

**EFFECTS OF GRAPHENE OXIDE COATING ON
THE PROPERTIES OF
POLYURETHANE/NANOFILLER
NANOCOMPOSITE FOAMS**

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2022**

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POLYURETHANE/NANOFILLER NANOCOMPOSITE FOAMS**

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Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

August 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled '**Effects of graphene oxide coating on the properties of polyurethane/nanofiller nanocomposite foams**'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia for providing sufficient resources, facilities and equipment throughout the period of my experiments. I am truly appreciating for the resources, facilities and equipment provided. Next, I would like to express my sincere gratitude and deep appreciation to my supervisor, Prof. Dr. Chow Wen Shyang for his continuous guidance and advice whenever I faced difficulties or problem in completing my final year project. His detailed reviews, constructive comments and suggestions allow me to have better understanding on my final year project. Without his guidance, I will not be able to complete this work successfully. Besides, I would like to thank all the laboratory technicians especially En. Mohammad Azrul bin Zainol, En. Mohd Faizal bin Mohd Kassim and En. Muhammad Sofi bin Jamil for their helps and advices throughout the period of my experiment. My experiment will not be able to run smoothly without their technical assistance and kindly support. Lastly, I would like to thank my family and friends who always motivate and support me. Their persistent help and encouragement always keep me motivated.

TABLE OF CONTENTS

DECLARATION.....	ii
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	iii
LIST OF TABLES	vi
LIST OF ABBREVIATIONS	vii
LIST OF SYMBOLS	viii
ABSTRAK	ix
ABSTRACT	x
CHAPTER 1	1
1.1 Overview	1
1.2 Background.....	1
1.3 Problem Statement.....	5
1.4 Objectives	6
1.5 Scope of Study.....	6
1.6 Thesis Outline	7
CHAPTER 2	8
2.1 Overview	8
2.2 Polyurethane	8
2.3 Polyurethane Foam	16
2.3.1 Polyurethane Nanocomposite Foam	25
2.3.2 Polyurethane Foam with Carbon Black.....	26
2.3.3 Polyurethane Foam with Carbon Nanotube.....	30
2.3.4 Polyurethane Foam with Graphene oxide.....	35
2.4 Electromagnetic Interference (EMI) and Electrostatic discharge (ESD)...	38
2.5 Summary of Literature Review.....	41
CHAPTER 3	43
3.1 Flow chart of research methodology	43
3.2 Materials	46
3.3 Preparation of foam samples.....	46
3.3.1 Preparation of unfilled PU foams	46
3.3.2 Preparation of PU nanocomposite foams.	47
3.3.3 Preparation of Graphene Oxide mixture.....	48
3.3.4 Preparation of GO coated PU nanocomposite foam.....	49

3.4 Sample Characterization	50
3.4.1 Foam Density	50
3.4.2 Scanning Electron Microscope (SEM)	51
3.4.3 Electrical Conductivity – Surface resistance	52
CHAPTER 4	53
4.1 Overview	53
4.2 Foam density	53
4.2.1 PU/CB nanocomposite foam	53
4.2.2 PU/MWCNT nanocomposite foams.....	54
4.2.3 Comparison between the foam densities of PU/CB and PU/MWCNT nanocomposite foams	56
4.3 Morphology characterization of PU nanocomposite foams	59
4.3.1 Effect of CB loading on the cell size of PU/CB nanocomposite foams	59
4.3.2 Effect of MWCNT loading on the cell size of PU/MWCNT nanocomposite foams.....	62
4.3.3 Microstructure evaluation of PU nanocomposite foams	64
4.3.4 Effect of graphene oxide coating on PU nanocomposite foams.....	68
4.4 Surface Resistance	71
4.4.1 Surface resistance of PU/CB nanocomposite foams	71
4.4.2 Surface resistance of PU/MWCNT nanocomposite foams	73
4.4.3 Comparison of CB and MWCNT on the surface resistance of PU nanocomposite foams	75
4.4.4 The effect of GO content on the surface resistance of PU nanocomposite foams.....	78
CHAPTER 5	80
5.1 Conclusion	80
5.2 Recommendations for future work	81
REFERENCES	82
APPENDICES	106

LIST OF FIGURES

Figure 2. 1: Classes of PU-based products (John et al., 2016).	9
Figure 2. 2: Polyurethane synthesis (Patti et al., 2021)	10
Figure 2. 3: Chemical structure of PU (Kemona et al., 2020).	12
Figure 2. 4: Applications of bio-TPU (Atika and Mustafa, 2021).....	13
Figure 2. 5: Schematic diagram of shape memory behaviour (Suman, 2017).....	14
Figure 2. 6: Global WPU market size (Verified Market Research, 2020).	15
Figure 2. 7: Polyurethane foam synthesis (Kausar, 2018).	17
Figure 2. 8: Preparation of free-rising PU foam (Haridevan et al., 2021).	18
Figure 2. 9: Schematic representation of nucleation, growth, and stabilization steps of foam formation. (Letizia et al., 2017)	19
Figure 2. 10: Homogenous and heterogenous nucleation in polymeric foams (Zimmermann et al., 2018).	20
Figure 2. 11: Rigid and flexible PU foams (Mona et al., 2019).	22
Figure 2. 12: Chemical reactions involved in PU foaming (Rao et al., 2017).....	24
Figure 2. 13: Cellular structure of carbon-based nanomaterial (Yuan et.al, 2019).25	
Figure 2. 14: Schematic diagram for the formation of conductive CB network in the polymer matrix (Zhang et al., 2019).	26
Figure 2. 15: SEM image of hybrid CB-GNP PU foam (Javad and Ali, 2018).....	28
Figure 2. 16: Structure of SWCNT and MWCNT (Marina and Vladimir, 2021)...	31
Figure 2. 17: SEM images of PU-CNT nanocomposite foam (Ciecierska et.al, 2015).	32
Figure 2. 18: Chemical structure of Graphene oxide (Gerani, Mortaheb, and Mokhtarani, 2016).	35
Figure 2. 19: SEM-EDS of graphene oxide layers (Balachandran 2015).	37

Figure 2. 20: Anti-static, conductive, and dissipative foam from the market.	38
Figure 2. 21: The illustration of EMI shielding mechanism (Yao et al., 2021).	39
Figure 2. 22: The surface resistance and surface resistivity classification for conductive foams used for packaging of electronic components based on ANSI- ESD S541.	41
Figure 3. 1: Phase I of research methodology.....	44
Figure 3. 2: Phase II of research methodology.	45
Figure 3. 3: Preparation of GO coated PU nanocomposite foams.	49
Figure 3. 4: Gas pycnometer.....	50
Figure 3. 5: PU nanocomposite foams prepared for SEM analysis.	51
Figure 3. 6: Surface resistance measurement of the PU nanocomposite foams.	52
Figure 4. 1: Foam density of PU/CB nanocomposite foams.	54
Figure 4. 2: Foam density of PU/MWCNT nanocomposite foams.....	55
Figure 4. 3: Foam densities of PU/CB and PU/MWCNT nanocomposite foams. ..	57
Figure 4. 4: Foaming of PU/MWCNT nanocomposite foams at various filler loading (from left to right – 1, 2.5, 5, 7.5 phr).	58
Figure 4. 5: Foaming of PU/CB nanocomposite foams at various filler loading (from left to right – 1, 2.5, 5, 7.5 phr).	58
Figure 4. 6: Average cell size of PU/CB nanocomposite foams at various filler loadings.	60
Figure 4.7: SEM images of PU/CB nanocomposite foams with 50X magnification.	61
Figure 4. 8: SEM images of PU/CB nanocomposite foams with 100X magnification.	61

Figure 4.9: Average cell size of PU/MWCNT nanocomposite foams at various filler loadings.	62
Figure 4. 10: SEM images of PU/MWCNT nanocomposite foams with 50X magnification.	63
Figure 4. 11: SEM images of PU/MWCNT nanocomposite foams with 100X magnification.	64
Figure 4.12: Average cell size of PU nanocomposite foams.	65
Figure 4.13: SEM observations of PU nanocomposite foams with 40X magnification.	66
Figure 4.14: SEM images of GO coated PU nanocomposite foams with 40X magnification.	69
Figure 4.15: SEM images of GO coated PU nanocomposite foams with different GO loadings.	70
Figure 4.16: Surface resistance of PU/CB nanocomposite foams at various filler loading. (Note: The grey area indicates the insulative region while the yellow area represents the dissipative region of the materials. If the surface resistance of material is located at yellow region, this means it is behaved dissipative.)	72
Figure 4. 17: Surface resistance of PU/MWCNT nanocomposite foams at various filler loading.....	74
Figure 4. 18: Surface resistance of PU/CB and PU/MWCNT nanocomposite foams at various filler loading	76
Figure 4.19: Surface resistance of PU nanocomposite foams at various GO loadings.	79

LIST OF TABLES

Table 1.1: Additives and the reasons for use in PU (John et al., 2016).....	11
Table 2.1: The category of ESD packaging materials (ANSI/ESD S541-2019 - Packaging Materials for The Protection of Electrostatic Discharge Susceptible Items).	40
Table 3.1: Materials composition and designation of the PU/CB nanocomposite foams.	47
Table 3.2: Materials composition and designation of the PU/MWCNT nanocomposite foams.....	48
Table 3.3: Materials composition of Graphene Oxide Solution.	49

LIST OF ABBREVIATIONS

AA	Ascorbic acid
CB	Carbon black
CNT	Carbon nanotube
CTF	Carbon black filled thermoplastic PU foam
EDS	Energy dispersive X-ray spectroscopy
EMI	Electromagnetic Interference
EMI – SE	Electromagnetic interference shielding effectiveness
ESD	Electrostatic discharge
FPUFs	Flexible PU foams
g-CB	Polyol grafted carbon black
GN	Graphene
GO	Graphene oxide
H ₂ O ₂	Hydrogen peroxide
MWCNT	Multiwalled Carbon nanotube
nm	Nanometer
o-CB	Oxidized carbon black
p-CB	Pristine carbon black
PU	Polyurethane
PUFs	Polyurethane foams
PUI	Polyurethane ionomers
RPUFs	Rigid polyurethane foams
SEM	Scanning electron microscope
SMPUs	Shape memory polyurethane
TEM	Transmission electron microscope
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
TiO ₂	Titanium oxide
TPUs	Thermoplastic polyurethane
WPU	Waterborne polyurethanes

LIST OF SYMBOLS

Appendix A	Foam density of PU/CB nanocomposite foams
Appendix B	Foam density of PU/MWCNT nanocomposite foams
Appendix C	Average cell size of PU/CB nanocomposite foams at various filler loadings.
Appendix D	Average cell size of PU/MWCNT nanocomposite foams at various filler loadings.
Appendix E	Average cell size of PU nanocomposite foams.
Appendix F	Surface resistance of PU/CB nanocomposite foams at various filler loading.
Appendix G	Surface resistance of PU/MWCNT nanocomposite foams at various filler loading.
Appendix H	Surface resistance of PU nanocomposite foams at various GO loadings.

KESAN SAPUTAN GRAFEN OKSIDA TERHADAP SIFAT-SIFAT BUSA NANOKOMPOSIT POLIURETANA/NANOFILLER

ABSTRAK

Dalam kajian ini, karbon hitam (CB) dan tiub nano karbon berbilang dinding (MWCNT) digunakan sebagai pengisi untuk penyediaan busa nanokomposit poliuretana (PU). Pemuatan CB dan MWCNT adalah dalam julat 1, 2.5, 5, 7.5 phr. Selanjutnya, salutan grafen oksida (GO) telah digunakan pada permukaan busa nanokomposit PU/CB dan PU/MWCNT untuk meningkatkan kekonduksian elektrik. Sifat-sifat busa nanokomposit PU telah dicirikan menggunakan pengujian ketumpatan busa, mikroskop elektron pengimbasan (SEM), dan ujian rintangan permukaan. Ketumpatan busa PU telah meningkat hasil daripada peningkatan kandungan CB atau MWCNT. Tambahan pula, busa nanokomposit PU/MWCNT mempunyai ketumpatan yang lebih tinggi daripada busa nanokomposit PU/CB pada pemuatan pengisi nano yang sama. Analisis struktur mikro busa nanokomposit PU mendapati bahawa saiz sel purata berkurangan apabila kandungan pengisi meningkat. Hal ini menunjukkan bahawa CB dan MWCNT boleh bertindak sebagai tapak nukleasi sel yang dapat menggalakkan pertumbuhan sel. Rintangan permukaan busa nanokomposit PU/MWCNT adalah lebih rendah daripada busa nanokomposit PU/CB pada kandungan pengisi yang sama. Yang menariknya, rintangan permukaan busa nanokomposit PU (formulasi PU-MWCNT-5wt%) berkurangan daripada $5.8 \times 10^{10} \Omega$ kepada $1.7 \times 10^8 \Omega$ dengan salutan GO. Hal ini menunjukkan bahawa salutan GO mampu meningkatkan kekonduksian elektrik busa nanokomposit PU. Secara keseluruhannya, busa nanokomposit PU yang berlakuan dissipatif telah berjaya dihasilkan menggunakan gabungan kaedah pengisi (terserak dalam matriks PU) dan salutan GO.

EFFECTS OF GRAPHENE OXIDE COATING ON THE PROPERTIES OF POLYURETHANE/NANOFILLER NANOCOMPOSITE FOAMS

ABSTRACT

In this study, carbon black (CB) and multiwalled carbon nanotube (MWCNT) were used as fillers for the preparation of the polyurethane (PU) nanocomposite foams. The CB and MWCNT loadings were in the range of (1, 2.5, 5, 7.5 phr). Further, graphene oxide (GO) coating was applied on the surface of the PU/CB and PU/MWCNT nanocomposite foams to increase the electrical conductivity which is determined by the surface resistance. The properties of the PU nanocomposite foams were characterised using foam density measurement, scanning electron microscopy (SEM), and surface resistance tests. The foam density of the PU was increased as a result of the increasing loading of CB or MWCNT. Furthermore, the PU/MWCNT nanocomposite foam has a higher density than the PU/CB nanocomposite foam at the same nanofiller loading. The microstructure analysis of the PU nanocomposite foams found that the average cell size is reduced as the filler loading increases. This indicates that the CB and MWCNT can act as cell nucleation sites to promote cell growth. The surface resistance of PU/MWCNT nanocomposite foam is lower than that of PU/CB nanocomposite foams at the same filler loading. Interestingly, the surface resistance of PU nanocomposite foams (formulation PU-MWCNT-5wt%) decreases from $5.8 \times 10^{10} \Omega$ to $1.7 \times 10^8 \Omega$ by the GO coating. This indicates that the GO coating is capable of increasing the electrical conductivity of the PU nanocomposite foam. Overall, the PU nanocomposite foam with dissipative behaviour was successfully produced using a combination of filler (dispersed in the PU matrix) and GO coating method.

CHAPTER 1

INTRODUCTION

1.1 Overview

In this chapter, the research background, problem statement, research objectives, research approach, research scope, and thesis outline of this study are covered. The background of polyurethane nanocomposite foam and characterization provide an overview on this research work. The problem faced in this field of research study has been pointed out in problem statement. There are several research objectives that need to be achieved in this study. The research approach and research scope were used to ensure that the research objectives were achieved. Lastly, the overall thesis outline of this study is summarized.

1.2 Background

Worldwide, polyurethane (PU) has been recognized as one of the most preferable, versatile engineering materials with its great diversity and simplicity in production for used in different applications (John et al., 2016). PU is classified as condensation polymers and it is synthesized by polymerization reaction between compounds with hydroxyl group (-OH) such as polyol and diisocyanate to form urethane linkages (-NH-CO-O-) arranged along the three-dimensional molecular network (Klemper and Sendjiarevic, 2004). The major repeating unit in PU is formed by the reaction of an isocyanate group (-N=C=O) with hydroxyl group (-OH) of the polyol. Moreover, the specific properties of PU (e.g., mechanical, physical, and chemical) can be tailored by compounding with the appropriate additives such as foaming agent, fillers, plasticizers, coupling agents, pigments, flame retardants, or surfactants to satisfy a wide range of specific applications. Furthermore, PU has high

processability which can be fabricated through injection moulding, extrusion, and also can be recycled by ammonolysis and aminolysis methods by using ammonia, amines, or alkanolamines to retrieve the monomeric polyol, which can be reused for the synthesis of PU.

Besides, continuous development in processing techniques and addition of additives in formulation had contributed to PU to be a special group of polymeric material which can be processed into different form based on its desired structure-property relationships such as rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants and elastomers (Szycher, 1999). This is due to PU can be synthesized from wide variety of sources such as ethers, esters, urea and some aromatic compounds which enable them to be used in wide range of specific applications (Khalid et al., 2014). PU can be applied in variety of applications due to its design versatility such as coatings, adhesives, sealants, elastomers, primer, sports goods, medical devices, textile finish, or adding nanofiller to produce nanocomposite foam (Khalid, Haq, and Ijaz, 2007). Thus, PU foam has become the most interested material to be investigated in the potential of filler addition to enhance its physical, chemical, and mechanical properties (Mahmoud et al., 2017).

In recent years, PU foam had become one of the most prominent PU-based products which is used in significant amounts from global market among other major applications due to the advantages such as light weight, ease of processability, low production cost, excellent abrasion resistance, and hardness. The global PU foams market is projected to grow from USD 42.8 billion in 2021 to USD 61.5 billion by 2026, at a CAGR of 7.5% from 2021 to 2026 (Research and Market, 2021). The major reasons for the growth of the PU foams market include growing end-use industries such as bedding and furniture, electronics, automotive, as well as building and construction, in

emerging economies like India, Thailand, and other countries. Some of the other like increased use of PU foams in building insulations for energy conservation and versatility and unique physical properties of PU foams are driving factors for growth of PU foams market.

Besides, incorporating of nanofillers into PU foams formulation was invented to produce PU nanocomposites with advanced properties in order to expand the potentialities of PU foams applications (Reid et al., 2014). Nanofillers, which have the particle size less than 100 nm is dispersed in the PU matrix and improve reinforcement of matrix as well as modification of cellular structure such as cell density, cell size, and size distribution (Samuel et al., 2012). For instance, PU nanocomposite foams are used in building and construction materials as roofing, floor, walls, or carpets cushion due to its advantages of low cost, easy to install, light weight but high mechanical strength, durable, and versatile.

Commonly, PU foam can be divided into open-cell and closed-cell foam which is used for different applications based on their physical properties (Ashida, 2006). Rigid PU foams are usually used for insulation and flotation, meanwhile flexible PU foams are used for cushioning and packaging. In addition, the PU foam can be tailored with desired properties such as tensile strength, electrical conductivity, and mechanical properties for specific applications by adding different types of fillers. This has been proven by previous researches done by scientists. For instance, Titanium dioxide (TiO_2) nanoparticles were used to improve tensile strength of PU nanocomposites foams (Saha et al., 2008). Other than that, carbon nanotube was commonly used to improve the electrical conductivity (Baughman et al., 2002) while nanoclay (Xu et al., 2007) was used to enhance the tensile and compressive strength of PU nanocomposite foams.

Due to the advantages of light density, compressible, easy processing, capable of withstanding cyclical vibration, and corrosion resistance, conductive PU nanocomposite foam has become the most preferable materials used in the electromagnetic compatibility design and rectification of electronic products (Faris et al., 2015). The electrical conductivity of PU nanocomposite foam is contributed by the formation of the conductive network of the nano-fillers in the PU matrix after compounding which given rise to their use in applications for Electromagnetic Interference (EMI) shielding as gap fillers between the components to provide a stable conductive connection (Huang et al., 2007). Electromagnetic interference or also known as radio frequency interference is a phenomenon in an electrical circuit caused by either human-made or natural sources which can result in malfunction of electrical circuit. Other than that, the conductive PU nanocomposite foams are ideal materials used for dissipating static build-up or transferring an electrical charge. Therefore, it is an ideal packing material for packing electronic components such as microelectronic devices, printed circuit board, integrated circuit, optoelectronic devices, and chip.

In this study, polyurethane nanocomposite foams of different nano-fillers (CB and MWCNT) at various nano-filler loadings were prepared. The morphology, foam density, and electrical properties of various nanocomposite foams were studied. The relationship between the electrical conductivity and the nano-filler concentration was investigated by further analysis. The foam densities of PU nanocomposite foams were obtained by gas pycnometer. Micro-structural analysis using scanning electron microscope (SEM) was carried out to verify and support the research findings. The electrical properties of various foams were determined by the surface resistance tests. Besides, the effect of GO coating with different GO content on electrical properties of PU nanocomposite foams was investigated.

1.3 Problem Statement

PU foam has become one of the most popular polymeric materials in industry due to its versatility to obtain desired properties such as densities, morphologies, rigidity or flexibility which enable PU foams to satisfy a wide range of technical requirements (Madaleno et al., 2013). Due to its excellent thermal insulation and impact absorption, PU foams can be used for comfort cushioning, automotive seats, shape memory foam, packaging, insulated wall in freezers, and sound absorbing materials (Verdolotti et al., 2011).

The ideal fillers used to improve electrical conductivity of insulative unfilled PU foams are carbon-based fillers such as carbon black, carbon nanotubes (CNT), or graphene (GN) (Xu et al., 2018) due to the advantages of high aspect ratio, high electrical conductivity, and excellent mechanical properties. However, the electrical conductivity improvement of PU nanocomposite foams is affected by the degree of dispersion of nanofiller which contribute to the formation of conductive network in the PU matrix with no agglomeration and entanglements as well as the improved nanotubes – resin interface adhesion (Xia and Mo, 2005). The poor dispersion of nanofillers will result in deterioration of other properties of conductive foams such as mechanical strength. Therefore, fabrication of highly electrically conductive PU foams is still a challenge due to its poor dispersion in polymeric matrix which limit the performance of nanocomposite.

So, in this study, the graphene oxide (GO) coating is a new approach to improve the electrical conductivity of the PU nanocomposite foam, with low percolation threshold and low loading of CB/CNT, while maintaining the foamability/processability of the PU nanocomposite foam. Besides, the effect of GO coating with different GO content on the surface resistance of PU nanocomposite foams is studied.

1.4 Objectives

The research objectives are:

- I. To determine the effect of CB and MWCNTs loading on density, morphology, and surface resistance of the PU nanocomposite foams.
- II. To investigate the effect of graphene oxide coating on the surface resistance of the PU nanocomposite foams.

1.5 Scope of Study

In this research, the carbon-based fillers (CB and MWCNTs) at various filler loadings in the range of 1, 2.5, 5, 7.5 phr were used to improve the electrical conductivity of PU nanocomposite foams. Further, the GO coating was applied on the surface of PU nanocomposite foams to improve its electrical properties (i.e., surface resistance). Subsequently, the graphene oxide layer was coated on the PU nanocomposite foams for further improvement in electrical properties of PU nanocomposite foams. The effect of carbon – based nanofiller (CB and MWCNTs) on the PU foam properties with different filler loading and the effect of graphene oxide coating on the electrical properties of the PU nanocomposite foams were investigated.

1.6 Thesis Outline

This thesis consists of 5 chapters, including this chapter 1.

Chapter 1: Introduction on background, problem statement, research objectives, scope of study, and thesis outline.

Chapter 2: Literature review of PU nanocomposite foams with different fillers (carbon black, carbon nanotube, and graphene oxide). This session also reviews the application of conductive PU foams in electromagnetic interference (EMI) shielding.

Chapter 3: Methodology of this study which include the research flows, methods used for sample preparation, characterization of PU nanocomposite foams, raw materials and equipment used in this research.

Chapter 4: Results and discussion on the PU foam properties such as density, morphology, and electrical properties – surface resistance.

Chapter 5: Conclusion on this research work as well as suggestion for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

The literature review of the background of polyurethane nanocomposite foams which including the advantages and limitation of PU foams, types of PU nanocomposite foams produced, challenges and applications of PU nanocomposite foams in Electromagnetic Interference (EMI) as well as the factors influence the electrical conductivity of polyurethane nanocomposite foams.

2.2 Polyurethane

Polyurethane (PU) was first discovered by Dr Otto Bayer and his team in the pre-world war II era (1937). In recent era, PU is one of the prominent commercial thermoplastic polymers which has been extensively used in several technical applications such as automotive, electronic, sound absorbing, construction, and aerospace due to high mechanical properties, low density, durability, ease of processing, excellent chemical resistance, and physical properties (Ahmed et al., 2015). The structural properties of PU are determined by the ratio of hard and soft segments, molecular weight, polydispersity, and crosslinking ability in which the enhancement of properties depends on the physical link formed by hydrogen bonding in PU (Kausar, 2017). The different classes of PU and examples of the PU-based products are shown in Figure 2.1.

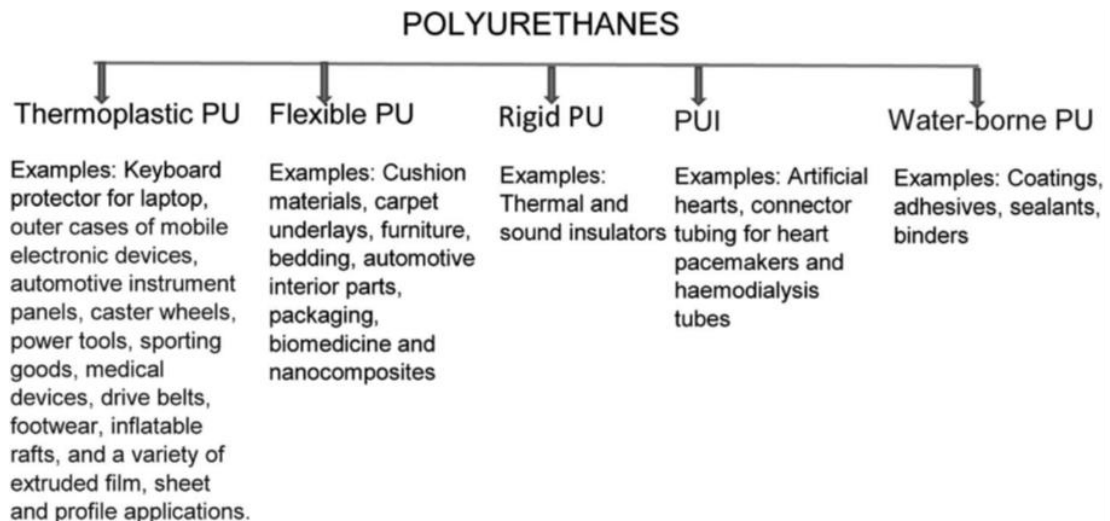


Figure 2. 1: Classes of PU-based products (John et al., 2016).

PU is a class of high-performance polymer which can be synthesised from the reaction between polyol and diisocyanate, or may involve other additives. Polyol is an organic compound which consist of more than one functional hydroxyl group e.g., ester, ether, amide, and acrylic as well. Meanwhile, diisocyanate is an organic compound which containing of two or more isocyanate (-NCO) groups per molecules, can exists in aliphatic, cycloaliphatic or aromatic, are essential building blocks for polyurethane synthesis. The soft segment in PU is made up from polyols while the hard segment is made up from the isocyanate. The polyols contribute to the flexible long segments which produce soft elastic polymers while the isocyanate is responsible for the PU reactivity and curing properties. Besides, PU can also be produced by several techniques including solution casting, precipitation, and in-situ routes (Sattar et al., 2015). The synthesis of polyurethane is shown in Figure 2.2.

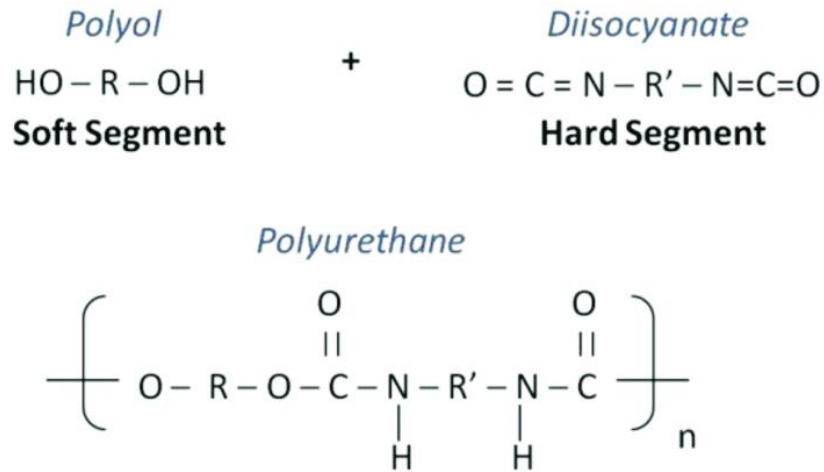


Figure 2. 2: Polyurethane synthesis (Patti et al., 2021)

In PU network structure, the major repeating unit is made up from the urethane group (NCOH) which is formed from the reaction between alcohol (polyol, -OH) and isocyanate (-NCO). PU can be categorized into different groups of materials in a wide range of specific applications such as rigid PU foam, flexible PU foam, thermoplastic PU (TPU), waterborne, binders, coating materials, adhesives, sealants, and elastomers. This is due to the PU can be tailored with variety of specific properties by adding additives or synthesised through different processing techniques such as two-step emulsification process (Peng et al., 2015), step growth polymerization (Fatoumata et al., 2014), polyaddition (Krishna et al., 2015), and polycondensation (Yi et al., 2015). Among the types of PU-based product, PU foam is one of the most famous PU-based products which is broadly used in variety of applications. Other than that, the PU can be incorporated with additives including flame retardants, cross-linkers, blowing agents, reinforcement filler, surfactants, and pigments to improve the performance of PU-based product. The additives and the reasons for use in the fabrication of PU composite are shown in Table 1.1. The chemical structure of PU is shown in Figure 2.3.

Table 1.1: Additives and the reasons for use in PU (John et al., 2016).

Additives	Reason for use
1. Isocyanate	As a reactive site for urethane linkages and curing properties (Zhou et al., 2015).
2. Polyols	Contributes flexible long segments which produces soft elastic polymers (Cardoso et al., 2012).
3. Catalysts	To speed up the reaction rate of urethane linkages formation between polyols and isocyanate.
4. Plasticizers	To reduce material hardness.
5. Pigments	To produce coloured PU product.
6. Cross-linkers/Chain extenders	To improve the mechanical properties of PU products.
7. Blowing agents	To aid the production of PU foams by controlling the bubbles formation and foam cell structure.
8. Fillers	To reduce the production cost and improve the mechanical properties such as hardness and tensile strength of PU products.
9. Flame retardants	To reduce the flammability of PU products (Mishra et al., 2020).

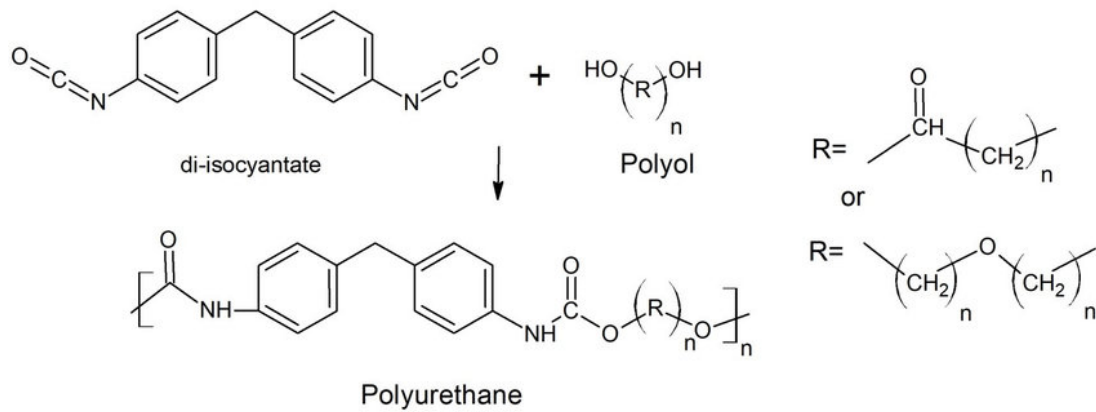


Figure 2. 3: Chemical structure of PU (Kemoni et al., 2020).

Rigid PU foams is commonly used engineering material as thermal insulation material, construction, impact absorption, refrigerators, and automotive industry due to its excellent properties of thermal insulation, chemical resistance, low density, and high mechanical properties (Yang et al., 2015). Rigid PU foams can be synthesised with two main types of polyols including petroleum-based polyols or bio-based polyols extracted from vegetable oils or plant-based lignin which exhibit different physical and mechanical properties in the PU foams produced (Heinen et al., 2014). Meanwhile, the flexible PU foams are mainly applied as cushion materials including carpet underlays, furniture, bedding, car seat, athletic equipment, packaging, filtration, biomedical (Singhal et al., 2013), and shape memory nanocomposite foams (Kang et al., 2013). Moreover, thermoplastic Polyurethane (TPUs) behave like thermoplastic which is melt-processable and can be fabricated using extrusion, blow, compression and injection moulding equipment (Claeys et al., 2015). TPUs has been incorporated to improve the durability of many products such as in automotive, footwear and construction due to the properties of high processability, good resistance to impact, abrasion, and weather (More et al., 2013). Figure 2.4 shows some of the applications of bio-TPUs as reported by Atika and Mustafa (2021).



Figure 2. 4: Applications of bio-TPU (Atika and Mustafa, 2021).

Apart from that, the Polyurethane Ionomers (PUI) is synthesized by adding ionic groups such as poly(propylene glycol), PPG, or poly(ethylene glycol), PEO, and di- (4-isocyanatophenyl) methane, MDI, butane-1,4-diol and cis-2-butene-1,4-diol in the polyurethane backbone chain to obtain better dispersion in polar solvent due to the enhanced hydrophobicity, improved thermal and mechanical properties (Jaudouin et al., 2012). Shape Memory Polyurethanes (SMPUs) is one of the products of PUI which is able to ‘memorize’ the temporary-deformed shape and recover to the original shape through different stimulus such as temperature, electric, humidity, pH, light, and magnetic energy. The schematic diagram for the shape memory behaviour is shown in Figure 2.5. Besides, PU is often used as coating materials due to its excellent mechanical, chemical-resistant, and physical properties (Rajput et al., 2014). PU adhesives can offer good bonding properties, whereas very tight seals may be obtained from PU sealants in filling the gap between masonry. A good PU coating must achieve good adhesive properties, high chemical resistivity, excellent drying, low temperature flexibility and adequate scratch resistivity.

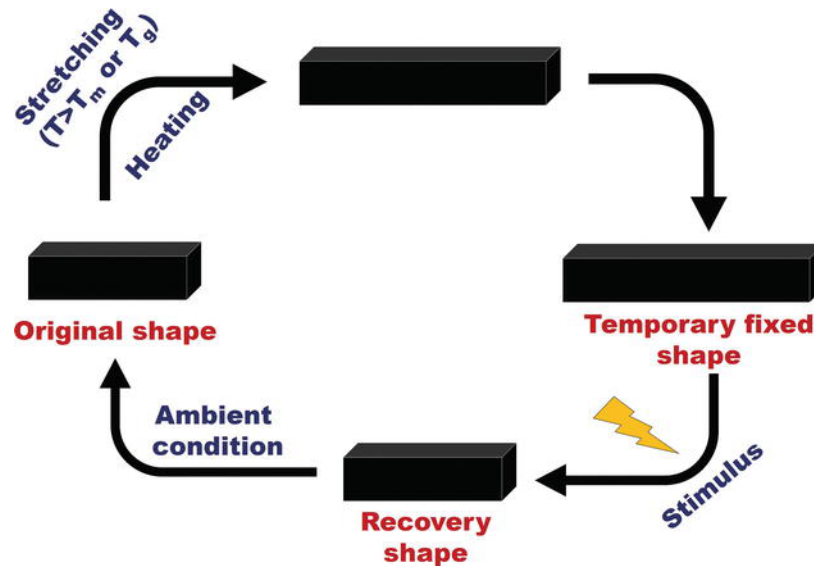


Figure 2. 5: Schematic diagram of shape memory behaviour (Suman, 2017).

In addition, PU binders are used to join different types of fibres and other materials to each other through permanent gluing effect between organic materials and long-strand lumbers, oriented strand boards, laminated veneer lumber, medium density fibre boards, particle boards and straw boards. The PU used for binder should consist of high hard-to-soft segments ratio and good thermal properties. PU binders are mainly used in elastomeric/rubbery flooring surfaces, wood panel manufacturing, ink-jet printing, foundry industries, and sand casting (Madbouly et al., 2013). Waterborne Polyurethanes (WPU) is referred to the coatings and adhesives in which the primarily solvent is water (Yan et al., 2010). The properties of the dispersion of WPU can be varied by the types and amount of polyol, isocyanate, ionomers and chain extender used. WPU has been used in most commercial and industrial applications due to there is no volatile organic compound and hazardous air pollutants contained in WPU which may cause pollution (Huber and Mecking, 2010).

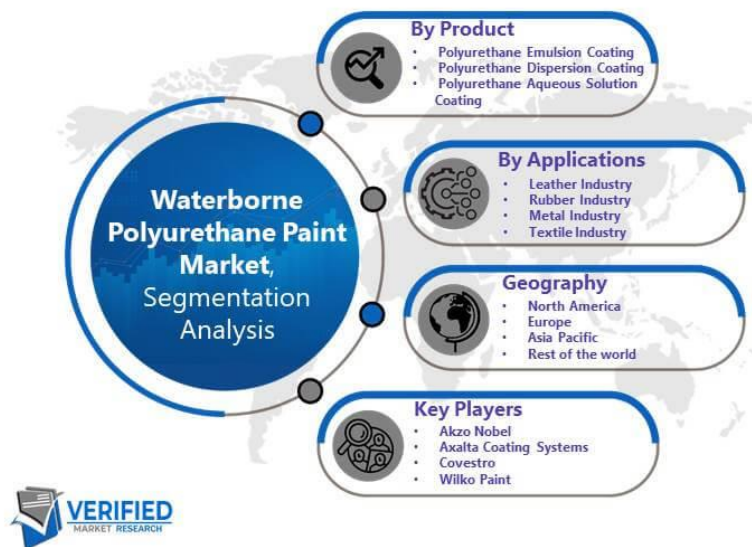


Figure 2. 6: Global WPU's market size (Verified Market Research, 2020).

In recent years, the research regarding the fabrication method, advanced additives, and characterization methods in order to improve the properties as well as the performance of PU nanocomposites has always been the most interested topic among scientists to tailor PU nanocomposites for use in variety of specific applications. Moreover, the trend of synthesis of hybrid PU nanocomposites by using more than one type of nanofiller has also become the interested topic among researchers. This is because the hybridization can reduce the production cost and also overcome the limitation of properties enhancement by only one nanofiller used through synergetic effect by adding of other nanofiller into the PU nanocomposites (Mogha, 2020).

2.3 Polyurethane Foam

Polyurethane foams (PUFs) are mainly classified as open-cell and closed-cell structures (Kausar, 2018). PU foams can exist as rigid, flexible or semirigid foam based on the composition of reactants (polyols and isocyanate) and its physical properties (Thirumal et al., 2008). In closed-cell foam, the distinct bubbles of gas are trapped individually by a membrane layer while the blowing agent is intact in the bubbles for long term. Closed-cell PU foams tend to have higher dimensional stability and low moisture content trapped as compared to open-cell foam due to its higher plastic content when it is measured at a same volume. For open-cell PU foams, the cell membrane within the material is broken which create a passage through the foam to allow the cell to be refilled with the surrounding air. The open-cell structure enables the immediate transfer of air or moisture through the ‘porous’ interconnected material structure. In order to be used in specific applications which require excellent material performances like mechanical strength, thermal stability, electrical conductivity, foaming behaviour, heat distortion temperature, and barrier properties, the incorporation of nanofiller into PU foams including carbon-based fillers (carbon black or carbon nanotubes), graphene derivatives, nano-clay, and nano-silica is the new trend among researchers (Ibeh et al., 2008). The synthesis of polyurethane foam is shown by Figure 2.7.

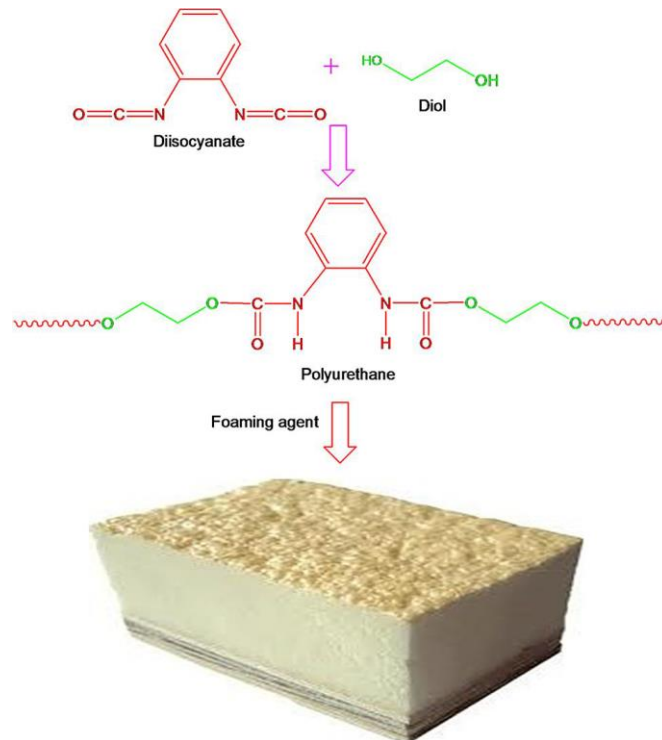


Figure 2. 7: Polyurethane foam synthesis (Kausar, 2018).

In addition, free-rising foaming is one of the most common used methodologies to produce PU foam or PU nanocomposite foams on small scale production. In this method, all of the materials such as polyol, isocyanate, or catalysts, blowing agents may be added are mixed based on the predetermined amount in a mould. The mixture is stirred and left to form foam at room temperature for a period of time. Figure 2.8 shows the preparation of free rising PU foam by previous research. Other than that, the thermoplastic PU-based foams can be fabricated through batch foaming process using carbon dioxide as blowing agent to create the fine cell structure due to the high diffusivity of carbon dioxide (Yeh et al., 2013). In addition, PU nanocomposite foams can be produced through three-step method including sonication, mixing, foam rising (Saha et al., 2008). In this method, the sonication technique was used to improve the dispersion and distribution of nanofillers in the Polyols matrix before mixing with isocyanate. After that, the mixture (polyols and nanofillers) was added into isocyanate

and stirrer well. Lastly, the foam was obtained through pouring the mixture in a preheated aluminium mould and cured with oven.

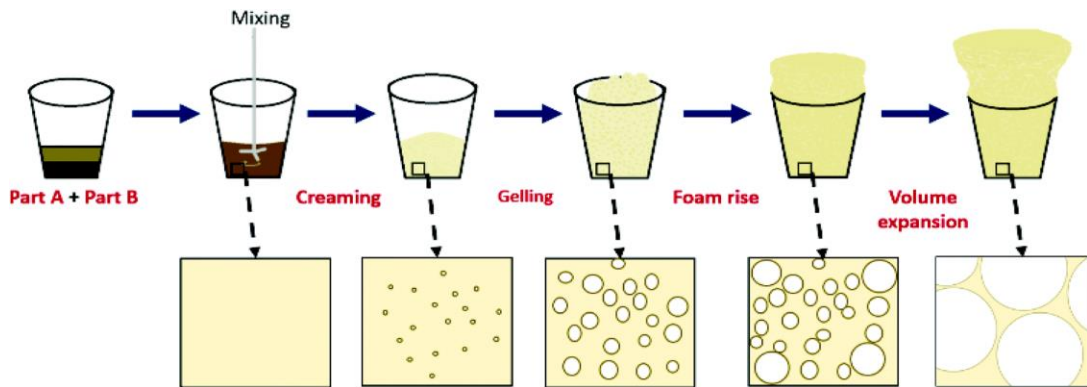


Figure 2. 8: Preparation of free-rising PU foam (Haridevan et al., 2021).

The fundamentals of the foaming process for polyurethane viscous medium can be briefly explained through a four-steps mechanism: gas formation, cell nucleation/bubble formation, bubble growth, and bubble stabilization (Letizia et al., 2017). The foaming process started with the formation of gas bubbles from the reaction between Isocyanate groups and water (blowing agents). After that, the bubbles nucleation occurs due to the expansion of blowing gas and additional gas molecules diffuse from the neighbouring polymeric matrix into the cells. Next, the expansion of blowing gas stimulate the nucleation of gas bubbles in either homogenous or heterogenous. Then, the bubble nucleation process is continued and stopped when all the spherical cells are closely packed in the PU viscous medium. The bubble nucleation occurs simultaneously when the partial pressure exerted by the carbon dioxide produced from the reaction between isocyanate and water surpass the total partial pressure of the system. Moreover, the foaming process only take place when the stable nuclei growth is achieved caused by the diffusion of gas from the viscous polymerization phase into the bubble phase (Niyogi et al., 2014). Lastly, the closely packed spherical cells will be converted to polyhedral cells when they contact with each other. The schematic

representation of nucleation, growth, and stabilization steps of foam formation is shown in Figure 2.9.

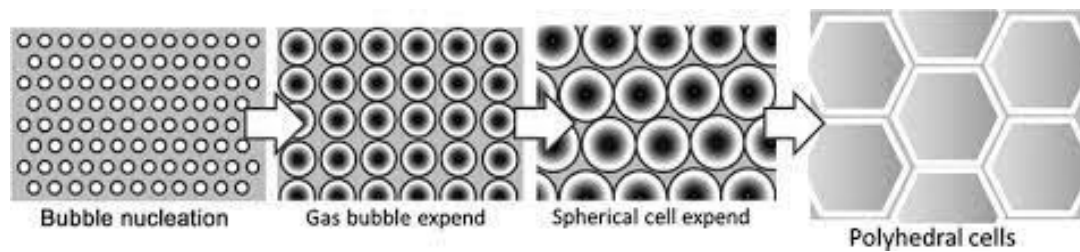


Figure 2. 9: Schematic representation of nucleation, growth, and stabilization steps of foam formation. (Letizia et al., 2017)

Generally, the bubble nucleation can occur in homogenous or heterogenous way. The homogenous nucleation occurs more vigorously than heterogenous nucleation due to the exothermicity of the polymerization reaction leading to wider cell size distribution. In the case of heterogenous nucleation, the existence of external surface (e.g., nanofiller) is required to promote the simultaneous cell formation in polymeric matrix for narrow cell size distribution. In other words, the foaming rate for heterogenous nucleation depends on the dispersion of nanofiller used inside the polymeric matrix which is influenced by the type, particle size, surface chemistry, and properties of nanofiller used based on the classical nucleation theory (Kalikmanov, 2013). As the cell start to grow and the gas pressure increases due to the diffusion of gas from neighbouring polyurethane matrix, the matrix resin will be pushed outwards in the radial direction when the internal pressure exceeds the surface energy. The schematic diagram of homogenous and heterogenous nucleation of nanocomposite foams are shown in Figure 2.10.

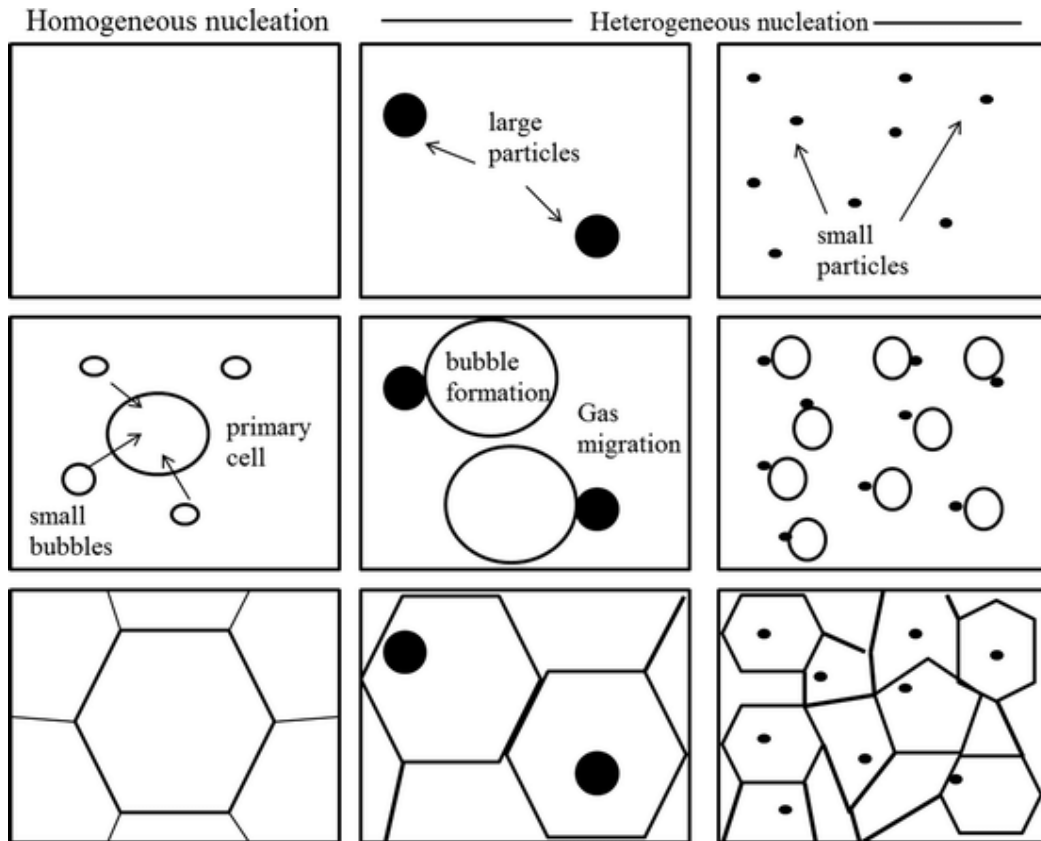


Figure 2. 10: Homogenous and heterogenous nucleation in polymeric foams (Zimmermann et al., 2018).

Other than that, the viscosity of PU resin increases as the polymerization rate increases due to there are more PU cross linkages are formed. Thus, the bubble growing will stop when the viscosity of PU matrix has achieved a very high value in which the PU starts to solidify. In short, the cellular structure of nanocomposite such as cell size, density, distribution, and thickness are affected by the properties of nanofillers in a significant manner. Nanofillers such as carbon nanotube, nano-clay or nano-silica due to their high aspect ratio and large surface area up to more than $1000 \text{ m}^2/\text{g}$ (Njuguna et al., 2008), can be used beneficially to improve the performance of nanocomposite such as mechanical properties, thermal stability, barrier properties, and electrical properties. However, the nanofillers has high tendency to agglomerate in the PU matrix because of their high surface energy which affect the nanofiller dispersion and also the performance of nanocomposite. Therefore, the optimization of nanofiller dispersion in

polyurethane matrix is crucial in order to ensure the properties of polyurethane nanocomposite foams produced satisfy with the specific applications.

Rigid polyurethane foams (RPUFs) which have closed-cell structure are normally used for insulation and flotation such as thermal insulation material to separate thermally sensitive components in electrical devices (Yang et al., 2021), potting material, and load bearing structure material. Rigid PU foam is one of the widely used engineering materials which has the excellent properties of thermal insulation, low-density due to the porous structure, high mechanical properties, and excellent energy saving insulation (Wang et al., 2019). It is also applied as insulation materials in building construction such as window insulations, barrier sealants for air, wall, and doors to reduce energy consumption. The rigid PU foams with high physical and mechanical properties can be synthesized by mixing of glycerine and castor oils (Letizia et al., 2017).

Nevertheless, the drawbacks of rigid PU foams such as low thermal resistance, high flammability, and high smoke production has limited the use of rigid PU foams in specific applications which require high material performance (Kirpluks et al., 2014). Therefore, the incorporation of nanofillers such as nano-clay (Widya and Christopher, 2005), nano-silica (Javni et al., 2002), multi-walled or single-walled carbon nanotubes (Yan et al., 2011), graphene oxide (Wicklein et al., 2014) or graphite (Qian et al., 2013) and the methods to improve the nanofillers dispersion in PU matrix has been proposed to enhance the PU foam properties. Nanofillers can exert various roles in nanocomposites due to their small size (Chen et al., 2012). Nanofiller act as nucleating agent which promotes the heterogenous nucleation sites to improve the crystallinity of nanocomposite. The morphological structure and density of the foam produced can be monitored by controlling the dispersion of nanofiller within the PU matrix. According

to the previous research, the addition of nano-silica at low loadings ($\sim 2.5\text{wt}\%$) in rigid PU foam is able to improve the mechanical properties, thermal and dimensional stability (Nikeje et al., 2010). This is because the addition of nano-silica has become the nucleation sites during cell formation and thus increase the cell density but decrease the cell size in rigid PU foams (Nikje and Tehrani, 2010). Figure 2.11 shows the rigid and flexible PU foams.



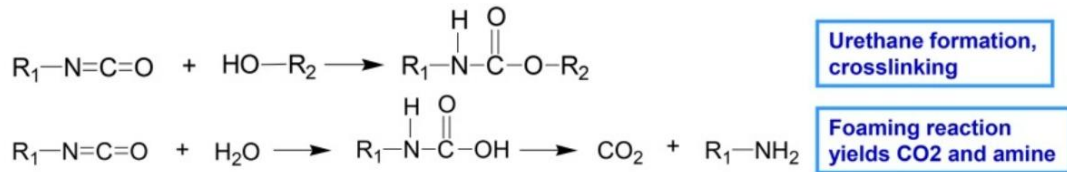
Figure 2. 11: Rigid and flexible PU foams (Mona et al., 2019).

Flexible PU foams (FPUFs), are block copolymers which have open cell structure, are built up from the phase separation between soft segment and hard segment. The flexibility of FPUFs is contributed by the compositional ratio of soft and hard segments (Cinelli et al., 2013). The hard segments which are physically cross-linked is contributed to the hardness while the soft segments are made up from stretchable chains which contributed to the elasticity of FPUFs. The FPUFs can be customized to desired stiffness for specific application by varying the compositional ratio of these segments. The hardness of FPUFs is determined by the foam density in

which there is an increase in 0.1 kPa in hardness for an increase of 1 kg/m³ in foam density (Irene et al., 2021). Generally, FPUFs are used for cushioning materials in bedding, furniture, carpet underlay, vibration dampening, packaging, automotive seating, biomedicine, and nanocomposite (Singhal et al., 2014). Other than that, the FPUFs are also applied in sound-absorption and noise-reduction materials. According to the previous studies, the sound absorption coefficient for PU foams used in the frequencies of 300 – 10000 Hz is 0.8 – 1.0 while the coefficient is 0 – 0.5 for the frequencies of 10 – 200 Hz (Ibeh and Bubacz, 2008).

Furthermore, the synthesis of FPUFs consists of two major reactions which are gelling and blowing reactions occurs simultaneously (Bernal et al., 2012). Gelling reaction is referred to the formation of backbone urethane linkages from the reaction of isocyanate and polyol which increase the molecular weight of polymer. For blowing reaction, carbon dioxide in the form of gas bubbles and disubstituted urea which expand the polyurethane structure into a foam, are formed from the decomposition of unstable carbamic acid results from the reaction between isocyanate and water (Choe et al., 2004). After that, this results in the formation of covalent cross-linking segments by extending the aromatic groups of isocyanates to form linear hard segments (Mahmoud et al., 2017). The chemical reactions involved in PU foaming process are shown in Figure 2.12.

Two key reactions: Isocyanate reaction with polyols and water



Various follow up reactions: Isocyanate reaction with amine, urea and urethane

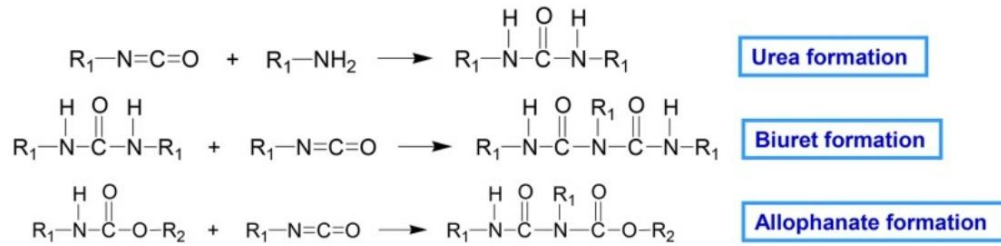


Figure 2. 12: Chemical reactions involved in PU foaming (Rao et al., 2017).

In summary, PU has become the most interesting commercial polymer due to its advantages of light density, ease of processing, and diversity in tailoring different desired properties into the PU based product for specific applications by adding nanofiller. In order to develop an optimum PU foam composite, the filler loading and filler dispersion in the polyurethane have to be considered to improve the properties of PU nanocomposites. This is due to the properties of PU foam are determined by the foam morphology such as cell size, cell density, and size distribution which are influenced by the filler content.