

**TRIBOLOGICAL EVALUATION OF HYBRID
NANOCOMPOSITE EPOXY COATING SYSTEM BASED
ON NOVEL FILLERS FOR DEMANDING INDUSTRIAL
APPLICATIONS**

BY

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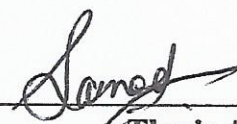
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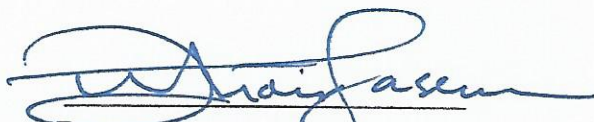
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*Dedicated to my parents and children for their continuous support
and prayers for my success*

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Table of Contents

ACKNOWLEDGEMENTS.....	iv
LIST OF FIGURES.....	x
LIST OF TABLES.....	xvi
LIST OF ABBREVIATIONS.....	xvii
ABSTRACT.....	xviii
ملخص الرسالة.....	xx
CHAPTER 1 INTRODUCTION.....	1
1.1 Background.....	1
1.2 Motivation and justification.....	2
1.2.1 The academic view.....	2
1.2.2 The industrial perspective.....	10
1.2.3 Defining the problem statement.....	11
1.3 Objectives.....	12
1.4 Research Methodology.....	13
1.5 Summary.....	17
CHAPTER 2 LITERATURE REVIEW.....	19
2.1 Introduction.....	19
2.2 Properties of the epoxy matrix.....	20

2.3	Incorporation of nano-fillers to improve the friction and wear properties of epoxy matrices.....	22
2.3.1	Types of commonly used fillers and their properties.....	22
2.3.2	Formulation of hybrid systems.....	29
2.3.3	Dispersion techniques.....	30
2.3.4	Tribology of epoxy bulk composites.....	38
2.3.5	Tribology of epoxy composite coating systems.....	40
2.4	Tribology of epoxy bulk composites.....	40
2.5	Tribology of epoxy composite coating systems.....	43
2.6	Summary.....	47
	CHAPTER 3 EXPERIMENTAL PROCEDURE.....	49
3.1	Introduction.....	49
3.2	Materials.....	49
3.2.1	Liquid epoxy resin system.....	49
3.2.2	Abrasives.....	52
3.2.3	Nano fillers.....	53
3.2.4	Mild steel, grade A36.....	56
3.3	Equipment.....	57
3.3.1	Specimen preparation equipment.....	57
3.3.2	Testing and characterization equipment.....	60
3.4	Sample preparation and characterization techniques.....	67

3.4.1	Samples for evaluation of the effect of various surface treatment techniques on adhesive strength.....	67
3.4.2	Samples for tribological characterization of epoxy nanocomposite coatings.....	71
CHAPTER 4 RESULTS AND DISCUSSIONS.....		77
4.1	Effect of various surface treatment techniques on adhesion strength....	77
4.1.1	Surface cleanliness.....	77
4.1.2	Surface texture, wettability and correlation with adhesive strength.....	82
4.1.3	Effect of plasma treatment on coating adhesion.....	88
4.1.4	Summary.....	91
4.2	Tribological characterization of epoxy-GO nanocomposite coatings.....	92
4.2.1	Effect of load on the tribological characteristics of pristine epoxy coatings.....	92
4.2.2	Effect of GO filler concentration on the tribological characteristics of epoxy-GO nanocomposite coatings.....	96
4.2.3	Summary.....	109
4.3	Tribological characterization of hybrid epoxy nanocomposite coatings...	111
4.3.1	Comparative studies of GO-Titania and GO-Alumina nanofiller loadings on the tribology of hybrid epoxy nanocomposite coatings.....	111
4.3.2	Correlation between coating hardness and wear life.....	121
4.3.3	Summary.....	122

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS.....	124
5.1 Conclusions.....	124
5.2 Recommendations for future work.....	130
REFERENCES.....	132
VITAE.....	138

List of Figures

Figure 1.1	The coating supply chain.....	11
Figure 1.2	The research methodology and organization of thesis.....	15
Figure 2.1	Fillers used to modify liquid epoxy resin systems (15).....	22
Figure 3.1	a) SEM image of GO nanoparticle at 50,000X b) SEM image of GO nanoparticle at 100,000X.....	53
Figure 3.2	a) SEM image of Titania nanoparticle at 50,000X b) SEM image of Titania nanoparticle at 100,000X c) SEM image of Titania nanoparticle showing particle size.....	55
Figure 3.3	a) SEM image of Alumina nanoparticles before sonication at 300,000X b) SEM image of Titania nanoparticle after sonication at 300,000X.....	56
Figure 3.4	Abrasive blasting in progress.....	58
Figure 3.5	Harrick air plasma cleaner, PDC-001.....	59
Figure 3.6	VCA optima contact angle tester.....	61
Figure 3.7	Pull-off adhesion test in accordance with ASTM D-4541.....	63
Figure 3.8	Quanta FEG 250 scanning electron microscope with EDS detector	64
Figure 3.9	Rigaku MiniFlex II desktop X-ray diffractometer.....	65
Figure 3.10	Bruker UMT TriboLab.....	66
Figure 3.11	Optical profilometer scans of ground and polished mild steel substrates.....	67

Figure 3.12	Lab fabricated spin coating and coating schedule adopted.....	72
Figure 4.1	a) Appearance of non-textured mild steel substrate b) Appearance of substrate textured using Olivine (OL 080) abrasive with SSPC SP 5 finish c) Appearance of substrate textured using Calcium Silicate (CS 085 abrasive) with SSPC SP 5 finish.....	79
Figure 4.2	a) and c) SEM image and corresponding EDS scan of mild steel substrate textured using Calcium Silicate (CS 085) b) and d) SEM image and corresponding EDS scan of mild steel substrate textured using Olivine (OL 080).....	82
Figure 4.3	Effect of surface texturing using Calcium Silicate (CS 085) and Olivine (OL 080) abrasives on the adhesive strength of high build coatings applied onto mild steel substrates.....	84
Figure 4.4	a) Topography of mild steel surface textured using Calcium Silicate (CS 085) b) Topography of mild steel surface textured using Olivine (OL 080).....	85
Figure 4.5	a) Apparent water contact angle measured on mild steel surface textured using Calcium Silicate (CS 085) b) Apparent water contact angle measured on mild steel surface textured using Olivine (OL 080).....	86
Figure 4.6	Variation of water contact angle (θ_y) with surface index.....	87

Figure 4.7	a) Variation in adhesive strength of the coating applied onto non-textured, non-plasma treated and non-textured, plasma treated substrates b) FTIR spectrum of non-textured, non-plasma treated mild steel c) FTIR spectrum of non-textured, plasma treated mild steel.....	89
Figure 4.8	Pristine epoxy coating tested at 35N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with corresponding EDS scan.....	93
Figure 4.9	Pristine epoxy coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with corresponding EDS scan.....	95
Figure 4.10	SEM image of wear track at high magnification (1500X) after tribological testing of pristine epoxy coating at 50N load.....	96
Figure 4.11	Effect of GO filler concentration on the wear life epoxy nanocomposite tested using a steel ball counterface at 50N normal load.....	97

Figure 4.12	Epoxy+0.5 wt.% GO nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan.....	100
Figure 4.13	SEM images showing a) Tribolayers b) Miniature waves due to fatigue wear mode c) Magnified image of wave like features.....	103
Figure 4.14	XRD spectrum of GO nanoparticles.....	104
Figure 4.15	XRD spectrum of Epoxy+0.5 wt.% GO nanocomposite coating.....	105
Figure 4.16	Epoxy+1.5 wt.% GO nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan.....	107
Figure 4.17	Low magnification SEM image (50X) of the wear track showing adhesive failure of the Epoxy+1.5 wt.% GO nanocomposite coating tested at 50N.....	108
Figure 4.18	XRD spectrum of Epoxy+1.5 wt.% GO nanocomposite coating...	109
Figure 4.19	Comparative wear life of hybrid nanocomposites.....	112
Figure 4.20	Epoxy + 0.5 wt.% GO + 5 wt.% Titania hybrid nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph	113

	b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan.....	
Figure 4.21	Epoxy+ 0.5 wt.% GO+ 5 wt.% Titania hybrid nanocomposite coating tested at 50N normal load presenting a) Low magnification (50X) SEM image of the wear track b) Angular shaped agglomerates.....	114
Figure 4.22	XRD spectrum of Epoxy+0.5 wt.% GO+5 wt.% Titania nanocomposite coating.....	115
Figure 4.23	Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing d) Ball image after acetone cleaning e) and f) SEM image of the wear track along with EDS scan.....	116
Figure 4.24	Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating tested at 50N normal load presenting a) Low magnification (50X) SEM image of the wear track with complete delamination of the coating from the center of the test zone b) Large agglomerates...	117
Figure 4.25	XRD spectrum of Epoxy+0.5 wt.% GO+5 wt.% Alumina nanocomposite coating.....	118

Figure 4.26	Initial and modified approaches adopted in preparation of GO-alumina hybrid nanocomposite powder.....	119
Figure 4.27	Effect of increased ultra-sonication time on wear life of Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating and comparison with other coatings produced using initial approach	120
Figure 4.28	Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating (produced using a modified approach) tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing d) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth.....	121
Figure 4.29	Comparison of hardness values of coatings.....	122

List of Tables

Table 1.1	Summary of works carried out on epoxy titania bulk and composite coatings.....	5
Table 2.1	Properties of base and solidifier components used in epoxy formulation (15).....	21
Table 2.2	Fillers used to modify epoxy systems and properties both inherent and imparted to the matrix (15).....	26
Table 2.3	Summary of various dispersion techniques used to uniformly disperse the nano-fillers in epoxy matrix (15).....	31
Table 2.4	Different types of coating techniques and pre-treatment methods used by researchers (15).....	42
Table 2.5	Partial summary of wear life and friction coefficient results.....	44
Table 2.6	Relative wear rates and friction co-efficient ratings from the pin-on-disk test (15).....	46
Table 3.1	Properties of Belzona [®] 1341.....	50
Table 3.2	Properties of Belzona [®] 4151.....	51
Table 3.3	Properties of Olivine abrasive.....	52
Table 3.4	Properties of Calcium Silicate abrasive.....	52
Table 3.5	Abrasive blasting parameters and environmental conditions.....	68
Table 3.6	Experimental matrix for tribological testing.....	76
Table 5.1	Summary of findings from phases 2 and 3 of this research.....	129

List of Abbreviations

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
CoF	Coefficient of friction
DGEBA	Diglycidylether of bisphenol A
DGEBF	Diglycidylether of bisphenol F
EDS	Energy dispersive X-ray spectroscopy
FPEK	Fluorinated poly (aryl ether ketone)
GO	Graphene-oxide
m	Meters
mL	Milli-liters
N	Newton
PTFE	Polytetrafluoroethylene
SEM	Scanning electron microscope
UV	Ultra-violet
Wt.	Weight
XRD	X-ray diffraction
θ_m	Measured contact angle
θ_y	Young's contact angle

ABSTRACT

Full Name	Bobby Satheesan
Thesis Title	Tribological evaluation of hybrid nanocomposite epoxy coating system based on novel fillers for demanding industrial applications
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Epoxies in the form of bulk and coatings have been used throughout the years for a wide spectrum of applications in industries. The success of any coating project lies in the quality of surface preparation achieved. Though a large variety of abrasives are available in the industry, coal slag (aluminium silicate) and garnet (mineral abrasive) have remained popular choices until now owing to their easy availability. However, depleting reserves of coal slag owing to stricter environmental regulations and shortage of good quality garnet have fueled the need to identify substitutes. While abrasive blasting is the most popular method for texturing of substrates prior to coating application, the present economic climate has forced huge coating manufacturers to invest a lot of time and effort into developing surface tolerant coatings.

The first phase of this research work began with the evaluation of the effect of texturing mild steel substrates using two novel abrasives namely, olivine (obtained from dunite rock) and calcium silicate (iron furnace slag) using a combination of techniques namely optical profilometry, replica tape method as per ASTM D-4417 (Method C) (height parameter) and scanning electron microscopy (secondary electron imaging/energy

dispersive X-ray spectroscopy analyses) for embedded particle composition analysis. Correlations were drawn to the wettability of metallic substrates textured using the selected abrasives. Adhesive strength tests were then performed in accordance with ASTM D-4541. The results of the various tests prove that both olivine and calcium silicate abrasives promise to be excellent alternatives to coal slag and garnet. Since elimination of abrasive blasting would be the preferred scenario, the effect of air plasma treatment on the adhesive strength of a high build epoxy coating system was also evaluated. A significant improvement in adhesive strength of the selected high-build epoxy coating system applied onto nontextured, plasma treated substrates was observed.

Following an in-depth literature review, it was understood that the application of epoxies in demanding tribological applications is often limited by the properties of the pristine epoxy matrix such as low load bearing capacity under severe p - v regimes combined with low thermal conductivity values. In this study, the load bearing capacity of the pristine epoxy coating system applied onto nontextured, plasma treated mild steel substrates was first evaluated under dry sliding conditions. Graphene oxide (GO) fillers in varying concentrations were then added to the pristine epoxy matrix to produce nanocomposite epoxy coatings. In the final phase of this study, titania and alumina fillers were added to the epoxy-GO nanocomposite to produce hybrid nanocomposite epoxy coatings. Tribological tests revealed that the addition of GO nanoparticles at 0.5 wt.% filler loading led to a significant improvement in wear life. Wear life analysis of hybrid nanocomposites showed that titania-GO based hybrids produced much better results when compared to alumina-GO based results.

ملخص الرسالة

الاسم الكامل : يوبي ساتيسان

عنوان الأطروحة : التقييم التريبولوجي لنظام الطلاء بالايوكسي الهجين غير المكون من مركبات من خلال نظام الحشوات الجديد في التطبيقات الصناعية

المجال الرئيسي : علوم وهندسة المواد

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استخدمت الايوكسيات السائبة والتي على شكل طلاء على مر السنين في مجال واسع من الاستخدامات في مختلف الصناعات. وإن نجاح أي مشروع طلاء أو تغليف بهذه المواد يكمن في جودة السطح المستخدمة عليه وجودة إعداده من أجل تطبيق هذه المواد عليه. وبالرغم من توفر العديد من المواد الكاشطة في الصناعة، إلا أن خبث الفحم (سيليكات الألمنيوم) والغارنيت (مادة كاشطة معدنية) بقيت الخيار الأكثر شيوعاً لغاية الآن بفضل سهولة توفرهم. ولكن قلة احتياطات خبث الفحم بسبب الأنظمة البيئية الصارمة والنقص في الغارنيت عالي الجودة قد ولدت الحاجة إلى إيجاد البدائل المناسبة. وبما أن الكشط بالرش الرملي هو الطريقة الأكثر شيوعاً لإعداد السطوح قبل تطبيق الطلاء، إلا أن المناخ الاقتصادي الحالي قد دفع عدد كبير من مصنعي مواد الطلاء لاستثمار وقتهم وجهدهم في تطوير أنواع طلاء الأسطح عالية التحمل والاستمرارية.

بدأت المرحلة الأولى من هذا البحث بتقييم أثر السطوح المعدنية باستخدام نوعين من المواد الكاشطة وهم بالتحديد مادة الأوليفين (التي تستخرج من صخر الدونيت) وسيليكات الكالسيوم (خبث الحديد) باستعمال مجموعة من التقنيات وبالتحديد التحليل الضوئي وطريقة الرغوة حسب المواصفة الأمريكية رقم د-4417 (الطريقة ج) (معطيات الارتفاع) وطريقة التصوير بالإلكترونات (التصوير الثانوي بالإلكترونات / التحاليل بالتصوير بالأشعة السينية) من أجل تحليل المكونات الجزيئية غير الظاهرة. تم ربط التماسك بقابلية السطوح المعدنية الداخلية للتبلل باستخدام مواد كاشطة محددة. ومن ثم تم إجراء اختبارات قوة المواد اللاصقة وفقاً للمواصفة الأمريكية د-4541. أثبتت نتائج مختلف

الاختبارات أن الكاشطات من الأوليفين وسيليكات الكالسيوم توعد بأنها بدائل ممتازة لخبث الفحم والغارنيت. وبما أن إزالة الرش الكاشط ستكون السيناريو المفضل، إلا أنه تم تقييم أثر المعالجة ببلازما الهواء على القوة اللاصقة لنظام الطلاء بالايوكسي. هناك تحسن مهم في قوة المادة اللاصقة من نظام الطلاء الذي تم اختياره المستخدم على السطوح غير النسيجية وتمت ملاحظة السطوح الداخلية المعالجة بالبلازما.

وبعد مراجعة عملية معمقة، تبين أن استخدام الايوكسيات في التطبيقات التريبولوجية يكون غالبا محدودا بخواص مجموعة الايوكسيات الأصلية مثل القدرة على التحمل في الحمل المنخفض تحت أنظمة $p-v$ الشديدة مجتمعة مع قيم الناقلية الحرارية المنخفضة. في هذه الدراسة، تم تقييم قدرة تحمل الحمل لنظام الطلاء بالايوكسي المطبق على السطوح غير النسيجية والسطوح المعدنية المعالجة بالبلازما وذلك تحت شروط التزليق الجاف. ومن قم تمت إضافة حشوات أكسيد الغرافين بعدة تركيزات على مجموعة الايوكسيات الأصلية لإنتاج طلاء ايوكسي غير مكون من مركبات. وفي المرحلة الأخيرة من هذه الدراسة، تمت إضافة حشوات من التايتانيا والألومينا إلى أكسيد غرافين لإنتاج طلاء ايوكسي هجين غير مكون من مركبات. وقد كشفت الاختبارات التريبولوجية أن حالة جزيئات أكسيد الغرافين عند الحشوة ذات الرطوبة 0.5 % قد أدت إلى تحسن مهم في عمر التآكل. تحليل عمر تآكل المادة الهجينة بين أن هجينات أكسيد غرافين التايتانيا قد ولدت نتائج أفضل بكثير بالمقارنة مع النتائج الناتجة عن أكسيد غرافين الألومينا.

CHAPTER 1

INTRODUCTION

1.1 Background

Since their inception, epoxy-based systems in bulk and coating forms have been used for the repair and protection of pressure vessels, flow handling equipment, heat exchangers, buildings, chemical containment areas, ships and off-shore structures owing to their excellent chemical and corrosion resistance properties. However, their use in tribo-environments involving high contact pressures (bearings, bio-medical implants etc. for instance) is limited by the low load bearing ability and poor thermal stability of the pristine epoxy matrix (1,2). Researchers over the years have invested a huge amount of time and effort in improving the tribological properties of the pristine epoxy matrix through reinforcement with micron and nano-sized fillers (3–7). These fillers, added either as stand-alone or hybrids and based on ceramics (1,8,9), carbon compounds (6,10,11), metals (12), polymers (13) and/or mineral silicates (14) impart desirable properties ranging from improved wear and impact resistance, lower frictional coefficient, hydrophobicity, ultra-violet resistance and thermal conductivity to the pristine epoxy matrix (15) and thereby help enhance the corrosion and wear resistance of neat epoxy matrices. While a lot of work has been carried out on epoxy-based systems, a closer look at present scientific

literature reveals that the major share of work has been confined to bulk epoxy composites with limited developments in the coatings' arena. A variety of filler combinations and their influence on the tribo-system are yet to be studied. Additionally, several discussions on tribological performance of coatings haven't been correlated with the morphology of the fillers used, thickness of the applied coating system or properties of the substrate-coating interface (15).

1.2 Motivation and justification

This research work has wide areas of application in both the academia and the industry. To begin with, problem statements were created further to a comprehensive review of published works in the scientific domain and based on inputs received from major coating manufacturers namely Belzona Polymerics Ltd, Harrogate, United Kingdom and Hempel Paints, Dammam, Saudi Arabia.

1.2.1 The academic view

From an academic perspective, the role of nano-sized graphene oxide, titania and alumina fillers or their hybrids in enhancing the tribological properties of epoxy composite coating systems are extremely limited. Our literature review reveals that almost no works involve high-build coating systems – coating systems that are categorized as 100% solids and applied at a high dry film thickness of greater than 300 microns in a single-coat without sagging. Moreover, combinations of the aforementioned fillers as hybrid reinforcements haven't been evaluated in any of the works. The lack of data on the properties of the

substrate itself, the substrate-coating interface properties, coating thicknesses, coating methods used to minimize the role of extraneous variables or correlation of tribological properties with the morphology of the fillers are voids in the current scientific domain that this research intends to fill. As noted by Friedrich et al. (16) in their works, homogenous dispersion of the nano-particles is a determining factor in obtaining the desired properties. A major factor hindering uniform dispersion of the nanoparticles in the matrix is their tendency to agglomerate which can act subsequently act as stress raisers within the bulk or coating matrix. Hence the dispersion technique being adopted is quite crucial to obtaining the desired properties from the selected fillers (1,8). The following sections will focus on the role played by titania and Graphene-Oxide fillers which led us to select these as the reinforcements for our epoxy matrix.

1.2.1.1 Graphene-Oxide as reinforcement

Traditionally produced using the Hummer's method or its modifications (17,18), graphene and graphene oxide are known to possess exceptional properties such as high fracture toughness, mechanical properties exemplified by the high values of Young's Modulus of 1 TPa and 130 GPa Tensile Strength, high thermal and electrical conductivities (19–21). Graphene oxide as a reinforcement is known to improve the glass transition temperature of the epoxy polymer and this makes it particularly useful while formulating higher temperature resistant coating and composite systems.

1.2.1.2 TiO₂ (Titania) as reinforcement

Zhang et al. (22) have shown through iterative trials that a combination of epoxy + 15 vol. % graphite + 5 vol. % nano-TiO₂ + 15 vol. % short-CF exhibits a specific wear rate of $3.2 \times 10^{-7} \text{ mm}^3/\text{N-m}$, which is about 100 times lower when compared to neat epoxy. In a separate study by Chang et al. (2), it was recognized that a complex mechanism existed for wear of short carbon fiber (SCF) based composites which include a multi-step process consisting of matrix wear and fiber thinning followed by the breaking of the fiber which leads to interfacial de-bonding and eventual peeling off of the fiber from the matrix. However, the addition of nano-TiO₂ particles combined with the effect of lubricant film forming PTFE and graphite fillers resulted in extremely high wear resistance under large *p-v* conditions demonstrated by a pin on disk test conducted in accordance with ASTM D3702. Nano TiO₂ particles in particular were found to play an important role by reducing the shear stresses at the interface of the mating interfaces owing primarily to their spherical morphology causing them to behave as roller bearings. Titania fillers have also been shown to improve wear and impact resistance of the base matrix when added as a reinforcement (22,23). It has also been shown through an extensive review by Pinto et al. (8) that TiO₂ fillers have resulted in improvement of fracture toughness values and enhancement of coating pull-off strengths from the substrate making it extremely attractive as an industrial coating filler. To conclude, works by Noori et al. (24) have proven that for the same conditions and filler loading, nano sized TiO₂ particles impart a higher degree of wear resistance to the epoxy matrix when compared to micro sized TiO₂

fillers. Table 1.1 presents a detailed summary of works carried out on epoxy-titania bulk composites and composite coatings.

Table 1.1 Summary of works carried out on epoxy titania bulk and composite coatings

Ref.	Year	Form	Filler	Main Topic	Important Findings
(24)	2013	Bulk	Nano-TiO ₂ , Micro-TiO ₂	Tribological characterization Type: Composite Pin on Steel Disk Load: 10N - 20N Sliding velocity: 0.06 - 0.12 m/s	Addition of 5 wt. % nano titania was found to produce the least wear rate. The wear rate was found to be increasing with load. In general, nano titania based epoxy composites exhibited better tribological characteristics when compared with micro titania composites.
(2)	2006	Bulk	Nano-TiO ₂	Tribological characterization Test method: Composite Pin on Steel Disk	Titania nanoparticles at 5 vol. %, 10 vol. % filler loadings act as third body particles and their spherical morphology produces a rolling effect thereby reducing the contact

Ref.	Year	Form	Filler	Main Topic	Important Findings
					temperature and the frictional coefficient.
(25)	2012	Bulk	Nano-TiO ₂	Tribological characterization Test method: Composite Pin on Steel Disk Load: 40N Rotational speed: 200 rpm	Titania nanoparticles at 5 wt. % filler loading produced the least wear rate. The wear mechanism was cited to include nucleation and development of cracks perpendicular to the sliding direction followed by the manifestation of a wave-like appearance culminating in production of wear debris. The addition of titania nanoparticles were postulated to hinder the development of cracks.

Ref.	Year	Form	Filler	Main Topic	Important Findings
(26)	2016	Coating	Nano-TiO ₂	Corrosion resistance	The addition of titania nanoparticles helped improve the corrosion resistance
(27)	2013	Bulk	Micro-TiO ₂	Mechanical performance	A filler loading of 20 wt. % titania resulted in significant increase in ultimate tensile strength and flexural strength. It was thought that the addition of micro titania would have helped the stresses to be transferred smoothly from the matrix to the filler. A strong interfacial adhesion between the matrix and the filler was cited to be important in this regard.

Ref.	Year	Form	Filler	Main Topic	Important Findings
(28)	2015	Coating	TiO ₂ Nano Tubes	Mechanical performance, Thermal Stability and Corrosion Resistance	Coatings were produced using conventional spray technique. Nano titania nanotubes were found to provide much better levels of adhesion strength (ASTM D4541) and impact strength (owing to excellent levels of dispersion achieved through ultrasonication and mechanical mixing), corrosion resistance due to the lamellar structure, thermal stability and mechanical performance as compared to micro titania modified epoxy composite coatings and significantly better results than the pristine matrix.

1.2.1.3 TiO₂ (Titania)-Graphene Oxide (TGO) hybrid as reinforcement

Works by Kumar (20) have shown that the TiO₂ (Titania)-Graphene Oxide (TGO) hybrid can be easily dispersed within the epoxy matrix and significantly improves the corrosion resistance characteristics of the pristine epoxy matrix. However, a significant gap exists in scientific research using the TGO hybrid as a filler to improve the tribological characteristics of the epoxy matrix. This served as a motivation to address this knowledge gap and hopefully open doors to more in-depth research in this field in addition to enhancing the scientific knowledge base.

1.2.1.4 Alumina (Al₂O₃) as reinforcement

The role of nano-sized, whisker and spherical shaped alumina fillers in enhancing the mechanical properties of epoxy matrices has been well studied (29). In their work, Johnsen et al. (29) observed that even at low filler loadings, and in spite of particle agglomeration, the mechanical properties of alumina modified epoxy matrices were found to have significantly improved. The glass transition temperature of the epoxy bulk composite across a range of filler loadings however remained unchanged. Similar observations were also made by Kozako et al. (30) in their work. While extensive research works on the effect of nanosized alumina fillers on the mechanical and electrical properties of alumina are available in literature, their role in a tribological environment haven't been as well documented. Subhash (31) showed that hybrid epoxy nanocomposites modified using alumina fillers led to a marked improvement of wear resistance under impact loading conditions. Tribological characterization of graphene oxide-alumina nanocomposite

epoxy coatings present an area of scientific domain where much research remains to be carried out.

1.2.2 The industrial perspective

A close look at the coating supply-chain presented in Figure 1.1 shows that abrasive blasting is a major component of any coating project. To begin with, inputs have been sought from Sibelco N.V., a corporation head quartered in Antwerp, Belgium and involved in mining, processing and world-wide distribution of surface preparation abrasives, on the present industrial outlook on surface preparation. As per Sibelco N.V., contractors and end users are facing project schedule overruns owing to fast depleting reserves of commonly used abrasives namely, coal-slag and garnet. Climate change concerns and a major shift towards renewable energy sources are fast depleting the available reserves of coal slag. Simultaneously, sourcing good quality garnet is becoming a major challenge by the day. The product specification sheets of at-least five different manufacturers reveal that all high-build coatings require application to be carried out onto substrates textured using angular abrasives to produce a surface roughness of 75 microns (height parameter of surface roughness only) and cleanliness level equal to ISO 8501-1, Sa 2½ (near-white metal finish). From an industrial perspective, surface texturing via abrasive blasting is a process riddled with health and safety risks as well as quality, cost and time constraints. The present economic climate, risk assessments involving community impact of accidents or incidents and increasingly stringent health and safety requirements of major corporations and asset owners have forced huge coating

manufacturers to invest a lot of time and effort into developing surface tolerant coatings – coatings that can be applied onto manually prepared surfaces. In this research work, nanocomposite epoxy coatings have been applied onto non-textured substrates. To add another dimension to this work, the role of plasma treatment and its influence on coating interface properties namely, the alteration of surface free energy characteristics, which in turn has been proven to improve adhesion, has also been evaluated.

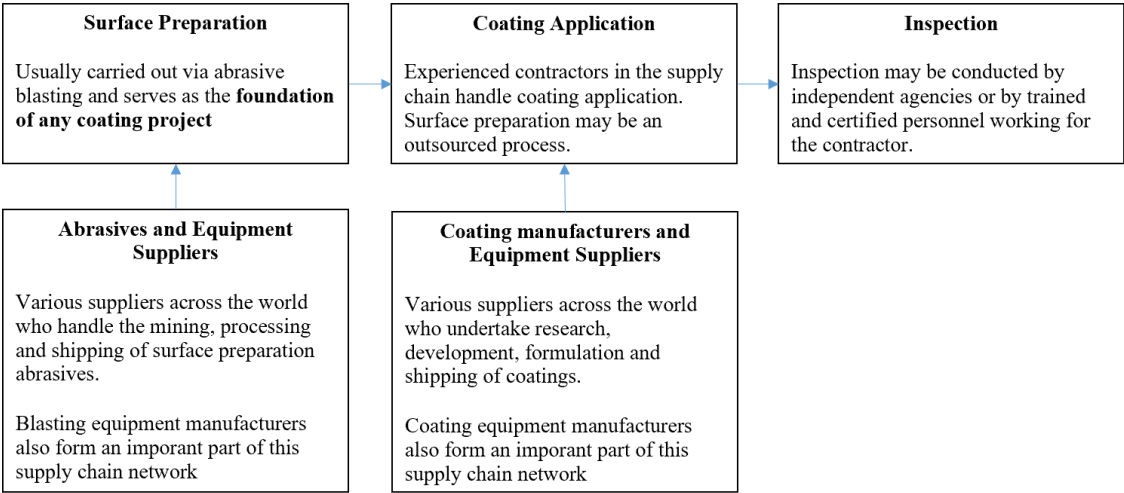


Figure 1.1 The coating supply chain

1.2.3 Defining the problem statement

This research work begins with an evaluation of various surface preparation techniques using novel abrasives namely Olivine and Calcium Silicate to address the present industrial need of finding suitable replacements for Coal Slag and Garnet. From here, the possibility of employment of air plasma treatment as an alternative to abrasive blasting is evaluated. It is believed that this study would help effect a possible paradigm shift higher up the coating supply chain in future while serving as a good starting point for researchers

in academia working with high build epoxy coating systems. The second half of this work deals with addressing the identified gaps in the academic arena with regard to tribology of hybrid nanocomposite epoxy coatings for demanding industrial applications.

1.3 Objectives

The objectives of this research work have been derived directly from the need to address the gaps in the academic and scientific domains. This research therefore seeks to address the following:

1. Carry out an extensive literature review on tribology of epoxy bulk composites and composite coatings to identify significant gaps in scientific research work.
2. Identify novel abrasives for surface preparation and determine the factors influencing the adhesion of high build epoxy coatings on textured mild-steel (A36) substrates.
3. Evaluate the effect of air plasma treatment on the adhesive strength of high build pristine epoxy coating on non-textured mild-steel (A36) substrates.
4. Determine the optimum concentration and best dispersion method of nano-sized graphene oxide filler to reinforce the pristine epoxy matrix.
5. Determine the optimum concentration and the best dispersion method of graphene oxide-titania fillers to formulate the hybrid epoxy nanocomposite system.
6. Determine the optimum concentration and the best dispersion method of graphene oxide-alumina oxide fillers to formulate the hybrid epoxy nanocomposite system.

7. Apply the formulated coatings onto non-textured mild-steel (A36) substrates using spin technique and evaluate their effect on the tribological properties.

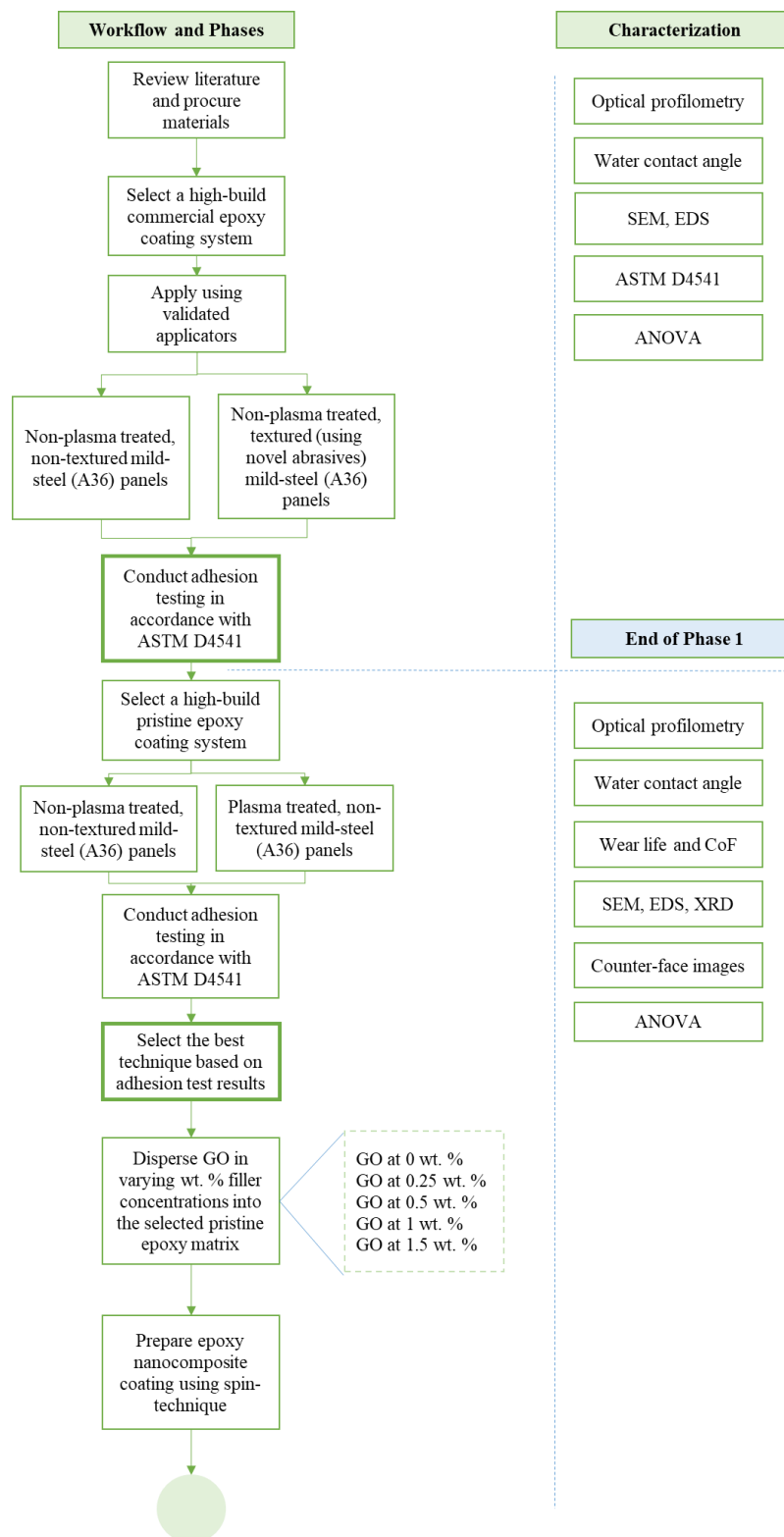
Fulfilment of the above objectives will result in the following:

- Address a pressing industrial problem of selecting the best alternative to conventional abrasives (coal slag and garnet), sources of which are now rapidly depleting owing to various reasons.
- Present to the industry, the possibility of considering air-plasma treatment as an alternate surface preparation technique for application of coatings onto non-textured or low surface energy substrates.
- Fill an important gap in the area of scientific research on tribology of hybrid epoxy nanocomposite coatings using graphene oxide, titania and alumina fillers on non-textured mild-steel (A36) substrates.
- Open doors to new research in the field of surface preparation and tribology of epoxy composite coating systems.
- Publications in the form of scientific journals, book chapters and conference papers.

1.4 Research methodology

This research work is intended to be undertaken in three distinct phases. Each phase has a clear milestone that must be crossed for the project to proceed to the next phase. The flow-chart presented in Figure 1.2 lays down the methodology and characterization techniques

that would be adopted to achieve the objectives of the proposed research. Milestones at the end of each phase have been clearly identified using bold outlines for clarity:



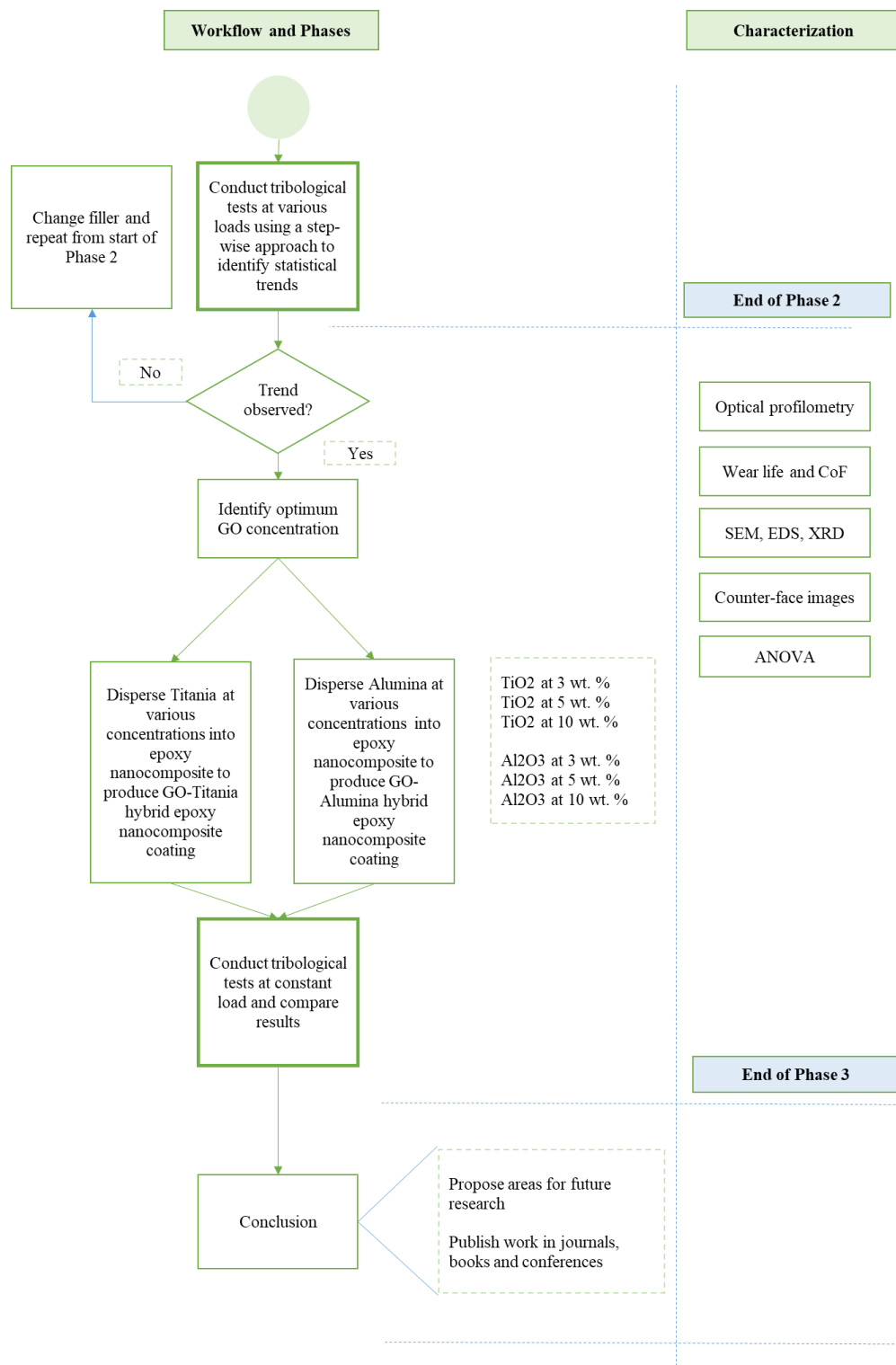


Figure 1.2 The research methodology and organization of thesis

1.5 Summary

This research work is intended to be undertaken in three distinct phases to address the gaps identified through discussions with industrial partners and based on review of scientific literature.

Phase 1

- In this phase, novel abrasives such as Olivine and Calcium Silicate will be evaluated for their effectiveness and as an alternative to commonly used Coal Slag and Garnet abrasives, thereby addressing an immediate industrial requirement.

Phase 2

- In this phase, the effect of air plasma treatment on adhesion of pristine high-build epoxy coatings on mild steel substrates will be investigated.
- This will be followed by the identification of the load bearing capacity of the selected pristine epoxy coating under dry sliding conditions.
- Further to this, epoxy-GO nanocomposite coatings will be prepared and tested at the failure load of the pristine epoxy coating. The effect of addition of GO nanofillers on the wear life of the formulated epoxy composite coatings will be investigated and the optimum GO filler concentration will be identified.
- A detailed analysis of the dispersion characteristics and wear morphology will be conducted.

Phase 3

- In this phase, Titania and Alumina fillers will be added to the pristine epoxy matrix in varying concentrations while keeping the GO filler concentration constant to produce hybrid nanocomposite epoxy coatings.
- Tribological tests will then be conducted at the failure load of the epoxy-GO nanocomposite coating and findings will be reported.
- A detailed analysis of the dispersion characteristics and wear morphology will be conducted.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Epoxy formulations are primarily classified into bulk composites and composite coating systems. Composite coating systems are generally recommended by specifying engineers of various organizations for applications demanding protection from a range of corrosive media while bulk composites find their use in load bearing applications such as in repair of machine components and airport runways. Though epoxy coating systems are known to be specified for certain applications involving heavy loads (as in a heavy traffic environment) and in fluid handling systems (where entrained solids in the fluid media cause severe abrasive wear), their use in various other demanding tribological environments - between sliding components of machines for instance - are known to be limited and this is often attributed to the property of the pristine epoxy matrix such as a low load bearing ability combined with poor thermal stability under severe p - v regimes. Researchers in both academia and industry have tried to enhance the tribological properties of the pristine epoxy matrix using a combination of several types of micro/nano sized fillers to produce hybrid nanocomposites. This review chapter focuses on the properties of the epoxy matrix, the types and properties of nano-fillers that have been

commonly used to develop epoxy bulk composites and epoxy composite coatings, dispersion techniques adopted, the effects each of these fillers (and their combinations) on the tribological properties of the system and most importantly, significant gaps existing in the current research domain highlighting the areas where future research works in the field of liquid epoxy coating may be directed towards.

2.2 Properties of the epoxy matrix

Epoxies can be classified into various types depending on the reactants used in their formulation. Durig (32) notes in his paper on waste water treatment that there are primarily three types of epoxy resins namely bisphenol-A, bisphenol-F and novolac. All three are produced by reactions between epichlorohydrin and phenolic compounds. While bisphenol A is produced by the reaction between phenol and acetone, bisphenol F is produced by the reaction between phenol and formaldehyde. Both bisphenol A and bisphenol F produced by the above reactions are then reacted with epichlorohydrin to produce diglycidylether of bisphenol-A (DGEBA) and diglycidylether of bisphenol-F (DGEBF) respectively. Novolac epoxy resins are modifications of bisphenol-F resins produced by reacting excess phenol and formaldehyde. It is important to note that in addition to the base resins used, the solidifier components, which are primary, secondary or tertiary amine compounds, also play a very important role in determining the properties of the cured system. The properties of base and solidifier components, typically used in the formulation of epoxies are summarized in Table 2.1 (15).

Table 2.1 Properties of base and solidifier components used in epoxy formulation (15)

Generic	Type	General Properties
Base	Bisphenol-A	A reaction product of phenol and acetone; bisphenol-A is further reacted with epichlorohydrin to give DGEBA; possesses good abrasion, wear and impact resistance
	Bisphenol-F	A reaction product of phenol and formaldehyde; bisphenol-F is reacted with epichlorohydrin to give DGEBF; imparts better chemical resistance when compared to bisphenol-A
	Novolac	A reaction product of excess phenol and formaldehyde; imparts high temperature resistance but makes the epoxy matrix more brittle than bisphenol-A or bisphenol-F
Solidifier	Aliphatic amines	Imparts fast cure properties and solvent resistance at the expense of limited flexibility
	Polyamides and amidoamines	Improved flexibility and wetting-out characteristics are imparted to the epoxy matrix along with improved adhesion and water tolerance
	Cycloaliphatic amines	High flexibility and good impact resistance

Aromatic amines	Lower heat resistance but good impact resistance
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2.3 Incorporation of nano-fillers to improve the friction and wear properties of epoxy matrices

2.3.1 Types of commonly used fillers and their properties

Various types of nano-fillers have been extensively used to improve the friction, wear and load bearing properties of pristine epoxy resins. Figure 2.1 presents a summary of commonly used fillers added to modify liquid epoxy resin systems (15):

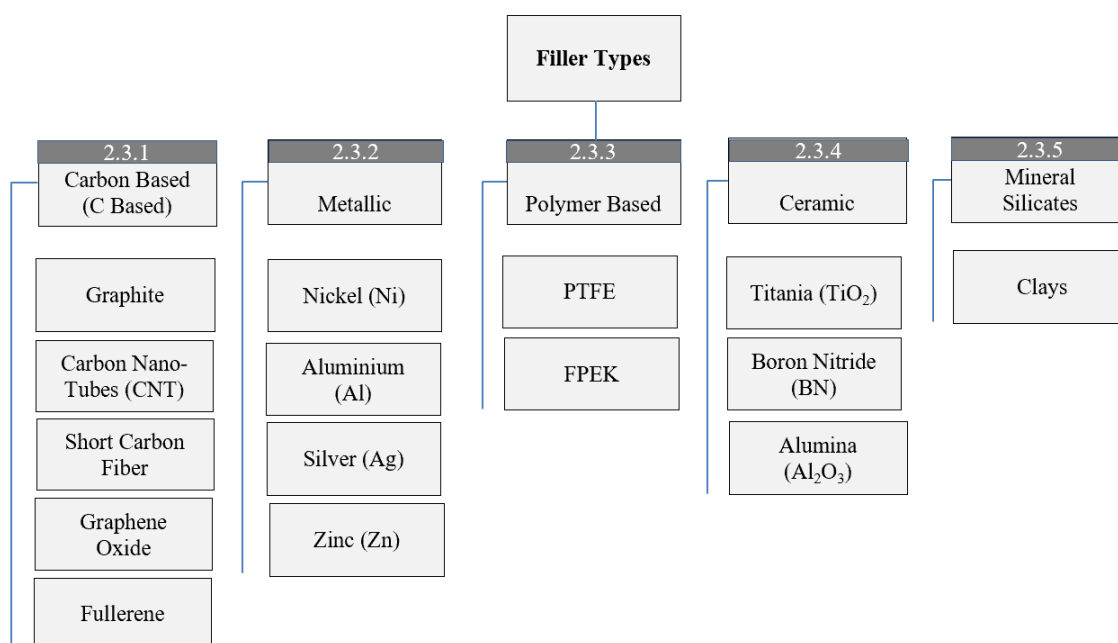


Figure 2.1 Fillers used to modify liquid epoxy resin systems (15)

2.3.1.1 Carbon based fillers

Graphite fillers, due to their layered structure with weak Van-Der Waals forces between the layers (22), are known to possess high electrical conductivities and also help in reducing friction and wear by forming a lubricant film between the contact surfaces (10). Carbon nano-tubes (both single-walled and multi-walled), discovered in the year 1991 by Iijima, are known to possess exceptional mechanical properties, thermal and electrical conductivities (3) making them an excellent filler for epoxy based composites and coatings (5). The short carbon fiber fillers used extensively by researchers Zhang et al. (22) have showed that incorporation of these into the epoxy matrix results in increased compressive strength and creep resistance. Any discussion on carbon-based fillers is incomplete without an in-depth review of graphene / graphene oxide fillers. Traditionally produced from graphene using the Hummer's method or its modifications (18,33), graphene and graphene oxide are known to possess exceptional properties such as high fracture toughness, mechanical properties exemplified by the high values of Young's Modulus of 1 TPa and 130 GPa Tensile Strength, high thermal and electrical conductivities (19–21,34). Even within the same filler group, it can be noted that slight chemical modifications to a compound can result in massive differences in the properties imparted. While graphene imparts water and oil tolerance properties to the epoxy matrix [9], graphene oxide increases the hydrophilic characteristics of the epoxy matrix (21). Both graphene and graphene oxide are known to improve the glass transition temperature of the epoxy polymer and this makes them particularly useful while formulating higher temperature resistant coating and bulk composite systems (21).

2.3.1.2 Metallic fillers

Brostow et al. (35) have studied the effect of addition of metallic fillers such as micron sized nickel, aluminium, zinc and silver powders on the tribological properties and surface energy characteristics of coatings applied on mild steel substrates. It was found that epoxy coating systems modified using aluminium fillers demonstrated the least friction and wear when subjected to a pin-on-disk test particularly due to their spherical shaped morphology that cause them to behave like roller bearings between the interacting surfaces.

2.3.1.3 Polymer based fillers

Polymer based fillers such as Fluorinated poly (aryl ether ketone) (FPEK) and Polytetrafluoroethylene (PTFE) have been used by Brostow et al. (35) and Zhang et al. (22) respectively in modifying the properties of epoxy based composites. While FPEK additives improve the scratch resistance of the epoxy matrix, PTFE fillers help reduce the coefficient of friction in the tribo-system. Such modifications have excellent applications in an industrial setting especially in fluid flow systems where a reduced coefficient of friction leads to lesser energy expenditure and improved efficiency.

2.3.1.4 Ceramic fillers

Ceramics are basically compounds of metallic atoms with oxides, carbides, borides, nitrides, silicides etc. and are generally known to possess hot hardness – the ability to retain mechanical properties at high temperatures (31). Nano-sized titanium dioxide fillers have been used by Zhang et al. (22) to improve the wear resistance and impact strength of composite epoxy systems. Pinto et al. (8) has carried out an extensive review on the mechanical properties of epoxy nanocomposites using titanium dioxide fillers as

reinforcement. Another ceramic filler worth mentioning is boron nitride which has been proven to exhibit up to 20% greater interfacial adhesion to the epoxy matrix when compared to CNTs and have shown exceptional results when subjected to wear and friction tests (1). It is also important to briefly mention the role of aluminium oxide fillers. Known for their high Young's Modulus values of approximately 347 GPa (9), the addition of these fillers are known to improve the compressive strength and wear resistance of pristine epoxy matrices (4). Mohanty et al. (9) have studied the improvement in mechanical properties of the epoxy matrix when reinforced with e-glass fibers. Though the performance of glass fibers may be weaker than their carbon based counterparts, this would often turn out to be a lower cost alternative while preparing hybrid composites and coating systems (9).

2.3.1.5 Mineral silicates

Another class of nano sized fillers used in modifying epoxies are montmorillonites commonly known as nano clays. Nano clays help improve both the mechanical strength and wear resistance; however, it requires a careful control over the filler loading due to the reason that a higher filler loading will result in particle agglomeration, non-uniform dispersion and properties contrary to what's desired (36,37). Pristine clay is known to be hydrophilic and also does not provide a good bond with the epoxy matrix (36). As such, it is necessary to modify the clay using silanes (commonly referred to as Silane Modified Clay or SMC) having amino-functional groups that can in-turn form bonds with the epoxide ring of the epoxies.

Table 2.2 presents a summary of the various nano-fillers used in modifying epoxy matrices along with their dominant properties (15).

Table 1.2 Fillers used to modify epoxy systems and properties both inherent and imparted to the matrix (15)

Fillers for Epoxy Matrix		
Name	Properties	Category
Graphite	High electrical conductivity (10); helps in formation of lubricant film between contact surfaces thereby reducing friction and wear (10); possesses a layered structure with weak Van-Der Waals force of attraction between the layers (22)	C Based
Carbon Nano-Tubes	Discovered in 1991 by S. Iijima; possesses low density (3); high electrical and thermal conductivities (38) and exceptional mechanical properties such as high strength and stiffness (3); addition of CNT leads to improved tensile strength, tensile modulus, flexural strength and flexural modulus (3); helps reduce wear by acting as roller bearings in between contacting surfaces (39)	C Based
Short Carbon Fiber	Carbon layers are oriented parallel to the fiber axis; mechanically strong, electrically and thermally	C Based

	conductive; helps improve the creep resistance and compressive strength (22)	
Graphene and Graphene Oxide	Graphene has high mechanical strength (40), fracture toughness (41), electrical and thermal conductivity (34); known to be better than CNTs in terms of dispersibility (34); incorporation of graphene into the epoxy matrix improves mechanical properties (41–43) and wear resistance (44); graphene has water and oil repellant properties, but graphene oxide is hydrophilic (34); both help increase the glass transition temperature (T _g) of the polymer and can be used to formulate elevated temperature resistant epoxy coatings (34)	C Based
Fullerenes (C₆₀)	Also called bucky balls, these additives impart extremely high tensile strength at lower filler loading when compared to ceramic fillers (6). They have lesser tendency to agglomerate owing to their spherical shape and are therefore much easier to disperse when compared to nano-clays and CNTs (6)	C Based
Ni, Al, Ag, Zn	Of these, the lowest friction and wear are exhibited by Al because of the spherical shape that act as roller	Metallic

	bearings and the highest friction and wear are exhibited by Zn / ZnO (35)	
PTFE	Plays the role of lubricant (13); One of the conventional fillers that can reduce the frictional coefficient by forming a transfer film (22); effective in the start-up regime (22)	Polymer
FPEK	Fluorinated poly (aryl ether ketone) is known to exhibit excellent hydrophobicity and also helps improve the scratch resistance of the epoxy matrix (35)	Polymer
TiO₂	Helps improve wear and impact resistance (22,23); improves fracture toughness and coating pull-off strengths (8); for the same conditions and filler loading, nano sized TiO ₂ particles are found to impart a higher degree of wear resistance to the epoxy matrix when compared to micron sized TiO ₂ fillers (24)	Ceramic
Boron Nitride (BN)	Considered to be more efficient than CNTs, shows good mechanical properties, high thermal conductivity (45), resistance to UV radiation, resistance to oxidation and possesses thermal	Ceramic

	stability (1); exhibit 20% greater interfacial adhesion to epoxy matrix than CNTs	
Al₂O₃	Alumina has been found to improve the compressive strength, mechanical properties (9) and also the wear resistance (4).	Ceramic
E-glass fibers	Glass fibers are very commonly used to reinforce polymer matrices and are known to improve the mechanical properties; however, their performance is much lower when compared to short carbon fiber reinforcements (9)	Ceramic
Nano Clay (Montmorillonite)	Very commonly used class of nano fillers, they are known to improve mechanical properties (36) and also impart a high degree of wear resistance (37). Particle agglomeration is a commonly associated problem with these fillers (37).	Mineral Silicates

2.3.2 Formulation of hybrid systems

Over the years, researchers have studied the combinative effects of adding several nano-fillers into the same pristine epoxy matrix (1,2,16,20,22,35). Such hybrid systems offer multiple advantages; and when dispersed uniformly in optimum concentrations, impart – in majority of the cases – the best of the properties of the various nano-fillers used (46). It

may be noted that given a set of fillers, multiple iterations (with regard to filler concentrations and dispersion techniques) need to be carried out to ensure that the best combination is arrived at in terms of enhanced wear resistance or reduced coefficient of friction values (14,16,22). The combination need not necessarily be limited to one class of fillers but may be selected from across carbon based, metallic, polymer based, ceramic and mineral silicate groups. Though hybrid systems are known to provide multiple advantages, it must not be construed that the combination would always result in better properties than stand-alone fillers as demonstrated by Hayrettin et al. (1) in their studies on hybrid epoxy resins modified using Multi-Walled CNT (MWCNT) and BN nanoparticles.

2.3.3 Dispersion techniques

In the development of epoxy bulk composites or epoxy composite coatings, one of the most important parameters for obtaining an effective improvement in wear resistance or reduced values for coefficient of friction is uniform dispersion of the nano-fillers in the epoxy matrix. It was observed during this extensive review that the preferred mode of dispersion for most researchers has been the sonication method using high frequency ultrasound waves (1,8,19,20,34). A summary of the dispersion techniques used by various researchers along with the types of fillers used are presented in Table 2.3 (15).

Table 2.3 Summary of various dispersion techniques used to uniformly disperse the nano-fillers in epoxy matrix (15)

Epoxy Bulk Composites				
Ref.	Filler	Filler category	Class	Dispersion Technique
(1)	0.3 wt. % MWCNT	C Based	Hybrid	BN nano-platelets / MWCNT combination added to epoxy and sonicated for 60 mins. followed by degassing
	0.5 wt. % BN	Ceramic		
	0.3 wt. % MWCNT+	Hybrid		
	0.5 wt. % BN			
(22)	PTFE	Polymer	Hybrid	Fillers pre-heated in oven @
		Based		70 ⁰ C, mechanical mixing
	TiO ₂	Ceramic		followed by vacuum treatment
	Graphite	C Based		
	Short Carbon Fiber (SCF)	C Based		

(3)	Pristine CNT	C Based	Non-	0.1 wt. % CNT added to epoxy
	Amino functionalized CNT	C Based	hybrid	and stirred for 5 minutes; High shear homogenization @ 20000 rpm (5 mins.) followed by ultra-sonication (700 Watts, 40% amplitude, 10 mins.); high shear and homogenization repeated; finally, vacuum desiccated at 400 mBar (1 hour)
(34)	FRGO (Functionalized Reduced Graphene Oxide)	C Based	Non-	100 mg of FRGO dispersed in 100 mL of acetone by sonication (2 hours) followed by addition of epoxy and mixture subject to sonication (1 hour); acetone removed by heating to 70 ⁰ C followed by vacuum treatment (12 hours) at 70 ⁰ C
	2 wt. % Al ₂ O ₃	Ceramic	Hybrid	Test specimen prepared in accordance with ASTM D 695-
(9)		C Based		10. Hardener added to epoxy and mechanically stirred for 5 mins.

(36)	Short glass fiber (SGF)			C Based	followed by addition of SGF & SCF. Finally, 2 wt. % Alumina added to the mixture and poured into molds lubricated with Silicon oil.
	Short carbon fiber (SCF)				
(36)	Montmorillonite	Mineral Silicate	Non-hybrid		4g of pristine clay dissolved in 120 mL of (De-ionized) DI water and stirred vigorously followed by addition of 800 mL of Acetone. Mixture filtered, washed with acetone and precipitate transferred to an acetone solution of γ -aminopropyl-trimethoxysilane (Silane mount is 10 wt. % of clay) followed by vigorous stirred to obtain SMC. SMC solution dispersed in epoxy using homogenizer at 10,000 rpm (1 hour) and acetone vaporized off thereafter by using

				a rotary evaporator followed by vacuum drying. Curing agent added and mixture cured at 100 ⁰ C (2 hours) followed by post-cure at 180 ⁰ C (5 hours)
(40)	Graphene	C Based	Non-Hybrid	Graphene sheets dispersed into Bis-F epoxy matrix using a mechanical stirrer at 1500 rpm (1 hour); evacuation of air carried out by degassing for 30 mins. followed by addition of hardener and degassing for 15 mins.
(6)	Fullerenes	C Based	Non-hybrid	0.1g of C ₆₀ dispersed in 50 mL of acetone using sonication at high amplitude (45 mins.); epoxy resin added to mixture and sonicated again (45 mins.); Acetone evaporated off using a Teflon coated magnetic bar (magnetic stir plate) at 70 ⁰ C (3 hours) followed by vacuum

				treatment at 70⁰C (12 hours). Epoxy hardener added and mixed using high shear mixer at 2000 rpm (4 mins.) and again subjected to vacuum treatment (20 mins.). Nano-composite poured into moulds and cured at ambient temp. (90 psi, 24 hours) and post-cured thereafter at 100⁰C (3 hours)
	ZnO	Ceramic	Hybrid	Epoxy resin dissolved in acetone at wt. % ratio of 10:2 and manually stirred (5 mins.); ZnO and PTFE added and stirred slowly followed by sonication (6 hours); Mixture placed in vacuum oven at 75⁰C (2 hours); Hardener added and mixture cured at 60⁰C (2 hours) followed by post-curing at 170⁰C (50 mins.)
(13)	PTFE	Polymer Based		

Epoxy Composite Coatings				
Ref.	Filler	Filler category	Class	Dispersion Technique
(10)	Graphite (10 - 60 wt. %)	C Based	Non-hybrid	Epoxy resin and agents dissolved in solvent of xylene and butanol; dispersed for 30 minutes at 500 rpm using SFJ-400 disperser; pre-wetted graphite added, and ball milled for 30 minutes. Resin with fillers then blended with the curing agent and coated onto tin plates and plastic substrates followed by curing in oven at 50°C – 60°C.
(20)	Graphene Oxide TiO ₂	C Based Ceramic	Hybrid	Titania colloidal suspension (0.05 M) prepared by dropwise addition of titanium (IV) isopropoxide to a solution of Ethanol and continuously stirred; 1.5 mg/ml of GO added to the TiO ₂ colloidal suspension and

				sonicated (30 minutes) followed by filtration, rinsing with DI water and drying at 60 ⁰ C (12 hours) to obtain TGO hybrid. TGO hybrid then dispersed in acetone, subjected to ultra-sonication (1 hour) and coated using the epoxy matrix.
(35)	10 wt. % FPEK 25 wt. % Ni, Al, Ag, Zn per 100 grams of epoxy	Polymer Based Metallic	Hybrid	FPEK dissolved in chloroform and epoxy resin added followed by vacuum treatment
(47)	10 wt. % Graphene 10 wt. % Graphite	C Based	Non-hybrid	Fillers added to the epoxy matrix and hand stirred for 15 minutes

2.4 Tribology of epoxy bulk composites

Zhang et al. (22) have shown through iterative trials that a combination of epoxy + 15 vol. % graphite + 5 vol. % nano-TiO₂ + 15 vol. % short-CF exhibits a specific wear rate of $3.2 \times 10^{-7} \text{ mm}^3/\text{N-m}$, which is about 100 times lower when compared to neat epoxy. In a separate study by Chang and Zhang (2) observed that a complex mechanism existed for wear of short carbon fiber (SCF) based composites which include a multi-step process consisting of matrix wear and fiber thinning followed by breakage of the fiber leading to interfacial de-bonding and eventual peeling off of the fiber from the matrix. However, the addition of nano-TiO₂ particles combined with the effect of lubricant film forming PTFE and graphite fillers resulted in extremely high wear resistance under large p - v conditions demonstrated by a pin on disk test conducted in accordance with ASTM D3702. It was concluded that the optimum composition involving nano-TiO₂, PTFE, graphite and short CF would be epoxy + 5 vol. % nano-TiO₂ + 5 vol. % PTFE + 5 vol. % graphite + 15 vol. % short-CF.

McCook et al. (13) determined the optimum concentration of Zinc oxide (ZnO) and Polytetrafluoroethylene (PTFE) hybrid at 1 vol. % ZnO and 14.5 vol. % PTFE nano-particles in order to obtain a reduction in friction and wear coefficient when subjected to pin-on-disk tests in reciprocating mode at 250 N normal load with an average reciprocating length of 25.4 mm and 50.8 mm/s sliding velocity. It was noted that the epoxy hybrid composite prepared using the above formulation had a wear resistance of

approximately 400 times greater than the pristine epoxy. When the concentration of ZnO was increased to 3.5 vol. % keeping the concentration of PTFE constant, the coefficient of friction was also found to have reduced by 7 times.

Hayrettin et al. (1) performed tribological tests using both stand-alone fillers and hybrids of the individual fillers. Friction and wear behaviors of 0.3 wt. % MWCNT, 0.5 wt. % BN and 0.3 wt. % MWCNT/0.5 wt. % BN hybrid were evaluated using a ball-on-disk set up at sliding velocities of 1.2 m/s and 1.5 m/s under a normal load of 10N under dry conditions. Scanning Electron Microscope images revealed both adhesive and abrasive wear modes. An interesting point stated in this work was though MWCNT/BN hybrid modification resulted in the best mechanical properties' enhancement, the minimum wear rates and friction coefficients were obtained for BN-modified specimens.

In order to improve the dispersion of nano-particles in the epoxy matrix, Luo et al. (48) used a chemical grafting method to modify nano-Si₃N₄ by covalently bonding polyglycidyl methacrylate (PGMA) onto the particles. Tribological tests were conducted using a pin-on-ring configuration at a constant velocity of 0.42 m/s and a pressure of 3 MPa. The addition of nano-Si₃N₄ particles in both normal and grafted forms were found to reduce both the friction coefficient and specific wear rate with the PGMA grafted nano-Si₃N₄ filled epoxy bulk composite faring slightly better in the tests.

In almost all cases, it is seen that the epoxy matrix selected for modification is based on Bisphenol-A which is then cured using an amine-based solidifier. However, Khun et al.(40) carried out modification of the Bisphenol-F matrix using Graphene as the stand-alone filler. Tribological properties were systematically investigated using a 100Cr6 steel ball-on-disk tribometer. Tribological properties were evaluated under varying sliding velocities under a constant load of 1N and sliding distance of 300 m. It was noted that increasing the Graphene content resulted in reduced coefficient of friction due to the formation of a lubricant film. It was noted that the wear resistance characteristics showed improvement when the Graphene content was increased over a range of 0 wt. % to 2 wt.%. A point worth mentioning is the tribo-layers' that were generated due to the compaction of wear debris generated with each revolution of steel ball along the wear track. The formation of these wave-like features was attributed to cyclic stresses created by the sliding steel ball causing sub-surface fatigue due to the embrittlement of the reinforced epoxy matrix. This theory was further confirmed by the non-existence of such features on the pristine epoxy owing to higher wear.

2.5 Tribology of epoxy composite coating systems

2.5.1 Coating techniques

Coatings are primarily classified into industrial coatings and decorative paints. While industrial coating systems are used for protecting substrates from corrosion, abrasion and other forms of wear, decorative coatings are used for aesthetic purposes and do not offer

the same levels of corrosion and wear resistance as industrial coatings. Industrial coatings are used for a wide spectrum of applications in *Oil and Gas*, *Petrochemical*, *Marine* (49,50), *Construction* (51), *Medical* (52), *Defense*, *Paper*, *Power*, *Metal Processing* and *Cement* sectors. Various techniques have been used by researchers to coat substrates with epoxy coatings in its pristine or composite forms. As opposed to bulk composites, the adhesive strength of the coating on the substrate over which it has been applied is an important aspect that determines the longevity of the coating and surface preparation, to a great extent, determines this feature.

Any substrate onto which coatings are applied must be free from contamination due to oil or water. It is recommended that substrates be cleaned using a suitable solvent such as acetone in accordance with SSPC SP-1 prior to performing any coating activity. Pre-treatment techniques such as oxygen-plasma treatment have also been used by researchers to improve the surface energy of the substrates to favor improved adhesion (47). In case of hi-build coatings – coatings that are applied at excessive thicknesses of 500 microns or more – a suitable anchor profile is required to promote mechanical adhesion as recommended by the manufacturer and these may be achieved through various methods such as abrasive blasting, bristle blasting or grinding to ensure a clean (as determined by visual inspection and comparison with relevant ISO, NACE or SSPC standards) and dry surface free of any salt contamination. Salts result in osmotic gradient and can cause blistering of coatings when immersed in high temperature media (53). At all stages of a coating project beginning from surface preparation to coating application, environmental

conditions must be recorded to ensure that the substrate is free from moisture resulting from condensation that could prove detrimental to the performance of the coating system. As a general rule of thumb, it must always be ensured that the surface temperature is at least 3⁰C greater than the dew point temperature (53).

The coating technique to be used depends largely on the application feasibility such as the geometry of the substrate to be coated, coating type, resin viscosity etc. and can vary widely between laboratory and industrial settings. Table 2.4 presents a summary of coating and pre-treatment techniques used by some researchers (15):

Table 2.4 Different types of coating techniques and pre-treatment methods used by researchers (15)

Ref.	Filler	Substrate	Pre-Treatment	Thickness	Coating Technique
(10)	Graphite (10 - 60 wt. %)	Tin plate	Not defined	Not defined	Not defined
(20)	Graphene Oxide TiO ₂	Mild Steel	Cleaned using Acetone	Not defined	Dip coating (1 minute) and then dried in oven @ 60 ⁰ C (18 hours)
(35)	10 wt. % FPEK 25 wt. % Ni, Al, Ag, Zn per 100 grams of epoxy	Mild Steel (ASTM A366)	Lab conditions; no other pre-treatment	Not defined	Brush

(47)	10 wt. % Graphene	Steel	Oxygen plasma for 2 minutes using	25 – 35 μm	Dip coating and then rotating the shaft at 50 rpm
	10 wt. % Graphite		plasma cleaner (PDC 32G)		

It can be seen from the above table that sufficient information with regard to coating properties such as thickness hasn't been provided. A closer look at the research works also reveal that in majority of the cases, interfacial properties such as surface roughness parameters, preparation techniques of the substrate etc. haven't also been well defined.

2.5.2 Tribological performance evaluation

Kumar et al. (47) investigated the use of epoxy composite coatings to enhance the wear life under dry and lubricated conditions. The coatings were separately modified using 10 wt. % graphene and graphite fillers and experiments were carried out using a ball on cylinder tribometer. A point contact resulted between the steel cylindrical shaft dip coated using the nanocomposite epoxy system (with a coating thickness of 25 – 35 microns) and the steel ball counter-face. Their findings are summarized in Table 2.5.

Table 2.5 Partial summary of wear life and friction coefficient results

Coefficient of Friction Results		
Type	Dry	Lubricated
Pristine epoxy	-	0.09
Epoxy / graphite	0.29	0.10
Epoxy / graphene	0.18	0.08
Test conditions	3N, 300 rpm, RH:40%	5N, 300 rpm, RH:40%
Wear Life Results (No. of Cycles)		
Type	Dry	Lubricated
Pristine epoxy	800	10000
Epoxy / graphite	6000	>20000
Epoxy / graphene	2000	>20000
Test conditions	5N, 300 rpm, RH: 40%	5N, 300 rpm, RH: 40%

The findings of Pan et al.(10) on graphite modified epoxy coatings applied to tin substrates are also quite significant. Nine different weight fractions of graphite were added to pristine epoxy using an SFJ-400 disperser. Tests were conducted under dry conditions, using a ring-block sliding contact apparatus at 22⁰C air with relative humidity maintained between 50 ± 10%. It was seen that both the friction coefficient and wear-rate drop until 30 wt. % of graphite content and the wear mechanism is noted to be predominantly adhesive. However, there was an increase of friction and wear coefficients at 40 wt. % due to the continuity of the epoxy matrix being compromised by the graphite flakes. However, at 50 wt. % of graphite, a considerable dip was once again on both the friction coefficients and wear rates primarily due to the formation of a transfer film on the counter-face.

A comparative study of tribological properties of fluoropolymer modified epoxy coatings in combination with metallic fillers such as nickel, aluminium, silver and zinc was carried out by Browstow et al. (35). The friction and wear rates were found to be dependent on the cure temperatures which were in-turn dependent on the curing agent. It was noted that among the epoxies modified using metallic powders, addition of Aluminium fillers resulted in the least coefficient of friction and wear when cured at lower temperatures owing to their spherical morphology resulting in rolling friction between the contacting surfaces during the pin-on-disk test. It was also noted that under low temperature curing regimes, addition of Zinc resulted in an increase in friction and wear coefficient possibly due to the formation of a secondary phase of Zinc oxide as tests were carried out in lab conditions exposed to air. However, these system properties were not found to hold true at higher cure temperatures possibly due to other mechanisms such as higher degree of cross-linking becoming predominant which nullifies the effect of addition of fillers. Table 2.6 gives an indication of the results that were obtained from the friction and wear coefficient tests (15).

Table 2.6 Relative wear rates and friction co-efficient ratings from the pin-on-disk test (15)

Wear Rates	Low Temp	High Temp
	Cure	Cure
Pristine Epoxy	6	3
FPEK Modified	3	1
Epoxy + FPEK + Ni	2	5
Epoxy + FPEK + Al	1	6
Epoxy + FPEK + Ag	4	2
Epoxy + FPEK + Zn	5	4

*** 1 represents the lowest wear rate**

Friction Coefficient	500 cycles		5000 cycles	
	Low Temp Cure	High Temp Cure	Low Temp Cure	High Temp Cure
Pristine Epoxy	1	2	6	1
FPEK Modified	4	1	1	3
Epoxy + FPEK + Ni	5	5	4	6
Epoxy + FPEK + Al	2	3	2	5
Epoxy + FPEK + Ag	3	4	3	2

Epoxy + FPEK + Zn	6	5	5	4
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*** 1 represents the lowest friction coefficient at both 500 and 5000 cycles and across various cure regimes**

2.6 Summary

Nanotechnology has gained quite a lot of importance in the field of tribology in the recent years (7,15,54,55). Due to its ability to enhance the mechanical properties and wear resistance of epoxy matrices, nano-fillers have aided the development of bulk composites and composite coatings. It can be concluded from this extensive literature review that most of the works in the field of tribological evaluation of hybrid epoxy systems have been carried out on bulk composites as opposed to coatings. Several authors have performed tribological tests under various conditions, using different concentrations of nano and micron sized fillers and mechanisms responsible for reduced coefficient of friction or enhanced wear resistance have been well studied. Some of them have managed to optimize the concentrations of these fillers over several iterations. In all cases involving the modification of surface properties of epoxy composites and coatings using nano – and sometimes micro – scale particles, due importance has been placed on obtaining a homogenous system with fillers uniformly dispersed within the epoxy matrix. Several methodologies for obtaining this and a range of test methods have been proposed by various teams of researchers and the same have been summarized in this chapter. Much work however remains to be carried out in the field of reinforced epoxy coatings for

tribological applications. The variables when it comes to coating development and application are numerous ranging from substrate texture characteristics, substrate treatment effects, filler type and morphology to filler modification approaches, coating techniques, thickness and adhesion that can in-turn affect the mode of delamination and resultant friction and wear characteristics (56).

The significance of this research stems from its fundamental and applied nature which begins with an evaluation of various surface preparation techniques using plasma treatment and employment of novel abrasives to effect a possible paradigm shift higher up the coating supply chain while proceeding to address the gaps in academia by using novel combinations of fillers to produce hybrid epoxy nanocomposite matrices and eliminating extraneous variables in the coating process by using a semi-automated spin technique. A range of characterization techniques have been employed throughout this study to support various findings and data collected during the course of this work have been subjected to rigorous statistical treatments to determine the statistical significance of various observations. Several aspects of this study are being presented for the first time in industrial and academic circles and will be of interest to both industrial professionals and scientific researchers.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

This chapter details the materials used in this work along with their properties, the techniques employed to disperse nanoparticles in the epoxy matrix, the coating methodology adopted to prepare specimens for tribological tests, the equipment employed in this research, the characterization techniques used and the testing program designed to accomplish the various research objectives.

3.2 Materials

3.2.1 Liquid epoxy resin system

The epoxy resin system used for the first phase of this research is Belzona[®] 1341 – a two component, high-build, 100% solids, commercial liquid epoxy coating system, based on Diglycidyl Ether of Bisphenol A (DGEBA Epichlorohydrin Polymer, CAS #25068-38-6) and cured using an amine solidifier. Properties of this epoxy resin system are provided in Table 3.1.

Table 3.1 Properties of Belzona® 1341

Description	Value
Component	Mixed
Mixing ratio (base: solidifier)	1:1 parts by volume
Viscosity of mixed material at 25°C	61 poise
Density of mixed material	1.42 g/cc
Working life at 20°C (68°F)	40 minutes
Time to immersion service at 25°C (77°F)	2 ½ days
Coverage rate	1.76 m ² (18.9 ft ²) / 1 kg at 400 microns (16 mils)
Compressive strength (ASTM D695)	57.2 MPa (8,300 psi) at 20°C (68°F) cure
Temperature resistance	60°C (140°F) immersed, 130°C (266°F) dry

In the second and third phases of this research work, the epoxy resin system used is Belzona® 4151 – a two component, pristine, 100% solids, amber colored resin system based on an equal volumetric combination of Diglycidyl Ether of Bisphenol A (DGEBA Epichlorohydrin Polymer, CAS #25068-38-6) and Novolac (Phenol, Polymer with Formaldehyde, Glycidyl Ether, CAS #28064-14-4) and cured using an amine solidifier. The base and solidifier components were supplied by Hajjan Trading and Industrial Services Co. Ltd., Saudi Arabia (exclusive distributor of

Belzona Polymerics Ltd. products within the Kingdom of Saudi Arabia). Important properties with regard to mixing and application are listed in Table 3.2.

Table 3.2 Properties of Belzona® 4151

Description	Value
Component	Base
Appearance	Clear, light amber
Density	1.16 g/cc
Component	Solidifier
Appearance	Clear, amber
Density	1.02 g/cc
Component	Mixed
Appearance	Clear, amber colour
Mixing ratio (base: solidifier)	2:1 parts by volume
Working life	12 minutes at 25 ⁰ C
Cure time	2.5 days at 35 ⁰ C
Heat distortion temperature (ASTM D648)	41 ⁰ C
Dry heat resistance (ISO 11357, DSC method)	200 ⁰ C

3.2.2 Abrasives

In phase one of this research work, mild steel (grade A36) plates are textured using two novel abrasives namely, Olivine and Calcium Silicate.

3.2.2.1 Olivine

Olivine is a naturally occurring mineral silicate abrasive produced from Dunite rock and has a light greenish tint. Chemically, olivine is magnesium iron silicate and is empirically expressed as A_2SiO_4 where A represents the elements Fe or Mg. The properties of the Olivine abrasive used in this study is presented in Table 3.3.

Table 3.3 Properties of Olivine abrasive

Abrasive Identifier	Particle Size Range	Mean Particle Size	Hardness (Mohs)
OL 080	0.2 mm - 1.4 mm	0.80 mm	6.5 – 7

3.2.2.2 Calcium Silicate

Calcium Silicate is also called iron furnace slag and is obtained from the blast furnace process. It has a light brown appearance with sandy texture. The properties of the Calcium Silicate abrasive used in this study is presented in Table 3.4

Table 3.4 Properties of Calcium Silicate abrasive

Abrasive Identifier	Particle Size Range	Mean Particle Size	Hardness (Mohs)
CS 085	0.2 mm - 1.5 mm	0.85 mm	>6

3.2.3 Nanofillers

In phases two and three of this research, the pristine epoxy resin system, Belzona® 4151, was proposed to be modified using various nanofillers. All nanosized fillers used in this research were procured by King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia and released towards this research. The properties of the individual fillers are provided below:

3.2.3.1 Graphene-oxide

Graphene oxide is a unique material possessing a single to few layers of graphite with various oxygen containing functionalities. Graphene oxide powders used in this work were procured from Ad-Nano Technologies, India. The initial loose bulk density of the nano-powder used in this study was determined to be ~ 0.731 g/cc. SEM scans of the graphene oxide powder used in this study presented in Figures 3.1 a) and 3.1 b) clearly depict the layered structure.

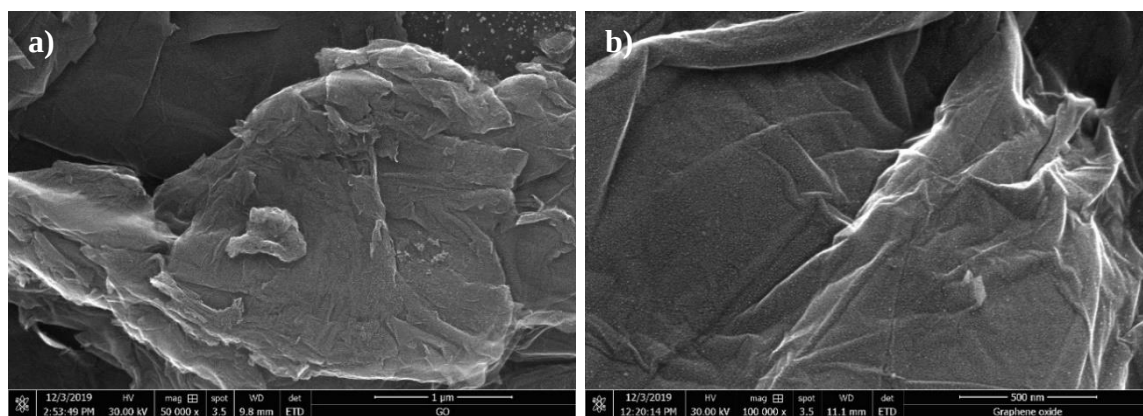


Figure 3.1 a) SEM image of GO nanoparticle at 50,000X b) SEM image of GO nanoparticle at 100,000X

3.2.3.2 Titania

Titania is a ceramic material and exhibits polymorphism i.e. it exists in a range of crystal structures. Depending on the crystal structure, titania is classified into rutile, anatase and brookite to name a few with rutile being the most common natural form of titania. Nanosized particles of titania however tend to crystallize in the metastable anatase phase owing to the lower surface energy of this phase when compared to the relatively stable equilibrium rutile phase at higher length scales. Titania nanoparticles of 99% purity used in this research were procured from Loba Chemie, India. The initial loose bulk density of these nano-powders was determined to be ~ 0.502 g/cc. SEM scans of the titania powder used in this study are presented in Figures 3.2 a) – c). The spherical morphology of the nanoparticles is clearly visible. In spite of agglomeration, individual particles with an average size of 85 nm (± 7 nm) diameter are clearly seen at higher magnifications (of 300,000x).

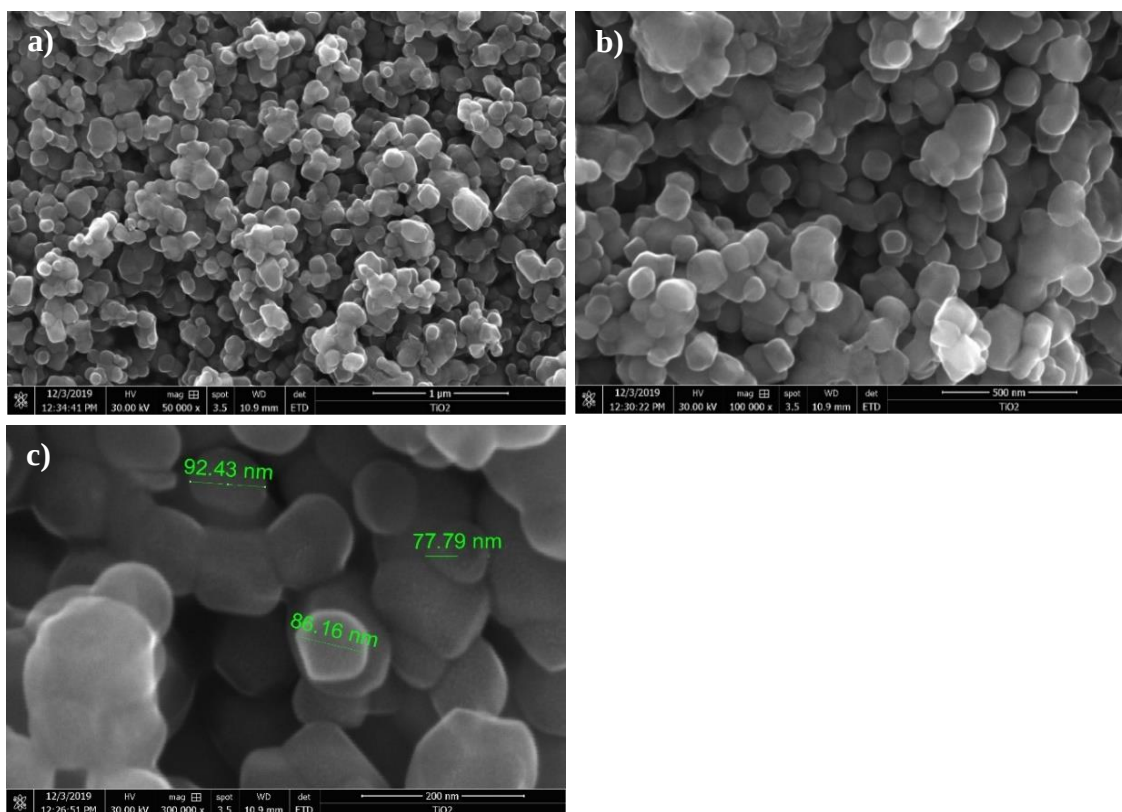


Figure 3.2 a) SEM image of Titania nanoparticle at 50,000X b) SEM image of Titania nanoparticle at 100,000X c) SEM image of Titania nanoparticle showing particle size

3.2.3.3 Alumina

Alumina is also a ceramic material and is significant in its use to produce aluminium metal, as a refractory material owing to its hot hardness and high melting point, as a catalyst in the Claus process and as an abrasive for surface preparation and other related applications. The Alumina powders (99.8% purity) were procured from Aldrich, USA. The bulk density of the powders used in this work was calculated to be ~ 0.045 g/cc. Owing to the extremely small particle size of approximately 13 nm (as specified by the supplier), high magnification images of the as-received alumina powders showed a great degree of agglomeration. As such, the nanoparticles, were subjected to ultrasonication and

reimaged. The SEM scans of the powder particles before and after ultrasonication are provided in Figures 3.3 a) and 3.3 b). The spherical morphology of the ultrasonicate nanoparticles can be clearly seen.

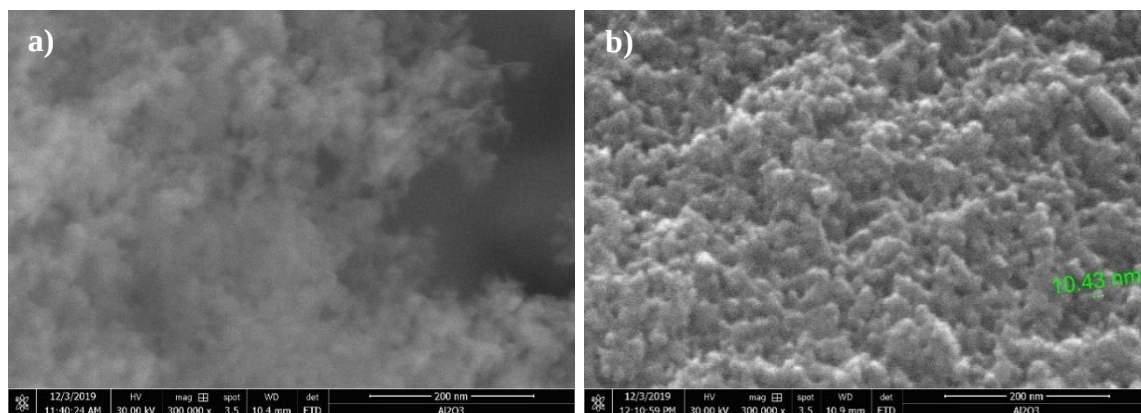


Figure 3.3 a) SEM image of Alumina nanoparticles before sonication at 300,000X b) SEM image of Titania nanoparticle after sonication at 300,000X

3.2.4 Mild steel, grade A36

All coatings formulated in this research are applied onto mild steel substrates of grade A36 (size: 75 mm X 75 mm X 4 mm) for the adhesion tests in the first phase and second phases of this research and onto mild steel substrates of grade A36 (size: 25 mm X 25 mm X 4 mm) for the tribological characterization studies in the second and third phases of this work. The mild steel plates were provided by King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

3.3 Equipment

The equipment used in this study have been divided into two types for clarity:

- Specimen preparation equipment
- Testing and characterization equipment

3.3.1 Specimen preparation equipment

3.3.1.1 Blasting equipment

Abrasive blasting, pictured in Figure 3.4 is a methodology by which solid particles called abrasives are entrained in a jet of compressed air and directed onto the surface that is to be textured and eventually coated. Abrasives may be spherical or angular shaped. Abrasives come in various types - steel shots, steel grit, glass beads, mineral abrasives, slags or more recently – walnut shells and dry ice to name a few. Within a particular abrasive type, there may be several grades or particle size ranges depending on the kind of surface roughness desired. In this work, texturing of mild steel substrates is carried out using two novel abrasives, Olivine and Calcium Silicate.



Figure 3.4 Abrasive blasting in progress

3.3.1.2 Spin-coater

For ensuring minimal operator skills / intervention and to reduce the effect of extraneous variables, a lab fabricated spin coater fitted with a variable speed drive is used (range: 0 – 800 rpm; least count: 1 rpm) to coat the mild steel substrates. This ensures a uniform coating with minimal variations in coating DFTs across the specimens.

3.3.1.3 Plasma treatment unit

Plasma treatment is commonly employed in academia to remove nanoscale contamination and alter surface chemistry without affecting bulk material properties. Air plasma treatment (or oxygen plasma treatment, as it is commonly known) helps in increasing the

surface free energy due to the introduction of dangling bonds on the surface of steel, thereby improving the interaction between the coating and the substrate (57). Though nitrogen is the major constituent of air by volume, the primary reason that this process is referred to as oxygen plasma treatment is due to the specific generation of oxygen containing functional groups on the mild steel substrate as opposed to nitrogen containing ones. This is due to the dissociation energy of nitrogen being higher (941 kJ/mol) than oxygen (494 kJ/mol), which causes elemental oxygen to dissociate into its nascent forms much more easily than nitrogen (58). In this research work, air plasma treatment is carried out using Harrick Air Plasma Cleaner, PDC-001, with a maximum RF power setting of 30W (see Figure 3.5).

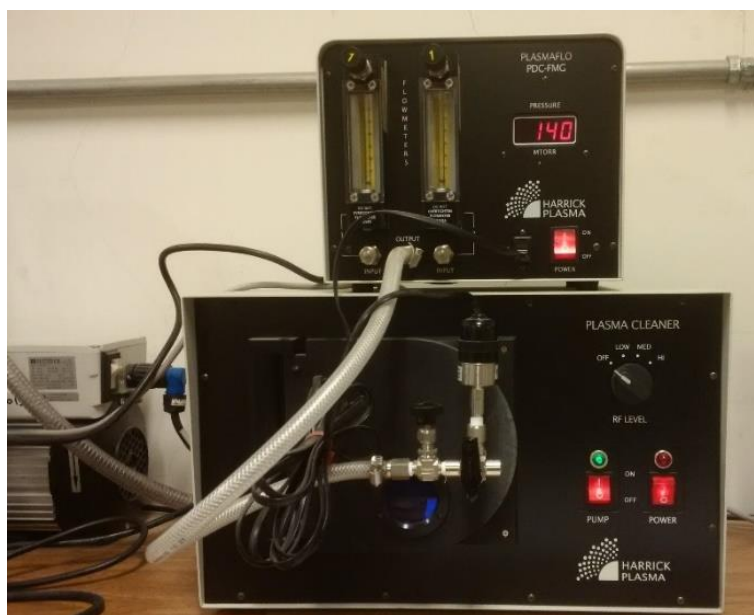


Figure 3.5 Harrick air plasma cleaner, PDC-001

3.3.2 Testing and characterization equipment

3.3.2.1 Optical profilometer

Optical profilometers are used to extract topographical data from a surface. It uses the principle of optical interference and help obtain data such as height, spatial and shape parameters of surface roughness. In tribological studies, it helps accurately measure the depth of the wear track and help set an initial point for coating failure evaluation. In our work, the Bruker ContourGT-K optical profilometer is used for characterizing the surface texture and determining the depth of the wear track after tribological testing.

3.3.2.2 Water contact angle tester

Water contact angle test is used to determine the surface free energy and provides a good indication of the wettability of a surface. When a liquid droplet is placed on a substrate, the degree of wetting is indicated by the contact angle that the liquid droplet makes with the surface. If the surface energy of the liquid droplet is greater than the substrate on which it is placed, the contact angle value will be $>90^{\circ}$ and is characterized by the formation of a liquid bead on the substrate. Contact angles $<90^{\circ}$ and closer to 0° indicates excellent wettability. This contact angle, also called Young's contact angle is indicated by θ_y . However, this is applicable only for relatively smooth surfaces. Where the surface is rough, the Young's contact angle varies from the measured contact angle by a factor known as the surface index, r , where ' r ' is the ratio of the actual surface area to the theoretical surface area. Equation (1) is used in this study for calculating the Young's contact angle:

$$\cos \theta_m = r \cos \theta_y \dots\dots\dots(1)$$

where θ_m represents the measured contact angle, r represents the surface index and θ_y represents the computed Young's contact angle. The VCA Optima contact angle tester, shown in Figure 3.6 has been employed in this study to determine the change in surface wettability characteristics prior to and after surface treatment. In this work, the apparent static water contact angle, θ_m , has been measured by placing a sessile, distilled water droplet of 1.2 μL , on treated mild steel substrates followed by the employment of the popularly used half-angle algorithm. Comparisons of surface free energy with control specimens have been drawn.



Figure 3.6 VCA optima contact angle tester

3.3.2.3 Dry-film thickness (DFT) gauge

Since all coatings used in this study are 100% solids, there is no shrinkage during cure. It is also essential that the dry-film thickness of coatings across specimens is kept constant to reduce the effect of extraneous variables. The DFT of all coatings is measured using Elcometer 456 gauge fitted with an FNF (ferrous/non-ferrous) probe. Prior to testing each batch, the gauge is site-calibrated by 480 μ foils using smooth calibration approach to keep errors during measurement within $\pm 1\%$. Five readings are taken on each plate and only coatings meeting the specified target DFT range of 350 $\mu\text{m} \pm 15\%$ (~300 μm minimum – 400 μm maximum) are utilized for subsequent tests. The spin-coating process ensures excellent repeatability and reproducibility and rejection rates owing to erratic DFTs are low.

3.3.2.4 Adhesion tester

A firmly adhered coating plays an important role in ensuring the longevity of a coating and this may also be partially attributed to the fact that a well adhered coating will mean a greater degree of effort is required to peel off the same using tensile or shear loads and as such would contribute to the durability of the applied protective system. In this work, the adhesive strength of coatings applied onto mild steel substrates are measured using a PosiTest AT-M Manual, Type V, Self-Aligning Tester from DeFelsko[®] Inspection Instruments. The tests are carried out in accordance with ASTM D-4541 using a 20 mm aluminium dolly (59–62). The ASTM D-4541 protocol is the most commonly used test in the industry for pull-off adhesion strength testing owing to its precision and accuracy. The

testing instrument records the amount of pressure required to pull-off the coating from the substrate. The test set-up is illustrated in Figure 3.7.

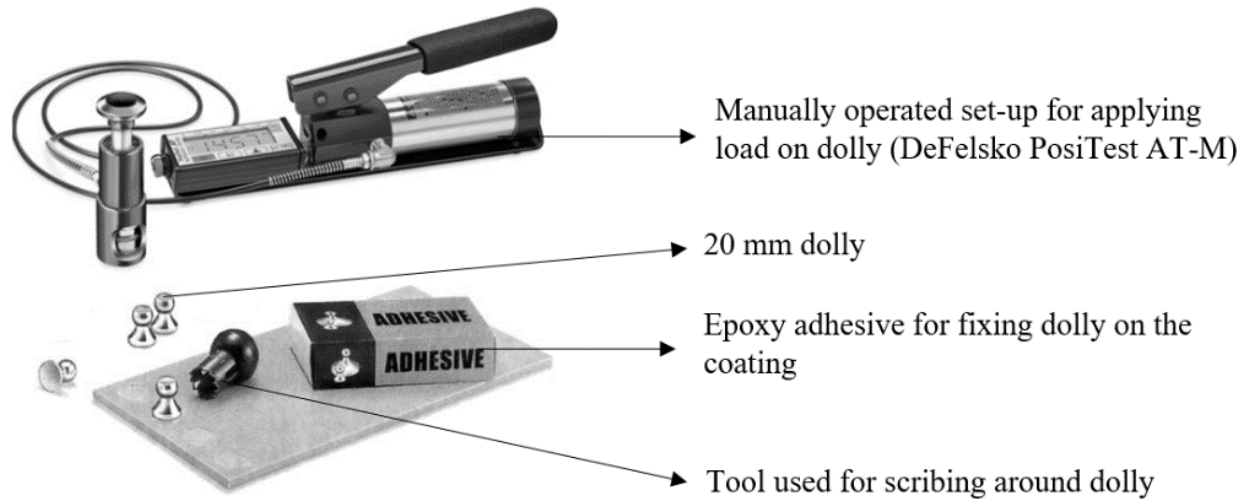


Figure 3.7 Pull-off adhesion test in accordance with ASTM D-4541

3.3.2.5 Scanning electron microscope

A scanning electron microscope (SEM) produces high resolution images of a sample, with a high depth of field, by scanning the surface of the specimen with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron source in a scanning electron microscope is an important element of the system and determines the resolution, beam stability, energy spread and brightness. They are generally classified into thermionic emission guns and field emission guns based on the type of electron gun used. While thermionic emission guns depend on the principle of resistive heating for ejecting electrons from the metal by overcoming the work function

of the metal, field emission guns utilize the principle of quantum-mechanical tunneling to remove electrons from the metal. Thermionic emission guns are further classified into Tungsten and LaB₆ guns while field emission guns are classified into Cold Field Emission and Schottky Field Emission guns. In this work, a Schottky Field Emission scanning electron microscope, Quanta FEG 250 fitted with an EDS (Energy-dispersive X-ray Spectroscopy) detector as shown in Figure 3.8 has been used. Prior to carrying out imaging works, the samples are gold coated to prevent charging.



Figure 3.8 Quanta FEG 250 scanning electron microscope with EDS detector

3.3.2.6 X-ray diffractometer (XRD)

XRD is an analytical technique used to identify the phase of a crystalline material. When an unknown sample is irradiated with X-rays, the sample diffracts the X-rays at certain characteristics angles denoted by θ . Diffraction of X-rays follows the Bragg's law given in Equation (2).

$$n\lambda = 2d \sin\theta \dots\dots\dots (2)$$

Where n represents the order of diffraction, λ is the wavelength of the X-ray source, d represents the inter-planar spacing and 2θ represents the diffraction angle. This θ value and the intensity of diffraction is unique to a specific compound and thus helps characterize the crystal structure of the material and also provides information on the degree of dispersion of a filler in the polymer matrix. Crystalline materials tend to show characteristics peaks whereas amorphous materials do not show any peaks in the XRD spectrum. Analysis of the XRD spectrum also helps give an indication of the particle size. For nanosized particles, peak broadening occurs, and particle size is usually measured using the *Debye-Scherrer* formula. For XRD characterization studies, the Rigaku MiniFlex II Desktop X-ray Diffractometer shown in Figure 3.9 has been employed.

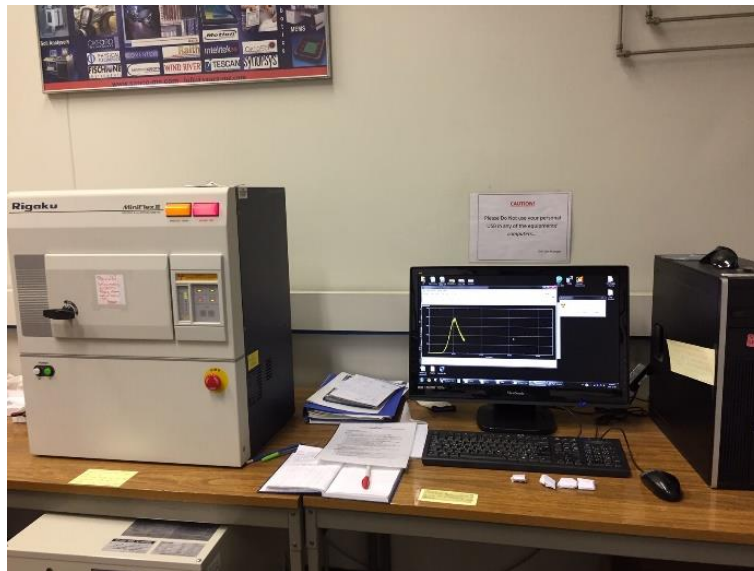


Figure 3.9 Rigaku MiniFlex II desktop X-ray diffractometer

3.3.2.7 Tribometer

A tribometer is an instrument that measures tribological quantities such as coefficient of friction, friction force, wear life and / or wear rate between two surfaces in contact. In this work, friction and wear tests on the formulated coatings are conducted using the Bruker UMT TriboLab equipment set to ball-on-disk configuration under dry conditions at room temperature and a relative humidity of $50 \pm 5\%$. Figure 3.10 represents the tribometer used in this research.



Figure 3.10 Bruker UMT TriboLab

3.4 Sample preparation and characterization techniques

This section details the procedures used in specimen preparation, testing and characterization.

3.4.1 Samples for evaluation of the effect of various surface treatment techniques on adhesive strength

This sub-section deals with the sample preparation and testing procedures adopted to evaluate the effect of various surface treatment techniques on the adhesive strength of high build coatings applied onto non-textured, textured and plasma treated non-textured substrates.

3.4.1.1 Preparation of non-textured, coated mild steel (grade A36) plates for phase one

Prior to coating application, all mild steel plates were ground and polished to obtain a roughness value of (R_a) of $0.7\mu \pm 0.15\mu$. Figure 3.11 a) and 3.11 b) presents the optical profilometer scans of two randomly selected mild steel plates for indicative purposes.

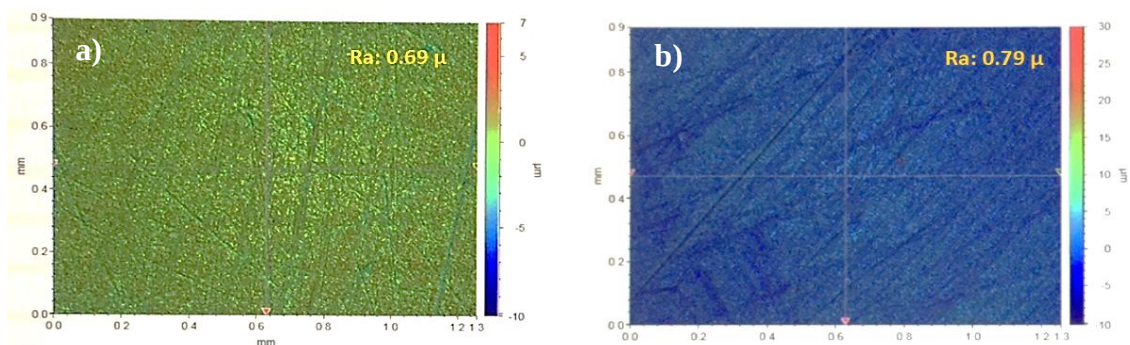


Figure 3.11 Optical profilometer scans of ground and polished mild steel substrates

For the first phase of this study, mild steel plates of size 75 mm X 75 mm X 4 mm were used. Prior to carrying out coating works, the steel plates were initially cleaned using acetone in accordance with SSPC SP-1 standard. A single coat of Belzona® 1341 was then applied using brush, by trained and validated applicators, at a wet film thickness of 400 µm – 500 µm in accordance with the manufacturer’s data sheets. The DFT of all coatings were verified using the DFT gauge, Elcometer 456. Any readings not falling within this coating thickness range were discarded.

3.4.1.2 Preparation of textured, coated mild steel (grade A36) plates for phase one

Following solvent cleaning in accordance with SSPC SP-1, another set of mild steel plates of size 75 mm X 75 mm X 4 mm were textured using the abrasive blasting process. Prior to abrasive blasting, and in accordance with industry best practices, the environmental parameters were checked to ensure that conditions are conducive to coating application. Further to this, all steel panels were cleaned using acetone in accordance with SSPC SP-1. Texturing of all steel panels were carried out simultaneously to prevent extraneous variables from affecting the experiment. All abrasive blasting works were carried out by trained and validated blasters under the conditions as shown in Table 3.5

Table 3.5 Abrasive blasting parameters and environmental conditions

Blast	Impact	Blast nozzle	Ta	Td	Ts	RH
pressure	angle	size	(°C)	(°C)	(°C)	
100–105 psi	70°–80°	2" (50.8 mm)	36.1	11.4	34.3	26.8%
Ta = Ambient temp. Td = Dew point temp. Ts = Surface temp. RH = Rel. humidity						

Two types of abrasives as discussed earlier were used for texturing the mild steel plates. For each abrasive, at-least five sample plates were prepared. The textured steel plates were again cleaned using acetone in accordance with SSPC SP-1 standard. A single coat of Belzona® 1341 was then applied using brush, by trained and validated applicators, at a wet film thickness of 400 µm – 500 µm in accordance with the manufacturer's data sheets. The DFT of all coatings were verified using the DFT gauge, Elcometer 456. Any readings not falling within this coating thickness range were discarded.

3.4.1.3 Preparation of non-textured, coated mild steel (grade A36) plates for adhesion studies in phase two

For adhesion studies in phase two, mild steel plates of size 75 mm X 75 mm X 4 mm were used. Prior to carrying out coating works, the steel plates were cleaned using acetone in accordance with SSPC SP-1 standard. A single coat of Belzona® 4151 was then applied using brush, by trained and validated applicators, at a wet film thickness of 300 µm – 400 µm in accordance with the manufacturer's data sheets. The DFT of all coatings were verified using the DFT gauge, Elcometer 456. Any readings not falling within this coating thickness range were discarded.

3.4.1.4 Preparation of non-textured, plasma-treated, coated mild steel (grade A36) plates for adhesion studies in phase two

For evaluating the effect of plasma treatment on adhesion, another set of mild steel plates of size 75 mm X 75 mm X 4 mm were used. Prior to carrying out coating works, the steel plates were cleaned using acetone in accordance with SSPC SP-1 standard. The cleaned

mild steel plates were then transferred to a plasma chamber. Air in the plasma chamber was then evacuated using a vacuum pump. After attainment of sufficient vacuum in line with standard operating procedures, fresh air was bled into the plasma chamber by adjusting the needle valve. This was followed by switching the plasma unit to maximum power setting. The optimum plasma generation level, characterized by a pink glow, was obtained by further adjusting the needle valve. Air plasma treatment was carried out for a period of 15 minutes. The mild steel plates were immediately transferred onto the coating bench for subsequent coating activities. A single coat of Belzona® 4151 was then applied using brush, by trained and validated applicators, at a wet film thickness of 300 µm – 400 µm in accordance with the manufacturer's data sheets. The DFT of all coatings were verified using the DFT gauge, Elcometer 456. Any readings not falling within this coating thickness range were discarded.

3.4.1.5 Adhesion tests in accordance with ASTM D-4541

Adhesion tests on coated mild-steel plates were carried out in accordance with ASTM D-4541. To begin with, all coated panels were left to fully cure in air in accordance with the manufacturer's data sheets. Next, aluminium dollies of 20 mm diameter were lightly abraded and attached to the cured coatings using Belzona® 1341 as the adhesive after lightly abrading the surface of the coating to remove the gloss and improve the surface energy. The dolly-adhesive-coating system was then allowed to cure for a further period in line with the manufacturer's data sheets. Once cured, the coating was carefully scribed around the dolly. Adhesive failure was defined as the point at which the coating

disbondment occurred from the substrate. It was noted during the pull-off tests that some runs produced cohesive failure in the coating or adhesive failure between the dolly and the adhesive used for fixing the dolly onto the coating. Such runs were considered void and the tests were repeated until three valid adhesive failure readings were obtained.

3.4.2 Samples for tribological characterization of epoxy nanocomposite coatings

This sub-section deals with the sample preparation, coating and testing procedures adopted to study the tribology of epoxy nanocomposite coatings applied onto mild steel substrates.

3.4.2.1 Preparation of control specimens and epoxy-graphene oxide (GO) nanocomposite coatings

In the second phase of this study, mild steel plates (grade A36), size 25 mm X 25 mm X 4 mm thickness were used as the substrate for developing the control specimens and epoxy-graphene oxide (GO) nanocomposite coating. All steel plates were ground and polished to a roughness (R_a) of $0.7\mu \pm 0.15\mu$. After grinding, the steel plates were cleaned using acetone followed by drying using an air blower. The air-dried steel plates were then subjected to air-plasma treatment using a Harrick Plasma cleaner for 15 minutes at a radio-frequency power of 30W.

Control specimens of pristine epoxy coatings were prepared by mixing 50 mL of the base and 25 mL of the solidifier components of Belzona® 4151 together for 2 minutes using a glass rod. The stated volume ratio of 2 parts of base to 1 part of solidifier was used based on product data sheets provided by the resin manufacturer. After this step, a known

volume (0.8 mL) of resin was deposited using a glass dropper onto the mild steel substrate. The mild steel plate was then carefully transferred onto the spin coater and spun at 350 rpm. A spin schedule as indicated in Figure 3.12 was used to ensure a coating DFT in the range of $350\ \mu\text{m} \pm 15\%$ ($\sim 300\ \mu\text{m}$ minimum – $400\ \mu\text{m}$ maximum). At the end of the spin cycle, the coated steel plates were transferred to a furnace and allowed to cure at 70°C for 15 hours followed by gradual cooling in air at room temperature for 72 hours prior to tribological testing.

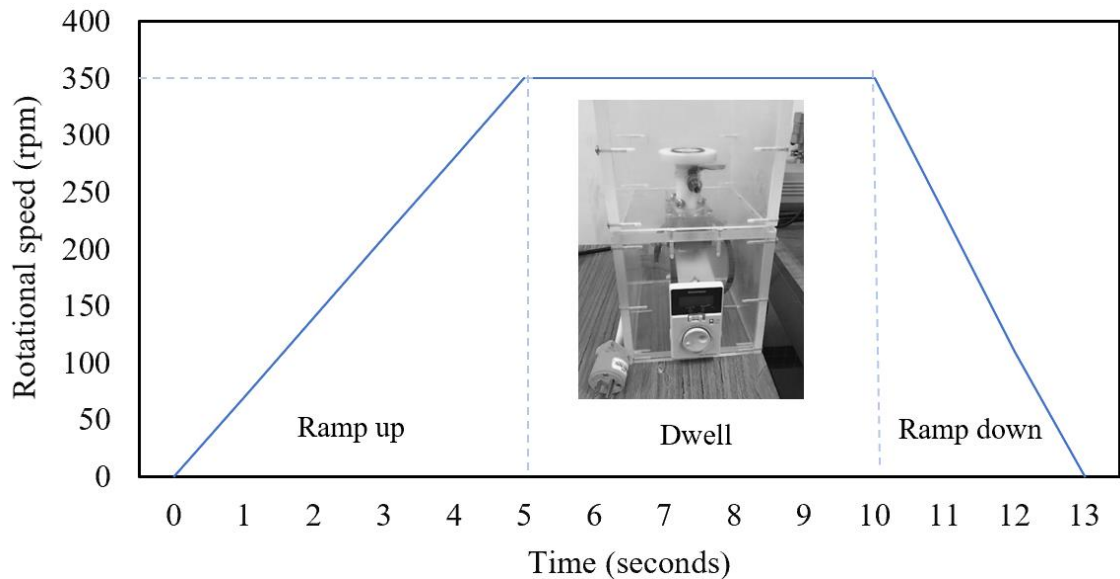


Figure 3.12 Lab fabricated spin coating and coating schedule adopted

For preparation of epoxy-GO nanocomposite coatings, different weight fractions of GO (0.25 wt.%, 0.5 wt.%, 1 wt.%, 1.5 wt.%) were incorporated into 50 mL of the base component of epoxy resin and stirred using an automatic mixer at 10000 rpm for 2 minutes. The viscosity of the epoxy base was found to have reduced within 1 minute of commencing the stirring process owing to the thixotropic nature of the epoxy base. 25mL

of the solidifier was then added to this mixture and mixed together for 2 minutes using a glass rod. At the end of this step, 0.8 mL of the epoxy-GO nanocomposite resin was deposited using a glass dropper onto the mild steel substrate. The mild steel plate was then carefully transferred onto the spin coater and spun at 350 rpm. At the end of the spin cycle, the coated steel plates were transferred to a furnace and allowed to cure at 70⁰C for 15 hours followed by gradual cooling in air at room temperature for 72 hours prior to tribological testing.

3.4.2.2 Preparation of hybrid epoxy nanocomposite coatings

In the third phase of this work, two types of hybrid epoxy nanocomposite coatings were prepared as listed below:

- Epoxy-GO-Titania hybrid nanocomposite coating
- Epoxy-GO-Alumina hybrid nanocomposite coating

For preparation of epoxy-GO-titania hybrid nanocomposite coatings, 0.5 wt.% of GO was dissolved in 75 mL of ethanol followed by ultrasonication for 10 minutes using a vibra-cell[®] VCX 130 ultrasonicator with an amplitude setting of 35% and pulse on/off cycle of 20/5 seconds. To this sonicated mixture, titania was added in varying proportions of 3 wt.%, 5 wt.% and 10 wt.% and the mixture was sonicated for another 10 minutes using similar settings. Further to this step, the mixture was placed on a hot plate set to 50⁰C and stirred using a magnetic pellet at 300 rpm for 60 minutes. At the end of 60 minutes, magnetic stirring was stopped, and the mixture was allowed to dry at 50⁰C for 72 hours. Dry GO-titania powder was obtained at the end of this process. Following this, the dry

hybrid powder in varying concentrations (0.5 wt.% GO + 3 wt.% titania, 0.5 wt.% GO + 5 wt.% titania, 0.5 wt.% GO + 10 wt.% titania) was incorporated into 50 mL of the base component of epoxy resin and stirred using an automatic mixer at 10000 rpm for 2 minutes. The viscosity of the epoxy base was found to have reduced within 1 minute of commencing the stirring process owing to the thixotropic nature of the epoxy base. 25mL of the solidifier was then added to this mixture and mixed together for 2 minutes using a glass rod. At the end of this step, 0.8 mL of the epoxy-GO-titania hybrid nanocomposite resin was deposited using a glass dropper onto the mild steel substrate. The mild steel plate was then carefully transferred onto the spin coater and spun at 350 rpm. At the end of the spin cycle, the coated steel plates were transferred to a furnace and allowed to cure at 70°C for 15 hours followed by gradual cooling in air at room temperature for 72 hours prior to tribological testing. Coated specimens were further analyzed using SEM and XRD for determining the nature and extent of agglomeration.

For preparation of epoxy-GO-alumina hybrid nanocomposite coatings, a similar procedure was adopted. To begin with, 0.5 wt.% of GO was dissolved in 75 mL of ethanol followed by ultrasonication for 10 minutes using a vibra-cell® VCX 130 ultrasonicator with an amplitude setting of 35% and pulse on/off cycle of 20/5 seconds. To this sonicated mixture, alumina was added in varying proportions of 3 wt.%, 5 wt.% and 10 wt.% and the mixture was sonicated for another 10 minutes using similar settings. Further to this step, the mixture was placed on a hot plate set to 50°C and stirred using a magnetic pellet at 300 rpm for 60 minutes. At the end of 60 minutes, magnetic stirring was stopped, and

the mixture was allowed to dry at 50°C for 72 hours. Dry GO-alumina powder was obtained at the end of this process. Following this, the dry hybrid powder in varying concentrations (0.5 wt.% GO + 3 wt.% alumina, 0.5 wt.% GO + 5 wt.% alumina, 0.5 wt.% GO + 10 wt.% alumina) was incorporated into 50 mL of the base component of epoxy resin and stirred using an automatic mixer at 10000 rpm for 2 minutes. The viscosity of the epoxy base was found to have reduced within 1 minute of commencing the stirring process owing to the thixotropic nature of the epoxy base. 25mL of the solidifier was then added to this mixture and mixed together for 2 minutes using a glass rod. At the end of this step, 0.8 mL of the epoxy-GO-alumina hybrid nanocomposite resin was deposited using a glass dropper onto the mild steel substrate. The mild steel plate was then carefully transferred onto the spin coater and spun at 350 rpm. At the end of the spin cycle, the coated steel plates were transferred to a furnace and allowed to cure at 70°C for 15 hours followed by gradual cooling in air at room temperature for 72 hours prior to tribological testing. Coated specimens were further analyzed using SEM and XRD for determining the nature and extent of agglomeration.

3.4.2.3 Tribological testing and characterization techniques

For carrying out tribological tests, a ball-on-disk configuration was used. Grade 440C stainless steel ball with a diameter of 6.3 mm and a hardness of 62 HRC, Rockwell, was used as the counterface. The experimental matrix used for the tests is shown in Table 3.6.

Table 3.6 Experimental matrix for tribological testing

Load (N)	Wear track	Cycles	RPM	Sliding dist.	Sliding velocity
35N	4 mm radius	100,000	239	~2500 m	0.1 m/s
50N	4 mm radius	100,000	239	~2500 m	0.1 m/s

Prior to every test, the counterface ball was cleaned thoroughly with acetone. In order to analyze the transfer film phenomenon, the counterface ball was examined under an optical microscope before and after cleaning of the ball after every run. For each set of samples, three wear tests were conducted. The depth of the wear track was measured using optical profilometry. The topography of the wear track was evaluated using SEM imaging and coating failure was confirmed via EDS spectrum analysis. For all coatings, hardness measurements were carried out using a micro-indentation tester by employing an indentation load of 0.2N and correlations with the coating wear life were drawn.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of various surface treatment techniques on adhesion strength

Surface treatment includes two major aspects that affect coating adhesion and therefore its longevity. They are a) surface cleanliness and b) surface texture

4.1.1 Surface cleanliness

Surface preparation constitutes the major element of any coating project and the quality of surface cleanliness required to be achieved must be clearly stated in the coating specification. The presence of loose rust, mill scale etc. have been cited by all coating manufacturers to affect the quality of adhesion. It can however be easily gathered that the presence of contaminants (such as oil) on any substrate can reduce its wettability and eventually impairing coatings' adhesion. Though studies in this regard cannot be found, findings reported later in this section should help the readers appreciate the importance of surface cleanliness in improving the adhesion of coatings on both nontextured and textured substrates. In this first phase of this work, mild steel plates have been textured using Olivine (OL 080) and Calcium Silicate (CS 085) abrasives as outlined in

Tables....and....The cleanliness of a substrate is analyzed via two methods namely a) visual evaluation and b) chemical analysis of textured substrates

4.1.1.1 Visual evaluation by comparison with SSPC VIS-1 standard

For substrates textured using abrasive blasting, visual evaluation of cleanliness is done in accordance with the SSPC VIS-1 standard. The SSPC VIS-1 standard is a visual standard and categorizes previously unpainted mild steel substrates into four main categories depending on the condition of the substrate at the time of assessment. The four categories can be briefly described as follows: a) condition A representing tightly adherent mill scale b) condition B representing rust and mill scale c) condition C representing a total rusted surface with little-to-no visible pittings d) condition D representing a fully rusted surface with visible pittings. Categorizing substrates this way is important since the initial condition of the previously unpainted substrate greatly affects the appearance of the textured surface and provides a means to check the quality of the blast while keeping subjectivity of the end result to a minimum. Four major levels of post-abrasive blasting cleanliness are often referred to within the industry. They are SSPC SP 5, SSPC SP 10, SSPC SP 6 and SSPC SP 7 of which SSPC SP 5 also referred to as a *white metal finish* representing the highest degree of achievable cleanliness with no oil, grease, visible rust or mill-scale leaving the substrate uniformly white in appearance. Major coating manufacturers often tend to specify SSPC SP 10 as an acceptable level of cleanliness for achieving excellent coating adhesion. Visual inspection of blasted surfaces showed that both Olivine (OL 080) and Calcium Silicate (CS 085) abrasives have produced surfaces

with an SSPC SP 5 level of finish. Figure 4.1 a) – c) illustrates the initial and final conditions of the mild steel substrates as determined using SSPC VIS-1. The final appearance of all images, taken using a digital camera under natural lighting are in agreement with the definition of SSPC SP 5 and can be used as a reference tool for end users wishing to employ the abrasives in this study in future.



Figure 4.1 a) Appearance of non-textured mild steel substrate b) Appearance of substrate textured using Olivine (OL 080) abrasive with SSPC SP 5 finish c) Appearance of substrate textured using Calcium Silicate (CS 085 abrasive) with SSPC SP 5 finish

4.1.1.2 Chemical analysis of textured substrates

Non-visible soluble salt contamination is another factor that affects the adhesion of coatings on a substrate. In addition to adhesive delamination of a coating, the presence of soluble salts on the substrate on which a coating is applied can prove to be detrimental to the life of a coating owing to a phenomenon known as osmotic blistering. Substrates can get contaminated with ionic salts of chlorides, sulphates, carbonates, ammonium and nitrates based on the service it is placed in. For example, a pump through which sea water flows will see a lot of chloride salts ingrained within the substrate. Similarly, another equipment operating in a fertilizer plant could see an increased amount of carbonate,

nitrate or ammonium salts on its substrates. It is essential that substrates are made free from dissolved salts prior to the application of a coating system. Soluble salt contamination in the industry is generally measured and reported as chloride ion concentration or total ion concentration (which is a sum of all ionic constituents such as chlorides, sulphates, carbonates, ammonium and nitrates, on the substrate). As discussed earlier, the type of test to be used in any given scenario is largely governed by the type of chemical media the substrate has been immersed under. The amount of chloride ions is often independently verified as it is understood that these ions due to their smaller size actively increase the rate of osmosis. Additionally, large temperature gradients between the internal and external surfaces of the equipment (caused by hot media inside and non-insulated equipment walls) can increase the osmotic gradient and is characterized by large blisters on the surface of the coating (the coating system in this case acts as a semi-permeable membrane). Though it may be argued that the permeability of the coating system has a role to play in the degree of osmotic blistering and that different coatings may blister to a different rate in a given environment, theoretical salt contamination levels (chloride ions or total ions) of the substrate ought to be zero. Practically, zero salt contamination is quite difficult to achieve, and acceptable levels are not governed by any industry standard. Several manufacturers, however, specify a maximum chloride ion or total salt contamination level that is acceptable based on in-house tests. Having said the above, it must be realized that the blasting abrasive should not be a source of salt contamination. The mining and production processes of abrasives can be a source of salt contamination as also the packaging and shipping processes. These salts can get

transferred to the substrate during the blasting process and be detrimental to the coating in the long run. Figures 4.2 a) and b) represent MS substrates textured using Calcium Silicate (CS 085) and Olivine (OL 080) abrasives respectively. EDS scans presented Figures 4.2 c) and d) also show no traces of chlorine ions proving that both abrasive types and grades can be used for all texturing substrates. For large and critical coating projects, the employment of EDS analyses with data generated from multiple points is advised as commonly available industrial tests often cannot detect extremely trace amounts. This can also be used as an abrasive screening test by end users for product pre-qualification purposes.

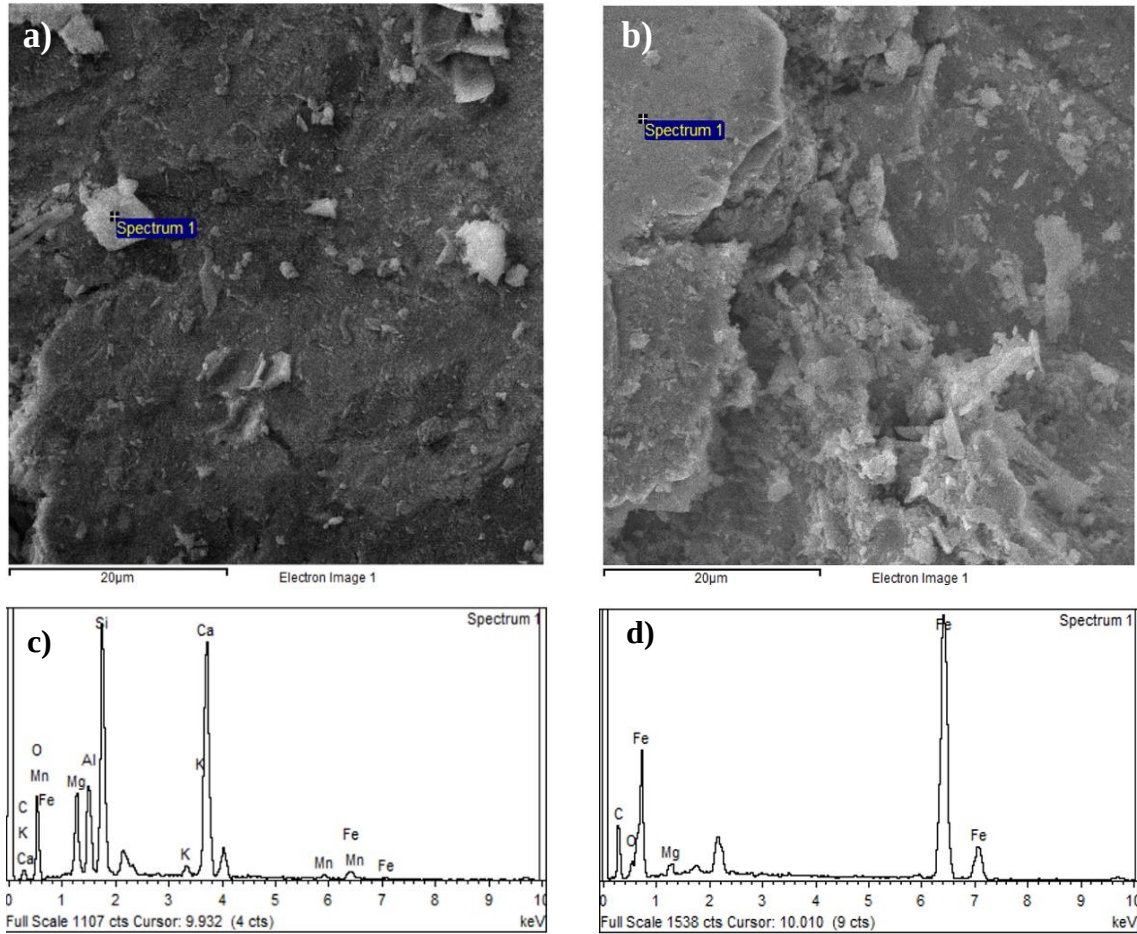


Figure 4.2 a) and c) SEM image and corresponding EDS scan of mild steel substrate textured using Calcium Silicate (CS 085) b) and d) SEM image and corresponding EDS scan of mild steel substrate textured using Olivine (OL 080)

4.1.2 Surface texture, wettability and correlation with adhesive strength

Surface texture is a complex terminology and involves several aspects namely: flaws, lay, waviness and roughness. Of these, the roughness aspect of surface texture is quite important as the adhesive strength of any coating is affected greatly by it (63,64). However, surface roughness itself is quite complicated and is usually characterized by various parameters such as, height parameters, spatial parameters and shape parameters.

Coating manufacturers always recommend an optimum surface roughness that need to be achieved prior to the application of a specific coating system. Commonly called anchor pattern or surface profile, this recommended value almost always considers only the height parameter of surface roughness. Earlier studies have shown that in addition to the height parameter, spatial parameters of surface roughness can also influence the coating adhesion levels (59,61). For the purpose of this work, only the height parameter of surface roughness is considered and correlated with the adhesion strength of the Belzona® 1341 coating system applied onto different substrates. To add another dimension to this study, the change in surface free energy characteristics of substrates prior textured using different abrasives has also been reported.

4.1.2.1 Role of surface texturing on promotion of mechanical bonding

The graph presented in Figure 4.3 highlights the effect of abrasive blasting on the adhesive strength of high build coatings applied onto mild steel substrates. It is clear that there is a dramatic increase in adhesive strength of the coating system when applied onto a textured surface. On non-textured surfaces, the adhesive strength values are measured to be <1000 psi (6.89 MPa); however, the mean adhesive strength is found to have improved by approximately three times when applied onto substrates textured using Calcium Silicate (CS 085) and Olivine (OL 080) abrasives. The reason for this can be attributed to two main mechanisms – mechanical interlocking and increased wettability.

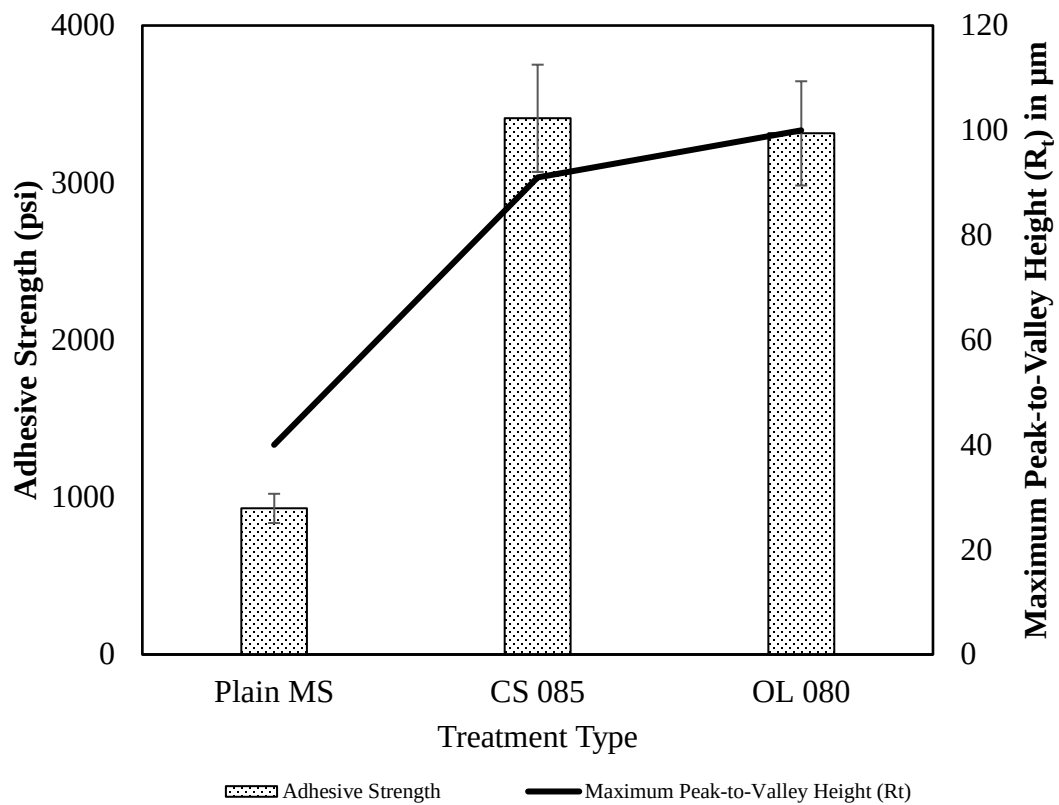


Figure 4.3 Effect of surface texturing using Calcium Silicate (CS 085) and Olivine (OL 080) abrasives on the adhesive strength of high build coatings applied onto mild steel substrates

Texturing of surfaces via abrasive blasting produces peaks and valleys on an otherwise flat and smooth surface (a theoretical flat and smooth surface has an ‘*r*’ value close to 1). Figures 4.4 a) and b) represent the SEM scans of the abrasive blast textured surfaces at 500X magnification. The substrate is characterized by the presence of peaks and troughs reflecting the angular nature of both types of abrasives chosen for this study. The presence of such peaks and valleys allow the coating to properly wet out the surface and promotes mechanical interlocking which subsequently makes it harder for the coating to be pulled

out adhesively off the substrate. Optical profilometric scans reveal that surface texturing using CS 085 abrasive generates a surface index of ~8.5 while surface texturing using OL 080 abrasive produces a surface index of ~11.5.

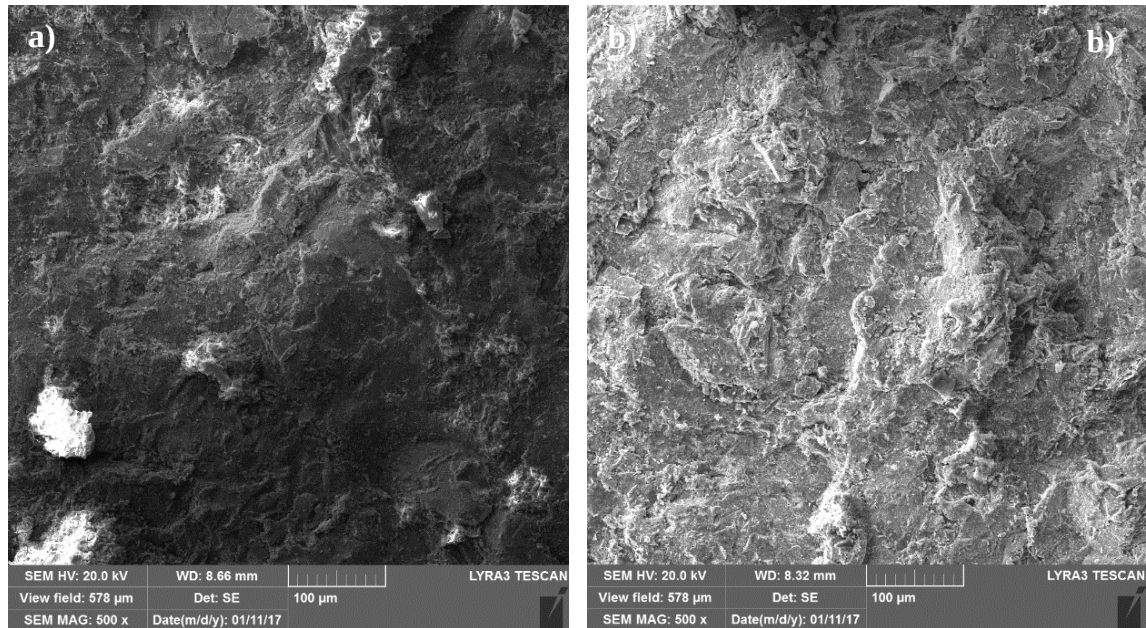


Figure 4.4 a) Topography of mild steel surface textured using Calcium Silicate (CS 085) b) Topography of mild steel surface textured using Olivine (OL 080)

In addition to the above, it may also be noted that there is also a strong positive correlation between the R_t values (maximum peak-to-valley distance) measured using the replica tape method (where the evaluation length is taken as the diameter of the micrometer anvil or spindle) in accordance with ASTM D-4417, Method C and the adhesive strength of the coating. Earlier studies have proven that optimum R_t values lie in the range of 90 – 110 μm for achieving highest levels of adhesion of high build coatings on mild steel substrates (61).

4.1.2.2 Effect of surface texturing on wettability

The Young's water contact angle (θ_y) values have been calculated using the apparent contact angle, θ_m and r . Figures 4.5 a) and b) shows the water contact angle images depicting the values of θ_m for Calcium Silicate (CS 085) and Olivine (OL 080) textured substrates respectively.

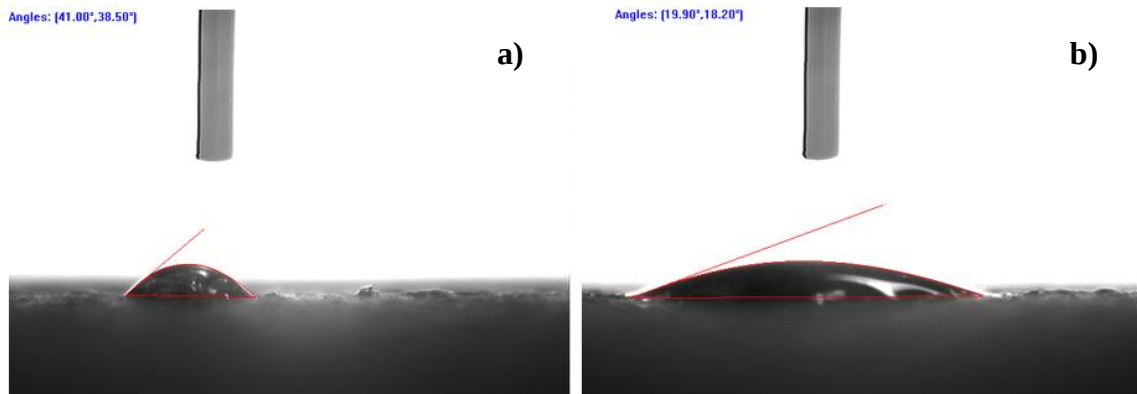


Figure 4.5 a) Apparent water contact angle measured on mild steel surface textured using Calcium Silicate (CS 085) b) Apparent water contact angle measured on mild steel surface textured using Olivine (OL 080)

The graph presented in Figure 4.6 indicate a strong negative correlation between surface index and θ_y . This implies that surface texturing directly results in improved wettability by enhancing the surface free energy. This subsequently helps the coating wet out the substrate better resulting in enhanced adhesion.

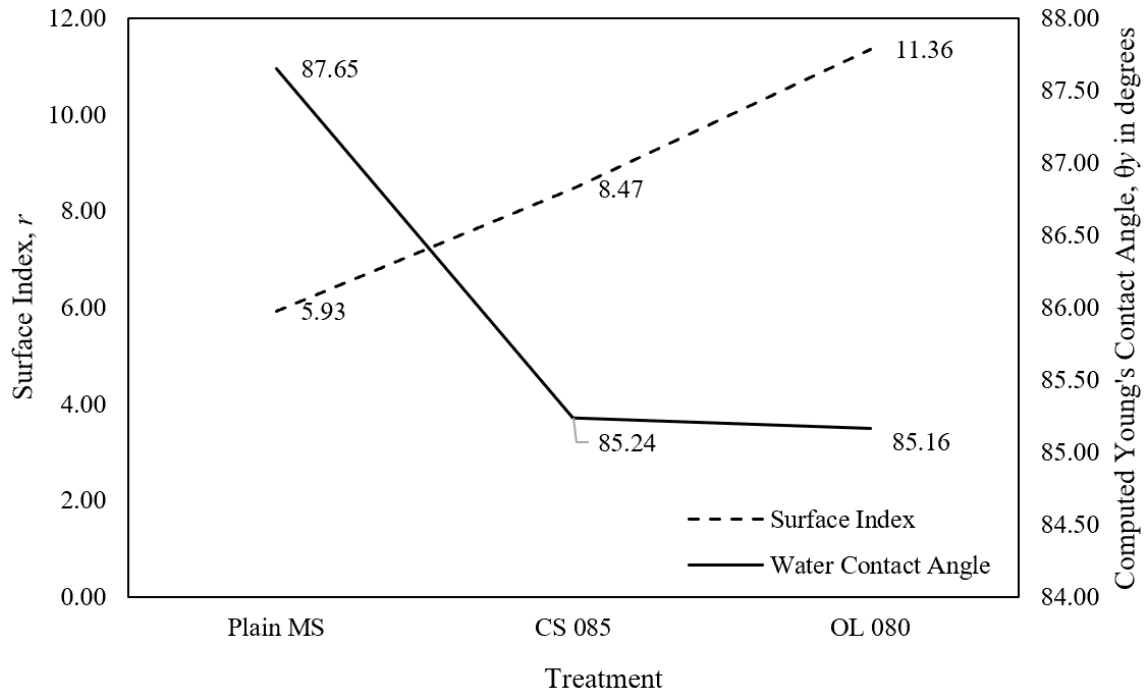


Figure 4.6 Variation of water contact angle (θ_y) with surface index

4.1.2.3 Analysis of variance (ANOVA)

To confidently conclude that the variation in adhesive strength is due to the treatments (no texturing v/s surface texturing using abrasives) and not random chance, ANOVA analysis on the obtained data have been carried out. The ANOVA technique has been widely employed in research and industry to identify variations between and within treated groups. An F-ratio value of 249.26 has been observed at $p < 0.05$ leading to the conclusion that the findings from the first phase of this study are statistically significant and that surface texturing using abrasive blasting leads to increased coating adhesion. No post-hoc analyses have been carried out as the statistical significance of the means are not important to this part of the study.

4.1.3 Effect of plasma treatment on coating adhesion

It is clear from earlier discussions that both mechanical interlocking and surface wettability (which is in-turn a function of surface free energy) play an important role in enhancing coating adhesion. One of the main objectives of this research is to evaluate the independent effect of surface free energy on adhesion by keeping the surface index constant or in other words, by studying the effect of plasma treatment on non-textured surfaces. For the second phase of this work, a new pristine coating system, Belzona[®] 4151 has been used and will form the basis for the rest of this research. The graph shown in Figure 4.7 a) presents the variation in adhesive strength of the coating applied onto non-textured, non-plasma treated and non-textured, plasma treated substrates.

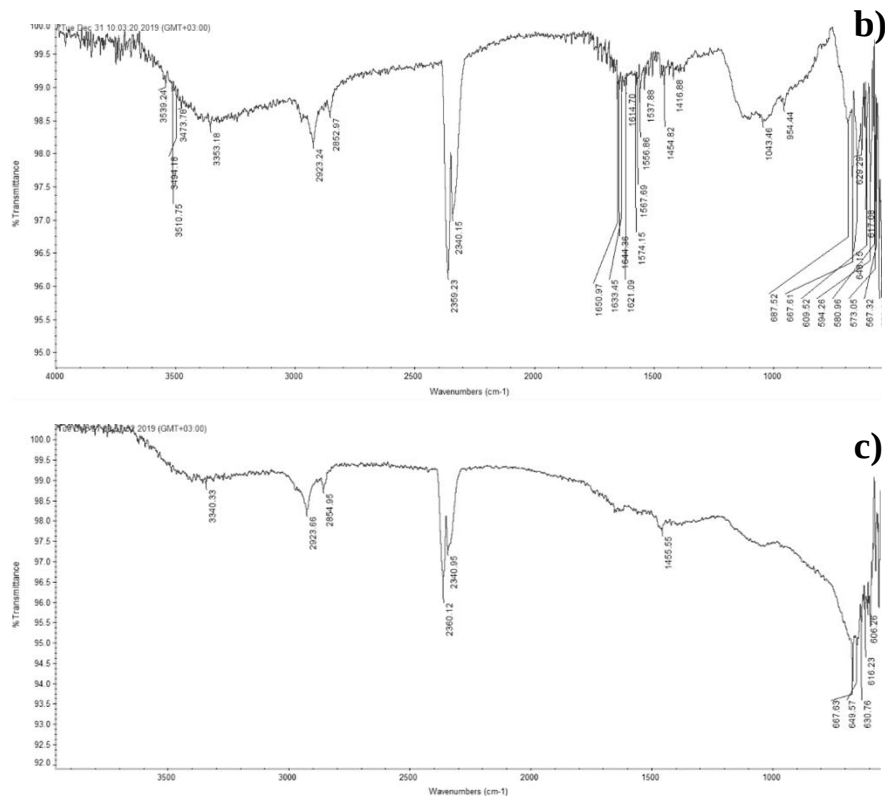
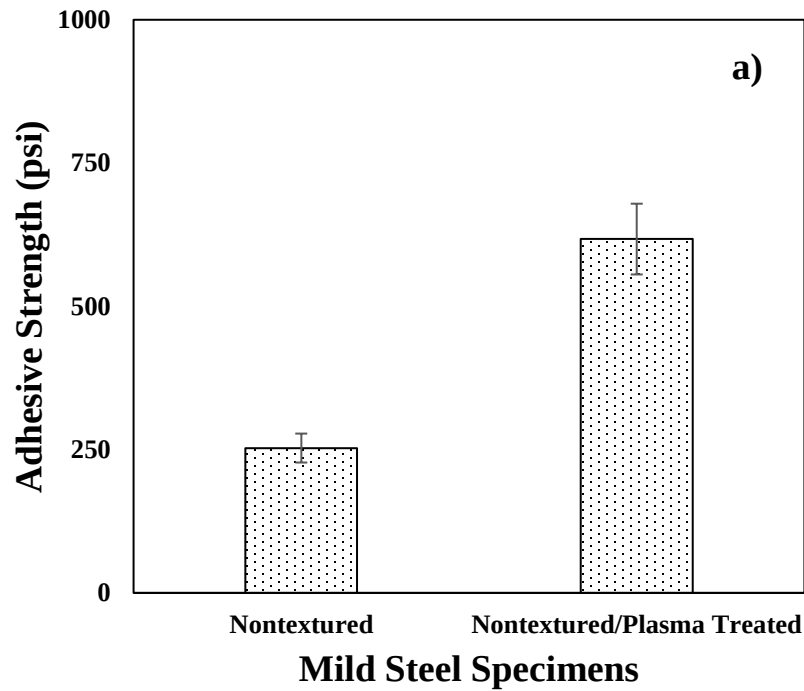


Figure 4.7 a) Variation in adhesive strength of the coating applied onto non-textured, non-plasma treated and non-textured, plasma treated substrates b) FTIR spectrum

of non-textured, non-plasma treated mild steel c) FTIR spectrum of non-textured, plasma treated mild steel

While the pristine epoxy system applied onto non-textured, non-plasma treated mild steel substrates fail at approximately 260 psi, the adhesive strength improves by nearly 2.5 times when the coating system has been applied onto plasma treated substrates. This improvement can be attributed to the improvement in surface free energy arising from increased chemical bonding sites available in the form of dangling bonds and oxygen containing functional groups. Comparative FTIR scans of non-textured, untreated and plasma-treated mild steel substrates presented in Figures 4.7 b) and c) clearly reveal that air plasma treatment has caused the removal of several low energy bond peaks in the fingerprint region of the spectrum which is indicative of the cleaning effect. Additionally, it can be observed from Figure 4.7 b) that there is a peak at 1650 cm^{-1} corresponding to the C=C alkene bond stretching in the non-plasma treated samples. Air plasma treatment has cleansed the surface from impurities as characterized by the absence of peaks in the $1600 - 1680\text{ cm}^{-1}$ band. Though a large amount of research work is available in literature citing the benefits of air plasma treatment (65,66), no such pre-treatment has been carried out for majority of the works involving epoxy coatings on metallic substrates. Furthermore, all works wherein air plasma treatment has been employed involve thin film coatings ($<100\text{ }\mu\text{m}$) while this work shows the impact of air plasma treatment on improving the strength of high build epoxy coatings ($>200\text{ }\mu\text{m}$) on mild steel substrates.

4.1.4 Summary

- The effect of surface texturing using novel abrasives namely Olivine and Calcium Silicate on the adhesive strength of a commercially available high-build epoxy coating has been evaluated. The results of the adhesion test prove that both Olivine and Calcium Silicate abrasives promise to be excellent alternatives to Coal Slag and Garnet.
- Air plasma treatment has improved the adhesive strength of the pristine high-build epoxy coating system applied onto nontextured substrates.

4.2 Tribological characterization of epoxy-GO nanocomposite coatings

4.2.1 Effect of load on the tribological characteristics of pristine epoxy coatings

Initially, the pristine epoxy coating, Belzona[®] 4151, is evaluated for its load bearing capacity at 35N load at a linear sliding velocity of 0.1 m/s and a wear track radius of 4 mm for 100,000 cycles (sliding distance = 2500 m). The pass criteria for each test load has been arbitrarily set at 100,000 cycles with no coating failure, where coating failure has been defined as metal-to-metal contact between the counterface and the substrate as indicated by a sharp variation in the coefficient of friction graph along with scar marks on the counterface and depth of wear track exceeding 350 μm as measured using optical profilometry. The coefficient of friction (CoF) graph presented in Figure 4.8 a) show no major variation in the CoF readings for the pristine epoxy coating tested until 100,000 cycles at 35N load. The images of the counterface ball before test, after test and after cleaning have also been presented in Figures 4.8 b) – d). The presence of no scar marks on the counterface are indicative of the fact that failure hasn't occurred. Optical profilometer scans presented in Figures 4.8 e) and f) also reveal that the depth of the wear track is < 350 μm . SEM images of the wear track along with the corresponding EDS spectrum shown in Figures 4.8 g) and h) also do not indicate any spikes for Fe ($K\alpha = 6.405$) confirming that the coating has withstood 100,000 cycles without failure at 35N load under the defined test conditions.

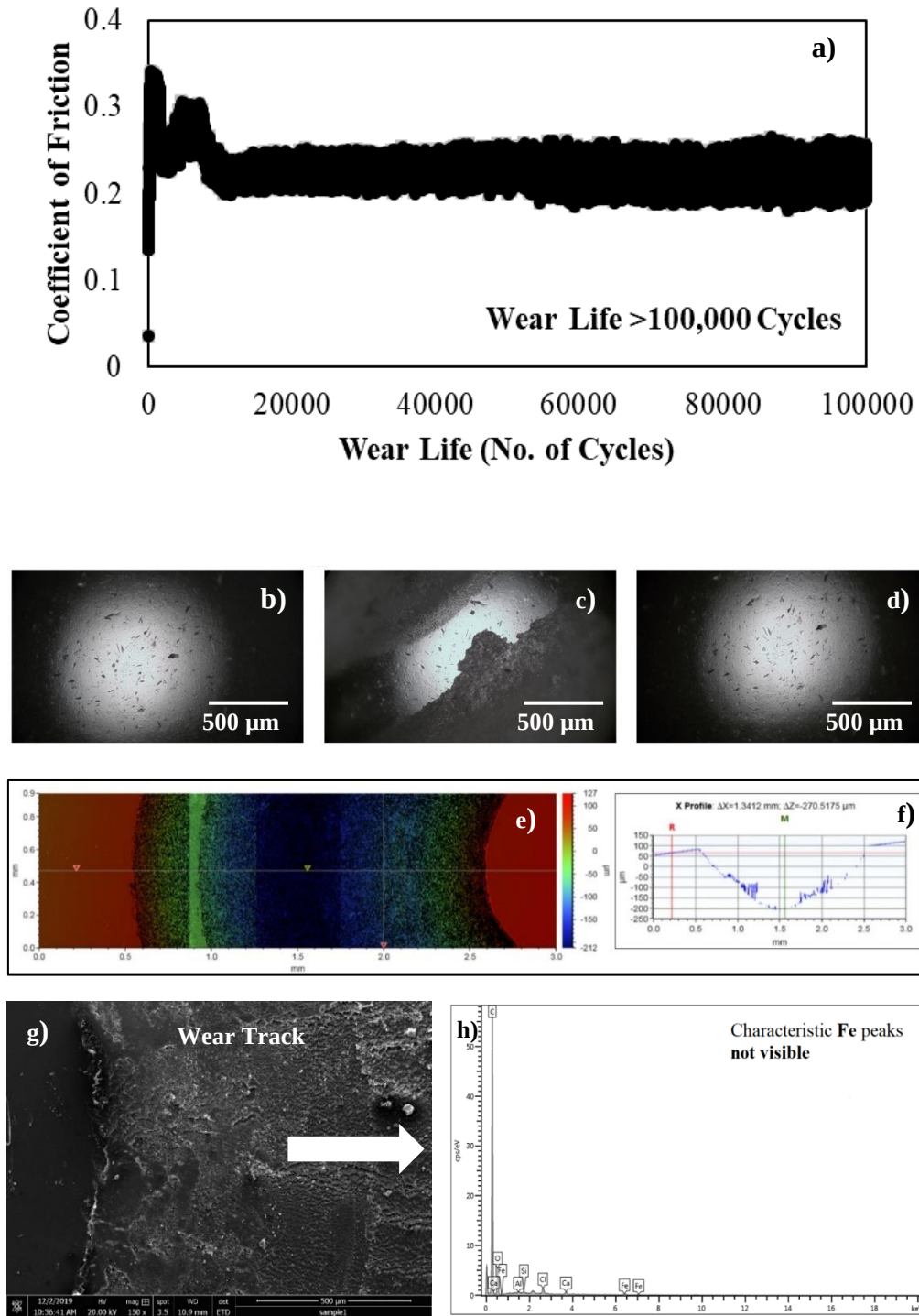


Figure 4.8 Pristine epoxy coating tested at 35N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with corresponding EDS scan

Increasing the load to 50N results in premature failure of the coating as evidenced by the spike in the CoF graph (shown in Figure 4.9 a)) at approximately 12,000 cycles and extending until about 13,500 cycles. The wear life calculated as an average of three runs is approximately 13,000 cycles. The presence of deep scar marks on the counterface immediately following testing, and as clearly evident from Figure 4.9 c), indicate that metal-to-metal contact (counterface ball with the steel substrate) could have occurred. Optical profilometer scans presented in Figures 4.9 e) and f) reveal that the depth of the wear track is $>350\text{ }\mu\text{m}$. This is one of the first evidences of coating failure. SEM images of the wear track along with the corresponding EDS spectrum presented in Figures 4.9 g) and h) indicate a sharp spike for Fe ($K\alpha = 6.405$) clearly showing that the mild steel substrate has been exposed and that the coating has failed.

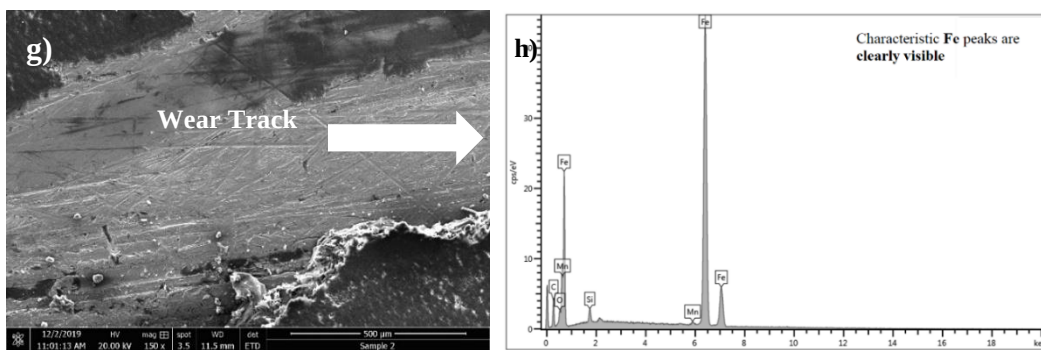
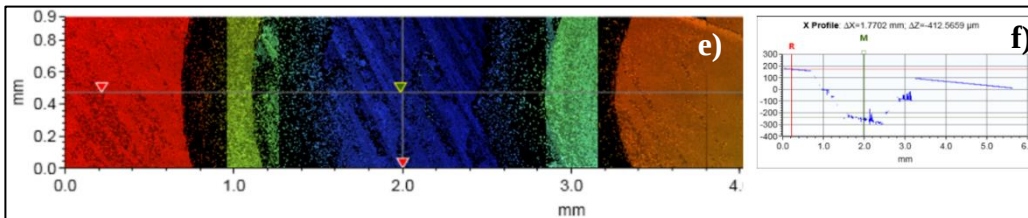
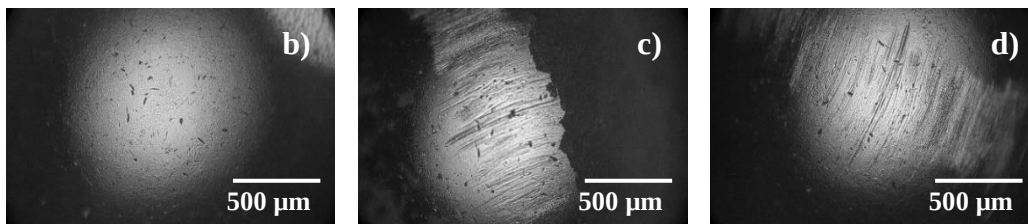
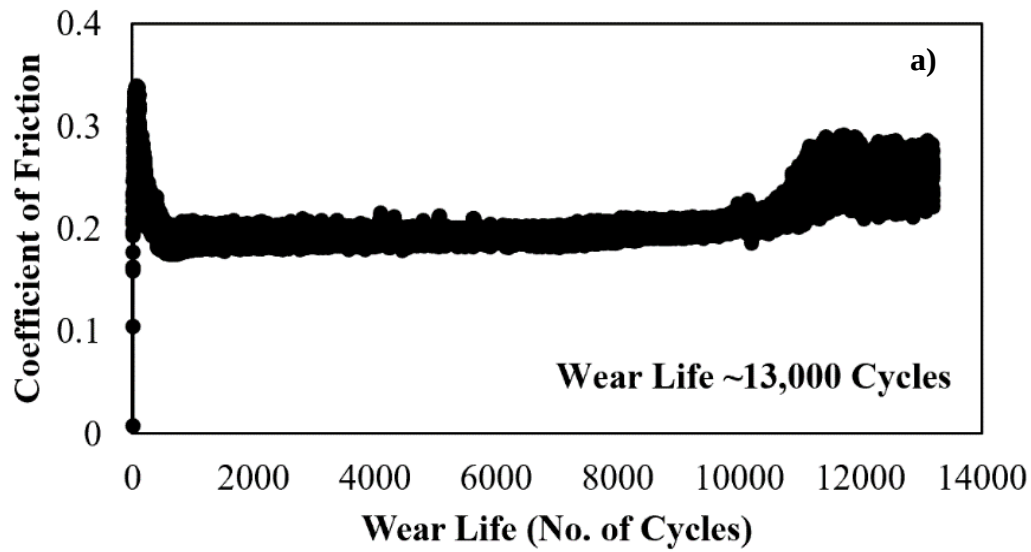


Figure 4.9 Pristine epoxy coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with corresponding EDS scan

In order to study the wear mode, high magnification (1500X) images of the wear track have been obtained. It is clear from Figure 4.10 that the pristine epoxy has undergone a high degree of rapid abrasive wear as characterized by the presence of groove like features all along the wear track within a short testing time (~13,000 cycles). Such crisscrossing features can be attributed to the formation of sharp wear debris particles during the testing process under high loads. These wear debris particles then act as abrasive third bodies between the counterface and the surface of the pristine epoxy thereby increasing the rate of wear.

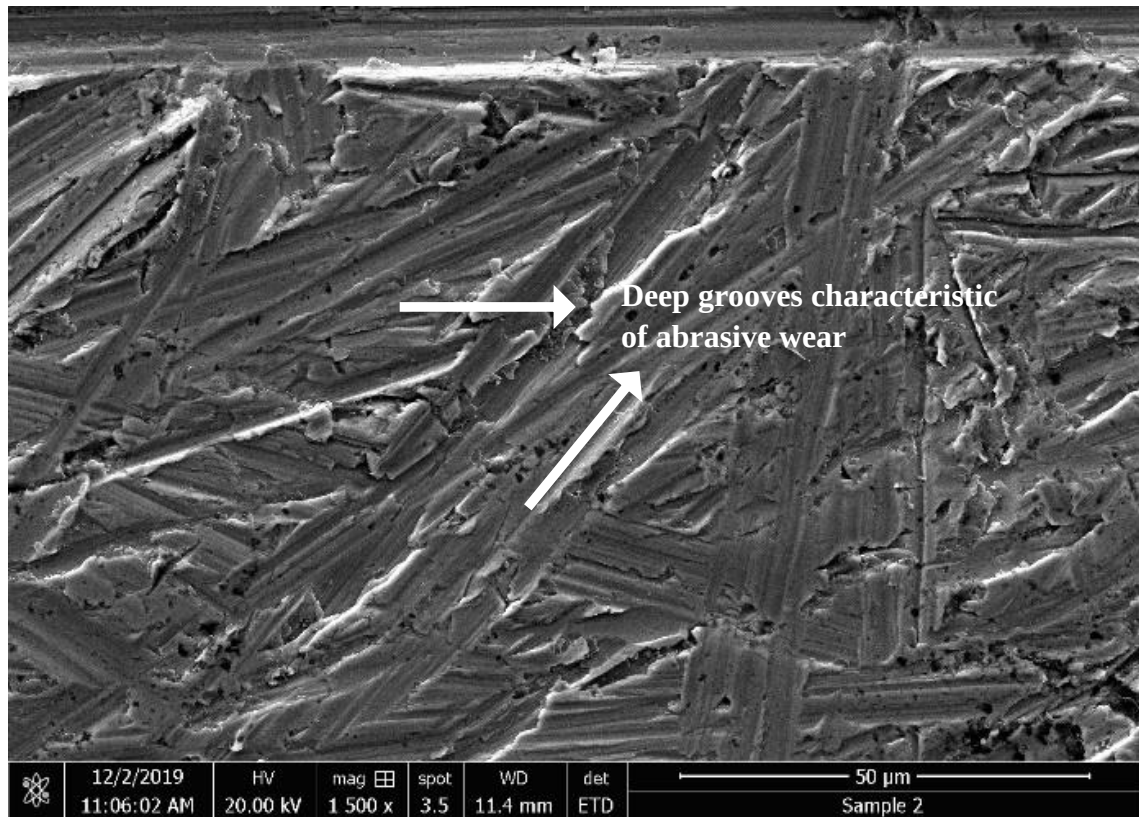


Figure 4.10 SEM image of wear track at high magnification (1500X) after tribological testing of pristine epoxy coating at 50N load

4.2.2 Effect of GO filler concentration on the tribological characteristics of epoxy-GO nanocomposite coatings

Following the tribological testing of pristine epoxy coating, the failure load has been ascertained as 50N. GO in varying concentrations (0.25 wt.%, 0.5 wt.%, 1 wt.% and 1.25 wt.%) have been added to the pristine epoxy matrix and tested at 50N load. The graph presented in Figure 4.11 show the effect of GO concentration on the wear life of the epoxy nanocomposite.

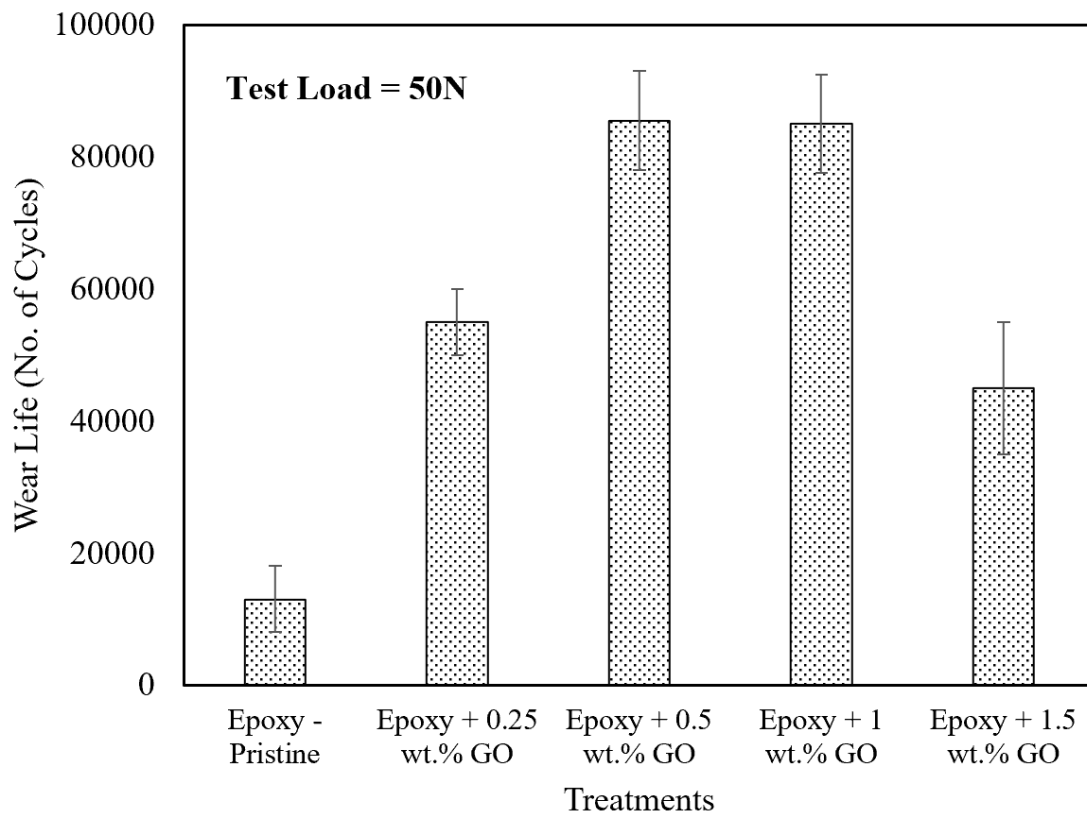


Figure 4.11 Effect of GO filler concentration on the wear life epoxy nanocomposite tested using a steel ball counterface at 50N normal load

It is clear that the addition of GO nanofillers has led to a substantial increase in wear life when compared to the pristine epoxy system. There is also a clear bell-shaped trend that is observed indicating that there is an optimum filler loading beyond which the improvement in wear life is not as pronounced. In this sub-section, two data points of interest namely, Epoxy + 0.5 wt.% GO and Epoxy+1.5 wt.% GO have been evaluated further to explain the reason for the improvement in wear life and subsequent decline respectively.

4.2.2.1 Tribology of Epoxy + 0.5 wt.% GO nanocomposite coating

The coefficient of friction (CoF) graph presented in Figure 4.12 a) show a spike in readings at around 85,500 cycles indicating that the coating could have failed at around this point. The average wear life has increased by approximately 6.5 times when compared to the pristine epoxy system. The counterface images presented in Figure 4.12 c) indicate that a transfer film of GO has formed on the surface during the testing process. This has protected the counterface from damage as evident from the absence of any wear marks. The absence of wear scars can also imply that the failure mode of the Epoxy-GO nanocomposite coating could be predominantly adhesive as opposed to abrasive wear as seen in the pristine epoxy system. Hayrettin et al. (1) have cited the importance of closely analyzing the effect of tribological tests on the counterface as the protection of both surfaces are important in a tribo-system. Optical profilometer scans presented in Figures 4.12 e) and f) reveal that the depth of the wear track is $>350\text{ }\mu\text{m}$ and is a clear evidence of coating failure as seen from earlier discussions. SEM images of the wear track along with

the corresponding EDS spectrum has been generated (see Figures 4.12 g) and h)) and the Fe ($K\alpha = 6.405$) spike clearly indicate coating failure.

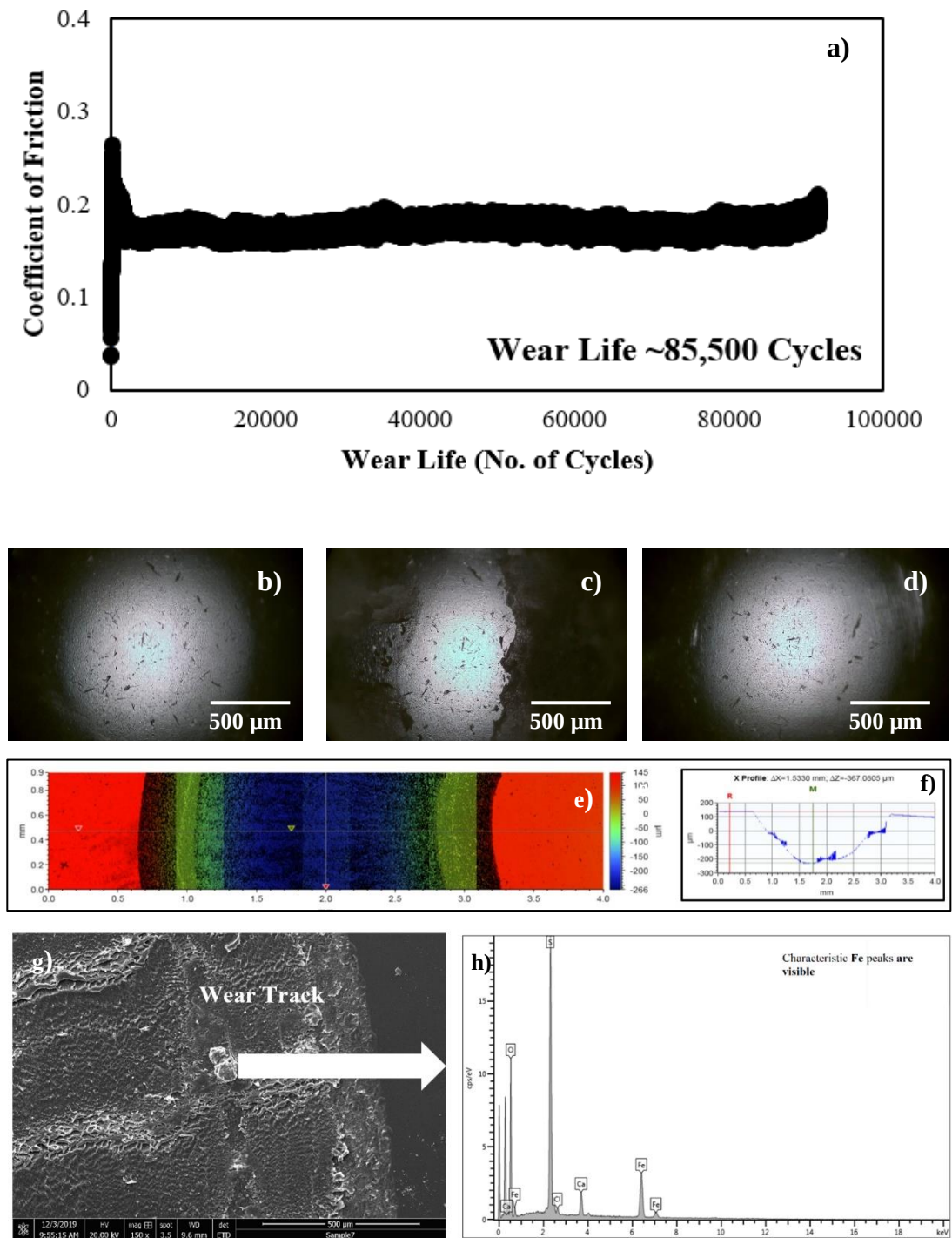


Figure 4.12 Epoxy+0.5 wt.% GO nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan

In order to ascertain the failure mode, SEM scans have been generated of the wear track at both low (50X) and high magnifications (1500X). Analysis of the images shown in Figures 4.13 a) – c) reveal a huge variation from the wear mode depicted by the pristine epoxy system under the same testing conditions and tribo-environment. A striking feature of the low magnification image is the presence of equidistant waves all along the wear track, extending radially and perpendicular to the sliding direction. The wear morphology can be described as constituting two distinct wear patterns a) large wave like features also called tribo-layers extending from end-to-end of the wear track as shown in Figure 4.13 a) and b) small wave like features of the order of 50 – 100 μm as presented in Figures 4.13 b) and c).

In sliding contacts, the maximum shear stress occurs at the surface due to high friction. The repeated sliding of the steel ball produces wear debris (via adhesive wear) and subsequent compaction of the so produced wear debris leads to the formation of tribo-layers. The absence of such features on the pristine epoxy system can be attributed to its much higher wear rate which prevents the formation of tribolayers.

The small wave like features which are observed in the high magnification SEM scans are characteristics of surface fatigue. During the wear test, the repeated sliding of the steel ball under high normal loads induces cyclic stress concentration in front of the steel ball, which in turn causes surface fatigue. The surface fatigue nucleates minute cracks in the surface and subsurface of the epoxy nanocomposite and propagates the cracks parallel as well as perpendicular to the sliding direction. Subsurface cracks that propagate down to

the substrate under repeated cyclic loading will cause subsequent adhesive delamination of the coating from the substrate-coating interface. Eventually, the formation of a network of microcracks produces miniature wave like features on the wear track.

Khun et al. (40) have also observed the formation of similar tribo-layers and miniature-wave like features in graphene sheets modified epoxy bulk composites slid against a 100Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for 300 m at a sliding speed of 0.03 m/s under a normal load of 1 N. It was postulated by the authors that the enhanced embrittlement of the epoxy-graphene sheets nanocomposite when compared to the pristine epoxy bulk was the reason for such miniature waves like features to be formed on the nanocomposite.

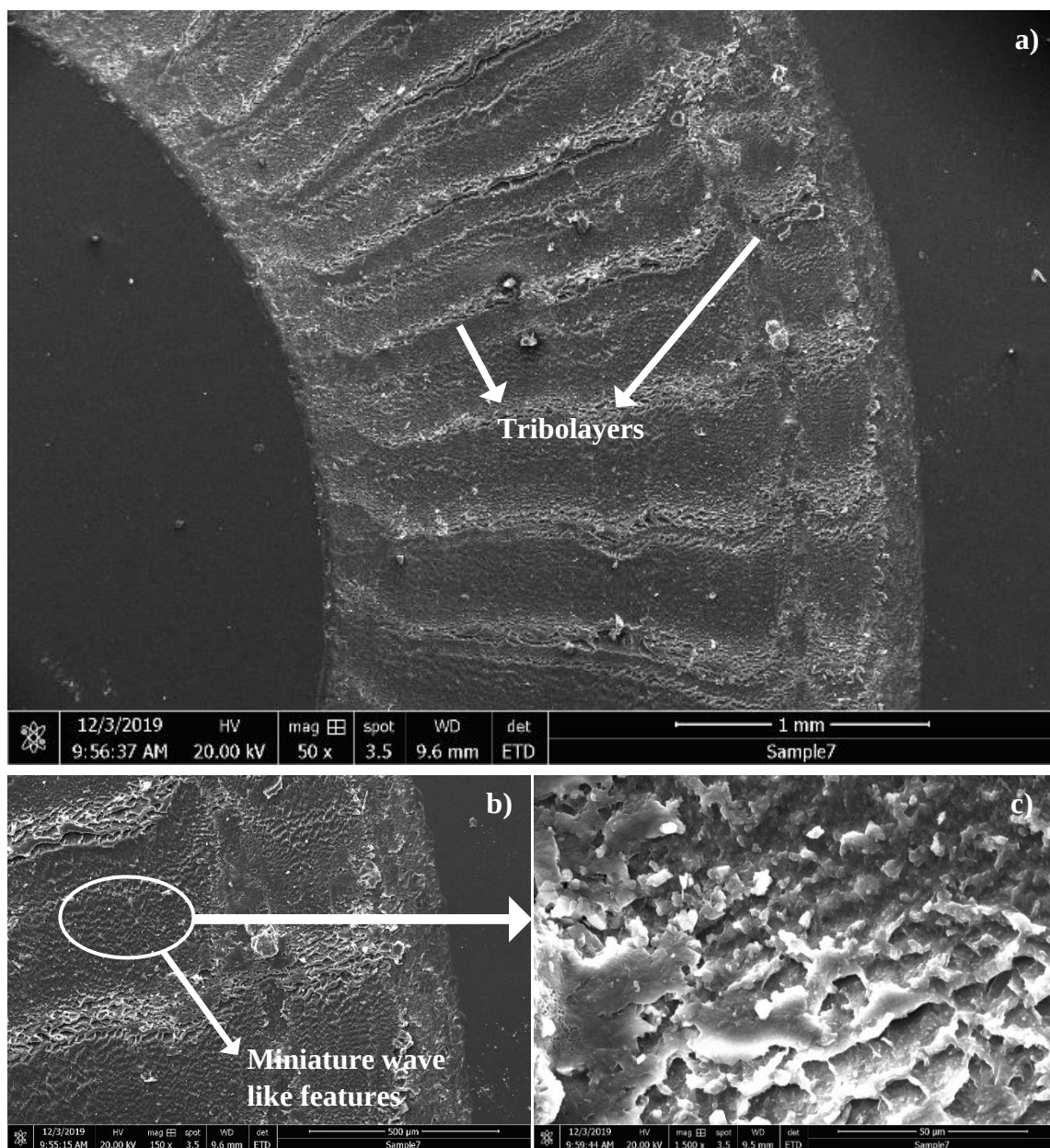


Figure 4.13 SEM images showing a) Tribolayers b) Miniature waves due to fatigue wear mode c) Magnified image of wave like features

In order to accurately cite the various reasons for this improvement in wear resistance when compared to the pristine epoxy coating system tested at 50N normal load, attention has been drawn towards the nature of the GO fillers. GO has a layered structure. Under

sliding wear regime, the GO nanoparticles are pulled out along with the wear debris. These particles then act as a solid lubricant between the steel ball and the epoxy nanocomposite matrix. This phenomenon is confirmed by comparing the frictional coefficient of the *steel ball – pristine epoxy coating* system to the *steel ball – Epoxy + 0.5 wt.% GO nanocomposite epoxy coating* system at 50N load. While the pristine epoxy coating tribo-system shows a steady-state friction coefficient of 0.21, the friction coefficient of the nanocomposite epoxy tribo-system is 0.17, a substantial reduction of almost 20 % in the frictional coefficient value.

In addition to this, proper dispersion of the nanoparticles within the epoxy matrix helps improve the strength of the nanocomposite by seamlessly transferring the stresses from the polymer to the GO nanoparticle network. The XRD spectrum of the GO nano-powders used in this study is presented in Figure 4.14. A sharp diffraction peak from the basal plane (001) at a diffraction angle of $2\theta = 10.6^\circ$ corresponding to a ‘d’ spacing of 0.419 nm has been observed.

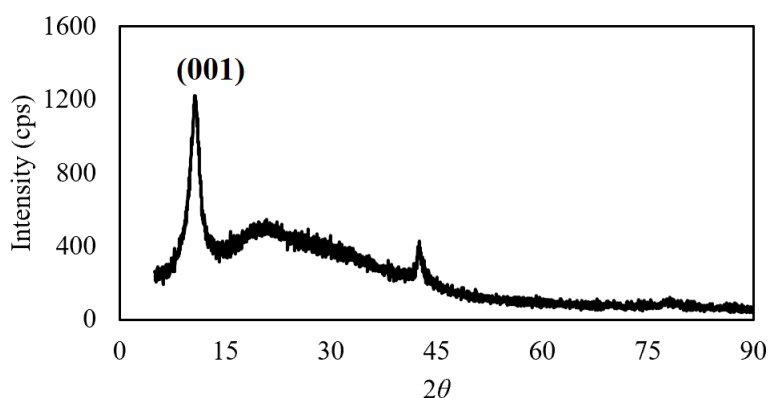


Figure 4.14 XRD spectrum of GO nanoparticles

Past studies have also shown that GO exhibits a sharp diffraction peak (001) at similarly low diffraction angles (67). The absence of such a peak in the XRD spectrum of the Epoxy-0.5wt.% GO nanocomposite coating shown in Figure 4.15 clearly indicates that homogeneous dispersion has been achieved through total exfoliation of GO sheets. Similar observations were also made by Abdullah and Ansari (68).

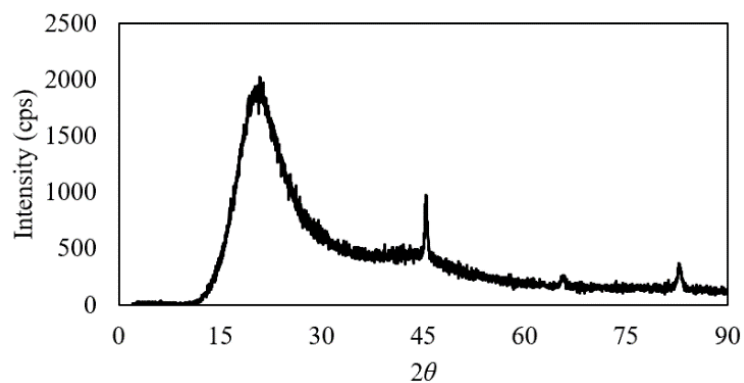


Figure 4.15 XRD spectrum of Epoxy+0.5 wt.% GO nanocomposite coating

In addition to the above, GO is also known to possess excellent thermal conductivity which could help reduce the interface temperature between the steel ball and the epoxy nanocomposite surface and further contributing to the improvement in wear resistance (69).

4.2.2.2 Tribology of Epoxy + 1.5 wt.% GO nanocomposite coating

Analysis of the coefficient of friction (CoF) graph presented in Figure 4.16 a) shows that the Epoxy + 1.5 wt.% GO system has failed much earlier than the Epoxy + 0.5 wt.% GO system. The counterface image presented in Figure 4.16 c) again indicate that a transfer film of GO has formed on the surface during the testing process thereby protecting the

same from damage. Coating failure has been established through optical profilometer scans (see Figures 4.16 e) and f)) which reveal the depth of the wear track to be $>350\text{ }\mu\text{m}$. SEM images of the wear track along with the corresponding EDS spectrum shown in Figures 4.16 g) and h) clearly indicate coating failure.

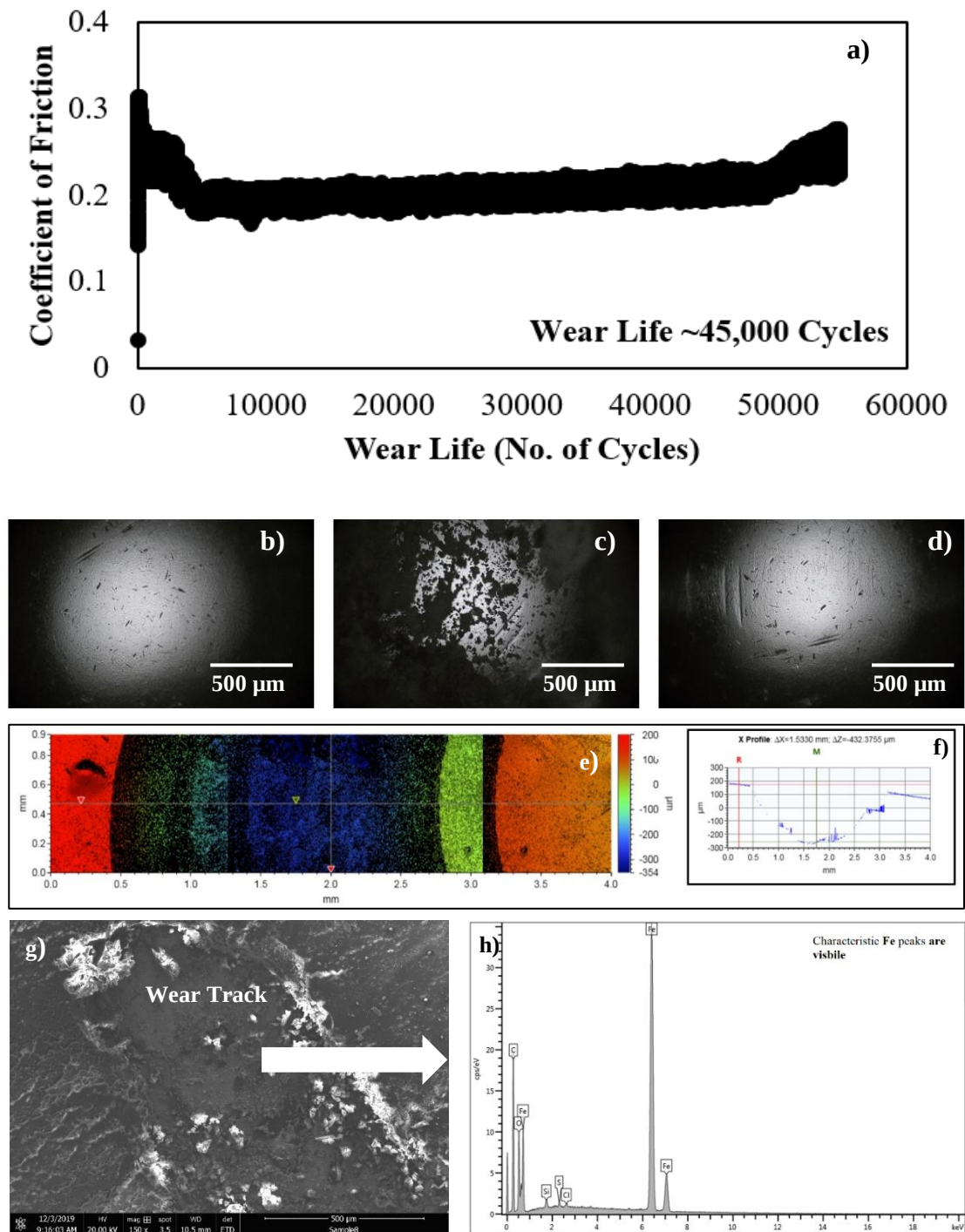


Figure 4.16 Epoxy+1.5 wt.% GO nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan

Low magnification (50X) SEM image of the wear track reveal adhesive failure mode. A closer look at the wear morphology presented in Figure 4.17 shows the presence of tribolayers on the outer perimeters of the defect and a few miniature wave-like features similar to that observed on the Epoxy + 0.5 wt.% GO nanocomposite's wear track. It is however clear that effective stress transfer from the matrix to the GO network hasn't occurred.

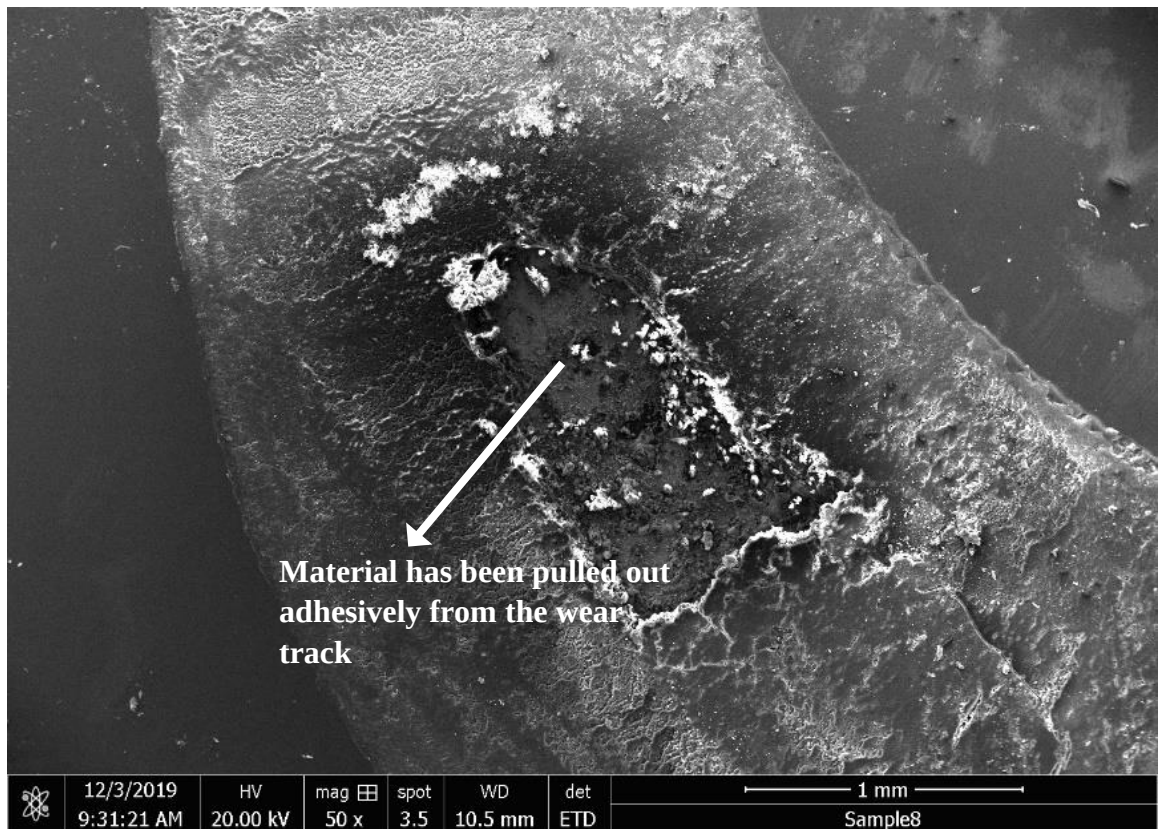


Figure 4.17 Low magnification SEM image (50X) of the wear track showing adhesive failure of the Epoxy+1.5 wt.% GO nanocomposite coating tested at 50N

Analysis of the XRD spectrum of Epoxy + 1.5 wt.% GO presented in Figure 4.18 does not show the characteristic peak of GO. However, a small peak at approximately 2° indicate that complete exfoliation of GO sheets hasn't taken place. Additionally, the CoF

value has also increased by ~23% to 0.21. It can therefore be hypothesized that particle agglomeration may have started to occur. These agglomerates can in-turn act as stress raisers and reduce the load bearing capacity of the matrix as seen in this case.

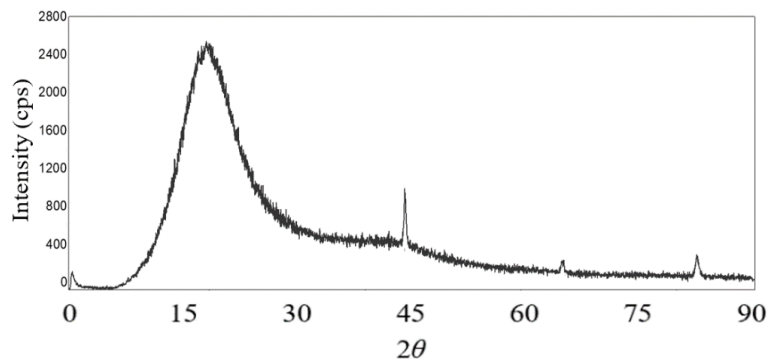


Figure 4.18 XRD spectrum of Epoxy+1.5 wt.% GO nanocomposite coating

4.2.3 Summary

- The pristine epoxy coating, Belzona® 4151, is evaluated for its load bearing capacity at 35N load at a linear sliding velocity of 0.1 m/s and a wear track radius of 4 mm for 100,000 cycles (sliding distance = 2500 m). While the pristine epoxy coating system passes the set target value of 100,000 cycles at 35N load, it is found to withstand only ~13,000 cycles when the load is increased to 50N.
- There is a substantial increase in wear life of the epoxy-GO nanocomposite coating system when compared to the pristine epoxy coating system.
- A filler loading of 0.5 wt.% GO has been determined to be optimal and produces a wear life of ~85,500 cycles. The reason for the same has been attributed to complete dispersion of the GO particles in the epoxy matrix. The failure mode also

changes from predominantly abrasive in case of the pristine epoxy coating system to a combination of adhesive and fatigue wear modes. The steel ball counterface in case of epoxy-GO nanocomposites also does not show any wear scars owing to the formation of a transfer film of GO that acts as a solid lubricant between the contacting surfaces.

- While the pristine epoxy coating tribo-system shows a steady-state friction coefficient of 0.21, the friction coefficient of the nanocomposite epoxy-GO tribo-system is 0.17, a substantial reduction of almost 20 % in the frictional coefficient value.
- The wear life is found to reduce to ~45,000 cycles at 1.5 wt.% GO filler loading owing to incomplete dispersion of the GO nanofillers in the pristine epoxy matrix.

4.3 Tribological characterization of hybrid epoxy nanocomposite coatings

4.3.1 Comparative studies of GO-Titania and GO-Alumina nanofiller loadings on the tribology of hybrid epoxy nanocomposite coatings

Since the highest wear life at 50N has been presented by Epoxy + 0.5 wt.% GO nanocomposite coatings, further addition of Titania and Alumina nanofillers in varying concentrations of 3 wt.%, 5 wt.% and 10 wt.% have been made to this concentration of GO. This produces three types of hybrid nanocomposite Epoxy-GO-Titania coatings (Epoxy + 0.5 wt.% GO + 3 wt. % Titania (E0.5GO3T), Epoxy + 0.5 wt.% GO + 5 wt.% Titania (E0.5GO5T) and Epoxy + 0.5 wt.% GO + 10 wt.% Titania ((E0.5GO10T)) and three variants of hybrid nanocomposite Epoxy-GO-Alumina coatings (Epoxy + 0.5 wt.% GO + 3 wt.% Alumina (E0.5GO3A), Epoxy + 0.5 wt.% GO + 5 wt.% Alumina (E0.5GO5A) and Epoxy + 0.5 wt.% GO + 10 wt.% Alumina (E0.5GO10A)). The graph presented in Figure 4.19 shows the comparative wear life of the hybrid nanocomposites. It is clear that the wear life of Epoxy-GO-Titania nanocomposites far exceed the wear life of Epoxy-GO-Alumina nanocomposites. The tribology of the hybrid epoxy nanocomposites has been analyzed at two data points namely: Epoxy + 0.5 wt.% GO + 5 wt.% Titania and Epoxy + 0.5 wt.% GO + 5 wt.% Alumina.

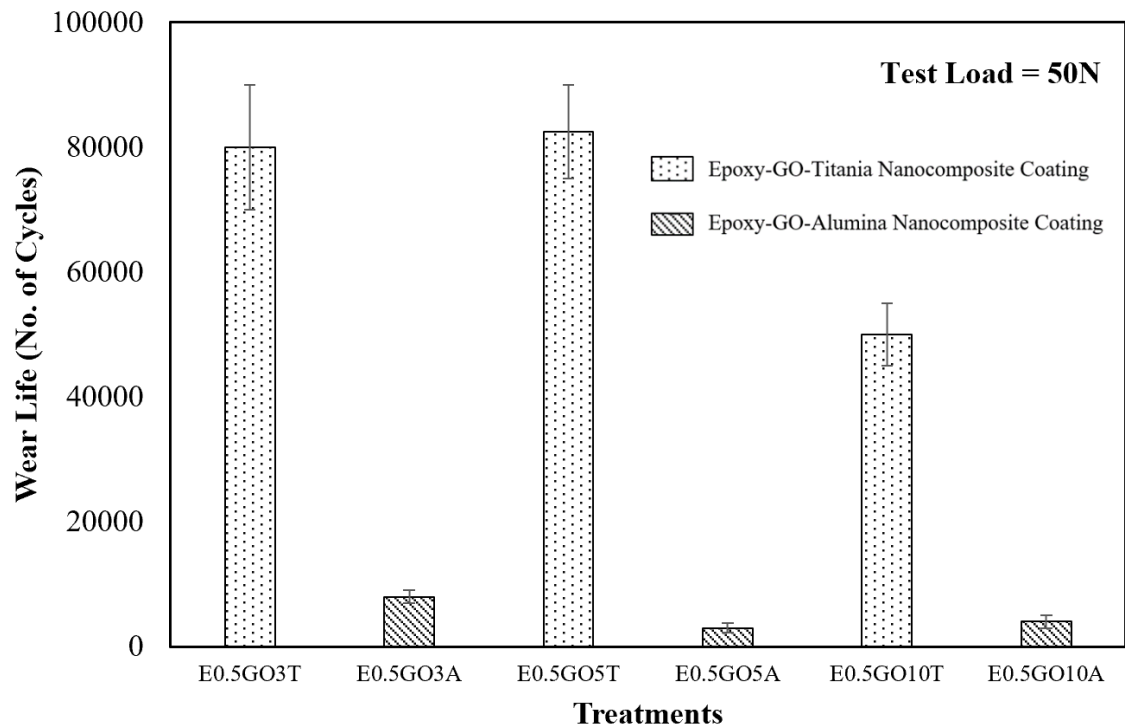


Figure 4.19 Comparative wear life of hybrid nanocomposites

4.3.1.1 Tribology of Epoxy + 0.5 wt.% GO + 5 wt.% Titania hybrid nanocomposite coating

The coefficient of friction (CoF) graph presented in Figure 4.20 a) show a spike in readings at around 82,500 cycles. The counterface image presented in Figure 4.20 b) show the presence of a transfer film and faint scar marks citing the possibility of both adhesive and abrasive wear. The abrasive wear of the counterface in this case could be from the hard Titania particles acting as abrasive third bodies. Coating failure has been established through optical profilometer scans which reveal the depth of the wear track to be >350 μm . SEM images of the wear track shown in Figure 4.20 g) along with the corresponding EDS spectrum with visible Fe ($K\alpha = 6.405$) spike clearly indicate coating failure.

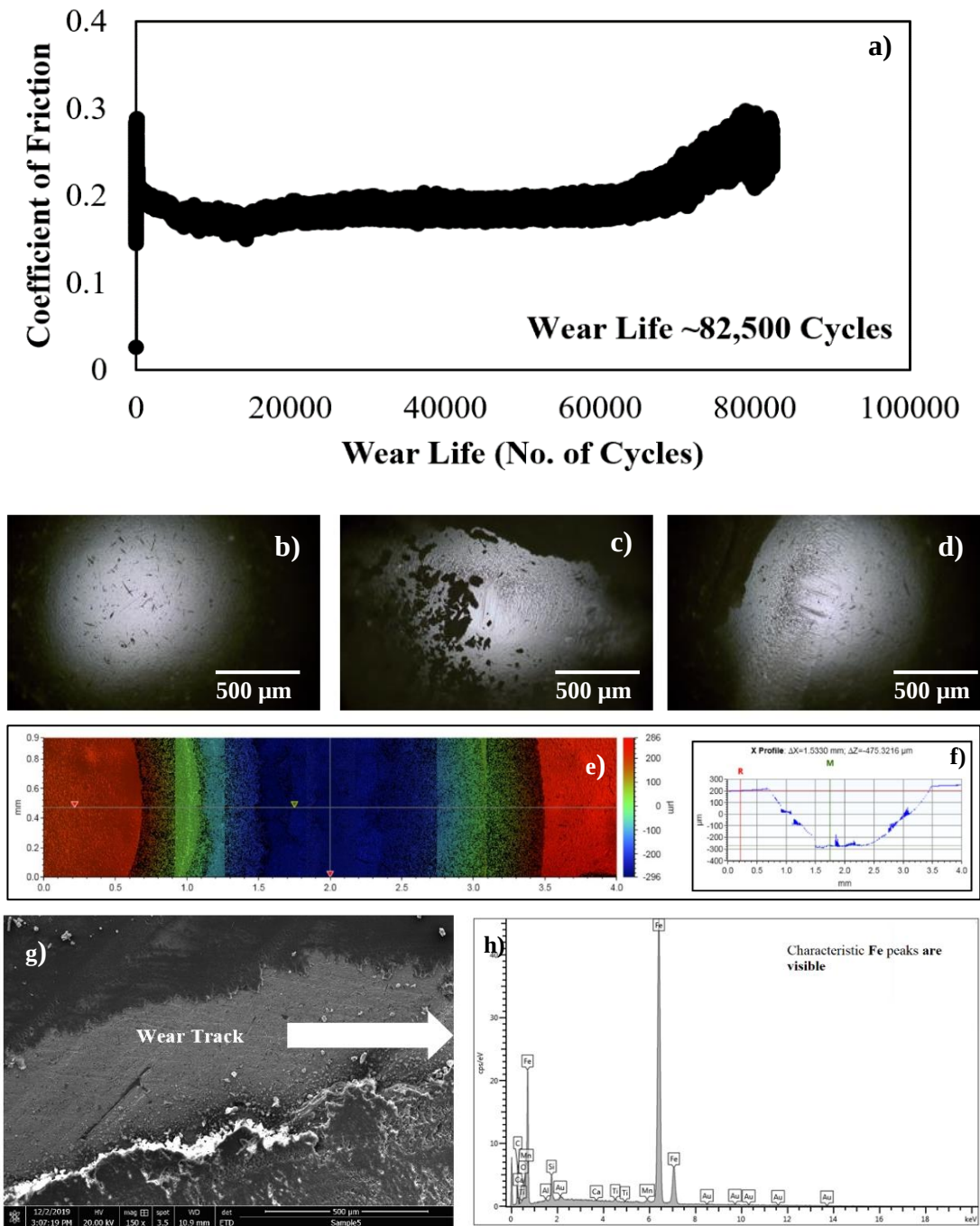


Figure 4.20 Epoxy + 0.5 wt.% GO + 5 wt.% Titania hybrid nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing c) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth g) and h) SEM image of the wear track along with EDS scan

Low magnification (50X) SEM image of the wear track shown in Figure 4.21 a) reveal both adhesive and abrasive failure modes. There is evidence of material pull-out and groove like features on the wear track. The reason for the same can be explained as follows. The high shear stresses produced by sliding friction causes the pull-out of Titania agglomerates from the surface and sub-surface. The Titania agglomerates then behave more like abrasive third bodies than roller bearings. Though the nanoparticles have been examined to possess spherical morphologies, a study of the SEM scans (Figure 4.21 b)) reveal that agglomerates tend to possess a more angular shape. Comparison with Epoxy + 0.5wt.% GO nanocomposite coating also shows that the addition of Titania nanoparticles have not shown any improvement in wear life. This could be likely due to the formation of agglomerates of Titania nanoparticles that can impede effective transfer of stress from the matrix to the nanoparticles thereby weakening the hybrid epoxy nanocomposite coating matrix. The coefficient of friction value has been recorded to be ~ 0.19 .

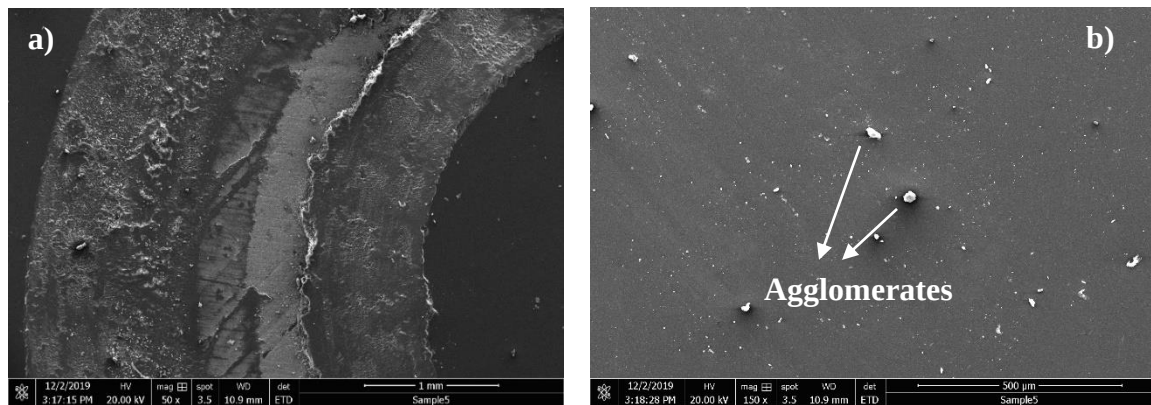


Figure 4.21 Epoxy+ 0.5 wt.% GO+ 5 wt.% Titania hybrid nanocomposite coating tested at 50N normal load presenting a) Low magnification (50X) SEM image of the wear track b) Angular shaped agglomerates

In order to confirm agglomeration of Titania particles, analysis of the XRD spectrum of the Epoxy-0.5wt.% GO-5 wt. % Titania nanocomposite coating has been carried out. The XRD spectrum presented in Figure 4.22 shows a clear phase separated morphology implying that homogeneous dispersion of the particles hasn't been achieved. Peaks of Titania corresponding to the crystal structure of anatase with strong diffraction peaks at approximately 25° (101) and 48° (202) have been observed (70).

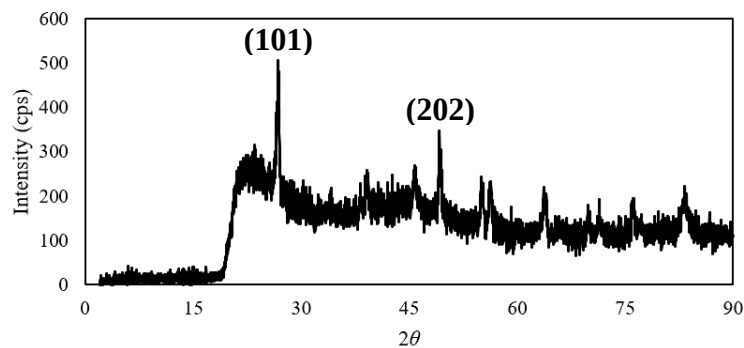


Figure 4.22 XRD spectrum of Epoxy+0.5 wt.% GO+5 wt.% Titania nanocomposite coating

4.3.1.2 Tribology of Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating

The coefficient of friction (CoF) graph presented in Figure 4.23 a) show that the alumina-based hybrid nanocomposite has failed quite early at approximately 3000 cycles. A very high CoF reading of around 0.37 has been noted citing the possibility of extremely high interface temperatures along with a high degree of wear. Examination of the counterface after test and after cleaning of the transfer film reveal abrasive scar marks (see Figure 4.23 c)). SEM images of the wear track shown in Figures 4.23 e) and f) along with the

corresponding EDS spectrum with visible Fe ($K\alpha = 6.405$) spike clearly indicate coating failure.

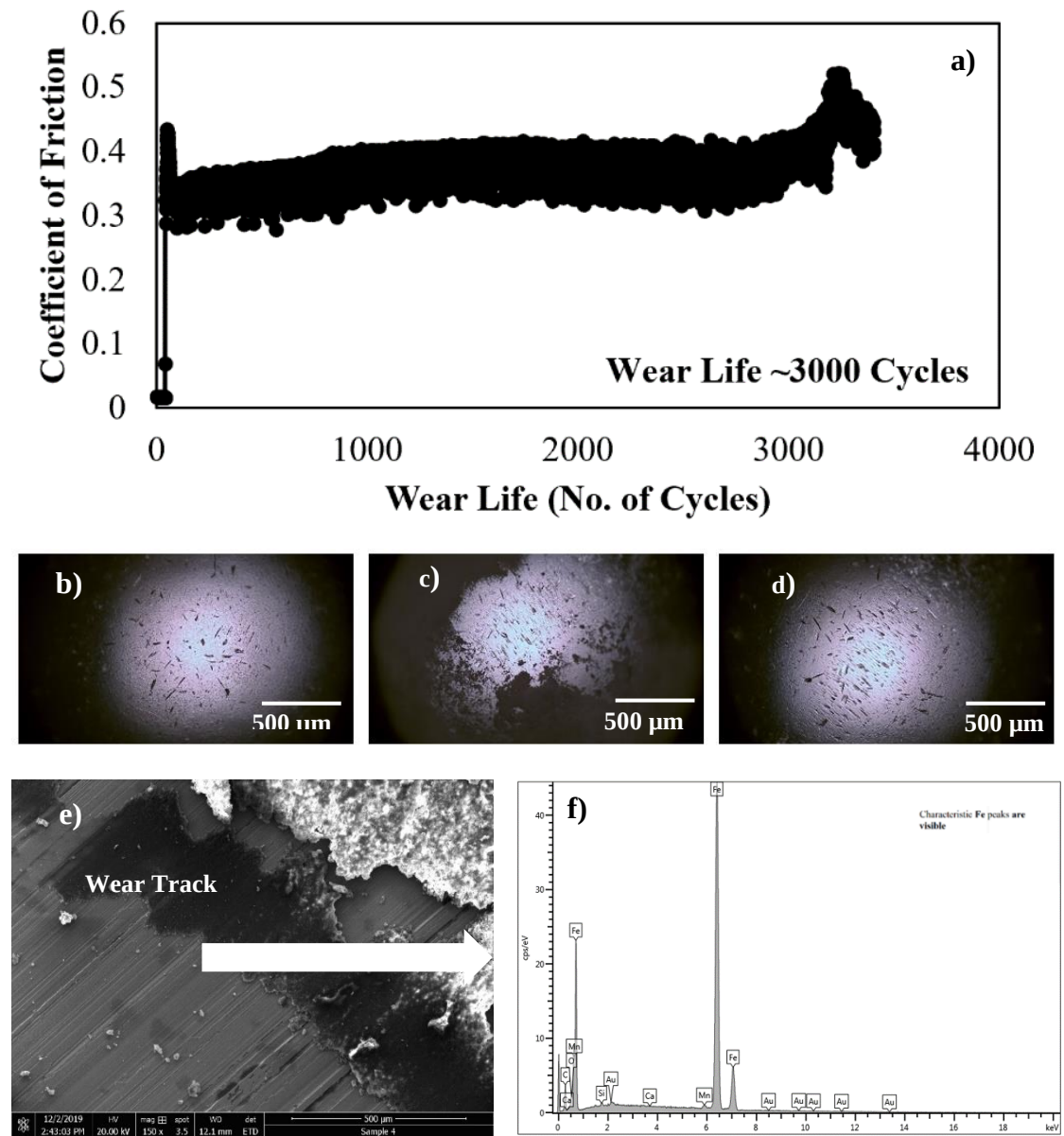


Figure 4.23 Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing d) Ball image after acetone cleaning e) and f) SEM image of the wear track along with EDS scan

A closer analysis of the region around the wear track shows that complete delamination of the coating from the wear track and also from center of the test zone (see Figure 4.24 a)) has occurred leading to the conclusion that the continuity of the epoxy matrix was affected at the coating formulation stage itself. It was observed during the formulation process that the affinity of the GO-Alumina fillers for the epoxy matrix was extremely low leading to extremely high surface run-off of the deposited resin during the spin coating process. Figure 4.24 b) shows an extremely high degree of agglomeration, of the order of a few millimeters, which has compromised the strength of the epoxy matrix.

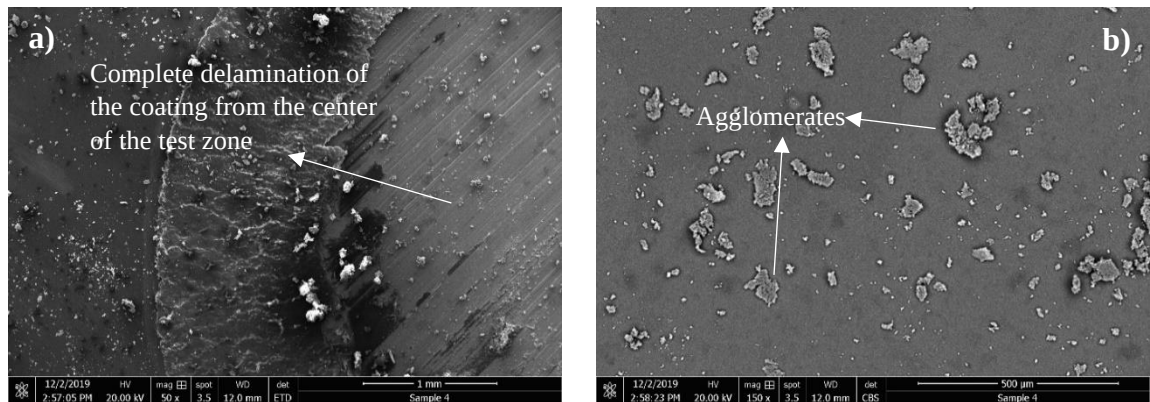


Figure 4.24 Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating tested at 50N normal load presenting a) Low magnification (50X) SEM image of the wear track with complete delamination of the coating from the center of the test zone b) Large agglomerates

The XRD spectrum of the Epoxy-GO-Alumina hybrid nanocomposite coating shown in Figure 4.25 reveals a phase separated morphology with sharp peaks at $2\theta = 45.3^\circ$ (200) and 82.9° (222).

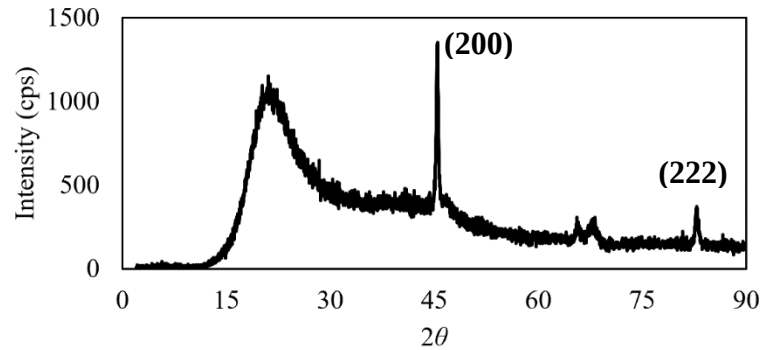


Figure 4.25 XRD spectrum of Epoxy+0.5 wt.% GO+5 wt.% Alumina nanocomposite coating

It is clear from the above discussions that the dispersion of the GO-Alumina hybrid fillers within the epoxy matrix is extremely poor. Regions of high stress arising from micrometer length scale aggregates coupled with an extremely low interfacial adhesion between the GO-Alumina hybrid fillers and the epoxy matrix leads to insufficient stress transfer and complete breakdown of the hybrid nanocomposite coating matrix under the aforementioned test conditions.

In order to improve the dispersion characteristics of the GO-alumina hybrid system within the epoxy matrix, the effect of increasing the sonication time has also been investigated as a part of this study. The initial and modified approaches used to produce the GO-Alumina hybrid nanocomposite powders have been presented in Figure 4.26.

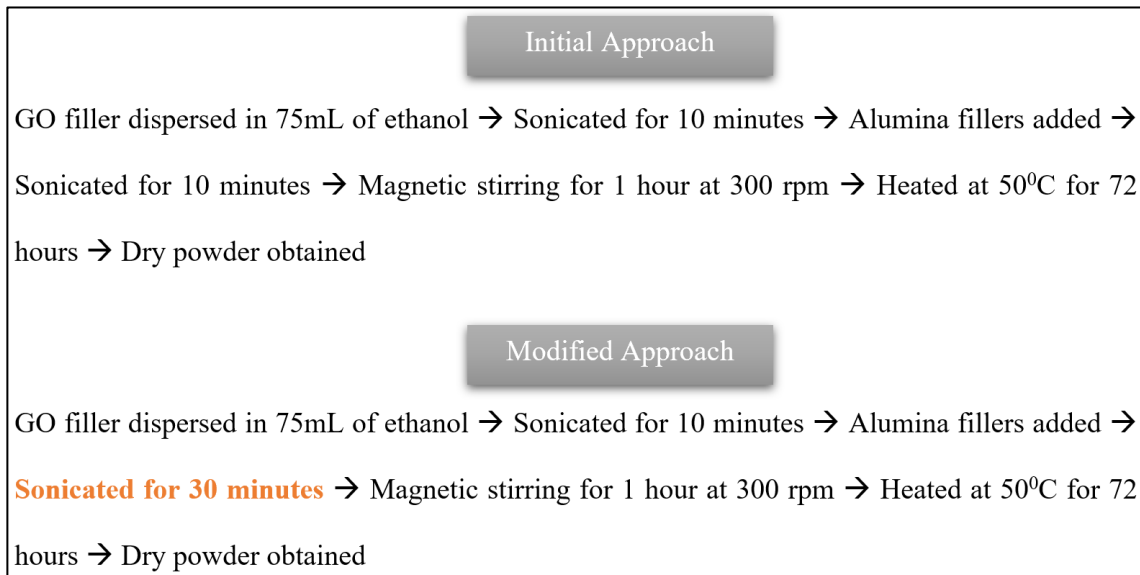


Figure 4.26 Initial and modified approaches adopted in preparation of GO- alumina hybrid nanocomposite powder

In both cases, application of the developed hybrid nanocomposite coatings onto mild steel substrates has been carried out using the approach detailed earlier. Figure 4.27 demonstrates a slight increase in wear life of the Epoxy-0.5wt. GO-5 wt.% Alumina hybrid nanocomposite coating produced using the modified approach when compared to the pristine epoxy system and a significantly higher improvement in wear life when compared to the Epoxy-0.5wt. GO-5 wt.% Alumina hybrid nanocomposite coating produced using the initial approach. It is evident that increasing the sonication time while keeping all other factors constant leads to improvement in wear life owing to better transfer of stresses from the filler to the matrix due to improved dispersion and better coating application characteristics.

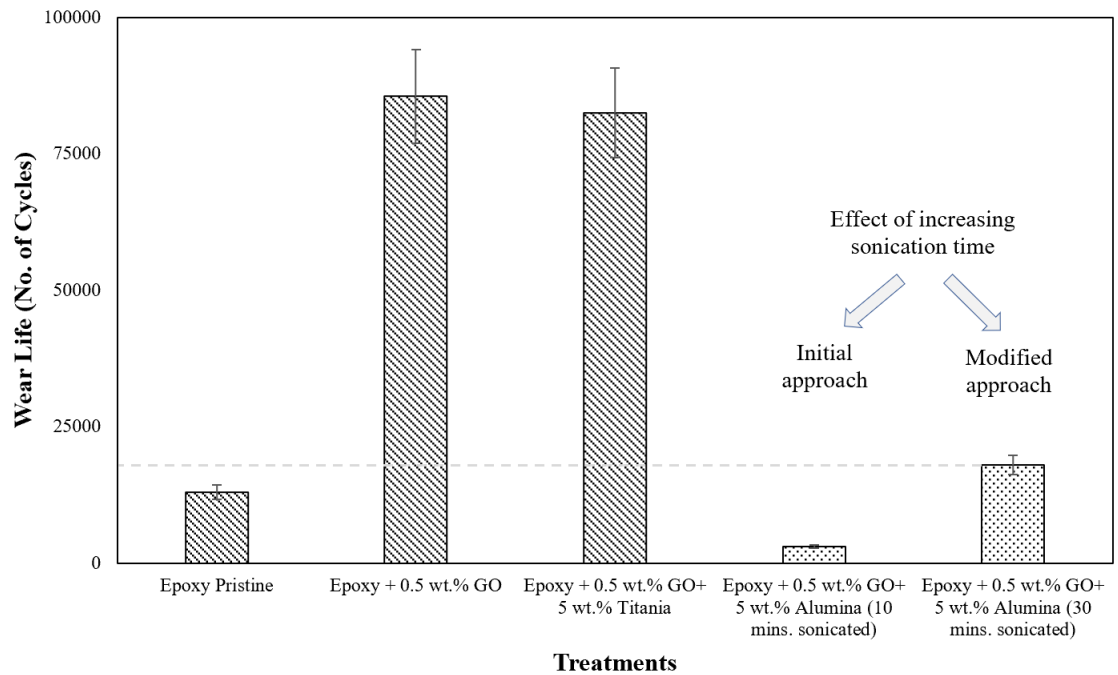


Figure 4.27 Effect of increased ultra-sonication time on wear life of Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating and comparison with other coatings produced using initial approach

The coefficient of friction (CoF) graph presented in Figure 4.28 a) show that the alumina-based hybrid nanocomposite produced using the modified approach has failed at approximately 18,000 cycles. A marked reduction in frictional coefficient when compared to the initially produced GO-alumina hybrid nanocomposite coating by approximately 40% (to ~0.22) has also been observed. Additionally, the coating has also not delaminated from the center of the test zone as visually observed at the time of stoppage of the test. This is indicative of the fact that the overall integrity of the hybrid nanocomposite system has improved with the increase in sonication time owing to improved dispersion and coating application characteristics.

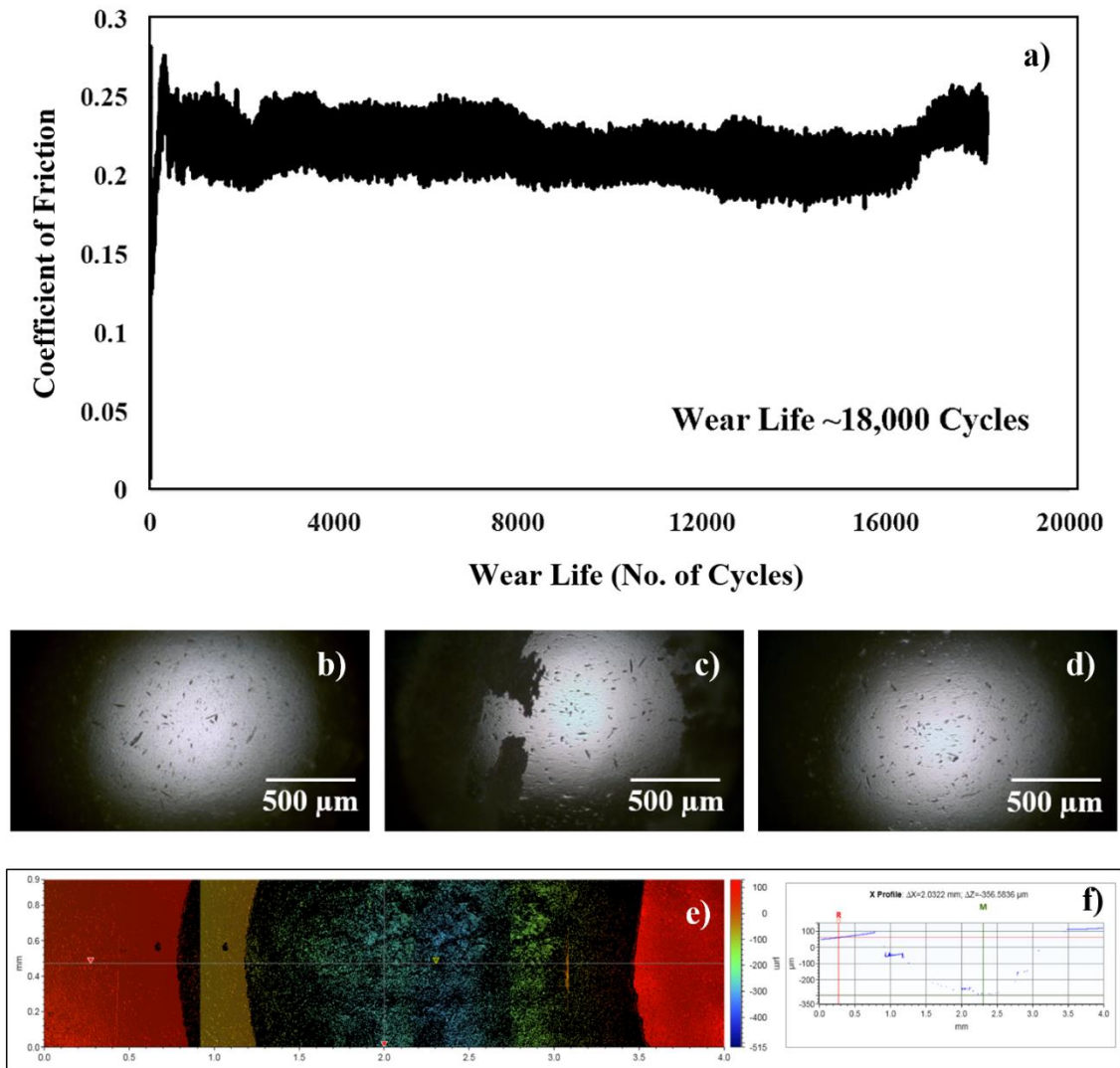


Figure 4.28 Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating (produced using a modified approach) tested at 50N normal load presenting a) Typical CoF graph b) Ball image before testing c) Ball image after testing d) Ball image after acetone cleaning e) and f) Optical profilometer scans and wear track depth

4.3.2 Correlation between coating hardness and wear life

The graph presented in Figure 4.29 shows the hardness values measured for coatings produced only using the initial approach for comparison purposes.

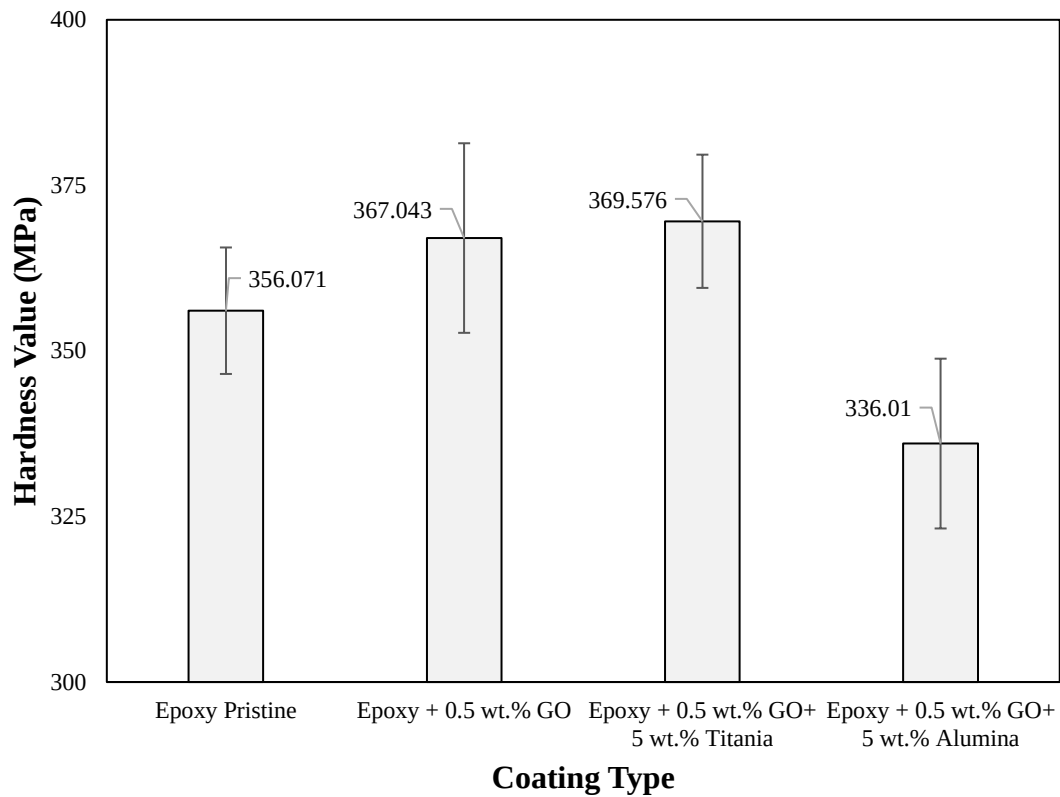


Figure 4.29 Comparison of hardness values of coatings

ANOVA analysis of the measured hardness values gives an F-ratio of 4.988 indicating that the results are statistically significant at $p < 0.05$. A strong positive correlation has also been observed between the wear life results and measured hardness values with a Pearson correlation coefficient of +0.77 (p value = 0.0035; 11 degrees of freedom).

4.3.3 Summary

- The wear life of Epoxy-GO-Titania hybrid nanocomposite coatings far exceed the wear life of Epoxy-GO-Alumina hybrid nanocomposite coatings across all filler loadings.

- The dispersion of Titania fillers in the Epoxy-GO nanocomposites is found to be less than optimal with XRD scans showing a phase separated morphology. There is no change in wear life of the Epoxy + 0.5 wt.% GO + 5 wt.% Titania hybrid nanocomposite coating when compared to the Epoxy+0.5 wt.% GO nanocomposite coating. This could be due to a high degree of particle agglomeration and the formation of abrasive third body particles which serve to increase the rate of wear.
- The wear life of the Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating is extremely low when compared to the Epoxy+0.5 wt.% GO nanocomposite coating or even the pristine epoxy coating. This is attributed to both the poor dispersion characteristics of the Alumina filler in epoxy-GO nanocomposite matrix as well as the formation of large agglomerates that act as stress raisers. This is also reflected in the high CoF value at ~0.37. Increasing the sonication time of alumina nanoparticles leads to a significant improvement in wear life coupled with a drastic reduction in frictional coefficient when compared to the Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating produced using the initial approach.
- Hardness values of the developed coatings are found to have a strong positive correlation with the wear life results obtained.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research was undertaken to address a range of problems identified through discussions with industrial partners and review of scientific literature.

Phase 1

In the first phase of this study, novel abrasives namely Olivine (OL 080) and Calcium Silicate (CS 085) were used to texture mild steel (A36) substrates. A series of tests ranging from visual examination of surface cleanliness in accordance with SSPC VIS-1, chemical analysis of textured mild steel surfaces using EDS and evaluation of adhesive strength of a commercially available high build epoxy coating on Olivine (OL 080) and Calcium Silicate (CS 085) textured mild steel substrates in accordance with ASTM D-4541 were carried out.

- The tests revealed that surface cleanliness levels equivalent to SSPC SP 5 could be achieved using either abrasive type.
- Additionally, the quality of the abrasives was deemed to be excellent owing to the absence of any chloride contamination.

- An adhesive strength improvement of nearly three times when compared to the coating system applied onto non-textured mild steel panels was observed.
- Olivine (OL 080) and Calcium Silicate (CS 085) abrasives can therefore be a suitable alternative to conventionally used Coal Slag and Garnet abrasives, the reserves of both of which are fast depleting owing to various reasons.

Phase 2

The second phase of this study began with the objective of evaluating the suitability of air plasma treatment on improving adhesion of high build coatings applied onto mild steel substrates. Since the remainder of this study would include works with pristine epoxy coatings, a neat epoxy resin was used for this phase of the study.

- The pristine epoxy coating applied onto non-textured, air plasma treated mild steel substrates showed an improvement of ~2.5 times in adhesive strength when compared to the pristine epoxy coating system applied onto non-textured, non-plasma treated mild steel substrates. This finding is expected to help researchers in academia and also industrial contractors wishing to apply coatings onto non-textured substrates.

In the latter part of the second phase, the load bearing capacity of the pristine epoxy coating system was evaluated. All coatings in this phase were produced using the spin coating technique to remove any extraneous variables and ensure a consistent DFT in the range of 300 μm – 400 μm .

- At 35N, the pristine epoxy coating was found to have withstood 100,000 cycles when tested at a sliding velocity of 0.1 m/s; however, the wear life reduced to ~13,000 cycles at 50N. The failure mode was characterized using SEM and the presence of severe abrasive wear marks were noted on the steel ball counterface as also on the wear track.
- GO nanofillers were then added in varying concentrations of 0.25 wt.%, 0.5 wt.%, 1 wt.% and 1.5 wt.% to the pristine epoxy matrix to produce epoxy-GO nanocomposite coatings and subjected to the same testing conditions under a normal load of 50N.
- There was a substantial improvement in wear life to ~85,500 cycles at a GO filler loading of 0.5 wt.%. XRD analysis showed excellent dispersion of the GO fillers within the epoxy matrix. A striking feature of the wear track was the presence of tribo-layers owing to the high shear stresses produced under repeated sliding. This repeated sliding of the steel ball was also found to have induced surface fatigue. Under high normal loads, cyclic stress concentrations in front of the steel ball were found to have produced minute cracks, parallel and perpendicular to the sliding direction which were then postulated to have coalesced into a network of micro-cracks and manifesting miniature wave like features on the surface of the wear track.
- The CoF in case of the Epoxy-0.5 wt.% GO nanocomposite coating system was also found to have reduced by approximately 20% when compared to the pristine epoxy matrix and this was attributed to the sheet like morphology of the GO

nanoparticles serving as a solid lubricant between the mating surfaces. The high thermal conductivity of the GO nanoparticles was also thought to have played a role in reducing the interface temperatures and improving the wear life of the Epoxy- 0.5 wt.% GO nanocomposite.

- Increasing the GO filler content to 1.5 wt.% resulted in a reduction of wear life to around 45,000 cycles. This was believed to have occurred due to incomplete dispersion of the GO fillers in the epoxy matrix.
- The CoF was also found to have increased by approximately 23% when compared to the Epoxy + 0.5 wt.% GO nanocomposite coating.

Phase 3

In the third phase of this work, Titania and Alumina nanofillers were added to the Epoxy + 0.5 wt.% GO matrix in varying concentrations of 3 wt.%, 5 wt.% and 10 wt.% to produce hybrid nanocomposites.

- The wear life of Epoxy-GO-Titania nanocomposites across all weight percentages of fillers were found to far exceed the wear life of Epoxy-GO-Alumina nanocomposites. This was attributed to the poor coating application characteristics of the Alumina based hybrid when compared to the Titania based system.
- While the Epoxy + 0.5 wt.% + 5 wt.% Titania hybrid nanocomposite coating exhibited a wear life similar to the Epoxy + 0.5 wt.% GO nanocomposite coating, the wear mode was found to be a combination of adhesive and abrasive types possibly due to the agglomerates of angular shaped Titania nanoparticles being

pulled out of the matrix and into the steel ball-coating interface. It was believed that these particles could have then acted as abrasive third bodies and increased the rate of wear.

- In the case of Alumina based hybrid nanocomposites, complete delamination of the coating from the wear track was found to have taken place. Additionally, agglomerates of the order of a few millimeters were observed during SEM scans. Using a modified approach by increasing the sonication time of alumina nanoparticles while keeping all other parameters constant was found to have eliminated several of the aforementioned issues as evidenced by a significant improvement in wear life (combined with a reduction in frictional coefficient) as compared to the Epoxy + 0.5 wt.% GO + 5 wt.% Alumina hybrid nanocomposite coating produced using the initial approach. A reduction in frictional coefficient by ~40% was also observed.
- XRD analyses of both the Epoxy +0.5 wt.% +5 wt.% Titania hybrid nanocomposite coating and Epoxy +0.5 wt.% +5 wt.% Alumina hybrid nanocomposite coating revealed a phase separated morphology owing to agglomeration.
- Hardness values of the developed coatings were found to be strongly positively correlated with the wear life readings.

Table 5.1 presents a summary of all the findings from phases 2 and 3 of this research work.

Table 5.1 Summary of findings from phases 2 and 3 of this research

Coating Type	Load	Wear Life	Counterface	Wear Mode	CoF
Pristine Epoxy	35N	>100,000 cycles	No visible wear scars; transfer film visible on the counterface	Predominantly adhesive	0.23
Pristine Epoxy	50N	13,000 cycles	Visible deep wear scars; transfer film discontinuous	Predominantly abrasive	0.21
Epoxy + 0.5wt.% GO	50N	85,500 cycles	No visible wear scars; transfer film visible on the counterface	Predominantly adhesive and characteristics of surface fatigue	0.17
Epoxy + 1.5wt.% GO	50N	45,000 cycles	No visible wear scars; transfer film visible on the counterface	Predominantly adhesive	0.21

Epoxy +	50N	82,500	Slightly visible	Predominantly	0.19
0.5wt.% GO +		cycles	wear scars;	adhesive with	
5 wt.% Titania			transfer film	a fair degree	
			visible on the	of abrasion	
			counterface		
Epoxy +	50N	3,000 cycles	Visible wear	Predominantly	0.37
0.5wt.% GO +			scars; transfer	adhesive with	
5 wt.%			film	a high degree	
Alumina			discontinuous	of abrasion	

It can be concluded that all the objectives outlined for the present study were successfully achieved and will serve as a good starting point for researchers in the industry and academia to build on the positives and determine alternate approaches for the negative outcomes witnessed during the course of this research.

5.2 Recommendations for future work

Some of the improvements that can be made to this work are as follows:

1. The role of the abrasives used in this study can be expanded from a study of adhesion characteristics of the applied coating system to the corrosion characteristics of the applied coating system, particularly in terms of performance under salt fog tests in accordance with ASTM B-117.

2. The UV-stability of the hybrid nanocomposites can be compared with the Epoxy – 0.5 wt.% GO nanocomposite to expand the range of possible industrial applications.
3. Surface modification of Titania and Alumina nanofillers using suitable chemical methods can be evaluated to further improve their dispersion in the epoxy-GO matrix. It can also be evaluated if other fillers (polymer based such as UHMWPE or PEEK) without surface modification can produce better load bearing characteristics when subjected to the same test conditions used in this study.
4. The tests can be repeated under water / oil lubricated conditions to determine the applicability of the produced epoxy nanocomposites in lubricated contacts.

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Journal Publications

Bobby S, Samad MA. Enhancement of tribological performance of epoxy bulk composites and composite coatings using micro/nano fillers: a review. Polymers for Advanced Technologies, Wiley Online Library, 2016

Bobby S, Samad MA. Evaluation of parameters affecting adhesive strength of high build epoxy coatings on textured and plasma treated metallic substrates. Journal of Adhesion Science and Technology, Taylor and Francis Online, 2017

Book Chapters

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Conference Papers

Bobby S, Samad MA. Effect of surface texturing and air-plasma treatment on the adhesive strength of high build epoxy coatings on metallic substrates, 6th World Tribology Congress, Beijing, China, September 17-22, 2017

Bobby S, Samad MA. Novel abrasives for texturing metallic substrates and evaluation of air plasma treatment process on adhesive strength of high build epoxy coating systems, 1st Materials Performance & Welding Technology (MPWT) Conference & Exhibition, Dammam, Saudi Arabia, September 11-14, 2017