

PREPARATION AND CHARACTERISATION OF GRAPHENE FILLED
UNPLASTICISED POLYVINYL CHLORIDE NANOCOMPOSITES FOR
MINING PIPE APPLICATION

YEE JOON WEE

UNIVERSITI TEKNOLOGI MALAYSIA

PREPARATION AND CHARACTERISATION OF GRAPHENE FILLED
UNPLASTICISED POLYVINYL CHLORIDE NANOCOMPOSITES FOR
MINING PIPE APPLICATION

YEE JOON WEE

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

MAY 2021

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to the management of Baerlocher company group. Without the company's support, it would have been very challenging for me to complete the study. I am most thankful towards my dissertation supervisor, Prof. Dr. Azman Bin Hassan who made sure that his office was open for me when I need to seek help from him throughout my research journey, writing and the submission of my PhD thesis. He encouraged me to look through different papers and journal articles to steer me in the right direction when I needed it.

Special thanks to Kak Lijah (chief of administrator assistant, academic school of chemical and energy engineering UTM) for guiding me through the administration procedure throughout the last 5 years and for giving her valuable comments on my thesis formatting before the final submission. I am thankful to everyone who had helped me throughout the research process and had encouraged me to complete the work and submit it on time.

Last but not least I am very thankful to my family as they have been with me from the beginning of my PhD journey, and for their endless support throughout the completion of my PhD.

Cheers to All of You!

ABSTRACT

This study was aimed to prepare and characterise a graphene filled unplasticised polyvinyl chloride (UPVC) nanocomposite for mining pipe application by means of a conventional dry-blending method. A pre-dispersed reduce graphene oxide (PDG) in Fischer-Tropsch (FT) wax was prepared by defining a melting method with ultrasonic probe. An investigation has been conducted on different types of graphene derivatives: graphene oxide (GO), reduce graphene oxide (rGO) and pre-dispersed rGO (PDG) in Fischer-Tropsch wax (FT wax) filled UPVC nanocomposites. The properties such as electrical, mechanical, rheological and thermal properties were benchmarked against the commercial carbon black (CB) filled UPVC composites for the mining pipe application. The nanocomposites were prepared using the dry-blending method involving different material formulations. The two-roll milling method and the hot press moulding were also employed to produce the test specimens. An environmental friendly stabiliser namely calcium-zinc stabiliser was used to replace the conventional lead stabiliser. The results showed that the specimen with 1.5 phr PDG filled UPVC nanocomposites has the lowest volume resistivity, comparable or higher tensile strength, tensile modulus and impact strength. The specimen was also possessed a wide processing parameter with sufficient heat stability and better cost performance efficiency, compared to the commercial CB filled UPVC composites. The evidences from the fourier transform infrared spectroscopy and scanning electron microscopy images of the surface-fractured specimens showed a well dispersed PDG into the PVC matrix and correlated with the impact strength result. The modulus of the PDG filled UPVC nanocomposites were simulated using the Halpin-Tsai model. The theoretical simulation for the random distribution of PDG supported the results of the experimental data. This study confirmed that the best cost performance of graphene filled UPVC nanocomposites can be achieved by maximising the dispersibility of graphenes within the PVC matrix. This study provides an opportunity for the PDG filled UPVC nanocomposites to be used for mining pipe application.

ABSTRAK

Kajian ini bertujuan untuk penyediaan dan pencirian komposit nano polivinil klorida tanpa pemplastik (UPVC) isian grafin untuk aplikasi paip perlombongan yang boleh dihasilkan melalui kaedah pencampuran kering konvensional. Grafin oksida terturun pra-serak (PDG) dalam lilin Fischer-Tropsch (FT) telah disediakan dengan menentukan kaedah leburan dengan kuar ultrasonik. Penyiasatan telah dijalankan terhadap jenis terbitan grafin yang berlainan: grafin oksida (GO), grafin oksida terturun (rGO) dan rGO pra-serak (PDG) dalam komposit nano UPVC isian lilin Fischer-Tropsch (lilin FT). Sifat-sifat seperti elektrik, mekanikal, reologi dan terma telah dijadikan sebagai penanda aras terhadap komposit UPVC isian karbon hitam (CB) komersial untuk penggunaan paip perlombongan. Komposit nano telah disediakan menggunakan kaedah pencampuran kering yang melibatkan formulasi bahan berlainan. Kaedah pengisaran dua giling dan pengacuan tekanan panas juga telah dijalankan untuk menghasilkan spesimen ujian. Satu sistem penstabilan mesra alam iaitu penstabil kalsium zink telah digunakan untuk menggantikan penstabil plumbum konvensional. Keputusan menunjukkan bahawa spesimen dengan kandungan 1.5 phr komposit nano UPVC isian PDG mempunyai kerintangan isipadu terendah, kekuatan tegangan, modulus tegangan dan kekuatan hentaman setanding atau lebih tinggi. Spesimen tersebut juga menghasilkan parameter pemprosesan yang lebih luas dengan kestabilan haba mencukupi dan kecekapan prestasi kos lebih baik berbanding komposit UPVC isian CB komersial. Bukti-bukti daripada spektroskopi inframerah jelmaan Fourier dan imej permukaan spesimen retak dari mikroskopi elektron pengimbasan menunjukkan penyerakan PDG yang baik ke dalam matriks PVC dan berkorelasi dengan keputusan kekuatan hentaman. Modulus komposit nano UPVC isian PDG disimulasikan menggunakan model Halpin-Tsai. Simulasi teori untuk taburan rawak PDG menyokong keputusan data eksperimen. Kajian ini mengesahkan bahawa prestasi kos terbaik komposit nano UPVC isian grafin boleh dicapai dengan memaksimumkan kebolehserakan grafin di dalam matriks PVC. Kajian ini memberikan peluang bagi komposit nano UPVC isian PDG untuk digunakan dalam penggunaan paip perlombongan.

TABLE OF CONTENTS

	TITLE	PAGE
	DECLARATION	iii
	DEDICATION	iv
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF ABBREVIATIONS	xviii
	LIST OF SYMBOLS	xxi
	LIST OF APPENDICES	xxiii
CHAPTER 1	INTRODUCTION	1
	1.1 Background of Study	1
	1.2 Problem Statement	4
	1.3 Significance of Study	5
	1.4 Objectives	5
	1.5 Scope of Study	6
CHAPTER 2	LITERATURE REVIEW	9
	2.1 Introduction to PVC	9
	2.1.1 Structure	9
	2.1.2 Polymerisation	12
	2.1.3 K-Value and Degree of Polymerisation	14
	2.1.4 Degradation of PVC	15
	2.2 Stabilisation of PVC	17
	2.2.1 Lead-based Stabilisation	18
	2.2.2 Calcium Zinc Stabilisation	20

2.2.3	Comparison Between Lead-based and Calcium Zinc Stabilisation	23
2.2.4	Development of Stabilisation System for UPVC Pipe Application	24
2.3	Additives	26
2.3.1	Lubricant	26
2.3.2	Processing Aids	30
2.3.3	Fillers	32
2.3.3.1	Calcium Carbonate	33
2.3.4	Pigments	34
2.3.4.1	Titanium Dioxide	34
2.3.4.2	Carbon Black	35
2.4	Sustainability of PVC	38
2.5	Introduction to Graphene	40
2.5.1	Properties and Application	42
2.5.2	Synthesis of Graphene	43
2.5.2.1	Micromechanical Exfoliation	45
2.5.2.2	Chemical Vapour Deposition (CVD) and Epitaxial Growth	45
2.5.2.3	Intercalation of Small Molecules by Mechanical Exfoliation	46
2.5.2.4	Graphene Oxide and the Reduction	48
2.5.2.5	Graphene via Mechanochemical Process	49
2.5.3	Review on Dispersion of Graphene in Polymer	51
2.5.3.1	Pre-dispersed Graphene in Solvent	52
2.5.3.2	Functionalisation of Graphene	53
2.5.3.3	Pre-dispersed Graphene in Waxes	55
2.6	Introduction of Fischer-Tropsch Waxes	57
2.6.1	Flow Behaviour of Wax	58
2.7	Review on Graphene Filled Polymer Composites	61
2.8	Mechanism of Nanoparticles in Polymer Matrix	65
2.9	UPVC Mining Pipe Application	68

CHAPTER 3	METHODOLOGY	71
3.1	Research Design	71
3.2	Materials	71
3.2.1	Pre-dispersed Graphene	71
3.2.2	Graphene filled UPVC Nanocomposites	71
3.3	Preparation of Pre-dispersed rGO in Fischer-Tropsch Waxes	74
3.4	Preparation of Graphene Filled UPVC Nanocomposites	75
3.4.1	Formulation Design	75
3.4.2	Preparation of Test Specimens	79
3.4.2.1	Dry-blend Mixing	79
3.4.2.2	Two-roll Milling	79
3.4.2.3	Hot Press Moulding	80
3.5	Characterisation of Graphene Filled UPVC Nanocomposites	81
3.5.1	Scanning Electron Microscopy (SEM)	79
3.5.2	Fourier-Transform Infrared (FTIR) Spectroscopy	79
3.5.3	Testing of Electrical Conductivity	82
3.5.4	Tensile Test	83
3.5.5	Impact Test	84
3.5.6	Study of Morphology	85
3.5.7	Testing of Rheological Behaviour	85
3.5.8	Differential Scanning Calorimetry	86
3.5.9	Congo Red Test	87
3.5.10	Thermogravimetric Analysis (TGA)	87
3.5.11	Bulk Density	88
CHAPTER 4	RESULTS AND DISCUSSION	89
4.1	Pre-dispersed Graphene with Fischer-Tropsch Waxes	89
4.1.1	Surface and Dispersion's Homogeneity Analysis	90
4.1.2	FTIR Spectroscopy Analysis	92
4.2	Analysis of Electrical Properties	94
4.3	Analysis of Mechanical Properties	100

4.3.1	Stress-Strain Properties of Graphene Filled UPVC Nanocomposites	100
4.3.2	Tensile Strength and Elongation at Break	101
4.3.3	Tensile Modulus	106
4.3.3.1	Halpin-Tsai Equations	108
4.3.4	Impact Strength	111
4.3.5	Scanning Electron Microscopy Analysis	113
4.4	Comparison of Electrical and Mechanical Properties Between CB Filled UPVC Composites with PDG Filled UPVC Nanocomposites	121
4.5	Rheological Behaviour	122
4.5.1	Analysis of Fusion Characteristics	122
4.5.2	Rheological Analysis	126
4.6	Thermal Analysis	132
4.6.1	Degree of Fusion	132
4.6.2	Congo Red Test	137
4.6.3	Thermogravimetric Analysis (TGA)	139
4.7	Cost Performance Efficiency	143
CHAPTER 5	CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORKS	151
5.1	Overall Conclusions	151
5.2	Recommendation for Future Works	153
REFERENCES		155
APPENDICES A-K		167-179

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Types of PVC Resin	14
Table 2.2	Comparison of Various Degrees of Polymerisation	15
Table 2.3	Various Types of Pb Stabilisers and its Properties	19
Table 2.4	Pros and Cons of Using Pb Stabilisers	20
Table 2.5	The Lubricating Effects of Lubricants	27
Table 2.6	Lubrication Properties of Different Type of Lubricants	30
Table 2.7	Expected Results of the Addition of Graphene to PVC	68
Table 3.1	Details on Formulation Design	77
Table 3.2	Details on Formulation Design	78
Table 4.1	Viscosity of PDG at Different Temperature (80 °C / 100 °C) and Stirrer Speed (1000 rpm / 2000 rpm)	90
Table 4.2	SEM Images on the Surface of Two Roll Mill Sheet (Unfilled UPVC and PDG Filled UPVC Nanocomposites)	91
Table 4.3	Comparison Between Commerical CB Filled UPVC Composites and 1.5 phr PDG Filled UPVC Nanocomposites on Volume Resistivity	100
Table 4.4	Comparison result of electrical and mechanical properties between CB filled UPVC composites and PDG filled UPVC nanocomposites	122
Table 4.5	Comparison of Rheological Properties Between CB Filled UPVC Composites Versus 1.5 phr PDG Filled UPVC Nanocomposites	126
Table 4.6	The Effect of End Torque on PDG Filled UPVC Nanocomposites, Unfilled UPVC and CB Filled UPVC Composites at Different Rotor Speeds	128
Table 4.7	Effect of Content of PDG Filled UPVC Nanocomposites compare with Unfilled UPVC and CB Filled UPVC Composites on n (power law index)	129
Table 4.8	Tg, Processing Temperature and Degree of Fusion of Unfilled UPVC, CB Filled UPVC Composites and PDG Filled UPVC Nanocomposites (0.5, 1.0 and 1.5 phr content)	135
Table 4.9	TGA Data of Unfilled UPVC, CB Filled UPVC Composites and PDG Filled UPVC Nanocomposites (0.5, 1.0 and 1.5 phr content)	143

Table 4.10	Derivation of Cost Per Unit Volume of Unfilled UPVC, PDG Filled UPVC Nanocomposites and CB Filled UPVC Composites	145
Table 4.11	Relationship between Volume Resistivity, Tensile Modulus, Impact Strength and Cost Per Unit Volume Versus Congo Red and Torque of Unfilled UPVC, PDG Filled UPVC Nanocomposites and CB Filled UPVC Composites (Sorted to 1-5 where 1 is the worst and 5 is the best to provide enhancement to respective properties)	148

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Reaction Paths for Productions of Vinyl Chloride	10
Figure 2.2	Polymerisation of VCM into PVC	11
Figure 2.3	Chain Reaction Processes (Initiation, Propagation, Chain Transfer and Termination)	12
Figure 2.4	Causes of PVC Degradation	16
Figure 2.5	Inhibitor of PVC degradation	16
Figure 2.6	Degradation of PVC	17
Figure 2.7	Ca and Zn Soaps Stabilisation Synergism	21
Figure 2.8	Recovery of Zn Stearate with Ca Stearate	22
Figure 2.9	Comparison Between Pb-based and Ca-Zn Stabilisation	23
Figure 2.10	Thermal Heat Stability is Portrayed in a Plot of ΔE Against Time	24
Figure 2.11	Production of Carbon Black	36
Figure 2.12	Illustration of Carbon Allotropes (Clockwise from top right) Graphite, which is a multi-layer stacked of graphene; fullerene (C60), wrapped graphene; CNT, graphene being rolled; and graphene, single layer, monoatomic-thick sheet of hexagonal-shaped lattice of carbon	41
Figure 2.13	Hypothetical Illustration of Graphene as a Hammock	42
Figure 2.14	Methods for the Production of Graphene	44
Figure 2.15	Microstructure and Morphology of the rGO by Micromechanical and Reduce Through Microware Process	50
Figure 2.16	Surface's Structure of the Nanocomposites Material after Homogenisation	52
Figure 2.17	Polar Functionalities on Graphene Surface	56
Figure 2.18	Physical Properties of Fischer-Tropsch Waxes	57
Figure 2.19	Gas to Liquid (GTL) Process	58
Figure 2.20	Types of Waxes	59
Figure 2.21	Effect of Temperature and Shear Rate on Viscosity	61
Figure 2.22	Structure of Nanocomposite in Polymer Matrix	67
Figure 3.1	Research Design Flowchart	73

Figure 3.2	Apparatus Setting for Dispersion Process	75
Figure 3.3	A Typical Temperature Diagram for UPVC Mixing	79
Figure 3.4	Setup of Volume Resistivity Tester	83
Figure 3.5	Sample Dimension for Tensile Test (Type IV)	84
Figure 3.6	Sample Dimension Izod Testing (ASTM D256)	85
Figure 3.7	Congo Red Test Setup	87
Figure 3.8	Bulk Density Apparatus, V32.02	88
Figure 4.1	(a) 30% Pre-dispersed rGO (PDG) in FT Wax Prepared at 80°C in Flake Form and (b) 30% Pre-dispersed rGO (PDG) in FT Wax Prepared at 120°C in Flake Form.	90
Figure 4.2	FTIR Spectra of rGO	93
Figure 4.3	Structure and Functional Group of rGO	93
Figure 4.4	FTIR spectra of Unfilled UPVC and PDG Filled UPVC Nanocomposites	94
Figure 4.5	Effect of Pb and Ca-Zn Stabiliser on Volume Resistivity	95
Figure 4.6	Effect of Different GO Content on Volume Resistivity	96
Figure 4.7	Effect of Different rGO Content on Volume Resistivity	97
Figure 4.8	Effect of Different PDG Content on Volume Resistivity	98
Figure 4.9	Comparison Between 5 phr GO and 5 phr rGO VS PDG filled UPVC Nanocomposites on Volume Resistivity	98
Figure 4.10	Stress-strain Curve of Graphene Filled UPVC Nanocomposites	101
Figure 4.11	Effect of Different GO Content on Tensile Strength and Elongation at Break	102
Figure 4.12	Effect of Different rGO Content on Tensile Strength and Elongation at Break	103
Figure 4.13	Effect of Different PDG Content on Tensile Strength and Elongation at Break	104
Figure 4.14	Schematic Models of Various Dispersion Types of Graphene Nanosheets in PVC Matrix	105
Figure 4.15	Effect of Different GO Content on Tensile Modulus	107
Figure 4.16	Effect of Different rGO Content on Tensile Modulus	108
Figure 4.17	Effect of Different PDG Content on Tensile Modulus	108
Figure 4.18	Tensile Modulus of the PDG Filled UPVC Nanocomposites and Halpin-Tsai Theoretical Models	110
Figure 4.19	Effect of Different PDG Content on Impact Strength	111

Figure 4.20	Toughening Mechanism of the PDG Filled UPVC Nanocomposites	112
Figure 4.21	Different Zone During the Fracture of the PDG Filled UPVC Nanocomposites	114
Figure 4.22	SEM of 1 phr PDG Filled UPVC Nanocomposites at Tip Point (Magnification x250)	115
Figure 4.23	SEM of 1 phr PDG Filled UPVC Nanocomposites at Tip Point (Magnification x2000)	115
Figure 4.24	SEM of 1phr PDG filled UPVC Nanocomposites at Midway Point (Magnification x250)	116
Figure 4.25	SEM of 1 phr PDG filled UPVC Nanocomposites at Midway Point (Magnification x2000)	116
Figure 4.26	SEM of 1 phr PDG Filled UPVC Nanocomposites at Hinge Point (Magnification x250)	117
Figure 4.27	SEM of 1 phr PDG Filled UPVC Nanocomposites at Hinge Point (Magnification x2000)	117
Figure 4.28	SEM of Unfilled UPVC Composites at Tip Point (Magnification x250)	118
Figure 4.29	SEM of Unfilled UPVC Composites at Tip Point (Magnification x2000)	118
Figure 4.30	SEM of Unfilled UPVC Composites at Midway Point (Magnification x250)	119
Figure 4.31	SEM of Unfilled UPVC Composites at Midway Point (Magnification x2000)	119
Figure 4.32	SEM of Unfilled UPVC Composites at End Point (Magnification x250)	120
Figure 4.33	SEM of Unfilled UPVC Composites at End Point (Magnification x2000)	120
Figure 4.34	Typical Torque Rheometer Curve of PDG Filled UPVC Nanocomposites	123
Figure 4.35	Effect of Fusion Time and Fusion Torque on Unfilled UPVC and PDG Filled UPVC Nanocomposites	124
Figure 4.36	Effect of Fusion Time and Fusion Temperature on Unfilled UPVC and PDG Filled UPVC Nanocomposites	125
Figure 4.37	Effect of End Torque on Unfilled UPVC and PDG Filled UPVC Nanocomposites	125
Figure 4.38	Log Torque vs Log Rotor Speed to Obtain n Value	129
Figure 4.39	Log Plot of Apparent Shear Stress Versus Apparent Shear Rate	130
Figure 4.40	Log Plot of Apparent Viscosity Versus Apparent Shear Rate	131

Figure 4.41	The Effect of loading level of PDG filled UPVC Nanocomposites and CB filled UPVC Composites on Apparent Viscosity at Various Rotor Speeds	131
Figure 4.42	Typical DSC Analysis Trace Obtained from 1.5 phr PDG Filled UPVC Nanocomposites	133
Figure 4.43	DSC Trace of Unfilled UPVC, CB Filled UPVC Composites and PDG Filled UPVC Nanocomposites (0.5, 1.0 and 1.5 phr content)	135
Figure 4.44	Effect of Congo Red Stability Time (min) on CB Filled UPVC Composite VS Unfilled UPVC VS PDG Filled UPVC Nanocomposites	139
Figure 4.45	TGA curve of unfilled UPVC, CB Filled UPVC Composites and PDG Filled UPVC Nanocomposites (0.5, 1.0 and 1.5phr content)	142
Figure 4.46	Relationship between Volume Resistivity, Tensile Modulus, Impact Strength and Cost Per Unit Volume Versus Congo Red and Torque of Unfilled UPVC, PDG Filled UPVC Nanocomposites and CB Filled UPVC Composites	150

LIST OF ABBREVIATIONS

AS/NZS	-	Australia / New Zealands Standards
ASTM	-	American Society for Testing and Materials
ATR	-	Attenuated Total Reflectance
C	-	Carbide
Ca	-	Calcium
Ca-Zn	-	Calcium Zinc
CaCO ₃	-	Calcium Carbonate
CAGR	-	Compound Annual Growth Rate
CB	-	Carbon Black
Cl	-	Chloride
CLP	-	Classification, Labelling and Packaging
C _n H _{2n+2}	-	Alkanes
CNT	-	Carbon Nanotube
COOH	-	Carboxylic Acid
CPPA	-	China Plastics Piping Association
CVD	-	Chemical Vapor Deposition
DBLP	-	Dibasic Lead Phosphite
DIN	-	German Institute for Standardisation
DMF	-	N, N-dimethylformamide
DSC	-	Differential Scanning Calorimetry
EBS	-	Ethylene Bis-Stearamide
EC and E _{Paral}	-	Young's modulus of the composites with unidirectionally
EDC	-	1, 2-dichloroethane
FT	-	Fischer-Tropsch
FTIR	-	Fourier-Transform Infrared Spectroscopy
GB	-	Guabiao (Chinese National Standards)
GHS	-	Globally Harmonised System
GIC	-	Graphite Intercalation Compound
GNFs	-	Graphite Nanofibers
GNFs	-	Graphite Nanofibers
GNP	-	Graphene Nanoplatelets

GO	-	Graphene Oxide
GTL	-	Gas to Liquid
GTL	-	Gas to Liquid
H ₂ S	-	Hydrogen Sulphide
HCl	-	Hydrogen Chloride
I	-	Initiator
ICIS	-	Independent Commodity Intelligent Services
L _G , T _G & V _G	-	Length, thickness and volume fraction of rGO in the
MEK	-	Methyl Ethyl Ketone
MGO	-	Modified Graphene Oxide
MLG	-	Multi-layer Graphene
MPVC	-	Modified Polyvinyl Chloride
<i>n</i>	-	Power-law index
NaBH ₄	-	Sodium borohydride
NaBH ₄	-	Sodium borohydride
NaNO ₃	-	Sodium Nitrate
Ni	-	Nickel
NMP	-	N-methylpyrrolidone
ODCB	-	Ortho-Dichloro Benzene
OH	-	Hydroxide
OPVC	-	Oriented Polyvinyl Chloride
Pb	-	Lead
Pb-St	-	Lead Stearate
PCMs	-	Phase Change Materials
PDG	-	Pre-Dispersed Graphene
PE	-	Polyethylene
PET	-	Polyethylene Terephthalate
PMMA	-	Poly-methylmethacrylate
PP	-	Polypropylene
PPVC	-	Plasticised Polyvinyl Chloride
PS	-	Polystyrene
PVC	-	Polyvinyl Chloride
R	-	Radicals
rGO	-	Reduce Graphene Oxide
S ₂ O ₈ ²⁻	-	Persulfate

SAWS	-	State Administration of Work Safety
Sb ₂ O ₃	-	Antimony Trioxide
SEM	-	Scanning Electron Microscopy
Si	-	Silicon
SiC	-	Silicon Carbide
Sn	-	Organotin
SWCNT	-	Single Wall Carbon Nano Tube
TBLS	-	Tribasic Lead Sulphate
T _g	-	Transition Glass Temperature
TGA	-	Thermogravimetric Analysis
THF	-	Tetrahydrofuran
THF	-	Tetrahydrofuran
TiO ₂	-	Titanium Dioxide
UPVC	-	Unplasticised Polyvinyl Chloride
UV	-	Ultraviolet
VCM	-	Vinyl Chloride Monomer
VDE	-	Association for Electrical, Electronic & Information
VR	-	Volume Resistivity
Zn	-	Zinc
ZnCl ₂	-	Zinc Chloride

LIST OF SYMBOLS

wt. %	-	Weight percent
S/m	-	Siemens per meter
η_{rel}	-	Relative viscosity
K	-	K-value
c	-	Concentration
%	-	Percent
°C	-	Degree Celsius
ml	-	Milliliter
ΔE	-	Delta E
μm	-	Micron Meter
Ωm	-	Ohm meter
Å	-	Angstrom
nm	-	Nanometer
N/m	-	Newton per meter
mg/m^2	-	Milligram per square meter
mg	-	Milligram
vol. %	-	Volume percent
mg/ml	-	Milligram per milliliter
mm^2/s	-	Millimeter square per second
Pa.Sec	-	Pascal-second
Sec^{-1}	-	Per second
S/cm	-	Siemens per centimeter
MPa	-	Mega Pascal
rpm	-	Revolutions per minute
phr	-	Part per hundred
kg	-	Kilogram
min	-	Minutes
g	-	Gram
sec	-	Second
Kv	-	Kilovolts
cm^{-1}	-	Reciprocal centimetre

ρ_v	-	Volume resistivity
D1	-	Diameter of the guarded electrode
R_v	-	Volume resistance
t	-	Thickness of the test piece
mm/min	-	Millimeter per minute
N/mm ²	-	Newton per Square Millimeter
KJ/m ²	-	Kilojoule per square meter
ml/min	-	Milliliter per minute
°C/min	-	Degree celsius per minute
cm ³	-	Cubic centimeter
J/g	-	Joule per gram
cP	-	Centipoise

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
Appendix A	Materials Origin and Technical Specification	167
Appendix B	Materials Origin and Technical Specification	168
Appendix C	Materials Origin and Technical Specification	169
Appendix D	Materials Origin and Technical Specification	170
Appendix E	Materials Origin and Technical Specification	171
Appendix F	Materials Origin and Technical Specification	172
Appendix G	Materials Origin and Technical Specification	173
Appendix H	Materials Origin and Technical Specification	174
Appendix I	Materials Origin and Technical Specification	175
Appendix J	Materials Origin and Technical Specification	176
Appendix K	Calculation to Relate Rotor Speed, Torque and Viscosity	177



INTRODUCTION

1.1 Background of Study

According to Independent Commodity Intelligent Services (ICIS) reports 2020, the global polyvinyl chloride (PVC) market is growing at a compound annual growth rate (CAGR) of 5 % and is projected to reach USD 80 billion by 2024 with the volume of 53,000 kmt.

PVC is the third most widely produced synthetic plastic polymer after polyethylene (PE) and polypropylene (PP) [14]. It has been extensively used in many industries such as building and construction, electrical and electronics, automotive, packaging, footwear, and others due to its low cost, ease of processing and blending, high tensile strength, and flame-resistant properties [1].

PVC is mainly available in two forms, namely, plasticised PVC (PPVC) and unplasticised PVC (UPVC). The UPVC is a typical insulating material primarily used in construction application such as windows, doors and pipes. The stabilisation of PVC pipes is commonly done using lead-based salts such as lead sulphate or lead stearate. Lead (Pb) is a heavy metal and it is classified as toxic, whereas calcium zinc (Ca-Zn) stabilisation is recognised as an eco-friendly process, hence, paving the way in replacing Pb-based stabilisation. For instance, Europe has successfully phased out Pb in year 2015. Asia followed the trend towards Pb-free and predicted realising it in the year 2025.

Typically, Ca-Zn stabiliser has slight inferiority in thermal heat stability and narrower processing window in comparison with conventional Pb-based stabiliser. Under-loading or over-loading of Ca-Zn stabiliser will reduce its performance. Therefore, rheology adjustment is more critical. Practical experience confirm that heat

stability of Ca-Zn stabiliser is sufficient for both extrusion and recycling. Compound or dry-blend formulations together with processing parameter need to be optimised in order to be cost effective.

Mining industry involves the transportation of clean water, fresh air, slurries, muds, as well as other infrastructures in and out from the quarry. Harsh surroundings in mining areas increase the chance of the piping network to be damaged. In the event of tunnelling or underground mining operation, the ventilation system must be suffice to dilute harmful exhaust pollutants where a single spark can lead to serious fire disasters. In certain circumstances, fire disasters might be triggered by electric charges and accumulate on pipe surfaces, resulting in static electric spark [2]. Due to this particular reason, considering the possibility for corrosion, impact, abrasion and ensuring electrical conductivity have been a challenge in designing mining pipe system with low cost.

UPVC pipes have high impact strength and flexibility together with the abrasion resistance required in slurry lines which make it an ideal material for the mining industry. Several methods had been developed over the years to enhance electrical conductivity of PVC materials [3-7], such as coating PVC with conductive layers and producing conductive polymer blend through the incorporation of inorganic/liquid anti-static. PVC coated with conductive layers is easily peeled off due to poor interfacial bonding.

Carbon black (CB) is one of the most extensively used conductive fillers due to its blending compatibility with PVC matrix and low production cost [8]. In order to achieve acceptable antistatic properties for mining pipe application, loading level up to 20 weight percent (wt. %) is required which reduces the mechanical strength and processing performance of the CB filled UPVC composites. Carbon Nanotube (CNT) was first introduced to replace CB as conductive filler in PVC. CNT greatly improve electrical conductivity of PVC nanocomposites with loading level as low as 0.1 wt. % due to its high intrinsic electrical conductivity and large aspect ratio [9]. However, issues of poor dispersion and much higher production cost restrict commercial application of the CNT filled UPVC nanocomposites.

Graphene exhibits exceptional properties of high electrical and thermal conductivity; high modulus could be used as a viable and better cost performance alternative to substitute CNT [11-13]. Researchers had come up with different methods for the production of graphene, which include bottom up and top down methods such as: mechanical/chemical exfoliation, graphene oxide (GO) and reduction, arc discharge, epitaxial growth, chemical conversion, chemical vapour deposition (CVD) etc. [7].

Graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO), modified graphene oxide (MGO), graphene nanoplatelets (GNP) and multi-layer graphene (MLG) are widely used as functional fillers for polymer nanocomposites. Garmor, a company based in Florida relies upon new advances mechanochemical technology to yield edge-oxidised graphene oxide (GO) composed of a few layers of graphene. Later, the GO undergoes a reduction step using a suitable thermal, chemical and electrochemical route which is via microwave process. The rGO has an immaculate surface with almost no residual oxidation and no corrugation or damaged sp² orbital and hence conserves graphene's highly prized electrical, thermal and mechanical properties.

However, pristine graphene is not compatible with organic polymers and does not form homogeneous composites resulting in inferior properties. In order to improve the properties, the dispersion of graphene in polymer matrices and the graphene-polymer interaction need to be improved [8].

The improvement in electrical, mechanical and thermal heat stability properties of PVC matrix with graphene derivatives has recently been reported in various literatures [5, 15-19]. Solution blending method had been used to prepare graphene filled PVC nanocomposite films. In the works of Vadukumpully et al. [5], it was reported that graphene filled PVC nanocomposites have high mechanical strength, thermal stability and good conductivity. Deshmukh and Joshi [19] prepared GO filled PVC nanocomposites films using colloidal blending method and reported an augmentation in the thermal stability because of the strong inter-linkage between PVC and GO. Pham et al. [15] produced graphene filled PVC nanocomposites using

colloidal blending methods which exhibit a low percolation threshold of 0.4 wt. % and an electrical conductivity as high as 46.5 S/m corresponding to 4.0 wt. % of graphene loading. The Colloidal blending method is used to fabricate graphene filled PVC nanocomposites as done by Dang et al. [16] and achieved a threshold of 0.3 wt. %. while the best conductivity value obtained was as high as 38.5 S/m corresponding to 4 wt. % graphene loading. Ma et al. [17] observed an augmentation in electrical conductivity of graphene grafted with polyaniline filled PVC nanocomposites, and the works of Joshi et al. [18] confirmed that graphene filled PVC nanocomposites prepared using solution blending showcased high electrical conductivity properties.

1.2 Problem Statement

Notably, with the breakthrough of various graphene derivatives availability in the market with low costs [19], the method of preparing graphene filled polymer nanocomposites in a cost-effective way has been a critical issue to be explored and pushing its practical application forward. A more attractive and cost effective, GO has oxygenated groups (epoxy, hydroxyl, carboxyl) that can, in principle interact with the chlorine atoms in the PVC through halogen bonding, which serves as active sites to anchor functional groups to ensure GO compatibility with PVC. However, GO is electrically insulating which limits its application as conductive polymers. GO is electrically insulating, but becomes conductive by the chemical reduction of GO into reduced graphene oxide (rGO), presumably by restoring the graphitic network sp² bonds. Nevertheless, rGO will easily aggregate due to high cohesive interaction making it difficult to disperse. This lack of homogeneous dispersion limits its ability to enhance electrical conductivity of graphene filled UPVC nanocomposites intended to be use for mining pipe application. To achieve optimum conductive pathways of graphene filled UPVC nanocomposites the dispersability of graphene should be maximised within the PVC matrix.

When it comes to the dispersion of graphene into PVC matrix, Renteria et al. [20] in their graphene dispersion research have selected a specific paraffin wax as a composite matrix medium for graphene dispersion which is intended to be used specifically in thermal phase change materials (PCMs) application. Fischer-Tropsch (FT) derived wax is a synthetic paraffin which consists largely of straight chain alkanes with a wide range of melting points and boiling points. The use of FT wax with low viscosity type SX 60 S is expected to have better compatibility, interaction, volume loading and degree of dispersion with rGO surface.

1.3 Significance of Study

Referring to the several literature reviews [5, 15-19], it is worth pointing out that most graphene filled polymer composites are mainly prepared using solvent or in-situ process for conductive film application inevitably resulting in complicated procedures, high cost, and environmental pollution. Furthermore, this solution method is extremely difficult to be applied for large-scale production of nanocomposites.

Dry-blending method is a conventional way to produce PVC pipe in a large-scale. Bearing in mind the above mentioned, there's a need to prepare and characterise a graphene filled UPVC nanocomposite which is expected to be a promising material for mining pipe application and can be manufactured using conventional dry-blending method. This research is expected to fill up the academic deficiencies in the current UPVC nanocomposites development.

1.4 Objectives

The aim of this study is to prepare and characterise a graphene filled UPVC nanocomposites which is expected to be a promising material for mining pipe application and can be manufactured by conventional dry-blending method. In order to achieve this aim, the following objectives are identified:

1. To prepare pre-disperse rGO in Fischer-Tropsch wax in order to ease dispersion and compatibility within PVC matrix using defining melt-mixing method.
2. To investigate the effect of different type of graphene derivatives: GO, rGO and pre-dispersed rGO (PDG) in Fischer-Tropsch wax (FT wax) filled UPVC nanocomposites with varying contents on electrical, mechanical, rheological, thermal properties.
3. To analyse cost performance efficiency of Ca-Zn stabilised pre-dispersed rGO in Fischer-Tropsch wax filled UPVC nanocomposites benchmarking against commercial Pb-based stabilised CB filled UPVC composites.

1.5 Scope of Study

In order to achieve the aim of this research, the scopes of this study are as follows:

- a. To identify the optimum content of PDG in FT wax with different temperature variations using ultrasonication.
 - i. Scanning electron microscopy (SEM) to confirm the nanocomposites surface and the dispersion's homogeneity.
 - ii. Fourier-transform infrared spectroscopy (FTIR) to confirm the presence of rGO.
- b. Design of experimental formulation followed by the preparation of sample, which involves the following stages:
 - i. high speed Mixing
 - ii. two-roll milling
 - iii. compression moulding

- c. Electrical conductivity test to determine:
 - i. the effect of Pb and Ca-Zn stabiliser on volume resistivity.
 - ii. the effect of various contents of GO, rGO and PDG on filled UPVC nanocomposites in term of volume resistivity.
 - iii. the optimum content of PDG filled UPVC nanocomposites in order to achieve comparable volume resistivity of commercial CB filled UPVC composites.
- d. Tensile test to determine the effect of various contents of GO, rGO and PDG on filled UPVC nanocomposites in term of tensile strength, elongation at break and Tensile modulus.
- e. The Halpin-Tsai equation was used to simulate the modulus of the PDG filled UPVC nanocomposites to study the distribution of graphene nanosheets in the polymer matrix.
- f. Impact test to determine the effect of various contents of PDG filled UPVC nanocomposites on impact strength.
- g. Scanning electron microscopy (SEM) to study the morphological and structural of fracture test specimens to correlate with the impact test results.
- h. To determine the effect of various contents of PDG filled UPVC nanocomposites on mechanical properties benchmarking against commercial CB filled UPVC composites.
- i. Torque rheometer (Brabender plasticoder) is used to study the processability of various contents of PDG filled UPVC nanocomposites benchmarking against commercial CB filled UPVC composites.
- j. Differential Scanning Calorimetry (DSC) analysis to determine transition glass temperature (T_g), degree of fusion and processing temperature of various content of PDG filled UPVC nanocomposites benchmarking against commercial CB filled UPVC composites.

- k. Thermogravimetric analysis (TGA) and congo red test to determine the thermal heat stability of various contents of PDG filled UPVC nanocomposites.
- l. Determine the cost performance efficiency of electrical, mechanical, processability and thermal heat stability of PDG filled UPVC nanocomposites at various contents benchmarking against commercial CB filled UPVC nanocomposites.

REFERENCES

1. Wilkes, C. E., Daniels, C. A., and Summers, J. W. 2005, PVC Handbook, Munich: Hanser Publishers.
2. Saad, A. L. G., Sayed, W. M., Ahmed, M. G. M. and Hassan, A. M. 1999, Preparation and properties of some filled poly(vinyl chloride) compositions, *J Appl Polym Sci*, 73(13), 2657-2670.
3. Mouley, S. 2010, Chemical modification of poly(vinyl chloride)- still on the run, *Prog Polym Sci*, 35(3), 303-331.
4. Saad, A. L. G., Aziz, H. A. and Dimitry, O. I. 2011, Studies of electrical and mechanical properties of poly(vinyl chloride) mixed with electrically conductive additives, *J Appl Polym Sci*, 49,(1), 198-205.
5. Vadukumpully, S., Paul, J., Mahanta, N. and Valiyaveetil, S. 2011, Flexible conductive graphene/poly(vinyl chloride) composite thin films with high mechanical strength and thermal stability, *Carbon*, 49(1), 198-205.
6. Ouyang, M. and Chance, C. M. 1998, Conductive polymer composites prepared by polypyrrole-coated poly(vinyl chloride) powder: relationship between conductivity and surface morphology, *Polymer*, 39(10), 1857-1862.
7. Saad, A. L.G., Hussien, L. I., Ahmed, M. G. M. and Hassan, A. M. 1998, Studies of electrical and mechanical properties of semiconductive poly(vinyl chloride) compositions, *J Appl Polym Sci*, 69(4), 685-693.
8. Zhou, S., Lei, J., Sun, Z. and Li, Q. 2006, Study on novel soft poly(vinyl chloride) with antistatic property, *Acta Chim Sin*, 64.
9. Mamunya, Y., Boudenne, A., Lebovka, N., Ibov, L., Candau, Y. and Lisunova, M. 2008, Electrical and thermophysical behaviour of PVC-MWCNT nanocomposites, *Compos Sci Technol*, 68(9), 1981-1988.
10. Broza, G., Piszczek, K., Schulte, K. and Sterzynski, 2007, Nanocomposites of Poly(Vinyl Chloride) with Carbon Nanotubes (CNT), *Compos Sci Technol*, 67(5), 890-894.
11. Stankovich, S., Dikin, D. A., Dommett, G. H. B. and Kohlhaas, K. M. 2006, Graphene-based composite materials, *Nature*, 442, 282-286.

12. Tang, G., Jiang, Z. G., Li, X., Zhang, H. B. and Hong, S. 2014, Electrically conductive rubbery epoxy/diamine-functionalized graphene nanocomposites with improved mechanical properties, *Compos*, 67, 564-570.
13. Du, J., Zhao, L., Zheng, Y., Zhang, L., Li, F., Liu, P. and Liu, C. 2011, Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/ high density polyethylene composites with a segregated network structure, *Carbon*, 49(4), 5820-5826.
14. Retrieved 15 May 2020, Plastic Europe, Association of Plastic Manufactures: <https://www.plasticseurope.org/en/about-plastics/what-are-plastics/large-family/polyvinyl-chloride>.
15. Pham, V. H., Dang, T. T., Hur, S. H. and Kim, E. J. 2012, Morphology and properties of segregated-network chemically converted graphene-poly(vinyl chloride) composite, *J Nanosci Nanotechnol*, 12,(7), 1094-2100.
16. Dang, T. T., Pham, V. H. and Chung, J. S. 2010, Preparation of poly (vinyl chloride) solvo thermally reduced graphene composite by latex technology, *Proceedings of International Forum on Strategic Technology (IFOST 2010)*.
17. Ma, F., Yuan, N. and Ding, J. 2012, The conductive network made up by the reduced graphene nanosheet/polyaniline/polyvinyl chloride, *J Appl Polym Sci*, 128(6), 3870-3875.
18. Joshi, G. M. and Deshmukh K. 2014, Optimized quality factor of graphene oxide-reinforced PVC nanocomposite, *J Electron Mater*, 43, 1161-1165.
19. Deshmukh, K. and Joshi, G. M. 2014, Thermo-mechanical properties of poly (vinyl chloride)/graphene oxide as high performance nanocomposites, *Polym Test*, 34 (4), 211-219.
20. Renteria, J. D., Nika, D. L. and Balandin, A. A. 2014, Graphene thermal properties: applications in thermal management and energy storage, *Appl. Sci.* 4(4), 525-547.
21. Allsopp, M. W. and Vianello, G. 2012, *Poly(Vinyl Chloride)*, Weinheim: Wiley-VCH.
22. Baumann, E. 1872, "Ueber einige Vinylverbindungen" (On some vinyl compounds), Munich: Justus Liebigs Annalen der Chemie.
23. Titow, W. V. 1990, *PVC Plastics Properties, Processing, and Applications*, Essex: Elsevier Science Publisher Ltd.

24. Brooks, B. 2010, Suspension Polymerization Processes. *Chemical Engineering and Technology*, 33 (11), 1737-1744.
25. Cowie, J. M. G. 1991, *Polymers: Chemistry and Physics of Modern Materials*, London: Blackie.
26. Geddes, W. C. 1967, The Thermal Decomposition of Polyvinylchloride – I. Kinetics of Dehydrochlorination, *European Polymer Journal*, 3(2), 267-281.
27. Braun, D. 1981), Thermal Degradation of Polyvinyl Chloride, *Pure and Applied Chemistry*, 26(2), 173-190.
28. Grossman, R. F. 2008, *Handbook of vinyl formulating*, New Jersey: John Wiley & Sons Inc.
29. Patrick, S. G. 2005, *Practical Guide to Polyvinyl Chloride*, London: Rapra Technology Limited.
30. Folarin, O. M. and Sadiku, E. R. 2011, Thermal Stabilizers for Poly(vinyl chloride): A Review, *International Journal of the Physical Sciences*, 6(18), 4323-4330.
31. Wypych., G. 2008, *PVC Degradation and Stabilization*, Toronto: ChemTec Publishing.
32. Zweifel, H., Maier, R. D., Schiller, M. and Amos, S. E. 2001, *Plastics Additives Handbook*. Cincinnati: Hanser Publications.
33. Mathur, K. K. and Vanderheiden, D. B. 1982, Precipitated Calcium Carbonates as Ultraviolet Stabilizers and Impact Modifiers in Poly (Vinyl Chloride) Siding and Profiles, *Polymer additives*, 26, 371-389.
34. Schwartz, G., Cervený, S. and Marzocca, A. J. 2000, A numerical simulation of the electrical resistivity of carbon black filled rubber, *Polymer*, 41(17), 6589-6595.
35. Titow, W. V. 1986, *PVC Technology – 4th Edition*. USA: USA: Elsevier Applied Science Publishers Ltd.
36. Pötschke, P., Dudkin, S. M. and Alig, I 2003, Dielectric spectroscopy on melt processed polycarbonate—multiwalled carbon nanotube composites, *Polymer*, 44(17), 5023-5030.
37. Leadbitter, J. 2002, PVC and Sustainability, *Progress in Polymer Science*, 27(10), 2197-2226.
38. The American Architectural Manufacturers Association (AAMA). 2012. Sustainable Vinyl. <https://aamanet.org/pages/vinyl-green-and-sustainability>.

39. Lucas, H. 2017, What's wrong with PVC?, London: Greenpeace.
40. Wagner, J. D. 2001. 7 Myths About PVC Debunked. <https://www.carlislesyntec.com/dfsmedia/c9a15d476f364981b1124520f6258acf/8965-source>.
41. The American Architectural Manufacturers Association (AAMA). 2008. Avoiding the Land Fill: The Recycling Vinyl Windows and Doors. http://www.aamanet.org/upload/file/The_Recycling_of_Vinyl_Windows_and_Doors.pdf
42. Commission of the European Communities. 2000. Environmental Issues of PVC. Brussels: Commission of the European Communities.
43. Singh, V., Joung, D., Zhai, L., Das, S., Khondaker, S. I. and Seal, S. 2011, Graphene based materials: Past, present and future, *Progress in materials science*, 56, 1178–1271.
44. Neto, A. H. C., Guinea, F., Peres, N. M. R., Novoselov, K. S. and Geim, A. K. 2009, The electronic properties of graphene, *Mod. Phys.*, 81, 109.
45. Class for Physics. 2010. Scientific Background on the Nobel Prize in Physics 2010. Sweden: Royal Swedish Academy of Sciences.
46. Derbyshire, D. 2010. Dailymail UK. Retrieved 18 February, 2016, from Dailymail UK: <http://www.dailymail.co.uk/sciencetech/article-2045825/G>.
47. Fuente, J. D. L., 2016, Graphene - What Is It? <https://www.graphenea.com/pages/graphene#.X2yMBUBuKM8>.
48. Vadukumpully, S. 2011, Preparation, Characterization And Property Studies of Carbon Nanostructures Derived From Carbon Rich Materials, Singapore: National University of Singapore.
49. Gudarzi, M. M. and Sharif, F. 2012, Enhancement of Dispersion and Bonding of Graphene Polymer Through Wet Transfer of Functionalized Graphene Oxide, *eXPRESS Polymer Letters*, 6(12), 1017–1031.
50. Salim, N. K., Ahmad, B., Mohd Nashrul, M. Z., Huang, N. M., Misni, M., Emad, S., Mehrali, M and Nur, I. S. 2015, Investigation on the use of graphene oxide as novel surfactant to stabilize weakly charged graphene nanoplatelets, *Nanoscale research letters*, 10.
51. Wang, H., Xie, G., Ying, Z., Tong, Y. and Zeng, Y. 2015, Enhanced Mechanical Properties of Multi-layer Graphene Filled Poly(vinyl chloride) Composite Films, *Journal of Materials Science & Technology*, 31(4), 340-344.

52. Gierz, I., Riedl, C., Starke, U., Ast, C. R. and Kern, K. 2008, Atomic Hole Doping of Graphene, *Nano Lett*, 8(12), 4603–4607.
53. Godovsky, D. Y. 2000, Device Applications of Polymer-Nanocomposites, *Adv Polym Sci*, 153, 163–205.
54. Kuilla, T., Bhadra, S., Yao, D., Kim, N. H., Bose, S. and Lee, J. H. 2010, Recent advances in graphene based polymer composites, *Progress in Polymer Science*, 35(11), 1350-1375.
55. Duguay A.J., Nader¹, J. W., Kiziltas, A., Gardner¹, D. J. and Dagher, H. J. 2014, Exfoliated Graphite Nanoplatelets-filled Impact Modified Polypropylene Composites: Influence of Particle Diameter, Filler Loading and Coupling Agent on Mechanical Properties, *Applied Nanoscience*, 4, 279 - 291.
56. Tripathi, P., Ravi, C. H., Patel, P., Shaz, M. A. and Srivastava, O. N. 2013, Synthesis of High-quality Graphene Through Electrochemical Exfoliation of Graphite in Alkaline Electrolyte. *Materials Science*, 1310.
57. Krane, N. 2001, Preparation of Graphene. *Selected Topics in Physics: Physics of Nanoscale Carbon*.
58. Enderlein, C. 2010, Graphene and its Interaction with Different Substrates Studied by Angular-Resolved Photoemission Spectroscopy. Berlin: Freie Universita et Berlin.
59. Juang, H. Y., Wu, C. Y., Lu, A. Y., Su, C. Y., Leou, K. C., Chen, F. R. and Tsai, C. H. 2010, Graphene Synthesis by Chemical Vapor Deposition and Transfer by a Roll-to-roll Process, *Carbon*, 48(11), 3169-3174.
60. Yu, Q., Lian, J., Siriponglert, S., Li, H., Chen, Y. P. and Pei, S. S. 2008 Graphene Segregated on Ni Surfaces and Transferred to Insulators. *Appl Phys Lett*, 93(11), 1-3.
61. Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V., Dresselhaus, M. S. and Kong, Jing. 2009, Large Area, Few-layers Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition, *Nano Lett*, 9(1), 30-35.
62. Kim, K. S., Zhao, Y., Jang, H., Lee, S., Kim, J. M., Kim, K. S., Ahn, J. H., Kim, P., Choi, J. Y. and Hong, B. H. 2009, Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes, *Nature*, 457, 706-710.
63. Juang, Z. Y., Wu, C. Y., Lo, C. W., Chen, W. Y., Huang, C. F., Hwang, J. C., Chen, F. R., Leou, K. C. and Tsai, C. H. 2009, Synthesis of Graphene on Silicon Carbide Substrates at Low Temperature. *Carbon*, 47(8), 2026-2031.

64. Reina, A., Thiele, S., Jia, X., Bhaviripudi, S., Dresselhaus, M. S., Shaefer, J. A. and Kong, Jing. 2009, Growth of Large-area Single- and Bi-layer Graphene by Controlled Carbon Precipitation on Polycrystalline Ni Surfaces. *Nano Research*, 2, 509-516.
65. Reina, A., Son, H., Jiao, L., Fan, B., Dresselhaus, M. S., Liu, Z. F., Kong, Jing. 2008, Transferring and Identification of Single- and Few-layers Graphene on Arbitrary Substrates, *J Phys Chem C*, 112(46), 17741-17744.
66. Chae, S. J., Güneş, F., Lim, K. K., Kim, E. S., Han, G. H., Kim, S. M., Shin, H. J., Yoon, S. M., Choi, J. Y., Park, M. H., Yang, C. W., Pribat, D. and Lee, Y. H. 2009, Synthesis of Large-area Graphene Layers on Poly-Nickel Substrate by Chemical Vapor Deposition: Wrinkle Formation, *Adv. Material*, 21(22), 2328-2333.
67. Obraztsov, A. N., Obraztsova, E. A., Tyurnina, A. V. and Zolotukhin, A. A. 2007, Chemical Vapour Deposition of Thin Graphite Films of Nanometer Thickness, *Carbon*, 45(10), 2017-2021.
68. Layek, R. K. and Nandi, A. K. 2013, A Review on Synthesis and Properties of Polymer Functionalized Graphene, *Polymer*, 54(19), 5087-5103.
69. Riedl, C., Coletti, C., Iwasaki, T., Zakharov, A. A. and Starke, U. 2009, Quasi Freestanding Epitaxial Graphene on Sic Obtained by Hydrogen Intercalation, *Phys. Rev. Lett*, 103(24).
70. Varykhalov, A., Sánchez-Barriga, J., Shikin, A. M., Biswas, C., Vescovo, E., Rybkin, A., Marchenko, D. and Rader, O. 2008, Electronic and Magnetic Properties of Quasifreestanding Graphene on Ni, *Phys. Rev. Lett.*, 101(15)
71. Abdala, A. A. 2012, Polymer Graphene Nanocomposites. The Sixth Jordan International Chemical Engineering Conference. Amman, Jordan.
72. Eda, G., Chhowalla, M. 2010, Chemically Derived Graphene Oxide: Towards Large-Area Thin-film Electronics and Optoelectronics, *Adv. Material*, 22(22), 2392-2415.
73. Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D., Adamson, D. H., Schniepp, H. C., Chen, X., Ruoff, R. S., Nguyen, S. T., Aksay, I. A., Prud'Homme R. K. and Brinson, L. C. 2008, Functionalized Graphene Sheets for Polymer Nano Composites, *Nat. Nano. Technol.*, 3, 327-331.

74. Geng, X., Guo, Y., Li, D., Li, W., Zhu, C., Wei, X., Chen, M., Gao, S., Qiu, S., Gong, Y., Wu, L., Long, M., Sun, M., Pan, G. and Liu, L. W. 2013, Interlayer Catalytic Exfoliation Realizing Scalable Production of Large Size Pristine Few Layer Graphene, *Sci. Rep.*, 3, 1134.
75. Kuilla, T., Bhadra, S., Yao, D., Kim, N. H., Bose, S. and Lee, J. H. 2010, Recent Advances in Graphene Based Polymer Composites, *Progress in Polymer Science*, 35(11), 1350-1375.
76. Kumar, M., Chung, J. S. and Hur, S. H. 2014, Controlled atom transfer radical polymerization of MMA onto the surface of high-density functionalized graphene oxide, *Nanoscale research letters*, 9, 345.
77. Atif, R. and Inam, F. 2016, Reasons and Remedies for the Agglomeration of Multilayered Graphene and Carbon Nanotubes in Polymers, *Beilstein journal of nanotechnology*, 7, 1174–1196.
78. Wei, J., Saharudin, M. S., Vo, T and Inam, F. 2017, N,N-Dimethylformamide (DMF) Usage in Epoxy/Graphene Nanocomposites: Problems Associated with Reaggregation, *Polymer*, 9(6), 193.
79. Sahoo, S., Hatui, G., Bhattacharya, P., Dhibar, S. and Das, C. K. 2013, One Pot Synthesis of Graphene by Exfoliation of Graphite in ODCB, *Graphene*, 2, 42-48.
80. Atif, R. and Inam, F. 2016, Modeling and Simulation of Graphene Based Polymer Nanocomposites: Advances in the Last Decade, 2016, 5, 96–142.
81. Šupová, M., Martynková, G. S. 2011, Effect of nanofillers dispersion in polymer matrices: a review, *Science of advanced materials*, 3(1), 1-25.
82. Shen, B., Zhai, W. T., Lu, D. D., Wang, J. and Zheng, W. G. 2012, Ultrasonication-assisted Direct Functionalization of Graphene with Macromolecules, *RSC Adv.*, 2, 4713-4719.
83. Renteria, J. D., Nika, D. L., Balandin, A. A. 2014, Graphene thermal properties: applications in thermal management and energy storage, *Appl. Sci.* 4(4), 525-547.
84. Goli, P., Legedza, S., Dhar, A., Salgado, R., Renteria, J. and Balandin, A. A. 2014, Graphene-enhanced hybrid phase change materials for thermal management of Li-ion batteries, *Journal of Power Sources*, 248, 37-43.
85. Al-Zahrani, S. M. and Al-Fariss, T. F. 1998, A general model for the viscosity of waxy oils. *Chemical Engineering and Processing*, 37(5), 433-437.

86. Gudarzi, M. M., Sharif, F. 2012, Enhancement of dispersion and bonding of graphene-polymer through wet transfer of functionalized graphene oxide, *eXPRESS Polymer Letters*, 6(12), 1017–1031.
87. Wang, Y., Lu, J., Tang, L., Chang, H. and Li, J. H. 2009, Graphene oxide amplified electrogenerated chemiluminescence of quantum dots and its selective sensing for glutathione from thiol-containing compounds. *Anal Chem.*, 81(23), 9710–9715.
88. Salavagione, H. J. and Martínez, G. 2011, Importance of covalent linkages in the preparation of effective reduced graphene oxide – Poly(vinyl chloride) nanocomposites, *Macromolecules*, 44(8), 2685–2692.
89. Hasan, M. and Lee, M. Y. 2014, Enhancement of the thermo-mechanical and efficacy of mixing technique in the preparation of graphene/PVC nanocomposites compared to carbon nanotubes/PVC, *Progress in Natural Science: Materials International*, 24(6), 579-587.
90. Wang, H., Xie, G., Fang, M., Ying, Z., Tong, Y. and Zeng, Y. 2015, Electrical and mechanical properties of antistatic PVC films containing multi-layer graphene, *Composites Part B: Engineering*, 79, 444-450.
91. Ovid'Ko. 2013, Mechanical properties of graphene, *Rev.Adv.Mater.Sci.*, 1(34), 1-11.
92. Deshmukh, K., Khatake, S. M. and Joshi, G. M. 2013, Surface properties of graphene oxide reinforced polyvinyl chloride nanocomposites, *J. Polym. Res.* 20, 286.
93. Xiang, J. and Drzal, L. T. 2011, Thermal conductivity of exfoliated graphite nanoplatelet paper, *Carbon*, 49(3), 773-778.
94. Gonçalves, G., Marques, P. A. A. P., Barros-Timmons, A., Bdkin, I., Singh, M. K., Emamic N. and Grácioa J. 2010, Graphene oxide modified with PMMA via ATRP as a reinforcement filler, *Journal Of Materials Chemistry*, 20, 9927-9934.
95. Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Bao, W. Z., Calizo, I., Teweldebrhan, D., Miao, F. and Lau, C. N. 2008, Superior thermal conductivity of single-layer graphene. *Nano Lett*, 8(3), 902-907.
96. Zhang, Q. H., Chen, D. J., et. al. 2020, Enhanced mechanical properties of graphene-based poly(vinyl alcohol) composites, *Macromolecules*, 43(5), 2357–2363.

97. Halpin, J. C., Kardos, J. L. 1976, The Halpin-Tsai equations: a review. *Polym. Eng. Sci.*, 16(5), 344-352.
98. Qian, D., Dickey, E. C., Andrews, R., Rantell, T. 2000, Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites, *Appl. Phys. Lett.*, 76(1), 2868.
99. Kulas, F. R., Thorshaug, N. P. 1974, The influence of stabilizers on the fusion of rigid poly (vinyl chloride), *Journal of Polymer Engineering and Science*, 14(5), 366-370.
100. Bower, J. D. 1986, The function of lubricant in processing of rigid poly(vinyl chloride), *Journal of Vinyl Technology*, 8(4), 179-182.
101. Casey, W. J., Okano, K. 1986, An investigation of acrylic processing aids for low molecular weight PVC, *Journal of Vinyl Technology*, 8(1), 37-40.
102. Ari, G. A., Aydin, I. 2011, A study on fusion and rheological behaviors of PVC/SiO₂ microcomposites and nanocomposites: The effects of SiO₂ particle size, *Polymer Engineering & Science*, 51(8), 1574-1579.
103. Chen, C. H., Teng, C. C., Su, S. F., Wu, W. C., Yang, C. H. 2005, Effects of microscale calcium carbonate and nanoscale calcium carbonate on the fusion, thermal, and mechanical characterizations of rigid poly(vinyl chloride)/calcium carbonate composites, *Journal of Polymer Physics*, 44(2), 451-460.
104. Rabinovitch, E. B., Summers, J. W. 1980, Poly (vinyl chloride) processing morphology, *Journal of Vinyl Technology*, 2(3), 165-168.
105. Matuana, L. M., Kim, J. W. 2007, Fusion characteristics of rigid PVC/wood-flour composites by torque rheometry, *Journal of Vinyl and Additives Technology*, 13(1), 7-13.
106. Krzewki, B. J., Collins, E. A. 1981, Rheology of PVC compounds. I. effect of processing variables on fusion, *Macromol Sci. Phys.*, 20(4). 443-464.
107. Hawkins, T. 1982, Evaluation of PVC compound on the brabender torque rheometer, *Journal of Vinyl Technology*, 4(3), 110-114.
108. Rabinovitch, E. B. 1982, Poly(Vinyl chloride) processing morphology part II—molecular effects on processing in the torque rheometer, *Journal of Vinyl Technology*, 4(2), 62-66.
109. Chen, C. H., Wesson, R. D., Collier, J. R., Lo, W. Y. 1995, Studies of rigid poly(vinyl chloride) (PVC) compounds. IV. Fusion characteristics and morphology analyses, *Journal of Applied Polymer Sciences*, 58(7), 1107-1115.

110. Chen, C. H., Lo, W. Y. 1999, Influences of chlorinated polyethylene and oxidized polyethylene on the fusion of rigid poly(vinyl chloride) compounds, *Journal of Applied Polymer Sciences*, 74(3), 699-705.
111. Faulkner, P. G. 1975, The use of a temperature programmable brabender mixing head for the evaluation of the processing characteristics of poly(vinyl chloride), *J. Macromol Sci-phys*, 11(2), 251-279.
112. Kalaitzidou K., Fukushima H., Drzal L. T. 2007, Multifunctional polypropylene composites produced by incorporation of exfoliated graphite nanoplatelets, *Carbon*, 45(7), 1446-1452.
113. Ghose S., Working, D. C., Connell, J. W., Smith, JG, J. R., Watson, K. A., Delozier, D. M., Sun, Y. P., Lin, Y. 2006, Thermal Conductivity of UltemTM/Carbon Nanofiller Blends, *High Perform Polym*, 18(6), 961-977.
114. Planes, E., Duchet, J., Maazouz, A., Gerard, J. F. 2008, Characterization of new formulations for the rotational molding based on ethylene-propylene copolymer/graphite nanocomposites, *Polym Eng Sci*, 48(4), 723-731.
115. Chen, C. H., Li, H.C., Teng, C. C., Yang, C. H. 2006, Fusion, electrical conductivity, thermal, and mechanical properties of rigid poly(vinyl chloride) (PVC)/carbon black (CB) composites, *J. Appl. Polym. Sci.*, 99(5), 2167-2173.
116. Byler, L. and Daane, J. 1967, An analysis of Brabender torque rheometer data. *Polymer Engineering and Science*, 7(3), 178-181.
117. Goodrich, J. E., & Porter, R. S. 1967, A rheological interpretation of torque-rheometer data. *Polymer Engineering and Science*, 7(1), 45-51.
118. Strankowski, M., Włodarczyk, D., Piszczyk, L. and Strankowska, J. 2016, Thermal and Mechanical Properties of Microporous Polyurethanes Modified with Reduced Graphene Oxide, *International Journal of Polymer Science*.
119. Wang, L., Hong, J., Chen, G. 2010, Comparison study of graphite nanosheets and carbon black as fillers for high density polyethylene, *Polym Eng Sci*, 50(11), 2176-2181.
120. Kalaitzidou, K., Fukushima, H., Drzal, L. T. 2007, Multifunctional polypropylene composites produced by incorporation of exfoliated graphite nanoplatelets, *Carbon*, 45(7), 1446-1452.
121. George, J. J., Bandyopadhyay, A., Bhowmick, A. K. 2008, New generation layered nanocomposites derived from ethylene-co-vinyl acetate and naturally occurring graphite. *J Appl Polym Sci*, 108(3), 1603-1616.

122. Kim, H., Macosko, C. W. 2008, Morphology and Properties of Polyester/Exfoliated Graphite Nanocomposites, *Macromolecules*, 41(9), 3317-3327.
123. Katbab, A. A., Hrymak, A. N., Kasmadjian, K. 2008, Preparation of interfacially compatibilized PP-EPDM thermoplastic vulcanizate/graphite nanocomposites: Effects of graphite microstructure upon morphology, electrical conductivity, and melt rheology, *J Appl Polym Sci*, 107(5), 3425-3433.
124. Gopakumar, T. G., Page, D.J.Y.S. 2004, Polypropylene/graphite nanocomposites by thermo-kinetic mixing, *Polym Eng Sci*, 44(6), 1162-1169.
125. Kim, H., Macosko, C. W. 2009, Processing-property relationships of polycarbonate/graphene composites, *Polymer*, 50(15), 3797-3809.
126. Xie, X. L., Liu, Q. X. I., Li, R. K. Y., Zhou, X. P., Zhang, Q. X., Yu, Z. Z., and Mai, Y. W. 2004, Rheological and mechanical properties of PVC/CaCO₃ nanocomposites prepared by in situ polymerization, *Polymer*, 45(19), 6665-6673.
127. Gilbert, M., Vyvoda, J. C. 1981, Thermal analysis technique for investigating gelation of rigid PVC compounds, *Polymer*, 22(8), 1134-1136.
128. Potente, H., Schultheis, S. M. 1987, Measurement of the degree of gelation of PVC with the DSC, *Kunststoffe*, 77, 401-404.
129. Wang, H., Xie, G., Yang, C., Zheng, Y., Ying, Z., Ren, W., Zeng, Y. 2017, Enhanced toughness of multilayer graphene-filled poly(vinyl chloride) composites prepared using melt-mixing method, *Polym. Compos.*, 38, 138-146.
130. Hu, J., Jia, X., Li, C., Ma, Z., Zhang, G., Sheng, W., Wei, Z. 2014, Effect of interfacial interaction between graphene oxide derivatives and poly (vinyl chloride) upon the mechanical properties of their nanocomposites. *J. Mater*, 49, 2
131. Salavagione, H. J., Martínez, G. 2011, Importance of Covalent Linkages in the Preparation of Effective Reduced Graphene Oxide– Poly (vinyl chloride) Nanocomposites. *Macromolecules*, 44, 2685-2692.943-2951.
132. Xie, X. L., Li, R. K. Y., Liu, Q. X., Mai, Y. W. 2004, Structure-property relationships of in situ PMMA modified nano-sized antimony trioxide filled poly (vinyl chloride) nanocomposites. *Polym*, 45, 2793-2802.
133. Ahmad, Z., Al-Awadi, N. A., & Al-Sagheer, F. 2008, Thermal degradation studies in poly(vinyl chloride)/poly(methyl methacrylate) blends, *Polymer Degradation & Stability*, 93(2), 456–465.

134. Nuñez, A. J., Kenny, J. M., Reboredo, M. M., Aranguren, M. I., & Marcovich, N. E. 2002, Thermal and dynamic mechanical characterization of polypropylene-woodflour composites. *Polymer Engineering & Science*, 42(4), 733–742.
135. Hu, J. M., Jia, X., Li, C. H., Ma, Z. Y., Zhang, G. X., Sheng, W. B., et al. 2014, Effect of interfacial interaction between graphene oxide derivatives and poly(vinyl chloride) upon the mechanical properties of their nanocomposites. *J Mater Sci*, 49(7), 2943-2951.
136. Comeaux, E. J., Chen, C. H., Collier, J. R., Wesson, R. D. 1994, Fusion study of polyvinyl chloride (PVC): relation of processing time and processing temperature to the degree of fusion, *Polymer Bulletin*, 33, 701-708.
137. Terselius, B., Jansson, J. F., Bystedt, J. 1985, Gelation of PVC. IV: Impact strength, *Plast Rubber Proc. Appl.* 5(1), 1-7.
138. Axtell, F. H., Sophanowong, W., Rujiranontapong, K. 1994, The influence of soft filler characteristics and fusion level on the impact strength of poly(vinyl chloride), *P1. Rubber Comp. Proc. Appl.*, 21 (1), 53-61.
139. Calvert, D. J., Haworth, B., Stephenson, R. C. 1991, Processing and fracture behaviour of impact-modified PVC, *Plast. Rubb. Compos. Roc. Appl.*, 15, 229.
140. Marshall, D. E., Higgs, R. P., Obande, O. P. 1983, International Conference on PVC Processing, London, 13.
141. Imery Group brochure, Production of Carbon Black, Malaysia.
142. Retrieved 21 June 2020, from ASEAN Vinyl Council: <http://aseanvinyl.com/>.
143. Cassel, R. B., Determine volatiles in Polyethylene Terephthalate using the Q5000 IT thermogravimetric analyser. TA Instruments, <http://www.tainstruments.com>.