

UNIVERSITI TEKNOLOGI MARA

**SYNTHESIS AND
CHARACTERIZATION OF NON-
ISOCYANATE POLYURETHANE
FROM RUBBER SEED OIL, OLEIC
OLIGOMER, AND OLEIC ACID AS A
RAW MATERIAL**

**RADEN SITI AMIRAH
BINTI HAMBALI**

Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy
(Science)

Faculty of Applied Sciences

March 2022

ABSTRACT

Polyurethane is a versatile material that is utilized for various applications. Conventional polyurethane is synthesized from polyols and polyisocyanates. However, the toxicity of isocyanate could cause health issues such as skin irritation and lung problems. Its toxicity is exposed during manufacturing and in the end-product. Therefore, the development of non-isocyanate polyurethane is an alternative that is environmentally safe to produce polyurethane. The non-isocyanate polyurethane is developed through chemical modification processes which involve epoxidation, carbonation and curing. During the epoxidation process, the double bond functionality of raw material was converted into an epoxide ring using peroxyformic acid generated in-situ. Carbon dioxide gas was introduced to the epoxide ring to form a cyclic carbonate ring. The cyclic carbonate ring was then reacted with ethylenediamine to yield a non-isocyanate polyurethane. The non-isocyanate polyurethane was synthesized from rubber seed oil, oleic oligomer, and oleic acid as raw material of different functionality numbers of $F \geq 3$, $F=2$, and $F=1$, respectively. Rubber seed oil was extracted using hexane via solvent extraction method in 7 hours. The extracted rubber seed oil's properties of viscosity, iodine value, acid value, and FFA were found at 35 mPa/s, 192.89 gI₂/100g, 25.5 mgKOH/100g, and 12.81 %, respectively. The oleic oligomer was synthesized from oleic acid and ethylene glycol. The optimum ratio of ethylene glycol to oleic acid for the oligomer conversion was found at 1.5:1. The oleic oligomer had iodine value, acid value, and FFA of 94 gI₂/100g, 7.21 mgKOH/100g, and 3.62 %, respectively. The reaction temperature and the ratio of hydrogen peroxide and formic acid to the double bond of oil were the parameters being investigated in epoxidation process. The optimum epoxidation condition to yield maximum epoxide conversion was found at 50 °C and the reactant ratio of 1:1:2 (oil : formic acid : hydrogen peroxide). The epoxide conversion of 73 % after 4.5 hours for epoxidized rubber seed oil, 63 % after 3 hours for epoxidized oleic oligomer, and 91 % after 3 hours for epoxidized oleic acid were achieved under the optimum parameter settings. The epoxidized oil then underwent a low-pressure carbonation process. The cyclic carbonate conversion was increased rapidly in the initial stage of the cyclic carbonated rubber seed oil and a gradual conversion for the cyclic carbonated oleic oligomer. The cyclic carbonated oleic acid conversion from epoxidized oleic acid was unsuccessful due to self-attack during the carbonation process where the carboxylic acid group of epoxidized oleic acid will attack its opened epoxide ring. The non-isocyanate polyurethane film was formed by curing the cyclic carbonated oil with ethylenediamine. The optimum percentage of ethylenediamine was found at 20 %. Pencil hardness test on the film resulted in hardness ranging from 2B to 4H for non-isocyanate polyurethane derived from rubber seed oil and 5B to 2H for oleic oligomer. The tensile strength and elongation percentage for non-isocyanate polyurethane derived from rubber seed oil were found at a range of 20 kg/cm²–35 kg/cm² and 20 %-85 %, respectively. While 5 kg/cm²–25 kg/cm² tensile and 28 %-75 % elongation for oleic oligomer. Thus, the non-isocyanate polyurethane derived from rubber seed oil had higher hardness, tensile strength, and elongation percentage compared to oleic oligomer as raw material. The degradation temperature of the non-isocyanate polyurethane was found at 224 °C.

ACKNOWLEDGEMENT

Firstly, I wish to thank God for allowing me to embark on my Ph.D. and for completing this long and challenging journey successfully. My gratitude and thanks go to my supervisor Dr. Ahmad Faiza Bin Mohd. Thank you for the support, patience, and ideas in assisting me with this project, and do not give up on me. I also would like to express my gratitude to my co-supervisors, Prof. Azemi Bin Samsuri and Assoc. Prof. Dr. Dzaraini Binti Kamarun for their guidance and support during my study.

My appreciation goes to the staff of the Polymer Technology Laboratory, especially En Hairul Nizam, Puan Nuridayu, and En Anuar for providing the facilities, knowledge, and assistance. Special thanks to my colleague, friends and siblings, especially Adillah Nurashikin Arshad, Siti Aisyah Jarkasi, Wan Siti Hafizah, Noorie Nabila Musa, Raden Nadhirah Aishah, Raden Ain Nabilah, and Raden Ameer Hanafi for endless emotional support during my Ph.D. journey.

Finally, this thesis is dedicated to my father, Hambali Hirzin and mother, Rohanie Amil for the vision and determination to educate me. Thank you for always being patient and trusting me. This piece of victory is dedicated to both of you. Alhamdulillah.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xix
LIST OF SYMBOLS	xxi
CHAPTER ONE INTRODUCTION	22
1.1 Background Study	22
1.2 Problem Statement	23
1.3 Limitation of Study	24
1.4 Significant of Study	25
1.5 Objectives of Study	27
CHAPTER TWO LITERATURE REVIEW	28
2.1 Natural Oil	28
2.1.1 Rubber Seed Oil	30
2.1.2 Extraction of Natural Oil	31
2.2 Oligomerisation	33
2.3 Chemistry of Polyurethane	34
2.3.1 Toxicity of Isocyanate	36
2.4 Non-isocyanate Polyurethane	39
2.4.1 Epoxidation	40
2.4.2 Carbonation	41

CHAPTER ONE

INTRODUCTION

1.1 Background Study

Polyurethane is a polymeric material with versatile properties used in various industries such as adhesives, coatings, footwear, furniture, and flexible foam. Polyurethane contains urethane linkage (-NH-CO-O-) which is formed from a chain growth reaction of polyisocyanates and polyols. According to Rosato (1993), polyurethane can be synthesized into different types such as rigid foam, flexible foam, and elastomers depending on the material and method used. Polyurethane has high strength, good chemical and abrasion resistance, and superior resistance to ozone, gasoline, and many solvents.

Exposure to petroleum or petroleum-based product could cause arthritis, lupus, allergies, and asthma. Fully reacted polyurethane should be chemically inert. However, even fully reacted polyurethane can produce dust that could induce mechanical irritation to the eyes and lungs. Some countries in Europe and some states in the United States of America have already banned the usage of polyurethane as raw material in home and domestic applications. In the conventional polyurethane system, the isocyanate is used as a monomer to form urethane linkage. Despite being a favourite intermediate product, the isocyanate is toxic and could cause skin irritation, difficulty to breathing, and other lung problems. Moreover, conventional polyurethane releases dangerous components such as isocyanate, carbon monoxide, and hydrogen cyanide during combustion.

Nevertheless, the polyurethane's excellent properties could not be replaced. The growing interest in renewable resources and safer materials and the need to replace the isocyanate inspire the development of other methods to synthesize polyurethane. Hence, the non-isocyanate route had been studied where polyurethane is synthesized without incorporating the isocyanate.

One of the methods is the non-isocyanate carbonation route where it was carried out by converting a double bond in the seed oil into an epoxide ring. The conversion was carried out using peroxyformic acid generated in-situ. Then, carbon dioxide gas was introduced to the epoxide ring to form a cyclic carbonate ring. The cyclic carbonate ring was reacted with ethylenediamine to yield a non-isocyanate polyurethane.