, it is very essential that the developed nanocomposite coating should have high wear resistance, high load-bearing capacity, and resistance against material degradation.

Polyether Ether Ketone (PEEK) is one such semi-crystalline, high-performance thermoplastic engineering material that provides a distinctive combination of properties, including excellent thermal stability, good chemical resistance, exceptional mechanical strength, and reasonably good tribological properties [2-5]. This unique balance of properties makes PEEK exhibit excellent performance in harsh environments that other most commonly used polymers like polyamide (PA), polytetrafluoroethylene (PTFE), and ultra-high-molecular-weight polyethylene (UHMWPE) fail to withstand. However, pristine PEEK exhibits a high coefficient of friction, between 0.30 – 0.38, in addition to a high wear rate [6,7]. Various researchers have modified these properties by reinforcing them with different nanofillers. Moreover, PEEK, like many polymers, faces degradation issues when exposed to ultraviolet (UV) radiation over time. The exposure can lead to photodegradation, affecting its surface properties and mechanical integrity [8,9]. Polymer nanocomposite coatings are highly effective in reducing mechanical stresses however not all reinforcements will provide resistance against UV and prolonged exposure to outdoor environments will result in degrading the polymer's molecular structure, leading to photooxidation, and a significant loss of mechanical integrity [10,11]. Ceria nanoparticles, a rare earth metal compound that exhibits exceptional mechanical strength, thermal stability, and resistance to UV radiation, make it highly desirable for use in demanding industrial environments and are added to improve the load-bearing capacity of the coating and to improve the mechanical properties and resistance against UV

exposure [12-15]. Hence the main objective of this work is to develop a nanocomposite coating of PEEK reinforced with cerium dioxide/ceria (CeO_2) for bearing applications under dry lubricated conditions.

Cerium dioxide is a versatile rare earth metal compound that finds usage in a wide range of biological and engineering fields. As a rare earth metal compound, ceria exhibits exceptional mechanical strength, thermal stability, and chemical resistance, making it highly desirable for use in demanding industrial environments [16,17]. Ceria's UV-blocking capabilities and its antioxidant properties are particularly beneficial in environments like the aerospace and automotive industries, where materials are often exposed to harsh sunlight and fluctuating temperatures [10,18]. Ceria's high hardness and wear resistance behavior make it compatible with applications involving heavy loads and high-speed operation, such as in the manufacturing of bearings, gears, and other mechanical components subjected to extreme force [19-21].

1.3 Objectives

*Hence in view of the above justification, we defined the main objective of our study to be as follows: **To evaluate the effect of composition and UV-exposure on the Mechanical, Tribological and scratch resistance properties of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria***

1.4 Project phases

To achieve the objective mentioned above, the overall project is divided into four different phases as described below.

Phase 1 - Evaluating the effect of surface texturing on the tribological properties of pristine PEEK coatings deposited on mild steel substrates

The ideal surface roughness required to achieve the optimum adhesion level, which directly affects the tribological properties of the deposited pristine PEEK coatings on mild steel substrates was evaluated. For this, an experimental study was conducted on samples with different surface roughnesses resulting in the best adhesion strength/tribological properties. The pre and post-heat treatments along with other coating parameters were also optimized in this phase of the study.

The following tasks were performed in this phase:

- **Task 1:** Selection of a proper coating process
- **Task 2:** Optimization of surface roughness parameters required for best adhesion/tribological properties
- **Task 3:** Optimization of the pre and post-heat treatment parameters during coating resulting in the best tribological properties

Phase 2 - Selection of a mixing technique to uniformly disperse the ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties

In this phase, the ideal dispersion technique required to obtain the homogeneous mixture required to develop PEEK/ceria nanocomposite coating was studied and optimized. The following tasks were performed in this phase:

- **Task 1:** Selection of the primary dispersion techniques based on literature survey
- **Task 2:** Development of homogenous mixtures from the selected dispersion techniques.
- **Task 3:** Development/deposition of nanocomposite coatings onto the substrate
- **Task 4:** Structural and mechanical characterization of coatings
- **Task 5:** Tribological characterization of coatings

Phase 3 – Optimizing the composition of the ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties

In this phase, nanocomposite coatings with different compositions of ceria nanoparticles were developed and characterized in terms of wear tests to obtain the optimized loading of ceria nanoparticles. The following tasks were performed in this phase:

- **Task 1:** Development/deposition of nanocomposite coatings with different ceria loadings (0.5, 1.5, 3 wt%) based upon the optimized parameters from phase 1 and phase 2.
- **Task 2:** Structural and mechanical characterization of coatings
- **Task 3:** Tribological characterization of coatings under dry conditions.

Phase 4 – Optimizing the composition of the ceria nanoparticles in the PEEK matrix, which would result in the best scratch resistance behavior of the nanocomposite coatings

In this phase, nanocomposite coatings with different compositions of ceria nanoparticles were developed and characterized in terms of scratch resistance tests to obtain the optimized loading of ceria nanoparticles. The following tasks were performed in this phase:

- **Task 1:** Development/deposition of nanocomposite coatings with different ceria loadings (0.5, 1.5, 3 wt%) based upon the optimized parameters from phase 1 and phase 2.
- **Task 2:** Structural and mechanical characterization of coatings
- **Task 3:** Scratch resistance characterization of coatings under dry conditions.

Phase 5 - Evaluating the effect of counterface material on the wear resistance of the optimized nanocomposite coating from Phase-3 and Phase-4

In this phase, the optimized nanocomposite coating from phase-3 and phase-4 was subjected to wear tests to determine the effect of various counterface materials on the developed coatings. Alumina, silicon nitride (SiN), tungsten carbide (WC) and 440C hardened steel balls were used to evaluate the tribological testings. The following tasks were performed in this phase:

- **Task 1:** Development of optimized nanocomposite coatings based upon the optimized compositions from phase 3 and phase 4.
- **Task 2:** Tribological characterization of coatings under dry conditions.

Phase 6 – Evaluating the Effect of UV exposure on the wear and scratch resistance of the optimized nanocomposite coating from Phase-3 and Phase-4

In this final phase, the wear and scratch resistance of the optimized coatings from phase-3 were evaluated before and after exposure to UV radiations. The following tasks were performed in this phase:

- **Task 1:** Structural and mechanical characterization of coatings before and after the test.
- **Task 2:** Tribological and scratch characterization of the optimized coating was evaluated before and after UV exposure.

Figure 1.1 shows the clear research methodology that was adopted during our research to meet all the objectives stated above.

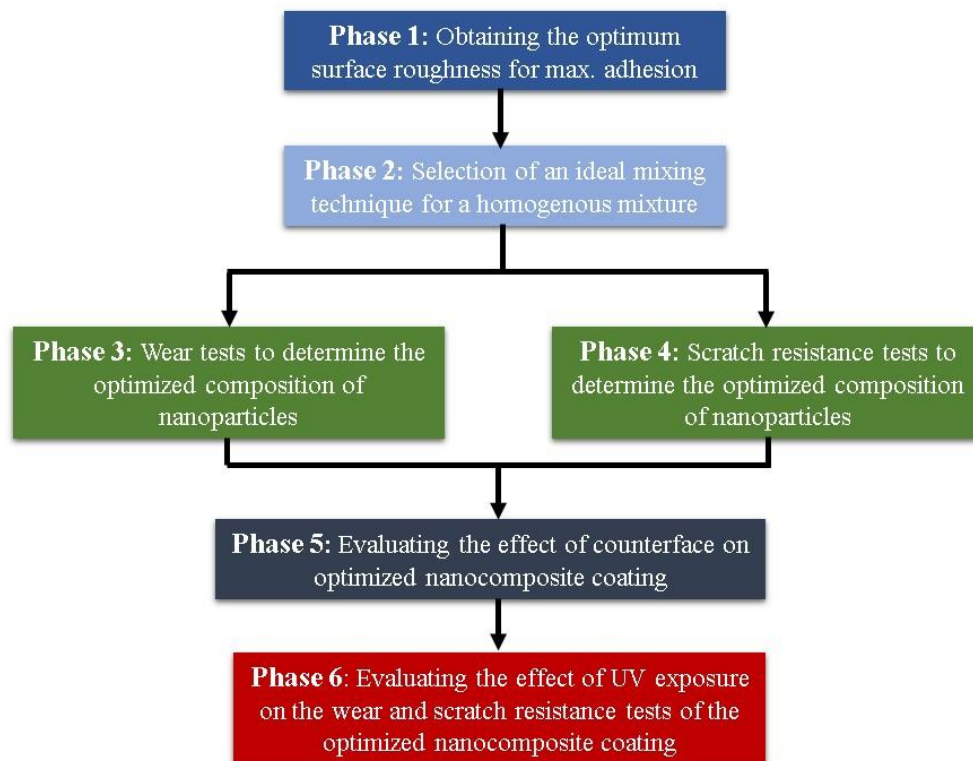


Figure 1.1 Research Methodology followed in the present study

1.5 Organization of the Thesis

In this thesis, Chapter 1 is related to the introduction part of the work. In Chapter 2, an extensive literature review is presented on the effect of surface roughness parameters, various dispersion strategies being used to obtain homogenous mixtures, and developments regarding polymer nanocomposite coatings particularly PEEK-based nanocomposite coatings in the perspective of the current research work. In Chapter 3, the experimental methods/procedures used in this study are described. Chapter 4 presents the experimental results and discussion related to all the project phases. Chapter 5 presents all the conclusions obtained from the work and suggests a few recommendations for the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Tribology

The science of interacting surfaces in their relative motion is known as Tribology. It is a multi-disciplinary field. It deals with the phenomenon of friction, wear, and lubrication to reduce energy loss as well as increase the operational life of components in a system. It plays an important role in modern machinery that involves sliding and rolling surfaces. Friction and wear are major concerns in practically all modern mechanical machines. A few examples are internal combustion and aircraft engines, automobiles, gears, cams, bearings, and seals. In a survey in 1966, it was estimated that about 4% of the GNP of the United States was wasted due to neglect of the role of Tribology. At present, about one-third of energy resources are wasted due to the involvement of friction directly or indirectly [1]. So, it is significant to consider the causes of friction and wear. The aim of research and development in tribology is to minimize losses due to friction and wear as much as possible. Today tremendous research is going on to achieve this aim and tremendous achievements have been achieved. People are using different fillers to make composites to get better tribological properties. However, research to improve further is still necessary.

2.2 Significance of polymer and polymer-based nanocomposite coatings in tribological applications

The tribology of polymers is not the same as that of metals, ceramic materials, and their derivatives because of differences in chemical and physical structures. The polymers have very low surface free energy [22]. Polymers show viscoelastic properties due to which they are being affected differently in terms of tribological behaviors. The effect of different tribo-system parameters on the wear of polymer is even stronger than that for metals [23].

Polymer coatings have become essential in many industries, primarily for their protective and aesthetic benefits. These coatings are used to enhance the durability, corrosion resistance, and chemical stability of materials. Some common types include epoxy, polyurethane, polytetrafluoroethylene (PTFE), ultra-high molecular weight polyethylene (UHMWPE), and polyether ether ketone (PEEK). Each type of polymer coating is selected based on specific requirements such as mechanical strength, temperature resistance, and environmental stability.

C. G. Clarke et al. [24] in their studies, evaluated the tribological behaviors of five different polymers (UHMWPE, PETP, P (A-I)/GR, POM, and PA6/MoS₂) under water lubrication for applications of bearing surfaces between the body of a hydraulic drill and tool holder. They proved that all parameters including counterface roughness, sliding velocities, and pressure had a great impact on the tribological behaviors of these polymers.

H. Meng et al. [25] compared the tribological behavior of CNTs reinforced polyamide 6 (PA6) composites with pristine polymer in dry and water-lubricated condition at different loads. They found that CNTs reinforced composites showed less COF and more wear resistance under dry and lubricated conditions as compared to that of pristine PA6 matrix.

Samad et al [26] evaluated the effect of temperature on tribological behavior of a CNTs reinforced UHMWPE nanocomposite coating on steel substrates with or without PFPE overcoat under dry as well as base oil lubricated conditions and found variation in the tribological results at different temperatures.

2.3 Limitations of these polymers

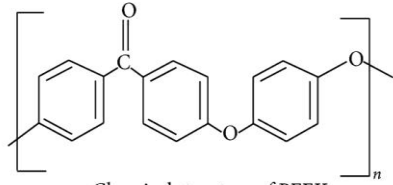
Despite their widespread use, traditional polymer coatings come with limitations. For example, epoxy coatings, although robust and resistant to chemical corrosion, can be prone to cracking under thermal stress [27]. Similarly, PVC coatings are widely used for their chemical resistance but degrade over time when exposed to UV light and harsh weather [28]. PTFE coatings, known for their non-stick properties and temperature stability, are less effective in environments that require abrasion resistance. These limitations drive the search for advanced coatings that can endure harsher conditions and offer superior performance.

2.4 Polyether Ether Ketone (PEEK)

PEEK is a high-impact polymer showcasing exceptional mechanical and physical properties. PEEK polymers are manufactured by step-growth polymerization by the dialkylation of bisphenol salts. PEEK has a low surface energy, due to which it displays a

low adsorption rate. PEEK was found to have a low water solubility range of 0.5 wt% even at temperatures around 260°C [29]. PEEK, a semi-crystalline material, exhibits an elastic modulus of around 3.1 GPa. This unique balance of properties makes PEEK exhibit excellent performance in harsh environments where other most commonly used polymers like polyamide (PA), polytetrafluoroethylene (PTFE), and ultra-high molecular weight polyethylene (UHMWPE) fail to withstand (Figure 2.1). Table 2.1 provides in-depth information of the various properties the PEEK exhibits and its chemical structure.

Table 2.1 Structural, mechanical, and thermal properties of PEEK [44,45]

PROPERTY	VALUE
Structure	 Chemical structure of PEEK
MECHANICAL	
Elongation at Break (%)	20-40
Impact Strength (KJ/ m²)	5-8.5 at 20 °C
Modulus of Elasticity (GPa)	3.3 – 4.0
Shear Stress (MPa)	90 – 120
Coefficient of friction	0.3-0.38
Density (g/cm³)	1.3 ± 0.02
Elongation (% strain)	0.3-1.5
THERMAL	
Coefficient of Thermal Expansion	4.7 – 6x10⁻⁶ K⁻¹

Melting Point ($^{\circ}$ C)	340-343
Specific Heat Capacity (J/(Kg K))	2100 - 2200 at 20 $^{\circ}$ C
Maximum Working Temperature ($^{\circ}$ C)	239-260
Poisson's Ratio	0.43

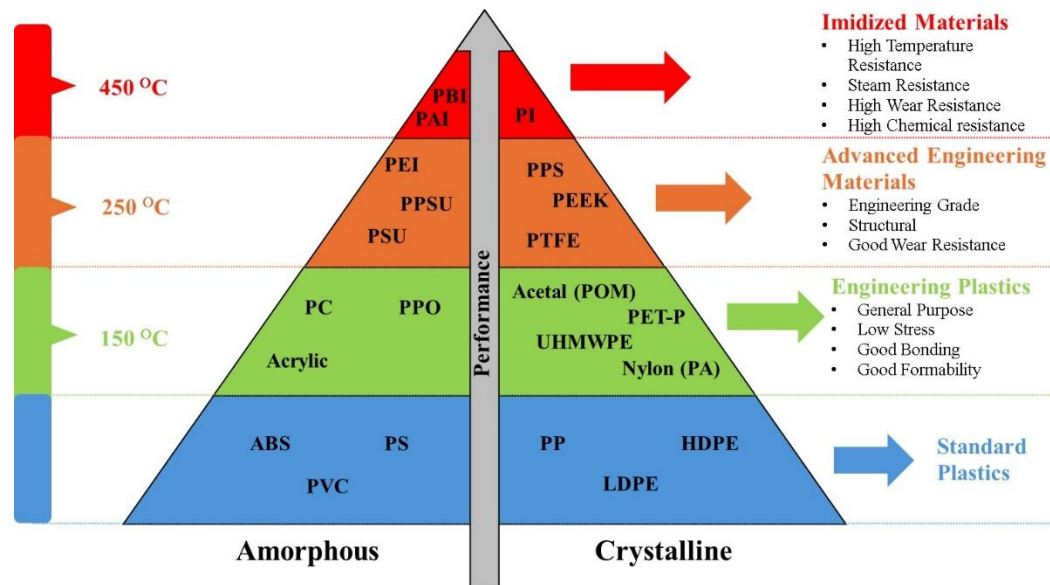


Figure 2.1 Polymer pyramid, listing PEEK with other thermoplastic polymers with regard to performance and formability

2.4.1 Applications of PEEK

Driven by the fuel efficiency demand, there is much impetus to replace metallic parts with lighter alternatives such as plastic or polymer materials. As discussed, the exceptional behavior of PEEK in extreme conditions makes it a suitable replacement in the manufacturing of automobile parts like seals, washers, and bearings. Aluminum is a popular choice in the aerospace industry due to its lightweight. PEEK, being a lighter material than aluminum, have become an alternative for the latter, especially in the

aerospace industry [32]. Nowadays, PEEK has also found its way into medical applications due to its biocompatible nature, which stems from its insolubility in most polymeric solvents [47,48]. It is also an appropriate choice for dental implants in composite form [35]. Being an excellent insulator, it has found its way into electrical instruments operating at high temperatures, such as handles of soldering irons [36]. Due to its exceptional chemical and heat resistance, it has been also used extensively in oil and gas applications [37].

2.4.2 Limitations of PEEK

Despite its excellent mechanical and physical properties, PEEK exhibits a high coefficient of friction (COF), between 0.30 – 0.38, in addition to a high wear rate [38]. A lot of research has been conducted on various polymers like ultra-high molecular weight polyethylene (UHMWPE) and polytetrafluoroethylene (PTFE) due to their low coefficient of friction in the range of 0.09 to 0.12 and 0.05 to 0.08 respectively. However, all these polymers exhibit poor thermal stability due to their low melting point, limiting their applications in extreme working environments under high load and speed.

2.4.3 How to overcome these limitations

To overcome these challenges, numerous kinds of research are conducted on thin polymer coatings. Polymer coatings are characterized by low friction, wear, low deposition cost, simple deposition techniques, etc. As a result, polymers like PTFE, UHMWPE, PEEK, etc. are being widely investigated. Among these, PEEK stands out showing excellent thermal and mechanical properties, which allows it to be widely used in extreme environmental conditions. However, as discussed earlier, pristine PEEK as thin coatings tend to show a high coefficient of friction and high wear rate. To enhance

the properties, fillers are added to the PEEK feedstock as reinforcements. Research has been conducted on incorporating PTFE, CF, graphite, CNT, etc. with PEEK to take advantage of the individual properties of each filler into one product. The quality and enhancement in the performance of the hybrid/composite coatings depend on the shape and size of the reinforcements used, the dispersion technique as well as the deposition methods employed.

2.5 Cerium dioxide/Ceria (CeO₂)

Cerium dioxide is a versatile rare earth metal compound that finds usage in a wide range of biological and engineering fields. As a rare earth metal compound, ceria exhibits exceptional mechanical strength, thermal stability, and chemical resistance, making it highly desirable for use in demanding industrial environments [53,54]. Moreover, ceria nanoparticles have also gained significant attention in both the cosmetic and materials science fields for their exceptional Ultraviolet (UV) protective properties. In sunscreens, ceria is valued for its ability to absorb and scatter UV radiation, effectively shielding the skin from harmful UV rays that can lead to sunburn, skin aging, and increased risk of skin cancer [55-57]. Ceria's UV-blocking capabilities and its antioxidant properties are particularly beneficial in environments like the aerospace and automotive industries, where materials are often exposed to harsh sunlight and fluctuating temperatures [58,59]. Polymer nanocomposite coatings are highly effective in reducing mechanical stresses however not all reinforcements will provide resistance against UV and prolonged exposure to outdoor environments will result in degrading the polymer's molecular structure, leading to photooxidation, and a significant loss of mechanical integrity [60,61]. This degradation compromises the protective function of the coatings, ultimately

reducing their performance and lifespan. As a result, enhancing the UV resistance of high-performance polymers such as PEEK has become a focal point of research. Ceria's remarkable ability to absorb UV radiation and prevent the breakdown of polymer structures has opened new avenues for enhancing the durability of polymers [48]. Ceria's unique electronic structure allows it to absorb and dissipate UV radiation, thus preventing the photo-oxidative reactions that typically degrade the polymer surface [49]. All these properties along with ceria's high hardness and wear resistance behavior make it compatible with applications involving heavy loads and high-speed operation, such as in the manufacturing of bearings, gears, and other mechanical components subjected to extreme forces [64-66].

In recent years, a lot of development in polymer/ceramic nanocomposites has been carried out due to the outstanding properties offered by these nanocomposites as compared to pristine polymers.

Kumar et al [53] evaluated the tribological and mechanical properties of thermally sprayed $\text{Al}_2\text{O}_3/\text{CeO}_2$ nanocomposite coatings and concluded that reinforcing CeO_2 helped in improving the mechanical characteristics of coating-substrate interface and also exhibited lower values of coefficient of friction and increased wear resistance even at high load and high sliding velocity.

Thappa et al [54] used high-velocity oxygen-fuel (HVOF) sprayed WC-Co-Cr coating reinforced with ceria for thermal applications. It was observed that WC-Co-Cr/ CeO_2 nanocomposite hybrid coating exhibited better erosion resistance and improved the

corrosion resistance and enhanced better thermal stability when compared to WC-Co-Cr coating.

2.6 Existing gaps in the literature and addressing the existing gaps

Current research on PEEK and its composites, while extensive in basic wear and friction studies, still lacks comprehensive evaluations under more demanding conditions, such as high load, high-speed wear tests, scratch tests, UV exposure, and the influence of different counterface materials. These factors are critical for understanding how PEEK and its composite coatings will hold up in real-world applications that involve intense mechanical stress, exposure to sunlight, and interaction with various materials.

In many applications, materials like PEEK are subjected to high-load and high-speed wear environments, such as in automotive or aerospace components. However, limited research explores how PEEK and its composites truly perform under these strenuous conditions. High load and high-speed tests are essential to determine the durability of PEEK, as they reveal how the material handles significant frictional heating and material deformation. Such tests allow us to evaluate wear depth, the rate of material loss, and whether reinforcements like ceria can reduce wear by enhancing load-bearing capacity and minimizing surface damage. In applications where consistent, long-term performance is vital, these high-stress wear tests provide crucial insights into PEEK's reliability and longevity. Another key area is the material's scratch resistance, especially in applications where surfaces might experience direct, sharp contact. Scratch tests simulate the impact of concentrated forces on the coating, helping to assess its resilience to cracking, surface deformation, and potential for wear initiation. Testing PEEK and PEEK/ceria

nanocomposite coatings under these conditions allows us to evaluate whether the addition of ceria strengthens the material's resistance to such damage, making it more suitable for harsh operational environments.

UV exposure testing also fills an important gap, as PEEK and PEEK composites may often be used in outdoor or high-UV settings. UV radiation can alter the material's surface properties, potentially leading to increased brittleness or surface degradation. By conducting UV tests on PEEK and PEEK/ceria nanocomposite coatings, we will be able to assess how these coatings maintain their wear resistance and structural integrity after prolonged exposure to UV light, which is especially valuable for applications like outdoor machinery and aerospace components. Finally, the effect of counterface materials has often been overlooked but is a critical factor in the performance of tribological coatings. The nature of the counterface, whether it is softer, harder, or has specific roughness can significantly impact wear characteristics, frictional behavior, and overall coating lifespan. Testing the developed nanocomposite coatings against various counterfaces provides insights into how these coatings interact with different materials, which is crucial for applications where components may encounter a wide range of surface types. This allows us to determine whether certain counterfaces accelerate or reduce wear and if the ceria enhanced PEEK coatings perform consistently well regardless of the counterface material.

Our research will address these gaps by conducting high load, high-speed wear tests, UV exposure assessments, scratch testing, and evaluations across different counterfaces, offering a robust understanding of how PEEK and PEEK/ceria coatings perform under

real-world stresses. This holistic approach provides insights that can guide material selection and optimization for industries requiring durable, wear-resistant, and versatile coatings.

2.7 PEEK coatings

Nowadays, many researchers are focusing on improving the characteristics of PEEK to be used as a bulk material as well as thin coatings on numerous substrates. Limited works have been carried out by using pristine PEEK as a coating on different substrates especially due to their high coefficient of friction and high wear. Selection of appropriate deposition technique which depends on respective material properties is critical to coating performance.

Zhang et.al [29] conducted the friction test on CO₂ and Nd: YAG remelted flame-sprayed PEEK coating by using an oscillating ball-on-disc tribometer. The CO₂ laser remelting resulted in a semi-crystalline structure whereas Nd: YAG laser remelting resulted in an amorphous structure of the coating. The tests were performed under the applied load of 2 N and speed of 0.3 m/s against a steel ball in dry sliding conditions. It was also observed that the peak value of the coefficient of friction obtained with both the CO₂ and Nd: YAG laser-remelted coatings was about 0.35. However, the CO₂ laser-remelted coating exhibited a slightly lower friction coefficient. This was ascribed to the difference in the crystal structure of remelted coatings. It is to be noted that the reported value of friction coefficient (~ 0.35) is higher compared to other polymer coatings.

Similarly, Kruk et. al [55] studied the effect of PEEK coating in improving the tribological performance of the Ti-6Al-4V substrate. A general improvement in wear

resistance by more than 100 times and a reduction in friction coefficient by two times (from 0.72 to 0.27) was reported with PEEK coating on the substrate. Further, the effect of coating structure on room temperature mechanical and scratch properties along with tribological properties (at Room temperature, 150 ° C, and 260 ° C) was also studied. Furnace cooling of the coated sample after the post-deposition heat treatment resulted in a semi-crystalline structure whereas water cooling resulted in an amorphous structure of the coating. Coatings with semi-crystalline structures exhibited greater micro-hardness, elastic modulus, and scratch resistance in comparison to amorphous structures. Additionally, higher wear resistance and relatively lower friction coefficient were also reported at all test temperatures. Therefore, slow cooling rates after post-deposition heat treatment appear to have a positive effect on tribological properties. Various deposition techniques reported in the literature for depositing pristine PEEK on metallic substrates are presented in Table 2.2.

Table 2.2 Effect of post-deposition treatment on coating characteristics

Ref.	Deposition Technique	Substrate	Coating Characteristics	Post-Deposition Treatment	Coating Characteristics after post-deposition treatment
[29]	Flame Spray	SS	Large porosity, Thin film, weak adhesion, Poor mechanical properties	Nd: YAG laser remelting	Dense and homogeneous coating
				CO ₂ Laser remelting	No complete elimination of porosities near the interface
[56]		Al	High porosity, poor mechanical properties	Nd: YAG laser remelting	No complete elimination of porosities near the interface
				CO ₂ Laser remelting	
		SS	Nd: YAG	Diminished	

				laser remelting	porosities near the interface
				CO ₂ Laser remelting	Dense and homogeneous coating
[55]	Electrophoretic	Ti-6Al-4V	Not Available	Heat-treatment in Oven	Dense, homogeneous, and continuous

2.7.1 PEEK nanocomposite coatings

The lubrication strategies have been the most common focus of research interest. Currently used techniques involve the usage of hard coatings and lubricants with additives to reduce wear and friction. However, these techniques suffer from their drawbacks.

The development of PEEK nanocomposite coatings presents several challenges. Substrate preparation is critical as it ensures proper adhesion between the coating and the substrate; improper cleaning or surface roughening can lead to coating delamination. Powder mixing of PEEK with ceria nanoparticles requires uniform dispersion to avoid agglomeration, as inconsistent mixing can lead to defects in the coating. Additionally, deposition techniques, such as thermal spraying or spin coating, require precise control of parameters like temperature, speed, and environment to achieve a consistent and defect-free coating layer. These steps demand careful optimization to maintain the coating's tribological and mechanical performance.

To overcome these challenges, numerous kinds of research are conducted on thin polymer coatings. Polymer coatings are characterized by low friction, wear, low deposition cost, simple deposition techniques, etc. As a result, polymers like PTFE,

UHMWPE, PEEK, etc. are being widely investigated. Among these, PEEK stands out showing excellent thermal and mechanical properties, which allows it to be widely used in extreme environmental conditions. However, as discussed earlier, pristine PEEK as thin coatings tend to show a high coefficient of friction and high wear rate. To enhance the properties, fillers are added to the PEEK feedstock as reinforcements. Research has been conducted on incorporating PTFE, CF, graphite, CNT, etc. with PEEK to take advantage of the individual properties of each filler into one product. The quality and enhancement in the performance of the hybrid/composite coatings depend on the shape and size of the reinforcements used, the dispersion technique as well as the deposition methods employed.

2.7.2 Significance of roughness parameters of the substrate on the tribological properties of PEEK coatings

Surface preparation is a crucial phase in coating applications since it ensures the durability, adherence, and overall performance of protective coatings on a variety of substrates. The procedure requires careful cleaning, treating, and at times modifying the surface to prepare it for coating. Neglecting or underestimating the importance of surface preparation can result in a variety of problems, including poor adhesion, premature coating failure, lower durability, and higher maintenance costs. Surface preparation for coatings is mandatory for a variety of reasons and factors such as the substrate's nature, ambient circumstances, and the type of coating system used all play important roles. Surfaces subjected to harsh weather, high humidity, or chemical exposure, for example, require more rigorous surface preparation to maintain the coating's long-term performance. During the coating time, monitoring environmental parameters like

humidity, ambient temperature, and accumulation of dust contaminations can indirectly affect the quality of the prepared surface [57]. The presence of these impurities forms a barrier that hinders the coating's proper substrate adhesion. Since a roughened surface offers greater anchoring for the coating to connect with, surface preparation may include altering the surface profile to improve the mechanical adherence of the coating. As a result, a well-adhered coating is of utmost importance in guaranteeing long-term performance, thereby assuring that a higher level of effort is required to peel off the coatings under tensile or shear loads [58,59]. Surface texturing is a technical term that involves several features like flaws, lay, waviness, and roughness. These are the features that need to be extensively observed while trying to justify the adhesive strength of the coating, primarily, the roughness parameter [60]. Before applying a particular coating to the system, coating manufacturers usually advise achieving an ideal surface roughness to improve the quality of the coatings. Several factors, including spatial and height parameters, can significantly influence the degree of adherence to the coating [61].

Texturing of surfaces is a common technique used by many researchers to obtain the required surface roughness for various coating applications. One of the ways to achieve it is by grit blasting the surface of the substrate by using specific abrasive grit. Several researchers have given substantial findings in achieving the desired adhesion by using this technique [62-64]. As a result, the topography becomes rougher and there are more contact regions, which promotes the coating and sample to mechanically interlock [65]. The cleanliness of the substrate also greatly affects the level of adhesion of the coatings along with the surface roughness [66]. This parameter also improves the wettability of the coated media to the substrate and promotes sites for mechanical interlocking [67].

However, a well-polished sample is also free from corrosion and contaminants, thereby creating a higher surface contact area between the two mediums. Thus, this characteristic appears to run counter to the previous debate on the significance of surface texturing.

Surface roughness describes the variations or imperfections present on the surface of a material. These imperfections can range from microscopic to macroscopic scales and can have a significant effect on how well the coating adheres to the substrate. Surface roughness parameters, such as average roughness (R_a), root mean square roughness (R_q), peak-to-valley height (R_z), the kurtosis, and the skewness of the peak and valley distributions directly affect the adhesion strength of the coating [68,69].

The average roughness (R_a) is a commonly used parameter to define the surface roughness of a material [70]. In terms of surface height deviations from the mean line, it is the arithmetic mean of their absolute values. A higher R_a value indicates a rougher surface, which can enhance the adhesion of the polymer coating if maintained within a certain limit. The increased surface area resulting from higher roughness provides more contact points for the coating to adhere to, improving its overall adhesion strength.

Root mean square roughness (R_q) is another important parameter that characterizes the surface roughness. It represents the square root of the average of the sum of the squared height deviations from the mean line. R_q provides a more comprehensive measure of the roughness, considering both the height and distribution of the irregularities. A higher R_q value signifies a more uneven surface, which can positively impact the adhesion of the polymer coating within a certain limit.

Peak-to-valley height (R_z) measures the vertical distance between the highest peak and the lowest valley within a sampling length (Figure 2.2). It provides information about the extreme irregularities present on the surface. Greater surface height variation, indicated by a higher R_z value, can promote adhesion by strengthening the mechanical interlocking between the coating and the substrate [70].

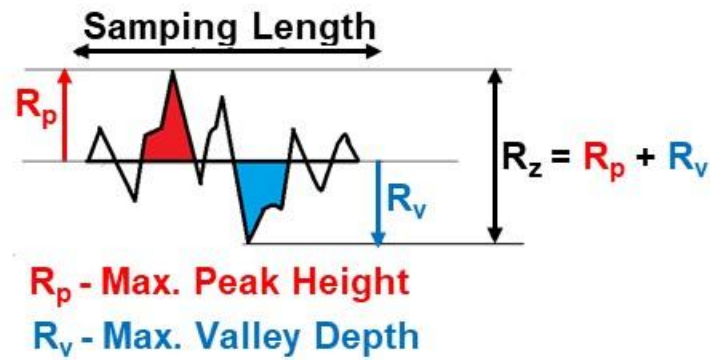


Figure 2.2 Schematic of Surface Roughness 2D profile showing the R_p , R_v , and R_z measurements

Skewness (R_{sk}) is a statistical measure that describes the asymmetry of the profile [69]. Surface roughness refers to the irregularities and variations in height on a surface, and analyzing the skewness of the profile can provide insights into the directional bias of these irregularities. A surface with zero skewness ($R_{sk} = 0$) in its roughness profile is considered symmetric (Figure 2.3a). This means that the peaks and the valleys on the surface are equally distributed on both sides of the mean line. A positively skewed roughness profile ($R_{sk} > 0$) indicates that there is a greater concentration of peaks on one side of the mean line (Figure 2.3a).

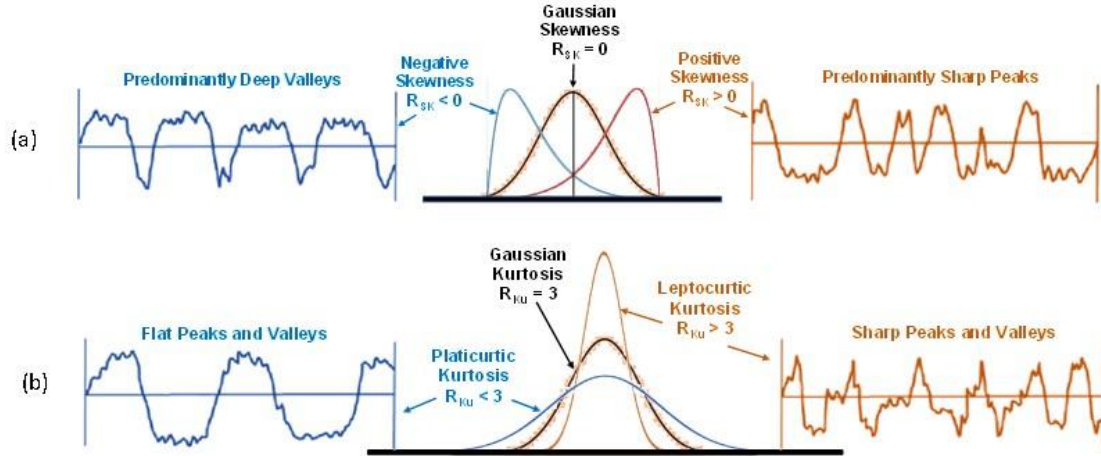


Figure 2.3 Representation of (a) skewness and (b) kurtosis

Conversely, a negatively skewed roughness profile ($R_{sk} < 0$) implies that there is a higher concentration of valleys on one side of the mean line. Similarly, kurtosis (Figure 2.3b) is another roughness parameter that provides information about the flatness or sharpness of the peaks and valleys in the surface profile [69]. A surface profile with positive kurtosis is said to be leptokurtic ($R_{ku} > 3$). This means that the surface has more pronounced and sharper peaks and deeper valleys than a normal distribution. A surface profile with negative kurtosis is considered platykurtic ($R_{ku} < 3$). In this case, the surface has flatter and more spread-out peaks and valleys compared to a normal distribution. Hence, optimizing the surface roughness parameters of the substrates is crucial for achieving the desired adhesion strength. However, it is important to note that there is no universal roughness value that guarantees optimal adhesion. The ideal roughness parameters depend on various factors, including the type of coating, substrate material, and intended application.

2.7.3 Various reinforcements used to fabricate the composite/hybrid PEEK coatings

The reinforcements that have been used to enhance the properties of PEEK coatings can be classified under seven groups: bioactive, ceramic, carbon-based, refractory, metallic, polymeric, and mineral-based materials as shown in Table 2.3. It also shows the characteristics of respective reinforcements that can impart the desired changes in the properties of PEEK coatings. Additionally, certain reinforcements that have been classified under ceramic, refractory, and metallic materials are reported by several studies to exhibit bio-activity, biocompatibility, cytocompatibility, hemocompatibility, anti-bacterial, anti-microbial and anti-inflammatory effects also.

Table 2.3 Classification and characteristics of reinforcements used in PEEK composite/hybrid coatings

Material	Reinforcement	Characteristics	References
Bioactive	Hydroxy Apatite	Bioactive agent, bone-bonding capability, accelerate bone cell growth	[71,72]
	Bioglass	Bioactive agent, rapid bonding with bone, accelerate bone cell growth degradable in body	[73-78]
Ceramic	Al ₂ O ₃	Hard, chemically inert, corrosion resistant, cytocompatibility	[79-83]
	SiO ₂	Hard, chemically inert, biocompatible	[84]
	k-SiO ₂	Hard, chemically inert, hydrophobic	[85]
	SiC	Hard, chemically inert	[86]
	Si ₃ N ₄	Hard, bioactive, accelerates bone repair, antibacterial effect	[87]
	h-BN	Self-lubricating, inert, high thermal conductivity, high thermal stability	[78,88,89]
	TiN	Hard, inert, stable, low friction coefficient	[90]
	WC-CoCr	Hard, chemically inert	[91]

Carbon Based	Graphite	Good load-bearing capability, solid lubricant,	[92,93]
		high electrical and thermal conductivity	
	GO	High strength and elastic modulus, excellent thermal and electrical conductivity	[94,95]
	RGO	High strength and elastic modulus, excellent thermal and electrical conductivity	[96]
	Carbon Fibre	High stiffness, tensile strength, strength-weight ratio,	[95,97]
		thermal and chemical stability	
Refractory	Ta	High heat, wear and corrosion resistance, biocompatible, hemocompatible	[98]
	TaN	High heat, wear and corrosion resistance, biocompatible, hemocompatible,	[99]
		anti-bacterial effect	
	TaB ₂	High heat, wear and corrosion resistance, anti-inflammatory effect	[100]
Metallic	Ag	High thermal and electrical conductivity, anti-bacterial and anti-microbial effect	[77]
	ZnS	High stability, non-toxic, anti-bacterial and anti-microbial effect	[71]
	MoS ₂	Self-lubricating, anti-bacterial effect against certain pathogens	[72]
Polymer	PTFE	Self-lubricating, hydrophobic, chemically inert	[85,101,102]
Minerals	Huntite	Flame retardant material with high decomposition temperature	[101]

2.7.4 Dispersion techniques of the reinforcements within the PEEK matrix

The reinforcements selected must be thoroughly and uniformly distributed within the PEEK matrix in order to obtain the targeted result. Non-uniform distribution can lead to the agglomeration of the particles, which will result in degrading the properties including the adhesion between film and substrate. Hence, a variety of dispersion techniques have

been used to disperse the reinforcements within the PEEK matrix for uniform dispersion, which are listed and discussed below.

a. Wet mixing

Ethanol is used as a solvent for the dispersion of powder particles. After adding the powder particles to ethanol, the mixture is sonicated in either an ultrasonic bath or by using a probe-sonicator. The sonication is performed to deagglomerate and uniformly disperse the powder particles. It is followed by mixing by magnetic stirring of the suspension as shown in Table 2.4. In some studies, mixing by magnetic stirring is performed first which is followed by sonication [71-73,77,78]. The prepared suspension is directly used in the electrophoretic coating process. On the other hand, for electrostatic and flame spray coating processes which require feedstock in the form of dry powder, the suspension is dried in an oven to completely evaporate the solvent. In preparation of composite powder for electrostatic spray coating [103], after adding the filler to ethanol, the solution was sonicated using a probe-sonicator for 30 minutes. After the deagglomeration and uniform dispersion of filler, the matrix powder (PEEK) was added followed by sonication for another 30 min. Similarly, in preparation of hybrid powder for electrostatic coating, the solution containing primary composite powders was magnetically stirred for 10 min. Then the secondary filler was added to this solution followed by magnetic stirring for 15 minutes. The different sonication and magnetic stirring times presented in Table 2.4 indicate that the choice of time is based on the researcher's practical observation.

Table 2.4 Dispersion parameters used for wet mixing of powders

Solvent	Particles to Disperse	Dispersing Time	Mixing Time	Solvent Evaporation	Coating Technique	Ref
Ethanol	Ta+PEEK	30 min in ultrasonic bath	30 min magnetic stirring	Not Applicable	Electrophoretic	[98]
	Al ₂ O ₃ +PEEK	30 min in ultrasonic bath	7 min magnetic stirring			[80]
	TaN+PEEK	30 min in ultrasonic bath	30 min magnetic stirring			[99]
	Bioglass+PEEK	30 min in ultrasonic bath	5 min magnetic stirring			[74]
	PTFE+PEEK	15 min in ultrasonic bath	10 min magnetic stirring			[101]
	ZnS+HA+PEEK	20 min in ultrasonic bath	10 min magnetic stirring			[71]*
	Graphite+PEEK	15 min in ultrasonic bath	5 min magnetic stirring			[92]
	Al ₂ O ₃ +PEEK	20 min in ultrasonic bath	5 min magnetic stirring			[79]
	Si ₃ N ₄ +PEEK	20 min in ultrasonic bath	10 min magnetic stirring			[87]
Ethanol + isopropanol	GO+PEEK	6 min probe-sonication	24 hour magnetic stirring			[94]
	RGO+PEEK	6 min probe-sonication	24 hour magnetic stirring			[96]
Ethanol	MoS ₂ +PEEK	20 min in ultrasonic bath				[104]
	MoS ₂ +PEEK+HA	10 min in ultrasonic bath	10 min magnetic stirring			[72]*
	Al ₂ O ₃ +PEEK	20 min in ultrasonic	5 min magnetic			[83]

Ethanol	Bioglass+Ag+PEEK	3-5 min in ultrasonic bath	3 min magnetic stirring	Not Applicable	Electrophoretic	[77]*
	Bioglass+PEEK	1 hour in ultrasonic bath	5 min magnetic stirring			[73]*
	Bioglass+h-BN+PEEK	30 min in ultrasonic bath	5 min magnetic stirring			[78]*
	SiC	30 probe-sonication		Dried in Oven	Electrostatic Spray	[103]
	SiC+PEEK	30 probe-sonication				
	PTFE+PEEK		10 min magnetic stirring			[85]
	PTFE+PEEK+k-SiO ₂		15 min magnetic stirring	80°C for 12 hours		
Ethanol	CF+PEEK	2 hours in ultrasonic bath		60°C for 6 hours	Flame Spray	[97]
Ethanol	CNT+PEEK	2 hours in ultrasonic bath		60°C for 6 hours		[105]

*: Magnetic stirring performed first followed by sonication.

b. Dry Mixing

Dry mixing appears to be the preferred dispersion method when the coating process requires feedstock to be in dry powder form as in the case of electrostatic and flame spray coating processes. It is generally accomplished using a ball mill. Zhu et. al [106] adopted the mechanical dispersion technique of blending. This mixture was then blended on a high-speed blender at room temperature. Before spraying the composite mixture, it was dried in a vacuum oven at 150 °C for 4 hours so as to remove any moisture content. Hedayati et. al [84] used Ball milling for the uniform blending of SiO₂ particles with

PEEK powder. The powders were physically blended and milled at a planetary ball milling machine for 15 hours at 280 RPM. Similarly, Li et al [105] also blended CNT particles with PEEK powders at a speed of 150 rpm for 90 minutes.

2.7.5 Tribology of PEEK nanocomposite coatings

It is well established that the tribological behavior of materials is different in different environments. Many researchers evaluated the tribological behavior of PEEK nanocomposite coatings which are discussed below.

Rehman et al [73] deposited PEEK/bioactive glass composite coating over 316 L stainless steel substrates using an electrophoretic deposition technique. After the coating, the samples were sintered at temperatures of 355 °C, 375 °C, 400 °C, and 450 °C for 30 min at a heating rate of 2 °C/min followed by cooling to ambient temperature at a cooling rate of 20 °C/min. Wear tests were performed by a pin-on-disc method at a normal load of 7 N. The scratch tests concluded that the coating heat treated at 400 °C was found to exhibit the highest wear resistance at the implantation load (Figure 2.4). However, the addition of bioactive glass has increased the COF when compared to pure PEEK coating (from 0.26 to 0.37). But is in direct relation to the wear behaviour of the coating for designing the implant in the study performed.

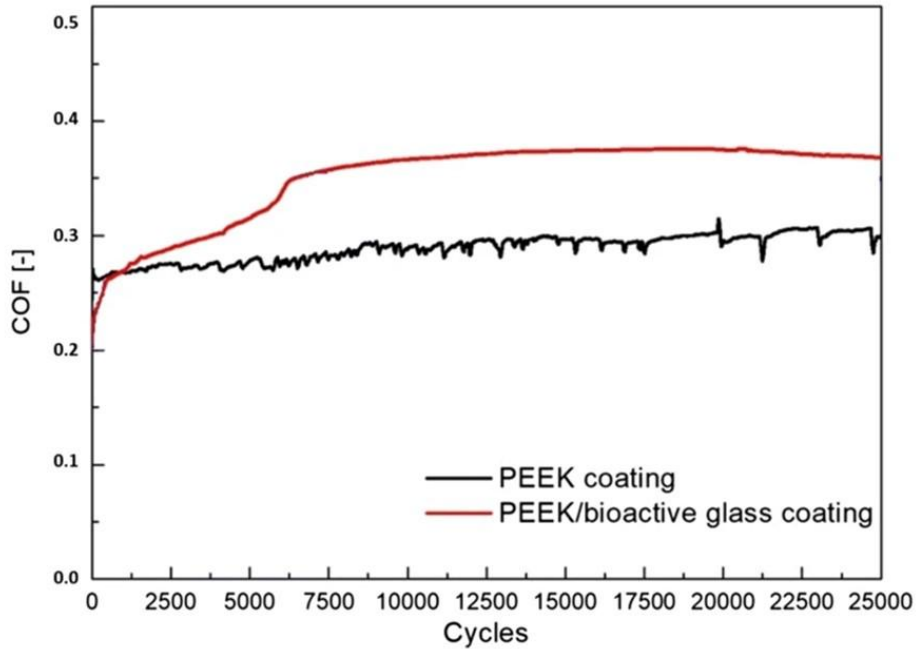


Figure 2.4 COF graph for PEEK and PEEK/BG coatings (sintered at 400 ° C) [73]

Moskalewicz et al [79] deposited $\text{Al}_2\text{O}_3/\text{PEEK}$ nanocomposite on Ti-13Nb-13Zr substrate using an electrophoretic deposition technique. The coated samples were dried at room temperature after EPD, then heated in a furnace for 20 min at a temperature of 350 ° C (heating rate of 4.5 ° C/min and cooling rate of 2.7 ° C/min). A ball-on-disk setup was used to study the friction and wear properties of the coatings with alumina (Al_2O_3) balls of 6 mm diameter as the counter face. Testing's were done at a normal load of 5 N at 120 rpm rotation speed corresponding to a sliding distance of 1000 m. A low coefficient of friction of 0.29 was recorded for $\text{Al}_2\text{O}_3/\text{PEEK}$ composite coating in comparison to coefficients of friction of 0.37 for pure PEEK coating. It also showed a two times lower specific wear rate than that of pure PEEK coating. The mean hardness and elastic modulus of the $\text{Al}_2\text{O}_3/\text{PEEK}$ coatings were equal to 0.34 ± 0.03 GPa and 6.2 ± 0.3 GPa, respectively. These values were higher by 15% to 25% compared with the

PEEK coating. The addition of ringer solution (a common electrolyte for corrosion study) was found to reduce the COF to a much lower value under lubricated testing conditions.

Al_2O_3 /PEEK composite coatings were applied by Moskalewicz et al. [83] using the electrophoretic deposition method to the Ti-6Al-4V substrate. The samples that had the coatings applied as-deposited underwent a 20-minute heat treatment at 380°C ($4.5^\circ\text{C}/\text{min}$). Two different cooling rates were used: one in room temperature water and the other in a furnace with a cooling rate of $2^\circ\text{C}/\text{min}$. A Vickers indenter was applied with a maximum load of 100 mN and a dwell time of 15 sec to determine the hardness values of the coatings. A Rockwell C indenter with a $200\text{ }\mu\text{m}$ diamond tip radius was used to evaluate the coatings' scratch resistance. The indenter was moved at a rate of 5 mm/min as the linear load increased from 0.03 to 30 N. The scratch length measured was 5 mm. Using a ball on disc tribometer, the friction and wear tests were conducted against Al_2O_3 balls. At room temperature, 150°C , and 260°C , with a sliding distance of 2000 m, the tests were conducted with a standard load of 5 N and a sliding velocity of 0.05 m/s. Coatings with a semi-crystalline, both Al_2O_3 /PEEK (0.35 GPa) and pure PEEK (0.32 GPa) demonstrated higher hardness values than those with an amorphous structure (0.22 GPa for composite and 0.19 GPa for pure PEEK). Similarly, coatings with a semi-crystalline structure demonstrated a higher scratch resistance as well when compared to the coatings having an amorphous structure. At room temperature, the Al_2O_3 /PEEK composite coatings showed a coefficient of friction of 0.25, whereas the pure semi-crystalline PEEK and pure amorphous PEEK coatings showed coefficients of friction of 0.3 and 0.33, respectively. Additionally, at room temperature, it demonstrated a five-fold reduction in wear rate compared to pure semi-crystalline PEEK coatings. The

Al₂O₃/PEEK composite coating's coefficient of friction rose to 0.37 and its wear rate increased seventeen times at 150 °C compared to room temperature. Tests conducted at 260 °C showed that the Al₂O₃/PEEK composite coating's coefficient of friction rose to 0.35 and its wear rate increased by 70 times compared to room temperature.

Hedayati et al [84] studied the tribological properties of PEEK coatings reinforced with SiO₂ nanoparticles deposited on plain carbon steel (st 37) using an electrostatic spray coating technique. The coated samples were transferred into an oven for post-heat treatment (30 min at 430 °C for pure PEEK and 50 min at 450 °C for nanocomposite coatings). Semi-crystalline coatings (P for pure PEEK coating and PS for nanocomposite coating) were obtained by cooling the coatings to room temperature while amorphous coatings were obtained by quenching the melted coatings on an ice-water medium (denoted by P-Q and PS-Q, respectively for pure PEEK and nanocomposite coatings). Vickers microhardness was used to determine the hardness measurement at a load of 25 gf. The friction and wear tests were done on a pin-on-disc configuration at varying loads (3, 7, and 11 N) and a sliding speed of 0.13 m/s corresponding to a sliding distance of 1000 m (Figure 2.5). Hardness values were found to increase with the addition of SiO₂. The semi-crystalline PEEK exhibited a higher hardness value (~19 HV) than the amorphous PEEK coatings (~15 HV). However, there were no comparable differences in the hardness values of the semi-crystalline nanocomposite coating (~26 HV) and the amorphous nanocomposite coating (~25 HV). The COF of the semi-crystalline and amorphous nanocomposite coatings was observed to be higher than the pure ones. Regardless of the crystalline structure of the matrix, after incorporating SiO₂ particles, the wear resistance of the coatings improved. At all three loading conditions, the semi-

crystalline nanocomposite coatings exhibited higher wear resistance than the amorphous nanocomposite coatings.

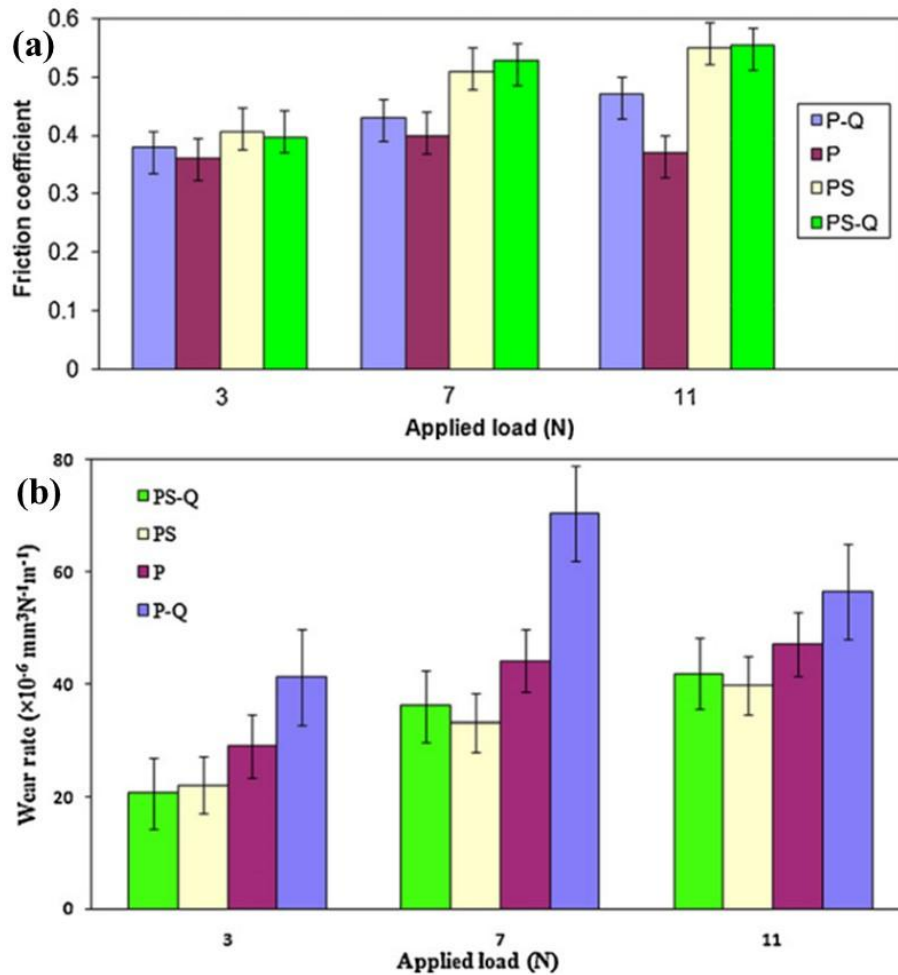


Figure 2.5 (a) The friction coefficients and (b) wear rates of the different coatings vs. the different applied loads [84]

Zhang et al [86] deposited SiC/PEEK composite coatings on an aluminum substrate using the printing technique. After depositing the powders, the coatings were heated to 370 °C for 5 min and then quenched into water at room temperature to obtain the desired coating having a thickness of 40 μm . Friction and wear tests were done on a ball-on-disc arrangement at varying loads (1, 5, and 9 N) and varying sliding velocities (0.2, 0.5, 0.8,

1.1, and 1.4 m/s) corresponding to a total sliding distance of 2000 m. Under low load (1 N), the friction coefficients decrease slightly while increasing the sliding velocity for pure PEEK coatings whereas, under high load (5 and 9 N) and low velocities, the COF remains almost the same. The SiC/PEEK composite coatings exhibited a slightly higher COF than pure PEEK coatings at lower loads but as the loading was increased, it was found to have a decrease in the values of COF. A lower wear rate was evident with the introduction of SiC nanoparticles. As the sliding velocities were increased, the nanocomposite coatings exhibited higher wear resistance when compared to pure PEEK coatings.

Tharajak et al [88] studied the friction/wear properties of PEEK coatings reinforced with hexagonal boron nitride (h-BN) deposited over low carbon steel (AISI 1040) by flame spray technique. A Vickers microhardness test setup (load = 300 gf, dwell time = 15 sec) was used to determine the coating's hardness values. The effect of different particle sizes (0.1, 0.5, and 1.5 μm) on the hardness values of the coatings was also investigated. Friction and wear tests were carried out using a ball-on-disc configuration for varying normal loads (5 & 25 N) and a sliding speed of 0.1 m/s for a sliding distance of 1000 m. The addition of h-BN with a particle size of 0.5 μm provided the highest hardness value. The specific wear rate was lowered by the addition of h-BN particles at an applied load of 5 N. Furthermore, the friction coefficient was lowered by adding larger amounts of h-BN, particularly 8 wt% h-BN to the PEEK covering. Since h-BN had a strong solid lubricating capacity, 8 wt% h-BN/PEEK composite coatings exhibited good efficiency of friction reduction for an applied load of 25 N. In addition, h-BN/PEEK coating with h-BN particle size of 0.1 μm exhibited the lowest specific wear rate, whereas h-BN/PEEK

composite coatings filled with larger-size h-BN particles (0.5 and 1.5 μm) revealed typical sliding grooves from the abrasive wear mechanism.

Moskalewicz et al. [90] deposited titanium nitride (TiN)/PEEK composite coatings on the Ti-6Al-4V substrate by the electrophoretic deposition technique. Samples with the as-deposited coatings were heat treated at a temperature of 390 $^{\circ}\text{C}$ for 40 minutes (heating rate of the samples 4.5 $^{\circ}\text{C}/\text{min}$) and were cooled down in a furnace (cooling rate of 2 $^{\circ}\text{C}/\text{min}$) after soaking. The scratch resistance of the coatings was tested using a Rockwell C indenter with a diamond tip radius of 200 μm for a scratch length of 5 mm and an indenter displacement rate of 5 mm/min for an increasing linear load from 0.03 to 30 N. The friction and wear tests were done on a ball-on-disc configuration for a normal load of 5 N at a rotational speed of 140 RPM corresponding to a sliding distance of 2000 m. No cohesive cracks or adhesive failures were observed in the composite coatings up to the maximum load of 30 N, indicating excellent scratch resistance. The TiN/PEEK708 coatings reduced the coefficient of friction from 0.70 (baseline alloy) to 0.30, indicating a significant improvement in frictional behavior (Figure 2.6). The wear rate of the TiN/PEEK coated oxygen hardened alloy was approximately 70 and 650 times lower compared to the oxygen hardened and baseline alloy respectively.

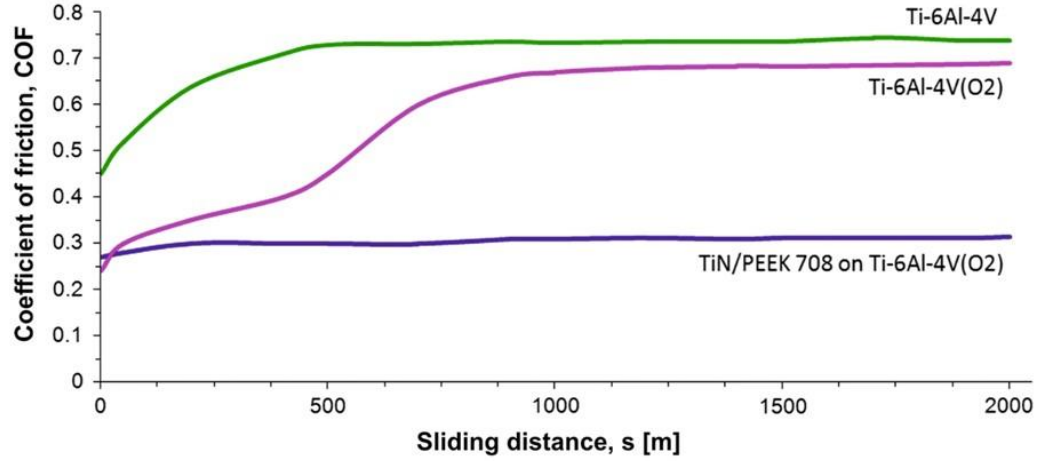


Figure 2.6 Coefficient of friction vs sliding distance for the baseline and oxygen-hardened Ti-6Al-4V alloy and TiN/PEEK708 coated oxygen-hardened alloy [90]

Fiolek et al [92] deposited PEEK/graphite composite coating over Ti-6Al-4V substrate using an electrophoretic deposition technique. The heat treatment consisted of heating the coated samples with the furnace to a temperature of 390 °C at a constant rate of 4.5 °C/min for 40 min, and then cooling with the furnace to room temperature with a cooling rate of 2 °C/min. The scratch tests were conducted using a Rockwell C diamond stylus with a tip radius of 200 µm. The test specimens were linearly loaded from 0.01 N to 30 N with a constant velocity of 5 mm/min on a scratch length of 5 mm. The introduction of graphite fillers was found to reduce the scratch resistance property of the coatings when compared to the unfilled PEEK coatings. It was also observed that the penetration depth of the indenter at the maximum load (30 N) was 75 µm and 65 µm for the composite and pure PEEK coatings respectively (Figure 2.7). The introduction of graphite fillers has however resulted in the reduction of COF. A low COF of 0.10 was observed for the PEEK/graphite composite coating in comparison to the COF of 0.12 for pure PEEK coating. The parallel orientation of the graphite particles embedded in the polymer were

found to be the most advantageous arrangement in terms of improving the friction process.

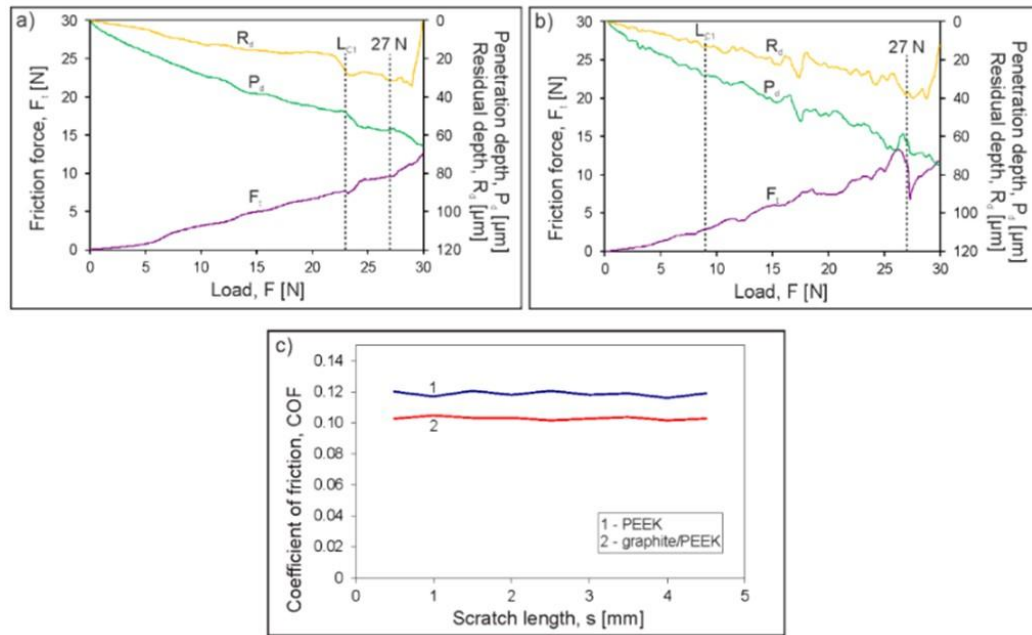


Figure 2.7 The scratch test results (friction force, penetration depth and residual depth signals) of (a) PEEK coating, and (b) graphite/PEEK coating, and (c) friction coefficient of the coatings vs. diamond stylus in a scratch test at 0.25 N constant load [92]

Lio et al [93] deposited PTFE/PEEK/graphite hybrid nanocomposite coating on titanium substrates using an electrophoretic technique. After drying the coating at room temperature for 12 hours, it was heat treated to a temperature of 390 °C for 60 minutes followed by cooling to ambient temperature. The friction and wear tests were performed using a ball-on-disk tribometer. The tests were performed under a normal load of 5 N and 10 N at a sliding velocity of 0.05 m/s at for a sliding distance of 1080 m. A low coefficient of friction of 0.1 was recorded for PTFE/PEEK composite coatings in comparison to coefficients of friction of 0.4 and 0.3 for pure PEEK and PEEK/graphite

coatings. It also showed a three times lower wear rate than that of pure PEEK coatings. The hybrid nanocomposite (PEEK/PTFE/graphite) coatings were found to exhibit a slightly higher wear rate than the PEEK/PTFE coating due to the low bonding strength exhibited by the graphite sheet and PEEK matrix. For tests performed at a normal load of 10 N, the coefficient of friction decreased to less than 0.1 for the PEEK/PTFE composite coating when compared to the pure PEEK and hybrid nanocomposite coatings. However, the wear rate showed that the hybrid nanocomposite coating performed well exhibiting the lowest wear rate due to the well-known load carrying capacity of graphite, and the exceptional lubricating capacity of the PTFE.

Li et al [97] deposited CF/PEEK composite coatings over 17-4PH martensitic stainless steel by flame spray technique. Two types of short carbon fibers (CFs) were used: 300-mesh CFs with intact morphology and 600-mesh CFs with fractured shape and higher graphitization degree. The tribological studies were conducted on a ball-on-disc configuration under normal loads of 5 and 7 N at sliding velocities of 0.2 m/s and 0.5 m/s over a sliding time of 120 min. 300-mesh CFs increased surface hardness by 1.31 times compared to pure PEEK coatings, while 600-mesh CFs led to significantly lower specific wear rates due to higher graphitization degree. The severe wear of the flame-sprayed CF/PEEK composite coatings with carbon fibers of 300 and 600 mesh in 30 wt% content is observed under the different loads and sliding speeds. The average friction coefficient of CF/PEEK composite coatings with different CF types and contents slightly increases with higher loads. Coatings with 10 wt% CF content also showed optimized nanoindentation behavior and tribological properties.

Cao et al [99] studied the effect of tantalum nitride (TaN) nanoparticles on the tribological properties of PEEK coatings deposited by electrophoretic deposition. After drying, all the coatings were heat treated at 390 °C for 60 min at a heating rate of 4.5 °C followed by cooling to ambient temperature. The friction and wear tests were performed against a ZrO₂ counterface ball (Ø = 5 mm) using a reciprocating ball on disk tribometer. The tests were performed under a normal load of 5 N and a sliding speed of 5 Hz for 120 min. A 31.25 % reduction in the COF (0.62 to 0.44) and an 82.80% reduction in the value of specific wear rate (94.2×10^{-6} to 16.2×10^{-6} mm³/Nm) was recorded for TaN/PEEK composite coatings (3 wt% TaN) in comparison to the pure PEEK coatings, thereby exhibiting excellent wear and lubrication effects provided by the TaN. The hardness values of the TaN/PEEK composite coatings (3 wt% TaN) were also found to be increased by 34% (0.35 GPa) compared to the pure PEEK (0.26GPa).

Huang et al [100] deposited (borated tantalum) TaB₂/PEEK composite coating on pure titanium (TA2) substrate by the electrophoretic technique. After the coating, all the samples were heat treated at 390 °C for 60 min at a heating rate of 4.5 °C/min followed by cooling to ambient temperature. The tribological testing was done on a reciprocating ball-on-disc configuration under lubricated conditions by using a simulated body fluid (SBF solution). The testings were conducted at a normal load of 5 N at a sliding speed of 5 Hz for 120 min using a ZrO₂ ball (Ø = 5 mm) as the counter face. The wear rate of TaB₂/PEEK (3 wt% TaB₂) coating in the simulated body fluid (SBF) was 72% lower than that of the PEEK coating, with a COF of 0.164 and a wear rate of 1.45×10^{-6} mm³.N⁻¹.m⁻¹, respectively. An improved hardness values were also observed by the addition of TaB₂

when compared to pure PEEK coatings, with the 3 wt% reinforcement exhibiting the highest value.

Fiolek et al [101] deposited PTFE/PEEK composite coating on Ti-6Al-4V substrates using an electrophoretic technique. After drying the coating was heated treated to a temperature of 450 °C for 20 minutes followed by furnace cooling at the rate of 2 °C/min. The friction and wear tests were performed against an Al₂O₃ ball using a ball on disk tribometer. The tests were performed under a normal load of 5 N and a sliding velocity of 0.05 m/s at Room temperature, 150 °C, and 260 °C for a sliding distance of 2000 m. A low coefficient of friction of 0.1 was recorded for PTFE/PEEK composite coatings in comparison to coefficients of friction of 0.27 and 0.33 for pure semi-crystalline PEEK and pure amorphous PEEK coatings respectively for room temperature testing (Figure 2.8). It also showed a seven times lower wear rate than that of pure semi-crystalline PEEK coatings at room temperature. For tests performed at 150 °C, the coefficient of friction increased to 0.17, and the wear rate increased by four times than that at room temperature for the PTFE/PEEK composite coating. The formation of self-lubricating polymer film due to the presence of PTFE resulted in a low coefficient of friction and wear rate. The coating could not withstand the test at 260 °C.

Kadiyala et al [103] studied the influence of nano and micron-sized SiC particles on PEEK coatings deposited over 316 stainless steel using an electrostatic powder spray technique. After coating, the samples were transferred into an oven at 370 °C for 30 min followed by cooling it to room temperature. Scratch testings were conducted at constant load test conditions (2 to 8 N, slider speed = 0.33 mm/s and traversing time = 15 sec) and dynamic loading conditions (slider speed = 0.33 mm/s and loading rate = 2 N/min). The

scratch hardness and adhesion of coatings improved significantly by two times when compared to pure PEEK coatings with an increase in micro-particles of SiC contents and the optimum concentration was found to be around 10–15 wt%. The nanoparticles (3 wt%) in composite coatings showed significantly improved friction and wear behavior by two times compared to their microparticles (3 wt%) counterparts. The inclusion of SiC particles also significantly improved the load-bearing capacity of the coatings.

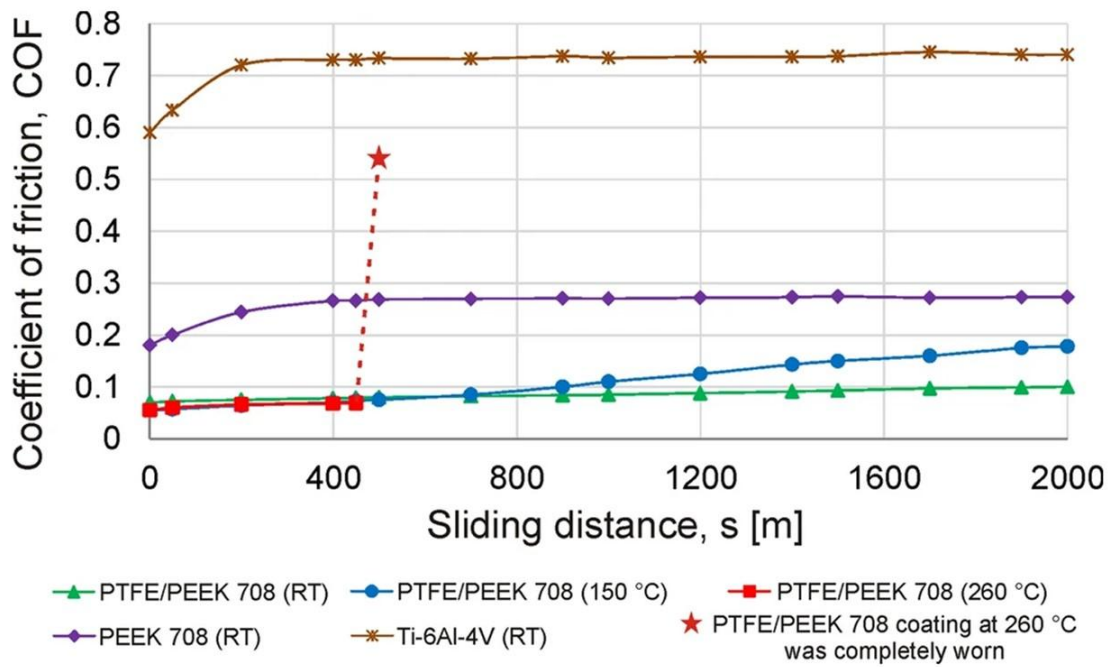


Figure 2.8 The friction coefficient of the uncoated and PTFE/PEEK 708 coated Ti-6Al-4V alloy during dry friction with an Al₂O₃ ball at RT, 150 °C, and 260 °C [101]

Zhu et al [106] deposited PEEK/PTFE composite coating over a stainless-steel substrate by electrostatic powder spray technique. After spraying the powders, all the coated samples were transferred into an oven for post-heat treatment at 380 °C for 5 min. The coatings were then quenched into ice water medium and annealed for 30 min at 260 °C

in an oven to obtain a uniform coating with a thickness of 200 μm . Friction and wear tests were performed on a ball-on-disc arrangement with a 100Cr6 steel ball ($\varnothing = 6 \text{ mm}$) as the counter face. The tests were conducted at a normal load of 10 N corresponding to a sliding distance of 697 m. The PTFE/PTFE composite coating (3 wt% PTFE) exhibited a COF of 0.133 in comparison to the COF of 0.149 for pure PEEK coatings. An improved wear resistance was observed by the addition of PTFE ($38 \times 10^{-6} \text{ mm}^3/\text{Nm}$) when compared to pure PEEK coatings ($44 \times 10^{-6} \text{ mm}^3/\text{Nm}$). However, the addition of PTFE was found to have no improvement in the hardness values.

Qin et al [107] deposited graphene oxide (GO)/carbon fibers (CF)/PEEK hybrid composite coatings on Ti-6Al-4V substrate by electrostatic powder spray technique. After spraying, the samples were put into a furnace at 385°C for post-heat treatment for 60 min at a constant heating rate of $5^\circ \text{C}/\text{min}$ followed by cooling naturally to room temperature. Friction tests were conducted by using a vertical reciprocating wear testing machine with Si_3N_4 as the counter face ball ($\varnothing = 5 \text{ mm}$) at a normal load of 5 N and a sliding speed of 2 Hz for 60 min. A low coefficient of friction of 0.08 was recorded for GO/CF/PEEK hybrid composite coatings in comparison to coefficients of friction of 0.19 for pure PEEK coatings. It was also observed that the addition of nanofillers to the PEEK coatings improved the hardness values (from 17.17 HV to 30.53 HV) in addition to the decreased COF and enhanced wear resistance.

Yeo and Polycarpou et al [108] studied the tribological performances of PTFE/PEEK composite coatings under oil-less compressor conditions deposited over gray cast iron using an electrostatic powder spray technique. The friction and wear tests were conducted on a pin-on-disc configuration at a normal load of 445 N under oscillatory (load = 445 N,

linear velocity = 0.22 m/s) and unidirectional motion (load = 445 N, linear speed = 3.75 m/s). Better performance with lower COF values and wear rates was obtained under unidirectional conditions than oscillatory operating conditions (Figure 2.9).

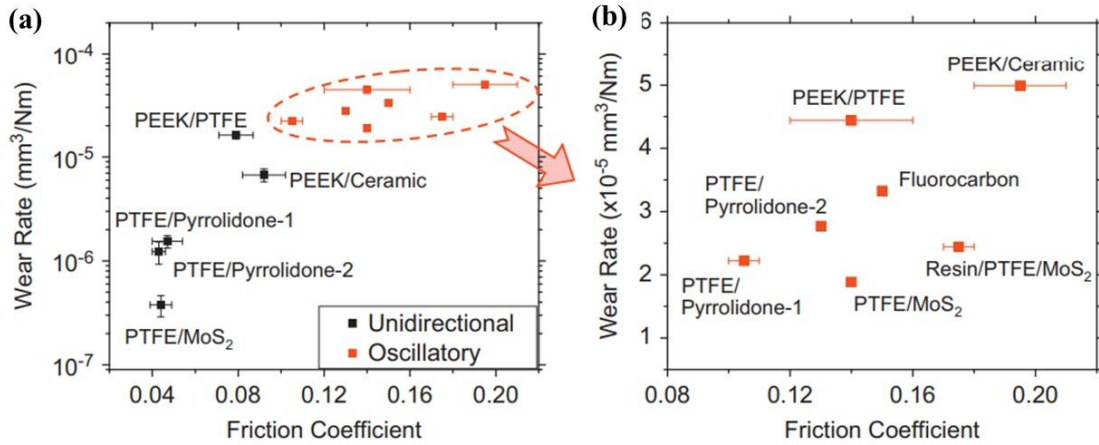


Figure 2.9 (a) Friction coefficient vs. wear rate of seven polymeric coatings under both unidirectional and oscillatory testing and (b) zoom-in of only oscillatory testing result [87]

A summary of the tribological evaluations conducted earlier is provided in Table 2.5.

Table 2.5 Tribological evaluations of the coatings performed under linear sliding conditions

Filler	Substrate	Load (N)	Speed (m/s)	Distance (m)	COF	Sp. Wear rate (X10 ⁻⁶ mm ³ /Nm)	Ref.
Al ₂ O ₃	Titanium alloy	5	0.05	2000	0.25	0.47	[83]
SiO ₂	Carbon Steel (st 37)	3	0.13	1000	0.4	30	[84]
h-BN	Low Carbon Steel	5	0.1	1000	0.2	14	[88]
		25			0.22	37	
TiN	Titanium alloy	5	0.04	2000	0.3	1.1	[90]

PTFE	Stainless Steel	10	NA	697	0.1328	38.57	[106]
SiC	Aluminum disc	9	1.4	2000	0.27	25	[109]
PTFE	Grey Cast Iron	100	4.8	8640	0.07	0.9	[110]
PTFE/Ceramic Blend					0.06	3.8	

* PTFE – Polytetrafluoroethylene, SiO₂- Silicon dioxide, SiC – Silicon Carbide, TiN – Titanium Nitride, Al₂O₃ – Alumina

2.8 Summary

Given the extensive literature review presented above it can be noted that there is still a lot of scope to further improve the properties of these polymer nanocomposite coatings so that they can be used in varying environments. The polymer or polymer nanocomposite coatings can be exposed to different environments during their operational life. For example, the coated components may be operated in extreme conditions as well as challenging environments. Hence, there is an urgent need to further enhance the properties of these coatings so that they will be able to function and protect the sliding components against wear and tear, irrespective of the environment they are exposed to. For this purpose, the developed nanocomposite coatings must have a low coefficient of friction, high wear resistance, high load-bearing capacity, and high resistance to corrosive environments and UV radiations.

As can be seen from the literature, Polyether Ether Ketone (PEEK) is one of the most suitable high-performance polymers among all other polymers which can be used for coating purposes in tribological applications because of its unique properties such as excellent mechanical and thermal properties. However, it has some limitations such as

high friction coefficient, low wear resistance, and faces degradation when exposed to UV radiation.

Ceria is one such filler that exhibits exceptional mechanical strength, thermal stability, and resistance to electrochemical and UV radiation, making it highly desirable for use in demanding industrial environments. As a result, it is one of the most effective nanofillers to be used as a reinforcement in different polymer matrices to improve the overall performance of the developed nanocomposite coating.

Hence in view of the above justification, we defined the main objective of our study to be as follows: ***To evaluate the effect of composition and UV exposure on the Mechanical, Tribological, and scratch resistance properties of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria***

CHAPTER 3

Experimental Work

The details of the materials, experimental procedure for the development of nanocomposite coatings and the characterization techniques used for evaluation of these coatings will be described in this chapter.

3.1 Materials

3.1.1 PEEK powder

Polyether Ether Ketone (PEEK) powder procured from Goodfellow Cambridge Corp (Cambridge, UK) having the following specifications: mean particle size = 50 μm and density = 1.30 g/cm^3 . Figure 3.1 is the SEM image of the received PEEK powder.

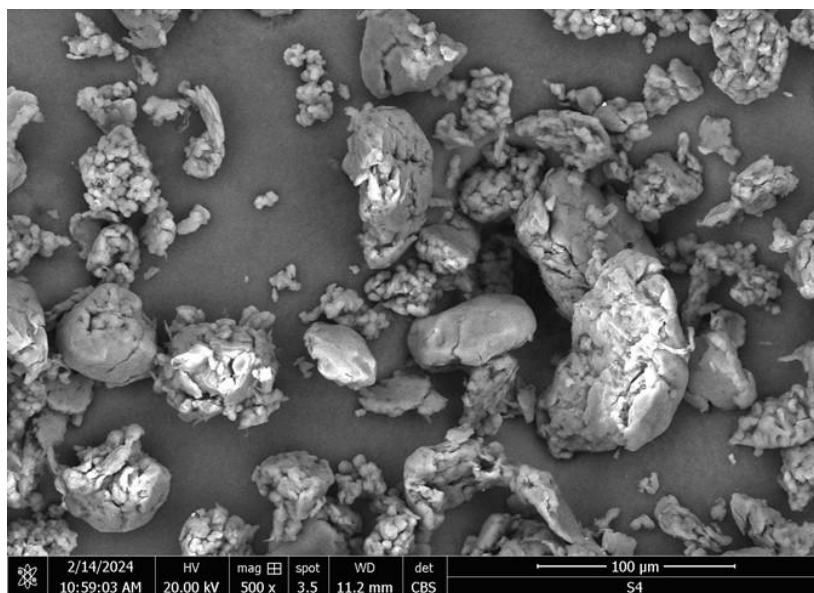


Figure 3.1 SEM image of PEEK powder

3.1.2 Cerium dioxide (CeO_2)

Cerium dioxide/ceria (CeO_2) was obtained from Sigma–Aldrich (USA) with mean particle size = 50 nm and density = 7.13 g/cm^3 . Figure 3.2 is the SEM image of the ceria nanoparticle.

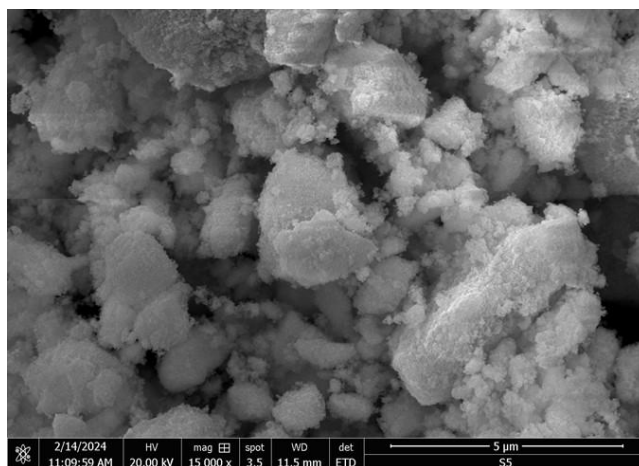


Figure 3.2 SEM image of ceria

3.2 Characterization techniques

3.2.1 X-ray diffraction (XRD)

The morphology of the prepared PEEK/Ceria nanocomposite powders using both methods was analyzed using an X-ray diffractometer (ultimate IV, Rigaku, Japan) having $\text{Cu (K}\alpha\text{)}$ X-ray source. The powders were analyzed from $2\theta = 10$ to 60° with a step size of 0.02° .

3.2.2 Fourier transform infrared (FTIR) spectroscopy

The ball-milled and sonicated powders were analyzed using FTIR spectroscopy with the DTGS KBr disc method, employing a Nicolet FTIR iS10 system (Thermo Scientific, USA), covering the wavelength range from 3500 to 450 cm^{-1} .

3.2.3 Dispersion analysis

A field emission scanning electron microscope (FE-SEM) assembled with a Schottky field emission gun (FEI Quanta FEG 250, USA) was used to analyze the typical dispersion of nanofillers in the PEEK matrix. The analysis was carried out with the help of a secondary electron detector and at a voltage of 30 kV. The samples were gold coated (for around 25 seconds) using a Quorum (Q150R S, UK) gold coating machine to prevent the charging effect and make it conductive prior to the SEM analysis.

3.2.4 Thickness measurements

FE-SEM was used to measure coating thicknesses by analyzing cross cross-sectional area of coated samples with the help of FE-SEM. The analysis was carried out with the help of a secondary electron detector and at a voltage of 30 kV. The samples were gold coated (for around 25 seconds) using a Quorum (Q150R S, UK) gold coating machine to prevent the charging effect and make it conductive prior to the SEM analysis. Four readings for each set of samples were taken and the average value of coating thickness was reported.

3.2.5 Hardness measurements

Vickers microhardness of the coatings was measured using a micro-combi tester (CSM instruments SA, Switzerland) with a load of 0.25 N for a dwell time of 15 seconds using a pyramidal-shaped diamond indenter. In order to prevent the substrate influence during

the indentation procedure, it was ensured that the penetration depth was less than 10% of the coating thickness for each coating. The hardness value provided for each coating was the average of five measurements

3.2.6 Tribological testing

Wear tests are conducted on a UMT-3 tribometer (Bruker, USA), using a ball-on-disc configuration, with an alumina ball ($\varnothing = 6.3$ mm) as the counterface at room temperature, with a relative humidity of $55 \pm 5\%$. Acetone was used to properly clean the balls before each experiment, followed by drying them using a blower. An optical microscope (MT7000, Meiji, Japan) was used to examine the counter face ball before the test and also after the test to investigate the phenomena of transfer film and scratch formation if any. To determine the effect of counterface materials in the tribological studies, three different balls of the same specifications, namely silicon nitride (Si_3N_4), tungsten carbide (WC), and stainless steel (SS) were used in addition to the alumina ball. Three wear tests were conducted for each set of samples and the average values of the COF and wear life were reported.



Figure 3.3 Tribometer used in the current study

3.2.7 Evaluation of wear morphology

After the wear tests, the examination of the wear track and subsequent investigation regarding the characteristics of wear and evaluation of the failure of the coatings were carefully studied by using a field emission scanning electron microscope (FE-SEM) coupled with (EDS). Prior to SEM analysis, a thin layer of gold coating was deposited on each sample to prevent surface charging of the polymer coatings. Furthermore, both two-dimensional (2D) and three-dimensional (3D) wear profiles were captured using a 3D optical profilometer (GTK-A, Bruker, USA) to quantify the depth of the wear track (Z) after each test. After analyzing the wear track, the specific wear rate (mm^3/Nm) was computed by dividing the total amount of material lost (mm^3) by the normal force (N) applied and the sliding distance (m).

3.2.8 Water contact angle (WCA) measurements

Contact angles may be used to compute thermodynamic parameters of a surface, such as the surface free energy because they are dependent on the liquid's interaction with the surface [111]. Our studies measured contact angles of the developed nanocomposite coatings, and optimized coating before and after exposure to ultraviolet (UV) of the coated samples using a VCA Optima (ACT Products Inc., USA) contact angle tester. The measurements were carried out on the developed coatings with distilled water (1.2 μ L) as the solvent. Multiple points were tested, and the average values were reported.

3.2.9 Ultraviolet (UV) radiation tests

UV-resistant behavior of coatings on steel panels (Q235) was evaluated using the QUV Accelerated Weathering Tester (QUV/Spray Gen 4, UK) for about 500 hours. The test was carried out according to ASTM G154 – 23 standards. The environmental conditions were set at 8-hour UV irradiation (UVA-340+) and water spray then 2-hour condensation. Temperature and humidity were 60 ± 3 °C and $50 \pm 5\%$ RH, respectively.

3.2.10 Scratch testing

Scratch tests were conducted on the samples using step 501 mechanical surface testing equipment (Anton Paar GmbH, Austria). Rockwell diamond indenter (O-138) with a conical angle of 120° and a tip radius of 100 μ m was used for the same. The test was conducted under a linear increase in load (0-30 N) with time (progressive) at a speed of 5 mm/min along a scratch length of 10 mm.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Phase 1 - Evaluating the effect of surface texturing on the tribological properties of pristine PEEK coatings deposited on mild steel substrates

Evaluating the effect of surface texturing on obtaining the optimum adhesion strength of PEEK coatings deposited on mild steel substrates has been evaluated in this phase of the study. A detailed explanation of the work conducted along with the methodology has been provided below (Figure 4.1).

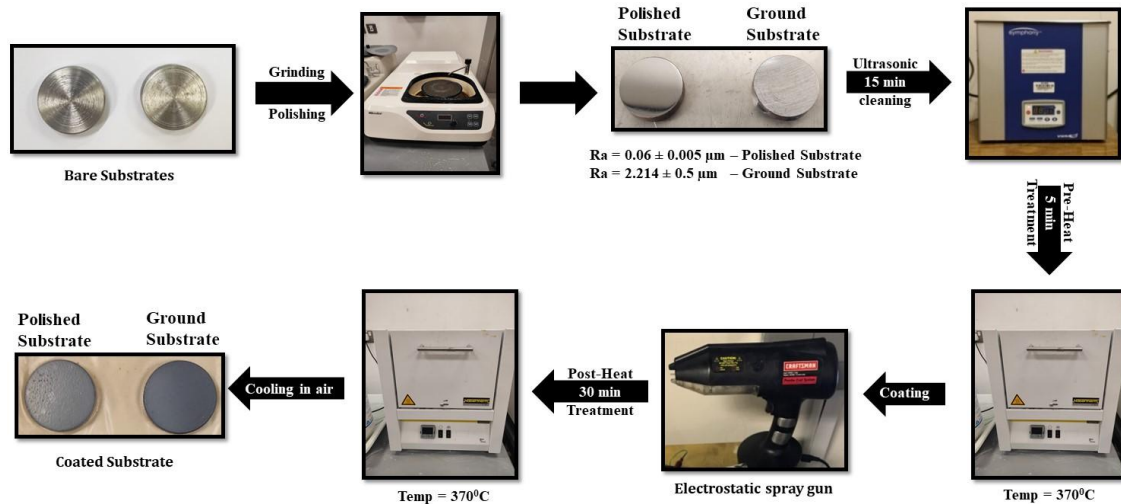


Figure 4.1 A flowchart illustrating the research methodology adopted in this study

In this phase, we have focused our research on the effect of texturing samples having two different surface roughness parameters – polished (sequential grinding by different grit sheets) and ground (grinding the substrate using a 120-grit grinding paper only).

Nevertheless, there hasn't been any prior research reported that thoroughly examined the various surface roughness parameters of the substrate and reported their effect on the tribological performances of PEEK coatings. The results are presented below.

4.1.1 Evaluation of coating thickness

Figure 4.2 shows a typical FE-SEM cross-section image of the substrate/coating system, whereby the coating thicknesses are shown. The values were obtained as an average of three readings conducted. In the case of both samples, the thickness was found to be approximately $100 \pm 5 \mu\text{m}$.

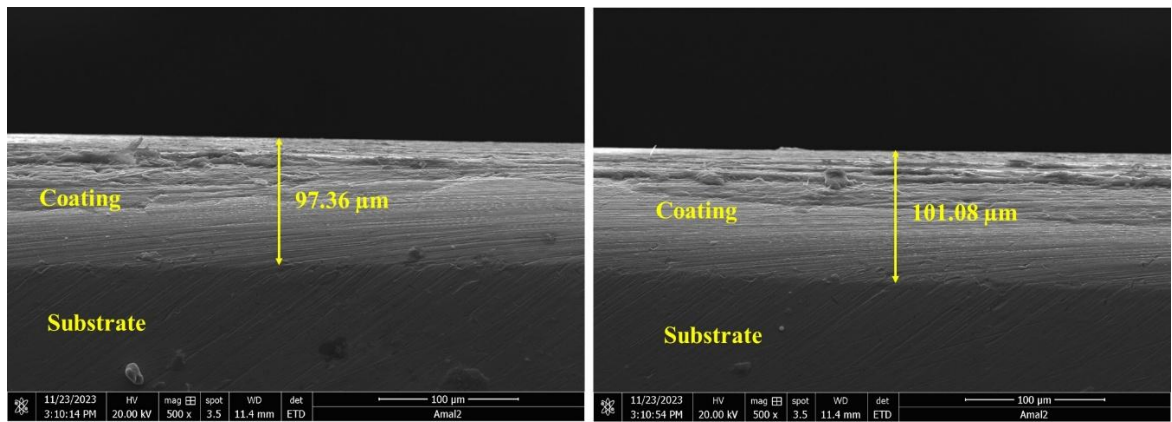


Figure 4.2 Cross-sectional FE-SEM images of the thickness of PEEK coatings on (a) polished and (b) rough samples respectively

4.1.2 Evaluation of the tribological performance of PEEK coatings deposited on the polished and ground substrates

As mentioned earlier, uni-directional sliding wear tests were conducted at varying normal loads (30 N, 40 N, and 50 N) at a constant sliding velocity of 0.2 m/s (637 rpm) for 10,000 cycles, corresponding to a sliding distance of 189 m. It is imperative to highlight

that the tests were terminated promptly in the event of an observed substantial coefficient of friction (COF) exceeding 0.5, indicative of a potential metal-to-metal contact and consequent coating failure. Figure 4.3 and Figure 4.4 illustrates that both the polished and the rough coatings were seen to exhibit quite comparable behaviour at 30 N as they did not peel off until 10,000 cycles. The average coefficient of friction values obtained were 0.2170 for polished and 0.3167 for the rough samples respectively (Figure 4.3h and Figure 4.4h). After examining the ball images (Figure 4.3d&f) and Figure 4.4d&f) taken before and after the test, it was observed that there were no noticeable scars on the balls that would have indicated a metal-to-metal contact. It is evident from the EDS spectra that the coatings did not fail or peel off as evident from the absence of the iron (Fe) peak (Figure 4.3c and Figure 4.4c) in the spectra.

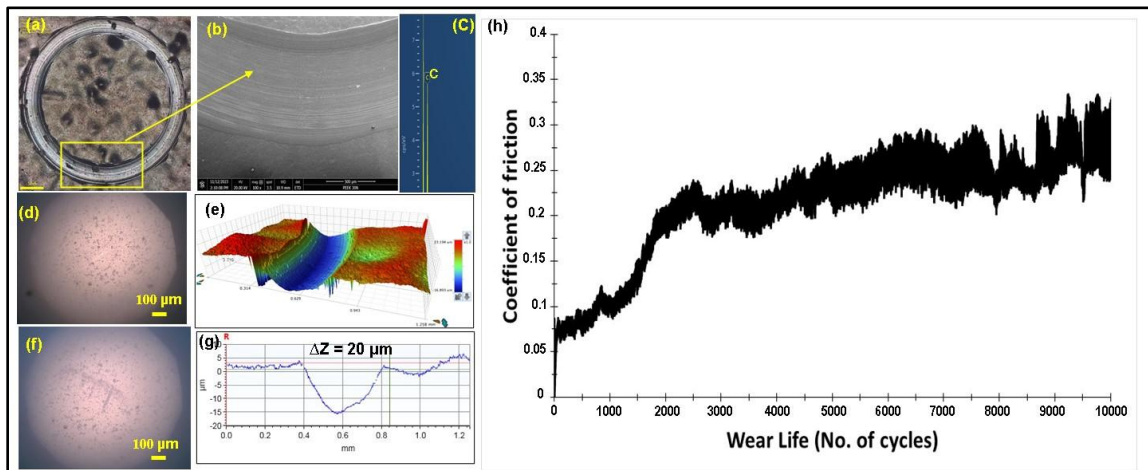


Figure 4.3 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph

Additionally, the wear track (Z) depth was only around 20 µm for both the polished and the rough samples (Figure 4.3g and Figure 4.4g), which is less than the coating's

thickness of approximately 100 μm confirming the non-failure of the coating. It can also be seen from the SEM images of the wear track that abrasive wear by plastic deformation was the primary wear mechanism (Figure 4.3b and Figure 4.4b).

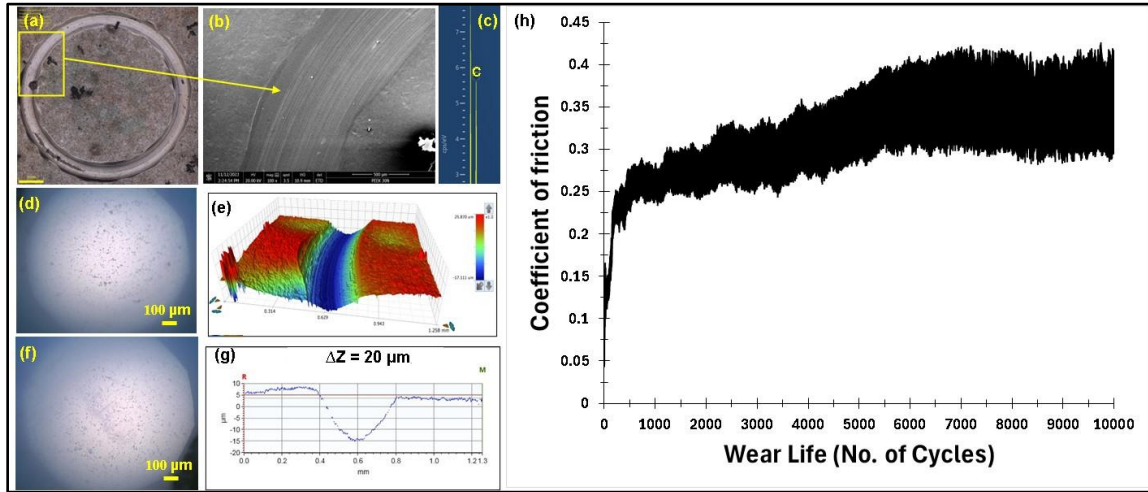


Figure 4.4 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph

As there were no clear indications of failure, the load was subsequently increased to 40 N for the same conditions as mentioned earlier and the tribological evaluations were studied. The average coefficient of friction values obtained were 0.2493 for the polished sample (Figure 4.5h) and 0.2405 for the rough sample (Figure 4.6h) respectively. Analyzing the optical images of the ball before and after the test (Figure 4.5d&f and Figure 4.6d&f) and in conjunction with the low values of coefficient of friction obtained, it was clear that the coatings on both the substrates did not fail as there was no evidence of metal-to-metal contact. However, to further confirm the same, SEM/EDS analysis was conducted on the wear track and the spectra obtained thereby contribute to the fact that

there was no tangible evidence of the coating's failure (Figure 4.5b&c and Figure 4.6b&c). This was further confirmed by the wear track depth of 25 μm for the polished and a depth of 20 μm for the rough sample, which was way below the thickness of the coating.

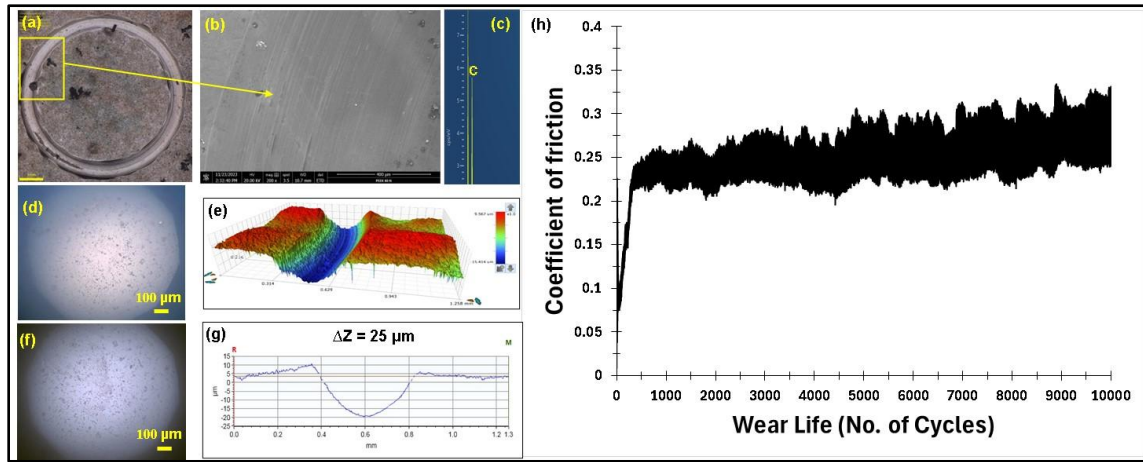


Figure 4.5 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph

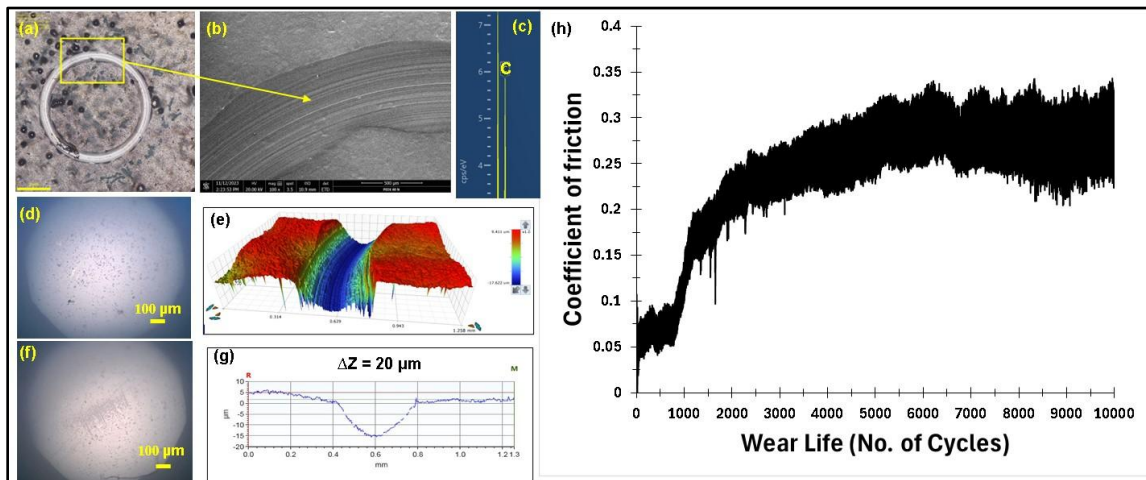


Figure 4.6 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph

Hence, the load was further increased to 50 N to evaluate the tribological performance of the PEEK coatings on both substrates. It was observed that the PEEK coating deposited on the rough sample was able to withstand a normal load of 50 N showing a wear life of 10,000 cycles, with an average coefficient of friction of 0.2369 (Figure 4.7h). The slightly lower value of the coefficient of friction can be attributed to the formation of transfer films on the counterface ball due to the possible high localized temperatures during the test under a higher normal load. Previous research has demonstrated that polymers have a propensity to create a transfer film on the counterface ball during the wear test, which has a significant impact on both the wear rate and coefficient of friction depending on how firmly the film adheres to the counterface [112]. As the loading was subsequently increased, a continuous and adherent formation of transfer layer would have formed over the counterface ball. This was one of the most plausible reasons for obtaining a lower COF throughout the test, thereby preventing direct contact of ball asperities with the coating surfaces. As the loading was increased, the amount of transfer film accumulated over the counterface ball was found to be larger than the previously used lower loadings. Further, it is well evident from the SEM image of the wear track (Figure 4.7b) that, when the load was increased to 50 N, there was a change in the wear mechanism from only abrasive wear to a combination of abrasive and adhesive wear.

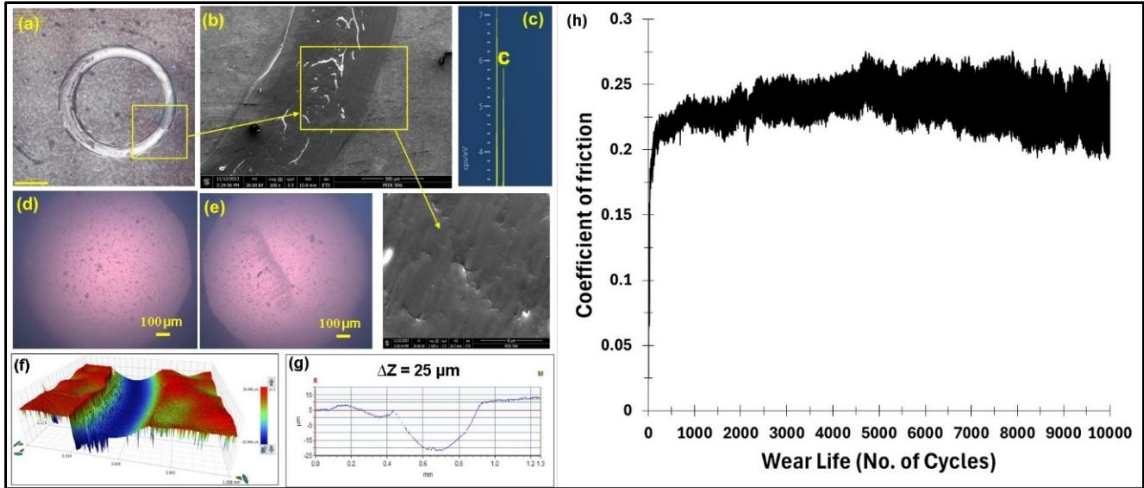


Figure 4.7 An illustration representing the (a) wear track, (b-c) corresponding SEM image and supportive EDS analysis, (d&f) the before and after test ball images, (e) the 3D profile, (g) the 2D profile indicating the wear track depth and (h) the frictional graph

The EDS spectra confirmed that the coating did not fail even until 10,000 cycles at a load of 50 N (Figure 4.7c). Furthermore, the wear track (Z) depth was only around 25 μm , which is way less than the coating's thickness of about 100 μm . From this, it can be attributed that increasing the loading from 30 N to 50 N did not result in a considerable increment in the wear rate of the coating deposited on the rough sample.

However, for the polished sample under 50 N, the coating completely peeled off, just after about ~ 200 cycles into the wear test as shown in Figure 4.8. The coefficient of friction graph and the counter face ball images are shown in Figure 4.8a-b. A substantial increase in the coefficient of friction to a value of ~ 0.6 was observed which is attributed to the coating failure resulting in metal-to-metal contact, which is also confirmed by a big scar mark on the counterface ball after the test.

Figure 4.9 shows the comparison of the specific wear rate of the coatings at different loading conditions at a sliding velocity of 0.2 m/s for 10,000 cycles. It can be seen that at all the loading conditions the PEEK coating deposited on the rough sample exhibited a lower wear rate as compared to the coating deposited on the polished sample. However, with increasing load both the coatings showed an increase in the wear rate as expected. Figure 4.10 compares the average wear life of the PEEK coatings deposited on the rough and the polished samples at a normal load of 30 N, 40 N, and 50 N respectively, at a linear sliding speed of 0.2 m/s. It is evident from Figure 4.10 that the coating deposited on both samples did not show any failure until 10,000 cycles under the loads of 30 and 40 N respectively. At 50 N, however, the polished sample failed just after ~ 200 cycles, whereas the coating deposited on the rough sample sustained until 10000 cycles.

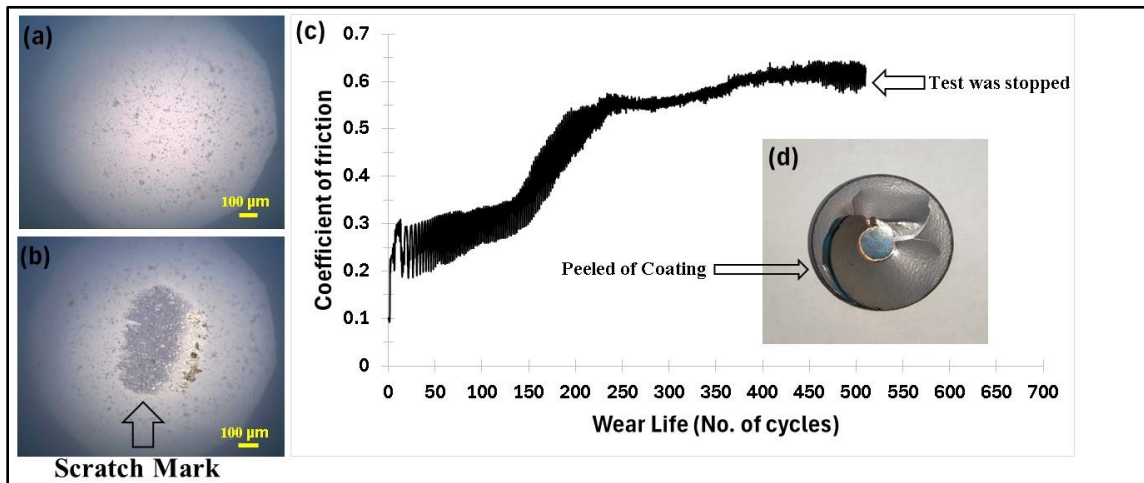


Figure 4.8 (a-b) The before and after test ball images, (c) the coefficient of friction graph, and (d) peeled-off coating at 50 N load, 0.2 m/s.

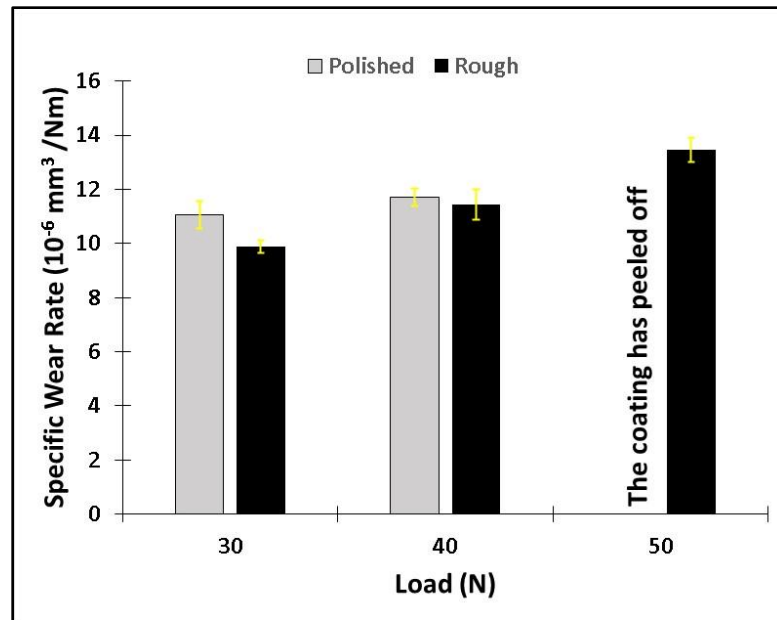


Figure 4.9 Comparison of the specific wear rate of the coatings at different normal loads at a sliding velocity of 0.2 m/s

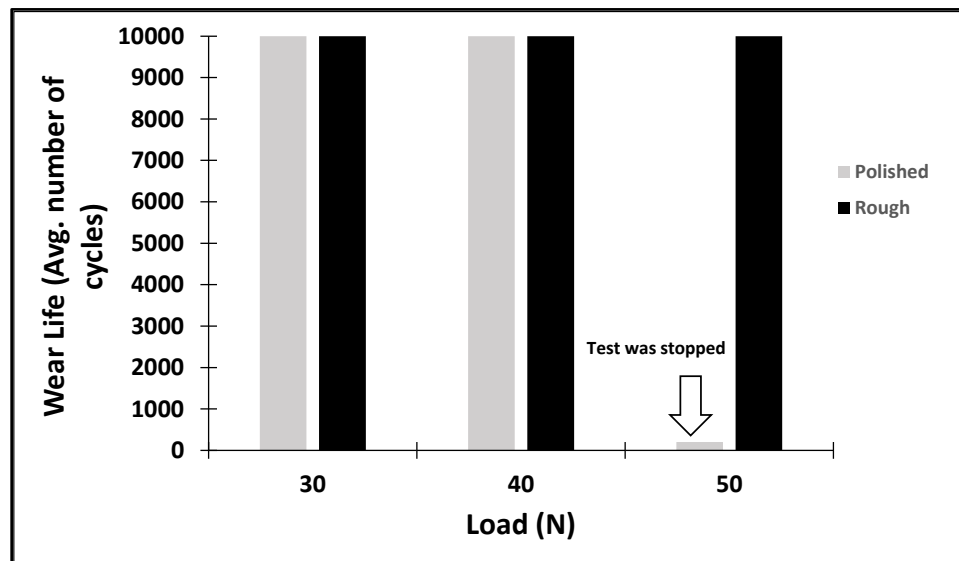


Figure 4.10 Comparison of average wear life of pristine PEEK at normal loads of 30 N, 40 N, and 50 N at a linear sliding speed of 0.2 m/s for 10,000 cycles

4.1.3 Discussion

As the PEEK coating deposited on the rough and polished samples exhibited contrasting tribological performance in terms of wear rate and wear life, it was imperative to investigate the effect of different surface roughness parameters on the performance of the coating. It is to be noted that there are three sets of roughness parameters, that play a very important role in tribology, namely, the height parameters such as average surface roughness (R_a), root mean square roughness (R_q), peak height (R_p), valley depth (R_v) and the maximum profile height (R_z), the spatial surface roughness parameters such as peak density (N_p) and then the statistical surface roughness parameters, such as the skewness (R_{sk}) and the kurtosis (R_{ku}) of the peak/valley distribution. Hence all these various surface roughness parameters were measured using a 3D Optical profilometer (Bruker, USA) and the values are presented in Table 4.1.

Table 4.1 The various surface parameters of the polished and rough samples

Type	Parameter (μm)	Polished	Rough
Height Parameters	R_a	0.06094	2.214
	R_q	0.14	2.7265
	R_p	2.0727	22.222
	R_v	-2.11	-12.656
	R_z	4.182	34.877
Statistical Parameters	R_{ku}	2.8022	7.6712
	R_{sk}	-0.1627	0.2135

4.1.4 Effect of height parameters on the tribological performance of the PEEK coatings

The height parameters have a significant effect on the adhesive properties of the coating/substrate system, which in turn play an important role in the tribological performance of the coating. An optimum R_z value, which is the sum of the maximum peak height and the maximum depth of the valley as depicted in Figure 2.2, results in a greater mechanical bonding between the coating and the substrate due to the higher number of anchorage points and increased surface area for bonding. As can be seen from Table 4.1, the polished sample has a lower R_z value, resulting in the substrate having lower anchoring points and reduced surface area leading to a decreased adhesion between the substrate and the coating, which is reflected in the failure of the coatings under higher loads of 50 N during the wear test. The same can be understood from Figure 4.11 which symbolizes the distinction in the height parameters between the two surfaces.

The root mean square (RMS – R_q) value of the substrates also provides some significant insights into the coating/substrate system's behavior during the wear tests. A higher R_q value signifies a rougher surface, which can positively impact the adhesion of the polymer coating to the substrate. As shown in Table 4.1, the higher R_q value of the rough sample (2.7265) as compared to that of the lower R_q value of the polished sample (0.14) has also contributed to an improved adhesion between the PEEK coating and the substrate resulting in its better tribological performance in terms of lower wear rate at all applied normal loads and increased wear life even at a higher load of 50 N.

The average roughness (R_a) is another commonly used parameter to quantify the surface roughness of a material. A higher R_a value indicates a rougher surface, which can enhance the adhesion of the polymer coating. It can be concluded that the higher surface roughness ($2.214\text{ }\mu\text{m}$) of the rough substrate promotes better mechanical interlocking of the PEEK coating to the substrate ensuring a better adhesive strength than the PEEK coatings on the polished surfaces (Table 4.1), which showed a lower R_a value of $0.06094\text{ }\mu\text{m}$. The peeling off of the coating on this substrate at 50 N can be attributed to the surface not providing many locations for mechanical interlocking for the PEEK coating. An increase in available surface area for adhesion or more mechanical interlocking sites for the PEEK to adhere to would explain this behavior as well.

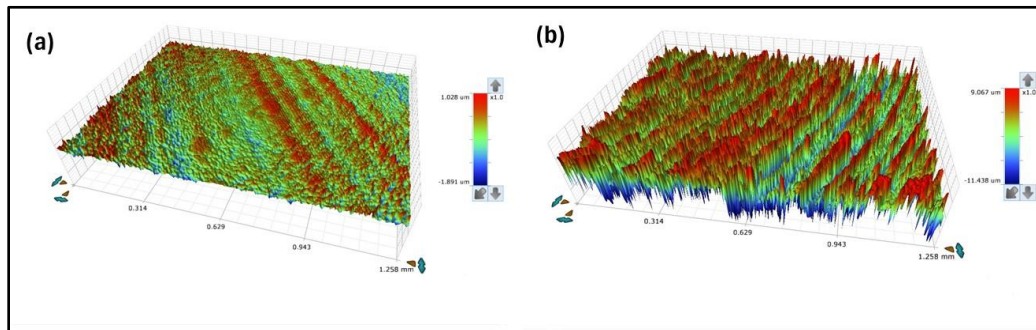


Figure 4.11 A 3-D optical profilometry image depicting the height parameter distinction between (a) polished and (b) rough sample

4.1.5 Effect of spatial parameters on the tribological performance of the PEEK coatings

The peak density distribution, one of the other important surface roughness parameters, illustrates on how the peaks on the substrates are packed on the surface. From Figure 4.12b, it is evident that the rough sample has a more uniform peak density distribution.

Here, the peaks are evenly distributed resulting in the coating to conform well to the substrate, thereby initiating a larger contact area for adhesion, promoting a stronger bond. On the contrary, the polished surface (Figure 4.12a) lacks significant peaks and valleys that resulted in reducing the mechanical interlocking and eventually leading to the coating failure at higher loads.

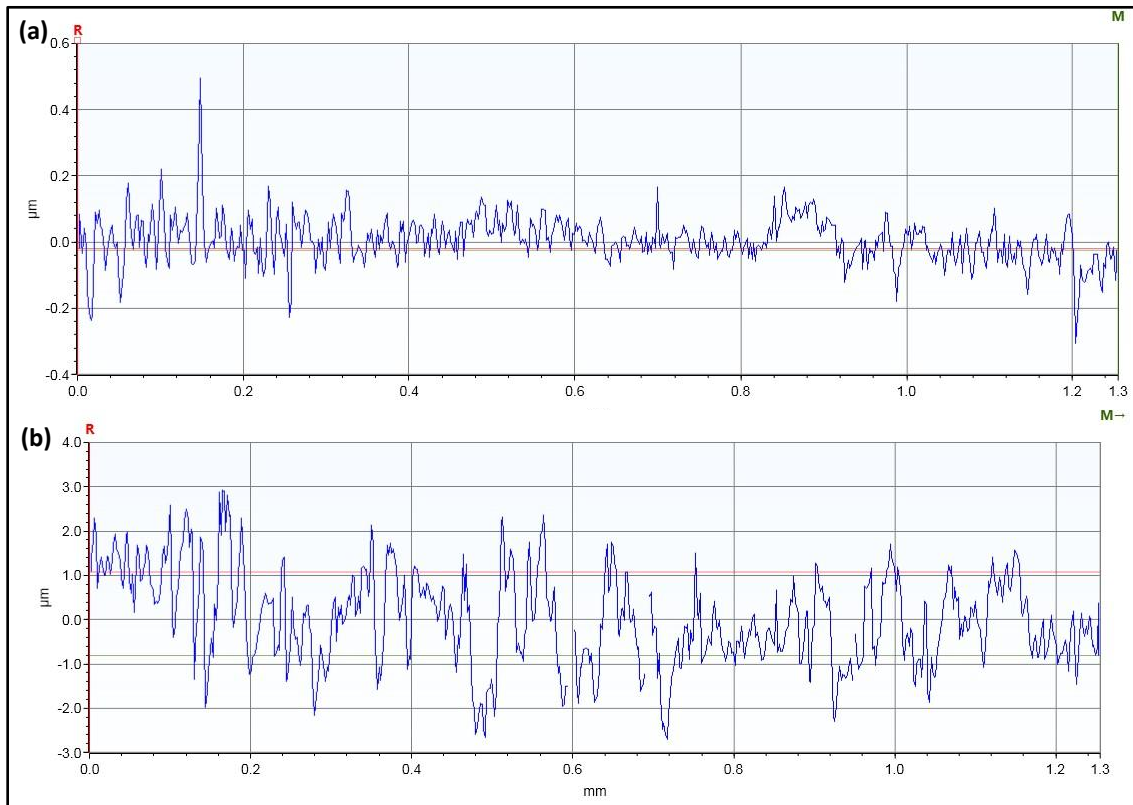


Figure 4.12 A graphical representation of the peak density of the surface profiles of (a) polished and (b) rough samples

4.1.6 Effect of statistical roughness parameters on the tribological performance of the PEEK coating

Statistical parameters such as the skewness and kurtosis of the peak/valley distribution across a profile also play a very significant role in determining the adhesive properties of

the coating/substrate system. As can be seen from Table 4.1, the polished sample had an average negative skewness value in the range of -0.1627 and the rough sample had an average skewness value in the positive range of 0.2135. As explained earlier and as shown in Figure 2.3, a negative skewness represents a profile with predominantly deep valleys and a positive skewness represents a profile with sharp peaks. Hence, on a negatively skewed surface, which in this case is the polished surface, the PEEK polymer during the post-heat treatment, would not flow into the deep and sharp valleys as much as it flows into the broad valleys due to the sharp peaks of a surface with a positive skewness value. This gives more available surface area for increased adhesion, as well as mechanical interlocking between the coating and the substrate surface.

The same principle can be related to the kurtosis (R_{ku}) as well. As shown in Figure 2.3, a surface having a kurtosis value higher than 3 will result in sharp peaks and valleys, thereby creating more anchoring points to improve the mechanical interlocking, which can be seen in the rough sample showing a R_{ku} value of 7.6712. The peaks and valleys for the polished surface were spread out and flattened as its kurtosis (R_{ku}) value was significantly less than 3 (Table 4.1), resulting in fewer anchoring sites, which in turn had an adverse effect on the adhesion between the coating and the substrate leading to its failure at higher loads.

Hence, the various surface roughness parameters provide us with crucial information on how the substrate surface must be designed or prepared to obtain an ideal coating.

4.1.7 Summary

- From this phase, it is found that the pristine PEEK coating deposited over polished substrates failed in the test at a load of 50 N and a sliding speed of 0.2 m/s. The failure is attributed to the poor adhesion between the coating and the substrate compared to the rough sample which sustained for a wear life of 10000 cycles.
- Optimal surface roughness is critical for achieving the required level of adhesion which thereby enhances the tribological performance of PEEK-coated mild steel applications.
- Kurtosis, skewness, average roughness (R_a), root mean square roughness (R_q), peak to valley height (R_z), and peak density (N_p) were investigated as key surface roughness parameters affecting PEEK coating performance.

4.2 Phase 2 – Selection of a mixing technique to uniformly disperse the ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties

In our findings presented in phase 1, we optimized the ideal surface roughness required to obtain the maximum adhesion between the coating and the substrate. In this section, we will be discussing on which dispersion technique will be ideal in developing the homogenous mixture required to develop the nanocomposite coatings in this study. From the literature survey conducted earlier, planetary high-energy ball milling is a widely preferred method for dispersing various fillers into the PEEK matrix [113-115]. It has also been extensively used by researchers to obtain a uniform distribution of ceria as a nanofiller or reinforcement in various parent matrices [116-119]. As a result, during the initial stages of our experimental investigation, ball milling was chosen as the primary method for dispersing ceria nanoparticles within the PEEK matrix. However, as the experimentation progressed, several unexpected results prompted us to reconsider this approach, which will be discussed in detail in the following sections. Given these limitations, probe sonication, which was also widely used by researchers to disperse the fillers in the PEEK matrix uniformly to graft bulk composites as well as powders for coatings [120-122] was selected for further experimental comparison and analysis. As a result, this gave us the motivation to compare and investigate the influence of ball milling (BM) and probe sonication (SON) on the particle dispersion of the two powders on developing PEEK/ceria nanocomposite powder for coating application and determine their effects on the tribological properties of the coatings developed from these mixtures. XRD, FTIR, TGA, and SEM analysis were used for structural characterization of

nanocomposite coatings. Later, tribological evaluation of coatings, coupled with SEM analysis and optical profilometry to study the wear mechanism involved, was carried out.

4.2.1 PEEK/1.5 wt% ceria composite powder preparation

Two methods namely, ball milling and sonication were implemented to make the PEEK/1.5 wt% ceria composite powders, and subsequently to evaluate the effect of these methods on the quality of the coating and subsequently its tribological properties. Regarding the selection of 1.5 wt% ceria for the analysis, this concentration was chosen based on existing literature and experimental evidence that suggested the optimal performance of composites is when ceria is used at lower weight percentages. Studies have shown that ceria concentrations typically range from 0.5 wt% to 5 wt%, with lower percentages providing the desired reinforcement without causing excessive agglomeration of the nanoparticles [123-125]. By selecting 1.5 wt%, we aimed to achieve a balance between obtaining uniform distribution and avoiding agglomeration.

The first method used to prepare the composite powders was probe sonication coupled with magnetic stirring. A pre-determined amount of ceria was sonicated for ten minutes in 50 milliliters of ethanol using a probe sonicator (VCX 750, Sonics, USA) at an amplitude of 30% and an on/off cycle time of 20/5 seconds. The sonicated solution containing the ceria powder was then magnetically stirred for two minutes at 1100 rpm to further disperse the ceria particles uniformly. Subsequently, a weighted amount of PEEK powder is added to the solution and subjected further to magnetic stirring for an additional hour. Finally, the mixture was heated in an oven at 80 °C for 24 hours, for the ethanol to evaporate and obtain the PEEK/ceria nanocomposite powder for further processing.

High-energy ball milling was the second method used to make the PEEK/Ceria nanocomposite powders using a planetary ball milling machine (Focucy, China). A weighted quantity of PEEK and ceria nanoparticles along with 5 mm diameter stainless steel balls with a ball-to-powder ratio (BPR) of 5:1 was put in a stainless-steel vial and milled for 30 minutes at a rotational speed of 250 rpm, with an on/off cycle of 5/55 minutes. The on/off cycle was carefully selected to prevent the overheating of the powders and provide sufficient time intervals for the cooling of the powder. Table 4.2 lists out the ball milling parameters used in this study.

Table 4.2 Ball milling process parameters

Diameter of balls (mm)	5
No. of balls	80
Ball to powder ratio (BPR)	5:1
On/Off Cycle	5/55
Rotational speed (rpm)	250
Temperature	Ambient

4.2.2 Quality assessment of the coatings formed by the powders using ball milling and sonication methods

The carefully prepared ball-milled and sonicated composite powders were deposited on the mild steel substrates using an electrostatic spraying gun following the same procedure

as listed above. As can be seen from Figure 4.13, the probe-sonicated composite powder resulted in a coating with a uniform thickness of $\sim 97 \mu\text{m}$. The coating was well adhered to the substrate as can be observed from Figure 4.13b.

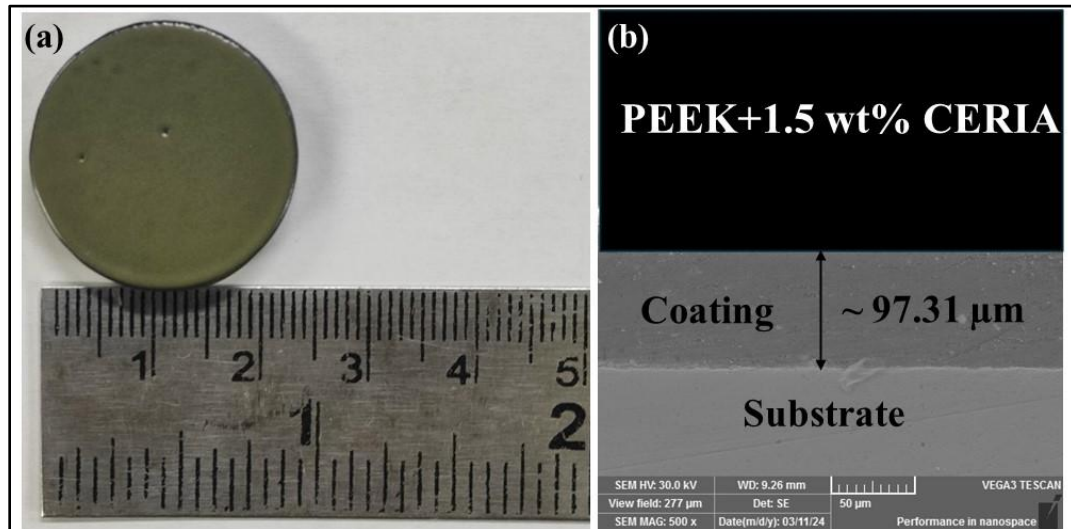


Figure 4.13 An illustration of the (a) coated sample with (b) corresponding cross-sectional SEM image of the PEEK/1.5 wt% Ceria powder prepared from probe sonication

However, the powder prepared using the ball milling process, when deposited onto the mild steel substrate and subjected to the 30-minute post-heat treatment process at 370°C , did not exhibit any melting as shown in Figure 4.14a&b. There was no consolidation of the nanocomposite powder coating on the substrate and the powder could be scrapped from the substrate very easily as can be seen in Figure 4.14b. This suggested that the powder retained its solid-state structure and remained in its solid form throughout the post-heat treatment process, showing no signs of phase change or melting. This prompted us to conduct a thorough investigation into this aspect to determine the reasons for this behavior of the PEEK/1.5wt% ceria nanocomposite powders. As mentioned, earlier,

different characterization techniques were used to evaluate the effect of the ball milling and the sonication methods on the morphology and thermal stability of the powders.

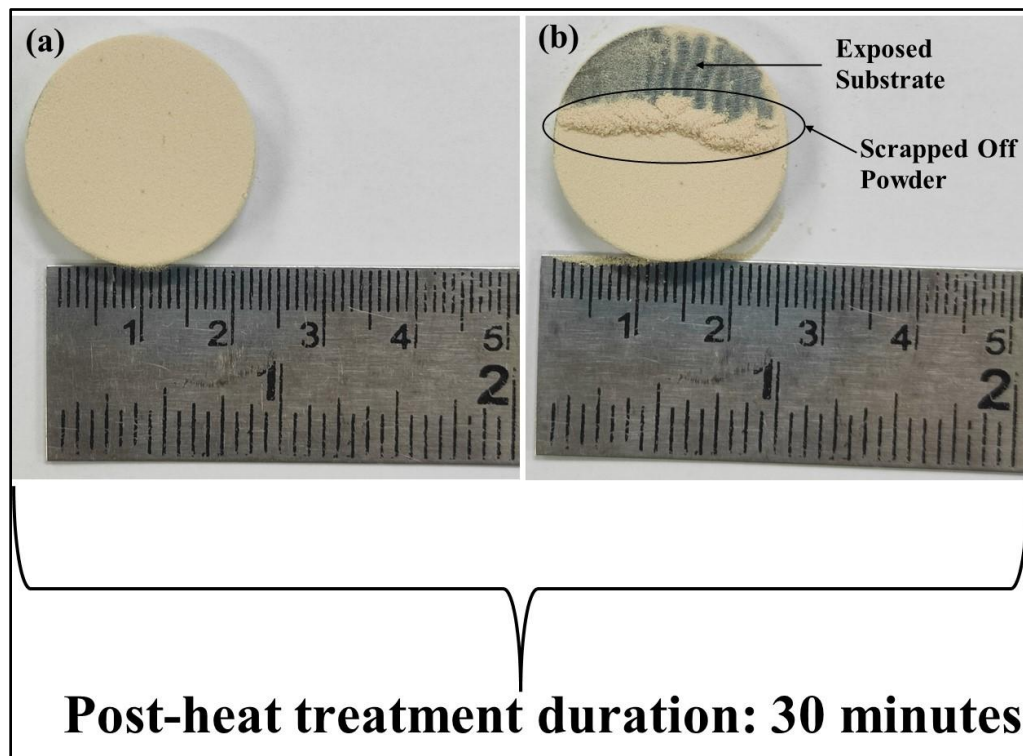


Figure 4.14 An illustration of the coated sample (a) after the pre-determined post-heat treatment, and (b) unmelted ball-milled powder after the post-heat treatment

4.2.3 X-ray diffraction (XRD) characterization of the nanocomposite powders

PEEK is a semi-crystalline polymer, and its XRD pattern typically exhibits sharp diffraction peaks corresponding to the crystalline regions. The primary peaks were observed around 2θ values of 18.8° , 21.6° , 22.8° , and 28.7° which correspond to the (110), (111), (200), and (211) crystal planes, respectively [126,127] (Figure 4.15). Ceria is a fluorite-structured oxide and its XRD patterns were characterized by distinct, sharp peaks corresponding to its cubic crystal structure. The most prominent peaks were

observed at 2θ values around 28.6° , 33.1° , 47.5° , and 56.3° , which correspond to the (111), (200), (220), and (311) planes, respectively [128-130].

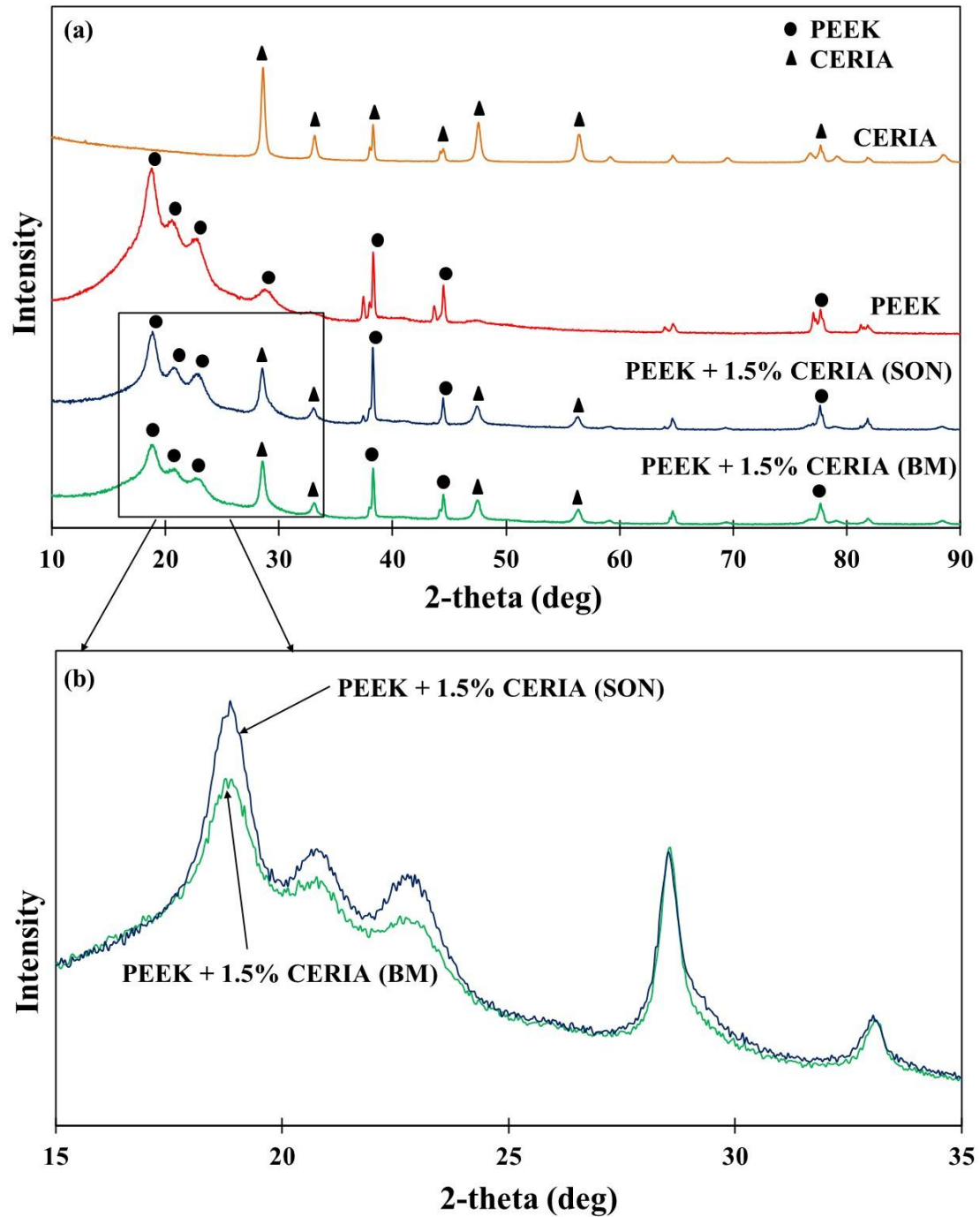


Figure 4.15 XRD patterns of pristine PEEK, ceria, and PEEK reinforced with ceria powders prepared through sonication and ball milling

Compared to the peaks of pristine PEEK and ceria, the XRD spectrum for the ball-milled and sonicated nanocomposite powders had broader peaks of lower intensity, at the corresponding 2θ values, however, it can be observed from Figure 4.15b, that the ball-milled PEEK/1.5 wt% ceria nanocomposite powder exhibited much lower intensity signature peaks at 18.8° , 21.6° , and 22.8° , respectively when compared to the sonicated powders. Ball milling is a high-energy process involving mechanical deformation and particle fracture, resulting in significant amounts of strain and defects. This mechanical energy present could have broken down the crystallinity, shifting the material into an amorphous state [113,131,132]. As crystallinity decreases, the sharp, well-defined peaks in the XRD pattern become broader, especially the primary peaks of PEEK, which explains the lower intensity observed in the ball-milled powder (at 18.8° , 21.6° , and 22.8°) when compared to the sonicated powder. As can be seen in Figure 4.15b, the crystallinity decreased for the ball-milled powder and is about 66.84% based on the XRD pattern. However, the sonicated powder exhibited sharp diffraction peaks illustrating a crystallinity of 76.46% suggesting that the ball milling process resulted in significantly reducing the crystallinity of PEEK as compared to the sonication process, which has resulted in the deterioration of the properties of the nanocomposite powder as a whole.

4.2.4 FTIR analysis of the nanocomposite powders

The FTIR wide spectra from 3000 to 450 cm^{-1} for pristine PEEK and ceria powders are shown in Figure 4.16. The FTIR spectra of PEEK exhibited a stretching of the carbonyl group at 1647 cm^{-1} and vibration of the skeletal ring at 1594 cm^{-1} , 1487 cm^{-1} , and 1411 cm^{-1} , respectively [133-135]. The peak at 1219 cm^{-1} was assigned to the stretching of C-OH and the peak at around 1154 cm^{-1} corresponds to C-O-C stretching [133,136]. The

vibration bands of the diphenyl ether group's asymmetric stretching were observed at 1277 cm^{-1} and 1185 cm^{-1} [137]. The absorbance observed between 926 cm^{-1} and 674 cm^{-1} correlates with the C-H out-of-plane bending vibrations [138]. Furthermore, the pristine ceria spectrum consisted of its signature peak at 2924 cm^{-1} corresponding to -CH₃ and -CH₂ asymmetric stretching [139]. The peak at 1624 cm^{-1} can be attributed to the interlayer stretching and bending vibration of molecular water [124]. The peak at 1337 cm^{-1} and 555 cm^{-1} is due to Ce-O stretching vibrations [140,141].

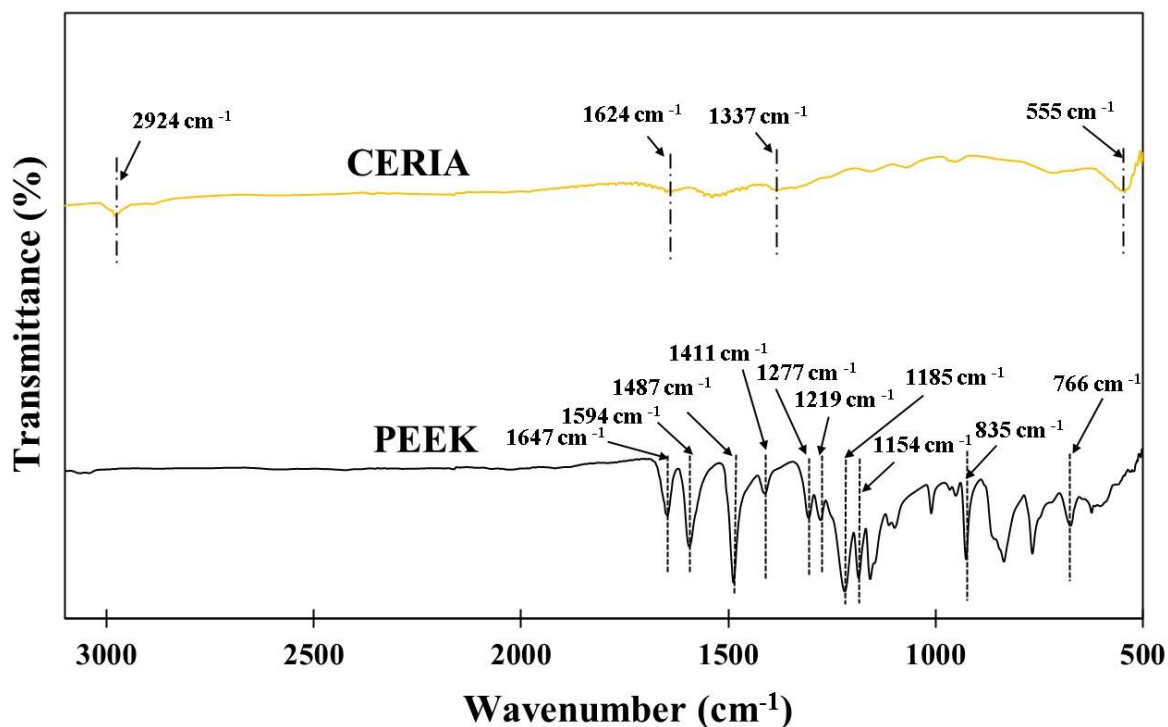


Figure 4.16 The FTIR spectra of PEEK and Ceria

Figure 4.17a shows the FTIR spectrum of the PEEK/1.5wt% ceria nanocomposite powders prepared by ball milling and sonication methods along with the pristine PEEK and ceria powders. It can be observed from the FTIR spectrum of the PEEK/1.5wt% ceria

nanocomposite powders prepared from both ball milling and probe sonication, both of them retained the signature peaks of PEEK with similar intensities, suggesting an increase in the PEEK chain mobility with the addition of ceria [135].

However, the ball-milled nanocomposite powder exhibited the characteristic peaks of PEEK in addition to the signature characteristic peak of ceria at 2924 cm^{-1} corresponding to $-\text{CH}_3$ and $-\text{CH}_2$ asymmetric stretching vibrations (Figure 4.17b), suggesting a non-uniform dispersion of the ceria particles within the PEEK matrix suggesting a possible agglomeration of the ceria nanoparticles. But on close observation of the FTIR spectrum of the sonicated nanocomposite powders, it was found that the spectrum did not show the characteristic peak of ceria at 2924 cm^{-1} but had all the characteristic peaks of PEEK (Fig. 4.17a&b), suggesting a uniform dispersion of the ceria nanoparticles within the matrix, and also that during the sonication process, the possibility of the PEEK polymer encapsulating the ceria nanoparticles lead to a different behavior as compared to the ball-milled powders.

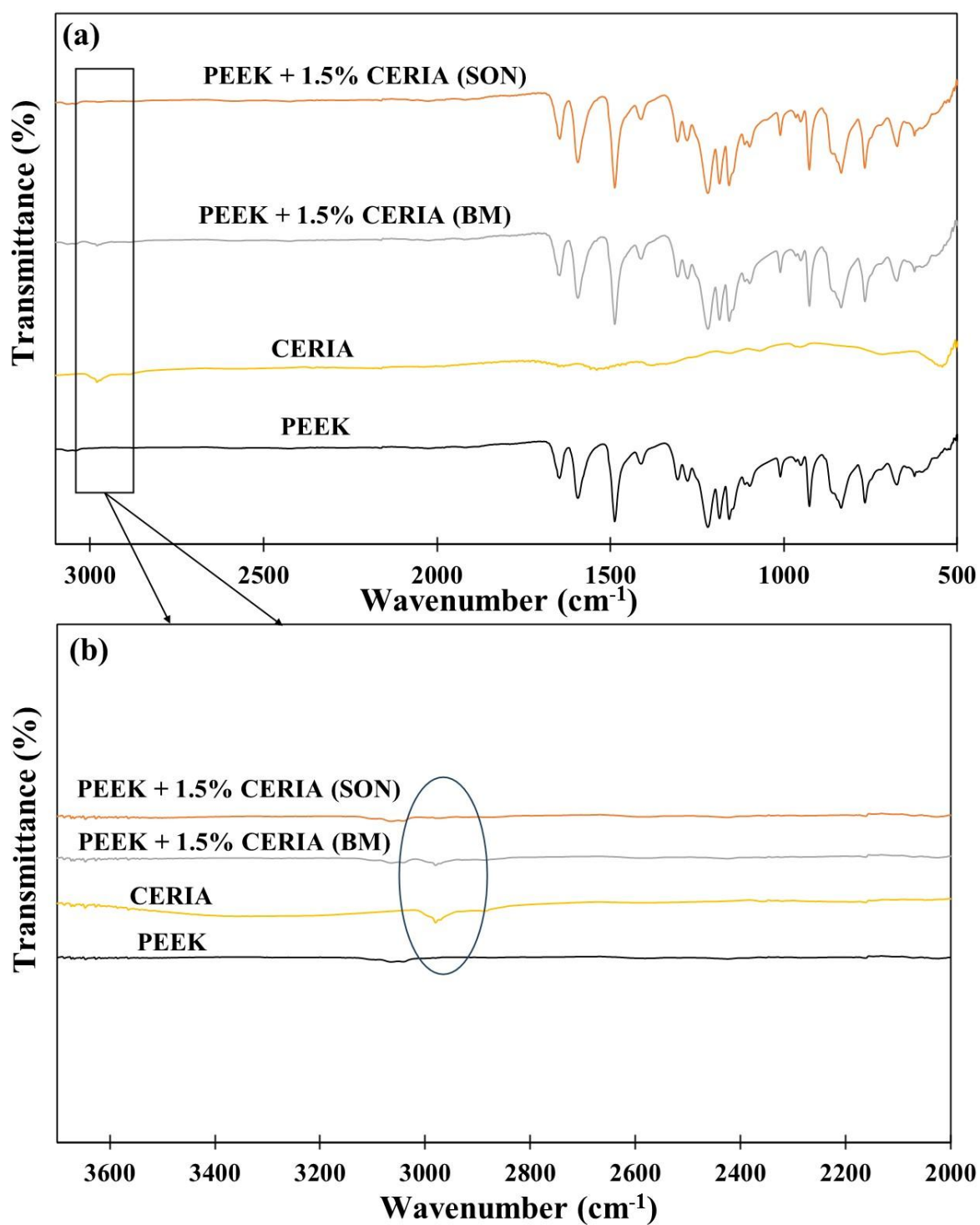


Figure 4.17 (a) The FTIR spectra of PEEK, ceria, and the nanocomposite powders prepared from sonication (SON) and ball milling (BM) and (b) the graph highlighting the signature peak of ceria among the nanocomposite powders

4.2.5 TGA analysis of the nanocomposite powders

Figure 4.18 shows the TGA curves of pristine PEEK powder along with the PEEK/1.5 wt% ceria nanocomposite powders prepared from ball milling and probe sonication, respectively. It can be observed that the pristine PEEK powder lost 20% of its weight at about 594 °C, while the nanocomposite powders prepared both by ball milling and sonication lost approximately the same percentage (20%) of their weight at a lower temperature of about 582 °C. However, as the temperature increased further, the pristine PEEK powder started degrading much faster as compared to the nanocomposite powders as it lost about 40% of its weight at about 616 °C, whereas at the same temperature, the composite powders lost about 36-37%, suggesting a better thermal stability for the nanocomposite powders at higher temperature. Furthermore, it can be observed that the ball-milled powders showed slightly better thermal stability than the sonicated powders, which could be one of the reasons for the ball-milled powders not resulting in a coating compared to the sonicated powders.

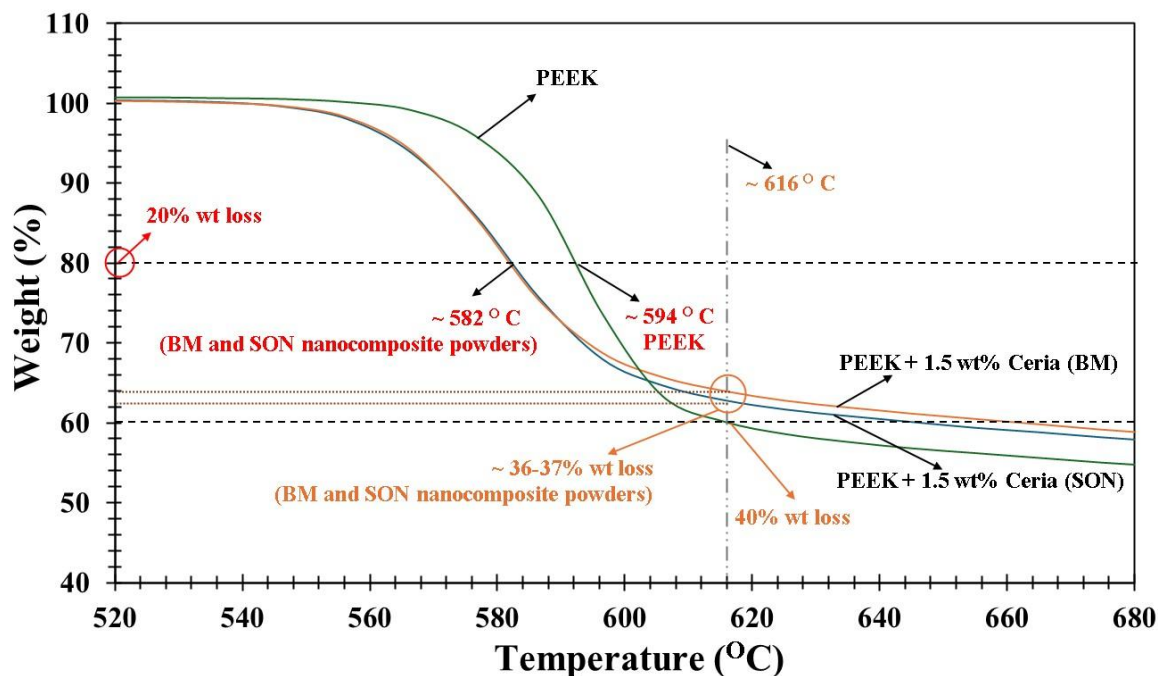


Figure 4.18 TGA thermograms of pristine PEEK and PEEK nanocomposite powders

Hence based upon the various characterizations carried out, it could be suggested that several reasons such as, change in crystallinity, the uniform dispersion along with a possible encapsulation of the ceria particles by the PEEK powder and a slightly lower thermal stability of the sonicated powders must have contributed to the formation of a uniform coating on the mild steel substrates as compared to that of the ball milled powders.

4.2.6 Tribological characterization of the nanocomposite coatings

However, the TGA analysis prompted us to increase the post-heat treatment duration for the ball-milled powders to 90 minutes as compared to the 30-minute post-heat treatment duration used initially for the ball-milled powders, in which case the composite powder

did not consolidate into a coating. As we increased the duration, we could see that the ball-milled powders also resulted in a coating on the mild steel substrates as shown in Figure 4.19. However, it could be observed from Figure 4.19b, that the interface between the coating and the substrate was not as sharp as compared to the one obtained with the sonicated powders as shown in Figure 4.13b, suggesting poor adhesion between the coating and the substrate.

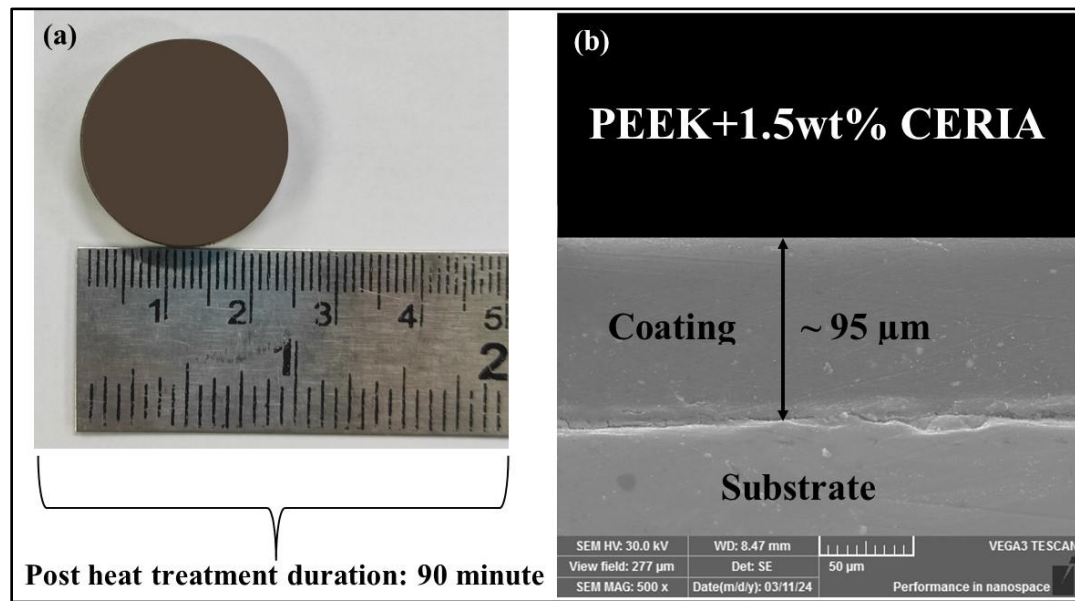


Figure 4.19 An illustration of the (a) coated sample with (b) corresponding cross-sectional SEM image of the PEEK+1.5 wt% Ceria powder prepared from ball milling after 90 minutes of post-heat treatment

To evaluate the tribological performance of the coatings formed by both the ball milled and the sonicated nanocomposite powders, wear tests were conducted at a normal load of 70 N and a constant sliding speed of 0.1 m/s (318 rpm) for 10,000 cycles corresponding to a sliding distance of 189 m. The wear track radius was kept constant at 3 mm. Three wear tests were conducted for each set of the coated samples and the average values of

the COF are reported. It can be observed from the frictional graph (Figure 4.20) that the coating that was deposited from the sonicated powders didn't fail until 10,000 cycles as no spike in the COF was observed suggesting that there was no metal-to-metal contact.

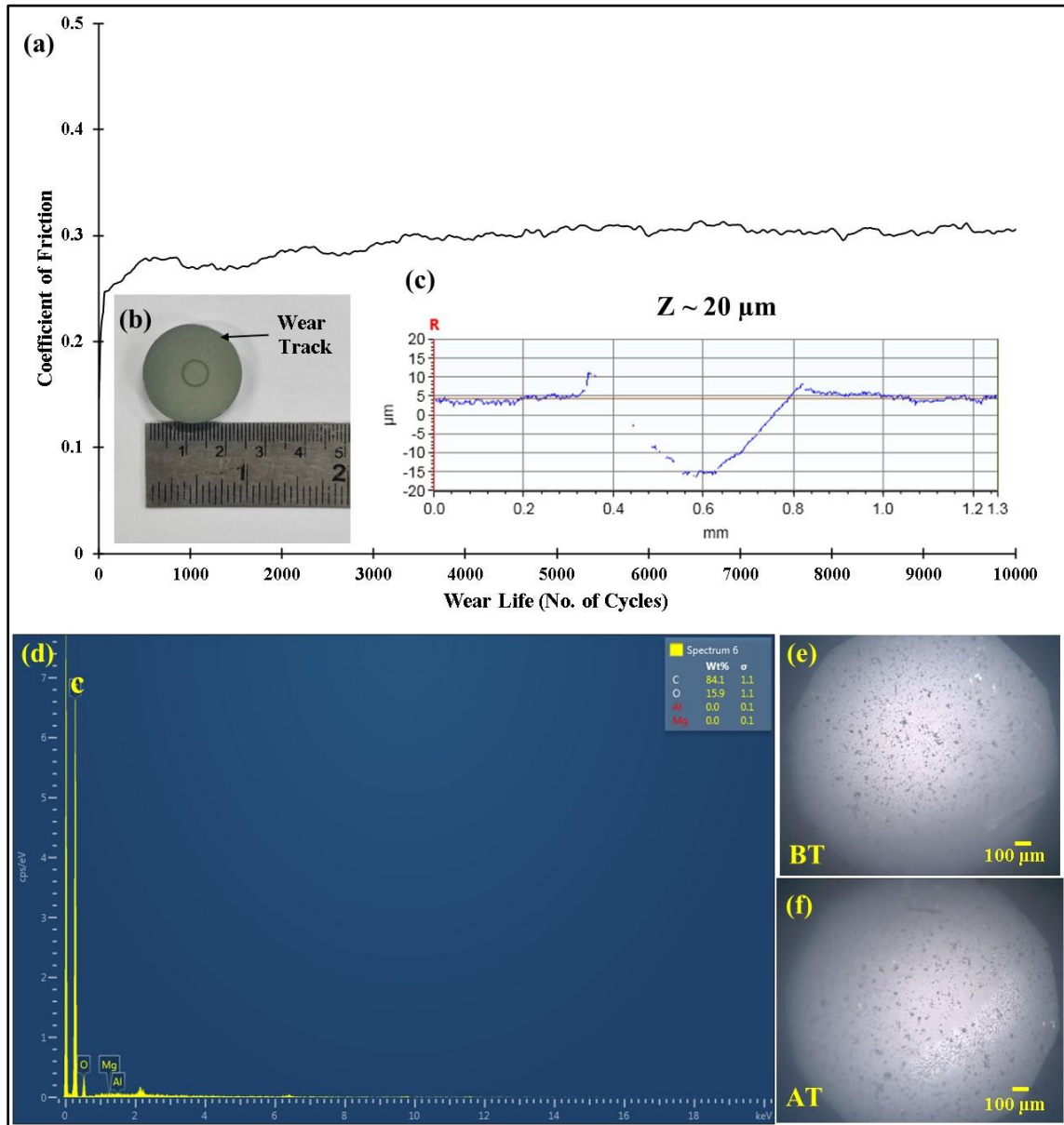


Figure 4.20 The (a) frictional graph of PEEK+1.5 wt% ceria nanocomposite coating prepared from probe sonication along with the (b) wear track photograph, (c) the 2D wear track depth, (d) the EDS scan, and (e) the counter face ball images before the test (BT) and (f) after the test (AT) at a normal load of 70 N for 10,000 cycles at 0.1 m/s.

This was also confirmed by the wear track depth measured from the 2D profile obtained from the optical profilometer. The wear track depth (Z) was found to be $\sim 20 \mu\text{m}$, which was significantly lower than the thickness of the coating ($\sim 97 \mu\text{m}$). Furthermore, the EDS scan over the wear track also confirms the non-failure of the coating due to the absence of iron (Fe) peaks.

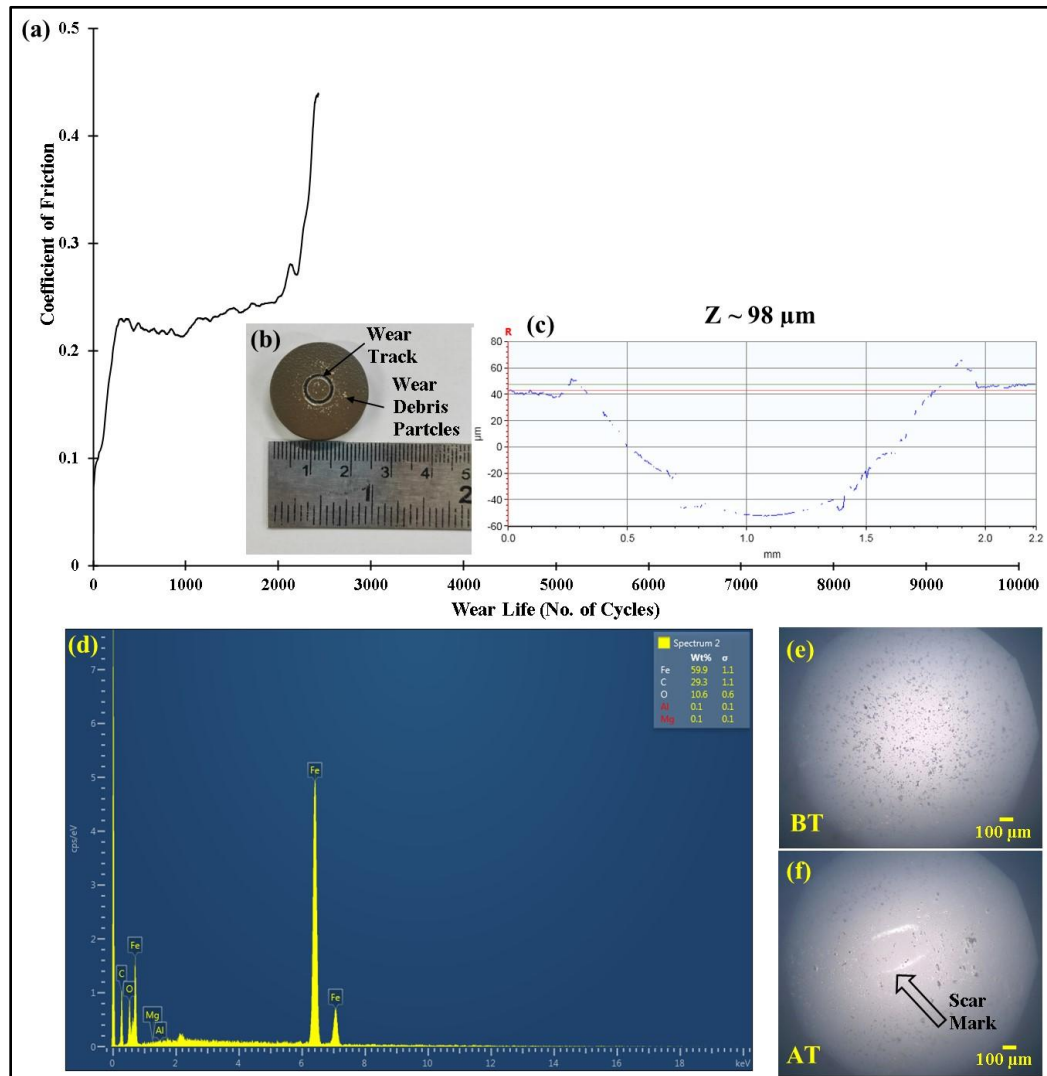


Figure 4.21 The (a) frictional graph of PEEK+1.5 wt% ceria nanocomposite coating prepared from ball milling technique along with the (b) wear track photograph, (c) the 2D wear track depth, (d) the EDS scan, and (e) the counter face ball images before the test (BT) and (f) after the test (AT) at a normal load of 70 N for 10,000 cycles at 0.1 m/s

However, when the coating deposited from the ball-milled powders with a post-heat treatment duration of 90 minutes was tested, it was found that the coating failed at ~ 2500 cycles as can be seen from the sudden spike in the frictional graph as shown in Figure 4.21a, suggesting of a possible metal to metal contact. The coating failure was also confirmed by the scar marks observed on the counter face ball as shown in Figure 4.21f suggesting a metal-to-metal contact. Furthermore, the EDS scan also confirms the failure of the coating with an evident presence of a Fe peak (Figure 4.21d) and the wear profile depths (Z) reached $\sim 98 \mu\text{m}$ which is more than the thickness of the coating. The long duration of post-heat treatment might have resulted in the degradation of the PEEK powder, thereby deteriorating the overall mechanical and tribological properties of the ball-milled composite powder. Furthermore, the weak interface between the coating and the substrate leading to reduced adhesion must have also played a role in the earlier failure of the coating. Hence it can be concluded that the probe sonication would be an ideal choice for mixing and dispersing ceria particles in the PEEK matrix as compared to the ball milling.

4.2.7 Summary

This study provides a comparative evaluation of two techniques, namely, ball milling and probe sonication to prepare PEEK/1.5 wt% ceria nanocomposite powders for depositing coatings on mild steel substrates. The results underscore the importance of selecting an appropriate method to achieve optimal material properties, particularly for high-performance applications. The tribological tests demonstrated that the coatings developed from the sonicated powders exhibited superior wear resistance and load-bearing capacity, successfully exhibiting a wear life of more than 10,000 cycles under a 70 N load without

failure. In contrast, the coatings from the ball-milled powders failed much earlier, at around 2,500 cycles. Overall, the findings indicate that probe sonication could be the preferred method for developing PEEK/ceria nanocomposite powders for coating application when the goal is to achieve superior mechanical and tribological properties. The study highlights the critical role of processing techniques in determining the final properties of nanocomposite materials, emphasizing the need for careful selection based on the specific requirements of the intended application.

4.3 Optimized parameters for substrate, dispersion, and coating preparations

Based on findings from Phase 1 and Phase 2, we have optimized the ideal surface roughness required for the coating to adhere well to the substrate to obtain the best tribological result. We have also obtained the dispersion technique that is required to obtain a homogenous mixture of matrix and filler to develop the nanocomposite coatings along with the ideal coating parameters needed to craft the coatings.

4.3.1 Preparation of nanocomposite powders for coating

Figure 4.22 below shows the nanocomposite powder preparation setup. PEEK/Ceria nanocomposite powder was produced by magnetic stirring in conjunction with the sonication process as concluded from phase 2. A probe sonicator (Sonics, Vibracell, USA) was used to sonicate a weighted quantity of ceria in 50 milliliters of ethanol for ten minutes at an amplitude of 30% and an on/off cycle duration of twenty/five seconds. To further distribute the ceria particles evenly, the sonicated solution with the ceria powder

was magnetically agitated for two minutes at 1100 rpm using magnetic stirrers. Subsequently, a weighted quantity of PEEK powder was added to the solution and was further subjected to magnetic stirring for one hour followed by heating in a furnace at 80 degrees Celsius for 24 hours to completely evaporate ethanol and retrieve the PEEK/ceria nanocomposite powder for further processing.

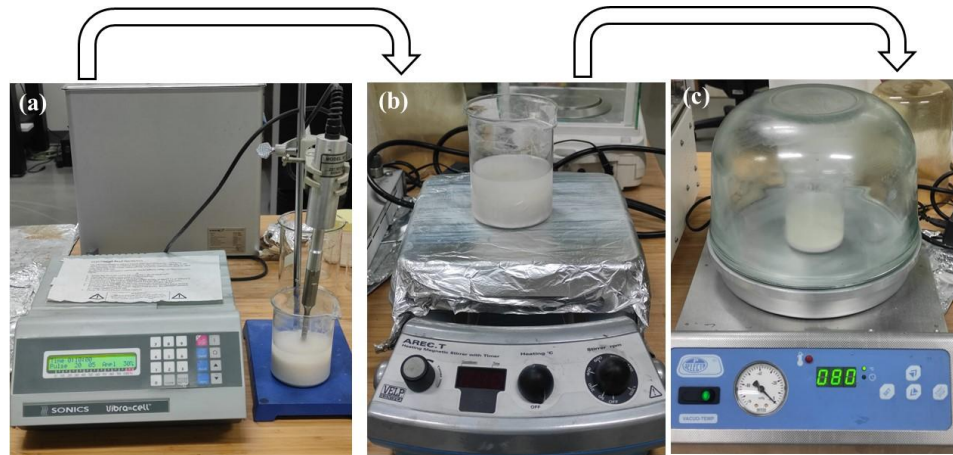


Figure 4.22 Nanocomposite powder preparation setup (a) Probe sonication of filler material (b) Mixing of filler and polymer matrix by magnetic stirring (c) Drying of nanocomposite powder

4.3.2 Substrate preparation before coating

Prior to coating, the mild steel substrates were subjected to surface roughening to improve the adhesion between the coating and the substrate. The grinding process was carried out using a metallographic manual grinder-polisher (Mikrosized, China) as shown in Figure 4.23. The substrates were ground using 120 grit size paper to obtain a final surface roughness of $2.214 \pm 0.5 \mu\text{m}$.



Figure 4.23 Grinding machine

4.3.3 Ultrasonic cleaning and drying

After grinding, samples were cleaned with acetone by using the ultrasonic cleaning method for 15 minutes. The benefit of ultrasonic cleaning is that sound waves hit the sample and remove the attached debris particle which is necessary prior to coating. After cleaning, samples were dried using an air blower. Figure 4.24 below is the ultrasonic bath cleaner used for cleaning purposes.



Figure 4.24 Ultrasonic cleaner

4.3.4 Coating procedure

Figure 4.25 illustrates the electrostatic spray gun (Model no 17288, Craftsman®) which was used for depositing the powders on the substrate. The benefits of using the electrostatic powder spray coating method over other conventional methods are as follows; it is quick, easy, has no requirement of different solvents for specific polymers, is environment-friendly, energy efficient, and results in less wastage of materials. The basic principle of an electrostatic spray gun is that negatively charged powder particles are deposited on a positively charged sample.

The ground and cleaned mild steel samples were pre-heated for 10 min at 370 °C in the oven and subsequently removed to deposit the coatings using a Craftsman® electrostatic spray gun (Model: 17288). The spray gun directed the powder flow to the grounded substrates to achieve a powder layer on the surface. The powder-coated samples were again placed in the oven at 370 °C for a post-heat treatment for 30 minutes followed by cooling to room temperature to obtain uniform coatings.



Figure 4.25 Electrostatic spray gun

4.4 Phase 3 - Optimizing the composition of ceria nanoparticles in the PEEK matrix, which would result in the best tribological properties of the nanocomposite coatings

From phase 2, we concluded that probe sonication is the optimized dispersion technique for obtaining homogenous mixtures to develop nanocomposite coatings. The tribological tests demonstrated that the coatings developed from the sonicated powders exhibited superior wear resistance and load-bearing capacity, successfully exhibiting a wear life of more than 10,000 cycles under a 70 N load without failure. Now in this phase, our findings from the tribological characterization and analysis of pristine PEEK and PEEK nanocomposite coatings reinforced with three different ceria loadings (0.5, 1.5, 3 wt%), deposited onto mild steel substrate under dry conditions, are discussed. XRD, FTIR, TGA and SEM analysis were used for structural characterization of nanocomposite coatings. Then thickness and hardness measurements were conducted. Later, tribological evaluation of coatings, coupled with SEM analysis and optical profilometry to study wear mechanism involved, was carried out.

4.4.1 XRD analysis of pristine and developed nanocomposite powders

The XRD patterns for the orthorhombic unit cell of pristine PEEK were obtained in the 2θ range of 10 to 60 °, which shows the characteristic diffraction peaks of crystalline PEEK in its α -phase at 18.8 °, 21.6 °, 22.8 ° and 28.7 ° corresponding to (110), (111), (200), and (211) of the diffraction planes respectively (Figure 4.26) [126,127]. The XRD patterns of ceria were also plotted in the 2θ range of 25 to 60 ° corresponding to (111), (200), (220), and (311) of the diffraction planes to provide a detailed understanding of the

intensity and shift in the XRD peaks obtained in the composites prepared for this study [130]. The X-ray diffractogram of the composites illustrated a similar pattern to the PEEK and ceria but with broader and less intense peaks. Even though having a very low composition of ceria for 0.5 wt% loading, there is a slight shift in peak intensities indicating potential interactions between PEEK and ceria nanoparticles, even though these effects may be subtle. In the XRD analysis of 1.5 and 3 wt% ceria loadings, more intense peaks emerged at 2θ angles corresponding to the presence of ceria nanoparticles, such as around 27-30 °. Similar intense peaks due to the presence of ceria were also observed around 45-47 ° and 56-58 ° respectively. The peak observed at around 37.5 ° in the XRD pattern of pristine PEEK represents a characteristic crystalline phase within the polymer matrix. The reduced peak intensity at 0.5 wt% ceria indicated that the PEEK's crystalline structure was reduced. The peak intensity did, however, increase once again at 1.5 wt% ceria, suggesting a more uniform dispersion of the nanoparticles and possible restoration of the crystalline structure. On the other hand, at 3 wt%, the peak completely disappeared, indicating substantial changes in the crystalline structure due to nanoparticle agglomeration.

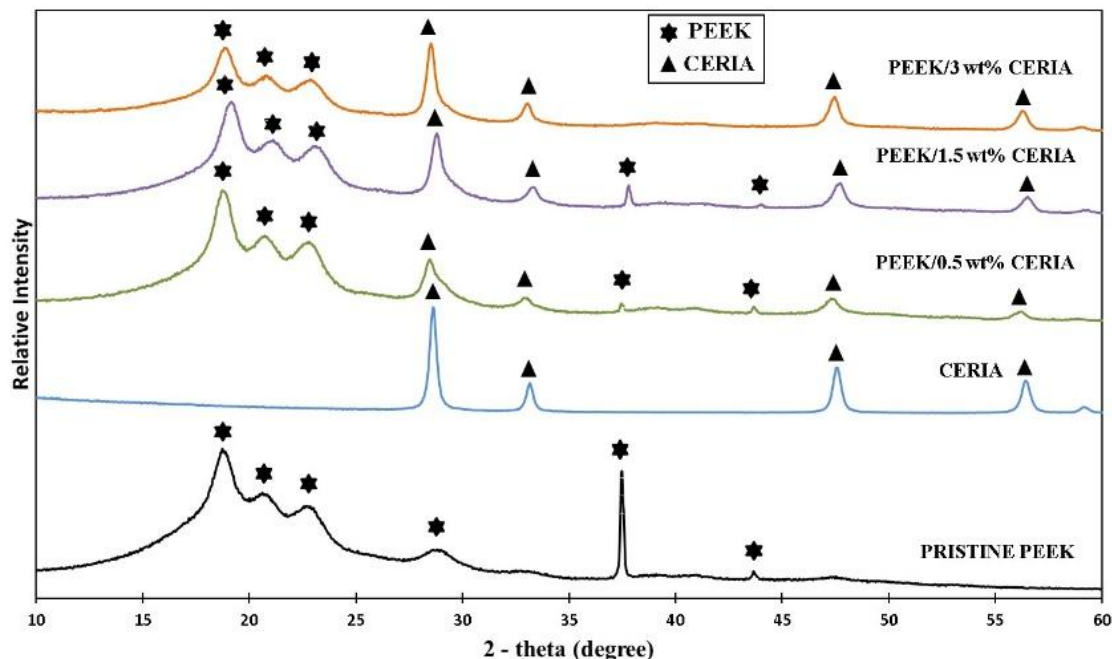


Figure 4.26 XRD patterns of pristine PEEK and PEEK reinforced with ceria at different loading conditions

4.4.2 FTIR analysis of pristine and developed nanocomposite coatings

Figure 4.27 shows the FTIR spectra of pristine PEEK, ceria and developed nanocomposite powders in the range between 3500 and 500 cm^{-1} . The FTIR spectra of PEEK exhibited a carbonyl group stretching at 1647 cm^{-1} and vibration of the skeletal ring at 1594 cm^{-1} , 1487 cm^{-1} , and 1411 cm^{-1} , respectively [133-135]. The peak at around 1154 cm^{-1} corresponds to C-O-C stretching [142]. The vibration bands of the diphenyl ether group's asymmetric stretching were observed at 1277 cm^{-1} and 1185 cm^{-1} [143]. The absorbance observed at 835 cm^{-1} and 766 cm^{-1} correlates with the aromatic out-of-plane bending vibrations [144]. Furthermore, the ceria nanoparticle consisted of the signature peak of ceria at 2924 cm^{-1} corresponding to $-\text{CH}_3$ and $-\text{CH}_2$ asymmetric stretching [145]. The peak at 1624 cm^{-1} can be attributed to the interlayer stretching and

bending vibration of molecular water (H-O-H) [135,141]. The peak at 1337 cm^{-1} and 555 cm^{-1} is due to Ce-O stretching vibrations of CeO_2 [125,141].

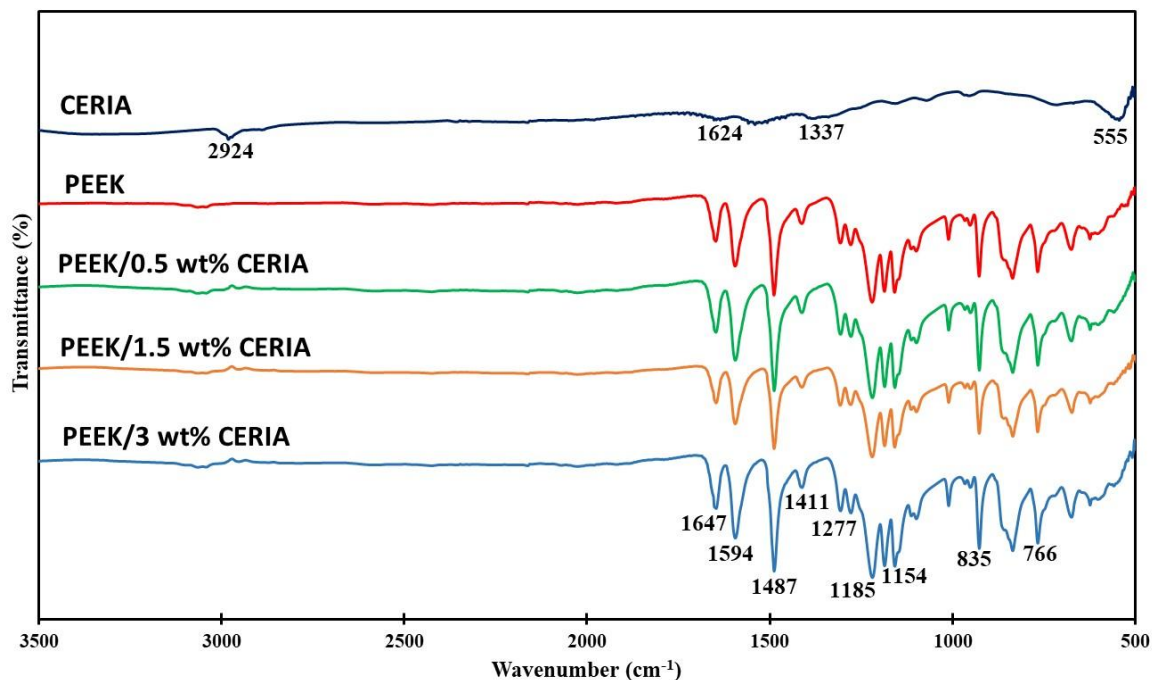


Figure 4.27 FTIR spectra of PEEK, ceria, and nanocomposite powders prepared from different wt% of ceria nanoparticles

The FTIR spectra of the PEEK/ceria composite powders with 0.5, 1.5, and 3 wt% ceria showed similar characteristic peaks to those observed in pristine PEEK powder (Figure 4.27). This suggests that the overall chemical structure of the PEEK matrix remained largely intact, despite the addition of ceria nanoparticles. Notably, the signature peaks typically associated with ceria were very weak in all the developed composite samples. This indicates that the ceria nanoparticles were effectively encapsulated by the PEEK matrix. The complete embedding of the ceria within the PEEK structure implies that the nanoparticles were well integrated into the polymer matrix.

4.4.3 Analysis of microhardness of the pristine and developed nanocomposite coatings

Figure 4.28 illustrates the variation in the hardness of the PEEK coatings with varying loadings of the ceria nanoparticles. In general, an increase in the hardness values of the coatings was observed with the addition of ceria nanoparticles. Incorporating well-dispersed nanoparticles into the parent matrix enhances the stiffness of the matrix by limiting the slippage, and mobility of polymer chains, consequently resulting in an elevation in hardness values [147,148]. Here, the smaller ceria nanoparticles have larger surface area-to-volume ratios thereby enhancing interfacial interactions. Reinforcing ceria has created a greater interfacial area between the two mediums facilitating efficient stress transfer between the nanoparticles and the polymer matrix, promoting effective resistance to indentation, and increasing microhardness.

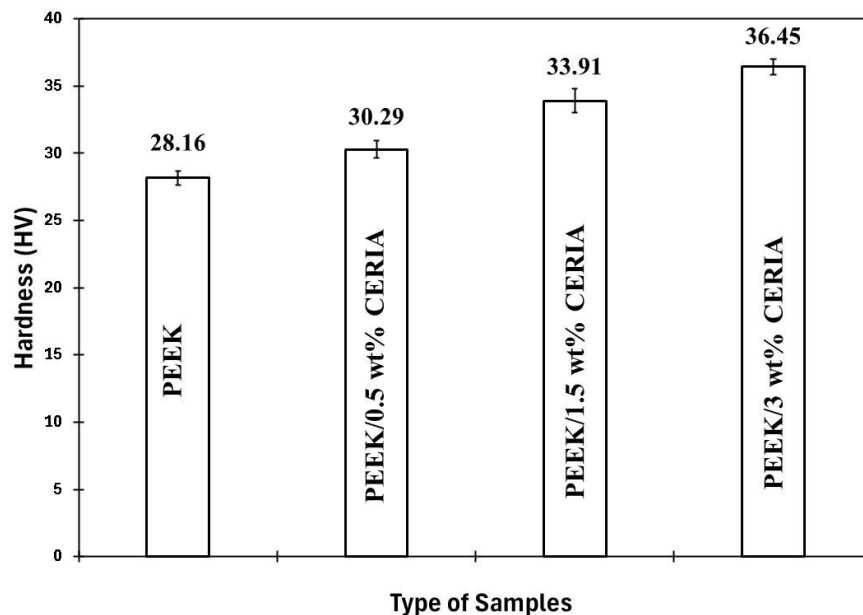


Figure 4.28 Comparison of the hardness values of PEEK nanocomposite coatings at different loadings of ceria

4.4.4 Analysis of the thickness measurements and dispersion of nanofillers in the polymer matrix

The thickness measurements of pristine PEEK and PEEK/ceria nanocomposite coatings are shown in Figure 4.29. It is observed that the addition of the nanofillers has no significant effect on the thickness values. The average value of the thickness readings of the coatings was found to be $\sim 100 \pm 5 \mu\text{m}$. Figure 4.30 depicts the EDS elemental maps of cerium (Ce) which offers insights into the distribution of ceria nanoparticles within the PEEK composite coatings at varying weight percentages. At 0.5 wt%, ceria nanoparticles demonstrate a lower concentration of nanofiller throughout the polymer matrix. However, at 1.5 wt%, the overall distribution is relatively uniform, indicating effective dispersion of the ceria nanoparticles within the PEEK polymer matrix. In contrast, at 3 wt%, very pronounced agglomerations of ceria nanoparticles become evident, suggesting non-uniform distribution within the polymer matrix. Various researchers performed such observations underlying the importance of dispersion analysis of the ceria nanoparticle in their studies [149,150].

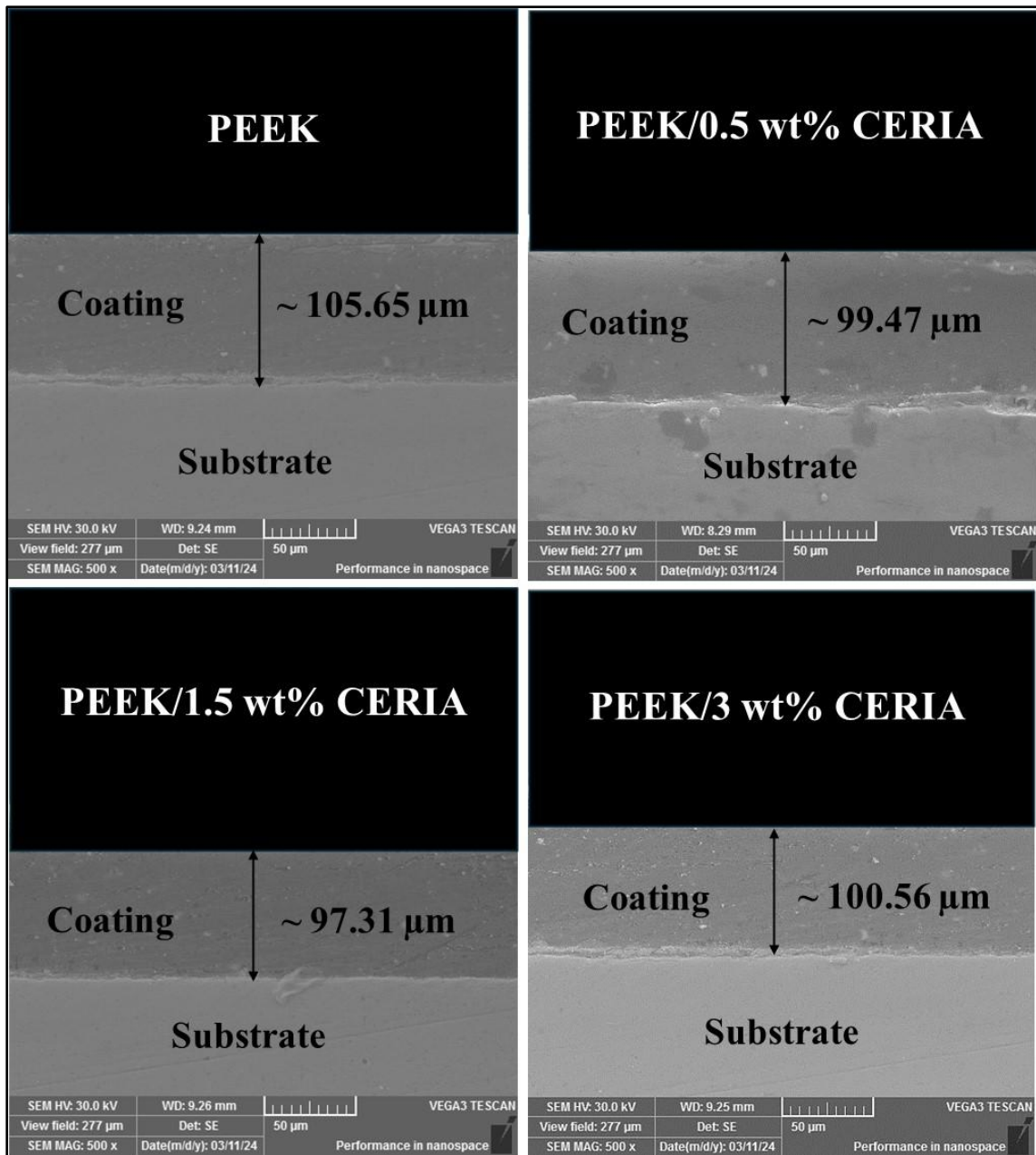


Figure 4.29 Cross-sectional SEM images of the coatings

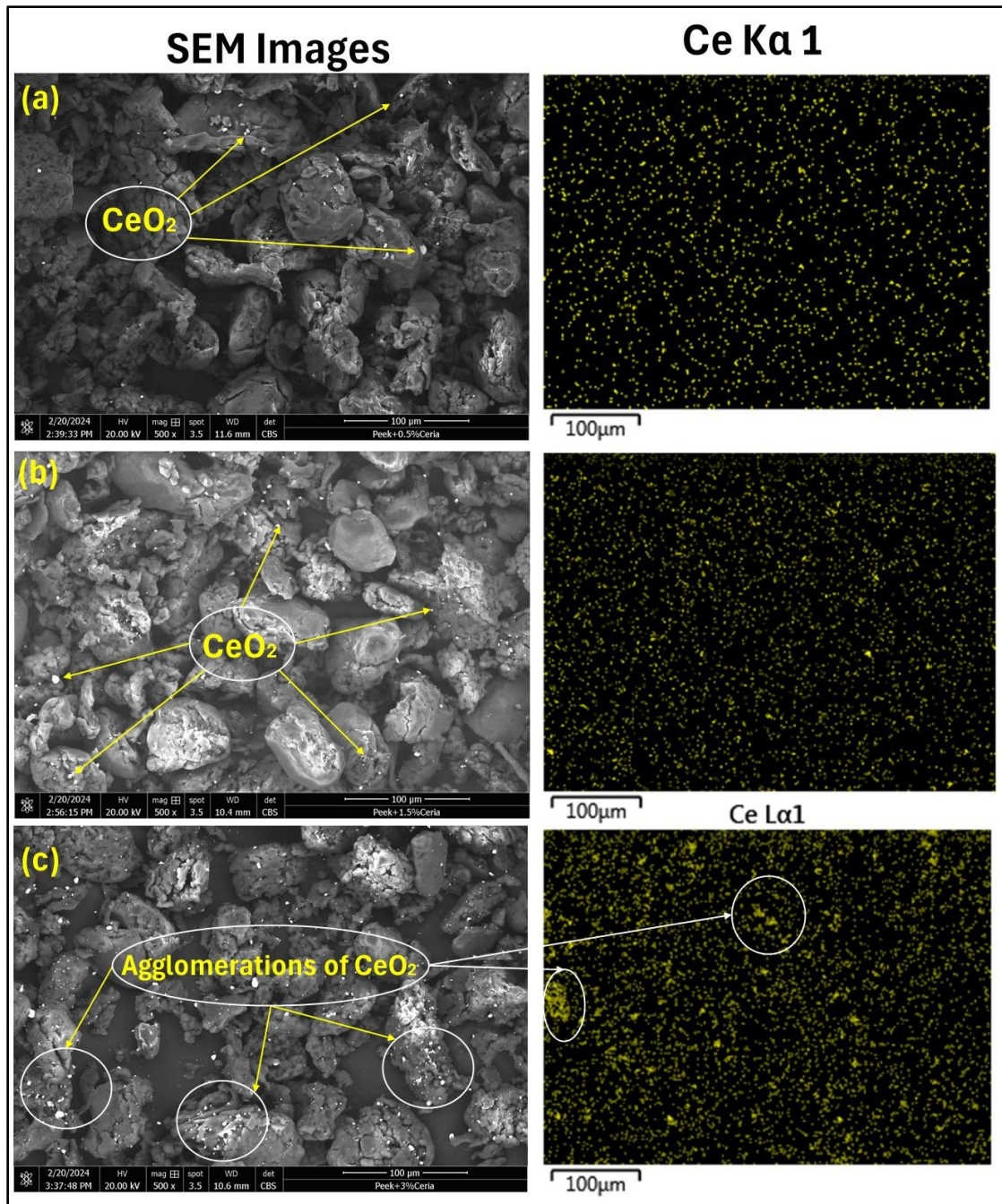


Figure 4.30 SEM images PEEK matrix reinforced with (a) 0.5wt%, (b) 1.5wt% and (c) 3wt% ceria loadings along with EDS maps for Cerium (Ce)

4.4.5 TGA analysis of the developed coatings

Figure 4.31 shows the TGA curves of pristine PEEK powder along with the PEEK/ceria nanocomposite powders. It is evident that the PEEK powder lost 10% of its weight at 590 °C, while the 0.5, 1.5, and 3 wt% reinforcements lost 10% of its weight at around 572 – 578 °C. As the temperature progressed, it can be concluded that a 40% weight reduction was observed for pristine PEEK powder at 617 °C while the nanocomposite powders exhibited a 40% weight reduction at 641 °C, 662 °C, and 647 °C for 0.5, 1.5 and 3 wt% reinforcements respectively.

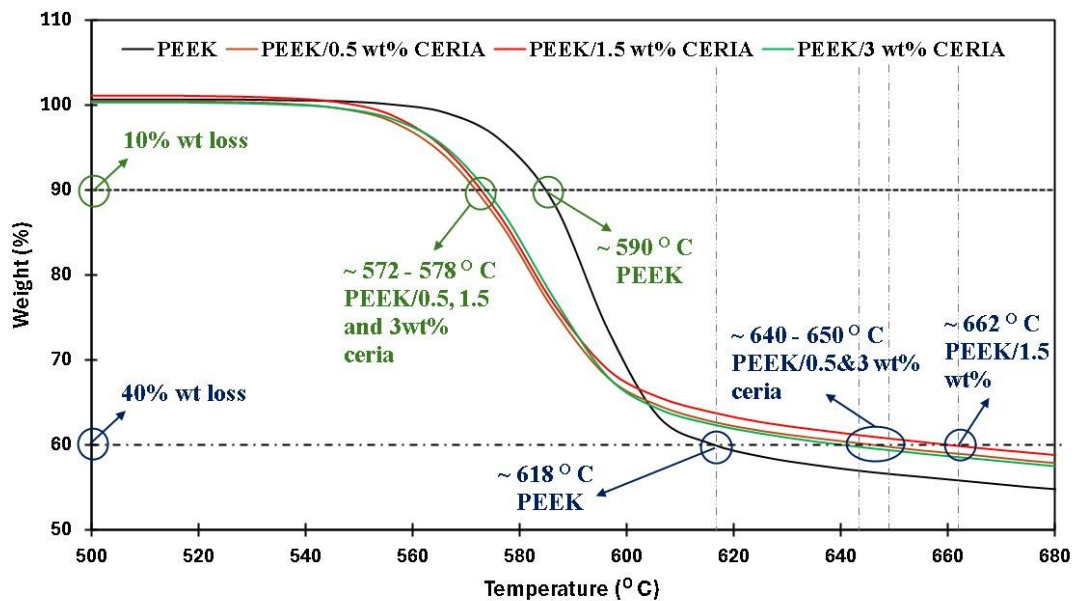


Figure 4.31 TGA thermograms of pristine PEEK and PEEK nanocomposite powders

At elevated temperatures, the presence of ceria has slowed down the decomposition process. This observation was in agreement with the TGA curves of pure PEEK exhibiting a lower weight loss at lower temperatures followed by a significant increment

in the weight loss as the temperature progressed when compared to its composite counterparts [151]. Similar observations were also reported by the ref [152] where the TGA curve of PEEK exhibited a similar trend.

4.4.6 Tribological performance of the pristine and developed nanocomposite coatings

The initial set of wear tests were conducted to determine the load-bearing capacity and the sliding speed limitation of pristine PEEK coatings deposited on mild steel substrates.

a. Effect of load and linear speed on the tribological performance of pristine PEEK coatings

To evaluate the load-bearing capacity of the pristine PEEK coatings, sliding tests were conducted at varying normal loads of 50 N, 60 N, and 70 N, respectively at a constant sliding speed of 0.1 m/s (318 rpm) for 10,000 cycles corresponding to a sliding distance of 189 m. The wear track radius was kept constant at 3 mm throughout the experimental study. It is critical to highlight that the tests were terminated promptly in the event of an observed substantial increase in the coefficient of friction (COF) exceeding 0.5, indicative of potential metal-to-metal contact and consequent coating failure. Figure 4.32 shows the frictional graph along with the data illustrating the wear track depth at normal loads of 50, 60, and 70 N respectively.

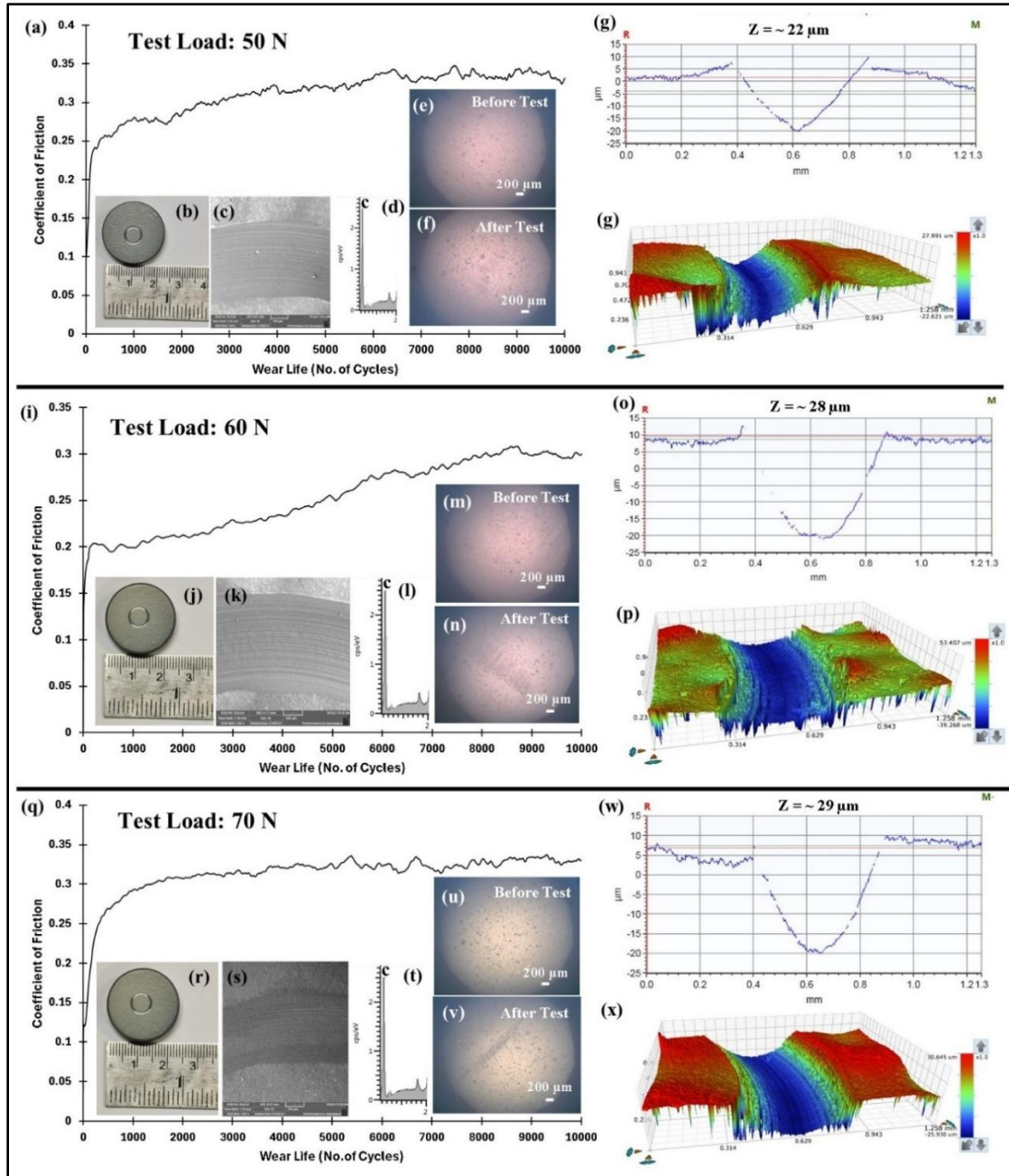


Figure 4.32 Comparison of the (a, i, q) frictional graph of pristine PEEK coatings along with (b, j, r) wear track photographs and (c, k, s) SEM images of the wear track with corresponding (d, l, t) EDS scans, the (e, m, u) counter face ball images before the test and (f, n, v) after the test, the (g, o, w) 2D wear track depth, and (g, p, x) 3D profile images at varying normal loads for 10,000 cycles at 0.1 m/s

It can be observed from the frictional graphs that the pristine PEEK coating did not fail until 10,000 cycles even as the loading was gradually increased from 50 N to 70 N. This

was confirmed by the wear track images as well as the wear track profile depths (Z) which were lower than the coating thickness of $\sim 100 \mu\text{m}$. It is also evident that, as the loading increased, the depth of the wear track increased due to increased contact pressures leading to more material removal and deeper wear tracks. However, the increase in the depth of the wear track was minimal as the normal load increased from 60 to 70 N indicating that the pristine PEEK coating may have reached a critical load threshold beyond which, an additional increase in normal load does not significantly affect the wear behavior at a sliding speed of 0.1 m/s. This threshold is attributed to the PEEK coating's inherent mechanical properties, such as its hardness, toughness, and wear resistance, which enabled it to withstand higher contact pressures without undergoing excessive wear. Further wear tests were conducted to study the effect of sliding speed on the tribological performance of pristine PEEK coatings. To evaluate this, the sliding speed was incrementally increased from 0.1 m/s to 0.5 m/s while maintaining the normal load at 70 N. The pristine PEEK coating tested at 0.2 m/s (637 rpm) exhibited a COF of 0.3178 and survived for 10,000 cycles without failure. The SEM image along with the EDS map confirms this (Figure 4.33). As the linear velocity was increased from 0.1 m/s to 0.2 m/s, there was a considerable increment in the wear track depth ($\sim 70 \mu\text{m}$). In such conditions, maximum shear stress occurs at the surface due to high friction. Due to the repetitive sliding of the counter face ball over the coating, miniature wave-like features were visible over the wear track. This is primarily due to the surface fatigue caused as a result of induced cyclic stresses caused due to the repetitive sliding of the counterface ball over the softer PEEK coating, causing the generation of subsurface cracks. However, as the linear speed was increased to 0.3 m/s (955 rpm), the coating failed just after $\sim$

7,500 cycles (Figure 4.34). It is to be noted that, with an increase in the sliding speed, the localized temperature becomes very high due to the less time available for heat dissipation, leading to the softening of the PEEK matrix resulting in the failure of the coating. This is evident from the TGA curves in Figure 4.31. As the temperature increases, the degradation rate of the PEEK polymer also increases. As a result, the material property gets drastically deteriorated resulting in the failure of coating at higher loads and speeds. Figure 4.35 summarizes the comparative wear life of the pristine PEEK coatings, clearly suggesting that the maximum load and speed that it could sustain for a wear test of 10,000 cycles, is 70 N and 0.2 m/s.

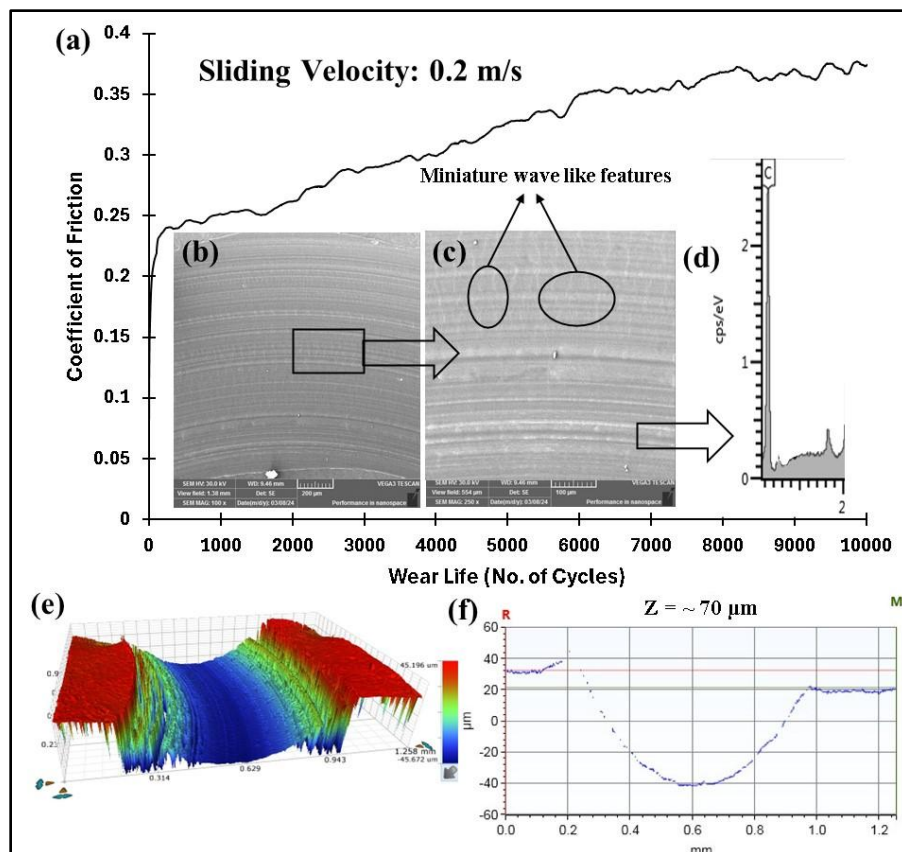


Figure 4.33 Pristine PEEK coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM image of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track

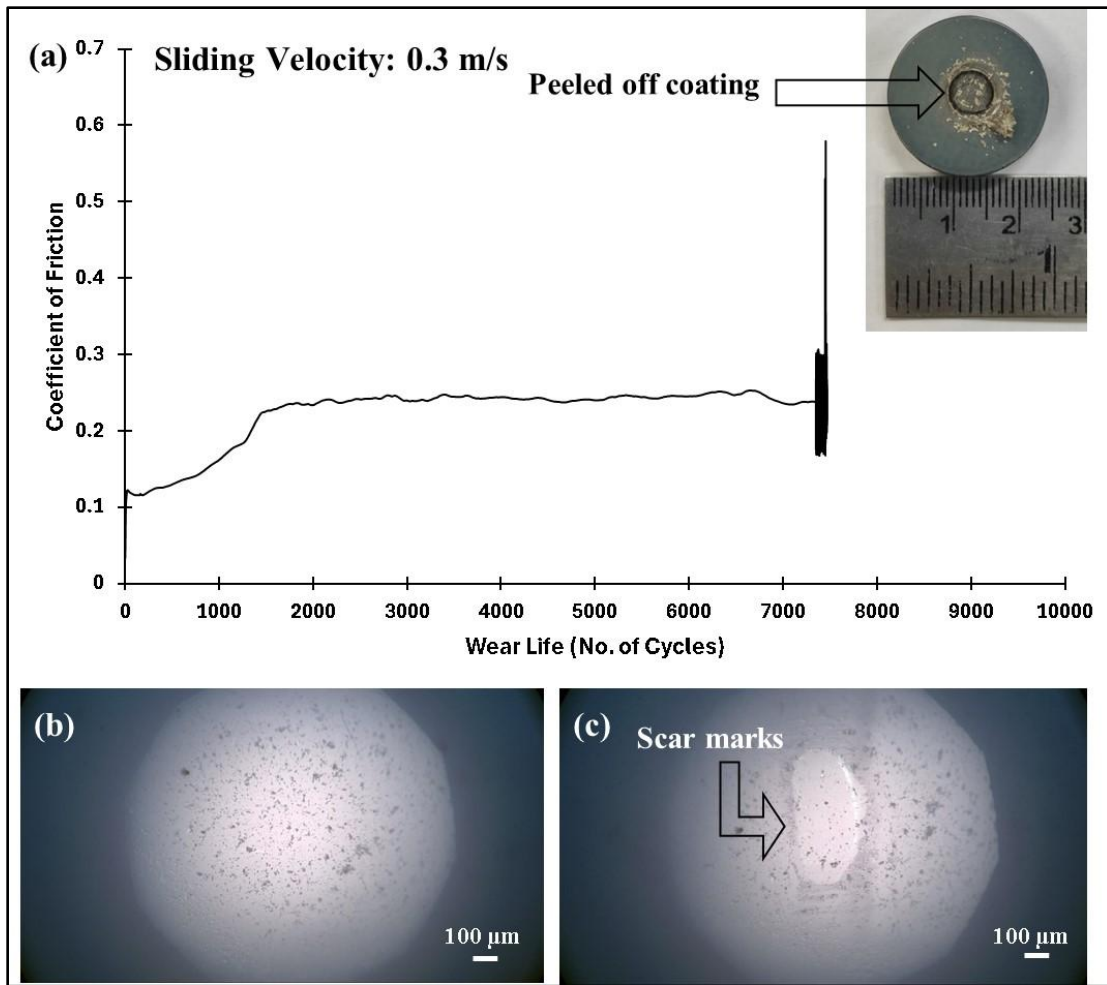


Figure 4.34 Pristine PEEK coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning

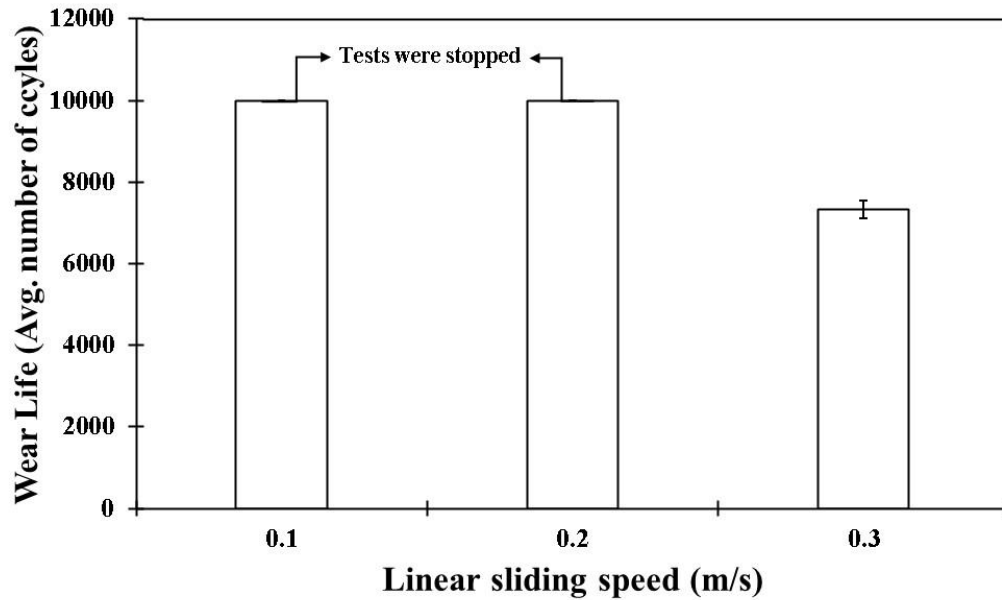


Figure 4.35 Comparative wear life of pristine PEEK coatings at a normal load of 70 N for 10,000 cycles at different sliding velocities

b. Effect of load and linear speed on the tribological performance of PEEK/Ceria nanocomposite coatings

Following the testing of the pristine PEEK coatings whereby the failure occurred at a normal load of 70 N and a sliding velocity of 0.3 m/s, nanocomposite coatings with different loadings (0.5, 1.5 and 3 wt%) of ceria were developed and their tribological and mechanical properties were evaluated at these conditions. It can be observed from Figure 4.36f, that the inclusion of ceria enhanced the wear resistance of the PEEK coating, as the wear track depth reduced significantly to $\sim 30 \mu\text{m}$ at a normal load of 70 N and 0.3 m/s as compared to the wear track depth of $\sim 70 \mu\text{m}$ for the pristine PEEK coating at a load of 70 N and a sliding speed of 0.2 m/s. Moreover, the COF also reduced significantly to a value of 0.2307 as compared to that of 0.35 for pristine PEEK coating. These

improvements are attributed to the increased hardness of the coating on the addition of 0.5 wt% of ceria. However, the PEEK/0.5 wt% ceria coating failed when the linear speed was increased to 0.4 m/s at a normal load of 70 N showing an average wear life of $\sim$ 3,100 cycles (Figure 4.37).

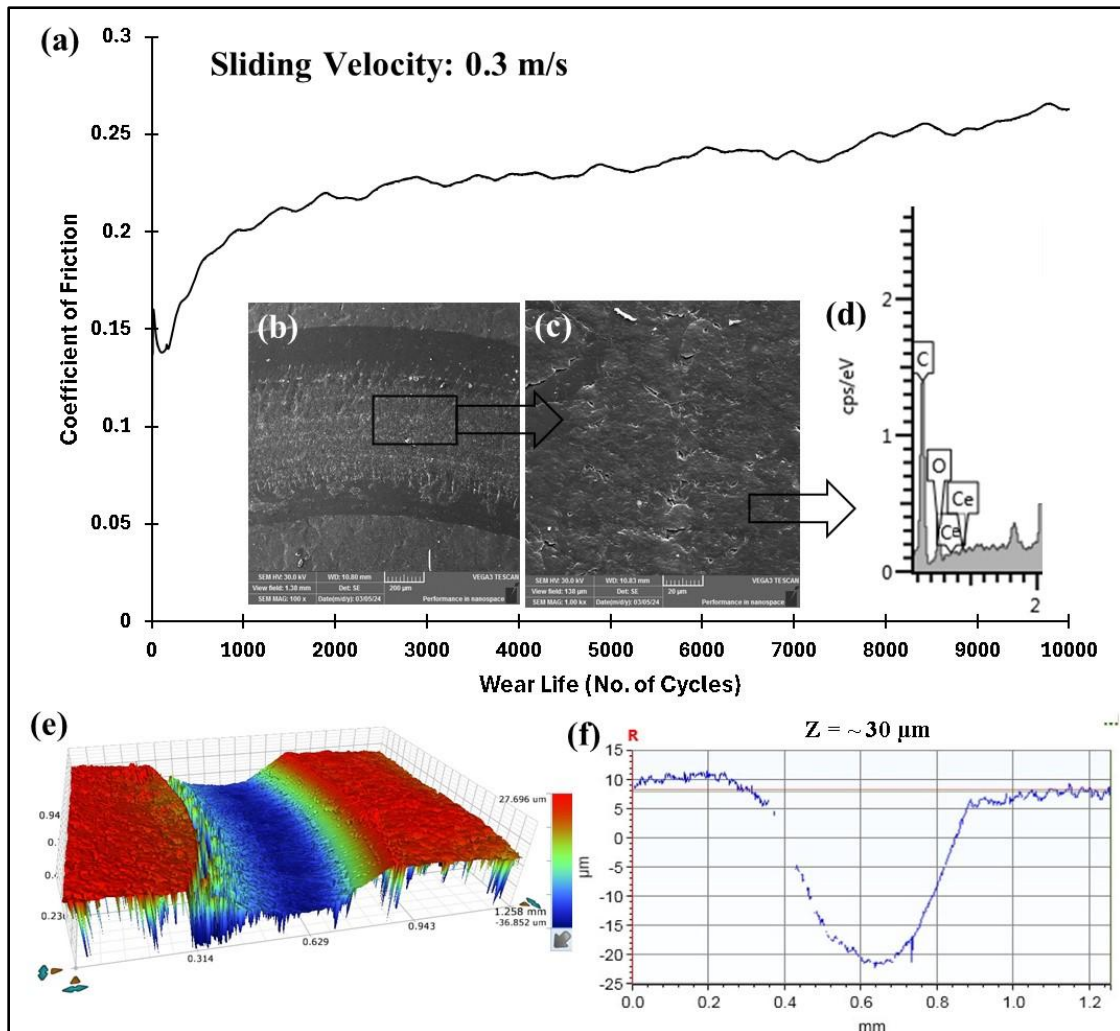


Figure 4.36 PEEK/0.5 wt% ceria coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM image of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track

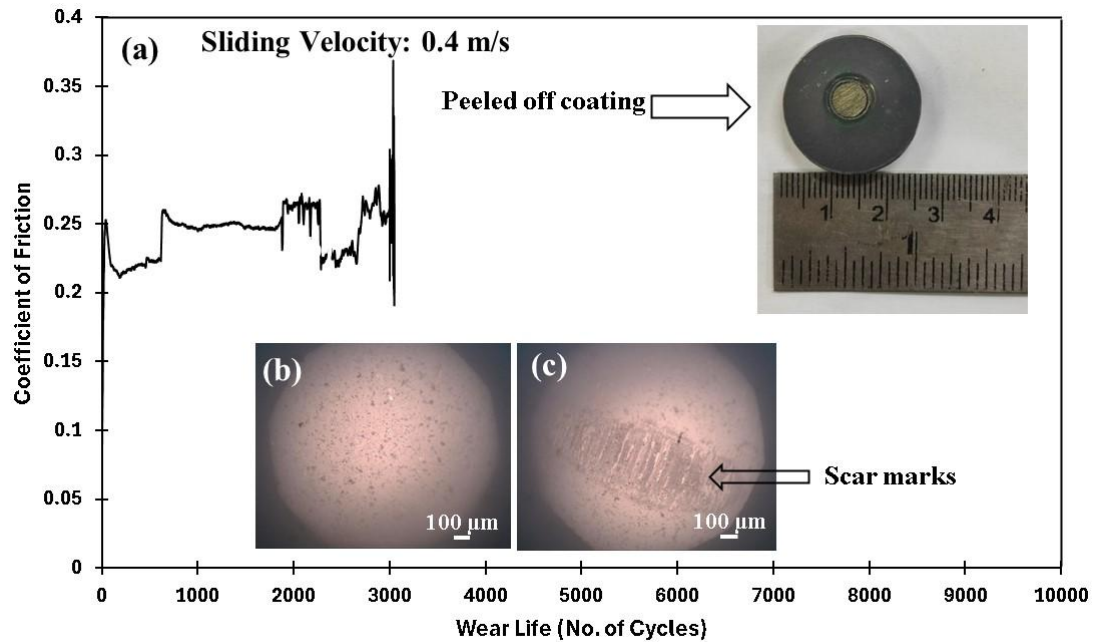


Figure 4.37 PEEK/0.5 wt% ceria coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning

As the sliding velocity is increased, the relative motion between the coating and the counterface medium intensifies, resulting in increased frictional forces and contact stresses at the interface, leading to a considerable generation of heat and increased localized temperatures at the interface. Hence the coating failure must have resulted due to the reduction in the mechanical properties as a result of the degrading of the coating at these elevated temperatures, signifying the fact that the 0.5 wt% of ceria was insufficient to provide the necessary protection to the coating at an increased speed of 0.4 m/s. The comparative wear life of PEEK/0.5 wt% ceria nanocomposite coatings is shown in Figure 4.38.

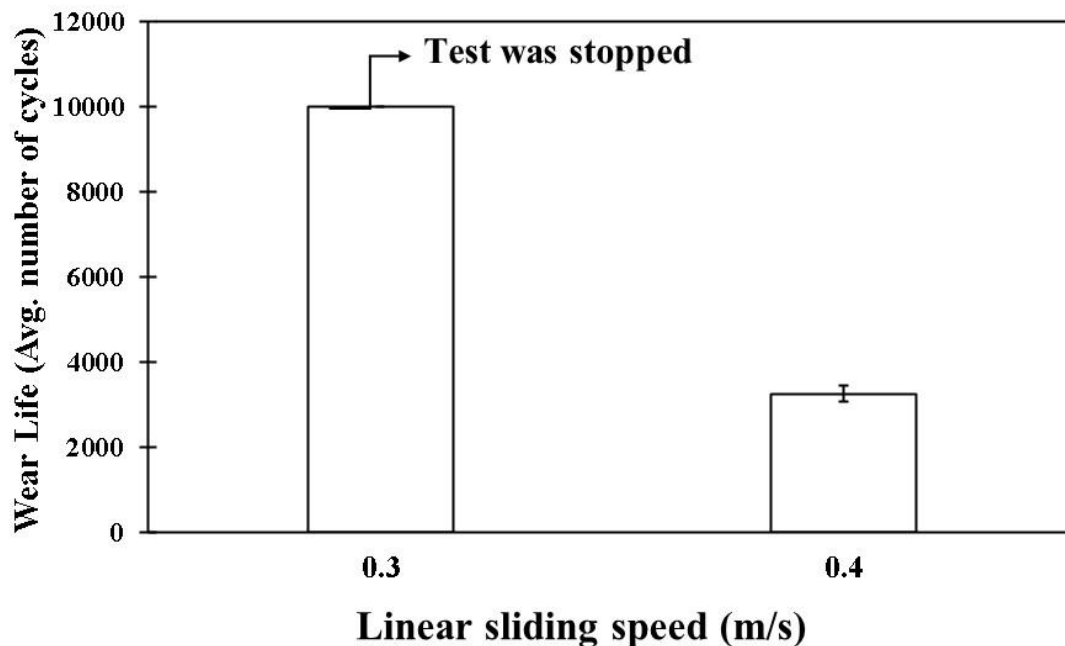


Figure 4.38 Comparative wear life study of PEEK/0.5 wt% Ceria coatings at a normal load of 70 N for 10,000 cycles at different sliding velocities

Since the PEEK/0.5 wt% ceria failed at 70 N and 0.4 m/s, we proceeded to conduct the wear test on PEEK/1.5 wt% ceria nanocomposite coating under these conditions. Figure 4.39a-f shows the performance of the PEEK/1.5 wt% ceria coatings at a load of 70 N and a linear speed of 0.4 m/s, and it can be observed that the nanocomposite coating did not fail until 10,000 cycles. The linear speed was further increased to 0.5 m/s and as can be seen from Figure 4.39g-l, the PEEK/1.5 wt% ceria nanocomposite coating did not fail until 10,000 cycles. This is confirmed by the 2D profiles of the wear tracks which show wear track depths of $\sim 26 \mu\text{m}$ and $\sim 28 \mu\text{m}$ respectively which are significantly lower than the coating thickness. It is also evident from the EDS scans that the coating didn't fail as there were no noticeable iron peaks (Fe). The increased and uniformly distributed ceria nanoparticles, which serve as effective reinforcements, along with greater

degradation temperatures obtained for the 1.5 wt% ceria loading (Figure 4.30) improved the mechanical as well as the thermal properties of the coating leading to improved wear resistance and subsequently increasing the wear life of the coating. The magnified SEM images of the wear track at 0.4 m/s and 0.5 m/s show that the predominant wear mechanism is a combination of abrasive wear and adhesive. To check, if an increased wt% of ceria would result in a further improvement in the wear resistance of the coatings, PEEK/3 wt% ceria nanocomposite coatings were tested at a load of 70 N and a sliding speed of 0.5 m/s. As can be seen from Figure 4.40, the PEEK nanocomposite coating reinforced with 3 wt% of ceria did not fail until 10,000 cycles showing a similar tribological performance as that of 1.5 wt% ceria loading. This was confirmed by the absence of the Fe peak in the EDS scan of the wear track, coupled with the lower wear track depth of $\sim 32 \mu\text{m}$ (lower than the coating thickness of $\sim 100 \mu\text{m}$).

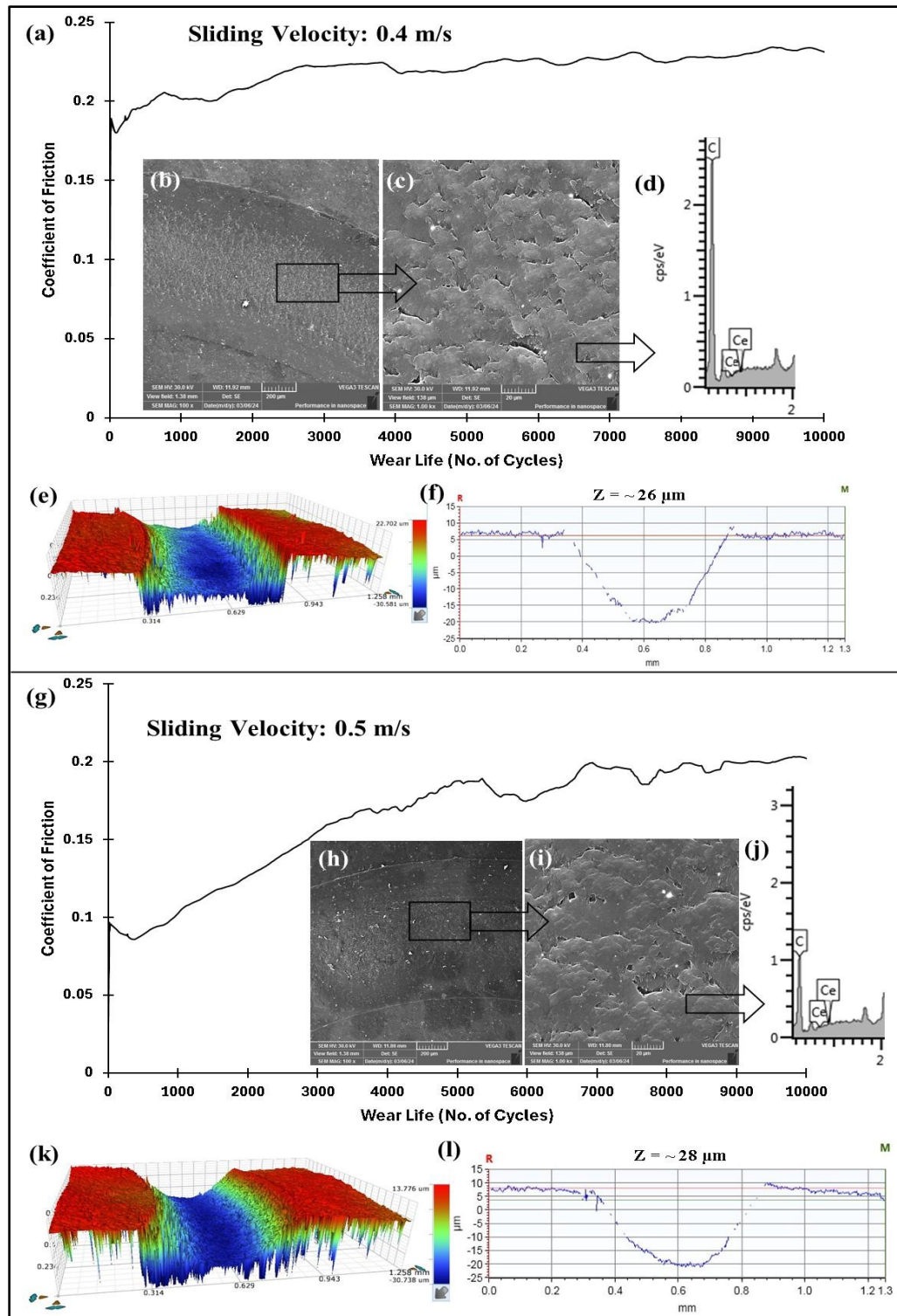


Figure 4.39 (a, g) Frictional graphs of PEEK/1.5 wt% Ceria coatings along with (b, c & h, i) SEM images of the wear track with corresponding (d, j) EDS scans, (e, k) 3D profile and (f, l) wear track depth images at varying sliding velocities for 10,000 cycles at 70 N

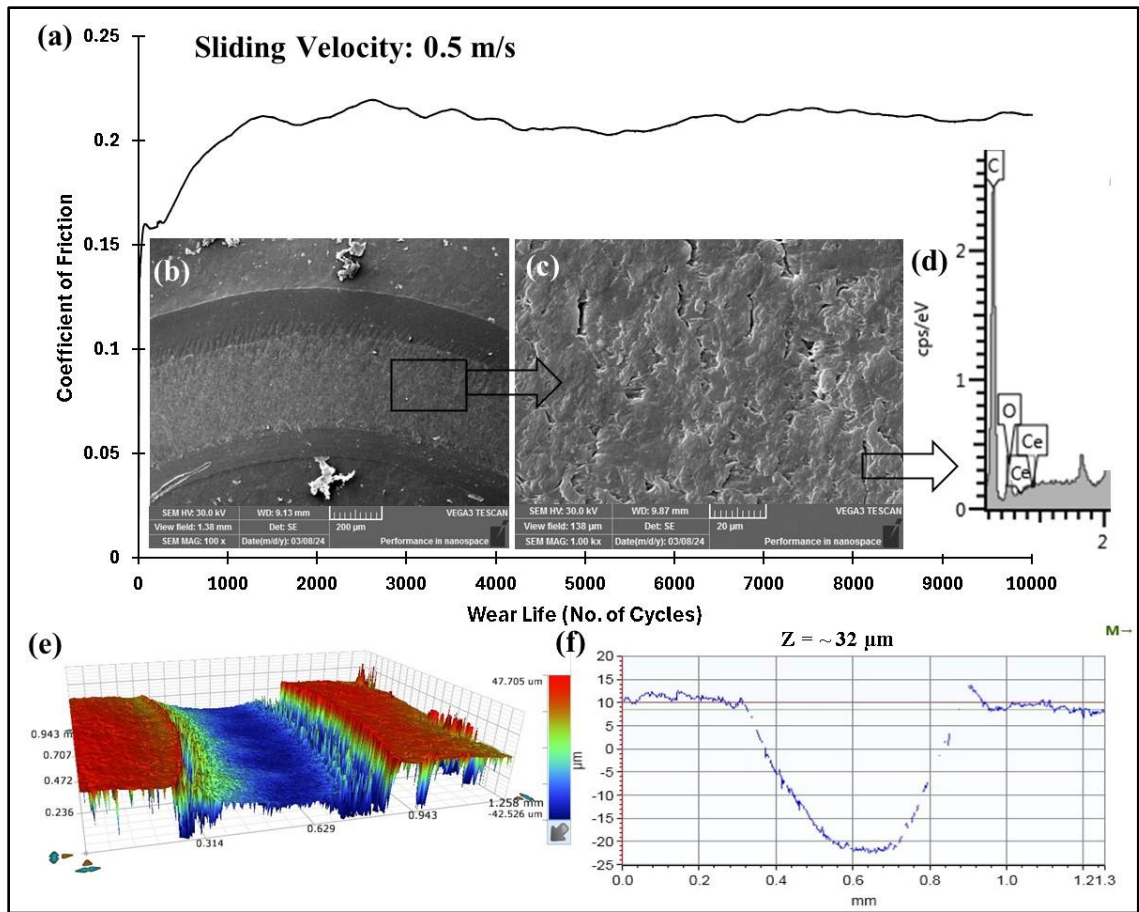


Figure 4.40 PEEK/3 wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph (b-c) SEM images of the wear track at along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track

c. Accelerated wear life testing

Since, both the 1.5 wt% and 3 wt% ceria reinforced PEEK coatings exhibited exceptional performance and did not fail under 70 N and 0.5 m/s for 10,000 cycles, long-term wear tests are performed to further evaluate their tribological performance. Hence, the coatings were tested at a normal load of 70 N and a linear sliding speed of 0.5 m/s for a prolonged duration of 50,000 cycles corresponding to a sliding distance of 1000 m. Figure 4.41 shows the frictional graph of PEEK/1.5 wt% ceria showing no failure of the coating even until 50,000 cycles (confirmed by the EDS scan in Figure 4.41d) indicating excellent

wear resistance, hence exhibiting its excellent potential in protecting the metallic component under such harsh experimental conditions. The wear track depth was found to be $\sim 50 \mu\text{m}$ (less than the coating thickness of $\sim 100 \mu\text{m}$). For an increment in the sliding distance from 189 m to 1000 m (around 430%), there was only around 79% increment in the wear track depth, which shows the excellent wear resistance property of the coating. The occurrence of plastic deformation and overlapping of the wear debris can be seen on the wear track as shown in Figure 4.41c, which are the characteristics of surface fatigue mechanisms that occur due to the continuous cyclic stresses experienced by the coating at such high speed and load.

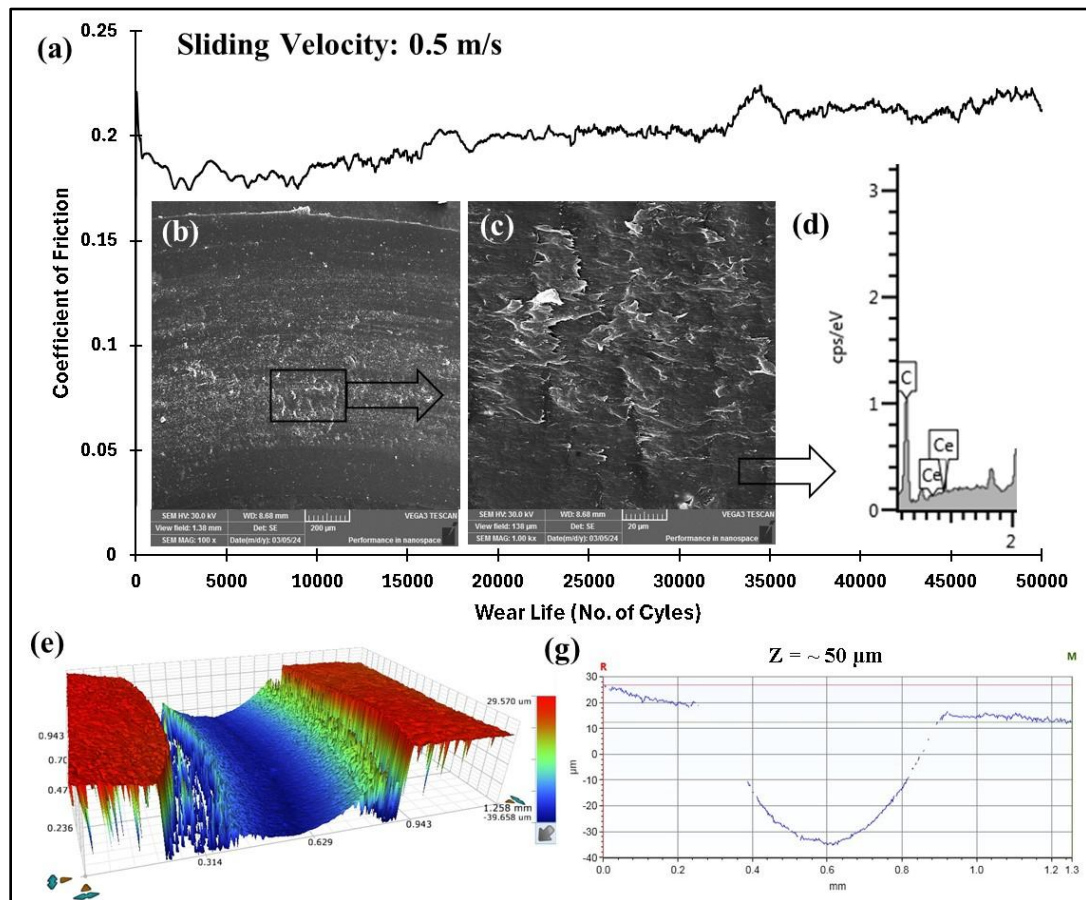


Figure 4.41 PEEK/1.5wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph (b) – (c) SEM images of the wear track along with (d) corresponding EDS scan (e) 3D optical scan of the wear track and (f) 2D optical scan of the wear track for 50,000 cycles

However, as can be seen from Figure 4.42, the nanocomposite coating reinforced with 3 wt% ceria failed under similar experimental conditions of 70 N normal load and a sliding speed of 0.5 m/s, when tested for a prolonged duration of 50,000 cycles corresponding to a sliding distance of 1000 m showing a wear life of only, ~ 26,000 cycles suggesting that the coating might have reached its endurance limit. This is attributed to a higher degree of agglomerations as observed from Figure 4.30c, which might have resulted in the deterioration of the coating due to the non-uniform properties. Figure 4.43 illustrates the average wear life of the coatings at a load of 70 N and a sliding velocity of 0.5 m/s for 50,000 cycles.

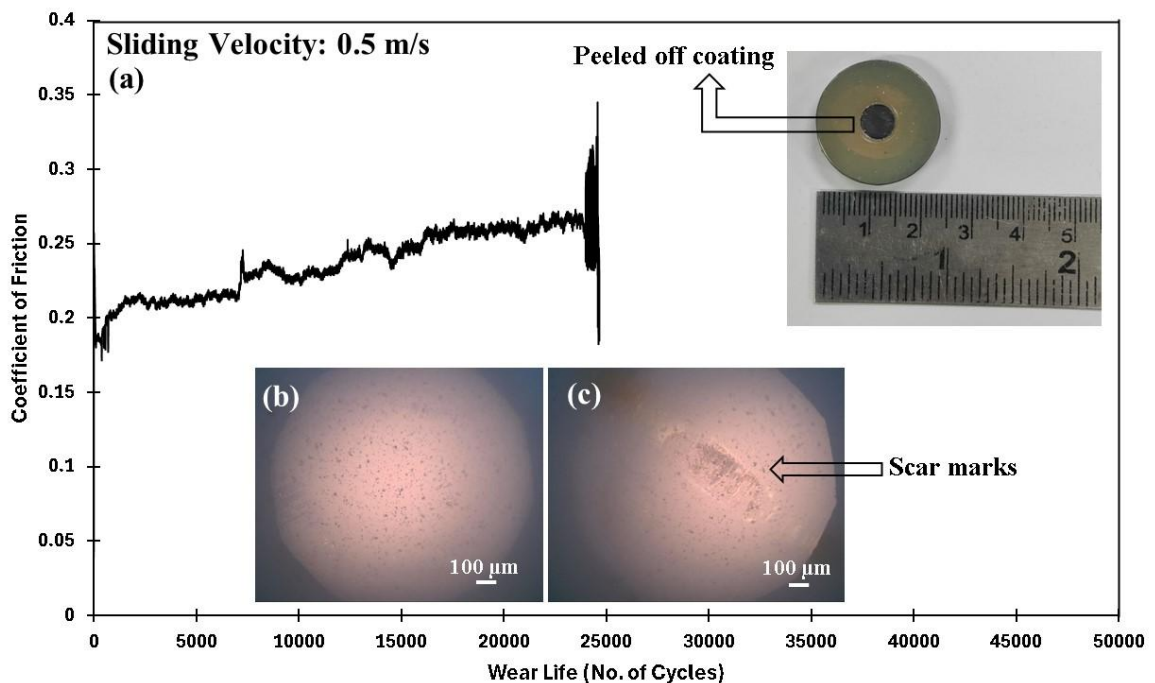


Figure 4.42 PEEK/3wt% Ceria coating at a normal load of 70 N presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning

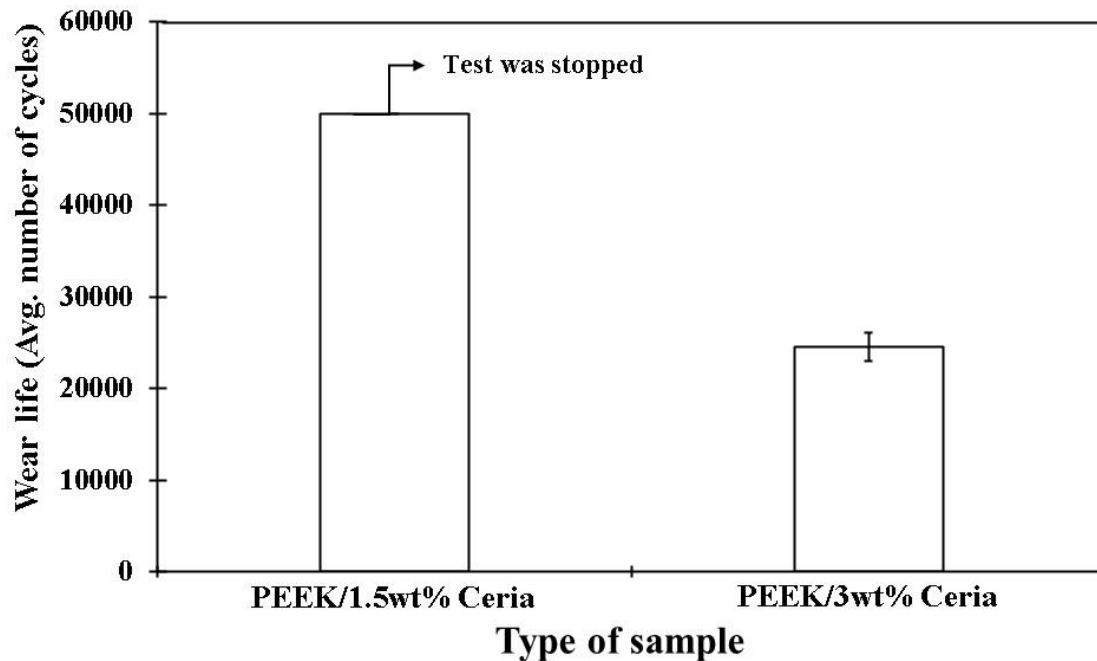


Figure 4.43 Comparative wear life study of nanocomposite coatings at a normal load of 70 N for 50,000 cycles at a sliding velocity of 0.5 m/s

d. Effect of normal load on the tribological performance of PEEK/1.5 wt% Ceria nanocomposite coatings

Following the previously conducted evaluations, it was ascertained that the 1.5 wt% ceria reinforced PEEK nanocomposite coating was providing wear resistance at a load of 70 N and a linear speed of 0.5 m/s. Tests were carried out at different normal loads of 80 N, 90 N, and 100 N, respectively, further, to examine the tribological performance of the optimized nanocomposite coatings at a constant linear speed of 0.4 m/s. Figure 4.44 shows the frictional graph along with the SEM images of the wear track with the corresponding EDS scan, and the 3D and 2D optical scan of the wear track at a sliding velocity of 0.4 m/s and normal loads of 80 N and 90 N. It can be observed that the coating didn't fail until 10,000 cycles. There wasn't a considerable increment in the wear track depth as well, which was $\sim 30 \mu\text{m}$ and $\sim 34 \mu\text{m}$ (less than the coating thickness of $\sim$

100 μm) as the normal load was increased, highlighting the excellent wear resistance exhibited by the coating. The wear track images highlight that the wear mechanism occurring was abrasive wear by plastic deformation. Furthermore, the EDS scan conducted on the wear track confirms the non-failure of the coating. However, the coating failed as the normal load was increased to 100 N exhibiting a wear life of $\sim 5,100$ cycles, which is attributed to the significant increase in the contact pressures resulting in an increased localized temperature leading to the complete degradation of the coating (Figure 4.45). Figure 4.46 shows a comparison of the wear life of the coating with varying loads.

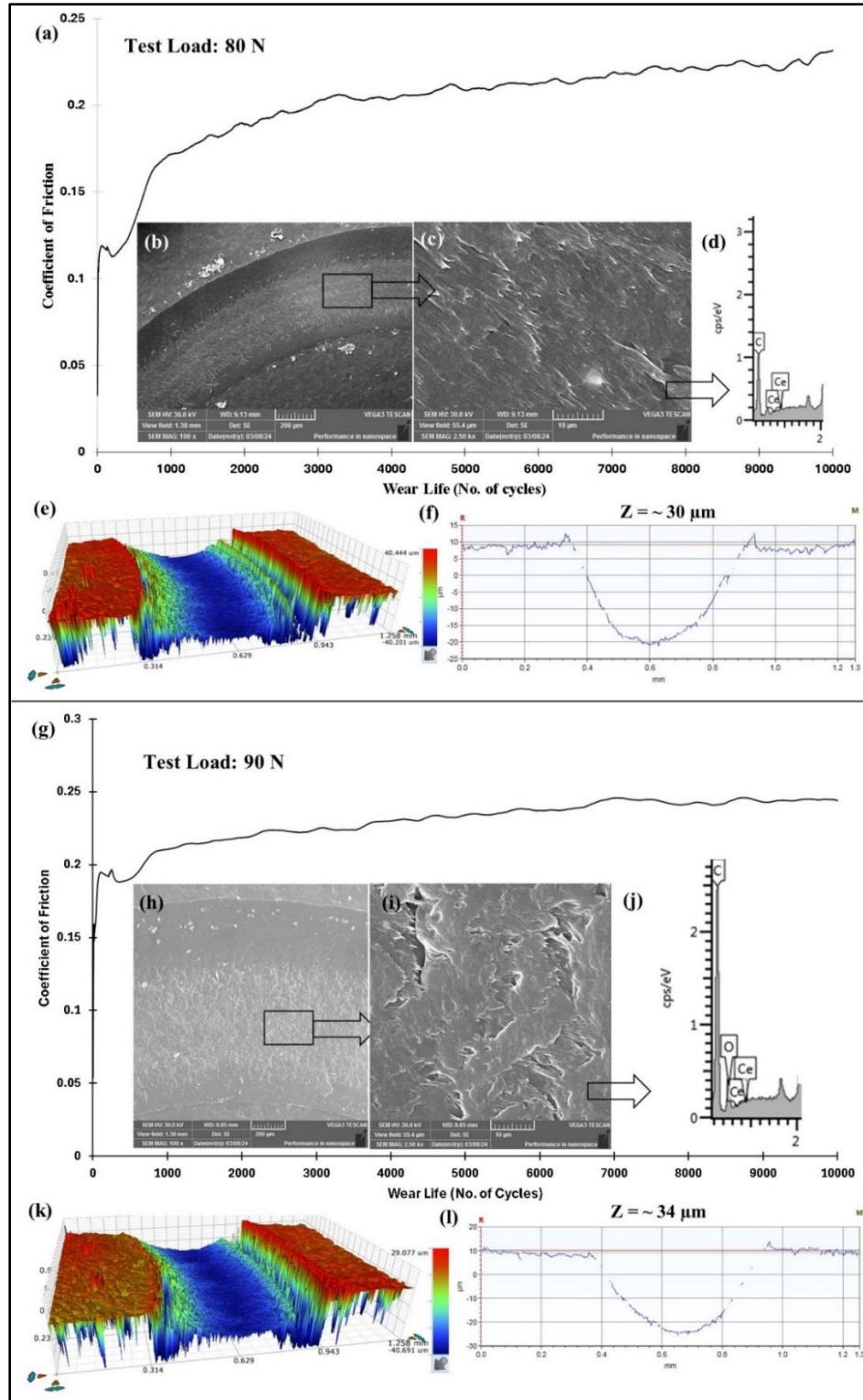


Figure 4.44 (a, g) Frictional graphs of PEEK/1.5 wt% Ceria coatings along with (b, c & h, i) SEM images of the wear track with corresponding (d, j) EDS scan, (e, k) the 3D profile and (f, l) the wear track depth images at varying normal load for 10,000 cycles at 0.4 m/s

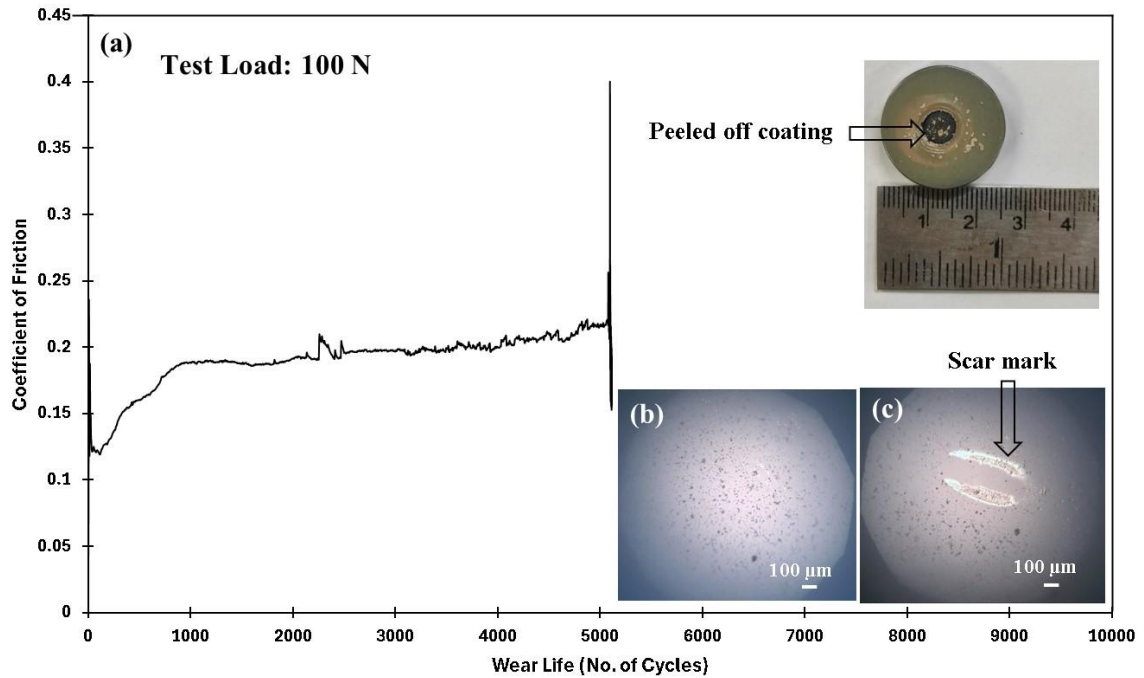


Figure 4.45 PEEK/1.5wt% Ceria coating at a sliding velocity of 0.4 m/s presenting (a) frictional graph along with the peeled-off coating with (b) ball image before testing and (c) ball image after testing with acetone cleaning

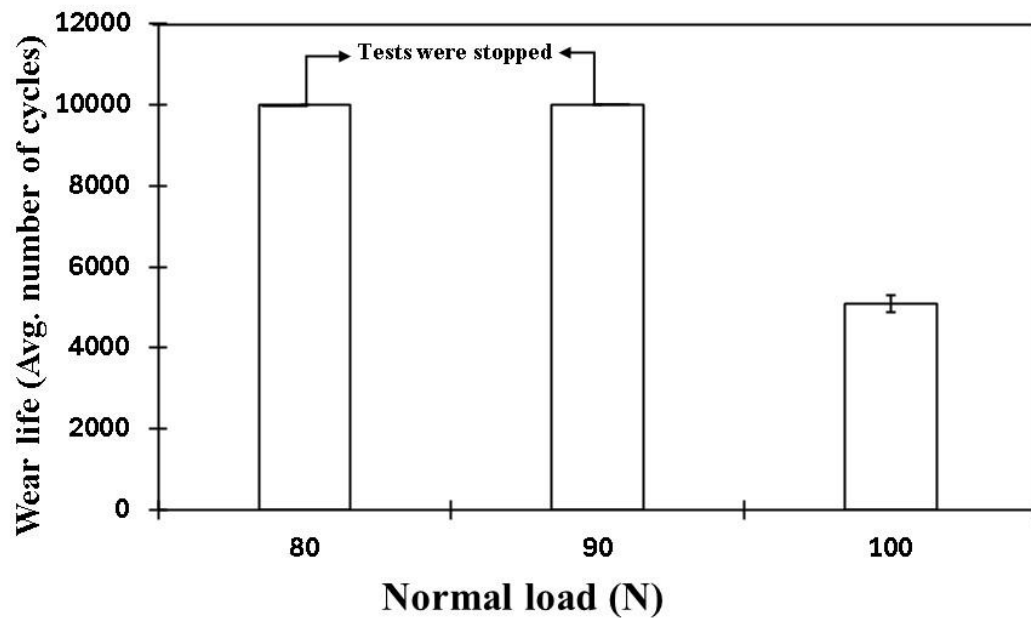


Figure 4.46 Comparative wear life study of PEEK/1.5 wt% Ceria coatings at a sliding velocity of 0.4 m/s for 10,000 cycles at different normal loads

e. Accelerated wear life testing of PEEK/1.5 wt% Ceria

Long-term wear tests were conducted on the optimized PEEK/1.5wt% ceria to determine the tribological properties of the nanocomposite coating. Tests were conducted at a normal load of 90 N and a sliding velocity of 0.4 m/s for 50,000 cycles corresponding to a sliding distance of 1000 m. Figure 4.47 shows the frictional graph showing no coating failure until 50,000 cycles. The SEM images of the wear track confirm that the wear mechanism was adhesive wear with plastic deformation. The EDS scan along with the wear track depth, which was found to be $\sim 48 \mu\text{m}$, confirms that the coating is still intact.

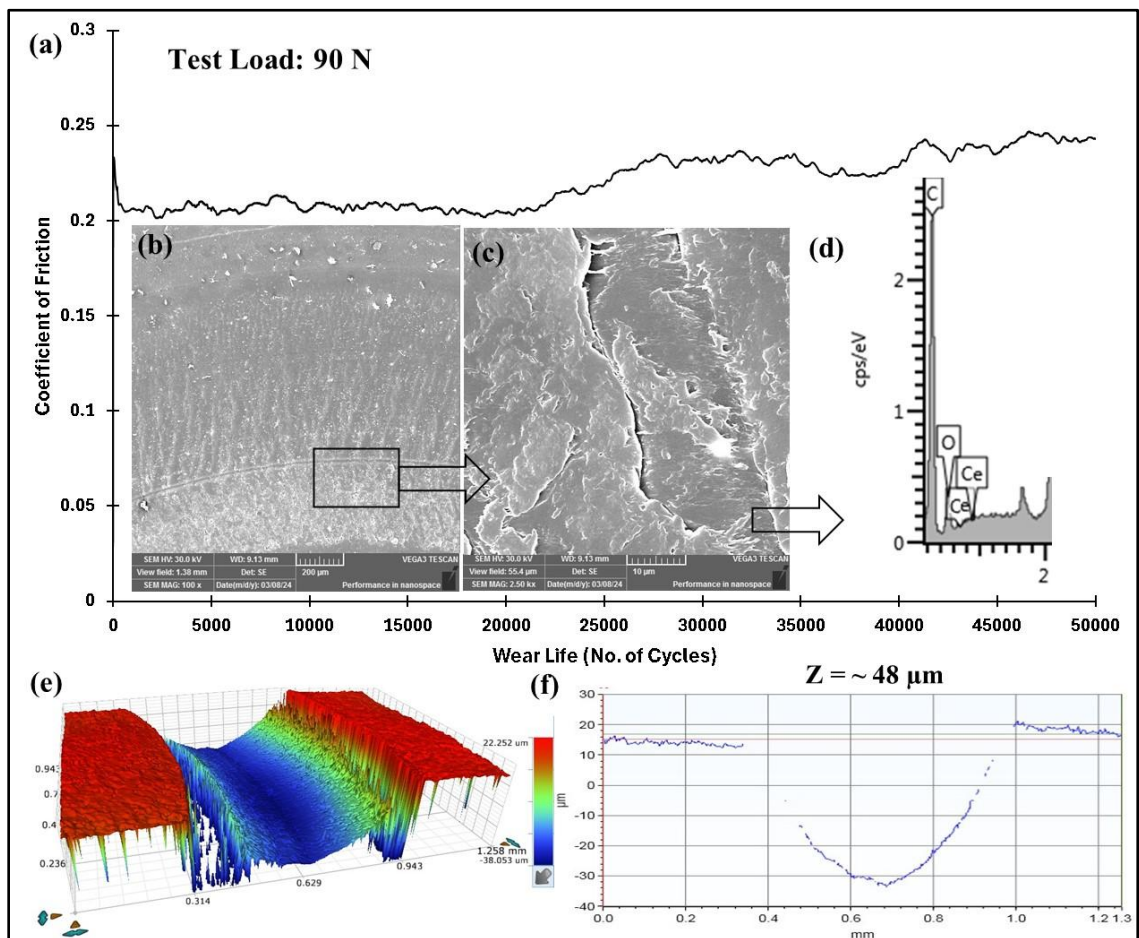


Figure 4.47 PEEK/1.5wt% Ceria coating at a normal load of 90 N presenting (a) frictional graph (b) – (d) SEM images of the wear track along with (e) corresponding EDS scan (f) 3D optical scan of the wear track and (g) 2D optical scan of the wear track for 50,000 cycles

Table 4.3 summarizes the performance of PEEK coatings reported in the literature with various reinforcements compared to the nanocomposite coating developed in the present study. It can be observed that the developed nanocomposite coatings exhibited an improved wear resistance by illustrating a lower specific wear rate value than the previously conducted research. Thomasz et al [44] have deposited $\text{Al}_2\text{O}_3/\text{PEEK}$ composite coatings on titanium alloy by electrophoretic technique. Tribological tests were conducted by a ball-on-disc configuration at a normal load of 5 N and a sliding velocity of 0.07 m/s for 2000 m. The specific wear rate obtained for the composite coatings was $1.9 \times 10^{-6} \text{ mm}^3/\text{Nm}$. Similarly, Thomasz et al [153] have deposited TiN/PEEK composite coatings on titanium alloy by electrophoretic technique and similar tribological tests were conducted by a ball-on-disc configuration at a normal load of 5 N and a sliding velocity of 0.04 m/s for 2000 m. The specific wear rate obtained for the composite coatings was $1.1 \times 10^{-6} \text{ mm}^3/\text{Nm}$. In comparison to the above-mentioned experiments, the developed coatings in the present study were able to sustain loads of 70 N and 90 N corresponding to sliding velocities of 0.5 m/s and 0.4 m/s exhibiting specific wear rate of $2.692 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $2.042 \times 10^{-6} \text{ mm}^3/\text{Nm}$ respectively. An increment in the sliding speed by almost ten times and an increment in the load by a factor of 20 has resulted in only an increase in the specific wear rate by approx. 2 folds. Coatings were subjected to increased mechanical stresses and frictional forces at these higher loads and velocities, which can accelerate the wear. Nevertheless, the developed coatings held up well under these harsh experimental conditions, indicating better material strength, cohesion, and substrate adherence. As a result, the engineered coatings in this study are well-suited for applications that need wear resistance throughout a broad range of loads

and speeds, in contrast to the low load low-speed objective attained by the researchers in the previously described studies.

Table 4.3 Comparison of results obtained in this study to past work

Ref	Filler	Conc. (wt%)	Substrate	Counter-Face	Speed (m/s)	Load (N)	Distance (m)	Wear track radius (mm)	Thickness (μm)	COF	Sp. Wear Rate (10 ⁻⁶ mm ³ /Nm)
[86]	Silicon carbide (SiC)	7	Aluminium	100Cr6 ball	1.4	9	2000	NA	40	0.27	20
[88]	Hexagonal boron nitride (h-BN)	1.5	Low carbon steel	Steel ball	0.1	25	1000	8	200	0.27	20
[153]	Titanium nitride (TiN)	1.3	Titanium Alloy	Alumina ball	0.04	5	2000	3	120	0.3	1.1
[154]	Teflon (PTFE)	3	Stainless Steel	100Cr6 Ball	NA	10	697	3	200	0.133	38
[155]	Silicon dioxide (SiO ₂)	10	Plain C Steel	steel pin	0.13	11	1000	NA	150	0.56	40
[156]	Carbon Fiber (CF)	10	Stainless Steel	Ceramic ball	0.2	7	1512	NA	150-200	0.4	75
[157]	Alumina (Al ₂ O ₃)	1.5	Titanium Alloy	Alumina ball	0.07	5	1000	6	120	0.29	1.9
*	Cerium dioxide (CeO ₂)	1.5	Mild Steel	Alumina ball	0.4	90	1000	3	100	0.22	2.042
					0.5	70				0.201	2.692

*Current Research

4.4.7 Summary

From this phase, it is found that PEEK/1.5 wt% ceria nanocomposite coating (optimized coating) exhibited excellent performance in the wear and resistance to scratch tests. The pristine PEEK coating failed at a normal load of 70 N and a sliding velocity of 0.3 m/s showing a wear life of ~ 7500 cycles. The coating's wear life has been significantly increased by the incorporation of ceria nanofillers; the ideal filler loading was found to be 1.5 wt%, resulting in a wear life of over 50,000 cycles at a normal load of 70 N and a linear speed of 0.5 m/s. Among the tested concentrations, the 1.5 wt% ceria also demonstrated optimal performance recording a wear life of over 50,000 cycles when tested at a load of 90 N having a linear speed of 0.4 m/s. Higher ceria content (3 wt%) led to reduced performance due to possible agglomeration, while 0.5 wt% showed only marginal improvement. The counterface materials had minimal impact on the tribological performance of the PEEK/1.5 wt% ceria nanocomposite coating, indicating that the coating effectively maintained its wear resistance and stability, regardless of the counterface in contact.

4.5 Phase 4 – Optimizing the composition of ceria nanoparticles in the PEEK matrix, which would result in the best scratch resistance behavior of the nanocomposite coatings

From the tribological testings, we concluded that 1.5 wt% ceria nanocomposite coating (optimized coating) did not fail at a normal load of 90 N at 0.4 m/s and at a load of 70 N at 0.5 m/s until 50,000 cycles. To further investigate and better understand the bonding strength and the degree of adhesion between the developed coatings and the substrate, a series of scratch tests were performed on PEEK and PEEK reinforced with different wt% of ceria nanoparticles (0.5, 1.5, and 3 wt%) under a linear increase in load (0-30 N) with time (progressive) at a speed of 5 mm/min along a scratch length of 10 mm. WCA, FTIR, and SEM analysis were used for structural characterization of nanocomposite coatings. Then thickness and dispersion analysis were conducted. Later, evaluation of scratch tests performed on the coatings, coupled with SEM analysis and optical profilometry to study the failure mechanism involved, was carried out.

4.5.1 Change in water contact angles of the developed coatings reinforced with different loadings of ceria

The contact angle formed between a water droplet and the surface provides insights into the balance of adhesive and cohesive forces at play. The contact angle formed between a liquid droplet and the surface provides quantitative information on the surface's hydrophobicity or hydrophilicity [158,159]. A lower contact angle indicates higher surface energy, meaning the surface has stronger interactions with the liquid, which

enhances wettability. Conversely, a high contact angle reflects lower surface free energy, corresponding to more hydrophobic behavior [160].

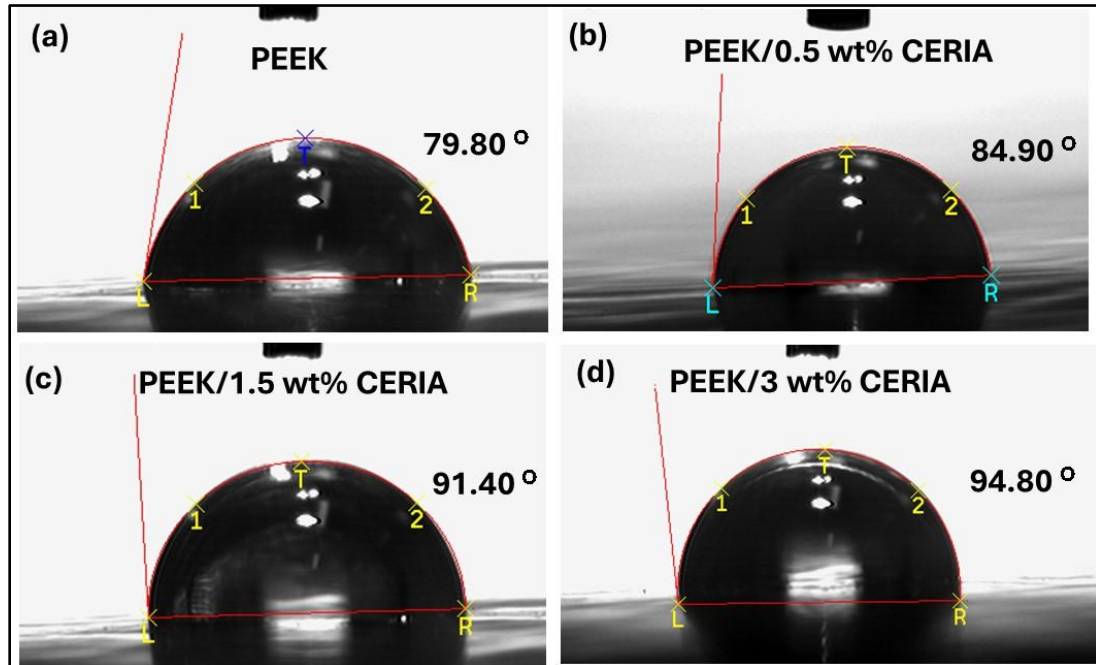


Figure 4.48 WCA measurements of 0, 0.5, 1.5, and 3wt% ceria nanoparticle reinforced PEEK nanocomposite coatings

It can be observed from Figure 4.48 that the addition of ceria has in fact contributed to increasing the hydrophobicity of the coatings. The developed pristine PEEK coating exhibited moderate hydrophobicity with a WCA of 79.80° which was predominantly due to the hydrophobic nature of PEEK [161,162]. As ceria nanoparticles are introduced, the hydrophobic characteristics of ceria start influencing the overall surface properties of the composite coatings [163,164]. The WCA measurements were 84.90° , 91.40° , and 94.80° for 0.5, 1.5 and 3 wt% nanocomposite coatings.

4.5.2 Scratch test results of the developed coatings reinforced with different loadings of ceria

Scratch tests were conducted to evaluate the interfacial bonding strength of coatings, particularly in composite materials like PEEK and ceria nanocomposites. The critical load (L_C) was determined as the point at which the coating has shown signs of failure through delamination, cracking, or complete detachment and could be observed through the variation of the acoustic emission (AE%) graph. For pristine PEEK coating (Figure 4.49), the coating has shown signs of failure at a load of 14 N. The variation in the AE% graph (Figure 4.49a) confirms the point at which the failure of the coating was initiated supported by the EDS scan performed at that particular scratch length. This can be attributed to the fact that PEEK coating does not form a particularly strong interfacial bond with the substrate resulting in its early failure.

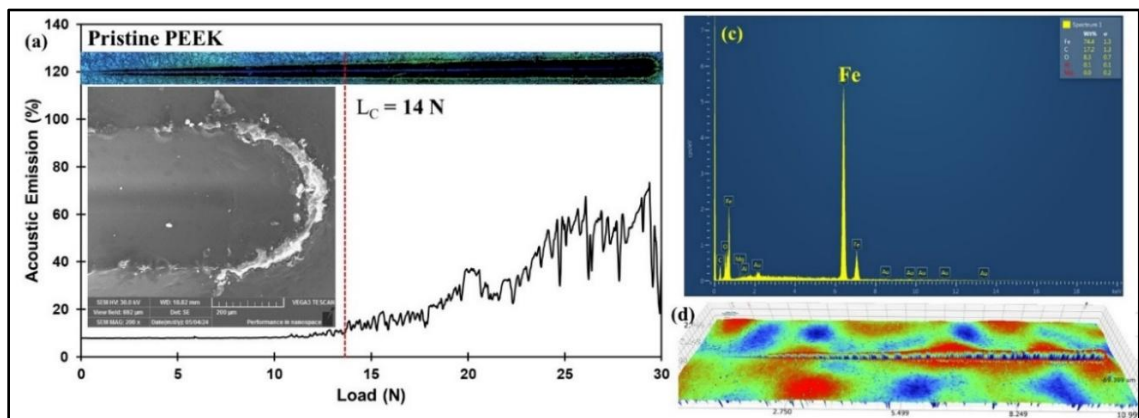


Figure 4.49 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK coating

PEEK reinforced with 0.5 wt% ceria nanocomposite coating demonstrated a noticeable spike in the intensity of the AE% graph (Figure 4.50a) at a load of 18 N illustrating signs of failure. The SEM images confirm the initiation of failure was due to microcracking of

the coatings (Figure 4.50b-c). The addition of ceria nanoparticles improved the performance of the coating. However, this improvement was marginal as the ceria content may have been too low (Figure 4.30) to significantly alter the microstructure or provide sufficient mechanical interlocking at the interface.

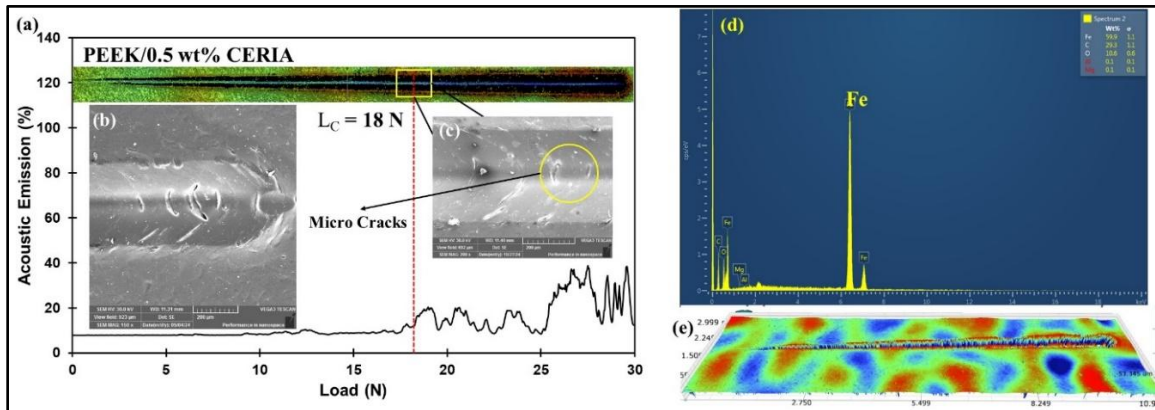


Figure 4.50 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on PEEK/0.5 wt% ceria nanocomposite coating

As can be observed from Figure 4.51, the PEEK/1.5 wt% ceria nanocomposite coating exhibited excellent performance in the scratch test as it didn't fail until a load of 30 N. The AE% graph (Figure 4.51a) illustrated no signs of failure and this was confirmed by the EDS scan (absence of Fe peak). This was possibly due to enhanced interfacial bonding that allowed the coating to resist delamination or cracking providing an efficient bridging effect anchoring the polymer chains resulting in an improved resistance to the coating failure. This exhibits the coating's superior performance and load-bearing capacity.

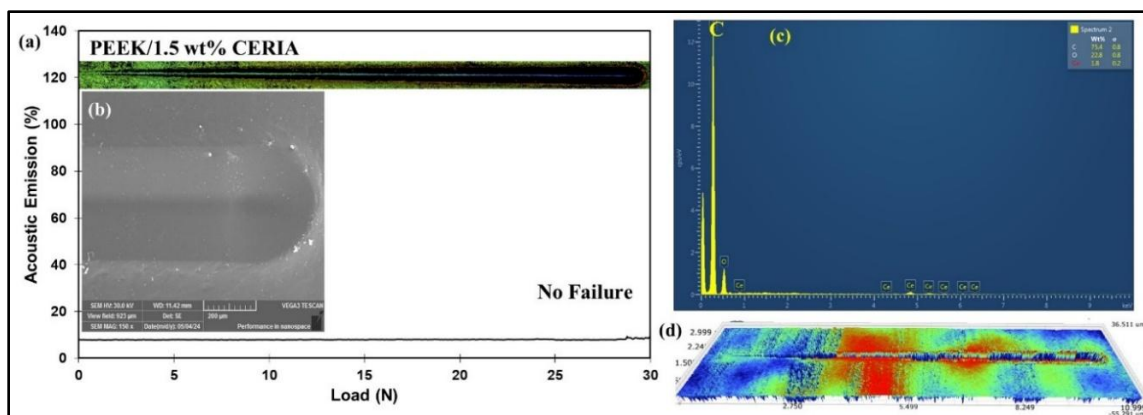


Figure 4.51 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on PEEK/1.5 wt% ceria nanocomposite coating

The failure of PEEK/3 wt% ceria nanocomposite coating at 24 N was confirmed through evidence from both the AE% graph (Figure 4.52a) and EDS scan (Figure 4.52d). The AE% graph showed a significant spike in signal intensity around the 24 N load, indicating noticeable crack initiation as illustrated in the SEM imaging (Fig. 4.52b-c). This suggests a possible agglomeration of the ceria nanoparticles at higher concentrations (Fig. 4.30) that likely reduced the overall load-bearing capacity of the developed coating causing it to fail at a lower load than the 1.5 wt% ceria composition. As a result, it was concluded that PEEK reinforced with 1.5 wt% ceria exhibited the best performance in terms of scratch resistance. Figure 4.53 illustrates the critical loads at which the coatings failed.

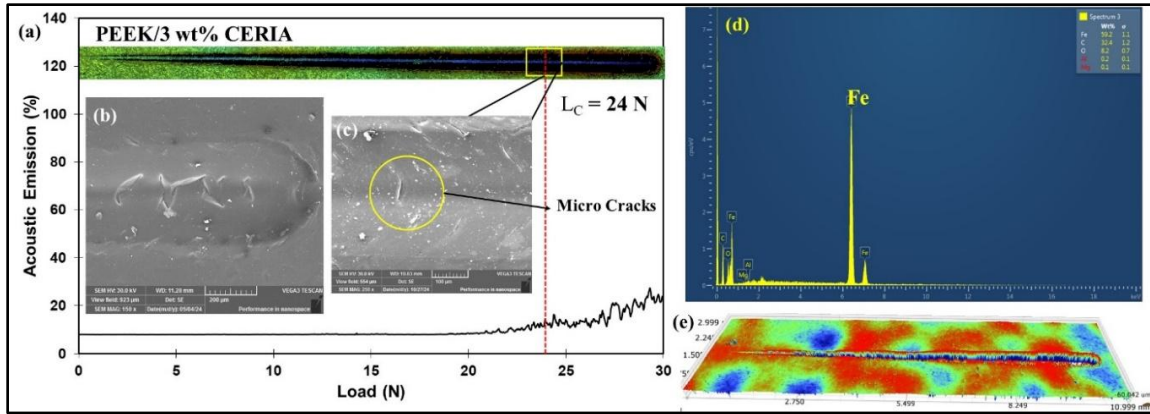


Figure 4.52 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on PEEK/3 wt% ceria nanocomposite coating

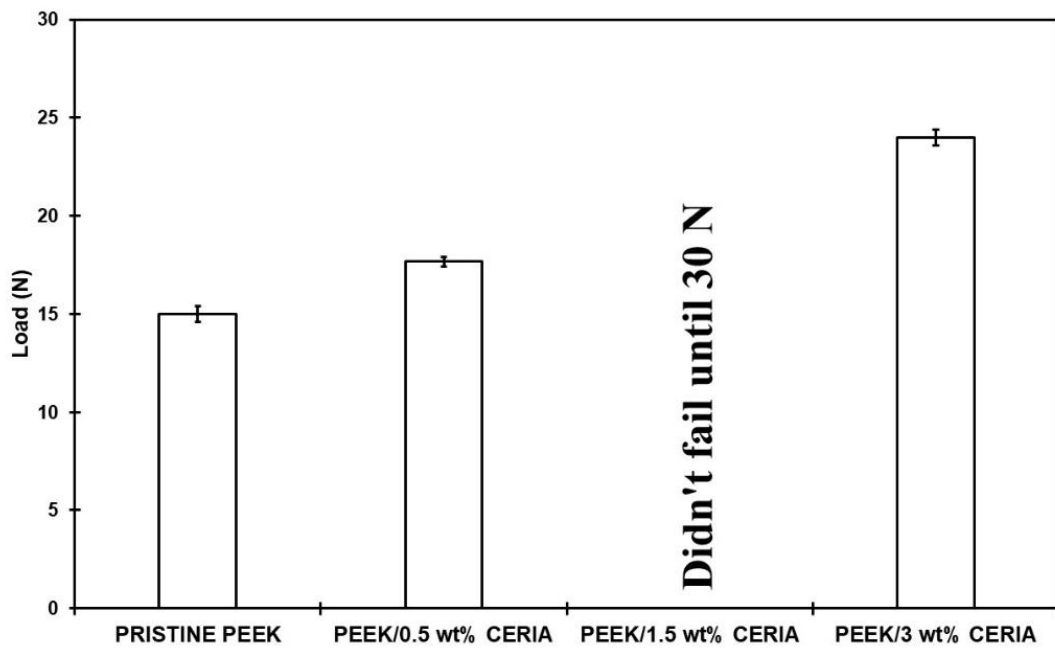


Figure 4.53 Critical loads of failure of the coatings

4.5.3 Summary

From this phase, it is found that PEEK/1.5 wt% ceria nanocomposite coating (optimized) exhibited superior scratch resistance, withstanding up to a load of 30 N without failure,

highlighting enhanced bonding and superior performance compared to other compositions. Higher ceria content (3 wt%) led to reduced performance due to possible agglomeration, while 0.5 wt% showed only marginal improvement. The counterface materials had minimal impact on the tribological performance of the PEEK/1.5 wt% ceria nanocomposite coating, indicating that the coating effectively maintained its wear resistance and stability, regardless of the counterface in contact.

4.6 Phase – 5 Evaluating the effect of counterface material on the wear resistance of the optimized nanocomposite coating from Phase - 3 and Phase - 4

From the results of the tribological and scratch tests, we observed that the PEEK/1.5 wt ceria nanocomposite coating (optimized) showed the best wear resistance and the highest degree of adhesion between the coating and substrate. While the coatings themselves were the primary focus, the interaction between the coatings and different counterface materials is crucial for determining real-world applicability. Counterfaces can affect wear mechanisms, friction coefficients, and the overall durability of the coatings under operational conditions. As a result, to further validate the results, in this study, tribological tests will be performed to evaluate the effect of counterpart on the wear tests by using different counterfaces (Alumina, Tungsten Carbide, Silicon nitride, and 440C Hardened Steel) on the developed coatings.

The tribological performances of PEEK/1.5 wt% ceria nanocomposite coatings were evaluated against different counterface materials: stainless steel (SS), tungsten carbide (WC), silicon nitride (Si_3N_4), and alumina at a normal load of 90 N, 0.4 m/s for 10,000 cycles. The roughness of the surface, coefficient of friction, and wear track depth of each counterface are reported in Table 4.4.

Table 4.4 Measurements of the roughness and water contact angles of the counterfaces

Material	Roughness (Ra/μm)	Coefficient of Friction	Wear track depth (μm)
440C Hardened Steel (SS)	3.141	0.2263	38
Alumina (Al)	3.187	0.2307	34
Tungsten Carbide (WC)	3.241	0.193	28
Silicon Nitride (Si_3N_4)	3.287	0.1693	26

The experimental results showed that the PEEK/1.5 wt% ceria nanocomposite coating exhibited consistent tribological performance across all tested counterface materials, including alumina (Figure 4.44), stainless steel, tungsten carbide, and silicon nitride (Figure 4.54). The wear track depths and overall wear behavior were similar for each counterface tested against the developed coating, indicating that the coating's performance did not have a significant effect on the differences in the counterfaces used. This suggests that the coating effectively mitigated the impact of varying surface interactions, maintaining its integrity and wear resistance regardless of the counterface in use. Its ability to deliver similar results, even under varying conditions, highlights its potential for use in various applications without being sensitive to the specific material it contacts.

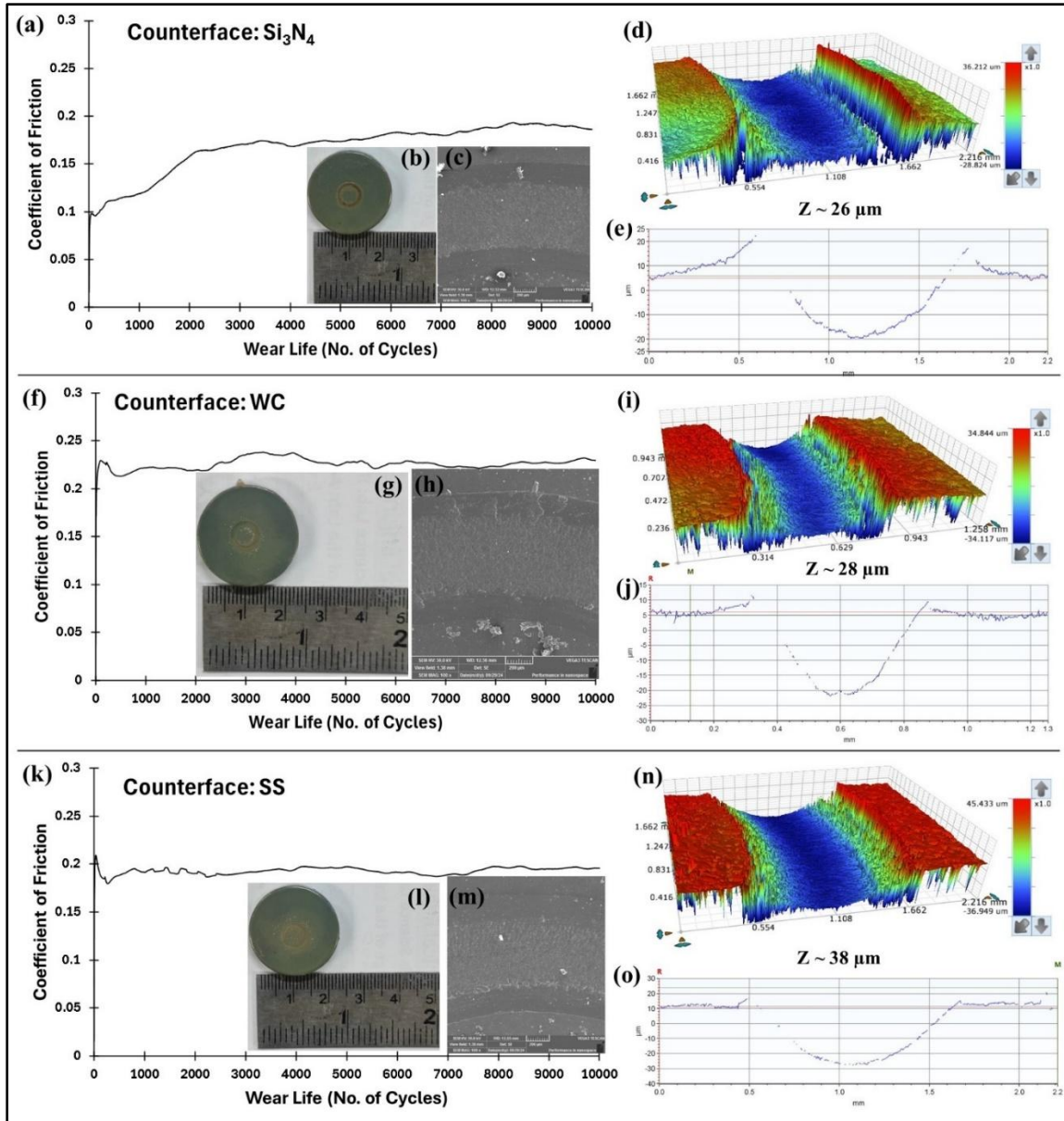


Figure 4.54 Comparison of the (a, f, k) frictional graph of PEEK+1.5 wt% ceria nanocomposite coatings along with (b, g, l) wear track photographs and (c, h, m) SEM images of the wear track with corresponding (d, i, n) 3D wear track depth images and (e, j, o) 2D profile images at normal load of 90 N at 0.4 m/s for 10,000 cycles

4.6.1 Summary

From this phase, it is found that counterface materials had minimal impact on the tribological performance of the PEEK/1.5 wt% ceria nanocomposite coating, indicating that the coating effectively maintained its wear resistance and stability, regardless of the counterface in contact. In conclusion, the developed PEEK/1.5 wt% ceria nanocomposite coating performed consistently well against all tested counterfaces, proving reliable and effective under diverse tribological conditions. This systematic testing strengthens the claim that the coatings performed well and were not overly sensitive to the type of counterface used.

4.7 Phase 6 – Evaluating the effect of UV exposure on the wear and scratch resistance characterization of the optimized nanocomposite coating from Phase-3 and Phase-4

In our findings presented in phase 3 and phase 4, we concluded that PEEK/1.5 wt% ceria nanocomposite coating (optimized coating) did not fail at high load high speed conditions and also performed extremely well in scratch tests. Hence to further explore the compatibility and durability of the developed coating, it was now exposed to UV exposure to determine coatings resistance to UV. Therefore, in this section, the tribological and scratch tests were conducted to evaluate the effect of UV exposure on the wear performance of the developed coatings along with a comprehensive observation on the bonding strength and the degree of adhesion between the coating and the substrate to quantify the extent of UV-induced degradation and its effect on the material's surface properties.

4.7.1 Analysis of the water contact angle measurements on UV exposed samples

Figure 4.55 illustrates the water contact angle measurements of the coatings before and after UV exposure. It can be observed that before UV exposure, the contact angle measurements of the coatings were 80.60° and 89.70° for the PEEK and PEEK/1.5 wt% ceria nanocomposite coatings. However, after 500 hours of UV exposure, the measurements of the coatings were gradually reduced to 28.40° and 43.80° . When exposed to UV light, PEEK undergoes photo-oxidation, a process that introduces polar functional groups onto its surface. These polar groups significantly increase the surface

energy of the material, enhancing its ability to interact with water molecules and thus making it more hydrophilic [165,166]. Ceria nanoparticles, due to their UV-absorbing properties act as a barrier against radiation that limit the formation of polar functional groups [167,168]. As a result, the coatings were found to be more hydrophobic when compared to the PEEK coating after the UV exposure. This suggests that ceria-reinforced coatings offer better long-term performance in environments where UV exposure is a concern, preserving surface properties such as reduced wettability and hydrophobicity.

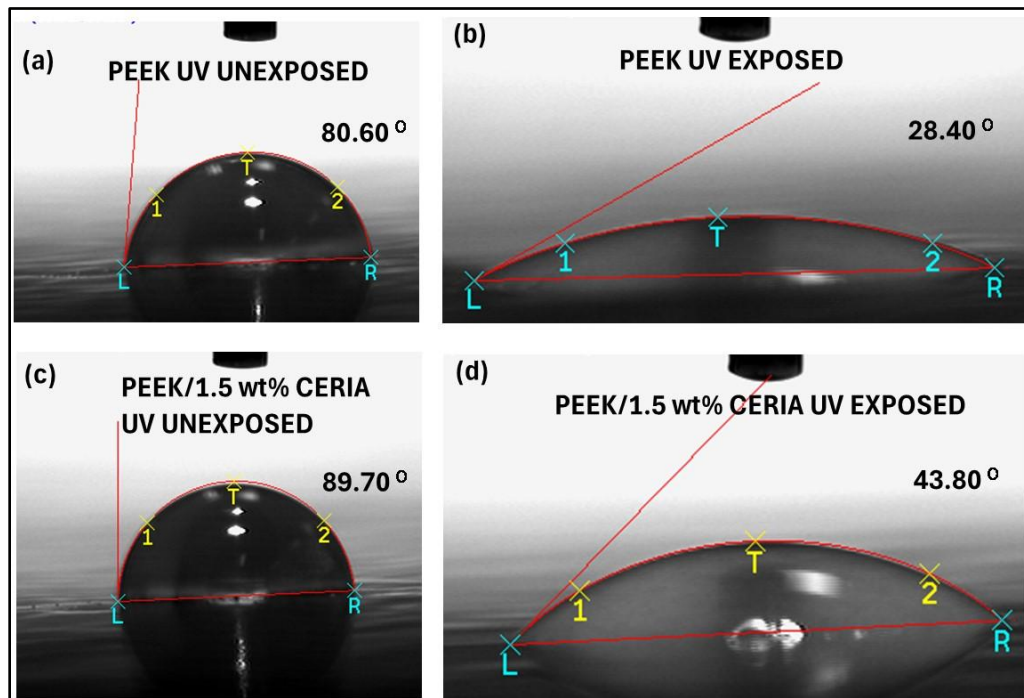


Figure 4.55 WCA measurements of PEEK and PEEK/1.5 wt% ceria nanocomposite coating obtained before and after 500 hours of UV exposure

4.7.2 FTIR analysis of PEEK and optimized PEEK/ceria nanocomposite coatings exposed to UV radiation

The FTIR spectra of the PEEK and PEEK/1.5 wt% ceria nanocomposite coatings exposed to UV radiation showed noticeable changes in the intensity of peaks when compared to their unexposed counterparts (Figure 4.56a&b). In the case of pristine PEEK coatings, after UV exposure (Figure 4.56a), there was a substantial reduction in the intensity of signature peaks of PEEK. This prolonged exposure to UV led to oxidative degradation, resulting in chain scission and the formation of oxidation products [163,164]. The overall intensity decrease reflects the PEEK's susceptibility to UV-induced damage. For the PEEK/1.5 wt% ceria coating (Figure 4.56b), the difference in FTIR spectra before and after UV exposure was noticeable, but the spectra consisted of more intense peaks when compared to the exposed PEEK coating. There was no shift in the characteristic peaks of PEEK as they remained relatively stable with only minor reductions in intensity. This suggests that the ceria nanoparticles prevented the PEEK matrix against UV degradation. The absence of major intensity changes, especially in the key functional groups, indicates that the ceria acted as a UV shield, mitigating the polymer breakdown and reducing the extent of oxidative damage [125,170,171]. Additionally, the signature peak of ceria was observed to be less intense compared to the unexposed coating, reflecting a change in its presence post-UV exposure. The overall stability of the spectra post-UV exposure reflects the enhanced UV resistance provided by the ceria nanoparticles improving the overall integrity of the nanocomposite coatings.

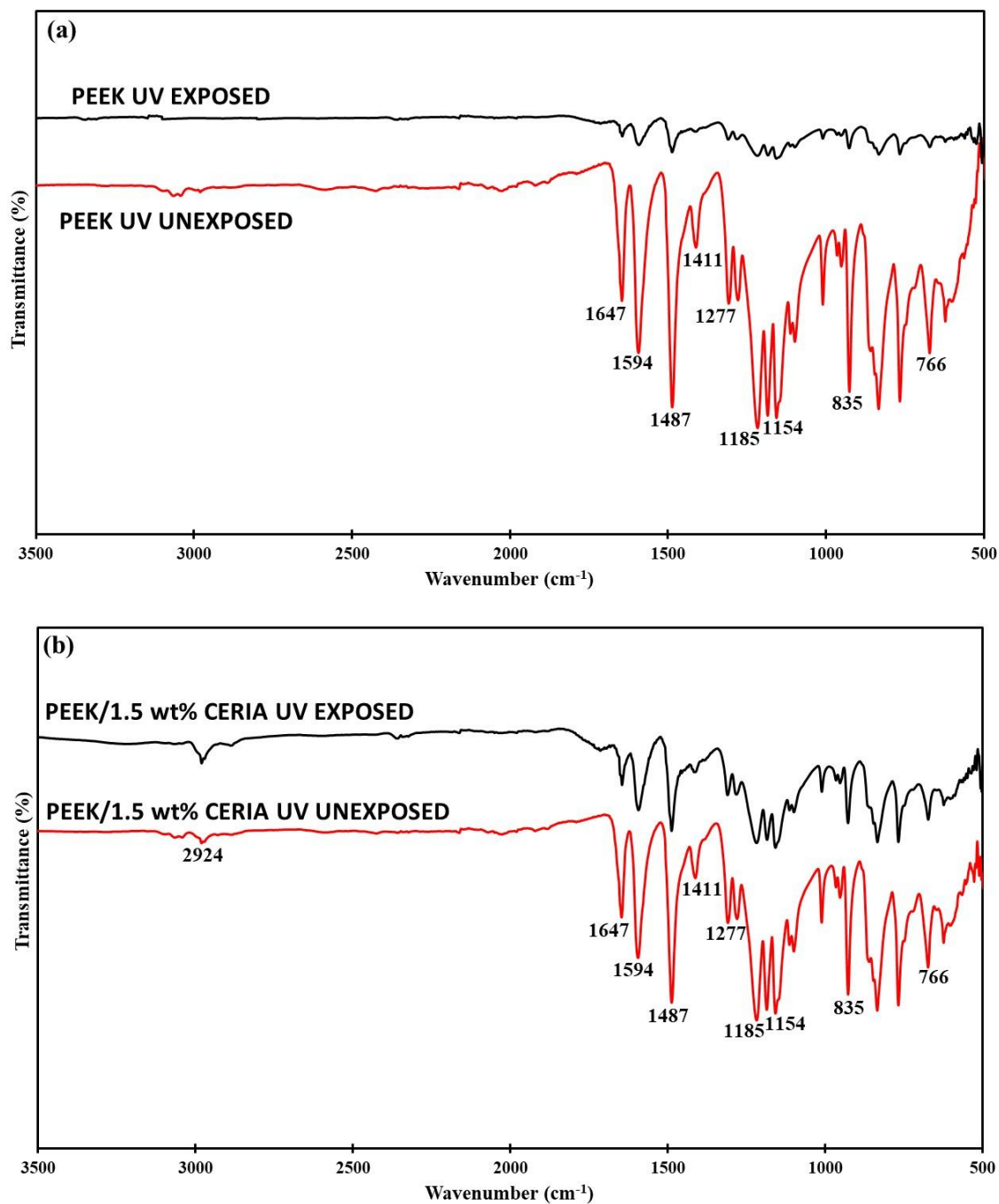


Figure 4.56 FTIR spectra of the UV unexposed and exposed (a) PEEK and (b) PEEK/1.5 wt% ceria coatings

4.7.3 Effect of UV-radiation on the tribological performance of pristine PEEK and PEEK/1.5 wt% ceria nanocomposite coatings

In this tribological study, tests were conducted on both PEEK and PEEK/1.5 wt% ceria composite coatings to evaluate their wear performance under identical conditions, both before and after UV exposure using the QUV Accelerated Weathering Tester (QUV/Spray Gen 4, UK) for about 500 hours. The tribological tests were conducted at a normal load of 50 N, a sliding speed of 0.1 m/s, and 10,000 cycles corresponding to a distance of 189 m. The goal was not to assess the longevity of the samples but to test how well these materials retain their wear resistance and structural integrity after prolonged UV exposure. The coating thickness was maintained at $\sim 100\ \mu\text{m}$ for both the coatings. The results indicated that the pristine PEEK coating exhibited a moderate wear depth (Figure 4.57e) in the unexposed condition ($\sim 17\ \mu\text{m}$). After UV exposure (Figure 4.57k), the wear track depth of the coating was found to have increased significantly ($\sim 50\ \mu\text{m}$).

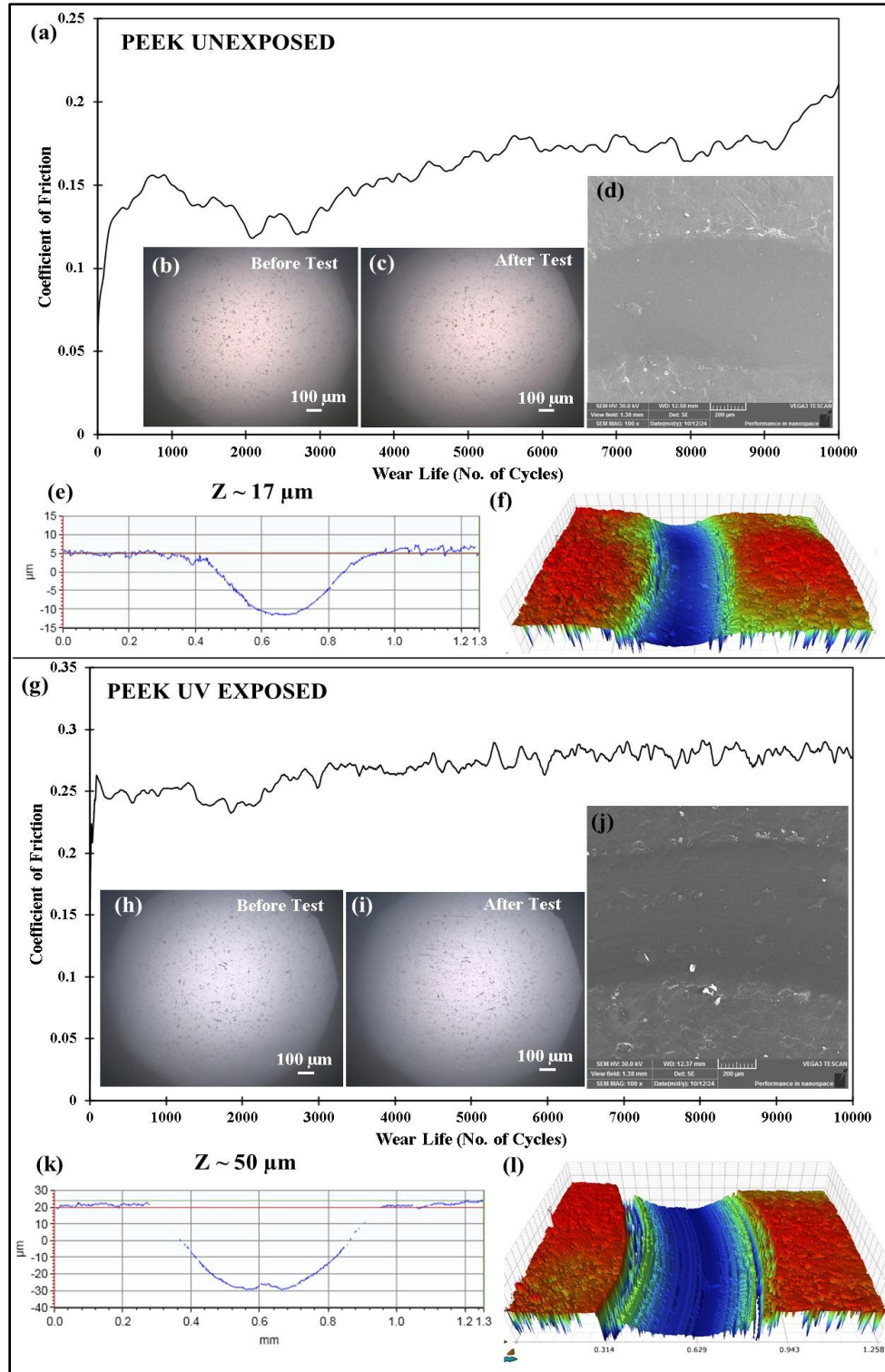


Figure 4.57 Comparison of the (a, g) frictional graph of PEEK coatings along with (b, h) before test ball and (c, i) after test ball images with (d, j) SEM images of the wear track with corresponding (e, k) 2D profile and (f, l) 3D profile wear track depth images at normal load of 50 N at 0.1 m/s for 10,000 cycles

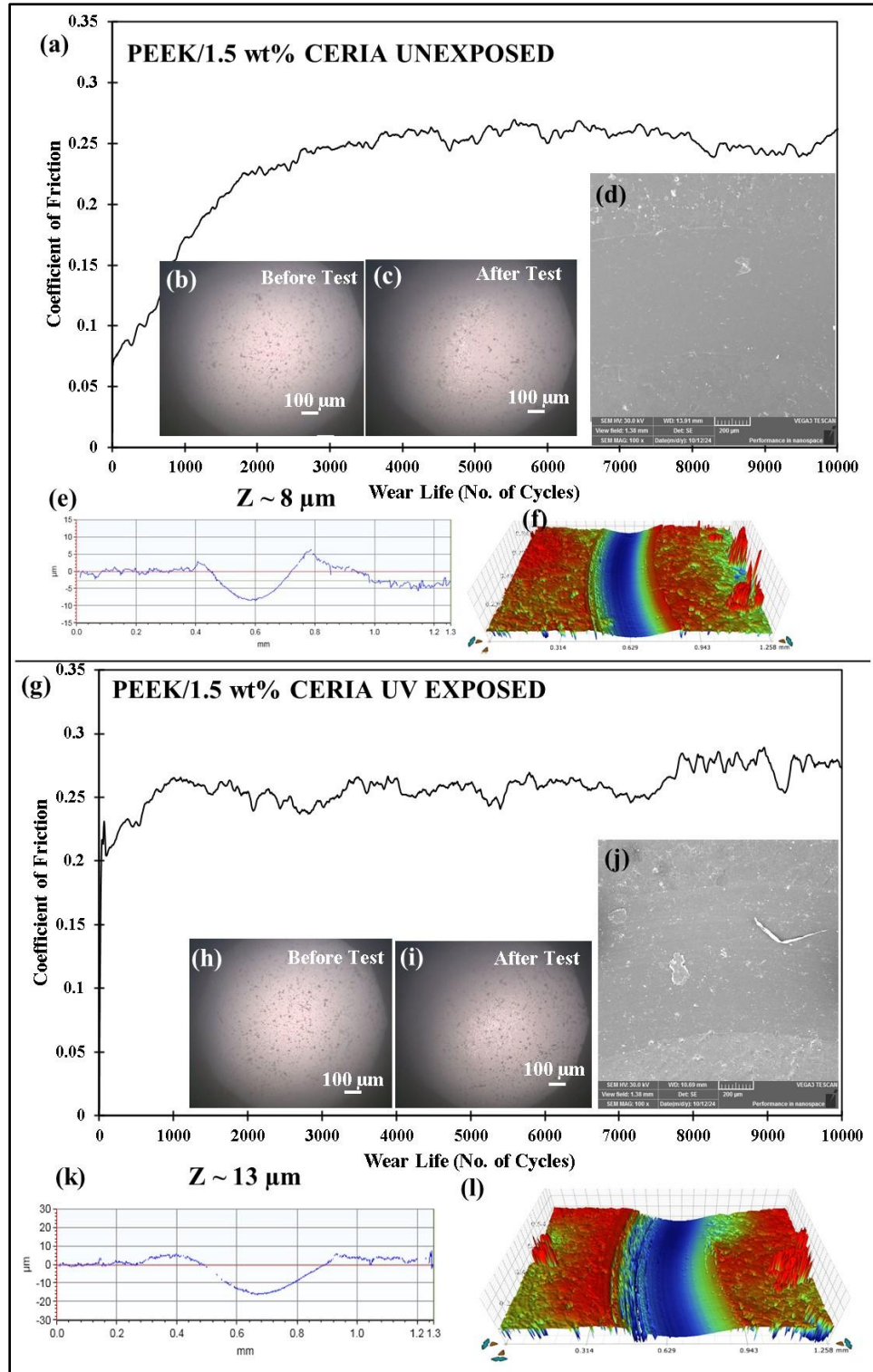


Figure 4.58 Comparison of the (a, g) frictional graph of PEEK/1.5 wt% ceria coatings along with (b, h) before test ball and (c, i) after test ball images with (d, j) SEM images of the wear track with corresponding (e, k) 2D profile and (f, l) 3D profile wear track depth images at normal load of 50 N at 0.1 m/s for 10,000 cycles

This might be due to the possible deterioration of the polymer structure due to photodegradation (Figure 4.56). In contrast, the PEEK/1.5 wt% ceria nanocomposite coatings demonstrated superior wear resistance in both unexposed and UV-exposed conditions, with much lower wear depth compared to pure PEEK. The unexposed nanocomposite coating exhibited a wear depth of only $\sim 8 \mu\text{m}$ (Figure 4.58e) and the UV-exposed coating demonstrated a wear depth of $\sim 13 \mu\text{m}$ only (Figure 4.58k). This was found to be attributed to the reinforcement effect of the ceria nanoparticles, which enhanced the mechanical strength of the coating. Furthermore, the nanocomposite coating maintained its performance even after UV exposure, with only a slight increase in wear depth. As a result, the PEEK/1.5 wt% ceria nanocomposite coating exhibited lower wear depth in both conditions, highlighting the benefits of adding ceria to enhance the durability and UV stability of PEEK.

4.7.4 Effect of UV-radiation on the scratch test results of pristine PEEK and PEEK/1.5 wt% ceria nanocomposite coating

The optimized coating was subjected to UV exposure and subsequently performed the scratch test in order to determine the coatings durability and debonding strength after prolonged UV radiation. The tests were conducted as per the ASTM G154 – 23 standards where the coatings were deposited over carbon steel samples (Ref: Q235) where the thickness of the coatings were maintained at $\sim 100 \pm 5 \mu\text{m}$. It can be observed from Figure 4.59 that the UV unexposed PEEK coating started to exhibit signs of delamination and micro-cracking at around 16 N, where there was noticeable spike in the AE%

intensity (Figure 4.59a). The SEM image (Figure 4.59b-c) and the EDS scan (Figure 4.59d) of the respective region confirms the coatings failure.

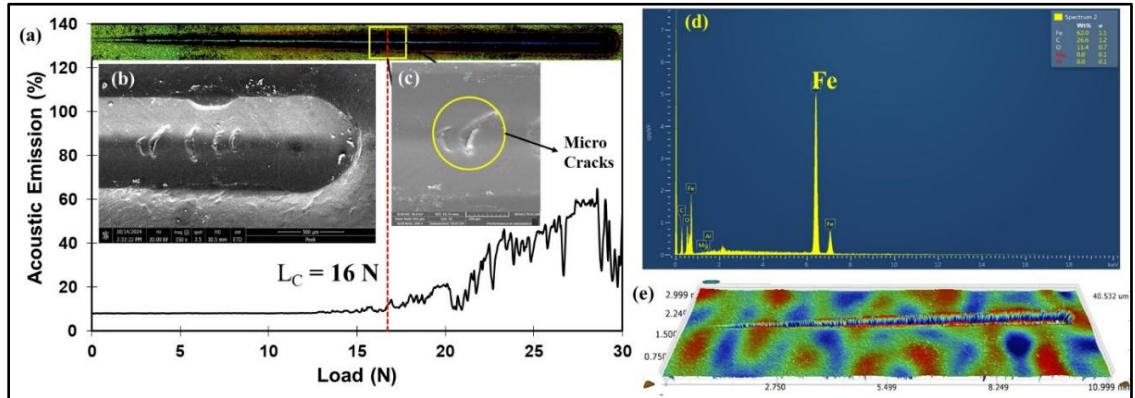


Figure 4.59 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on pristine PEEK coating before exposure to UV radiation

After exposing the PEEK coatings to UV, it was observed that the coating exhibited signs of failure at around 12 N. The AE% data presented in Figure 4.60a supports these observations as it illustrated frequent and intense spikes, indicating continuous cracking and delamination of the coating after the critical load has been reached. These spikes indicate the micro-cracking occurred at a lower load (Figure 4.60c), as the UV exposure led to the oxidative degradation of the polymer chains within PEEK weakening its structural integrity, thereby reducing the coating's resistance to the applied stress.

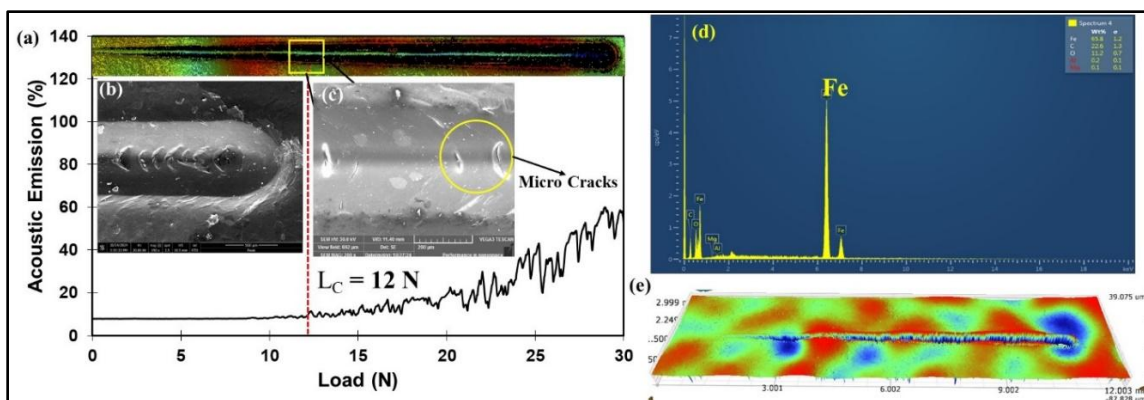


Figure 4.60 (a) Acoustic emission graph with corresponding (b-c) SEM images along with (d) EDS scans and (e) 3D optical image of the scratch conducted on pristine PEEK coating after exposure to UV radiation

On the other hand, PEEK/1.5 wt% ceria nanocomposite coating demonstrated noticeable performance both before and after UV exposure. As shown in Figure 4.61, the coating did not fail even at the maximum applied load of 30 N. This superior load-bearing capacity is primarily attributed to the uniform dispersion of ceria nanoparticles within the PEEK matrix, which enhanced the interfacial bonding strength between the coating and the substrate. The AE% graph in Figure 4.61a supports this observation, as there were no noticeable spikes, indicating that no significant cracking or delamination occurred during the test. Additionally, the EDS analysis confirms this as there were no noticeable peaks of iron (Fe). This further highlights the excellent mechanical stability of the unexposed nanocomposite coating, making it highly resistant to failure under mechanical stress. After UV exposure, the PEEK/1.5 wt% ceria nanocomposite coating continued to perform remarkably well, as seen in the post-UV scratch test results (Figure 4.62). The coating did not fail at the maximum load of 30 N as the ceria nanoparticles played a critical role in absorbing and mitigating the harmful effects of UV radiation, thereby

protecting the PEEK matrix from photodegradation. The AE% graph (Figure 4.62a) illustrated no spike in the peak intensity indicating that the coating withstood the applied load without significant cracking or delamination. This was confirmed by the EDS analysis as shown in Figure 4.62c.

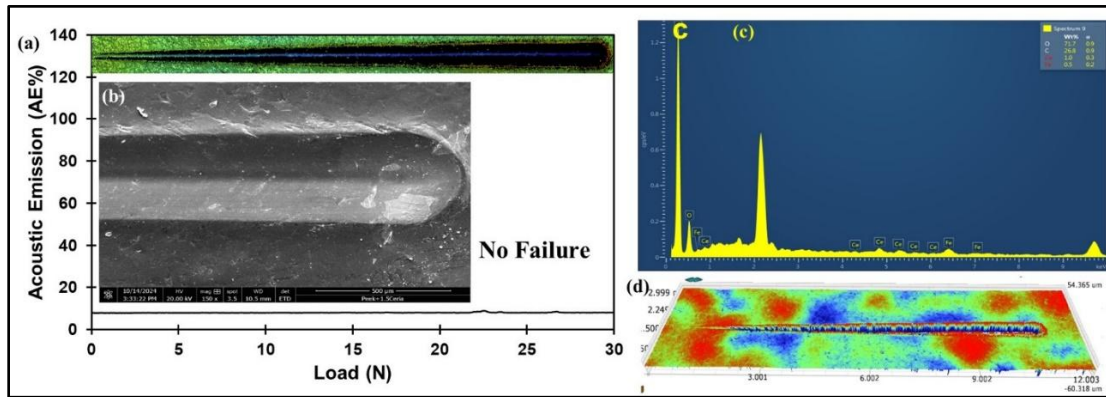


Figure 4.61 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK/1.5 wt% ceria nanocomposite coating before exposure to UV radiation

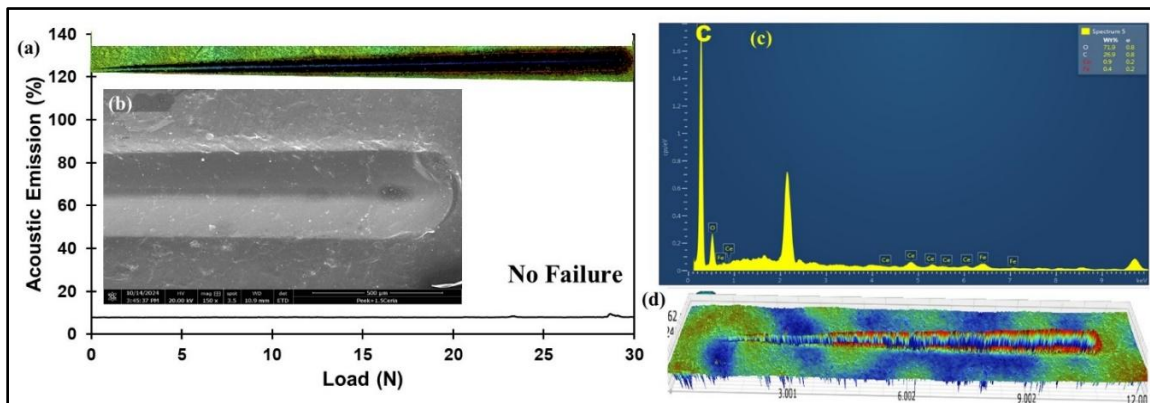


Figure 4.62 (a) Acoustic emission graph with corresponding (b) SEM images along with (c) EDS scans and (d) 3D optical image of the scratch conducted on pristine PEEK/1.5 wt% ceria nanocomposite coating after exposure to UV radiation

4.7.5 Summary

From this phase, it was concluded that UV exposure degrades PEEK's wear performance, while the addition of ceria nanoparticles was found to significantly enhance UV resistance, thereby improving the mechanical properties of the coating. After UV exposure, the PEEK/1.5 wt% ceria coating maintained higher WCA values compared to pristine PEEK, demonstrating better protection against surface degradation. Ceria reinforcement significantly improved UV resistance. After 500 hours of UV exposure, the PEEK/1.5 wt% ceria coating retained much of its mechanical property, while pristine PEEK showed early signs of failure. Both unexposed and UV-exposed PEEK/1.5 wt% ceria coatings showed no significant coating failure, confirming the durability of the nanocomposite under mechanical and UV stresses.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the mechanical, tribological, and resistance to UV exposure performance of pristine PEEK coating was enhanced by reinforcing it with different loadings of ceria nanofiller. Effects of normal load, linear sliding speed, and resistance to scratch tests were evaluated on the developed nanocomposite coatings. The following conclusions can be deduced from this study which are summarized below. The conclusions are presented for each phase of the project:

PHASE 1

The present research systematically examined the effect of various roughness parameters, including the height parameters (R_a , R_q , R_p , R_v , R_z), spatial parameters (N_p) and statistical parameters (R_{sk} , R_{ku}), on the tribological performance of the PEEK coatings deposited on two contrasting samples namely, a polished and a rough sample. The coatings deposited on the rough samples showed exceptional tribological characteristics as compared to the polished samples. Even though the coatings on the samples did not fail at lower loads of 30 and 40 N respectively, the coatings deposited on the rough sample showed a lower wear rate. However, at an increased load of 50 N, the PEEK coating on the polished

sample completely peeled off after ~ 200 cycles, which is attributed to the poor adhesion between the coating and the substrate as compared to the rough sample which sustained for a wear life of 10000 cycles.

Based on a thorough investigation of both surfaces, it was concluded that there was a direct correlation between the surface roughness and adhesion strength of the coating/substrate system, which indirectly determined the tribological performance in terms of wear rate and wear life of the PEEK coatings. PEEK coatings deposited on substrates with higher R_a , R_q , and R_z values exhibited significantly enhanced adhesion, showcasing the importance of meticulous control over these parameters during the surface preparation stage. Notably, the analysis of peak density distribution emerged as one of the other key factors influencing the mechanical interlocking and, consequently, contributing to improved tribological performance of the PEEK coating. Furthermore, the statistical parameters such as skewness and kurtosis of the peak/valley distribution were found to be influential in enhancing the adhesion of the coating/substrate system, which was well reflected in the tribological performance of the PEEK coatings deposited on the rough samples as compared to those deposited on the polished samples. Hence, this study highlights the delicate balance required in selecting and controlling roughness parameters to achieve an optimal equilibrium between mechanical interlocking and reduced friction. The implications of our findings extend to the practical design and application of PEEK coatings in industrial settings, where both adhesion strength and tribological characteristics are pivotal. By understanding and manipulating surface roughness, manufacturers can tailor PEEK-coated components to meet specific performance requirements, leading to increased reliability and longevity in real-world applications.

Our research advances the knowledge base in surface engineering and coatings, offering a foundation for further exploration and development in the realm of PEEK-coated materials.

PHASE 2

From phase 1, we obtained the required surface topography to obtain maximum adhesion between the developed coatings and the substrate. Therefore, in this current study, a comparative evaluation of two dispersion techniques, namely, ball milling and probe sonication to prepare PEEK/1.5 wt% ceria nanocomposite powders for depositing coatings on mild steel substrates. The results underscore the importance of selecting an appropriate method to achieve optimal material properties, particularly for high-performance applications. The observations are as follows:

- The XRD analysis revealed that the PEEK + 1.5 wt% ceria nanocomposite powders prepared via ball milling indicated a lower crystallinity of 66.84%. In contrast, the sonicated powders retained a higher crystallinity of 76.46% which is evident by sharper and more intense XRD peaks. The high-energy ball milling process induced mechanical deformation and introduced defects into the polymer matrix, leading to partial amorphization of the material.
- In both the sonicated and ball-milled powders, the FTIR analysis illustrated that the characteristic peaks of PEEK were consistently observed which confirms the retention of PEEK's molecular structure. However, in the ball-milled powders, the signature peak of ceria (at 2984 cm^{-1}) was noted indicating non-uniform dispersion and

potential agglomeration of ceria nanoparticles. In contrast, this peak was absent in the sonicated powders, suggesting that sonication achieved uniform encapsulation of ceria nanoparticles within the PEEK matrix, preventing agglomeration and leading to a more homogenous distribution.

- The TGA results illustrate that the ball-milled powders had a slower decomposition rate at elevated temperatures compared to both the sonicated and pristine PEEK powders.
- The tribological tests demonstrated that the coatings developed from the sonicated powders exhibited superior wear resistance and load-bearing capacity, successfully exhibiting a wear life of more than 10,000 cycles under a 70 N load without failure. In contrast, the coatings from the ball-milled powders failed much earlier, at around 2,500 cycles.

Overall, the findings indicate that probe sonication could be the preferred method for developing PEEK-ceria nanocomposite powders for coating application when the goal is to achieve superior mechanical and tribological properties. The study highlights the critical role of processing techniques in determining the final properties of nanocomposite materials, emphasizing the need for careful selection based on the specific requirements of the intended application.

PHASE 3

From phase 2, we concluded and obtained the ideal dispersion technique required to obtain the homogenous mixture for developing the nanocomposite coatings. As a result,

this study focuses on a comprehensive investigation into the mechanical and tribological, performances of pristine PEEK and PEEK reinforced with cerium dioxide (Ceria/CeO₂) under varying operating conditions. In our experiments, we incorporated different concentrations of ceria (0.5, 1.5, and 3 wt%) into the PEEK matrix and tested the coatings thereby investigating the effect of ceria reinforcement on wear resistance, wear life, and resistance to scratch performances of the coatings. Hence, the conclusions are summarized as follows:

- The pristine PEEK coating failed at a normal load of 70 N and a sliding velocity of 0.3 m/s showing a wear life of ~ 7500 cycles.
- The coating's wear life has been significantly increased by the incorporation of ceria nanofillers; the ideal filler loading was found to be 1.5 wt%, resulting in a wear life of over 50,000 cycles at a normal load of 70 N and a linear speed of 0.5 m/s.
- Among the tested concentrations, the 1.5 wt% ceria also demonstrated optimal performance recording a wear life of over 50,000 cycles when tested at a load of 90 N having a linear speed of 0.4 m/s.
- Less amount of ceria concentration providing insufficient bridging effect and formation of agglomerations were found to be the leading reasons for the premature failure of the 0.5 and 3 wt% loadings.

PHASE 4

From phase 4, we conducted a comprehensive investigation into the scratch resistance performances of pristine PEEK and PEEK reinforced with cerium dioxide (Ceria/CeO₂) under varying operating conditions. In our experiments, we incorporated different

concentrations of ceria (0.5, 1.5, and 3 wt%) into the PEEK matrix and tested the coatings thereby investigating the effect of ceria reinforcement on the resistance to scratch performances of the coatings. Hence, the conclusions are summarized as follows:

- The PEEK/1.5 wt% ceria nanocomposite coating exhibited superior scratch resistance, withstanding up to a load of 30 N without failure, highlighting enhanced bonding and superior performance compared to other compositions.
- The PEEK/0.5 wt% ceria nanocomposite coating showed only marginal improvement when compared to the pristine PEEK coating which failed at a critical load of 18 N while the pristine PEEK showed signs of failure at 14 N.
- Higher ceria content (3 wt%) failed at a critical load of 24 N which was due to possible agglomeration that led to reduced performance.
- Less amount of ceria concentration providing insufficient bridging effect and formation of agglomerations were found to be the leading reasons for the premature failure of the 0.5 and 3 wt% loadings.

PHASE 5

In this phase, the effect of different counterface materials on the tribological properties of the optimized PEEK/1.5 wt% ceria nanocomposite coatings was studied. The conclusion showed that the counterfaces did not significantly impact the performance of the coatings, as similar wear track depths and observations were noted across all tests. The following conclusions were obtained:

- The counterface materials had minimal impact on the tribological performance of the PEEK/1.5 wt% ceria nanocomposite coating (optimized), indicating that the coating effectively maintained its wear resistance and stability, regardless of the counterface in contact.
- When looking closely, the hardened steel and alumina counterface exhibited the highest wear depth (38 and 34 μm) with Si₃N₄ and WC counterparts illustrating comparatively lower wear track depths (26 and 28 μm).

PHASE 6

In this phase, initially, the experimental study was conducted to determine the resistance to wear and scratch performances of PEEK coating by reinforcing it with ceria nanoparticles. By preparing nanocomposite coatings with different ceria concentrations (0.5, 1.5, and 3 wt%) and subjecting them to tribological and scratch tests, the research evaluated the coating's ability to withstand mechanical stress and UV-induced degradation. As a result, the following were concluded:

- Water contact angle (WCA) measurements indicated that the PEEK/ceria coatings had better hydrophobicity. After UV exposure, the PEEK/1.5 wt% ceria coating maintained higher WCA values compared to pristine PEEK, demonstrating better protection against surface degradation.
- FTIR analysis revealed that ceria reduced the extent of UV-induced chemical changes in the PEEK matrix, minimizing oxidation and polymer chain scission, thereby improving the long-term stability of the nanocomposites.

- After 500 hours of UV exposure, the PEEK/1.5 wt% ceria coating retained much of its mechanical property, while pristine PEEK showed early signs of failure.
- The pristine PEEK coating exhibited a significant increase in the wear track depth before and after UV exposure (17 μm and 50 μm) at a normal load of 50 N and a sliding velocity of 0.1 m/s.
- Ceria reinforcement significantly improved UV resistance. For the PEEK/1.5 wt% ceria nanocomposite coating, there was no substantial increment in the wear track depths of the coating before and after exposure to UV radiation (8 μm and 13 μm) resulting in a wear life of over 10,000 cycles at a normal load of 50 N and a linear speed of 0.1 m/s.
- The PEEK/1.5 wt% ceria nanocomposite coating exhibited superior scratch resistance, withstanding up to a load of 30 N without failure before and after UV exposure, highlighting enhanced bonding and superior performance when compared to the pristine PEEK coating that failed at critical loads of 16 N and 12 N before and after to UV exposure.
- Both unexposed and UV-exposed PEEK/1.5 wt% ceria coatings showed no significant coating failure, confirming the durability of the nanocomposite under mechanical and UV stresses.

5.2 Achievements

From this work, we were able to publish one review paper and submit four Journal Papers which shall add value to the field of surface engineering. Following is the list of published and submitted works.

- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “A Comprehensive Review on the Tribological Evaluation of Polyether ether ketone (PEEK) Pristine and Composite Coatings”, **published in *Polymers (MDPI)***
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “A Comparative Study on the Effect of Roughness Parameters on the Adhesion and Tribological Properties of PEEK Coatings Deposited on Mild Steel Substrates”, **submitted to *Journal of Adhesion Science and Technology***
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Tribological Evaluation of PEEK/Ceria Composite Coatings Prepared from Powders Using Ball Milling and Sonication Methods”, **submitted to *Progress in Organic Coatings***
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Tribological Evaluation of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria – Effect of Composition, Counterface and UV-Exposure”, **final draft prepared and ready to be submitted.**
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Evaluation of Scratch Resistance of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria – Effect of Composition and UV-Exposure”, **final draft prepared and ready to be submitted.**

- Attended **International Tribology Conference (SETCOR) – 2024** to present my work “A Comparative Study on the Effect of Roughness Parameters on the Adhesion and Tribological Properties of PEEK Coatings Deposited on Mild Steel Substrates” from April 17 – 19, 2024 at **Vienne, Austria.**
- **Patent Filed** – “A Methodology To Develop, Wear Resistant And UV Resistant Peek Coatings Reinforced With Ceria Particles”

5.3 Recommendations

The following are some recommendations to increase the scope of work for some other different applications under different environments

1. Developed nanocomposite coating can be tested under different environments
2. The performance of this nanocomposite coating needs to be evaluated under lubricated conditions, most preferably under a liquid medium.
3. Erosion and corrosion prevention by using this coating can be evaluated to expand its application in various fields.

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Conferences and Publications

- Seenath, A. A., Baig, M. M. A., Katiyar, J. K., & Mohammed, A. S. (2024). A Comprehensive Review on the Tribological Evaluation of Polyether Ether Ketone Pristine and Composite Coatings. *Polymers*, 16(21), 2994. <https://doi.org/10.3390/polym16212994>
- Seenath, A. A., & Sarhan, A. a. D. (2024). A State-of-the-Art Review on Cutting Tool Materials and Coatings in Enhancing the Tool Performance in Machining the Superior Nickel-Based Superalloys. *Arabian Journal for Science and Engineering*, 49(8), 10203–10236. <https://doi.org/10.1007/s13369-024-08745-9>
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “A Comparative Study on the Effect of Roughness Parameters on the Adhesion and Tribological Properties of PEEK Coatings Deposited on Mild Steel Substrates”, **submitted to *Journal of Adhesion Science and Technology***
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Tribological Evaluation of PEEK/Ceria Composite Coatings Prepared from Powders Using Ball Milling and Sonication Methods”, **submitted to *Progress in Organic Coatings***

- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Tribological Evaluation of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria – Effect of Composition, Counterface and UV-Exposure”, **final draft prepared and ready to be submitted.**
- Amal A. Seenath, M.M.A. Baig, M. Abdul Samad, “Evaluation of Scratch Resistance of Polyether Ether Ketone (PEEK) Nanocomposite Coatings Reinforced with Ceria – Effect of Composition and UV-Exposure”, **final draft prepared and ready to be submitted.**
- Attended **International Tribology Conference (SETCOR) – 2024** to present my work “A Comparative Study on the Effect of Roughness Parameters on the Adhesion and Tribological Properties of PEEK Coatings Deposited on Mild Steel Substrates” from April 17 – 19, 2024 at **Vienne, Austria.**
- **Patent Filed** – “A Methodology To Develop, Wear Resistant And UV Resistant Peek Coatings Reinforced With Ceria Particles”