



## Synthesis and Characterization New Polyurethane Membrane From Hydroxylated Rubber Seed Oil

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### ABSTRACT

New polyurethane membrane from hydroxylated rubber seed oil has been prepared in this study. Hydroxylated process of rubber seed oil improved 135.30% of hydroxyl number and decreased 73.91% of iodine number of rubber seed oil. Optimum polyurethane membrane was obtained at the composition of hydroxylated rubber seed oil:hexamethylene-1,6-diisocyanate was 5:7 v/w. The membrane was homogeneous, dry, smooth, slightly stiff and brownish yellow. The clean water flux and rejection factor of the membrane were 0,544L / m<sup>2</sup>.h.bar and 98.86%, respectively. FTIR spectra indicated the formation of urethane bond (N-H at 3308 cm<sup>-1</sup>). Thermal analysis showed two stages of decomposition at 223°C and 386°C. The membrane exhibited a strong and elastic properties with a tensile strength of 1.13 kgf/mm<sup>2</sup> and elongation 215.36%.

**Keywords:** Rubber seed oil, Hexamethylene-1,6-diisocyanate,  
Synthesis, Polyurethane membrane, Characterization.

### INTRODUCTION

Indonesia is an agricultural country which has a wide range of biological, one of them is rubber plant (*Hevea brasiliensis*)<sup>1</sup>. The products of rubber plant are only put emphasis on the processing of latex and trunks, while other products such as its seed has not received more attention. Rubber seeds are the by products of rubber plantations which can be utilized for biodiesel<sup>2,3</sup>. To improve the

diversification of plant products, an effort is needed to increase the added value of these plants.

Rubber seed contains 40.76% (w/w) of oil. Rubber seed oil contains 38.59% of oleic acid, 41.06% of linoleic acid, 10.43% of stearic acid and 9.92% of palmitic acid. Rubber seed oil has a hydroxy number 40.33 mgKOH/g and 154.05 g<sub>2</sub>/g of iodine number<sup>4</sup>. Rubber seed oil has a color (lovinbond) 22R; 23,2Y, 0.916 of specific gravity (30 ° C), 43.62

mg KOH/g of acid number, free fatty acids 21.4, 202.91 mg KOH/g saponification number and 136.21 g I<sub>2</sub>/100 g of iodine numbers<sup>5</sup>.

Hydroxylation process is the addition of a hydroxy group into a compound by performing addition -OH group to the double bond<sup>6</sup>. The reaction takes place in two stages, where the first stage is protonated alkene to produce a carbocation. The second stage is nucleophilic addition to the carbocation. Both of reactions take place according to Markovnikov rule. Hydroxylation process in vegetable oils can increase the concentration of hydroxyl<sup>6</sup>.

In our previous research, polyurethane membranes have been prepared by using vegetable oil. The free fatty acids and oxidized fatty acids of castor oil were used as a source of hydroxyl and 2,4-toluene diisocyanate (TDI) as the source of isocyanate<sup>7</sup>. polyurethane membrane of rubber seed oil with HMDI had been synthesized, the resulting membrane has a homogeneous, dry, elastic, brownish yellow, wavy with the flux and rejection factor were 0544 L/m<sup>2</sup>.h.bar and of 100%, respectively<sup>4</sup>. Therefore, in this study hydroxylated rubber seed oil and hexamethylene-1,6-diisocyanate (HMDI) were used for polyurethane membrane preparation.

## MATERIALS AND METHODS

### Materials

The raw material was rubber seed taken from the plantation residents in the village Gunong Kleng, Meureubo, West Aceh, Aceh Province, Indonesia. Chemicals used were hexamethylene-1,6-diisocyanate (HMDI) purchased from Merck, chloroform, acetic acid, KOH, KI, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, starch indicator, n-hexane, NaCl, H<sub>2</sub>SO<sub>4</sub>, and methanol were purchased from Sigma–Aldrich.

### Instrumentation

FTIR spectra of rubber seed oil and polyurethane membrane used (Agilent resolution pro Cary 630 FTIR spectrometer), membrane morphology viewed using SEM (Tabletop microscope 3000), thermal analysis of polyurethane membrane using TGA and DTA (SDT Q600) and mechanical strength of the membrane was tested with (Control computer series 10-100 KN)

### Rubber seed oil extraction process

Rubber seeds were cleaned, peeled, dried at room temperature and crushed into powder. Rubber oil extraction was carried out by n-hexane at 80° C for 4 hours. A rotary evaporator was used to separate the rubber seed oil and n-hexane at 60°C for 30 minutes.

### Hydroxylation process of rubber seed oil

25 mL of rubber seed oil was added to 2.5 mL of H<sub>2</sub>SO<sub>4</sub> 35%, then stirred for 90 minutes, and then chloroform was added to separate the remaining water phase. 5 grams of anhydrous Na<sub>2</sub>SO<sub>4</sub> was added to the organic phase and then filtered. The filtrate obtained was evaporated using a rotary evaporator and the oil obtained was characterized.

### Preparation of polyurethane membrane

5 mL of hydroxylated rubber seed oil and 1,6-hexamethylene diisocyanate (with a series of composition) were mixture by using a magnetic stirrer at a temperature of 90-100°C for 60 min. Then poured in a petri dish, cured an oven at a temperature of 115-120°C for 8 hours. Once the membrane had been formed, then the membrane was released in the flowing water with the aid of a spatula.

## RESULT AND DISCUSSION

### Characterization of hydroxylated rubber seed oil

Hydroxylation process of rubber seed oil was conducted by using water in acidic solutions. H<sup>+</sup> as a catalyst break the double bond of rubber seed oil resulting in the addition reaction with -OH groups from water. The proposed of addition reaction of linoleic acid can be seen in Fig 1.

Hydroxylated rubber seed oil has a hydroxyl number 94,903 mgKOH/g and iodine number 40.185 g I<sub>2</sub>/g. There was an increase for the hydroxyl number and a decrease in iodine number of 40.333 mgKOH/g and 154.052 g I<sub>2</sub>/g<sup>4</sup>. Hydroxylation process had improved hydroxyl number amount up to 135.30%.

FTIR spectra of rubber seed oil and hydroxylated rubber seed oil are shown in Fig 2. The -OH groups of hydroxylated rubber seed oil at wave number 3400 cm<sup>-1</sup> was appear broader comparing to the spectrum of rubber seed oil. Peak of -CH alkene

bond at wave number  $3010\text{ cm}^{-1}$  in the spectrum of rubber seed oil seems clearer with high intensity comparing the spectrum of hydroxylated rubber seed oil. It shows that the hydroxylation process of rubber seed oil has reduced the number of double bonds and those results also supported by reduction of iodine number.

#### Polyurethane membrane preparation

The preparation of a polyurethane membrane from hydroxylated rubber seed oil and hexamethylene-1,6-diisocyanate through addition

reaction can be seen in Fig 3. The visual results of the membrane with HMDI composition is shown in Table 1.

Table 1 shows the visual of polyurethane membrane with composition variation of HMDI. The optimum composition of hydroxylated rubber seed oil and HMDI was 5: 7 v / w with a polymerization temperature of  $90\text{-}100^\circ\text{C}$  and a curing temperature of  $115\text{-}120^\circ\text{C}$ . It showed better results than the other variations. The obtained polyurethane membrane was homogeneous, smooth, dry (not greasy), a little rigid and brownish yellow.

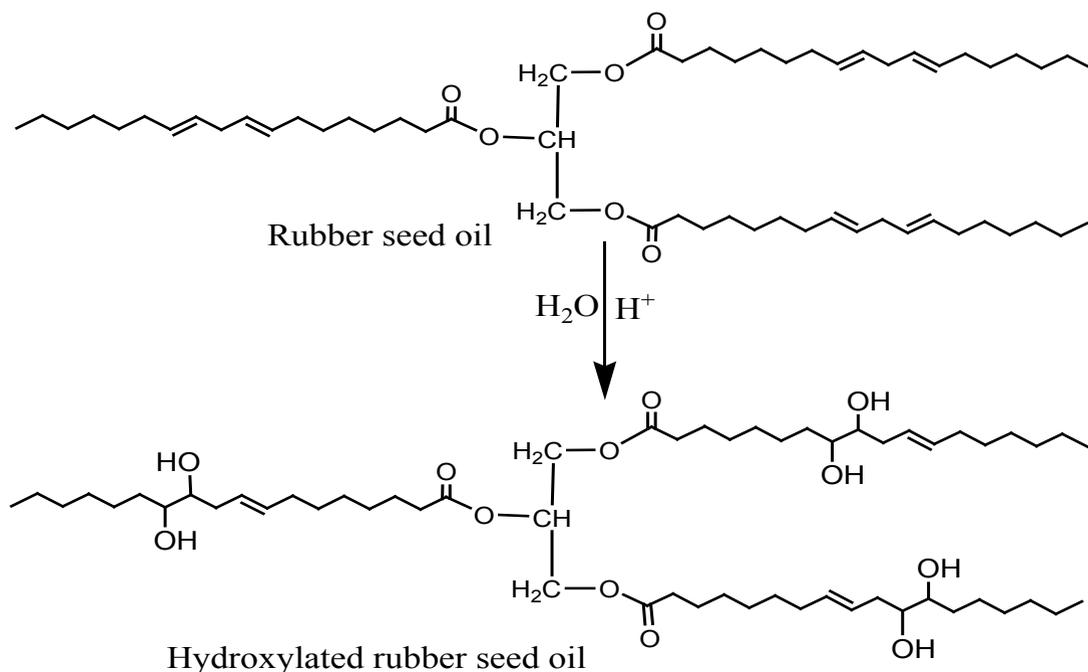


Fig. 1: The Proposed of addition reaction

Table 1: Variations in composition in the preparation of polyurethane membrane

HRSO <sup>1</sup> (ml)	HMDI <sup>2</sup> (grams)	Visual description polyurethane membrane
5	4	homogeneous, dry, slightly elastic, yellow, slightly bubbly
5	5	homogenous, slightly bubbly, a little stiff, dry, tawny,,
5	6	homogeneous, slightly bubbly, stiff, dry, tawny,
5	7	homogeneous, smooth, slightly stiff, dry, tawny,
5	8	homogeneous, smooth, stiff, dry, tawny,

<sup>1</sup> HRSO : Hydroxylated rubber seed oil

<sup>2</sup> HMDI : Hexamethylene-1,6-diisocyanate

### Characterization of polyurethane membrane

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

Rejection factor was obtained by calculating the concentration of mercury in the feed and permeate using atomic absorption spectrophotometry (AAS). Decoys are used in the form of mercury-contaminated

water with a mercury concentration of 0.0703 ppb, resulting permeate contains 0.0008 ppb mercury. So that the resulting rejection factor was 98.86%.

The results of the flux and rejection factors show that the polyurethane membrane can be used for mercury filtration from water. The membrane type was reverse osmosis membrane (RO) base on a linear relationship between the pressure applied and the flux.

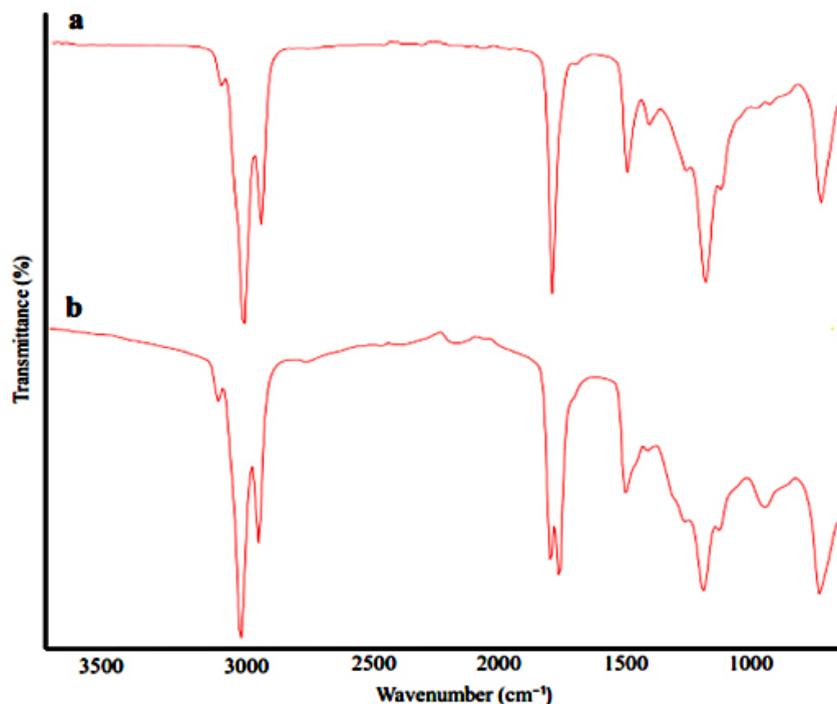
The FTIR spectrum of polyurethane membran is shown in Fig 4. The spectrum shows that the urethane bond had been formed. Urethane bond marked by the wavenumber 3308 cm<sup>-1</sup> of N-H, wave number 1373 cm<sup>-1</sup> of CN, wave number 1739 cm<sup>-1</sup> of -C=O and the absence of -NCO absorption at wave number 2280 cm<sup>-1</sup> for spectrum of polyurethane membrane.

Polyurethane membrane morphology was observed in cross sectional with magnification 100x and 500x as shown in Fig 5. The cross urethane

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

HRSO (ml)	HMDI (grams)	Flux L/m <sup>2</sup> .h.bar	rejection factor %
5	4	0,680	*
5	5	0,612	*
5	6	0,748	*
5	7	0,544	98,86
5	8	0,680	*

\*Not analyzed

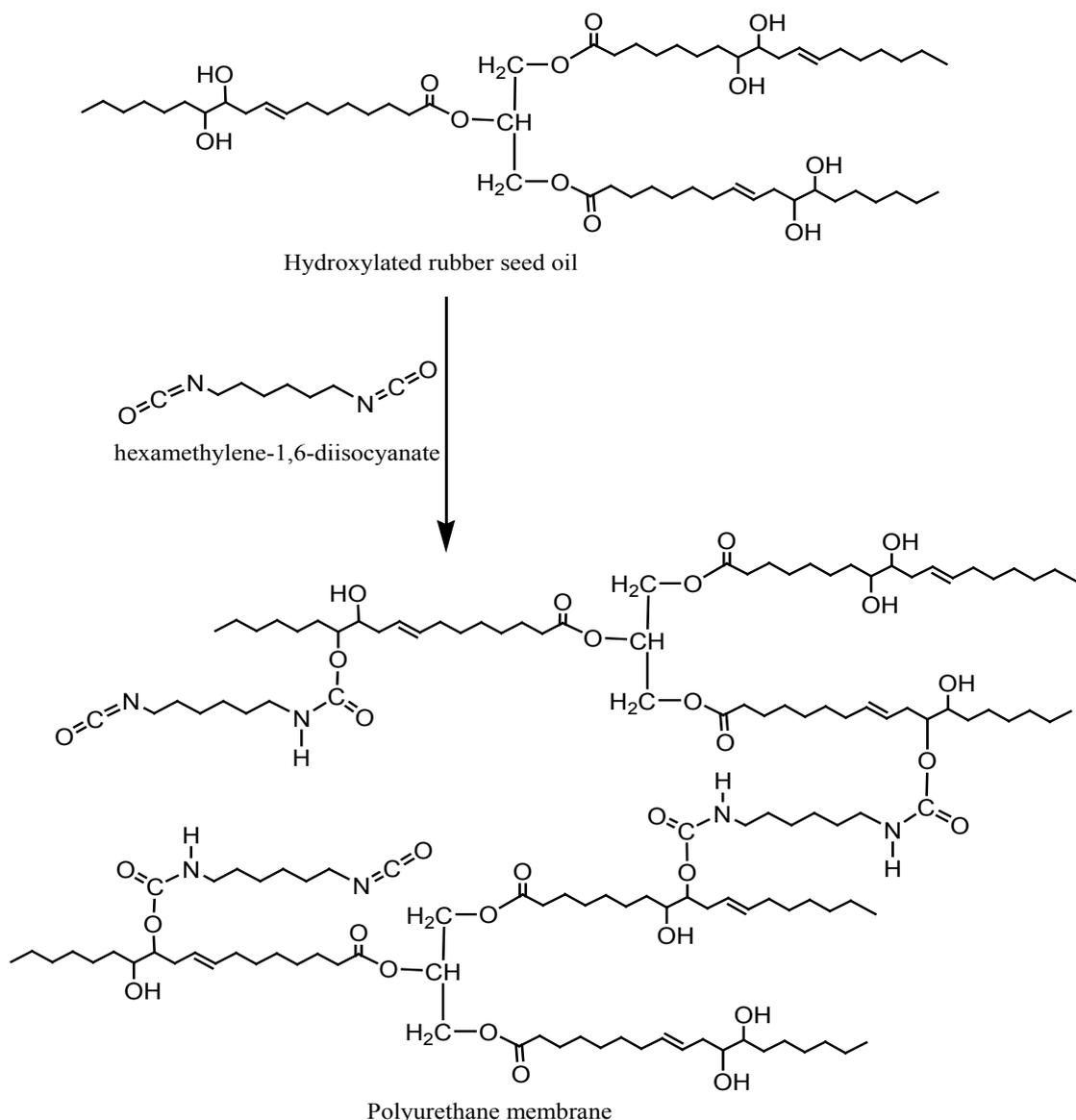


**Fig. 2: FTIR spectra of (a) rubber seed oil and (b) hydroxylated rubber seed oil**

bond was formed on the membrane. The structure was randomly or amorphous. Irregularities made polyurethane membrane morphology becomes hollow.

There here two stages of decomposition of the membrane, which has characterized by weight loss at temperature 223p C and 386p C. The first decomposition was occurred at the weakest point in the structure of macromolecules.

The and decomposition happen urethane, bond, the thermostable ware aromatic groups and ester groups of the soft segment in the structure of macromolecules<sup>8,9,10,11</sup>. Polyurethane membrane weight loss of 50% at a temperature of 410p C, weight loss of 90% at a temperature of 472p C and residual 4.3% at a temperature of 500p C. Thermal analysis using TGA showed two stages of decomposition as shown in Fig 6.



**Fig. 3: Suggested Hydroxylated reaction between linoleic acid and hexamethylene-1,6 diisocyanate**

Thermal analysis using DTA shows that the value  $T_g$  polyurethane membrane synthesized from hydroxylated rubber seed oil was 63°C. As seen in Fig 7, the glass transition was an endothermic shift at baseline because of the heat capacity of the sample was increase

Results of mechanical analysis showed that the polyurethane membrane was strong and

elastic, with a tensile strength of 1.13 kgf/mm<sup>2</sup> and elongation 215.36% Fig 8. Polyurethane membrane of rubber seed oil has more hydroxylated crosslinked (hard segment), so that when withdrawn are not prone to elongation, but the effect of the cross-linking of the membrane become stronger. Crosslinking result in higher tensile strength, so that the young modulus was also high.

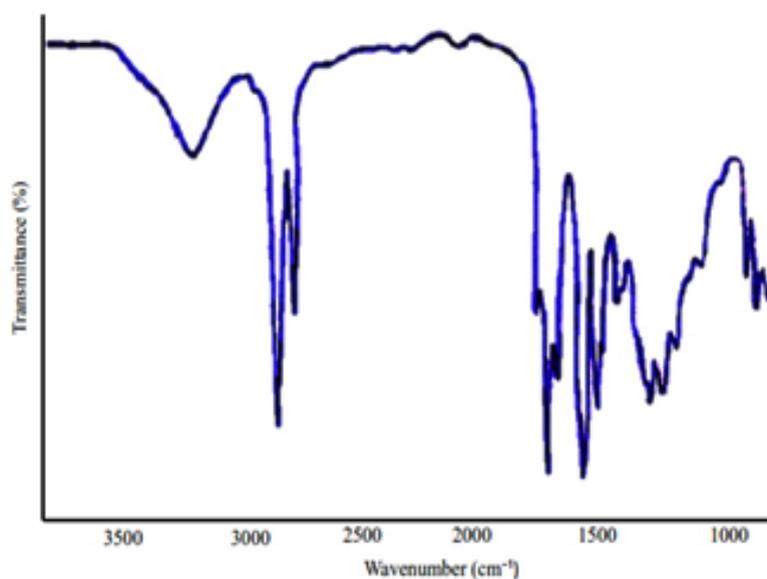


Fig. 4: FTIR spectra polyurethane membrane

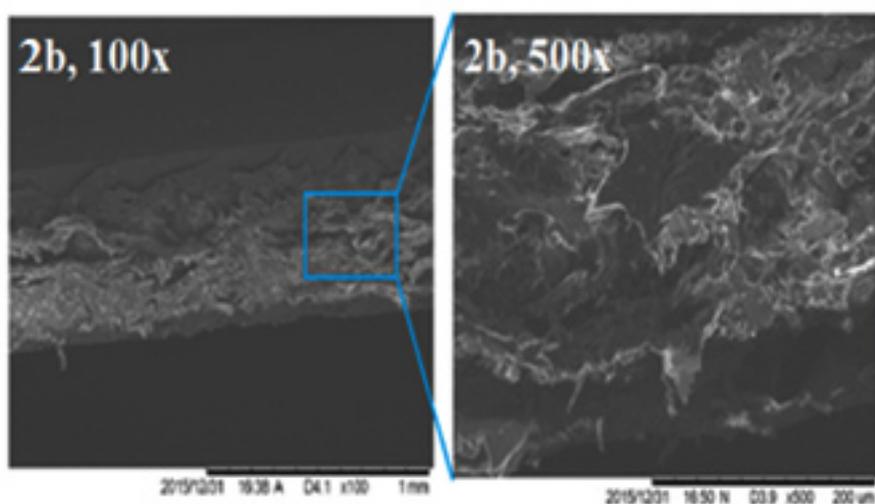


Fig. 5: SEM of polyurethane membrane with a magnification (2a) 100x and (2b) 500x

Hydroxylation process can improve hydroxyl number 135.30% and decrease 73.91% of the iodine number. Increasing hydroxyl number indicates an increase in the -OH group in the rubber seed oil. Hydroxylated rubber seed oil was reacted with hexamethylene-1,6-diisocyanate to produce polyurethane membrane. The optimum composition of the polyurethane membrane synthesized from hydroxylated rubber seed oil and hexamethylene-1,6-diisocyanate was 5:7 (v/w). The obtained membrane had properties of homogeneous, smooth,

dry (not greasy), a little stiff, brownish yellow, flux of 0,544 L/m<sup>2</sup>.h.bar and rejection factor of 98.86%. The results of characterization of polyurethane membrane indicated the formation of a urethane bond at wave number 3308 cm<sup>-1</sup>, has two stages of decomposition at 223°C and 386°C. The glass transition point 63°C, tensile strength 1,13 kgf/mm<sup>2</sup>, elongation 215.36%. The obtained polyurethane membrane can be classified on the type of reverse osmosis membrane.

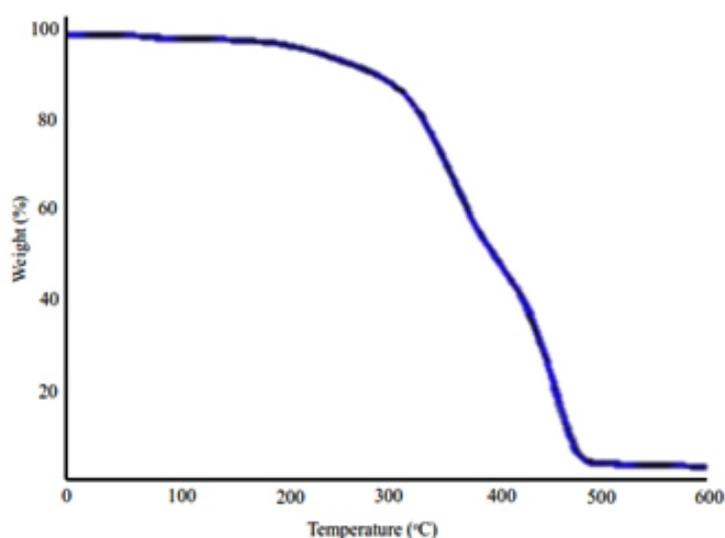


Fig. 6: TGA curves polyurethane membrane

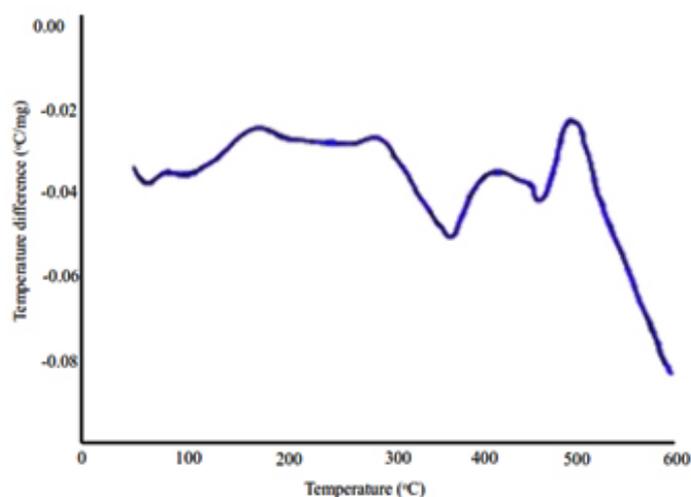
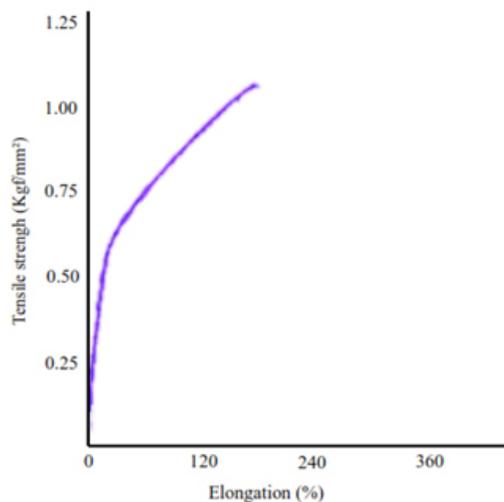


Fig. 7: DTA curve polyurethane membrane



**Fig. 8: Strain-stress curve polyurethane membrane**

#### ACKNOWLEDGEMENTS

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