

# Synthesis of Polyurethanes Membranes from Rubber Seed Oil and Methylene Diphenyl Diisocyanates (MDI)

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**Abstract.** Rubber seed oil and methylene diphenyl diisocyanates (MDI) based polyurethane membrane has been prepared in this study. The main objective of this research is manufacture of polyurethane membranes from avocado seed oil, as a filter of this membrane use as a filter of metals from water such as mercury (Hg). In this study, the polyurethane membrane had been synthesized by varying compositions of rubber seed oil and MDI, with ratios of 10:0.2; 10:0.4; 10:0.6; 10:0.8; 10:1.0; 10:1.2; 10:1.4; 10:1.6; 10:1.8 and 10:2.0 (v/w) at 80°C and 170°C as polymerization and curing temperatures, respectively. Optimum polyurethane membrane was obtained at rubber seed oil: MDI 10: 0.8 v/w, it was dry, non-sticky, smooth and blackish brown. The membrane flux was 5,8307 L / m<sup>2</sup>.h.bar and rejection factor was 35,3015 %. The results of characterization indicated the formation of urethane bonds (NH at 3480 cm<sup>-1</sup>, C=O at 1620 cm<sup>-1</sup>, CN at 1374 cm<sup>-1</sup>, -OC-NH- at 1096 cm<sup>-1</sup> and no -NCO at 2270 cm<sup>-1</sup>), the value of Tg was 55°C. The polyurethane membrane which treated at the optimum treatment conditions were used to the filter of metals from water such as mercury (Hg).

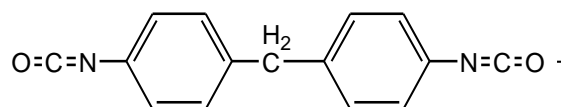
## 1. Introduction

Rubber seed oil contains triglycerides or esters of glycerol and free fatty acids. These free fatty acids containing two functional groups, namely the hydroxy group and the double bond can be used as a source of OH [1] According Nurman et al, 2015 rubber seed oil from the village Gunong Kleng, District Meurebo, West Aceh District, Aceh Province, can be used as the manufacture of polyurethane membrane, because it has a hydroxyl number 40.33 mgKOH/g and iodine number 154.05 gI<sub>2</sub> / g.

Polyurethanes can be synthesized by polyaddition reaction between isocyanate (toluene diisocyanate (TDI), hexamethylenediisocyanate (HMDI) and methylene diphenyldiisocyanate (MDI)) and alcohol or other compounds containing active hydrogen atoms [2-7]. Polyurethanes are polymers or copolymers



heteropolymer composed of different monomers, thus naming polyurethane was taken from the type of formed bond [7]. In this experiment, the compound methylene diphenyldiisocyanate (MDI) for the manufacture of membranes for having two isocyanate groups opposing directions (Figure 1). With the aim of the resulting membrane has a better performance.



**Figure 1.** Structure of methylene diphenyldiisocyanate

Nurman et al [8] have synthesized polyurethane membrane from rubber seed oil and hexamethylene diisocyanate (HMDI), resulting membrane is homogeneous, dry, elastic, corrugated and brownish yellow membrane, with glass transition point (T<sub>g</sub>) 65°C. Marlina et al [9,10] have synthesized a polyurethane membrane from jatropha seed oil and methylene diphenyldiisocyanate (MDI). The resulting membrane has a glass transition point 161°C.

In this study, the polyurethane membranes were fabricated by crosslink method. The optimum parameters of treatment were researched. Finally, the polyurethane membranes which treated at the optimum conditions was used to the filter of metals from water such as mercury (Hg) treatment and the nanofiltration performance was studied.

## 2. Methodology

### 2.1 Equipment and Materials

The equipment used in this study were glassware, analytical balance, soxhlet apparatus, rotary evaporator, oven, hotplate, magnetic stirrer, Fourier transform infrared (FTIR) spectrophotometer, differential thermal analyser (DTA). And materials used in this study were, methylene diphenyldiisocyanate (MDI), n-hexane. The sample (rubber seed) was collected from the plantation residents in the village GunongKleng, Meureubo sub-district, West Aceh District, Aceh Province.

### 2.2 Rubber Seed Oil Extraction

The extraction process of rubber seed oil starts from the cleaning process rubber seed, shelled and dried at room temperature, crushed into powder, extracted using soxhlet with solvent n-hexane at 80°C for 4 hours. To separate the rubber seed oil and n-hexane was used a rotary evaporator at 60°C for 30 minutes.

### 2.3 Preparation of Polyurethane Membranes

Manufacture of polyurethane membranes by reacting rubber seed oil with MDI. 10 mL of rubber seed oil, plus MDI composition variation 0.2; 0.4; 0.6; 0.8; 1.0; 1.2; 1.4; 1.6; 1.8 and 2.0 grams, was stirred using a magnetic stirrer at 80°C for 30 min, printed in a petri dish, then curing in the oven at 170°C for 24 hours. Once the membrane is formed, then the membrane is released in the flowing water with the aid of a spatula.

### 2.4 Characterization of Polyurethane Membranes

#### 2.4.1 Analysis of functional groups

Analysis of the functional groups polyurethane membrane using the Fourier transform infrared (FTIR) (Agilent pro carry 630 resolution FTIR spectrometer), conducted at the Laboratory Instruments, Department of Chemistry, State UNSYIAH, Banda Aceh.

### 2.5.5 Thermal analysis

Polyurethane membrane differential thermal analysis thermal analysis (DTA) (SDT Q600), conducted at the Laboratory of Integrated USU, Medan.

## 3. Results and Discussion

### 3.1 Polyurethane Membranes

Rubber seed oil is used to synthesize the results soxhletation polyurethane membrane. Manufacture of polyurethane membranes by varying the composition of methylene diphenyldiisocyanate to obtain optimum membrane. Table 1 and Figure 2 shows the variations in the composition of methylene diphenyldiisocyanate, which produces polyurethane membranes of different characteristics. Composition of methylene diphenyldiisocyanate 0.2 and 0.4 gram produce polyurethane membrane that is not dry and sticky. This is because there are still many traces of oil that does not react. While the composition of methylene diphenyldiisocyanate 1.4; 1.6; 1.8 and 2.0 gram produce polyurethane membranes were dry, slightly stiffer and less elastic. It shows that the composition of methylene diphenyldiisocyanate is already excessive.

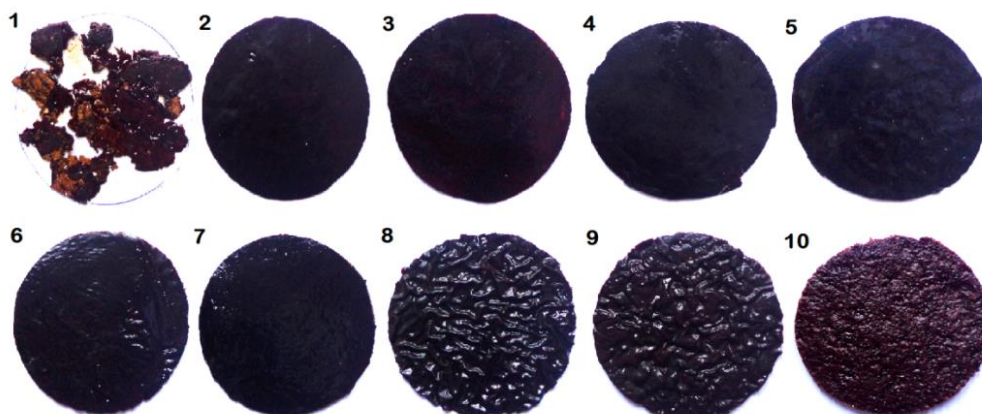
**Table 1.** Variation of compositions in the manufacture of polyurethane membrane.

No	MBK <sup>a</sup> (mL)	MDI <sup>b</sup> (grams)	Visually remarks polyurethane membrane
1	10	0.2	not dry, sticky
2	10	0.4	a little dry, sticky, smooth
3	10	0.6	dry, non-sticky, smooth
4	10	0.8	dry, non-sticky, smooth
5	10	1.0	dry, slightly wavy
6	10	1.2	dry, slightly wavy
7	10	1.4	dry, slightly stiff, smooth
8	10	1.6	dry, slightly stiff, wavy
9	10	1.8	dry, slightly stiff, wavy
10	10	2.0	dry, brittle, foamy

<sup>a</sup>MBK = rubber seed oil

<sup>b</sup>MDI = methylene diphenyldiisocyanate

Table 1 shows the visual polyurethane membrane with composition variation of MDI. The optimum composition of rubber seed oil and MDI was 10:0.8 v/w with a polymerization temperature of 80°C and 170°C curing temperature. It showed better results than the other variations. The obtained polyurethane membrane was homogeneous, dry (not oily), not sticky, soft and blackish brown.



**Figure 2.** Polyurethane membrane with composition variation MDI (1) 0,2 grams, (2) 0,4 grams, (3) 0,6 grams, (4) 0,8 grams, (5) 1,0 g (6) 1,2 grams, (7) 1,4 grams, (8) 1,6 grams, (9) and 1,8 grams (10) 2,0 grams

### 3.2 Characterization of Polyurethane Membranes

#### 3.2.1 Flux and Rejection

The polyurethane membrane which treated at the optimum treatment conditions filtration processes was done by using mercury-contaminated water. The membrane surface area used was 22.051 cm<sup>2</sup> with a pressure of 7 bar and a filtration time of 20 minutes. The results of the flux and rejection factors can be seen in Table 2.

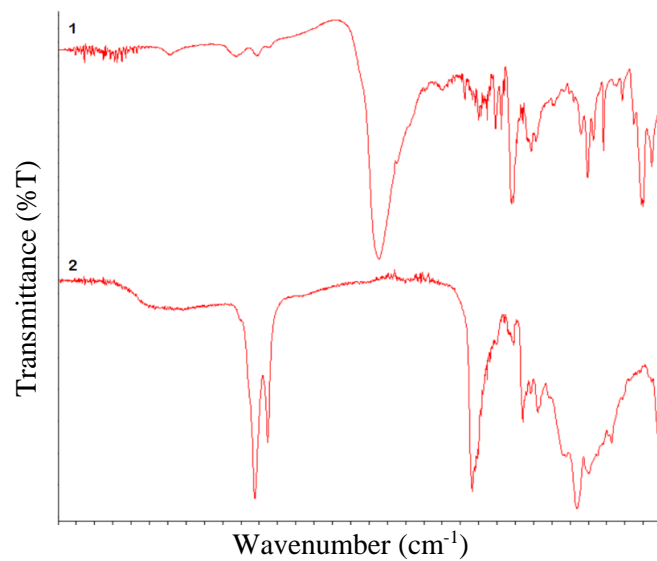
**Table 2.** Results of flux and rejection factor

Feed (ppb)	Permeate (ppb)	Flux (L/m <sup>2</sup> .h.bar)	Rejection Factor (%)
0,2388	0,1545	5,8307	35,3015

The results of the flux and rejection factors indicate that polyurethane membrane can be used to filter the mercury in the water. but not optimal because of the rejection that found only 35%. The resulting membrane type is nanofiltration base on a linear relationship between the pressure applied and the resulting flux.

#### 3.2.2 FTIR Spectroscopy

Figure 3 shows the FTIR spectrum of methylene diphenyldiisocyanate (1) and a polyurethane membrane (2). The spectrum of the polyurethane membrane showed the formation of a urethane bond. Urethane bond marked by the uptake of the bond -NH at wave number 3480 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>, -CN at wave number 1374 cm<sup>-1</sup>, -C = O at wave number 1620 cm<sup>-1</sup>, -OC-NH- at wave number 1096 cm<sup>-1</sup>. And the absence of -NCO absorption at wave number 2280 cm<sup>-1</sup> for spectrum polyurethane membrane. It shows that the isocyanate (-NCO) of methylene diphenyldiisocyanate has completely reacted to form a urethane rubber seed oil.

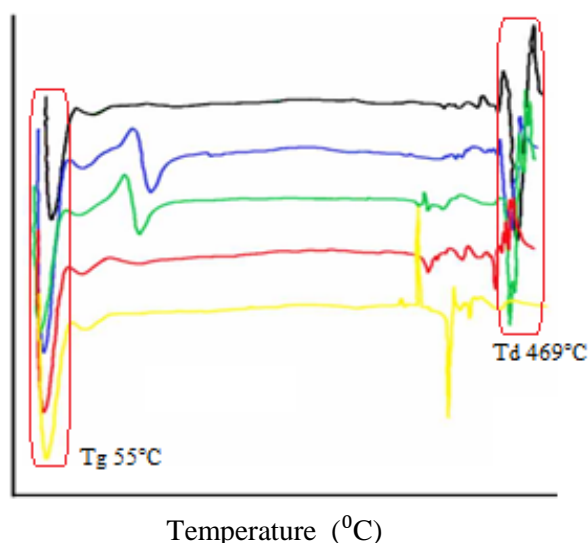


**Figure 3.** The FTIR spectrum of MDI and polyurethane membranes.

### 3.2.3 Thermal Resistance

The results of thermal analysis using a differential thermal analysis (DTA). Figure 4 shows the DTA curve analysis results of the sample with a composition ratio between rubber seed oil and methylene diphenyldiisocyanate 10:0.6 (black), 10:0.8 (blue), 10:1.0 (green), 10:1.2 (red), 10:1.4 (yellow), from the curve shown that the absence of a significant difference to the glass transition point. Glass transition point polyurethane membrane produced in this study the average temperature of 55°C. This result differs from the glass transition point reported by Nurman [9] is 65°C. It is caused by different types of isocyanates are used, in which the polyurethane membranes formed from HMDI has a structure that is straight so that it has a high-density polyurethane while the membrane is formed from MDI has branching structure so that the lower density levels. The density of the membrane can affect the thermal properties of the membrane.

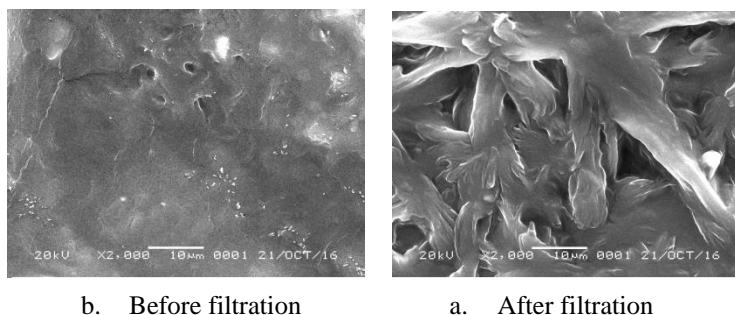
Raw materials with a high-OH source will also affect the thermal properties of the membrane. Marlina et al<sup>[7]</sup> have used the premises jatropha seed oil major components ricin oleic acid containing three -OH groups (more than rubber seed oil) to produce polyurethane membrane with a glass transition point of 161°C is resistant to heat, as well as proposed by Humberto<sup>[6]</sup>.



**Figure 4.** DTA curves of polyurethane membrane.

#### 3.2.4 Analisis of Morfologi

Polyurethane membrane morphology seen in cross sectional with magnification 2000x as shown in Figure 5. Morphological analysis performed on the membrane before filtration (a) and after filtration (b) Membrane surface before filtration shown not homogeneous. This is caused the membrane printing was done manually, so that the different thickness of the surface formed, There was also the solution has not completely dissolved at the time of preparation of the dope solution. After filtration, membrane pores showed that more and more large, these caused of the membrane filtration has been tested at a high pressure (7) bar. These PU membranes resistant to pressure and not teared when filtration test, so it can have applied in large scale.



**Figure 5.** SEM of polyurethane membrane

## 4. Conclusion

Synthesis of polyurethane membranes by using a rubber seed oil as a source of OH reacted with methylene diphenyldiisocyanate as a source of -NCO. The optimum composition of the synthesis of polyurethane membranes is 10:0.8 (v/w). The resulting membrane had properties of dry, non-sticky, smooth and blackish brown. The membrane flux was 5,8307 L / m<sup>2</sup>.h.bar and rejection factor was 35,3015 %. IR results indicate the formation of a urethane bond (NH at 3480 cm<sup>-1</sup>, C=O at 1620 cm<sup>-1</sup>, CN at 1374 cm<sup>-1</sup>, -OC-NH- at 1096 cm<sup>-1</sup> and no -NCO at 2270 cm<sup>-1</sup>), DTA results showed average glass transition temperature of several samples at 55°C.

### Acknowledgments

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### Reference

- [1] Bakare I O, Okieimen F E, Pavithran C, Abdul H P S K and Brahmakumar M 2010 Mechanical and thermal properties of sisal fiber-reinforced rubber seed oil-based polyurethane composites, *Material and Design*, **31**(2) 4274-4280
- [2] Alam M, Akram D, Sharmin E, Zafar F and Ahmad S 2014 Vegetable oil based eco-friendly coating, materials *Arabian Journal of Chemistry* **7**(2) 469-479.
- [3] Das B, Konwar U, Mandal M and Karak N 2012 Sunflower oil based biodegradable hyperbranched polyurethane as a thin film material *Industrial Crop and Products* **44**(2) 396-404.
- [4] Datta J and Głowińska E 2014 Effect of hydroxylated soybean oil and bio-based propanediol on the structure and thermal properties of synthesized bio-polyurethanes *Journal Industrial Crop and Products* **61**(3) 84-91.
- [5] Gurunathan T, Mohanty S and Nayak S K 2014 Isocyanateterminatedcastoroil-based polyurethane prepolymer: synthesis and characterization *Journal Progress in Organic Coatings* **80**(2) 39-48.
- [6] Min M A, Yaakob Z, Kamarudin S and Chuah L A 2014 Synthesis and characterization of jatropha (*jatropha curcas l.*) oil-based polyurethane wood adhesive, *Industrial Crops and Products* **60**(2) 177-185.
- [7] Stevens M P 1989 Polymer chemistry *Oxford University Press Inc University of Hartford USA*
- [8] Nurman S, Marlina, Saiful and Sitti S 2015 Sintesis dan karakterisasi membran poliuretan dari minyak bijikaret dan heksametilen-1,6-diisosianat *Jurnal Rekayasa Kimia dan Lingkungan* **10**(4) 188-195.
- [9] Marlina, Hizir S, Sitti S and Dedek S W 2010 The use of castor oil and methylene diphenyl diisocyanate in polyurethane membrane preparation *ICYC*
- [10] Humberto J S A J, Assunpcao D B, Meneguzzi A, Arthur C F and Dani F R A 2013 Castor oil and commercial thermoplastic polyurethane membrane modified with polyaniline: a comparative study, *Journal Materials Research*, **16**(4), 860-866.