# PREPARATION AND CHARACTERIZATION OF POLYVINYL CHLORIDE (PVC)/ RECLAIMED BUTADIENE RUBBER (rNBR)

EE YU FENG

UNIVERSITI TUNKU ABDUL RAHMAN

# PREPARATION AND CHARACTERIZATION OF POLYVINYL CHLORIDE (PVC)/ RECLAIMED BUTADIENE RUBBER (rNBR)

EE YU FENG

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Petrochemical Engineering

Faculty of Engineering and Green Technology Universiti Tunku Abdul Rahman

September 2024

## DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature: Name: Ee Yu Feng ID No.: 18AGB05405 Date: 13/05/2024

#### **APPROVAL FOR SUBMISSIOM**

I certify that this project report entitled "PREPARATION AND CHARACTERIZATION OF POLYVINYL CHLORIDE (PVC)/ RECLAIMED BUTADIENE RUBBER (rNBR)" was prepared by Ee Yu Feng has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Petrochemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature	:
Supervisor	: <u>Dr.Yamuna a/p Munusamy</u>
Date	:
Signature	:
Co-Superviso	or : <u>Dr Mathialagan a/l Muniyadi</u>

Date :\_\_\_\_\_

The copyright of this report belongs to the author under the terms of the copyright Act 1987 as qualified by Intellectual Property Policy of Universiti Tunku Abdul Rahman. Due acknowledgement shall always be made of the use of any material contained in, or derived from, this report.

© 2024, Ee Yu Feng. All right reserved.

Specially dedicated to

My beloved supervisor, co-supervisor, moderator, lecturers, parents, and friends

for all their help.

#### ACKNOWLEDGEMENTS

I would like to thank everyone who had contributed to the successful completion of this project. I would like to express my gratitude to my research supervisor, Dr.Yamuna a/p Munusamy and Dr Mathialagan a/l Muniyadi for their invaluable advice, guidance, and enormous patience throughout the development of the research.

In addition, I would also like to express my gratitude to my loving parent and friends who had helped and given me encouragement throughout this period. Lastly, I would also like to thank the lab officers and assistants for providing me their technical support and guidance during the setup and analysis of experimental work in this research.

# PREPARATION AND CHARACTERIZATION OF POLYVINYL CHLORIDE (PVC)/ RECLAIMED BUTADIENE RUBBER (rNBR)

#### ABSTRACT

Recycling of waste nitrile butadiene rubber is very hard to implement due to its threedimensional crosslink network, which exists between NBR chains. This threedimensional network is hard to be cleavage and break down. NBR with crosslinks cannot be re-compounded, cannot flow and re-molded into new products. Thus, the recycling and end of life use of NBR waste are limited to grinding it to powder to be used as filler material or through pyrolysis, respectively. Bridge Fields Resources Group (BFR) started their research with Universiti Tunku Abdul Rahman (UTAR) from 2012 to develop a new technique to reclaimed NBR (rNBR). The developed technology is used to devulcanize NBR using plant-based chemicals at room temperature and pressure using existing rubber processing equipment. The rNBR could be re-compounded, flow and re-molded into an entirely new product. In this project, the rNBR will be blended with plasticized PVC in various compositions (100/0, 90/10, 80/20, 70/30, 60/40, 50/50) and its properties will be studied. The properties will be compared with standard specification requirement given for anti-slip bathroom mat product by CY Handee Rubber Moulding Sdn. Bhd. Minimum specifications needed for an anti-slip bathroom mat application include ultimate tensile strength of 5 MPa, 25% of elongation at break with a maximum water absorption of 2.5%, and a Shore A hardness of 75–83. In this project, testing such as tensile strength, hardness test, morphological analysis of fracture surface, water absorption test, thermal decomposition analysis, thermal aging, process torque, curling and shrinkage was conducted to determine the best replacement percentage of plasticized PVC by

reclaimed NBR. Application of rNBR into this compound will reduce the need to use virgin PVC and provide more valuable application or market use for reclaimed NBR. Findings from this work shows that, optimum plasticized PVC/rNBR blend which fulfils these requirements is plasticized PVC/rNBR blends with ratio of 80/20. This blend exhibits 5.25 MPa ultimate tensile strength, 107.20% elongation at break, 2.4276% water absorption, and 75.5 Shore A hardness.

# **TABLE OF CONTENTS**

DECLARATION	iii
APPROVAL FOR SUBMISSION	iv
ACKNOWLEDGEMENTS	vii
ABSTRACT	viii
TABLE OF CONTENTS	X
LIST OF TABLES	xiii
LIST OF FIGURES	XV
LIST OF SYMBOLS/ ABBREVIATIONS	xvii
CHAPTER 1	1
INTRODUCTION	1
1.1 Background of Study	1
1.1.1 Background of Nitrile Butadiene Rubber (NBR)	1
1.1.2 Background of Polyvinyl Chloride (PVC)	4
1.1.3 Floor Mats	6
1.2 Problem Statement	8
1.3 Objective	10
CHAPTER 2	11
LITERATURE REVIEW	11
2.1 Introduction to rubber	11
2.1.1 Synthetic Rubber	11
2.1.2 Nitrile Butadiene Rubber (NBR)	14
2.1.3 Recycling and reclaiming nitrile butadiene rubber waste	19
2.2 Recycling method for rubber	20
2.2.1 Method of devulcanization/ reclaimed of crosslinked rubbers.	21
2.2.1.1 Thermo-mechanical devulcanization of crosslinked rubber	21

2.2.1.2 Thermo-chemical devulcanization of crosslinked rubber	23
2.2.1.3 Chemical devulcanization/ reclaimed method of crosslinked	
rubber	24
2.2.1.4 Microwave devulcanization of crosslink rubber	25
2.2.1.5 Biological devulcanization method of crosslink rubber	26
2.2.1.6 Ultrasonic devulcanization method of crosslink rubber	27
2.2.1.7 Devulcanization / reclaimed method of nitrile butadiene rubl	ber
in Bridge Fields Resources Sdn. Bhd.	28
2.2.1.8 Comparison about method of devulcanization/ reclaimed	
method of nitrile butadiene rubber	30
2.2.2 Specification of reclaimed nitrile butadiene rubber produced by	
Bridge Fields Resources Sdn. Bhd	33
2.3 Polyvinyl Chloride (PVC)	35
2.4 Thermoplastic Elastomer	38
2.4.1 Polyvinyl Chloride / Nitrile Butadiene Rubber (PVC/NBR)	
thermoplastic elastomer (TPE) blend	40
2.4.2 Recent studies on Polyvinyl Chloride/ Nitrile Butadiene rubber	
(PVC/NBR) thermoplastic elastomer (TPE) blends.	43
2.5 Application of Polyvinyl Chloride/ Nitrile Butadiene rubber (PVC/NBR)	46
2.5.1 Anti slip bathroom mat	47
CHAPTER 3	<b>48</b>
METHODOLOGY	<b>48</b>
3.1 Introduction	48
3.2 Research Flowchart	48
3.3 Materials	50
3.4 Preparation of plasticized polyvinyl chloride /reclaimed nitrile butadiene	
rubber blend	51
3.5 Characterization and Testing	54
3.5.1 Tensile Test	54
3.5.2 Hardness Test	56
3.5.3 Water Absorption Test	56
3.5.4 Thermogravimetric Analysis (TGA)	57
3.5.5 Thermal Aging Evaluation	57
3.5.6 Dimensional Stability	58

3.5.6.1 Curling Test	58
3.5.6.2 Shrinkage Test	59
CHAPTER 4	60
RESULT AND DISCUSSION	60
4.1 Introduction	60
4.1.1 Standard requirement of commercial anti -slip bathroom mat	61
4.2 Mechanical properties evaluation	62
4.2.1 Tensile properties	62
4.2.2 Hardness Test	64
4.2 Morphological analysis of fracture surface	66
4.3 Water Absorption Test	70
4.4.1 Thermal Decomposition Analysis	74
4.4.2 Thermal Aging	79
4.5 Process ability studies	82
4.5.1 Process torque	82
4.6 Dimensional Stability	84
4.6.1 Curling Test	84
4.6.2 Shrinkage Test	86
4.7 Cost analysis for plasticized PVC/rNBR blend for 80/20.	89
CHAPTER 5	90
CONCLUSION AND RECOMMENDATIONS	90
5.1 Conclusion	90
5.2 Recommendation	92
REFERENCE	93
APPENDICES	107

# LIST OF TABLES

#### TABLE

#### TITLE

#### PAGE

Table 1.1:	1.1: Supply and demand balance of the China nitrile butadiene		
	rubber from 2017 to 2021 (NBR: Domestic Market Slows		
	down Supply and Demand, 2022).		
Table 1.2:	Type of floor mats and application (Alec, 2023).	6	
Table 2.1:	General Information of Nitrile Butadiene Rubber.	15	
Table 2.2:	Synthesis of Nitrile Butadiene Rubber.		
Table 2.3:	Physical and Mechanical Properties of Nitrile Butadiene		
	Rubber.		
Table 2.5:	Chemical resistance of nitrile butadiene rubber.	18	
Table 2.6:	Environmental performance of nitrile butadiene rubber.	19	
Table 2.7:	Comparison about method of devulcanization method for	30	
	nitrile butadiene rubber		
Table 2.8:	Compounding formulation of Grenviro-NBR 30.	33	
Table 2.9:	Physical properties of Grenviro-NBR 30.	34	
Table 2.10:	Comparison of rigid and flexible PVC (M. S. Esmail,		
	2020).		
Table 2.11:	Difference properties between PVC and NBR.	41	
Table 2.12:	Advantages and disadvantages of PVC/NBR blends.	42	
Table 2.13:	Reviews on research and development of PVC/NBR	43	
	blends.		
Table 2.14:	Application of Polyvinyl Chloride/ Nitrile Butadiene	46	
	rubber (PVC/NBR).		
Table 3.1:	Material for the research	50	
Table 3.2:	Sample ratio of the plasticized PVC/rNBR.	52	

Table 4.1:	Standard specification requirement given for anti-slip	
	bathroom mat product by CY Handee Rubber Moulding	
	Sdn. Bhd	
Table 4.2:	Mean for tensile strength test result.	62
Table 4.3:	Shore A hardness test	64
Table 4.4:	Water absorption (wt%) test results	71
Table 4.5:	Thermogravimetric Analysis for PVC/NBR	74
Table 4.6:	Mean of curling (cm) and variation in length (%)	85
Table 4.7:	Mean of length, width and thickness of shrinkage	87
Table 4.8:	Cost analysis and calculation for plasticized PVC/rNBR	89
	blend of 80/20.	

# LIST OF FIGURES

FIGURE	TITLE	PAGE
Figure 1.1:	Prediction of Polyvinyl chloride (PVC) market size from	5
	2021 to 2023 (USD billion) (Precedence Research, 2022).	
Figure 1.2:	Vulcanization process of the raw rubber (Dorigato et al.,	9
	2023).	
Figure 2.1:	Synthetic rubber demand in 2020 by rubber types and the	12
	applications (Boon et al., 2022).	
Figure 2.2:	Vulcanization of natural rubber (Alarifi, 2022).	13
Figure 2.3:	Twin screw extruder (Chittella et al., 2021)	22
Figure 2.4:	Screw configuration used to perform thermomechanical	22
	devulcanization (Seghar et al., 2019)	
Figure 2.5:	Schematic of the ultrasonic twin screw extruder.	27
Figure 2.6:	Devulcanization process of NBR using Bridge Field	29
	resources technology.	
Figure 2.7:	Grenviro-NBR 30 (Bridge Fields Resources About Us,	33
	2023).	
Figure 2.8:	Synthesis of polyvinyl chloride (Sastri, 2022).	35
Figure 2.9:	Structural composition of TPEs (Conrad, 2021).	39
Figure 2.10:	PVC/NBR blend.	40
Figure 2.11:	Anti-slip bathroom mat (Supply, 2024).	47
Figure 3.1:	Research flowchart for the plasticized PVC/rNBR blends	49
Figure 3.2:	Brabender® Plastograph® EC 815652 Internal Mixer.	51
Figure 3.3:	Sample of plasticized PVC/rNBR after melt blending.	52
Figure 3.4:	Hydraulic hot and cold press equipment.	53
Figure 3.5:	Sample of PVC/NBR after going through hot and cold press.	53
Figure 3.6:	Universal testing machine model Tinius Olsen H10KS-	55
	0748.	

Dumbbell press and cutter and dumbbell shape samples.	55	
Micrographs of PVC/rNBR 100/0 (a) magnification of 500x		
(b) magnification of 1000x		
Micrographs of PVC/rNBR 90/10 (a) magnification of 500x	67	
(b) magnification of 1000x		
Micrographs of PVC/rNBR 80/20 (a) magnification of 500x	68	
(b) magnification of 1000x		
Micrographs of PVC/rNBR 70/30 (a) magnification of 500x	68	
(b) magnification of 1000x		
Micrographs of PVC/rNBR 60/40 (a) magnification of 500x	69	
(b) magnification of 1000x		
Micrographs of PVC/rNBR 50/50 (a) magnification of 500x	69	
(b) magnification of 1000x		
Thermogravimetric analysis.	75	
Weight loss derivate curves for decomposition of samples	76	
Impact of thermal aging on E-Modulus	79	
Impact of aging on ultimate tensile strength.	80	
Impact of aging on elongation break (%).	80	
Process torque.	83	
rNBR thermogravimetric analysis (TGA) result.	107	
PVC thermogravimetric analysis (TGA) result.	107	
PVC/rNBR 90/10 thermogravimetric analysis (TGA) result.	108	
PVC/rNBR 80/20 thermogravimetric analysis (TGA) result.	108	
PVC/rNBR 70/30 thermogravimetric analysis (TGA) result.	109	
PVC/rNBR 60/40 thermogravimetric analysis (TGA) result.	109	
PVC/rNBR 50/50 thermogravimetric analysis (TGA) result.	110	
	Dumbbell press and cutter and dumbbell shape samples. Micrographs of PVC/rNBR 100/0 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 90/10 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 80/20 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 70/30 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 60/40 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 50/50 (a) magnification of 500x (b) magnification of 1000x Micrographs of PVC/rNBR 50/50 (a) magnification of 500x (b) magnification of 1000x Thermogravimetric analysis. Weight loss derivate curves for decomposition of samples Impact of thermal aging on E-Modulus Impact of aging on ultimate tensile strength. Impact of aging on elongation break (%). Process torque. rNBR thermogravimetric analysis (TGA) result. PVC thermogravimetric analysis (TGA) result. PVC/rNBR 90/10 thermogravimetric analysis (TGA) result. PVC/rNBR 80/20 thermogravimetric analysis (TGA) result. PVC/rNBR 70/30 thermogravimetric analysis (TGA) result. PVC/rNBR 60/40 thermogravimetric analysis (TGA) result.	

# LIST OF SYMBOLS / ABBREVIATIONS

°C	Degree Celsius
cm	centimeter
g	Gram
J	Joule
Κ	Kelvin
kt	kiloton
kV	kilovolt
kJ/mol	Kilo joule per mole
m	Meter
min	Minute
mm	millimeter
Pa	Pascal
MPa	Megapascal
Ν	Newton
psi	Pounds per square inch
rpm	Revolution Per Minute
T <sub>50%</sub>	Temperature at 50 % Mass Loss
T450°C	total mass loss at 450°C
W	Watt
wt %	Weight Percent
BFR	Bridge Fields Resources Group
С	Carbon
CaCO <sub>3</sub>	Calcium Carbonate
Cl	Chlorine
CO <sub>2</sub>	Carbon Dioxide
DINCH	Diisononyl Cyclohexane Cicarboxylate

DOP	Dioctyl Phthalate
DOTP	Dioctyl Terephthalate
DTG	Derivative Thermogravimetry
FESEM	Field Emission Scanning Electron Microscopy
GTR	Ground Tire Rubber
Н	Hydrogen
HCl	Hydrogen Chloride
HNT	Halloysite Nanotubes
MBTS	2,2-Dibenzothiazole disulfide
NBR	Nitrile Butadiene Rubber
NR	Natural Rubber
0	Oxygen
PHR	Per Hundred Rubber
PVC	Polyvinyl Chloride
rNBR	Reclaimed nitrile butadiene rubber
S	Sulphur
scCO <sub>2</sub>	Supercritical Carbon Dioxide
SBR	Styrene Butadiene Rubber
TMTD	Tetramethyl Thiuram Disulfide
TGA	Thermogravimetric Analysis
UTAR	Universiti Tunku Abdul Rahman
UTS	Ultimate Tensile Strength
ZnO	Zinc Oxide

#### **CHAPTER 1**

#### **INTRODUCTION**

#### **1.1 Background of Study**

#### 1.1.1 Background of Nitrile Butadiene Rubber (NBR)

Nitrile butadiene rubber (NBR) is a synthetic rubber and made through butadiene and acrylonitrile polymerization. Without reinforcing fillers and crosslinks, NBR have poor tensile strength and limited tear propagation resistance and do not crystallize under stress. In order to increase tensile strength, crosslinking and reinforcing fillers like carbon black, calcium carbonate and talc are typically utilized (Kaliyathan et al., 2020). Reinforced NBR vulcanizates have a lower rip strength than natural rubber (NR) compounds, although the difference is less pronounced at higher strain rates and temperatures. Additionally, there is less abrasion loss in NBR compared with NR (Chandrasekaran, 2010). NBR vulcanizates also exhibits excellent chemical and weathering resistance (Nihmath & Ramesan, 2020).

Numerous sectors, including those in the building, automobile, petroleum and aerospace, employ NBR products. It is the most sought-after rubber particularly for uses involving contact with natural gas, fuels and petroleum (Ghowsi & Jamshidi, 2023). NBR production capacity in China remained at roughly 250,000 tons/year with an average annual compound growth rate of 6.2% from 2017 to 2021 based on **Table 1.1**. On average during the year 2017 to 2021, there was 77,000-tonne yearly difference

between supply and demand of NBR. China's apparent NBR consumption in 2021 was roughly about 277,000 tons. **Table 1.1** shows the supply and demand balance sheet for NBR in China from 2017 to 2021. The production volume from 2017 increased until 2019 but then dropped from 2019 to 2021 due to COVID-19 crisis. Between 2022 to 2026, China's NBR supply and demand may continue to expand steadily with anticipated increase in supply by 3.7% yearly (Chi, 2022). By 2025, the market for NBR anticipated to reach \$2.59 billion, expanding at a 3.3% compound annual growth rate (CAGR) (Market focus, 2018).

Year	Production volume (10kt)	Import volume (10kt)	Export volume (10kt)	Apparent consumption (10kt)
2017	16.6	9.1	0.7	25.0
2018	18.6	8.0	1.2	25.4
2019	21.1	8.4	1.3	28.1
2020	20.3	9.6	1.2	28.6
2021	19.6	8.9	0.9	27.7

Table 1.1: Supply and demand balance of the China NBR market from 2017 to2021 (NBR: Domestic Market Slows down Supply and Demand, 2022).

\*kt = kilotons

NBR waste, like other rubbers, does not naturally decompose over a long period of time due to the presence of chemical crosslinks between its chains. An estimated 5.5 million tons of NBR waste were produced on a global scale in 2023. The waste was from several sources, including the post-industrial waste, tyres, and consumer goods (Association of Natural Rubber Producing Countries, 2023). Nowadays, many industries are exploring into technologies to recycle rubbers and

bring the rubber waste back to the consumption cycle as a raw reclaimed elastomer. Some of the well-known recycling methods used for this purpose includes biological treatment, reclaiming, and chemical devulcanization methods (Kohjiya & Ikeda, 2021).

In this study, reclaimed NBR (rNBR) produced through patented technology by researcher in Universiti Tunku Abdul Rahman and Bridge Field Resources Sdn. Bhd are blended with plasticized polyvinyl chloride (PVC) with various compositions to produce bathmats. PVC/rNBR is a popular type of rubber-plastic compound because they effectively combine oil resistance and superior mechanical qualities. PVC/rNBR mixes are widely utilized in a variety of sectors, including wire and cable coatings, insulation for sound and heat foams, and oil-fuel seals (Lai, S et al., 2023b).

#### 1.1.2 Background of Polyvinyl Chloride (PVC)

Poly (vinyl chloride) (PVC) became important in industrial production as early as 1939, and due to gradual improvements in manufacturing technology, PVC accounted for nearly 30% of the total amount of globally produced plastics by the end of the 1950s, with more than half of this amount being processed into plasticized PVC. PVC is still one of the most frequently used polymers in the world today, owing to its incredible adaptability (Klempová et al., 2023). According to figures on worldwide plastics production in 2021, PVC was the third-most manufactured polymer, accounting for over 13% of total global plastics output (Liu et al., 2020).

The major drivers of the robust expansion seen in the worldwide PVC market during this time were the fast development of the electrical and electronics, building, packaging, and automotive industries. The market for PVC was anticipated to expand from its value of USD 82.52 billion to USD 105.8 billion from year 2022 to year 2023, with a forecasted compound annual growth rate of 3.15%. **Figure 1.1** shows the market size of PVC from 2021 to 2023. In 2021, the PVC market in the United States was USD 18.5 billion. The size of PVC market in China is anticipated to grow at a CAGR of 7.9% from 2022 to 2030, reaching USD 18.7 billion in 2023. In addition, PVC market at Germany and Latin America anticipated to develop at CAGR of 3.5% and 7.6% respectively within the same years (Precedence Research, 2022).



Figure 1.1: Prediction of Polyvinyl chloride (PVC) market size from 2021 to 2023 (USD billion) (Precedence Research, 2022).

Floor mats are commonly found in homes, offices, and commercial spaces. They perform a range of functions, including improving the aesthetic attractiveness of an area and ensuring safety and comfort. With so many variations available, it might be difficult to select the best floor mat for needs (Alec, 2023). **Table 1.2** shows the type of floor mat and their applications.

Floor mats	Application			
Entrance mat	The entrance mat major function is to collect dirt, debris, and			
	moisture off shoes, preventing it from being tracked indoors.			
	Entrance mats are available in a variety of materials,			
	including rubber, nylon, and coir, and may be personalized			
	with logos and patterns.			
Anti-fatigue mat	Anti-fatigue mats are intended to give comfort and ease the			
	stress on the body, especially in locations where people			
	stand for extended periods of time. The anti-fatigue mat are			
	widely utilized in commercial kitchens, workshops, and			
	manufacturing facilities. These mats contain cushioning			
	features that help to decrease tiredness and tension in the			
	feet, legs, and back.			
Kitchen mat	Kitchen mats have a non-slip surface, which prevents			
	accidents caused by damp flooring. These mats are			
	commonly constructed of rubber or vinyl, which are both			
	easy to clean and stain and oil resistant.			
Gym mat	Gym mats are necessary for providing a safe and			
	comfortable training environment. The mat offer cushioning			
	and stress absorption, lowering the likelihood of injury			
	during activity. Gym mats come in a variety of thicknesses			
	and materials, such as foam or rubber, to accommodate a			
	wide range of fitness exercises such as yoga, weightlifting,			
	and martial arts.			

 Table 1.2: Type of floor mats and application (Alec, 2023).

<b>Bathroom mat</b>	Bathroom mats are used to absorb water and prevent	
	slipping in wet areas like bathrooms or shower rooms. The	
	mat is usually made of absorbent materials like cotton or	
	microfiber and have a non-slip backing for added safety.	
	Bathroom mats come in various sizes and designs to	
	complement any bathroom decor.	

In this project, the blend of reclaimed NBR and PVC are produced to make the anti-slip bathroom mat. An important safety component for any bathroom is an anti-slip mat. Falling and slipping are less likely with anti-slip mat, which is helpful because damp bathroom floors may be particularly hazardous (Home, 2024).

#### **1.2 Problem Statement**

Implementing waste NBR recycling is very challenging. This is due to the irreversible and difficult-to-break three-dimensional crosslink network that exists between NBR chains. Crosslink rubbers are insoluble, thermally stable, will not melt and flow thus difficult to recycle. Vulcanization is often carried out using sulfur. Each crosslinking bonds requires 40–55 sulphur atoms and occurs primarily at C=C (double bonds) by the chemical reaction between sulphur and rubber hydrocarbons (Nakanishi et al., 2021). **Figure 1.2** shows the vulcanization process of the rubber (Dorigato et al., 2023). The cross-linked nature of the rubbers them from flowing and taking on new shapes after curing.

However, recently lot of research has been conducted on recycling NBR to bring it back into the product cycle as a raw decrosslinked rubber. Some of the popular methods to recycle the NBR are using biological treatment, ultrasound techniques, microwave radiation and chemical treatment (Ghowsi & Jamshidi, 2023). These methods can break down the NBR crosslink networks so it can easily be recycled, flow and reshaped into new product. NBR recycling provides a waste management option, but the existing processes have several disadvantages. Biological treatments might be time consuming and ineffective (Valdés et al., 2021b) while ultrasound technique require high energy inputs (Genovés et al., 2022). On the other side, chemical treatments have the potential to be dangerous and produce undesirable byproducts. These restrictions make it more difficult to recycle NBR efficiently and sustainable for the environment, which calls for the creation of better techniques (Gobetti et al., 2024).



Figure 1.2: Vulcanization process of the raw rubber (Dorigato et al., 2023).

Bridge Fields Resources Group (BFR) started their research with Universiti Tunku Abdul Rahman (UTAR) from 2012 to develop a new technique to reclaimed NBR. The developed technology is used to reclaimed rubber using plant-based chemicals at room temperature and pressure using existing rubber processing equipment. No solvents and carcinogenic chemicals are employed in this process which makes the process ecologically beneficial to the environment. This technology has led to production of reclaimed NBR with the brand name Greenviro<sup>®</sup>. BFR uses the reclaimed NBR to be compounded into other useful composition or product that can be used in our daily life. Some of the targeted products to be developed by BFR includes O-ring, safety boots and floor mats.

This project is about preparation and characterization of PVC/rNBR blends for production of anti-slip bathroom mats. In this project, the devulcanized NBR will be blended with plasticized PVC at various compositions (10 - 40 phr) and its properties will be studied. PVC/NBR blends generally is a highly profitable and miscible physical composition. The elastomeric component of NBR serves as a permanent plasticizer for PVC. It can increase the thermal ageing, chemical resistance, and abrasion resistance of PVC (Senake Perera et al., 2001).

In the global market, industries produce PVC/ NBR blends by using virgin NBR and PVC. However, in this project, reclaimed NBR is utilized to promote the recycling of NBR, reduce usage of virgin NBR, reduce the fraction of virgin PVC, and solve some problems associated with NBR waste. The cost of the overall product could also reduce. However, the challenge in using the rNBR is to find the best replacement ration of rNBR into the composition that could still fulfill the product standard. Through the implementation of this project, the best replacement of plasticized PVC by rNBR could be devised and the compound could be compared with standard required to produce anti-slip bathroom mat. The success of this project will provide more market acceptance and application for rNBR.

## 1.3 Objective

- To prepare polyvinyl chloride (PVC)/reclaimed nitrile butadiene rubber (rNBR) blends with different composition of PVC (10-40 phr).
- To test the mechanical, thermal, and physical properties of the PVC/rNBR blends.
- To compare the properties of the PVC/rNBR blend with commercial anti-slip bathroom mat product's standards.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Introduction to rubber

Rubber is a versatile material used in a variety of industries. It is a natural polymer, which means it is made up of long chains of organic molecules produced mostly from the latex sap of some plants, such as the rubber tree, or synthesized from petroleum wastes in the case of synthetic rubber (He et al., 2021).

#### 2.1.1 Synthetic Rubber

The evolution of synthetic rubber was particularly rapid and vast due to the development of polymerization chemistry. This was partly caused by the fact that attempts to create rubber were started long before anybody had the slightest clue about how polymerization processes worked. Such endeavors started very shortly following Williams' (1859) excellent analytical work, which discovers that Hevea rubber was "composed" of isoprene (Mark et al., 2013). Any artificial rubber made from natural or petroleum-derived monomers is called synthetic rubber. However, most of the synthetic rubbers used today are derived from the former. Since the first successful synthesis of synthetic polyisoprene in 1887, many different types of synthetic rubbers have been developed. Over 20 different types of synthetic rubber are already available on the market (Celeiro et al., 2021). **Figure 2.1** displays information on synthetic

rubber demand and distribution by application in 2020. Synthetic rubbers offer a broader range of uses beyond the many uses that are comparable to those of natural rubber. The main reason for this is that the synthetic rubber, in contrast to natural rubber, which usually only has one chemical structure, is made up of many monomers, which enables the design of different rubber qualities. For instance, the nitrile butadiene rubber (NBR) has excellent oil resistance because of the polar nitrile group from the acrylonitrile monomer. The butadiene monomer contributes to the flexibility and elastic properties. By adjusting the proportion of butadiene to acrylonitrile repeating units, the rubber's mechanical characteristics, oil resistance, and chemical resistance could be tailored based on application requirement (Boon et al., 2022).



Figure 2.1: Synthetic rubber demand in 2020 by rubber types and the applications (Boon et al., 2022).

Rubber products are created by a series of activities that entail the addition of value-adding material through chemical reactivity and irreversible physical feature modification. Extrusion, calendaring, and vulcanization are the procedures of the utmost significance when it comes to physical and chemical modification of rubber product (Lapkovskis et al., 2020). Rubber processing begins from harvesting and gathering of latex sap. Acid is added to latex to bulk out the substance. This fluid is then molded into sheets using a mill that sprays water to dry it. The sheets are prevulcanized through low-temperature chemical reactions. The rubber sheets become harder from the heating. The rubber is mixed with activators, accelerators, and sulphur

to promote chemical vulcanization process. The long rubber chains are cross-linked, which increases tensile strength, hardness and weather resistance (Alarifi, 2022). **Figure 2.2** shows the vulcanization of natural rubber.



Figure 2.2: Vulcanization of natural rubber (Alarifi, 2022).

The crosslinked rubber materials are strong, have high abrasion resistance, good dimensional stability, and chemical stability (Speight, 2020). Monosulfide crosslinks are formed by the interaction of one sulphur atom and two polymer chains. During vulcanization, sulfur molecules react with carbon-carbon double bonds (C=C) in NBR chains to generate mono-sulfur bridges between neighboring chains. These bridges assist in maintaining the polymer network, which improves mechanical durability and resilience (Kong et al., 2023). Disulfide (-S-S-) linkages are used to create bridges between two polymer chains using two sulphur atoms. Disulfide bridges, which are more stable than monosulfide bonds, are created when sulphur molecules react with many C=C bonds during vulcanization. Disulfide crosslinks reinforce the

polymer network even further, improving its overall mechanical qualities and ability to withstand heat and deformation (Sarkar et al., 2021). Longer sulphur chains are formed between polymer chains in polysulfide crosslinks. When there is too much sulphur present during vulcanization, this happens. When too much sulphur interacts with many C=C bonds, polysulfide bonds are created. Polysulfide crosslinks permit some chain movement while preserving the overall integrity of the network structure thus it enhances the polymer flexibility and durability (Kruželák et al., 2016).

#### 2.1.2 Nitrile Butadiene Rubber (NBR)

Random copolymers of butadiene and acrylonitrile are used to create nitrile rubber, often referred to as NBR, Buna-N, and acrylonitrile butadiene rubber. Although the nitrile composition affects the NBR's physical and chemical qualities, this type of synthetic rubber is typically resistant to fuel, oil, and other chemicals. By adding more nitrile, the adhesion qualities of NBR can be improved. Additionally, the polymer's resistance to oils increases with nitrile content while the material's elasticity will decrease. NBR have a wide range of fillers and modifiers that are very compatible with them, providing the compounder a wide range of characteristics (Petrie, 2021).

Depending on the end use of the polymer, different grades of NBR are produced. Low nitrile rubber is typically used in gaskets, O-rings and adhesives because of its flexibility at low temperatures. The medium nitrile content type is used for less flexible items such as shoe soles and kitchen rugs. Polymers with a high acrylonitrile content are used in fuel tanks, hoses, plumbing and gaskets because the NBR are stiffer and highly resistant to hydrocarbon derivatives and oils (Singh et al., 2021). But it also makes materials less elastic and frost resistant (Kapitonov et al., 2021). Like most unsaturated thermoset elastomers, NBR must be formulated with additional chemicals and undergo further processing to produce useful products. Reinforcers, plasticizers, protectors, and vulcanizing agents are often used as additional ingredients. The processing steps of NBR include mixing, performing into the desired shape and applying to substrates, extrusion, and curing. Extruders, internal

mixers and open mills are generally used for mixing and processing of NBR. (Thomas, 2017). **Table 2.1** shows the information related to NBR. (WYPYCH, 2016).

Parameter	Value	
Common name	• Acrylonitrile-butadiene elastomer, Nitrile butadiene rubber	
CAS name	<ul> <li>Polymer with 1,3-butadiene; nitrile rubber,</li> <li>2-propenenitrile</li> </ul>	
Acronym	• NBR	
Person to discover the Nitrile Butadiene Rubber	• Semon, W L	
CAS number	<ul> <li>9003-18-3; 9005-98-5</li> </ul>	

Table 2.1: General Information of Nitrile Butadiene Rubber.

Emulsion polymerization is used for producing NBR. The following ingredients: water, soap, the monomers butadiene and acrylonitrile and the radical generating activator are discharge into the reaction vessel. An emulsion technique produces a polymer latex that is then coagulated using calcium chloride or aluminum sulphate to create crumb rubber, which is then dried and pressed into bales. **Table 2.2** shows the synthesis of NBR. (Atef et al., 2019).

Parameter	Unit	Value
Monomer(s) structure	-	$CH_2 = CHCN$ ; $CH_2 = CHCH$ = $CH_2$
Monomer(s) CAS number(s)	-	107-13-1; 106-99-0
Monomer(s) molecular weight(s)	dalton, g/ mol, amu	53.06; 54.09
Acrylonitrile content	%	15-51
Number average molecular weight, $M_n$	dalton, g/ mol, amu	58,00-75,000
Mass average molecular weight, $M_w$	dalton, g/ mol, amu	199,000-600,000
Polydispersity, $M_w/M_n$	-	2-6

Table 2.2: Synthesis of Nitrile Butadiene Rubber.

NBR has good physical and mechanical properties. The hardness range of NBR is 20 - 95 Shore A. The tensile strength is 200 - 3500 psi and the elongation is 350% - 650%. NBR has high adhesion to the metal, high adhesion to rigid materials and high tear resistance. However, NBR only has medium flex cracking resistance, medium impact resistance and medium vibration dampening. **Table 2.3** shows the physical and mechanical properties of NBR (NBR - Nitrile rubber, 2017).

Physical Properties				
Properties	Range			
Hardness	20 - 95 Shore A			
Tensile Strength	200 - 3500 psi			
Elongation	350% - 650%			
Mechanical Properties				
Properties	Grade			
Adhesion resistance	High			
Adhesion to the metal	High			
High adhesion to rigid materials	High			
Tear Resistance	High			
Flex cracking resistance	Medium			
Impact resistance	Medium			
Vibration dampening	Medium			

# Table 2.3: Physical and Mechanical Properties of Nitrile Butadiene Rubber.

Synthetic NBR is known for its high chemical resistance to various chemicals. NBR has medium acid and alkaline chemical resistance. However, it is highly resistant to the fuel oils, mineral oils and petroleum. NBR also has high resistance to solvent. **Table 2.4** shows the chemical resistance properties of NBR (Braihi et al., 2020).

Properties	Grade
Acids, Dilute	Medium
Acids, Concentrated	Low
Acids, Organic (Dilute)	Medium
Acids, Organic (Concentrated)	Low
Acids, Inorganic	Medium
Alkalies, Concentrated	Medium
Fuel Oils	High
Mineral Oils	High
Oil Resistance	High
Petroleum Aromatic	Medium
Petroleum Non-Aromatic	High
Solvent	High

Table 2.5: Chemical resistance of nitrile butadiene rubber.

NBR have high color ability, gas permeability and water resistance. It has medium resistance to ozone, oxidation, radiation, steam, sunlight and weather. **Table 2.6** shows the environmental performance of NBR (NBR - Nitrile rubber, 2017).
Properties	Grade
Color ability	High
Gas permeability	High
Ozone Resistance	Medium
Oxidation Resistance	Medium
Radiation Resistance	Medium
Steam Resistance	Medium
Sunlight Resistance	Medium
Weather Resistance	Medium
Water Resistance	High

 Table 2.6: Environmental performance of nitrile butadiene rubber.

## 2.1.3 Recycling and reclaiming nitrile butadiene rubber waste

NBR products are used in a variety of industries including automotive, construction, aerospace, petroleum and more. The most demanded rubber is NBR, especially for applications where it is exposed to fuels, oils, and gases (Cui et al., 2020). Like other rubber scraps, NBR scraps take a long time to decompose. This is caused by formation of three-dimensional crosslink structure between NBR chains. Due to environmental issues and the large amount of scrap rubber that is generated today, scrap rubber recycling has become a topic of interest to scientists. A major problem in rubber scraps are insoluble, thermally stable, and difficult to recycle. The cross-linked nature of the rubbers prevented them from flowing and taking on new shapes after curing (Gumede et al., 2021b).

### 2.2 Recycling method for rubber

The disposal and recycling of cross-linked rubber waste is an important issue in our society. Polymeric materials are persistent, making their disposal a major environmental concern (Sabzekar et al., 2015). Industrial rubber waste and rubber goods that have reached the end of their useful lives are now posing a significant environmental issue. Despite efforts to recycle scrap rubber, much of it still ends up in landfills (Molino et al., 2018). Rubber waste can be incinerated to reduce waste volume and recover heat. However, the treatment of the secondary pollutants released, such as sulphur and nitrogen oxides, increases the financial burden on the company. Thermomechanical technology, which is often used to recycle plastic waste, is not suitable for recycling reclaimed rubber waste because the heating process cannot melt and shape it (Cheng et al., 2023). In fact, the accumulation of rubber scraps encourages the growth of mice and mosquitoes, and also creates the possibility of fire through spontaneous heating. Recycling rubber is challenging due to its three-dimensional structure and multi-component composition, and therefore poses a modern technological challenge. However, in recent decades, a few techniques have been developed to recycle scrap rubber (Asaro et al., 2018). One of the options is to grind this waste into powder or granules, which can then be used as reinforcing fillers for concrete, bituminous mixtures or polymers (Seghar et al., 2019).

The best method to recycle crosslink rubber waste would be to intentionally break the carbon-sulphur (C-S) bonds or sulphur-sulphur (S-S) bonds without breaking the carbon-carbon (C-C) bonds that make up the backbone polymer chain. The energy required to break S-S and C-S bonds (227 and 273 kJ/mol, respectively) is not significantly different from the energy required to break C-C bonds (348 kJ/mol), making this task challenging (Ramarad et al., 2015; Sabzekar et al., 2015). Recycling is also a sustainable practice as it saves raw materials and energy, has positive impact on the environment and continues to provide a source of income for many families whose livelihoods depend on the collection of recyclable materials (de Sousa et al., 2017).

### 2.2.1 Method of devulcanization/reclaimed of crosslinked rubbers.

Numerous studies have been conducted on recycling rubbers and returning them to the consumption cycle as a raw vulcanizable elastomer (Akca et al., 2018). The known methods that use to reclaimed NBR are thermo-mechanical, thermo-chemical, chemical, microwave, biological and ultrasonic approaches (Saputra et al., 2021).

## 2.2.1.1 Thermo-mechanical devulcanization of crosslinked rubber

Thermomechanical method is the one the best suited method for industrial adaptation. This is since it is based on the usage of an extruder, which is a piece of standard machinery in the thermoplastic and rubber industries and can create a high degree of devulcanization. Additionally, this method is simple to use, well-suited to mass manufacturing, and benefits from continuous operation, which enables the treatment of significant volumes of NBR waste (Valentini et al., 2020). In the last ten years, in particular, thermo-mechanical devulcanization has been extensively studied in the literature. It has been used to reclaimed waste NBR in a twin-screw extruder, and the results show that temperature and screw rotation speed were the key variables throughout the process (Brunella et al., 2022). Study by Seghar et al., showed that in a massive twin-screw extruder, the rubber was reclaimed at various barrel temperatures ranging from 80 to 100°C. **Figure 2.3** shows the twin screw extruder and **Figure 2.4** shows the screw configuration used to perform thermomechanical devulcanization in the study (Seghar et al., 2019).



Figure 2.3: Twin screw extruder (Chittella et al., 2021)



Figure 2.4: Screw configuration used to perform thermomechanical devulcanization (Seghar et al., 2019)

Rubber devulcanization was performed using a twin-screw extruder with five heating zones, a length to screw diameter ratio (L/D) of 40, and a maximum screw speed of 150 rpm. The barrel temperature was adjusted for the final three heating zones, while the temperature for the first two zones remained constant at 200°C. The rubber was reclaimed at 220°C initially, then increased to 250°C in heating zones (Parsamanesh et al., 2023). The system starts with a gravimetric feeding mechanism that feeds free-flowing rubber waste into the extruder continuously. The system consists of a central co-rotating twin-screw extruder, vacuum extraction, and degassing parts. The extruder heats and shears the rubber, breaking the bonds formed during vulcanization. A cooling tank and transport line are used to reduce the temperature of the material exiting the extruder. The reclaimed rubber is then collected (Costamagna et al., 2022).

### 2.2.1.2 Thermo-chemical devulcanization of crosslinked rubber

In this approach, crosslinked rubber recycling uses supercritical water, tetrahydrofuran, ethanol, n-butanol and toluene for devulcanization. These fluids are primarily used to convert rubber shavings into low molecular weight hydrocarbons (Gumede et al., 2022a). Most recently supercritical carbon dioxide ( $scCO_2$ ) is used for this purpose. The common theory behind the  $scCO_2$  devulcanization process is that when  $CO_2$  reaches a supercritical state, it promotes multiple chemical reactions in rubber vulcanizates, rapidly swelling them and increasing the vibrational amplitude of their atoms. This allows the release agent to effectively penetrate the stretched sulphur crosslinks and break them up with ease (Worlee et al., 2021).

Depending on temperature and pressure,  $ScCO_2$  exhibits high diffusivity, low viscosity, and high thermal conductivity. This liquid has an easily accessible critical point, non-toxic, cheap, and nonflammable. It also detaches easily from the rubber chains. The dispersion coefficient of diphenyl disulfide in  $scCO_2$  is about four orders of magnitude higher than that of toluene, (Mangili et al., 2014a).

The chemical method has been reported to be successful in devulcanization of NBR. Nitric acid or HNO<sub>3</sub>, a powerful oxidizing agent, reacts with various types of sulphur groups, oxidize the sulphur bonds and aids in the devulcanization of the rubber. The corrosive effect of nitric acid on rubber surfaces was first identified in 1985 by using scanning electron microscopy (SEM) (Rios et al., 2006). This method offers great potential for devulcanization of rubber using only readily available and inexpensive HNO<sub>3</sub> oxidizer. To start the process, the sulphur lattices are first oxidized. However, there are two other competing processes, nitration, and oxidation, that generate -NO<sub>2</sub> and -COOH groups. Under severe conditions, severe oxidation also occurs with fragmentation of the polymer chain, resulting in water-soluble, heavily oxidized and low-molecular-weight compounds (Sabzekar et al., 2015).

Other chemical reclamation techniques can lower rubber molecular weight without devulcanization events. Nitrous oxide was utilized to break down rubber by converting unvulcanized carbon-carbon double bonds into ketones. This technique produced homogenous rubber with a consistent structure, allowing for separation from fabric and steel wires (Bockstal et al., 2019). Additionally, the major chains were oxidatively cleaved using periodic acid. Rubber reclamation was successful but cannot be utilized in tire production to create fresh reclaimed rubber. However, it may still be used in other rubber product manufacturer (Thaicharoen et al., 2010).

### 2.2.1.4 Microwave devulcanization of crosslink rubber

Due to the high production potential and good material properties, microwave devulcanization is currently one of the most promising processes. The process uses microwaves to volumetrically heat the material, allowing for more uniform heating than is possible with traditional conduction and convection heating techniques. Other than that, no chemicals are used at any of the stages of the process. This is a type of thermal devulcanization, or controlled degradation, that applies a significant amount of energy to the material in a short period of time, resulting in high efficiency and is considered an environmentally friendly (de Sousa et al., 2017). The rubber is heated, which promotes the breaking of sulphur crosslinks. Non-polar elastomers like tire rubber can absorb microwave energy, but due to their limited absorption and dissipation this is not possible without the addition of some particles like carbon black. The devulcanization process can only be performed with this filler because it is known to absorb electromagnetic radiation through a phenomenon known as Maxwell-Wagner polarization (Garcia et al., 2015). However, because the process is a form of controlled degradation, the parameters must be tightly managed to prevent material degradation (Simon et al., 2019).

Microwave devulcanization of ground tire rubber was performed in a BP-125/50 laboratory microwave oven. The 100g of room temperature ground tire rubber was treated at heating rates of 1, 2, 3, 6, 12, and 18°C/min, with ultimate temperatures of 120, 140, 160, 180, and 200°C. In certain cases, we also used a 30-minute holding phase at the ultimate temperature in the microwave oven following the heating cycle (Simon & Bárány, 2023). In addition, the employed heating profiles with two distinct heating rates during the same devulcanization operation. There are certain challenges this method, such as optimizing microwave power, exposure duration, and temperature to accomplish successful devulcanization without damaging rubber (Ghamarpoor & Jamshidi, 2023a).

## 2.2.1.5 Biological devulcanization method of crosslink rubber

Biological tire devulcanization techniques have a few advantages over conventional approaches, which typically involve the release of toxic compounds, the use of hazardous chemicals, or a lot of energy (Valdés et al., 2021b). Additionally, because microorganisms have a variety of desulfurization enzymes, it may pick out and break certain cross-linked sulphur bonds on rubber surfaces. Recently, many studies have been conducted on microbial desulfurization of NBR using various bacteria that can oxidize sulphur to sulphate such as *T.thiooxidans, T.ferrooxidans, T.Thioparus, Thiobacillus* (Valdés et al., 2020a), *Sphingomonas, Gordonia, Gordonia* (Tatangelo et al., 2016), *Amycolatopsis, Psedomonas, Nocardia, Mycobacterium* and *Psedomonas* (Ghavipanjeh et al., 2018).

In reclaimed rubber, the bacteria can selectively cleave the sulphide bridges (S-S and C-S bonds), but leave the polymeric backbones intact (Cheng et al., 2023). A variety of sulphur-oxidizing microorganisms, both heterotrophic and autotrophic, have been studied for rubber devulcanization. *At. ferrooxidans, At. Thiooxidans* (Li et al., 2011), and *Sulfolobus acidocaldarius* (Bhowmick et al., 2023) are acidophilic. The sulphur oxidizing organisms thrive in acidic environments. Solvent leaching procedures are often employed to minimize the toxicity of GTR before microbial devulcanization (Allan et al., 2021).

### 2.2.1.6 Ultrasonic devulcanization method of crosslink rubber

This process takes place without the use of chemicals, as ultrasound can cause cavitation, which dissolves the three-dimensional network in the rubber matrix within seconds (Li et al., 2022). In previous studies, this recovery process was investigated on different types of rubber using an ultrasonic single-screw extruder (Byun et al., 2020). Recently, an ultrasonic component has been added to twin screw extruder to improve efficiency. Without the addition of fresh rubber, the resulting reclaimed tire rubber can be directly mixed with vulcanizing agents and reclaimed (Mangili et al., 2015b).

The **Figure 2.5** show an ultrasonic co-rotating twin screw extruder used for devulcanization and compounding. The rubber was conveyed using two 16 mmdiameter screws. Through a horn installed within the barrel, 40 kHz ultrasonic waves were delivered to the rubber (Dong et al., 2021). However, scalability and technological breakthroughs in extruder design may be required for large-scale industrial applications (Shabani & Jamshidi, 2022).



Figure 2.5: Schematic of the ultrasonic twin screw extruder.

# 2.2.1.7 Devulcanization / reclaimed method of nitrile butadiene rubber in Bridge Fields Resources Sdn. Bhd.

In Bridge Fields Resources Sdn. Bhd, it uses two roll mills for decrosslinking rubber products including natural rubber (NR), styrene butadiene rubber (SBR), NBR and chloroprene rubber. The rubbers are put into two roll mills and after that, plant-based chemicals are added to break down the sulphur linkages between the rubber chains After a few min, the rubber could be reclaimed with same processability as virgin rubber. The process also can be carried out by using extrusion for continuous production means. The technology used by Bridge Fields Resources combines chemical and mechanical processes without the use of external heat supply. The heat generated from friction and shear in the processing equipments are exploited. This invention was patented by the company with inventors from Universiti Tunku Abdul Rahman (Bridge Fields Resources About Us, 2023). Compared to other patented technology, this invention does not involve the usage of hazardous chemicals and inorganic solvents which is commonly used to swell the rubber before devulcanization. The process of NBR devulcanization using Bridge Field technology is summarized in **Figure 2.6**.



Figure 2.6: Devulcanization process of NBR using Bridge Field resources technology.

# 2.2.1.8 Comparison about method of devulcanization/reclaimed method for nitrile butadiene rubber

Researchers has attempted to reclaimed NBR rubber waste but often these technologies are not being commercialized because the process involves usage of solvent, new costly equipment, and technology such as ultrasound and microwave technology, uses hazardous chemicals and happens in batch processes. **Table 2.7** highlights the comparison of the methods being studied and its advantage and disadvantages.

Method Advantage Disadvantage Reference No **Thermo-mechanical** Continuous Operation. High shear force. (Seghar et al., 1 devulcanization Easy to implement. Oxygen has negative effects on 2019) • Can treat large amounts of the the devulcanization. rubber. Low temperature between 80 °C to 100 °C. Experience of many years for improvement. Thermo-chemical 2 Supercritical carbon dioxide scCO<sub>2</sub> properties is not well (Gumede et al., ۲ ۲ devulcanization (scCO<sub>2</sub>) as devulcanization is low 2022a) understood. price, chemically inert, non-toxic scCO<sub>2</sub> will create several •

Table 2.7: Comparison about method of devulcanization method for nitrile butadiene rubber

		<ul> <li>and non-flammable.</li> <li>scCO<sub>2</sub> has an easily accessible critical point at temperature and pressure of 31.1 °C and 7.39 MPa</li> <li>scCO<sub>2</sub> is easily removed after the devulcanization process.</li> </ul>	competing chemical reactions during the devulcanization process and increase the variation amplitude of the atoms.	
3	Chemical devulcanization	<ul> <li>Generally, use in reclaiming rubber industries.</li> <li>High potential for devulcanization of rubber.</li> </ul>	<ul> <li>It will generate by products such as -NO<sub>2</sub> and -COOH groups.</li> <li>Involves the usage of hazardous and corrosive chemicals such as nitric acid which is a strong acid.</li> </ul>	(Sabzekar et al., 2015)
4	Microwave devulcanization	<ul> <li>High production potential.</li> <li>Good material properties.</li> <li>More uniform heating because of volumetric heating by microwave.</li> <li>Eco friendly.</li> <li>No chemicals involved.</li> </ul>	<ul> <li>High amount of energy.</li> <li>Parameters involved need to be controlled well to prevent degradation of material.</li> <li>Need setup of new equipment; microwave facilities</li> </ul>	(de Sousa et al., 2017)

5	Biological devulcanization method	<ul> <li>Do not use hazardous chemicals.</li> <li>Low energy consumption.</li> <li>Do not release toxic chemicals.</li> <li>Low discharge of secondary pollutants.</li> </ul>	<ul> <li>Need to have more research towards the microorganism.</li> <li>Requires large space for biological treatment of waste.</li> </ul>	(Ghavipanjeh et al., 2018), (Cheng et al., 2023)
6	Ultrasonic devulcanization	<ul> <li>Without any chemicals.</li> <li>Can break the 3D network in the rubber matrix in a few seconds.</li> </ul>	<ul><li>Required high temperature.</li><li>Requires new facility setup</li></ul>	(Mangili et al., 2015b)
7	Bridge Fields Resources Sdn. Bhd devulcanization method rubber	<ul> <li>Without the use of heat.</li> <li>Do not have hazardous waste.</li> <li>Stable and mature process.</li> <li>Uses environmentally friendly green chemicals.</li> <li>.</li> </ul>	• Storage stability (Improvement continuous study)	(Bridge Fields Resources About Us, 2023), (Drobny, 2014)

# 2.2.2 Specification of reclaimed nitrile butadiene rubber produced by Bridge Fields Resources Sdn. Bhd

The brand name of reclaimed NBR produced by Bridge Fields Resources Sdn. Bhd is Grenviro-NBR 30 (Off grade) (Bridge Fields Resources About Us, 2023). **Figure 2.7** shows the Grenviro-NBR 30 produced by Bridge Fields Resources Sdn. Bhd.



Figure 2.7: Grenviro-NBR 30 (Bridge Fields Resources About Us, 2023).

A compounding formulation is a combination of components used to produce a rubber compound with specific characteristics. **Table 2.8** shows the compounding formulation of Grenviro-NBR 30 while **Table 2.9** shows the physical properties of Grenviro-NBR 30 (Bridge Fields Resources About Us, 2023).

Material	Per Hundred Rubber (PHR)
NBR 30	100
ZnO	6
Stearic acid	3
Sulphur	1

Table 2.8: Compounding formulation of Grenviro-NBR 30.

2,2-Dibenzothiazole disulfide (MBTS)	0.3
Tetramethyl Thiuram Disulfide	0.1
(TMTD)	

# Table 2.9: Physical properties of Grenviro-NBR 30.

Grenviro-NBR 30		
Tensile strength (Mpa)	$14.8 \pm 3$	
Elongation (%)	$630 \pm 60$	
Specific gravity (%)	$0.98 \pm 0.05$	
Rubber hydrocarbon (%)	97 ± 3	
Acetone extract (%)	3 ± 3	
Mooney viscosity	60 ± 15	
Acronitrile content (%)	$33 \pm 3$	

### 2.3 Polyvinyl Chloride (PVC)

With 57% by weight chlorine, polyvinyl chloride (PVC), also known as vinyl or under the IUPAC nomenclature "chloroethane" or "poly(chloroethanediyl)", is a type of "infrastructure thermoplastic" material. PVC, with the chemical formula  $C_2H_3Cl$ , composed of repeating vinyl (ethenyl) groups with one hydrogen atom per repeating unit replaced by chlorine (Torgal et al., 2016). Vinyl chloride, which is a gas at room temperature, is used to make PVC. Through the process of free radical polymerization, vinyl chloride is polymerized using the suspension, bulk, emulsion, and solution techniques. **Figure 2.8** shows the fundamental free radical polymerization procedure for PVC (Sastri, 2022).

Virgin PVC is an odorless white powder that is stable at normal pressure and temperature up to about 200°C before it begins to discolor and decompose, releasing hydrogen chloride (HCl) gas. PVC can be processed with all common plastic processing methods such as extrusion, injection molding and blow molding as it is a thermoplastic that softens when heated and hardens when cooled. PVC materials are cost effective as offer relatively low material prices per volume due to their relatively low density. Due to its affordability and excellent chemical and mechanical properties, PVC is currently one of the most widely used economic and bulk resins (Torgal et al., 2016).



Figure 2.8: Synthesis of polyvinyl chloride (Sastri, 2022).

Plasticized polyvinyl chloride was first introduced in the United States in the 1930's. It first attracted attention during World War II as a replacement for natural rubber in applications such as cable insulation (Chaudhary, et al., 2016). The addition of plasticizers creates flexible soft plasticized PVC that can be used for industrial

tubing, gaskets, flexible automotive parts and electrical wire sheathing where flexibility is important. This plasticized PVC has high tensile and fatigue strength, rubber-like elasticity and is flexible (Torgal et al., 2016). The polar polymer PVC contains 10% fine crystallites. Plasticizers are polar compounds that bond readily to PVC and have little or no volatility. The presence of a plasticizer does not significantly affect the structure of the PVC chains, allowing for a high degree of plasticization. The glass transition temperature of PVC is 80°C. This could be further reduced by adding a plasticizer. The material will appear like an elastomer as the transition temperature decreases below room temperature as the plasticizer content increases (Aji et al., 2020).

PVC has applications that are both rigid and plasticized. **Table 2.10** shows the comparison of rigid PVC and flexible PVC. Applications for rigid PVC include, storage tanks, construction materials, pipes, sheets, and particular molded goods and containers. Some of its applications in construction include PVC window frames, transparent roof sheeting, and rainwater pipes and gutters. Leather cloths, sheets, footwear, films, packing goods, tubes, pipes, hoses, toys, molded things, containers, belting, wire insulation, and cables are flexible or semi-rigid uses of plasticized PVC (M. S. Esmail, 2020).

Rigid PVC		Flexible PVC		
Advantage	Disadvantage	Advantage	Disadvantage	
<ul> <li>Excellent corrosion resistance.</li> <li>High dielectric properties.</li> <li>Good toughness.</li> <li>Abrasion resistance.</li> <li>Good weather ability.</li> </ul>	• Easily to stain. More difficult to process	<ul> <li>Highly flexible.</li> <li>High dielectric properties.</li> <li>Good chemical resistance.</li> <li>Good weather resistance.</li> <li>Low cost.</li> </ul>	<ul> <li>Become stiff at low temperature.</li> <li>Easily to stain.</li> <li>Some plasticizers migrate to the surface.</li> <li>Easier to process</li> </ul>	

Table 2.10: Comparison of rigid and flexible PVC (M. S. Esmail, 2020).

#### 2.4 Thermoplastic Elastomer

Thermoplastic elastomers (TPEs) developed almost 55 years ago and have become an integral part of the elastomer industry. TPE the fastest-growing polymer systems, are finding more and more uses in places where conventional thermoset rubbers have previously been employed (Subramanian et al., 2021). Growth of 6% per year up to 2015 was recorded, with the global demand for these raw materials around 6 million tons (Wang et al., 2019).

Most of the world's consumption of TPEs is in the automotive industry. Slower growth in established industries such as footwear and asphalt finishing could be witness for TPEs. Medical and healthcare supplies represent a small but significant new application area for TPEs (Musa et al., 2022). In practice, the homogeneity of the TPEs, which usually results from mechanical blending, is of crucial importance. The morphology and structure of the TPEs that are formed during the mixing process determine their properties and it is crucial to characterize the phase structure of TPE accurately at the microscopic level (Dai et al., 2020). Compared to traditional thermoset rubber materials, TPEs have several benefits, including quicker fabrication times, lower energy usage, greater quality control, and cheaper costs per volume (Ramya et al., 2022).

TPEs exhibit considerable flexibility due to their molecular structure. Both crystalline and amorphous domains are present in every TPE. These can be physical alloys or blends of crystalline and amorphous polymers, or block copolymers, which are chemical mixtures of crystalline and amorphous domain blocks in a polymer chain. **Figure 2.9** shows the structural composition of TPEs (Conrad, 2021).



Figure 2.9: Structural composition of TPEs (Conrad, 2021).

Advantages of TPE include the ability to recycle waste, lower processing costs, and the availability of standard and consistent grades (Robertson et al., 2023). Compared to the cycles required to press or transfer typical rubbers which is a batch process, TPEs are molded or extruded using standard plastic processing equipment which is a continuous process. The most common TPEs used in industry is styrene-butadiene-styrene (SBS) (Kaya et al., 2020), styrene-isoprene-styrene (SIS) (Dedduwakumara et al., 2024), thermoplastic vulcanizates (TPVs) (Ghahramani et al., 2020) and PVC/NBR blends.

In TPE, the hard blocks determine the plastic properties of the finished product, such as simple processing, temperature resistance, chemical resistance, and mechanical properties such as tear and tensile strength. The elastic properties are contributed by soft blocks. The soft blocks determine the degree of permanent deformation and material properties such as hardness and flexibility (Katheria et al., 2022).

# 2.4.1 Polyvinyl Chloride / Nitrile Butadiene Rubber (PVC/NBR) thermoplastic elastomer (TPE) blend

Materials that bridge the property gap between ordinary rubber and plastic have been created by advances in polymers over the past 50 years. These include many types of TPEs and elastomer-modified thermoplastics. PVC/NBR are well-known commercial polymer blends. Bergish-Gladbach brought PVC/NBR mixtures onto the market for the first time in 1936. Most commercial PVC/NBR blends contain 50–90% by weight NBR. **Figure 2.10**, shows the function of PVC as permanent plasticizer in PVC/NBR blends which then makes it easier to process the TPE (Payne & Rader, 2020).



Figure 2.10: PVC/NBR blend.

PVC is frequently used in engineering construction, food, and agriculture sectors due to its low cost and high performance. However, PVC has poor toughness and affects its further growth. Therefore, PVC has to overcome the properties problem. Good compatibility is a requirement for material modification since compatibility has a big impact on the mechanical properties, thermal characteristics, and other properties of blended materials (Xia et al., 2021). On the other hand, NBR is only used in applications that require high oil resistance, ozone resistance, heat oil resistance and chemical resistance (Vijayan et al., 2021). The differences between the properties of both constituents are compared in **Table 2.11**.

Property	Polyvinyl Chloride (PVC)	Nitrile butadiene Rubber (NBR)
Hardness	Hard	Soft
Flexibility	Rigid	Flexible
Abrasion resistance	Poor	Good
Water resistance	Good	Good
Chemicals resistance	Good	Good
Weather resistance	Good	Good
Oil resistance	Poor	Good
Aging resistance	Poor	Good

Table 2.11: Difference properties between PVC and NBR.

Due to their complete compatibility with plasticized polyvinyl chloride, NBR and PVC can be combined to create homogeneous mixes (alloys) with outstanding qualities (VINYL - NITRILE RUBBER BLENDS (NBR / PVC), 2022). NBR and PVC have good compatibility and comparable solubility properties thus NBR can be used to replace some parts of PVC in certain applications. Addition of NBR could decrease brittleness of PVC while addition of PVC into NBR improves its aging resistance. weather and chemical resistance (Xia et al., 2021). Therefore, PVC/NBR blends are known to have excellent resistance to ozone, oil and abrasion. PVC and NBR combine to generate a miscible blend with a single  $T_g$  that is between the  $T_g$  of the pure components (Subramanian et al., 2021). PVC is more miscible with NBR with acrylonitrile content between 23-45%. The advantages and disadvantages of PVC/NBR blends are summarized in **Table 2.12**.

Advantages	Disadvantages
<ul> <li>Improved thermal aging, ozone resistance and chemical resistance (Vijayan et al., 2021).</li> <li>Improved elasticity and weather resistance (Xia et al., 2021).</li> <li>Lower the cost for processing and shaping NBR when PVC is added (Vijayan et al., 2021).</li> </ul>	<ul> <li>The strength of PVC will be reduced by using rubber modification (Xia et al., 2021).</li> <li>Sometimes it might be challenging to form and process well dispersed PVC/NBR blends (Nitrile butadiene rubber/PVC blend, 2021).</li> </ul>

Table 2.12: Advantages and disadvantages of PVC/NBR blends.

# 2.4.2 Recent studies on Polyvinyl Chloride/ Nitrile Butadiene rubber (PVC/NBR) thermoplastic elastomer (TPE) blends.

In the current decade, many studies had been conducted to develop a PVC/NBR TPE blends with various properties to cater many industrial and consumer needs. **Table 2.13** critically reviews the important findings related to the development of these blends. Most of these studies focuses in improving the compatibility between the NBR and PVC phase and understanding the structural impact of the phases on the final properties.

Title	Important	Reference
The structure and properties of mechanochemically modified acrylonitrile butadiene rubber (NBR) /poly (vinyl chloride) (PVC) scraps and fresh NBR composites	It was successful to replace the new NBR with recycled and repurposed PVC and NBR insulating materials. Comprehensive studies of co-vulcanized rubber containing NBR/PVC with milling cycles of 0, 10, 15, 20, 30, and 35 have been conducted to examine its composition, structure, and performance. The study found that replacing 20% of NBR with PVC is the best, while 40% is the maximum practical proportion.	(Lai et al., 2023b)
Mechanochemically-induced C–S bond transalkylation exchange in the waste nitrile rubber (NBR)/Poly (vinyl chloride) (PVC) insulation	The dynamic reversible vitrimer-like network in the NBR/PVC insulating materials was created from the irreversible C-S cross-linked bonds by a mechanochemical mechanism. The result of the testing was an enhanced NBR/PVC continuity and compactibility .	(Lai et al., 2023a)

 Table 2.13: Reviews on research and development of PVC/NBR blends.

materials		
Rubber–rubber blends: A critical review	Report on the use of Brabender plasticorder to mix PVC and NBR at different rubber content levels (5 to 40 wt% rubber). It is demonstrated that as NBR concentration increases, the final tensile strength and modulus drop. The optimum value of tensile strength and modulus was achieved at NBR loading of 15 wt%	(Vayyaprontav ida Kaliyathan et al., 2019)
Studies on the effect of halloysite nanotubes (HNT) on the mechanical and hot air ageing properties of nitrile-polyvinyl chloride rubber nano-composites	NBR/PVC nanocomposite materials containing 2, 4, and 6 phr of HNT were melt blended on a two-roll open mill. The PVC properties increase by 34% with NBR loading of HNT.	(Subramanian et al., 2021)
High performance oil resistant rubber	The results of combining different kinds of rubber with PVC showed that PVC/NBR blends had remarkable resistance to hydraulic and motor oil.	(Khalaf, 2012)
Direct visualisation of the nanoscopic three-phase structure and stiffness of NBR/PVC blends by AFM	This research explains how the cross-linked rubber phase (cured rubber) in the NBR/PVC blends may be easily identified using the PeakForce QNM method. Based on the findings, it is demonstrated that the mixed phase considerably influences the mechanical properties of NBR/PVC blends. Because of the	(Wang et al., 2019)

nanomechanical mapping	viscoelastic differences between the phases, NBR/PVC blends exhibit a three-	
	phase coexistence of an unmixed NBR phase, a mixed phase, and PVC micro	
	crystallites. The nanomechanical examination can also identify the crosslinked	
	rubber phase in cured rubber.	

# 2.5 Application of Polyvinyl Chloride/ Nitrile Butadiene rubber (PVC/NBR)

PVC and NBR are two workhorse polymers with numerous uses. PVC is well-known for its durability and affordability, whereas NBR is regarded for its superior oil and abrasion resistance. These two materials, which are frequently used alone or combined to obtain certain qualities, play an important role in a wide range of sectors (Thoral et al., 2024). The properties of several PVC/NBR blends and its applications extracted from few research studies are listed in **Table 2.14**.

Table 2.14: Application of Polyvinyl Chloride/ Nitrile Butadiene rubber(PVC/NBR).

Properties	Application	Reference
<ul><li>High oil resistance</li><li>High abrasion resistance</li></ul>	Hose	(Ratnam et al., 2011)
<ul><li>High chemical resistance</li><li>Good thermal aging</li></ul>	Gasket	(Esmizadeh et al., 2011)
• Good thermal aging	Printing roll cover	(Esmizadeh et al., 2011)
<ul><li>High oil resistance</li><li>High ozone resistance</li><li>High abrasion resistance</li></ul>	Shoe soles	(Ratnam et al., 2011)
<ul><li>High ozone resistance</li><li>Good thermal aging</li><li>High chemical resistance</li></ul>	Conveyor belt cover	(Vijayan et al., 2021)
<ul><li>Good thermal aging</li><li>Flexible</li><li>Easy to shape</li></ul>	Wire and cable insulation	(Vijayan et al., 2021)

## 2.5.1 Anti slip bathroom mat

In this research reclaimed NBR is being blended with plasticize PVC to produce this anti-slip bathroom mat. This is an effort to utilize the reclaimed NBR into useful applications. An anti-slip bathroom mat is an important safety component in every bathroom. It helps to reduce slips and falls, which are especially hazardous on damp bathroom floors. There are several varieties of anti-slip bathroom mats available, so it may select one that suits for the preferences and requirements (Pro, 2024).

The anti-slip bathroom mats feature a rough surface that grips the floor, making them particularly efficient in preventing slips. The mat is also extremely resilient and easy to clean (Supply, 2024). **Figure 2.11** shows the anti-slip bathroom mat.



Figure 2.11: Anti-slip bathroom mat (Supply, 2024).

# **CHAPTER 3**

# METHODOLOGY

# **3.1 Introduction**

The aim of this chapter is to mainly discuss the preparation of polyvinyl chloride/ reclaimed nitrile butadiene rubber (PVC/rNBR) blends. The rNBR from waste NBR gloves was produced with collaboration with industry. In this project the rNBR will be blended with plasticized PVC at various weight fraction. The blend will be used to produce anti-slip bathroom mat. Additionally, in this chapter the test methods to characterize and evaluate PVC/rNBR blends are presented in detail.

# **3.2 Research Flowchart**

The outline of the experimental flow applied in this study is shown in Figure 3.1.





# **3.3 Materials**

The properties of the research materials are tabulated in **Table 3.1**.

Material	Info
• Plasticized polyvinyl chloride (PVC) supplied by CMY Handee	• Density: 1140 kg/m <sup>3</sup>
• reclaimed Nitrile Butadiene Rubber	• Density: 996 kg/m <sup>3</sup>
(rNBR) supplied by Bridge Field Resources Sdn Bhd	• Hardness: 70.1

# 3.4 Preparation of plasticized polyvinyl chloride /reclaimed nitrile butadiene rubber blend

The plasticized PVC was melted and blended with rNBR using a Brabender internal mixer Model Brabender Plastograph EC 815652 from Brabender GmbH & Co KG, Germany, **Figure 3.2**. The ratio of plasticized PVC to rNBR is shown in **Table 3.2**. The internal mixer was set to the temperature of 165°C and mixing speed of 60 rpm. Plasticized PVC was discharged into the internal mixer first and after 2 minutes rNBR was discharged into the chamber of the mixer. The mixing was continued up to 7 minutes until the torque time curves reaches stabilization. The processing torque values were recorded to study the processability of the blends. After 7 minutes, the sample as shown in **Figure 3.3** was taken out from the internal mixer and let to cool down to room temperature. The sample is needed to be taken out carefully to prevent contamination with other particles.



Figure 3.2: Brabender® Plastograph® EC 815652 Internal Mixer.

Ratio for PVC/rNBR	Mass of PVC (g)	Mass of rNBR (g)
100:0	50	0
90:10	45	5
80:20	40	10
70:30	35	15
60:40	30	20
50:50	25	25

Table 3.2: Sample ratio of the plasticized PVC/rNBR.



Figure 3.3: Sample of plasticized PVC/rNBR after melt blending.

After that the blended plasticized PVC/rNBR TPEs will be hot pressed into 1 mm thick sheets using Hydraulic Moulding Press, Model GT-7014-H supplied by GOTECH Testing Machines Inc., Taiwan, **Figure 3.4**. Heat is applied by the hot press machine to soften the sample, making it simpler to shape. Cold press machines employ

pressure to compress the sample without heating it to avoid warpage and promote even shrinkage of the sample. The temperature set for the pre-heat and compression is 175°C. Cooling was done using chilled water circulation at 2°C. The time for preheating was set to 10 minutes to increase the temperature of the sample and soften it. After that, the time for hot press was set to 2 minutes to press the sample and make the sample flow and fill the mold. The cooling time applied was 2 minutes. **Figure 3.5** shows the sample after going through hot and cold press. These steps were repeated to produce samples with different ratios of plasticized PVC and rNBR the pressed sheets were used for further testing and evaluations.



Figure 3.4: Hydraulic hot and cold press equipment.



Figure 3.5: Sample of PVC/rNBR after going through hot and cold press.

#### **3.5 Characterization and Testing**

# 3.5.1 Tensile Test

Tensile test was performed in accordance with ASTM D638 standard to determine the plasticized PVC/rNBR blends ultimate tensile strength (UTS), elastic modulus, and elongation at break. The test was performed using lightweight tensile tester, Model H10KS from Tinius Olsen Testing Machine Company supplied by Leader Technology Scientific Malaysia, Figure 3.6. 500N load cell, and the crosshead speed of 50 mm/min was set for the test. Before performing the tensile test, samples were cut into dumbbellshaped pieces as illustrated in Figure 3.7 by using a dumbbell press and cutter. Five test pieces were used for each blend ratio and average results were calculated. The cross-sectional morphology of the fractured samples was next examined using Field Emission Scanning Electron Microscopy (FESEM) model JOEL JSM 6701F supplied by JOEL, USA. Inc. at various magnifications. The samples were sputter coated with gold particles prior to scan. Tensile tests are performed to determine the amount of stress or load required for a polymer sample specimen to reach its breaking point. The collected information can be used to analyze and develop parts that can sustain tensile forces during application and implementation and to offer important insights for different materials.


Figure 3.6: Universal testing machine model Tinius Olsen H10KS-0748.



Figure 3.7: Dumbbell press and cutter and dumbbell shape samples.

The hardness of the plasticized PVC/rNBR samples was measured by using Shore A Durometer handheld machine in accordance with ASTM D 2240 A method. Shore A durometer measures the indentation hardness of the plasticized PVC/rNBR samples with the higher number indicating harder sample. The pressed PVC/rNBR sheets are stacked together to reach minimum height of 3mm in order to perform the test. Five readings recorded at different locations of the same samples and average was calculated.

#### 3.5.3 Water Absorption Test

Water absorption test was carried out following ASTM D570 standard. Specimens with length x width x thickness of 20 mm x 20 mm x 3 mm respectively were prepared and dried for two hours at 60°C in an oven supplied by Tuff OEM Lab Equipment, Malaysia, Model TVAC-53 before being cooled in a desiccator for the water absorption test. Upon cooling down, the samples are weighed right away, and the weight was recorded as conditioned weight. After that, the samples were submerged in water at room temperature for 120 hours Periodically the samples were also removed at 24, 48, 72, 96, 120 hours. Upon removal from water, the specimens were patted dry using lint-free cloth and then weighed. The weight was recorded as wet weight. The percent of water absorption calculated using **Equation 3.1**. Five test specimen was used for each blend ratio and water absorption percentage was calculated.

 $Increase in weight, \% = \frac{wet weight - conditioned weight}{conditioned weighr} x \ 100$ 

**Equation 3.1: Water absorption percentage.** 

Thermogravimetric analysis (TGA) is a technique used to measure the change in mass of a plasticized PVC/rNBR TPE sample as a function of temperature. TGA was used to evaluate the decomposition temperature and weight loss percentage of the blend in order to assess their thermal stability. The study was conducted using thermogravimetric analyser supplied by Mettler Toledo (M) Sdn. Bhd., Model: TGA/SDTA851e/1100. The test was conducted by heating 10 mg of the sample at a heating rate of 10°C/min from room temperature to 700°C under nitrogen gas flow.

#### 3.5.5 Thermal Aging Evaluation

A thermal exposure test at elevated temperature for plasticized PVC/rNBR samples were carried out to evaluate the thermal aging resistance of the blend. The plasticized PVC/rNBR samples were cut into dumbbell shape and placed in an air circulated drying oven at temperature of 100°C for 72 hours (Chaabane et al., 2021). The samples were taken out from the oven after 72 hours and left to cool down to room temperature in desiccator. After that, tensile test in accordance with ASTM D638 test method was carried out on the aged samples. Five test specimens were used for each blend ration and average results were calculated. The ultimate tensile strength, modulus, and elongation of break for aged samples were compared to unaged samples.

#### 3.5.6 Dimensional Stability

When a material can hold to its original dimensions and shape throughout time and in different environmental conditions, it is said to exhibit dimensional stability. This is an important characteristic for floor mats in general because the floor mat supposed to lay flat on the floor surface without curling and only minimum level of shrinkage could be accepted. Remedial actions such as addition of fillers into the formulation could be taken with proper dimensional stability evaluation results. Curling test and shrinkage test were carried out to evaluate the dimensional stability of the blends when pressed into sheets.

### 3.5.6.1 Curling Test

EN 434.94 test procedure was used to conduct the curling test. Test pieces with dimension width x length x thickness of 10 cm x 5 cm x 3 mm, PVC/rNBR samples respectively was prepared and sandwiched between two steel plates. A predetermined load (5 kg in this study) was placed on top of the plate. The plate together with the test pieces was stored in the drying oven at  $80 \pm 2^{\circ}$ C for  $360 \pm 15$  min. After stipulated time, the load on the side of the plates was then removed, and the test piece was left to cool to room temperature for 24 hours in the desiccator. Measurements were made on the dimensions and curl variations.

All samples underwent one hour of shrinkage testing in a hot air oven at 80°C. Samples with dimension of width x length x thickness of 10 cm x 5 cm x 3 mm, respectively were used. After one hour, the samples were taken out from the oven, cooled in desiccator to room temperature. After that all the dimensions of the samples are measured and compared to the original dimensions. The difference in the dimension is calculated as percentage of shrinkage. A mean value was computed using five samples for each blend ratio (Su et al., 2022).

# **CHAPTER 4**

# **RESULT AND DISCUSSION**

# **4.1 Introduction**

This chapter covers the results and discussion of various testing done on the plasticized polyvinyl chloride/ reclaimed nitrile butadiene rubber (PVC/rNBR) thermoplastic elastomer (TPE) blend. The properties of the blends were analyzed and compared with standard requirement for commercial anti slip bathroom mat. Blend ratios that fulfill the requirement of standard set will be recommended to Bridge Field Resources Sdn. Bhd. for pilot run.

#### 4.1.1 Standard requirement of commercial anti -slip bathroom mat

**Table 4.1** shows the essential properties and standards requirements for anti-slip bathroom mat provided by CY Handee Rubber Moulding Sdn. Bhd. By offering a range of acceptable values or expected values, it serves as a reference by which the actual experimental results can be analyzed. Through this comparison, we can evaluate the reliability and correctness of our findings. **Table 4.1** will be used as a comparison for the experiment result obtained to find the best plasticized PVC/rNBR composition ratio from this project which could fulfill the standard requirement of the product. Following this standard, we can get the best blend of plasticized PVC/rNBR and reduce the usage of virgin PVC and NBR to protect the environment.

Table 4.1: Standard specification requirement given for anti-slip bathroom matproduct by CY Handee Rubber Moulding Sdn. Bhd

Parameters	Desired values
Ultimate tensile strength (MPa)	> 5 MPa
Elongation at break (%)	> 25 %
Water absorption (swelling percentage) wt%	< 2.5 wt%
Hardness (Shore A)	75 - 83

### 4.2 Mechanical properties evaluation

The mechanical properties of the blend will provide information on how the product can still be operational and function to its purpose when subjected to different modes of force. For anti-slip bathroom mat the tensile properties and hardness are important mechanical properties that need to be considered.

### 4.2.1 Tensile properties

Findings from tensile test of the plasticized PVC/rNBR blend are summarized in **Table 4.2**. Young's Modulus gauges the stiffness of the blend whereas UTS indicates the strength of the generated blends and the highest stress it can withstand before buckling under strain.

PVC/rNBR	E-Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)
100/0	$5.62\pm0.15$	$13.73 \pm 0.15$	$349.30 \pm 14.15$
90/10	$5.92 \pm 0.54$	$5.09\pm0.49$	$111.50 \pm 12.41$
80/20	$5.95\pm0.16$	$5.25\pm0.05$	$107.20 \pm 25.43$
70/30	$6.02\pm0.31$	$5.39\pm0.21$	$101.10 \pm 22.78$
60/40	$6.73\pm0.27$	$4.03\pm0.40$	$122.70 \pm 15.09$
50/50	$6.99 \pm 0.44$	$4.22 \pm 0.80$	$158.60 \pm 14.59$

Table 4.2: Mean for tensile strength test result.

Plasticized PVC/rNBR blend stiffness can be evaluated using the E-modulus. As rNBR loading rises, the E-modulus also increases. Based on **Table 4.2**, the elastic modulus of plasticized PVC/rNBR blends increases from 5.62 MPa for blends without any rNBR to 6.99 MPa for blends with 50 wt% rNBR. The reason for this significant rise in E-modulus is because rNBR has hanging cleavage sulphur bonds which could be reutilized to form crosslinking during melt blending in internal mixer. This kind of vulcanization is known as dynamic vulcanization. rNBR will be stiffer due to formation of three-dimensional network between its rubber chains. When this stiffer material is blended into plasticized PVC, the E-modulus will increase.

Ultimate tensile strength (UTS) represents the strength of the produced blends and the maximum amount of the stress it can stand before buckling under strain. Data analysis in **Table 4.2** shows that UTS for all the plasticized PVC/rNBR blends are lower than UTS for virgin plasticized PVC. However, samples at plasticized PVC/rNBR blend ratio of 90/10, 80/20 and 70/30 fulfills the standard requirement for UTS of anti-slip bathroom mat. Tensile strength decreases because rNBR naturally has lower strength compared to plasticized PVC. Presence of rNBR limits the flexibility of PVC chains, preventing them from moving freely under stress and causing an increase in the distance between them due to a lack of crosslinking. (Al-Mosawi et al., 2019).

Elongation at break is very susceptible to the incompatibility between components of the blends. Based on **Table 4.2**, it was observed that the elongation at break of PVC/rNBR blends are lower than the elongation at break for plasticized PVC/rNBR.When 10 wt% of rNBR is initially added into the PVC, elongation at break experienced a drastic reduction from 349.3% to 111.5%. After that, adding 20 and 30 wt% of rNBR decrease the elongation of break percentage. However, when 40 and 50 wt% of rNBR blends is added with the PVC, the elongation of break percentage increased. All the blends can fulfill the elongation at break requirements for anti-slip bathroom mat as presented in **Table 4.1**. Following the standard in **Table 4.1** given by CY Handee Rubber Moulding Sdn. Bhd., the UTS and elongation at break need to be larger than 5MPa and 25%, respectively. the PVC/rNBR blends.

### 4.2.2 Hardness Test

Hardness is a measurement of how easily a material may be indented by another material. The Shore A hardness for PVC/rNBR blends are shown in **Table 4.3**.

PVC/rNBR	Shore A hardness
100/0	$68.0 \pm 4.86$
90/10	$70.6 \pm 2.60$
80/20	75.5 ± 1.95
70/30	76.1 ± 2.11
60/40	76.3 ± 1.54
50/50	76.8 ± 1.17
0/100	70.1 ± 1.56

Table 4.3: Shore A hardness test

As rNBR loading increases, hardness increases from 68 to 76.8. This result is in accordance with the increment of E-modulus with increment of rNBR. The Shore A hardness for 100 rNBR is 70.1 and this value was measured for rNBR samples as supplied without any further blending or pressing at high temperatures. The Shore A hardness for the processed blends with 20, 30, 40 and 50 wt% of rNBR is higher than 100% rNBR because in the processed blends the rNBR is subjected to heat and recrosslinks. This crosslinking increases the hardness of rNBR component. Formation of three-dimensional crosslinking between rNBR chains will reduce the mobility of polymeric chains and increases hardness (Santiagoo et al., 2020). Moreover, ionic cross-linking formation involving CN groups in rNBR and -Cl groups in PVC may be the cause of the rise in hardness values of the blends compared to its 100 wt% PVC and 100 wt% rNBR components (Sudhakaran & Avirah, 2023). Therefore, the blends get tougher and stiffer as more NBR wt% integrated.

To put it briefly, hardness was observed to rise gradually with NBR wt%. It was discovered that PVC/rNBR 80/20, PVC/rNBR 70/30, PVC/rNBR 60/40, and PVC/rNBR 50/50 were the only mixes that met the 75–83 requirement by referring to the the specification provided by CY Handee Rubber Moulding Sdn. Bhd. for the hardness test. Since the Shore A hardness of PVC/rNBR 90/10 was less than the Shore A hardness standard's minimum, it fell outside of the acceptable range.

#### 4.2 Morphological analysis of fracture surface

The application of the image processing methodology with Field Emission Scanning Electron Microscopy (FESEM) was useful in analyzing the blend dispersion and potential agglomerates formation in the tensile fractured plasticized PVC/rNBR blends. The resistance of materials towards crack propagation and their strength may be estimated using surface roughness and matrix tearing on the fracture surface. It is generally believed that morphology with significant matrix tearing, and surface roughness has a strong resistance to fracture propagation, allowing the materials to endure larger stresses and deform (Vijayan et al., 2021).

The micrographs of pristine plasticized PVC surfaces that have been tensile fractured are shown in **Figures 4.1(a-b)**. The fracture produces a smooth surface with very fine matrix tearing. Crack propagation planes could not be observed which indicates homogenous single component matrix with no hard segments to deviate cracks. This morphology corresponds to the higher elongation at break and low E-Modulus of pristine plasticized PVC. The same surface fracture morphology for plasticized PVC was reported by Apchain (Apchain, 2022).



Figure 4.1: Micrographs of PVC/rNBR 100/0 (a) magnification of 500x (b) magnification of 1000x

Adding 10% rNBR to plasticized PVC resulted in increased surface roughness and severe matrix tearing during tensile fracture. **Figures 4.2(a-b)** indicates good adhesion between plasticized PVC and rNBR where no phase separation between the two components of the blends was observed. Good compatibility between PVC and NBR had been reported in various research works (Rad et al., 2019) (Khalil & Rabie, 2019). PVC and NBR has good compatibility because NBR improve the elasticity and flexibility of PVC, whereas PVC increases NBR's resilience to chemicals, ozone and abrasions. The increased E-modulus of PVC/ rNBR 90/10 in comparison to PVC can be attributed to the superior resistance of the matrix deformation to applied load. Moreover, step like crack propagation pathway could be seen on the fractured surface which might be caused by deviation of crack propagation by hard segments of recrosslinked rNBR component of the blends.



Figure 4.2: SEM imaging of PVC/rNBR 90/10 (a) magnification of 500x (b) magnification of 1000x

In **Figures 4.3(a-b)**, at 80/20 plasticized PVC/rNBR blend ration more matrix tearing could be observed. **Figures 4.4(a-b)** demonstrate a transition from elastic to more brittle fracture surface with sharp edges on the fracture steps and rougher matrix tearing, indicating the stiffness of the matrix. As the loading of rNBR was further increased to 40 and 50 wt%, the fracture surface becomes more brittle with more step like fractures and rougher matrix tearing as shown in **Figures 4.5 (a-b)** and **4.6(a-b)**. The formation of more well-defined step like fracture indicates that the rNBR hard segments does not allow crack propagation and deviates the propagation to longer pathway. It is also noteworthy that even at 50/50 ratio of plasticized PVC/rNBR, no phase separation was observed. This morphology also confirms the flowability of the rNBR during melt blending which allows the rubber to homogeneously mix with plasticized PVC and forms a homogenous blend.

Even though the FESEM images showed no phase separation and many crack propagation deviation pathway, the UTS of the blends drops significantly. This could be contributed by the low UTS of rNBR. In future, the UTS of rNBR could be improved by adding crosslink ingredients into rNBR or using a pre-compounded rNBR.



Figure 4.3: Micrographs of of PVC/rNBR 80/20 (a) magnification of 500x (b) magnification of 1000x



Figure 4.4: Micrographs of PVC/rNBR 70/30 (a) magnification of 500x (b) magnification of 1000x



Figure 4.5: Micrographs of of PVC/rNBR 60/40 (a) magnification of 500x (b) magnification of 1000x



Figure 4.6: Micrographs of PVC/rNBR 50/50 (a) magnification of 500x (b) magnification of 1000x

### 4.3 Water Absorption Test

The ability of a blend to take up moisture from its surroundings is known as water absorption. High water absorption above permissible level will reduce the strength of plastic and the glass transition temperature. The impact can be reversed by drying. In addition, water absorption can also cause the polymer structure to irreversibly degrade (Water absorption 24 Hours, 2024). Interfacial region between the two component of the blends is where water penetrates most readily. Thus, compatibility between the two components of a blend is important to reduce water absorption.

rNBR is a reclaimed product from latex gloves which commonly contains calcium carbonate fillers (Tay et al., 2023). The absorption results are presented in **Table 4.4**. It is evident that when rNBR content increased, so did the equilibrium water absorption for the blends. The polymer matrix absorbed more water as filler content in the overall blends increases as the rNBR loading increases (Nur Farahana Ramli et al., 2022).

Table 4.4: Water absorption (wt%) test results	
--	--

	Mean Water Absorption (wt%)				
PVC/rNBR	24 hours	48 hours	72 hours	96 hours	120 hours
100/0	$0.2717 \pm 0.1040$	$0.3487 \pm 0.1578$	$0.3901 \pm 0.2331$	$0.3901 \pm 0.2331$	$0.3901 \pm 0.2331$
90/10	$1.2165 \pm 0.2354$	$1.6203 \pm 1.7088$	$1.7088 \pm 0.2580$	$1.8414 \pm 0.2333$	$1.9293 \pm 0.2650$
80/20	$1.5142 \pm 0.2217$	$2.0342 \pm 2.2781$	$2.2781 \pm 0.2206$	$2.3573 \pm 0.2096$	$2.4276 \pm 0.2916$
70/30	$2.1855 \pm 0.0822$	$2.9280 \pm 3.2228$	$3.2228 \pm 0.1588$	3.3696 ± 0.1664	$3.5935 \pm 0.2394$
60/40	$2.6968 \pm 0.0771$	$3.6884 \pm 4.2464$	$4.2464 \pm 0.0609$	$4.5559 \pm 0.1506$	$4.8990 \pm 0.1234$
50/50	$3.7752 \pm 0.2663$	$4.9975 \pm 5.7606$	$5.7606 \pm 0.3420$	$6.1973 \pm 0.4464$	$6.6948 \pm 0.4832$

As can be seen from the water absorption results, the least amount of water was absorbed by neat, plasticized PVC. The highest water adsorption percentage is for plasticized PVC/rNBR blend with ratio of 50/50. The neat PVC showed 0.2717 wt% of water absorption in 24 hours and the water absorption reaches equilibrium and remains constant at a value of 0.3901 wt% in 72 hours. This indicates that the water molecules were absorbed to the surface of the sample and got saturated without further continuous penetration of water molecules to the inside structure of the polymer matrix. PVC does not have any polar groups in its structure which could cause high water absorption and it is hydrophobic in nature. The water absorption value recorded by the PVC might be contributed by the polar plasticizer in PVC. Influence of plasticizer in water absorption was previously reported by Abdel-Hakim (Abdel-Hakim, 2021). However, the water absorption for plasticized PVC/rNBR at blend ratio of 90/10 has increased by four-fold to a value of 1.2165 wt% in 24 hours and continuously increases to 1.9293 wt% in 120 hours. The water absorption value reach equilibrium at 120 hours. Similar trend was observed for plasticized PVC/rNBR blend with ratio of 80/20. This result indicates the significant effect of rNBR addition on water absorption.

For rNBR loading of 30, 40 and 50 wt%, the water absorption increases significantly with no equilibrium reached up to 120 hours. For instance, the plasticized PVC/rNBR blend with ratio 50/50 showed 3.7752 wt% of water absorption in 24 hours and this value increases to almost two-fold to 6.6948 wt% of water absorption in 120 hours. No equilibrium of absorption reached. The water molecules continuously penetrate into the samples through diffusion and up to 120 hours no saturation point was achieved. Thus, it can be concluded that the rNBR amount has a significant impact on the percentage increase in water absorption. The proportion of water absorbed increases with the amount of NBR blends. This is because NBR has acrylonitrile (ACN) in its backbone structure. This polar group coupled with the pre-existing fillers in rNBR increases the water absorption in the blends.

According to the specification given by CY Handee Rubber Moulding Sdn. Bhd., pkasticized PVC/rNBR blends must not exceed 2.5 wt% of water absorption. However, only two blend ratios of plasticized PVC/rNBR blends could fulfill the standard required which are PVC/rNBR at blend ratio of 90/10 and 80/20. Plasticized PVC/rNBR with blend ratio 90/10 shows 1.9293 wt% of water absorption in 120 hours while plasticized PVC/rNBR with blend ratio 80/20 shows 2.4276 wt% of water absorption in 120 hours.

#### 4.4.1 Thermal Decomposition Analysis

The thermal stability of the blend is strongly influenced by the plasticized PVC to rNBR ratio. When compared to pure PVC, a larger rNBR concentration will usually result in a lower initial deterioration temperature. Apart from that, the way PVC and NBR interact may have an impact on how they behave during thermal breakdown.

The TGA thermograms of plasticized PVC/rNBR blends are shown in **Figure 4.7**, and the important decomposition parameters are summarized in **Table 4.5**. It was found that the decomposition of rNBR happened in single stage. On the other hand, there were double stage of thermal breakdown for plasticized PVC/rNBR blends and pure PVC. NBR only has single stage thermal decomposition which occurs between 200°C to 485°C. This is the critical breakdown step in which the NBR polymer chain degrades. Chemical bonds in the NBR backbone break, resulting in formation of smaller molecules (Liu et al., 2016). Some of the broken-down components may combine to generate a carbonaceous residue (Ammineni et al., 2022). For neat, plasticized PVC and PVC/rNBR blends, double stage thermal decomposition was observed. The first region of thermal decomposition is between 225°C to 335°C. The PVC/rNBR blends weight losses at all temperature ranges differ very little from one another (Ghowsi & Jamshidi, 2023). The second region of thermal decomposition is in the range of 425°C to 485°C. This result can be confirmed by the presence of one or two peaks in the DTG curve in **Figure 4.8**.

PVC/rNBR	Temperature at 50% mass loss (°C)	Total mass loss at 450 °C (%)	Total mass loss at 900 °C (%)
0/100 (rNBR)	440.67	78.75	91.20
100/0 (PVC)	294.50	58.72	88.36
90/10	297.67	78.98	91.38
80/20	302.67	75.87	88.57

Table 4.5: Thermogravimetric Analysis for PVC/rNBR

70/30	364.67	73.99	90.76
60/40	392.67	73.24	91.71
50/50	400.50	69.05	85.79



Figure 4.7: Thermogravimetric analysis.



Figure 4.8: Weight loss derivate curves for decomposition of samples

. The thermal breakdown for rNBR occurred in a single phase at a temperature between 250°C and 335°C. Chain scission is taking place in the rNBR as a result of heat deterioration. According to an analysis of the bond strengths, the thermal cleavage occurs mostly at bonds beta to the C-N bond and at tertiary carbon atoms in the NBR macromolecular structure (Pappa et al., 2011). Other than that, the rNBR might have water molecules in the structure which could vapourise at lower temperature during TGA analysis (Ghamarpoor & Jamshidi, 2022b).

For neat PVC double stage thermal decomposition occurs. The first region of thermal decomposition is from 225°C to 335°C and the second region of thermal decomposition is from 425°C to 485°C. In the first stage, hydrogen chloride is released from PVC when the C–Cl link breaks (Meng et al., 2021). At this point, the primary cause of the weight loss is due to the release of these volatile tiny molecules. **Figure 4.8** shows that at a temperature of around 300°C, the thermal breakdown rate is comparatively high. This is because the PVC breaks down more quickly due to the hydrogen chloride gas produced during the breakdown process at 300°C (Xia et al., 2021). The second stage of thermal decomposition involves more cracking and pyrolysis, resulting in formation of low hydrocarbons with either a linear or cyclic structure (Ennadafy et al., 2024). Based on the **Figure 4.7**, neat PVC is more thermally

stable at the temperature below 225°C with mass loss under 1% only. However, the mass loss started to increase around 225°C.

In the **Figure 4.7** plasticized PVC/rNBR blends, show two step mass loss. The first step thermal decomposition is from 225°C to 335°C and the second step thermal decomposition is from 425°C to 485°C. The first step of thermal decomposition is the creation of conjugated polyene sequences, which is a consequence of the volatilization of hydrogen chloride molecules. The carbonaceous conjugated polyene sequences undergo thermal cracking, which is represented by the second step of thermal decomposition (EL-Sayed et al., 2018). In **Figure 4.8**, the DTG graph shows that the plasticized PVC/rNBR blend with ratio of 90/10 have the highest thermal breakdown rate at a temperature of around 300°C compared with all of the blends.

**Table 4.5** shows that neat, plasticized PVC had the lowest temperature at 50% mass loss ( $T_{50\%}$ ), which is 294.50°C. It could be noted that starting with blends containing 10 wt% rNBR, the PVC/rNBR thermal breakdown started to shift to higher temperatures. The  $T_{50\%}$  increases when the rNBR wt% increases. The plasticized PVC/rNBR blend with ratio 90/10 have lowest  $T_{50\%}$  which is 297.67°C and the blends with 50/50 ratio has the highest  $T_{50\%}$  which is 400.50°C. The  $T_{50\%}$  mainly depends on the rNBR instead of the PVC. Through its mass transport barrier, NBR blends function as an insulator against the development of HCl, causing PVC to decompose more slowly (Tuong & Viet, 2023).

Furthermore, the temperature at 50% mass loss ( $T_{50\%}$ ) indicates the production of char, which are carbonaceous leftovers. The thermal breakdown of the plasticized PVC/rNBR blend slowed down at any temperature higher than  $T_{50\%}$ . The reason for this is that char prevents volatile breakdown products from the blends from diffusing out of the blend by acting as a barrier between the blend and the heat source. Blends require a greater temperature to decompose since the char thickens (Huey, 2019). Other than that, it might be the synergistic impact of the blend components, which produced a more stabilized product than the individual components, the char residue was likely enhanced in plasticize PVC/rNBR blends (Rotaru et al., 2023). For the total mass loss at 450°C ( $T_{450°C}$ ) shown in **Table 4.5**, the neat, plasticized PVC has the lowest mass loss because most of the PVC mass loss occurs in the first stage decomposition at temperature below 350°C. As rNBR was added and as the loading increases into the blend, more mass loss is being observed at second stage compared to the first stage. It is also noteworthy that the  $T_{450°C}$  decreases when the rNBR wt% increases into the blend. The PVC/rNBR blends 90/10 have highest  $T_{450°C}$  which is 78.98% and the PVC/rNBR blends 50/50 have lowest  $T_{450°C}$  which is 69.05%. In summary, it can be said that thermal decomposition depends on the rNBR component of the blends instead of the PVC. The PVC/rNBR blends of 70/30 gives better results compared to others.

## 4.4.2 Thermal Aging

Thermal ageing test is conducted to evaluate the degradation of plasticized PVC/rNBR, like many other polymers, when it is subjected to high temperatures over prolonged periods of time. Tertiary hydrogen atoms are present in the polymer chain and upon exposure to continuous heat these atoms will form radicals and causes molecular degradation. The long chain backbone of the polymer that interacts with one another will be broken apart by the high temperature. (Jawaid et al., 2019). **Figure 4.9 - 4.11** shows the tensile properties of blends before and after thermal aging.



Figure 4.9: Impact of thermal aging on E-Modulus



Figure 4.10: Impact of aging on ultimate tensile strength.



Figure 4.11: Impact of aging on elongation break (%).

Comparison between the the data before and after thermal aging shows that the E-modulus does not show significant change. Plasticized PVC/rNBR 50/50 have the highest E-modulus after thermal aging which is 7.87 MPa and pure plasticized PVC have the lowest E-modulus after thermal aging which is 4.75 MPa. The highest difference of E-modulus before and after thermal aging is 16.55% which was recorded for plasticized PVC/rNBR blend with the ratio of 90/10. PVC and rNBR degrade by a variety of processes at high temperatures, including chain scission, which breaks polymer chains, and dehydrochlorination, which causes PVC to lose its hydrochloric acid (Cruz et al., 2021). The material becomes less stiff and has a lower E-modulus as a result of these processes that weaken the polymer structure.

Same trend was observed for UTS. When compared with the data before and after thermal aging, the UTS does not show significant change. The highest difference of UTS between the blends before and after thermal aging was recorded to be 13.15% for plasticized PVC/rNBR blend with ratio off 60/40. **Figure 4.11** shows that the percentage of the elongation break does not significantly alter when compared to the data collected before and after thermal aging which is 379.4 % and plasticized PVC/rNBR blends with ratio 70/30 have the lowest elongation break after thermal aging which is 101.1%. The highest difference of elongation breaks between the blends before and after thermal aging is for plasticized PVC/rNBR blend with the ratio 90/10. The difference recorded was 31.93%. The percentage reduction in UTS and elongation break caused by thermal aging is dependent upon the rNBR content. The greater of UTS decline with aging is often correlated with higher rNBR concentration. This is because the total strength of the mix can be greatly impacted by the deterioration of rNBR, which usually has a lower tensile strength than PVC (Al-Mosawi et al., 2019).

In summary, the plasticized PVC/rNBR blends of 80/20 and 70/30 ratio have better thermal aging resistance with no significant changes in E-modulus, UTS and elongation in break before and after thermal aging. Process ability studies are an essential tool for figuring out how to make the manufacturing or production processes more reliable and consistent.

### 4.5.1 Process torque

In terms of material qualities and processing parameters, an engineering model that represents the evolution of torque and temperature during the melt processing stage in a laboratory internal mixer is provided. The model might be used to fully simulate the system and forecast torque and temperature as functions of time, in addition to estimating melt viscosity from torque and temperature (Alves et al., 2016). Generally, the viscosity, stiffness, and processability of the mixed compounds can be determined by measuring the mixing torque. On the other hand, stabilization torque represents the ultimate torque measured after achieving a homogenous mixing of a polymer blend.

The processing torque values acquired during the compounding of the blends are displayed in **Figure 4.12**. Plasticized PVC and rNBR were mixed for seven minutes at 165°C at rotor speed of 60 rpm. First the PVC was discharged into the internal mixer then let it melt and mix until stable. After 2 minutes, rNBR was discharged inside the internal mixer. Initially, plasticized PVC and rNBR are in the solid form and when they are discharged into the chamber the resistance to rotor rotation increases the torque values and will be observed as a peak. The torque increased rapidly until it reached a peak known as the loading torque because of the mechanical resistance the unmelted PVC pellets placed on the rotors. As the PVC pellet started to melt under shear and temperature, torque progressively decreased because of the viscosity reduction. **Figure 4.12** also shows the increasing viscosity of PVC/rNBR blends. For the plasticized PVC/rNBR blends at ratio of 90/10, 80/2070/30, the torque level increased and generated a second peak torque. After the PVC and rNBR successfully melted together, the torque value started reducing and reaching stabilization. The torque is found to stabilize around 5 minutes. However, for PVC/rNBR 60/40 and 50/50, the torque level continuously increased and does not reach stabilization. These might be due to recrosslinking of the high amount of rNBR. It is mentioned worthy that even at the blend ratio of 90/10, 80/20 and 70/30 the rNBR will still recrosslink but the fraction of the rNBR is lower and the flowability of the blend will be facilitated by plasticized PVC.



Figure 4.12: Process torque.

The viscosity of the polymer melt is reflected in the loading torque. The melting viscosity increases with increasing loading torque. The loading torque was found to increase with increment of rNBR in the blends based on **Figure 4.12**. Mixing will be greatly hampered by the elastic nature of rNBR mixes. As flow resistance rises, the resulting increase in melt viscosity means that higher shear stress levels are needed to overcome the high viscosity, which raises torque values. Plasticized PVC/rNBR blends become stiffer with decreased processability as the degree of resistance to deformability increases along with the increase in rNBR blends and reduction in plasticized PVC content (Huey, 2019). In summary, the plasticized PVC/rNBR blends at the ratio of 60/40 and 50/50 are not suitable to be produced because the torque value increases and makes the processing becomes energy intensive and difficult.

#### 4.6 Dimensional Stability

When a material can hold its original dimensions and shape throughout time and in different environmental conditions, it is said to exhibit dimensional stability.

# 4.6.1 Curling Test

Specifically, for sheet materials like plasticized PVC/rNBR, the curling test is a widely used technique to evaluate the dimensional stability of materials. Curling test is required for applications such as floor mat to ensure that the placed floor mat will not curl upon its service life. A rapid assessment on the resistance of plasticized PVC/rNBR blends to warping or deforming due to temperature variations may be obtained using this rather easy test (International, 2020). In curling, dimensional stability is the capacity of a material to hold its size and form under pressure.

In **Table 4.6**, the mean of curling for plasticized PVC/rNBR blends is very low. The plasticized PVC/rNBR blends at the ratio of 90/10, 80/20 and 50/50 did not have any curling. The mean of curling for plasticized PVC/rNBR blends at ratio70/30 and 60/40 are 0.10% and 0.06%, respectively. The percentage mean of variation in length decreases when rNBR content in the blends increase. It shows that the rNBR can increase the dimensional stability of the blend. The neat plasticized PVC has the highest percentage mean of variation in length which is 1.35%. while plasticized PVC/rNBR blends with ratio of 50/50 have the lowest percentage mean of variation in length which is 0.15%. The increment of dimensional stability of the blend with increment of rNBR loading is due to the recrosslinking or rNBR. Crosslinking produces thermosets which has higher dimensional stability compared to thermoplastics such as PVC.

PVC/rNBR	Curling (cm)	Variation in length (%)
100/0	0 ± 0	$1.35 \pm 0.2000$
90/10	$0\pm 0$	$0.80 \pm 0.2915$
80/20	$0\pm 0$	$0.35\pm0.2449$
70/30	$0.10\pm0.0894$	$0.30 \pm 0.2550$
60/40	$0.06 \pm 0.0583$	$0.20 \pm 0.1871$
50/50	$0\pm 0$	$0.15\pm0.1225$

Table 4.6: Mean of curling (cm) and variation in length (%)

PVC has a high impact strength and is less stiff. However, it has lower temperature resistance (PVC properties, 2019). For example, in application such as in PVC pipes, PVC are often resistant to temperatures as high as 60°C but start to show dimensional instability above that temperature. The restricted dimensional stability of PVC at elevated temperatures is one of its disadvantages. PVC can soften, warp, or deform as it becomes hot. Applications subjected to high temperatures may have issues as a result (Meena Rezkallah, 2023). NBR in the other hand have good tensile strength, elasticity, and temperature resistance. Furthermore, NBR exhibits thermal stability over a broad temperature range of -40°C to 120°C (Admin, 2023). NBR is resistant to permanent deformation, thus it can withstand a variety of environmental stresses without losing its dimensional stability. In this research, the increment of dimensional stability of the blend with increasing rNBR content shows that the rNBR exhibit the same properties as virgin NBR in term of its dimensional stability. This behavior could facilitate the replacement of virgin NBR with rNBR.

The volume contraction of polymers is indicated by the shrinkage test. Shrinkage occurs when the polymer products cool down during processing. A portion of the shrinkage can be attributed to the density differential between the melted and solidified states of the polymer. In this research both plasticized PVC which is the soft segment in the blend and rNBR which is hard segment in the blend is expected to have different intrinsic shrinkage and their final synergistic shrinkage level as a blend has to be evaluated. Better dimensional stability is shown by lower shrinkage values, which is important for many applications.

Based on the observation in **Table 4.7**, the mean of length shrinkage percentage decreases when the rNBR loading in the blends increase. The neat plasticized PVC has 1.65% of length shrinkage which is the highest shrinkage. The plasticized PVC/rNBR at blend ratio of 50/50 has only 0.2% of length shrinkage which is the lowest shrinkage. The mean of width shrinkage percentage shows similar trend. The plasticized neat PVC has 2% of width shrinkage which is the highest shrinkage and plasticized PVC/rNBR blend at ratio of 50/50 has 0.2% of width shrinkage which is the lowest shrinkage which is the lowest shrinkage. However, for mean thickness shrinkage percentages increases from neat plasticized PVC to plasticized PVC/rNBR blends with ratio up to 80/20, then decreases from blend ratio of 80/20 to 50/50. This might cause by the plasticizer in PVC which migrates and swell the samples.

PVC/rNBR	Length shrinkage	Width shrinkage	Thickness shrinkage
	(%)	(%)	(%)
100/0	$1.65 \pm 0.2550$	$2.00 \pm 0.4472$	$1.3743 \pm 0.9480$
90/10	$0.95\pm0.1871$	$1.35\pm0.5099$	$1.8722 \pm 1.1304$
80/20	$0.65\pm0.3742$	$0.95\pm0.3742$	$3.0484 \pm 3.4281$
70/30	$0.35\pm0.1225$	$0.90\pm0.9165$	$0.7190 \pm 0.1934$
60/40	$0.30 \pm 0.2449$	$0.30 \pm 0.2449$	$0.6626 \pm 0.2158$
50/50	$0.20\pm0.1871$	$0.20 \pm 0.2449$	$0.6554 \pm 0.2816$

Table 4.7: Mean of length, width and thickness of shrinkage

The interaction between the PVC and rNBR chains determines how much shrinkage occurs in plasticized PVC/rNBR blends. PVC has significant intermolecular forces between its polymer chains, mainly dipole-dipole interactions and van der Waals forces. During manufacturing and subsequent chilling, these interactions result in the PVC chains packing closely together. The chains try to reorganize into a more structured, crystalline form when the product cools. However, it is sometimes challenging to obtain perfect crystalline packing because of the inherent rigidity of PVC strands. Internal tension is created in the material as a result. Shrinkage results from the material contracting to release this tension when the temperature decreases more (Czogała et al., 2021). Compared to stiff PVC, the NBR is an elastomer, and has more flexible chains. NBR chains may function as internal lubricants during processing. This makes it possible for PVC chains to move more easily, which lowers the trapped tension that accumulates because of chain packing being inhibited during cooling. This stored tension has a significant role in PVC shrinking. rNBR and PVC chains might entangle when they are compatible. The tightly packed crystalline form that PVC chains seek for during cooling is physically hampered by this entanglement. As a result, the ideal packing is disturbed and the general propensity towards shrinking is decreased (Mensah et al., 2023).

In summary, managing the shrinkage of PVC/rNBR blends requires knowledge of the relationship between the strong interactions of the PVC chains and the ability of the rNBR to increase chain mobility and prevent packing. Manufacturers can achieve the right balance between dimensional stability and other material properties by optimizing rNBR concentration, production conditions and possibly the use of additives.

### 4.7 Cost analysis for plasticized PVC/rNBR blend for 80/20.

It the summary, the minimal requirements for an anti-slip bathroom mat application are an ultimate tensile strength of 5 MPa, 25% elongation at break with a maximum swelling of 2.5%, and a Shore A hardness of 75–83. PVC/rNBR blends with an 80/20 ratio have  $5.25 \pm 0.05$  MPa ultimate tensile strength,  $107.20\% \pm 25.43$  elongation at break, 2.4276% water absorption, and 75.5 Shore A hardness, making them the best choice for meeting these criteria. Therefore, **Table 4.8** show the cost analysis and calculation for plasticized PVC/rNBR blend of 80/20.

Table 4.8: Cost analysis and calculation for plasticized PVC/rNBR blend of 80/20.

Material	Cost
Plasticized PVC	RM 3.77/kg (1688 Alibaba, 2024a)
Virgin NBR	RM 10.39/kg (1688 Alibaba, 2024b)
rNBR	RM 0.71/kg
Plasticized PVC/ virgin NBR of 80/20	RM 5.10/kg
Plasticized PVC/rNBR blend of 80/20	RM 3.16/kg

### **CHAPTER 5**

### CONCLUSION AND RECOMMENDATIONS

# 5.1 Conclusion

In conclusion, polyvinyl chloride (PVC) and reclaimed nitrile butadiene rubber (rNBR) thermoplastic elastomerblends are successfully prepared with different composition ratios by using a brabender internal mixer. The blends were melt processed at temperature of 165 °C for 7 minutes at rotor speed of 60 rpm. Following melt mixing, plasticized PVC/rNBR blends were heated to 175 °C and pressed into sheets using a hydraulic hot and cold press machine. The mixes were heated for ten minutes, then compressed for two minutes, and finally cooled for two minutes in the hydraulic hot and cold press machine.

The tensile test shows an increase of the E-modulus but a decrease of ultimate tensile strength (UTS) and elongation break when rNBR content increases. The Shore A hardness increases when rNBR content increases. The FESEM scan of the fractured sample revealed that the surface has increased stress resistance and stiffens with increasing rNBR content and the fracture transition from elastic to brittle fracture surface as the rNBR content increases. The percentage of water absorption for plasticized PVC/rNBR increases when the rNBR content increases due to its polarity and filler content in the recycled material. In term of thermal decomposition 70/30 plasticized PVC/rNBR blend produces superior results. T<sub>50%</sub> for PVC/rNBR blends 80/20 and 70/30 is 302.67°C and 364.67°C, respectively. Thermal aging test showed that the plasticized PVC/rNBR blends with ratio of 80/20 and 70/30 exhibit superior stability because of low changes in E-modulus, UTS, and elongation at break after thermal aging.
The viscosity of plasticized PVC/rNBR blends rose with increment of rNBR loading, according to an analysis of the processing characteristics derived from the torque development curves. As NBR loading increases, the blends become harder to process, with raise in loading and stabilization torque. The plasticized PVC/rNBR at blend ratio of 60/40 and 50/50 are unsuitable to be processed commercially due to the continuous increase of torque value without reaching stabilization upon 7 minutes of processing. In term of dimensional stability, the plasticized PVC/rNBR blends do not show significant change in curling and shrinkage. The dimensional stability for the blend is stable even in a high temperature environment. This kind of stability is contributed by the thermoset nature of rNBR.

The minimum specifications needed for an anti-slip bathroom mat application are including ultimate tensile strength of 5 MPa, 25% of elongation at break with a maximum swelling of 2.5%, and a Shore A hardness of 75–83. The optimum plasticized PVC/rNBR composition which fulfils these requirements are PVC/rNBR blends with ratio of 80/20, which have the values of  $5.25 \pm 0.05$  MPa ultimate tensile strength,  $107.20\% \pm 25.43$  elongation at break, 2.4276% water absorption, and 75.5Shore A hardness.

## **5.2 Recommendation**

- Fillers such as fibres might be used. With little to no loss of flexibility, they can increase tensile strength, tear resistance, and abrasion resistance.
- PVC/rNBR mix performance may be effectively increased by adding coupling agents. With one end compatible with the PVC matrix and the other end compatible with the rNBR phase, coupling agents have a special molecular structure (Pan et al., 2022). As a result, the two polymers have a stronger bond, which enhances adhesion and dispersion.
- Preheat time during hot and cold press can increase to 12 minutes to let the PVC/rNBR blends become softer and easier to press.
- Instead of using standard DOP, use non-phthalate plasticizers with better environmental profiles, such as Hexamoll DINCH (diisononyl cyclohexane dicarboxylate) or DOTP (diethylehexyl terephthalate) (Plastics, 2021).

## REFERENCE

- Abdel Hakim, A. et al. (2021) 'Effect of fiber coating on the mechanical performance, water absorption and biodegradability of sisal fiber/natural rubber composite', Polymer International, 70(9), pp. 1356 1366. doi:10.1002/pi.6207.
- Admin (2023) What is nitrile rubber? properties, applications, and benefits, Delta Rubber supply Rubber Matting | Rubber Sheet | Washers | Extrusions | Viton | Neoprene bespoke and custom rubber products in the UK. Available at: https://www.deltarubber.co.uk/what-is-nitrile-rubber-properties-applications-and-benefits.html#:~:text=Nitrile%20rubber%20has%20a%20closed,gaskets%2C%20se als%2C%20and%20hoses. (Accessed: 15 March 2024).
- Admin (2023) What is nitrile rubber? properties, applications, and benefits, Delta Rubber supply Rubber Matting | Rubber Sheet | Washers | Extrusions | Viton | Neoprene bespoke and custom rubber products in the UK. Available at: https://www.deltarubber.co.uk/what-is-nitrile-rubber-properties-applications-and-benefits.html#:~:text=Nitrile%20rubber%20has%20a%20closed,gaskets%2C%20se als%2C%20and%20hoses. (Accessed: 15 March 2024).
- Aji, M.M. et al. (2020) 'Utilization of waste polyvinyl chloride (PVC) for ultrafiltration membrane fabrication and its characterization', Journal of Environmental Chemical Engineering, 8(2), p. 103650. doi:10.1016/j.jece.2019.103650.
- Akca, E., Gursel, A. and Sen, N. (2018) 'A review on Devulcanization of Waste Tire Rubber', Periodicals of Engineering and Natural Sciences (PEN), 6(1), p. 154. doi:10.21533/pen.v6i1.167.
- Alarifi, I.M. (2022) Synthetic engineering materials and nanotechnology. Amsterdam, Netherlands: Elsevier.
- Alec (2023) Different types of floor mats: Quality Matting: Save 70%, Pvc Floor Tile. Available at: https://www.pvcfloortile.co.za/different-types-of-floor-mats-and-theiruses/ (Accessed: 26 April 2024).
- Allan, K.M. et al. (2021) 'The microbial devulcanisation of waste ground tyre rubber using at. Ferrooxidans Dsmz 14,882 and an unclassified sulphur-oxidising consortium', Waste and Biomass Valorization, 12(12), pp. 6659–6670. doi:10.1007/s12649-021-01468-0.

- Al-Mosawi, A.I. et al. (2019) 'Mechanical properties of acrylonitrile-butadiene rubber (nbr)/poly (vinyl chloride) resin binary blend', OALib, 06(12), pp. 1–7. doi:10.4236/oalib.1105956.
- Alves, T.S. et al. (2016) 'Process simulation of laboratory internal mixers', Polymer Testing, 50, pp. 94–100. doi:10.1016/j.polymertesting.2016.01.002.
- Ammineni, S.P., Nagaraju, C. and Lingaraju, D. (2022) 'Thermal degradation of naturally aged nbr with time and temperature', Materials Research Express, 9(6), p. 065305. doi:10.1088/2053-1591/ac7302.
- Apchain, E. et al. (2022) 'A comparison between TGA, SEM-EDX and Raman spectroscopy to assess PVC plasticizer loss', Journal of Cultural Heritage, 57, pp. 79–87. doi:10.1016/j.culher.2022.07.008.
- Asaro, L. et al. (2018) 'Recycling of rubber wastes by devulcanization', Resources, Conservation and Recycling, 133, pp. 250–262. doi:10.1016/j.resconrec.2018.02.016.
- Association of Natural Rubber Producing Countries (2023) The Association of Natural Rubber Producing Countries (ANRPC). Available at: (Accessed: 05 July 2023).
- Atef, S. et al. (2019) 'Effect of gamma irradiation and lead content on the physical and shielding properties of PVC/NBR polymer blends', Polymer Bulletin, 77(10), pp. 5423–5438. doi:10.1007/s00289-019-03022-4.
- Bhowmick, A. et al. (2023) 'Heat shock response in Sulfolobus acidocaldarius and first implications for cross-stress adaptation', Research in Microbiology, 174(8), p. 104106. doi:10.1016/j.resmic.2023.104106.
- Bockstal, L. et al. (2019) 'Devulcanisation and reclaiming of tires and rubber by physical and Chemical Processes: A Review', Journal of Cleaner Production, 236, p. 117574. doi:10.1016/j.jclepro.2019.07.049.
- Boon, Z.H., Teo, Y.Y. and Ang, D.T.-C. (2022) 'Recent development of biodegradable synthetic rubbers and bio-based rubbers using sustainable materials from biological sources', RSC Advances, 12(52), pp. 34028–34052. doi:10.1039/d2ra06602e.
- Braihi, A.J. et al. (2020) 'Chemical resistance of nr/SBR rubber blends for surfaces corrosion protection of metallic tanks in Petrochemical Industries', Koroze a ochrana materialu, 64(2), pp. 65–71. doi:10.2478/kom-2020-0010.
- Bridge Fields Resources About Us (2023) About Us. Available at: <u>http://www.bridgefields.com/main/3150/index.asp?pageid=154206&amp;t=about-us</u> (Accessed: 06 July 2023).
- Brunella, V. et al. (2022) 'Recycling of EPDM via continuous thermo-mechanical devulcanization with co-rotating twin-screw extruder', Polymers, 14(22), p. 4853. doi:10.3390/polym14224853.

- Celeiro, M. et al. (2021) 'Evaluation of chemicals of environmental concern in crumb rubber and water leachates from several types of synthetic turf football pitches', Chemosphere, 270, p. 128610. doi:10.1016/j.chemosphere.2020.128610.
- Chaabane, M., Ding, N. and Zaïri, F. (2021) 'An approach to assess the thermal aging effects on the coupling between inelasticity and network alteration in filled rubbers', International Journal of Non-Linear Mechanics, 136, p. 103783. doi:10.1016/j.ijnonlinmec.2021.103783.
- Chandrasekaran, V.C. (2010) 'CHAPTER 6 Rubbers, Chemicals and Compounding for "O" Rings and Seals', in Rubber Seals for fluid and hydraulic systems. Oxford: William Andrew, pp. 57-69.
- Chaudhary, B. et al. (2016) Reference module in materials science and materials engineering. Elsevier.
- Cheng, X., Xia, M. and Yang, Y. (2023) 'Biodegradation of vulcanized rubber by a gut bacterium from plastic-eating mealworms', Journal of Hazardous Materials, 448, p. 130940. doi:10.1016/j.jhazmat.2023.130940.
- Chi Hongquan (2022) Vol 33, NBR: Domestic Market Slows down Supply and Demand. publication. China: China Chemical Reporter, pp. 27–30.
- Chittella, H. et al. (2021) 'Rubber Waste Management: A review on methods, mechanism, and prospects', Polymer Degradation and Stability, 194, p. 109761. doi:10.1016/j.polymdegradstab.2021.109761.
- Conrad, R. (2021) What is TPE? learn about thermoplastic elastomer material kuraray, Kuraray Specialty Chemicals: Elastomer Division. Available at: <u>https://www.elastomer.kuraray.com/blog/what-is-tpe/</u> (Accessed: 09 August 2023).
- Costamagna, M. et al. (2022) 'Environmental assessment of rubber recycling through an innovative thermo-mechanical devulcanization process using a co-rotating twinscrew extruder', Journal of Cleaner Production, 348, p. 131352. doi:10.1016/j.jclepro.2022.131352.
- Cruz, P.P. et al. (2021) 'Thermal dehydrochlorination of pure PVC polymer: Part I thermal degradation kinetics by thermogravimetric analysis', Journal of Applied Polymer Science, 138(25). doi:10.1002/app.50598.
- Cui, J. et al. (2020) 'A comparative study on enhancement of mechanical and tribological properties of nitrile rubber composites reinforced by different functionalized graphene sheets: Molecular dynamics simulations', Polymer Composites, 42(1), pp. 205–219. doi:10.1002/pc.25819.
- Czogała, J., Pankalla, E. and Turczyn, R. (2021) 'Recent attempts in the design of efficient PVC plasticizers with reduced migration', Materials, 14(4), p. 844. doi:10.3390/ma14040844.

- Dai, S. et al. (2020) 'Direct synthesis of polar functionalized polyethylene thermoplastic elastomer', Macromolecules, 53(7), pp. 2539–2546. doi:10.1021/acs.macromol.0c00083.
- De Lannoye, K. et al. (2024) 'The influence of experimental conditions on the mass loss for TGA in fire safety science', Fire Safety Journal, 144, p. 104079. doi:10.1016/j.firesaf.2023.104079.
- de Sousa, F.D.B. et al. (2017) 'Devulcanization of waste tire rubber by microwaves', Polymer Degradation and Stability, 138, pp. 169–181. doi:10.1016/j.polymdegradstab.2017.03.008.
- Dedduwakumara, H.T. et al. (2024) 'The macromolecular design of poly(styreneisoprene-styrene) (SIS) copolymers defines their performance in flexible electrothermal composite heaters', ACS Applied Materials & amp; Interfaces [Preprint]. doi:10.1021/acsami.3c19541.
- Does NBR absorb water? (2024) Does NBR Absorb Water? Available at: https://www.haozechem.net/news/do-nbr-absorb-water.html#:~:text=Water%20Absorption%20in%20NBR%20Rubber,other%20elas tomers%20like%20natural%20rubber (Accessed: 15 March 2024).
- Dong, H., Zhong, J. and Isayev, A.I. (2021) 'Manufacturing polypropylene (pp)/waste EPDM thermoplastic elastomers using ultrasonically aided twin-screw extrusion', Polymers, 13(2), p. 259. doi:10.3390/polym13020259.
- Dorigato, A., Rigotti, D. and Fredi, G. (2023) 'Recent advances in the devulcanization technologies of industrially relevant sulfur-vulcanized elastomers', Advanced Industrial and Engineering Polymer Research, 6(3), pp. 288–309. doi:10.1016/j.aiepr.2022.11.003.
- Drobny, J.G. (2014) Handbook of Thermoplastic Elastomers. Amsterdam etc.: Elsevier/WA, William Andrew.
- EL-Sayed, E.-S., Elnaggar, M. and Hassan, M. (2018) 'Thermo-mechanical properties of poly vinyl chloride/vulcanized nitrile butadiene rubber blends cured by gamma irradiation', Egyptian Journal of Radiation Sciences and Applications, 0(0), pp. 0–0. doi:10.21608/ejrsa.2018.1815.1023.
- Ennadafy, H. et al. (2024) 'Thermogravimetric analysis of rigid PVC and animalorigin bio-composite: Experimental study and comparative analysis', International Journal of Heat and Technology, 42(1), pp. 39–49. doi:10.18280/ijht.420105.
- Esmizadeh, E. et al. (2011) Optimal Parameter Design by Taguchi Method for Mechanical Properties of NBR/PVC Nanocomposites [Preprint]. doi:file:///C:/Users/User/Downloads/Optimal\_Parameter\_Design\_by\_Taguchi\_Met hod\_for\_Mec.pdf.
- Garcia, P.S. et al. (2015) 'Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times', Express Polymer Letters, 9(11), pp. 1015–1026. doi:10.3144/expresspolymlett.2015.91.

- Genovés, V. et al. (2022) 'Micronized recycle rubber particles modified multifunctional polymer composites: Application to ultrasonic materials engineering', Polymers, 14(17), p. 3614. doi:10.3390/polym14173614.
- Ghahramani, N. et al. (2020) 'Rheology of Thermoplastic vulcanizates (tpvs)', Journal of Rheology, 64(6), pp. 1325–1341. doi:10.1122/8.0000108.
- Ghamarpoor, R. and Jamshidi, M. (2022b) 'Preparation of superhydrophobic/superoleophilic nitrile rubber (NBR) nanocomposites contained silanized nano silica for efficient oil/water separation', Separation and Purification Technology, 291, p. 120854. doi:10.1016/j.seppur.2022.120854.
- Ghamarpoor, R. and Jamshidi, M. (2023a) 'Synergistic effect of microwave assisted devulcanization of waste NBR rubber and using superhydrophobic/superoleophilic silica nanoparticles on oil-water separation', Alexandria Engineering Journal, 69, pp. 67–84. doi:10.1016/j.aej.2023.02.002.
- Ghavipanjeh, F., Ziaei Rad, Z. and Pazouki, M. (2018) 'Devulcanization of ground tires by different strains of bacteria: Optimization of culture condition by Taguchi Method', Journal of Polymers and the Environment, 26(8), pp. 3168–3175. doi:10.1007/s10924-017-1169-0.
- Ghowsi, M.A. and Jamshidi, M. (2023) 'Recycling waste nitrile rubber (NBR) and improving mechanical properties of re-vulcanized rubber by an efficient chemomechanical devulcanization', Advanced Industrial and Engineering Polymer Research, 6(3), pp. 255–264. doi:10.1016/j.aiepr.2023.01.004.
- Gobetti, A. et al. (2024) 'Characterization of recycled nitrile butadiene rubber industrial scraps', Journal of Material Cycles and Waste Management [Preprint]. doi:10.1007/s10163-024-01932-8.
- Gumede, J.I. et al. (2021b) 'Organic Chemical Devulcanization of rubber vulcanizates in supercritical carbon dioxide and associated less eco-unfriendly approaches: A Review', Waste Management & amp; Research: The Journal for a Sustainable Circular Economy, 40(5), pp. 490–503. doi:10.1177/0734242x211008515.
- Gumede, J.I. et al. (2022a) 'Devulcanization of natural rubber/styrene-butadiene rubber unfilled blend in supercritical carbon dioxide using Tulbaghia violacea crude extract', Journal of Cleaner Production, 362, p. 132478. doi:10.1016/j.jclepro.2022.132478.
- He, L. et al. (2021) 'Research on the properties of rubber concrete containing surfacemodified rubber powders', Journal of Building Engineering, 35, p. 101991. doi:10.1016/j.jobe.2020.101991.
- Hirayama, D., Scuracchio, C.H. and Saron, C. (2016) 'Microwaves devulcanization of SBR containing Carbon Black', Journal of Research Updates in Polymer Science, 5(2), pp. 52–59. doi:10.6000/1929-5995.2016.05.02.1.

- Home, C. (2024) Bath mats, Canopy Home Malaysia. Available at: https://www.canopyhome.my/collections/bath-mats (Accessed: 24 April 2024).
- Huey, O.M. (2019) Development of thermoplastic elastomer using polyvinyl chloride and for anti-slip bathroom mat application.
- International, A. (2020) Standard test method for determining dimensional stability and curling properties of resilient flooring after exposure to heat, F2199. Available at: https://www.astm.org/f2199-20.html (Accessed: 26 April 2024).
- Jawaid, M., Tariq, M. and Saba, N. (2019) Durability and life prediction in biocomposites, fibre-reinforced composites and hybrid composites. Duxford, United Kingdom: Woodhead Publishing, an imprint of Elsevier.
- Kaliyathan, A.V. et al. (2020) 'Carbon black distribution in natural rubber/butadiene rubber blend composites: Distribution driven by morphology', Composites Science and Technology, 200, p. 108484. doi:10.1016/j.compscitech.2020.108484.
- Kapitonov, E.A. et al. (2021) 'Enhanced physical and mechanical properties of nitrilebutadiene rubber composites with N-cetylpyridinium bromide-carbon black', Molecules, 26(4), p. 805. doi:10.3390/molecules26040805.
- Katheria, A., Nayak, J. and Das, N.Ch. (2022) 'A journey of thermoplastic elastomer nanocomposites for electromagnetic shielding applications: From bench to Transitional Research', Materials Advances, 3(6), pp. 2670–2691. doi:10.1039/d1ma00989c.
- Kaya, D. et al. (2020) 'Aging effects on the composition and thermal properties of styrene-butadiene-styrene (SBS) modified bitumen', Construction and Building Materials, 235, p. 117450. doi:10.1016/j.conbuildmat.2019.117450.
- Khalaf, A., Yehia, A., Ismail, M. & El-Sabbagh, H. (2012). High performance oil resistant rubber. Open J. Org. Polym. Mater., 2, 89–93, <u>https://doi.org/10.4236/ojopm.2012.24013</u>.
- Khalil, A.M. and Rabie, S.T. (2019) 'Mechanical, thermal and antibacterial performances of acrylonitrile butadiene rubber/polyvinyl chloride loaded with moringa oleifera leaves powder', Journal of Thermal Analysis and Calorimetry, 143(4), pp. 2973–2981. doi:10.1007/s10973-019-09194-5.
- Klempová, S., Oravec, M. and Vizárová, K. (2023) 'Analysis of thermally and UV-vis aged plasticized PVC using UV-vis, ATR-FTIR and Raman spectroscopy', SSRN Electronic Journal [Preprint]. doi:10.2139/ssrn.4347291.
- Kohjiya, S. and Ikeda, Y. (2021) Chemistry, manufacture, and applications of natural rubber. Duxford, United Kingdom: Woodhead Publishing.
- Kong, Y. et al. (2023) 'Evolution of crosslinking structure in vulcanized natural rubber during thermal aging in the presence of a constant compressive stress', Polymer Degradation and Stability, 217, p. 110513. doi:10.1016/j.polymdegradstab.2023.110513.

- Kruželák, J. et al. (2016) 'Relationship between the cross-link structure and properties of peroxide and sulfur-cured magnetic composites based on NR and NBR', Journal of Elastomers & amp; Plastics, 49(6), pp. 459–480. doi:10.1177/0095244316672094.
- Kutz, M. (2017) Applied Plastics Engineering Handbook: Processing, materials, and applications. Amsterdam Netherlands: Elsevier.
- Lai, S. et al. (2023a) 'Mechanochemical reclaiming and thermoplastic re-processing of waste acrylonitrile-butadiene rubber (nbr)/poly (vinyl chloride) (PVC) insulation materials', Waste Management, 158, pp. 153–163. doi:10.1016/j.wasman.2023.01.019.
- Lai, S., Cheng, C., Liao, Y., et al. (2023b) 'The structure and properties of mechanochemically modified acrylonitrile butadiene rubber (nbr)/poly (vinyl chloride) (PVC) scraps and fresh NBR composites', Waste Management, 159, pp. 93–101. doi:10.1016/j.wasman.2023.01.021.
- Lapkovskis, V. et al. (2020) 'Crumb rubber as a secondary raw material from waste rubber: A short review of end-of-life mechanical processing methods', Recycling, 5(4), p. 32. doi:10.3390/recycling5040032.
- Li, J. et al. (2022) 'Internal de-crosslinking of scrap tire crumb rubber to improve compatibility of rubberized asphalt', Sustainable Materials and Technologies, 32. doi:10.1016/j.susmat.2022.e00417.
- Li, Y., Zhao, S. and Wang, Y. (2011) 'Microbial desulfurization of ground tire rubber by thiobacillus ferrooxidans', Polymer Degradation and Stability, 96(9), pp. 1662–1668. doi:10.1016/j.polymdegradstab.2011.06.011.
- Liu, J. et al. (2016) 'Investigation of aging behavior and mechanism of nitrilebutadiene rubber (NBR) in the Accelerated Thermal Aging Environment', Polymer Testing, 54, pp. 59–66. doi:10.1016/j.polymertesting.2016.06.010.
- Liu, Y. et al. (2020) 'Stocks and flows of polyvinyl chloride (PVC) in China: 1980-2050', Resources, Conservation and Recycling, 154, p. 104584. doi:10.1016/j.resconrec.2019.104584.
- M. S. Esmail, A.H. (2020) 'Impact of insulation and sheathing PVC mixture on the physical properties', Scholars International Journal of Chemistry and Material Sciences, 03(03), pp. 24–30. doi:10.36348/sijcms.2020.v03i03.002.
- Mangili, I. et al. (2014a) 'Characterization and supercritical CO2 devulcanization of cryo-ground tire rubber: Influence of devulcanization process on reclaimed material', Polymer Degradation and Stability, 102, pp. 15–24. doi:10.1016/j.polymdegradstab.2014.02.017.
- Mangili, I. et al. (2015b) 'Modeling and optimization of Ultrasonic devulcanization using the response surface methodology based on central composite face-centered

design', Chemometrics and Intelligent Laboratory Systems, 144, pp. 1–10. doi:10.1016/j.chemolab.2015.03.003.

Market focus (2018) in Nitrile butadiene market to top \$2.4 billion. Rubber World, pp. 10–10.

McKeen, L.W. (2016) Fatigue and tribological properties of plastics and elastomers. 3rd edn. Norwich, NY: Plastics Design Library.

Meena Rezkallah, P.Eng. (2023) Piping material, usage, and maximum temperature, Little P.Eng. Available at: https://www.littlepeng.com/single-post/piping-materialusage-and-maximumtemperature#:~:text=Maximum%20Temperature%3A%20The%20maximum%20te mperature%20limit%20for%20PVC%20pipes%20depends,C%20(140%C2%B0F). (Accessed: 26 March 2024).

- Meng, T.-T. et al. (2021) 'Comparing the effects of different metal oxides on low temperature decomposition of PVC', Journal of Analytical and Applied Pyrolysis, 159, p. 105312. doi:10.1016/j.jaap.2021.105312.
- Mensah, B. et al. (2023) 'A systematic study of the effect of graphene oxide and reduced graphene oxide on the thermal degradation behavior of acrylonitrilebutadiene rubber in air and Nitrogen Media', Scientific African, 19. doi:10.1016/j.sciaf.2022.e01501.
- Molino, A. et al. (2018) 'Waste tire recycling process for production of steam activated carbon in a pilot plant', Resources, Conservation and Recycling, 129, pp. 102–111. doi:10.1016/j.resconrec.2017.10.023.
- Mousa, A. et al. (2012) Utilization of agrowaste polymers in PVC/NBR alloys: Tensile, thermal, and morphological properties, International Journal of Chemical Engineering. Available at: https://www.hindawi.com/journals/ijce/2012/121496/ (Accessed: 15 March 2024).
- Musa, L. et al. (2022) 'A review on the potential of polylactic acid based thermoplastic elastomer as filament material for fused deposition modelling', Journal of Materials Research and Technology, 20, pp. 2841–2858. doi:10.1016/j.jmrt.2022.08.057.
- Nakanishi, Y. et al. (2021) 'Effects of mixing process on spatial distribution and coexistence of sulfur and zinc in vulcanized EPDM rubber', Polymer, 218, p. 123486. doi:10.1016/j.polymer.2021.123486.
- NBR Nitrile rubber (2017) Rahco Rubber. Available at: https://rahco-rubber.com/materials/nbr-nitrile-rubber/ (Accessed: 26 July 2023).
- Nihmath, A. and Ramesan, M. (2020) 'Comparative evaluation of oil resistance, dielectric properties, AC conductivity, and transport properties of nitrile rubber and chlorinated nitrile rubber', Progress in Rubber, Plastics and Recycling Technology, 37(2), pp. 131–147. doi:10.1177/1477760620925490.

- Nitrile butadiene rubber/PVC blend (2021) Clwyd Compounders. Available at: https://www.clwydcompounders.com/polymer/nitrile-butadiene-rubber-pvc-blend/ (Accessed: 25 August 2023).
- Nur Farahana Ramli *et al.* (2022) 'Effects of poly(vinylchloride)-maleic anhydride as coupling agent on mechanical, water absorption, and morphological properties of eggshell powder filled recycled high density polyethylene/ethylene vinyl acetate composites', *Journal of Advanced Research in Applied Sciences and Engineering Technology*, 28(1), pp. 33–43. doi:10.37934/araset.28.1.3343
- Pan, Z. et al. (2022) 'Mechanical properties of PVC concrete and mortar modified with silane coupling agents', Construction and Building Materials, 348, p. 128574. doi:10.1016/j.conbuildmat.2022.128574.
- Papaspyrides, C.D. and Kiliaris, P. (2014) 'Chapter 18 Fire Retardancy of Elastomers and Elastomer Nanocomposites', in Polymer green flame retardants. Amsterdam: Elsevier, pp. 597–651.
- Pappa, A. et al. (2011) 'Tg-ms analysis of nitrile butadiene rubber blends (NBR/PVC)', Journal of Analytical and Applied Pyrolysis, 92(1), pp. 106–110. doi:10.1016/j.jaap.2011.05.003.
- Parsamanesh, M. et al. (2023) 'Thermomechanical devulcanization of butyl rubber using twin-screw extruder: Process parameters, viscoelastic and compatibility properties', Progress in Rubber, Plastics and Recycling Technology [Preprint]. doi:10.1177/14777606231207000.
- Payne, M.T. and Rader, C.P. (2020) 'Thermoplastic elastomers: A rising star', Elastomer Technology Handbook, pp. 557–596. doi:10.1201/9780138758851-14.
- Peng, B.-Y. et al. (2023) 'Unveiling the residual plastics and produced toxicity during biodegradation of polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC) microplastics by mealworms (larvae of Tenebrio molitor)', Journal of Hazardous Materials, 452, p. 131326. doi:10.1016/j.jhazmat.2023.131326.
- Petrie, E.M. (2021) Handbook of Adhesives and sealants. New York: McGraw-Hill.
- Plastics, P. (2021) What does 'non-phthalate' mean? Phthalate free non phthalate plasticizers, Piper Plastics Corp. Available at: https://www.piper-plastics.com/2019/07/30/what-does-non-phthalate-mean/#:~:text=Non%2Dphthalates%20are%20essentially%20plasticizers,line%20o f%20soy%2Dbased%20plasticizers. (Accessed: 08 April 2024).

Precedence Research (2022) Polyvinyl chloride (PVC) market size to hit USD 105.8 bn by 2030, GlobeNewswire News Room. Available at: https://www.globenewswire.com/en/newsrelease/2022/08/04/2492922/0/en/Polyvinyl-Chloride-PVC-Market-Size-to-Hit-USD-105-8-Bn-by-2030.html (Accessed: 27 August 2023). Pro, H. (2024) Bath mats - anti-slip mats: Inspired by HomePro, HomePro. Available at:

https://www.homepro.com.my/c/BAT020201#:~:text=These%20mats%20are%20d esigned%20to,more%20visually%20appealing%20and%20functional. (Accessed: 26 April 2024).

PVC properties (2019) Vinidex Pty Ltd. Available at: https://www.vinidex.com.au/technical-resources/material-properties/pvcproperties/#:~:text=PVC%20(plasticised)%20is%20less%20rigid,has%20lower%20 ultimate%20tensile%20strength. (Accessed: 26 March 2024).

PVC's physical properties (2019) ECVM. Available at: https://pvc.org/aboutpvc/pvcs-physicalproperties/#:~:text=PVC%20has%20an%20amorphous%20structure,atoms%20in% 20its%20molecular%20structure. (Accessed: 26 March 2024).

- Rad, A.S. et al. (2019) 'Enhancement in the mechanical property of NBR/PVC nanocomposite by using sulfur and electron beam curing in the presence of cloisite 30b nanoclay', Journal of Macromolecular Science, Part A, 57(2), pp. 123–130. doi:10.1080/10601325.2019.1673663.
- Ragaert, K., Delva, L. and Van Geem, K. (2017) 'Mechanical and chemical recycling of solid plastic waste', Waste Management, 69, pp. 24–58. doi:10.1016/j.wasman.2017.07.044.
- Ramarad, S. et al. (2015) 'Waste tire rubber in polymer blends: A review on the evolution, properties and future', Progress in Materials Science, 72, pp. 100–140. doi:10.1016/j.pmatsci.2015.02.004.
- Ramya, A.N. et al. (2022) 'An efficient molecular luminophore based on tetraphenylethylene (TPE) enabling intracellular detection and therapeutic benefits of hydrogen sulfide in alzheimer's disease', Sensors and Actuators B: Chemical, 355, p. 131118. doi:10.1016/j.snb.2021.131118.
- Ratnam, C.T., Kamaruddin, S. and Abdullah, Z. (2011) 'Irradiation modification of PVC/NBR Blend', Polymer-Plastics Technology and Engineering, 50(8), pp. 833–838. doi:10.1080/03602559.2011.551973.
- Rios, R.R.V.A. et al. (2006) 'Devulcanization of styrenebutadiene (SBR) waste tire by controlled oxidation', Journal of the Brazilian Chemical Society, 17(3), pp. 603–608. doi:10.1590/s0103-50532006000300027.
- Robertson, M. et al. (2023) 'Direct synthesis of ordered mesoporous materials from thermoplastic elastomers', Nature Communications, 14(1). doi:10.1038/s41467-023-36362-x.
- Rotaru, I.M. et al. (2023) 'Optimization of the composition of polyvinyl chloride based composite materials with rubber matrices and fly ash additions respectively', Polymer Testing, 129, p. 108280. doi:10.1016/j.polymertesting.2023.108280.

- Sabzekar, M. et al. (2015) 'Influence of process variables on chemical devulcanization of & nbsp;sulfur-cured natural rubber', Polymer Degradation and Stability, 118, pp. 88–95. doi:10.1016/j.polymdegradstab.2015.04.013.
- Santiagoo, R. et al. (2020) 'The effect of epoxy resin compatibilizer on polypropylene (pp) / recycled acrylonitrile butadiene rubber (NBRR) / banana skin powder (BSP) composites', IOP Conference Series: Earth and Environmental Science, 616(1), p. 012021. doi:10.1088/1755-1315/616/1/012021.
- Saputra, R. et al. (2021) 'Current progress in waste tire rubber devulcanization', Chemosphere, 265, p. 129033. doi:10.1016/j.chemosphere.2020.129033.
- Sarkar, S., Banerjee, S.L. and Singha, N.K. (2021) 'Dual responsive self healable carboxylated acrylonitrile butadiene rubber based on dynamic Diels Alder "click chemistry" and disulfide metathesis reaction', Macromolecular Materials and Engineering, 306(3). doi:10.1002/mame.202000626.
- Sastri, V.R. (2022) Plastics in medical devices: Properties, requirements, and applications. San Diego: Elsevier, William Andrew Applied Science Publishers.
- Seghar, S. et al. (2019) 'Thermo-Mechanical Devulcanization and recycling of rubber industry waste', Resources, Conservation and Recycling, 144, pp. 180–186. doi:10.1016/j.resconrec.2019.01.047.
- Senake Perera, M.C., Ishiaku, U.S. and Mohd. Ishak, Z.A. (2001) 'Characterisation of PVC/NBR and PVC/enr50 binary blends and PVC/ENR50/NBR ternary blends by DMA and solid state NMR', European Polymer Journal, 37(1), pp. 167–178. doi:10.1016/s0014-3057(00)00085-9.
- Shabani, M. and Jamshidi, M. (2022) 'Recycling Nr/SBR waste using probe sonication as a new devulcanizing method; study on influencing parameters', RSC Advances, 12(40), pp. 26264–26276. doi:10.1039/d2ra04726h.
- Simon, D.Á. and Bárány, T. (2023) 'Microwave devulcanization of ground tire rubber and its improved utilization in natural rubber compounds', ACS Sustainable Chemistry & amp; Engineering, 11(5), pp. 1797–1808. doi:10.1021/acssuschemeng.2c05984.
- Simon, D.Á. et al. (2019) 'Microwave devulcanization of ground tire rubber and applicability in SBR compounds', Journal of Applied Polymer Science, 137(6). doi:10.1002/app.48351.
- Simon, D.Á. et al. (2019) 'Microwave devulcanization of ground tire rubber and applicability in SBR compounds', Journal of Applied Polymer Science, 137(6). doi:10.1002/app.48351.
- Singh, A., Brown, T. and Mashtizadeh, A. (2021) 'NBR', Proceedings of the 26th ACM SIGPLAN Symposium on Principles and Practice of Parallel Programming [Preprint]. doi:10.1145/3437801.3441625.

- Speight, J.G. (2020) Handbook of Industrial Hydrocarbon Processes. Cambridge, MA: Gulf Professional Publishing, an imprint of Elsevier.
- Su, P. et al. (2022) 'Investigation of the mechanical and shrinkage properties of plasticrubber compound modified cement mortar with recycled tire steel fiber', Construction and Building Materials, 334, p. 127391. doi:10.1016/j.conbuildmat.2022.127391.
- Subramanian, N., Senthilvel, K. and Prabu, B. (2021) 'Studies on the morphology and physico-mechanical properties of NBR/PVC hybrid nanocomposites', Materials Today: Proceedings, 38, pp. 2810–2816. doi:10.1016/j.matpr.2020.08.739.
- Subramanian, N., Senthilvel, K. and Prabu, B. (2021) 'Studies on the morphology and physico-mechanical properties of NBR/PVC hybrid nanocomposites', Materials Today: Proceedings, 38, pp. 2810–2816. doi:10.1016/j.matpr.2020.08.739.
- Sudhakaran, G. and Avirah, S.A. (2023) 'Application of carboxy terminated liquid natural rubber as a polymeric compatibilizer in commercial nano silica filled nr/NBR and PVC/NBR blends', Materials Today: Proceedings [Preprint]. doi:10.1016/j.matpr.2023.11.059.
- Supply, N.H. (2024) White Rubber Bath mats, National Hospitality Supply. Available at: https://www.nathosp.com/product/dhy57/hotel\_bath\_mats (Accessed: 26 April 2024).
- Tatangelo, V. et al. (2016) 'Biological devulcanization of ground natural rubber by Gordonia Desulfuricans DSM 44462T strain', Applied Microbiology and Biotechnology, 100(20), pp. 8931–8942. doi:10.1007/s00253-016-7691-5.
- Tay, J.Y. et al. (2023) 'Development of microporous breathable polyethylene film using different types of linear low-density polyethylene with calcium carbonate as filler', Solid State Phenomena, 349, pp. 95–100. doi:10.4028/p-vga64b.
- Thaicharoen, P., Thamyongkit, P. and Poompradub, S. (2010) 'Thiosalicylic acid as a devulcanizing agent for Mechano-Chemical Devulcanization', Korean Journal of Chemical Engineering, 27(4), pp. 1177–1183. doi:10.1007/s11814-010-0168-9.
- Thomas, S. (2017) Progress in rubber nanocomposites. Duxford: Woodhead Publishing is an Imprint of Elsevier.
- Thoral, C. et al. (2024) 'Impact of photo- and thermooxidative ageing of NBR/PVC blends on the formation of cracks', Polymer Degradation and Stability, 220, p. 110633. doi:10.1016/j.polymdegradstab.2023.110633.
- Torgal, F.P., Jalali, S. and Fucic, A. (2016) Toxicity of building materials. Oxford etc.: Woodhead Publishing Limited.
- Valdés, C. et al. (2020a) Desulfurization of vulcanized rubber particles using biological and chemical methods [Preprint]. doi:10.21203/rs.3.rs-82519/v1.

- Valdés, C. et al. (2021b) 'Desulfurization of vulcanized rubber particles using biological and couple microwave-chemical methods', Frontiers in Environmental Science, 9. doi:10.3389/fenvs.2021.633165.
- Valentini, F., Dorigato, A. and Pegoretti, A. (2020) 'Evaluation of the role of Devulcanized rubber on the Thermo-mechanical properties of polystyrene', Journal of Polymers and the Environment, 28(6), pp. 1737–1748. doi:10.1007/s10924-020-01717-8.
- Vayyaprontavida Kaliyathan, A. et al. (2019a) 'Rubber–rubber blends: A critical review', Progress in Rubber, Plastics and Recycling Technology, 36(3), pp. 196–242. doi:10.1177/1477760619895002.
- Vijayan, K., Muniyadi, M. and Munusamy, Y. (2021) 'Impact modified polyvinyl chloride based thermoplastic elastomers: Effect of nitrile butadiene rubber and graphene oxide loading', Journal of Engineering Science, 17(1), pp. 51–74. doi:10.21315/jes2021.17.1.4.

VINYL - NITRILE RUBBER BLENDS (NBR / PVC) (2022) NBR-PVC. Available at: <u>https://polymerdatabase.com/Polymer%20Brands/NBR-</u> <u>PVC.html#:~:text=Depending%20on%20the%20PVC%20and,with%20increasing</u> <u>%20level%20of%20PVC</u>. (Accessed: 28 July 2023).

Vulcanization and accelerators - [PDF document] (2015) vdocument.in. Available at: https://vdocument.in/vulcanization-and-accelerators.html (Accessed: 08 July 2023).

- Wang, W. et al. (2019) 'Direct visualization of the nanoscopic three-phase structure and stiffness of NBR/PVC blends by AFM nanomechanical mapping', Journal of Polymer Science Part B: Polymer Physics, 57(11), pp. 662–669. doi:10.1002/polb.24821.
- Water absorption 24 Hours (2024) Water Absorption 24 Hour (ASTM D570) Test of Plastics. Available at: https://omnexus.specialchem.com/polymer-property/water-absorption-24-hours (Accessed: 14 March 2024).
- Worlee, A. et al. (2021) Significant factors affecting the Thermo-chemical devulcanization efficiency of Tire Rubber, University of Twente Research Information. Available at: https://research.utwente.nl/en/publications/significant-factorsaffecting-the-thermo-chemical-de-vulcanizatio (Accessed: 25 April 2024).

WYPYCH, G. (2016) Handbook of Polymers. S.l.: ELSEVIER.

- Xia, Y. et al. (2021) 'Study on preparation and properties of PVC/NBR/PVC-G-PMMA composite film', Journal of Macromolecular Science, Part A, 58(9), pp. 636–641. doi:10.1080/10601325.2021.1921597.
- 1688 Alibaba (2024a) High performance natural PVC plastic raw material compound pellets transparent PVC granules 60-70 a for shoes sole, High Performance Natural Pvc Plastic Raw Material Compound Pellets Transparent Pvc Granules 60-70 A For Shoes Sole – Buy Pvc Compounds,Soft Pvc Shoes Compounds,Pvc Granules Product

on Alibaba.com. Available at: <u>https://www</u>.alibaba.com/product-detail/High-performance-natural-PVC-plastic-

raw\_1600537376410.html?spm=a2700.galleryofferlist.normal\_offer.d\_title.30a83a c6HgigLz (Accessed: 10 May 2024).

1688 Alibaba (2024b) NBR LG6280/nitrile butadiene rubber LG 6240 /raw materials/Kunhu/synthetic, Nbr Lg6280/nitrile Butadiene Rubber Lg 6240 /raw Materials/kunhu/synthetic - Buy Rubber Raw Material 6280 Kunhu lg Nbr Rurbber Product on Alibaba.com. Available at: https://www.alibaba.com/product-detail/NBR-LG6280-Nitrile-Butadiene-Rubber-

LG\_1600697922973.html?spm=a2700.galleryofferlist.normal\_offer.d\_title.77c36e6 fDCg9GR (Accessed: 10 May 2024).

## APPENDICES



Figure 6.1: rNBR thermogravimetric analysis (TGA) result.



Figure 6.2: PVC thermogravimetric analysis (TGA) result.



Figure 6.3: PVC/rNBR 90/10 thermogravimetric analysis (TGA) result.



Figure 6.4: PVC/rNBR 80/20 thermogravimetric analysis (TGA) result.



Figure 6.5: PVC/rNBR 70/30 thermogravimetric analysis (TGA) result.



Figure 6.6: PVC/rNBR 60/40 thermogravimetric analysis (TGA) result.



Figure 6.7: PVC/rNBR 50/50 thermogravimetric analysis (TGA) result.