

SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR  
POLYMER BASED ON LINOLEIC ACID OF SUNFLOWER OIL

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SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR  
POLYMER BASED ON LINOLEIC ACID OF SUNFLOWER OIL

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For my beloved husband and son who always be patient, give me support  
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## ABSTRACT

This research was intended to produce and characterize the supramolecular polymer based on linoleic acid of sunflower oil. The synthesis involved a three steps reaction. The first step was the preparation of dimer acid from linoleic acid of sunflower oil by using *Diels-Alder* reaction. The second step was preparation of oligoamides by condensation process of dimer acid and diethylenetriamine. The third step was the reaction of the oligoamides with urea to produce supramolecular polymers. The structure of supramolecular polymer as analyzed by Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) techniques reveals not only the main triglycerides but also primary and secondary amine functional groups which may present as free amine and amine bonded through hydrogen bond. FTIR analysis showed that free amine functional groups appear at  $3426\text{ cm}^{-1}$  and  $3348\text{ cm}^{-1}$  representing N-H stretching of primary and secondary amines as well as at  $1614\text{ cm}^{-1}$  and  $1603\text{ cm}^{-1}$  representing N-H deformation of primary and secondary amines, respectively. The presence of amine bonded hydrogen bonds in the supramolecular polymer is indicated by peaks at  $780\text{ cm}^{-1}$  and  $706\text{ cm}^{-1}$  owing to out-of-plane N-H deformation of primary and secondary amines. NMR analysis also show the appearance amine functional groups at peak 5.4 ppm in  $^1\text{H}$  NMR representing proton in amine functional group and peaks at 151 ppm and 156.6 ppm in  $^{13}\text{C}$  NMR representing carbon in amine functional groups. Moreover, the presence of hydrogen bonding is indicated by infrared peaks in the region  $2300\text{ cm}^{-1}$  to  $3700\text{ cm}^{-1}$  representing hydrogen bonded hydroxyl group from primary and secondary amines. The existence of hydrogen bonding in supramolecular polymer is also detected by the appearance of an endothermic peak in the region of  $116 - 131\text{ }^\circ\text{C}$  as indicated by Differential Scanning Calorimetry (DSC). This peak has broad and low intensity indicating limited numbers of supramolecular polymer formed via hydrogen bondings. All results confirmed that sunflower oil-based supramolecular polymer was formed from oligoamides connected via hydrogen bond.

## ABSTRAK

Penyelidikan ini bertujuan untuk menghasilkan dan mencirikan polimer supramolekul berasaskan asid linoleik daripada minyak bunga matahari. Sintesis melibatkan tindak balas tiga langkah. Langkah pertama ialah penyediaan asid dimer daripada asid linoleik minyak bunga matahari melalui tindak balas *Diels-Alder*. Langkah kedua ialah penyediaan oligoamida melalui proses kondensasi asid dimer dan dietilenatriamina. Langkah ketiga ialah tindak balas oligoamida dengan urea untuk menghasilkan polimer supramolekul. Struktur polimer supramolekul seperti yang dianalisis oleh spektroskopi inframerah jelmaan Fourier (FTIR) dan salunan magnet nuklear (NMR) menunjukkan bukan sahaja trigliserida utama tetapi juga kumpulan berfungsi amina primer dan sekunder yang mungkin hadir sebagai amina bebas dan amina terikat melalui ikatan hidrogen. Analisis FTIR menunjukkan kumpulan berfungsi amina bebas muncul pada  $3426\text{ cm}^{-1}$  dan  $3348\text{ cm}^{-1}$  yang mewakili regangan N-H untuk amina primer dan sekunder serta pada  $1614\text{ cm}^{-1}$  dan  $1603\text{ cm}^{-1}$  yang mewakili perubahan N-H untuk amina primer dan sekunder, masing-masing. Kehadiran ikatan hidrogen yang terikat pada amina dalam polimer supramolekul ditunjukkan oleh puncak pada  $780\text{ cm}^{-1}$  dan  $706\text{ cm}^{-1}$  disebabkan oleh perubahan N-H amina primer dan sekunder dikeluarkan satah. Analisis NMR juga menunjukkan kemunculan kumpulan berfungsi amina pada puncak 5.4 ppm di  $^1\text{H}$  NMR yang mewakili proton dalam kumpulan berfungsi amina dan pada puncak 151 ppm dan 156.6 ppm dalam  $^{13}\text{C}$  NMR mewakili karbon dalam kumpulan berfungsi amina. Selain itu, kehadiran ikatan hidrogen terbukti dengan kehadiran puncak FTIR di sekitar kawasan  $2300\text{ cm}^{-1}$  hingga  $3700\text{ cm}^{-1}$  yang mewakili kumpulan hidroksil terikat hidrogen daripada amine primer dan sekunder. Kewujudan ikatan hidrogen dalam polimer supramolekul juga dikesan oleh kemunculan puncak serap haba pada suhu  $116\text{ }^\circ\text{C}$  hingga  $131\text{ }^\circ\text{C}$  seperti diberikan oleh permeteran kalori pengimbangan kebezaan (DSC). Puncak ini mempunyai intensiti yang lebar dan rendah menunjukkan bilangan polimer supramolekul yang terbentuk melalui ikatan hidrogen adalah terhad. Semua hasil mengesahkan bahawa polimer supramolekul berasaskan minyak bunga matahari telah dapat dihasilkan dari oligoamida tersambung melalui ikatan hidrogen.

**TABLE OF CONTENTS**

<b>CHAPTER</b>	<b>TITLE</b>	<b>PAGE</b>
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENTS</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	x
	<b>LIST OF FIGURE</b>	xi
	<b>LIST OF SCHEME</b>	xiii
	<b>LIST OF ABBREVIATIONS</b>	xvi
<b>1</b>	<b>INTRODUCTION</b>	1
	1.1 Background of Research	1
	1.2 Problem Statement	4
	1.3 Objectives	5
	1.4 Scope of Research	5

<b>2</b>	<b>LITERATURE REVIEW</b>	<b>6</b>
2.1	Supramolecular Polymer	6
2.2	Supramolecular Polymer with Healing Ability	14
2.2.1	Non-Autonomic Healing Supramolecular Polymer	15
2.2.2	Autonomic Healing Supramolecular Elastomer	17
2.3	Sunflower Oil based Supramolecular Polymer	25
2.4	Preparation Dimer Acid Using <i>Diels-Alder</i> Reaction	27
<b>3</b>	<b>METHODOLOGY</b>	<b>30</b>
3.1	Materials	30
3.2	Synthesis Apparatus	30
3.3	Methods	32
3.3.1	Preparation Dimer Acid	33
3.3.2	Preparation of Oligoamide	33
3.3.3	Synthesis of Supramolecular Polymer	34
3.4	Characterization of Supramolecular Polymer	34
3.4.1	Fourier Transform Infrared Spectroscopy	34
3.4.2	Nuclear Magnetic Resonance Analysis	35
3.4.3	Differential Scanning Calorimetry	35
3.4.4	Thermogravimetric Analysis	36
3.4.5	Melt Flow Index	36
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>38</b>
4.1	Dimer Acid	38
4.1.1	Infrared Analysis	38
4.1.2	NMR Analysis	42
4.2	Oligoamide	47
4.2.1	Infrared Analysis	47
4.2.2	NMR Analysis	50
4.3	Supramolecular Elastomer	54
4.3.1	Infrared Analysis	54
4.3.2	NMR Analysis	56



4.4	Differential Scanning Calorimetry	64
4.5	Thermogravimetric Analysis	66
4.6	Melt Flow Index	68
<b>5</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>70</b>
5.1	Conclusions	70
5.2	Recommendation	71
	<b>REFERENCES</b>	<b>72</b>

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Stoichiometry for the first and second step synthesis (Montarnal <i>et al.</i> , 2008)	20
2.2	The quantities of reagents used for the synthesis self-healing rubber (Montarnal <i>et al.</i> , 2009)	22
2.3	Characteristics and Fatty Acid Composition for Sunflower Oil (Chakrabarty, 2003)	26
3.1	Materials that were used in synthesis of supramolecular polymer	31
3.2	The formulation of supramolecular polymer	31
3.3	Specific temperature and load for MFI test	37
4.1	FTIR data of sunflower oil	40
4.2	FTIR data of dimer acid	42
4.3	FTIR data of oligoamide	48
4.4	FTIR data of supramolecular polymer	56

**LIST OF FIGURES**

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Mechanism of supramolecular polymerization (Zhao and Moore, 2003)	7
2.2	Self-healing supramolecular rubber at room temperature. (a) Cut parts were brought into contact at 20 °C immediately after being cut (waiting time <5 min). (b) Cut parts were kept apart for 6 hours and then mended at 20 °C. (c) As in (b) but cut samples were kept apart for 18 hours. (d) Time-dependent infrared experiments (Cordier <i>et al.</i> 2008)	19
2.3	Infrared spectra of the synthesis PA2.3/400 after 10 min, 2 h, 7 h, and 25 h of reaction (Montarnal <i>et al.</i> , 2008)	20
2.4	Stress-strain curves for materials C (green) and D (blue) recorded at 5 mm/min and 50 °C (Montarnal <i>et al.</i> , 2009)	23
3.1	Flow chart of preparation of supramolecular polymer	32
4.1	FTIR spectra of sunflower oil	39
4.2	FTIR spectra of dimer acid	41
4.3	<sup>1</sup> H NMR spectrums of dimer acid	45
4.4	<sup>13</sup> C NMR spectrums of dimer acid	46
4.5	FTIR spectra of Oligoamide	47
4.6	<sup>1</sup> H NMR spectrum of oligoamide	52

4.7	<sup>13</sup> C NMR spectrum of oligoamide	53
4.8	FTIR spectra of supramolecular polymer	55
4.9	<sup>1</sup> H NMR spectrum of supramolecular polymer	58
4.10	<sup>13</sup> C NMR spectrum of supramolecular polymer	59
4.11	DSC curves of supramolecular polymer at heating rate 10 °C/min	65
4.12	TGA curves of supramolecular polymer for the first, second and third heating at temperature ranges of 30 to 150 °C, 30 to 200 °C and 30 to 800 °C, respectively	66
4.13	TGA curve of supramolecular polymer	67

**LIST OF SCHEME**

<b>SCHEME NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Two types of supramolecular polymer (a) main chain and (b) side chain (Ghosh, 2009)	8
2.2	Modification of polybutadiene with 4-phenyl-1,2,4-triazoline-3,5-dione (Stadler and Freitas, 1986)	9
2.3	Illustration (two-dimensional) representation of association polymers formed by 3-carboxyphenylurazole groups of different stereochemistry (Hilger and Stadler, 1990)	10
2.4	(a) Speculated model of rubber structure. (b) Speculated model of cross-linking moiety (six-point hydrogen bonding) (Chino and Ashiura, 2001)	11
2.5	(a) Three steps synthesis i.e. 1 = epoxidation, 2 = oxirane ring-opening and 3 = sulfonyl isocyanate addition. (b) Illustration of three possible hydrogen bond complexes between two sulfonylurethane groups (Peng and Abetz, 2005)	12
2.6	Synthesis of TPEs 1 and 2 from telechelic hydroxy-terminated poly(2-methyl-1,3-propylene adipate) and the functional IPDI-UPy-IPDI or HDI-Upy-HDI isocyanate synthons (Sontjens <i>et al</i> , 2008)	13

2.7	Hydrogen bonding types in the sulfonyl isocyanate end-capped oligomer polyamide (Chen <i>et al.</i> , 2012)	14
2.8	(a) Schematic representation of the cross-linked supramolecular polymer contains covalent (red blocks) and non-covalent bonds (blue/green blocks). (b) Illustration of hydrogen bonds between the amides, urea, and imidazole (Khor <i>et al.</i> , 2012)	16
2.9	Conversion of hyperbranched PEI into the urea-functional polyethylenimines [R = phenyl (ph), hexyl (hexl)] (Schüssele <i>et al.</i> , 2012)	16
2.10	Synthesis pathway of self-healing rubber (Cordier <i>et al.</i> , 2008)	17
2.11	Synthesis of self-healing rubber (Montarnal <i>et al.</i> , 2008). Step 1, reaction between DETA and carboxylic acid produce 1-acyl, 1,7-diacyl and imidazoline derivatives. Step 2, reaction between oligoamidoamines and urea produce supramolecular rubbers	21
2.12	Three step synthesis of supramolecular rubber (Montarnal <i>et al.</i> , 2009).	22
2.13	Two step synthesis of hybrid networks. Step 1 : partial amidation of a mixture of dicarboxylic and tricarboxylic acids with UDETA. Step 2 : cure of the epoxy resin with the remaining carboxylic acid functions (Montarnal <i>et al.</i> , 2010)	24
2.14	Triglyceride structure of sunflower oil. Where R <sub>1</sub> , R <sub>2</sub> , and R <sub>3</sub> are fatty acid chains (Belgacem and Gandini, 2011)	25
2.15	Diels-Alder reaction	27
2.16	C-21 dicarboxylic acid formula (Kadesch, 1979)	28
4.1	Structure of triglyceride (Beckett, 1995)	43
4.2	Preparation of dimer acid via Diels-Alder reaction	44
4.3	Plausible structure dimer acid and related peaks assignment of <sup>1</sup> H NMR chemicals shift	45

4.4	Plausible structure of dimer acid and related peaks assignment of $^{13}\text{C}$ NMR chemicals shift	46
4.5	The structure of amide I, amide II and amide III band of secondary amide and $\alpha$ -brached aliphatic secondary amides (Berhanu, <i>et al.</i> , 2010)	49
4.6	Amine functional groups in oligoamide structure. Where $1^\circ$ amine = primary amine and $2^\circ$ amine = secondary amine	50
4.7	Reaction between dimer acid and DETA	51
4.8	Plausible structure of oligoamide and related peaks assignment of $^1\text{H}$ NMR chemical shift	52
4.9	Plausible structure of oligoamide and related peaks assignment of $^{13}\text{C}$ NMR chemical shift	53
4.10	Amine functional groups in supramolecular polymer structure. Where $1^\circ$ amine = primary amine, $2^\circ$ amine = secondary amine, and $3^\circ$ amine = tertiary amine	55
4.11	Reaction of oligoamide with urea	57
4.12	Plausible structure of supramolecular polymer and related peaks assignment of $^1\text{H}$ NMR chemical shift	59
4.13	Plausible structure of supramolecular polymer and related peaks assignment of $^{13}\text{C}$ NMR chemical shift	60
4.14	Plausible structure of supramolecular polymer (model 1)	60
4.15	Plausible structure of supramolecular polymer (model 2)	61
4.16(a)	Plausible structure of supramolecular polymer (model 3a)	62
4.16(b)	Plausible structure of supramolecular polymer (model 3b)	63
4.17	Plausible structure of supramolecular polymer (model 4)	64

**LIST OF ABBREVIATIONS**

ASTM	-	American society for testing and materials
DETA	-	diethylene triamine
DA	-	<i>Diels-Alder</i>
DGBA	-	diglycidylether of bisphenol A
DSC	-	differential scanning calorimetry
E1016	-	empol 1016 (dimer acid)
FTIR	-	fourier transform infrared spectroscopy
HDI	-	hexamethylene diisocyanate
HDPE	-	high density polyethylene
IPDI	-	isophorone diisocyanate
PA	-	poly amide
PEB	-	polyethylenebutylene
PEI	-	polyethylenimine
MFI	-	melt flow index
NBR	-	nitrile butadiene rubber
NMR	-	nuclear magnetic resonance
NR	-	natural rubber
P1017	-	pripol 1017 (dimer acid)
SMRL	-	Standard Malaysian Rubber Light
SR	-	supramolecular rubber
TGA	-	thermogravimetric analysis
TPE	-	thermoplastic polymer
T <sub>c</sub>	-	crystallization temperature
T <sub>m</sub>	-	melting point
T <sub>g</sub>	-	glass transition temperature



UDETA	-	2-aminoethylimidazolidone
Upy	-	uridopyrimidinone
$\Delta H_f$	-	heating enthalpy
$\Delta H_c$	-	cooling enthalpy

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1. Background of Research**

Rubber is a class of polymers that are rubbery and has large elastic behavior after vulcanization. They are lightly crosslinked polymers. When rubber is stretched, it can elongate from 100 to 1000 % and quickly return to its original shape and size when the load is released. Application of rubber includes tires, belts, gaskets, o-rings, seals, hoses, tubings, engine mounts, wires and cables. The serious problem in the rubber products is cracking, especially in the tire. The tire has four year warranty for cracking protection but, cracking can occur earlier if a tire has poor maintenance practices. When cracking happens, the tire should be replaced by the new one (Baldwin and Bauer, 2008).

Beside tires, cracking can also be found in gaskets, o-rings, hoses and bearings. Cracks in fuel pipes are very dangerous. The growing cracks from the outside surface to inside pipe will cause a fuel leakage and fire can happen. The same hazard may occur in seals, such as diaphragm seals in airlines. Diaphragm seals are very useful for the operation of pneumatic controls. If the seals crack, all functions of the systems will be lost (Lewis and Hainsworth, 2005).

Thermoplastic elastomers (TPEs) are different from conventional rubber. Although TPEs have rubber properties but they can be recycled and reused. TPEs are a class of copolymers or physical mixture of polymers (usually a plastic and a rubber) which have thermoplastic and elastomeric properties. These materials are connected in a network by physical associations such as small glassy or crystalline domains, ionic aggregates or multiple hydrogen bonds (Cordier *et al.*, 2008). The other advantages of TPEs are easier in processing and TPEs scrap material can be reprocessed. The application of TPEs includes bearings, tubings, exterior bumpers, hoses, gears, cables, ski boots, soccer shoes, athletic shoes, soles, golf ball covers, tents and many more. Cracking also happens in TPEs products and it should be replaced (Mark *et al.*, 2005).

Rubber and TPE undergo failure and fatigue during their normal utilization. The idea to eliminate the failure through a self-healing concept holds the promise of increasing lifetimes and eternal strength (Wool, 2008). The studies about the synthesis of TPE have grown in recent years, but just a few that have the ability of self-healing.

The synthesis of TPE that connected by hydrogen bonds was introduced by Stadler and Freitas (1986). Polybutadiene was modified using 4-phenyl-1,2,4-triazoline-3,5-dione. Hydrogen bonding between the highly polar urazole groups creates a formation of a thermoreversible elastomer and strongly influences the mechanical properties. The rheological properties (Stadler and de Lucca Freitas, 1986) and molecular dynamics of this thermoreversible network (Muller *et al.*, 1995) have been reported. Urazola groups were found to enhance the stress relaxation time of polybutadiene. Rubber-like elastic materials were made by substituting phenyl-urazole groups with urazolylphenyl benzoic acid groups (Dardin *et al.*, 1993; Hilger *et al.*, 1992). The formation of these bonds were not only pairwise but aggregation to create a very robust crosslinks.

The aggregation of poly(dimethylsiloxane)s with bisurea end groups was studied by Colombani *et al.* (2005). They found that the elastomeric properties was obtained through the aggregation of the end groups into three dimension crystalline domains. In order to obtain tensile properties, crystallization should occur through the formation of hydrogen bonds. Sivakova *et al.* (2005) also found the same conclusions. The polymers with film-forming properties could be formed through very weak interaction between end to end groups when the end groups phase separated.

The effect of combining very strong end-to-end association via ureidopyrimidinone (Upy) quadruple hydrogen bonding with polyethylenebutylene (PEB) chains have been studied by Kautz *et al.* (2006) leading to the formation of viscoelastic polymers that has much longer relaxation time.

Montarnal *et al.* (2008) have synthesized a self-healing supramolecular rubbers from dimer or trimer fatty acids of vegetable oils. A supramolecular network was obtained from oligomers with many functional groups that associated via hydrogen bonds. These materials had an ability to re-join after tearing into pieces.

It is desirable to provide a new polymer that has an ability of self-healing to overcome cracking problems. In addition, this new polymer does not need vulcanization process to become elastic. Hopefully, in the future, this strategy can be applied in conventional rubber such as tires and bridge bearings.

## 1.2 Problem Statement

Generally, rubber is not sufficiently elastic and strong for practical use. It should be vulcanized to become elastic and strong. Besides, after crosslinking, it cannot be re-used and recycled. Cracks may happen in rubber products. For example tires, although, anti-aging chemicals are included in the formulation of rubber compounds, tire can lose its elasticity because of certain conditions, such as acid rain, brake dust, harsh chemicals, direct sunlight, summer's heat and winter's cold (Gobinath *et al.*, 2008). In such conditions, initiation of crack can occur. Then the tire should be replaced when the crack reaches deep into the rubber. The damage can also occur by an external mechanical force. These damages are not repairable.

Crack in elastomer is known as tearing. A tearing happens when the elastomers experience higher strains. When a crack is initiated, the crack will become bigger if the elastomer is subjected to large or repeated stress. If the crack is repaired by using a certain polymer, the repaired elastomer will not have the same properties with the original elastomer (Keller *et al.*, 2009).

The cracks may be prevented by using a self-healing strategy. In this strategy, a new polymer having self-healing capability is synthesized to give a supramolecular which is formed through interaction of oligomers and small molecules that associated via hydrogen bonds.

In this work, a supramolecular polymer was prepared from linoleic acid of sunflower oil. Synthesis on sunflower oil based supramolecular polymer has not been done before. However, there are some researchers reported the supramolecular synthesis based on vegetable oil, they used fatty acid derivatives (Cordier *et al.* (2008), Montarnal *et al.* (2008), Rogers *et al.* (2007), and Chen *et al.* (2005)).

For this work, synthesis was carried out in three steps, the first was the preparation of dimer acid, the second was the preparation of oligoamide, and the third was the synthesis of self-healing polymer by reacting oligoamide with urea.

### **1.3 Objectives**

The purpose of this research is to produce a supramolecular polymer from linoleic acid of sunflower oil. The objectives of this work are :

- 1) To produce dimer acid from linoleic acid of sunflower oil.
- 2) To react dimer acid with diethylene triamine to obtain an oligoamide.
- 3) To synthesize supramolecular polymer by reacting the oligoamide with urea.
- 4) To characterize the supramolecular polymer.

### **1.4 Scope of Research**

To achieve the goal of this research, the scopes are listed below :

- 1) In synthesis of supramolecular polymer, the scopes are the preparation of dimer acid from linoleic acid of sunflower oil, the preparation of oligoamide by condensation process, and the synthesis of supramolecular polymer by reacting the oligoamide with urea.
- 2) The characterization of supramolecular polymer was done by using Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Melt Flow Index (MFI).

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