POLYURETHANE MEMBRANE PROPERTIES BASED ON TREATMENT AND ITS COMPOSITION

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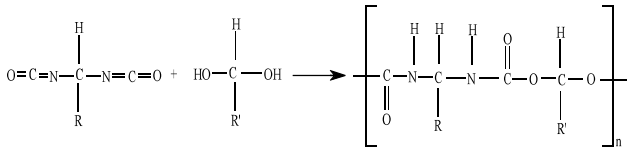
ABSTRACT: Protected process by acetylation on hydroxy groups affected free fatty acid properties as a monomer in polyurethane (PU) membrane synthesized. Synthesis process reached the optimum composition at OH : TDI 1.2 : 0.41 (mole/mole) for unprotected membranes and 1.2 : 0.52 (mole/mole) for protected membranes. Optimum performance in reverse osmosis aplication was reached at pressure 20 atm, indicating by flux of 29.61 L/m^2 h and rejection factor of 44,3 %. The result obtained was a transparent, elastic and strong film, with characteristics were polymerization completely occurred, i.e. hydrogen bonding index (HBI) of 0.43; glass transition temperature of 127.02 ^{o}C; decomposition temperature of 401.55 ^{o}C; crystallinity of 60.34 %; tensile strength of 328.45 Mpa, strain of 2.29 %, bursting strength of 767 Kpa, homogenouseous and smooth morphology before and after reverse osmosis application.

KEYWORDS: Free fatty acid, protection, acetylation, hydration, reverse osmosis

1. INTRODUCTION

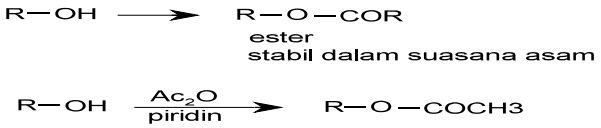
Polyurethane (PU) is a polymer which is produced by synthesis of various materials containing hydroxyl (-OH) groups, both of mono or poly with various diisocyanates. Some of polyhidroxy are polyethylene glycol (PEG), lactic acid, phenol, carbonimide, and residual sugar, and various diisocyanate are toylulene diisocianate (TDI), methylenediphenil diisocyanate (MDI), and isocyanate polymer (PMDI). Polyurethane is a well known polymer, it can be used as bed, sofa, car accessories, fiber, elastomer, and coating materials. PU products have various forms, from soft linear till thermosetting form, which is hard and rigid [1,2] , which the polymerization reaction is:



Castor Oil is derived from *Ricinus communis* L. seeds, belonging to Euphorbiacea family from Nangroe Aceh Darussalam, by soxhletation process using n-hexane as a solvent. Oil rendement per gram of castor bean is 45 – 48 % with viscous and had as same as properties the standard resulted by *The Association of Official Analytical Chemistry* (AOAC) and *American Standard for Testing Materials* (ASTM), which is indicated by physico-cemistry properties. Free fatty acid obtained from CO by coloum chromatography using n-hexanes and diklorometha ne as a solvent. Free fatty acid contain ricinoleic acid as a main compound (80 %) Ricinoleic acid having 3 double bond that can used as hydroxyl resource in polyurethane synthesis.

To make a membrane with dense pores and strong properties, the double bond structure of free fatty acid had to be modified to result hydroxy groups (-OH) by hydroxylation process. The aim of hydroxylation process is to add hydroxy groups into the double bond of oleic acid, so that crosslinking occurs with TDI, and to prevent deformation of polymer chains [7]. One of the hydroxylation process is hydration, where in this research hydration has carried out by using sulphuric acis as oxidator. Before applying the hydration process, the hydroxyl group of free fatty acid must be protected to prevent side reaction between hydroxyl group with sulphuric acid in use.

Protected process of hydroxyl (OH) or alcohol group will change the -OH group to be come ester or ether by specific reaction using specific reagent [5,8,9,10] , as example:



The result of protected process indicated by decreasing of hydroxyl number, change in refractive index, boiling point, and the structure.

Membrane is a diaphragma which is a porous material, where smaller size materials can diffuse through it. Membrane properties depend on monomers as membranes source material and the ways of membranes produced.

2. MATERIALS

All materials used in this works have pure analysis grade, i.e. n-hexane as a solvent, Na_2SO_4 anhydride, bentonite, cloroform, aquadest, acetyl anhydride, pyridin, NaOH, dimethyl sulphate, dimethyl formamide (DMF), K_2CO_3, H_2SO_4 as an oxidator, 2,4 toylulene diisocyanate (TDI), ethanol 95 % phenoftalein (pp), KOH 0,1 N, acetic acid glasial, I_2, Br_2, KI 15 %, $Na_2S_2O_3$ 0,1 N, amylum 1%, $K_2Cr_2O_7$, glycerine, dextrane, NaCl solution 2500 ppm, and CO.

Procedure

1. Free fatty acid Preparation

Free fatty acid derived from CO by extraction, using chloroform as a solvent. Free fatty acid yielded then evaporated and weighed (AOAC, 1995).

2. Hydroxylation Process

(i) Protection

Sample ca. 25 mL added acetic anhydride and pyridine ca. 0. 5 mL, cooling at 20 ^{o}C, then mix for 2 hours. Product extracted using chloroform, and then the organic phase evaporated by rotary evaporator. The result (oleic acid) was a viscous solution. Protected gathering by acetylation using acetyl reagent and pyridine as a base catalyst, at low temperature (20 ^{o}C).

(ii) Hydration

In this process, sample (protected product) amount 25 mL was added with water and a variation concentration of H_2SO_4 solution (5 - 35 %) ca. 2,5 mL in base condition, and mix for 90 min. Adding alkaline solution to release protective hydroxyl group, and then exracted using chloroform to remove residual water content. Organic phase i.e hydrated acid added Na_2SO_4, filtered, and evaporated.

(iii) Characterization

Measurement of all properties of pree fatty acid base on AOAC Official Methods of Analysis (1995).

3. Synthesis of Membranes

Dope solution of polyurethane made by polymerization of hydrated free fatty acid with TDI at various concentration, temperature and times. Membrane casted on glass plate, cured in oven at temperature 80 ^{o}C for 3 hours. Membrane resulted release from glass plate in flow water.

Measurement of membranes characterization includes hydrogen bonding index (HBI) using FT-IR Shimadzu 200-91538, glass trasition temperature using Differential Thermal Analysis (DTA) *General V4.1C Du Pont 2000*, crystalinity with X-Ray Difraction (XRD) Diano, tensile strength using Shimadzu Autograph AG-500 B, bursting strength *Mullen*, and apllied at reverse osmosis (RO) process.

3. RESULT AND DISCUSSION

A. Effect of Treatment

Table 1 showed the comparison of composition between -OH groups from free fatty acid and –NCO groups from isocyanate, by protected and unprotected occors on –OH groups. *Trial and error* process resulted optimum composition between free fatty acid and TDI, i.e.:

Table 1. Monomer Composition on PU Membrane Synthesis

Process	Concentration of OH:NCO (mole/mole)
Hydration (unprotected)	1,2 :0,41
Acetylation-Hydration	1,2 :0,52

Table 1 indicated that protected process affected polymerization reaction on PU membrane synthesis, This table also describes that protective free fatty acid has a higher hydroxyl value than the non-protective one, so it needed more TDI.

B. Effect of Diisocyanate Concentration

TDI concentration also affected on PU membrane properties yielded. If concentration of TDI more than as shown in table 1, so that the dope solution resulted more viscous, and PU membrane properties were strong and rigid. When concentration of TDI more than –OH, the membranes would be a rigid foam. This phenomenon showed that hard segment are produced more than soft segment in PU.

C. Characterization

Membranes obtained above were characterized included physico-chemical properties. Infrared analysis showed that no –CO from NCO absorption at wave number of 2272.9 cm^{-1} and –OH groups absorption at 3100 – 3300 cm^{-1} for membrane from acetylation-hydrated free fatty acid, but for membranes non protected was obtained. As a result, there was a new absorption at wave number of 3365 $cm^{-}1$, indicated as urethane group. This indicated that polymerization process has well occurred and completely. But, spectra of membranes from non protected free fatty acid showed that the absorption of -CO and –OH groups were weak, indicating that polymerization process did not occur completely.

Hydrogen bonding index (HBI) had measured from infra red structure, i.e. 0.49 for protective membrane and 0.43 for non protective one. This phenomenon caused by interaction between molecules in hard segment of protective membrane more than in soft segment.

Differential thermal analysis for measuring glass transition and decomposition temperatures showed that membrane from –acetylatated-hydration free fatty acid has this property higher than the other. This is caused due to of more cross linking and more harder segment formation in this membrane. So, to change it from solid to melt condition needed more energy. This result was supported by XRD analysis, where PU membrane from ptotective free fatty acid has a degree of crystalinity of 70.48 %. This value was higher than for other membrane, and indicated that the obtained was membrane strong and elastic enough for reverse osmosis application. Data of DTA and XRD measurements can be seen at table 2.

Table 2 Data of DTA and XRD analysis

Membranes	DTA		Crystalinity (%)
	Tg (°C)	TD (°C)	
Hydration	113.75	401.55	60.34
Acetylated Hydration	127.02	410.59	70.48

Data of stress-strain and bursting strength analysis are shown at table 3. Stress-strain measurement indicated that PU membrane from hydrated free fatty acid had a higher percentage of elongation than other. The membrane was transparent, elastic and strong. But, the results of bursting strength test gave the different results, where membrane from acetylatilated-hydration free fatty acid needed higher energy to breaking it than other membrane. This is caused of still existing double bond and some cross link occurred in this membrane, so that to break it made difficult.

Table 3 Data of stress-strain and bursting strength analysis

Membrane of	Stress-strain Analysis		Bursting strength (Kpa)
	Stress (Mpa)	Strain (%)	
Hydrated	328,45	2,29	767
Acetylated-Hydration	231,75	1,99	860

D. Reverse Osmosis

Membrane resulted above then applied at reverse osmosis process, using NaCl solution 2500 ppm as a feed, where pressure applied were from 10 to 20 atm.

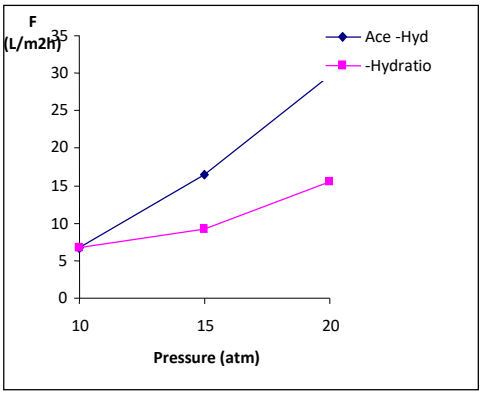


Figure 1 Flux vs pressure on reverse osmosis process

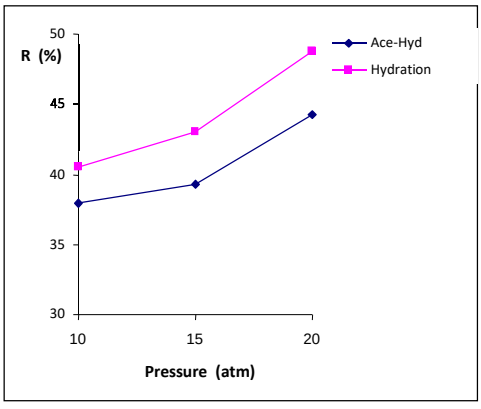


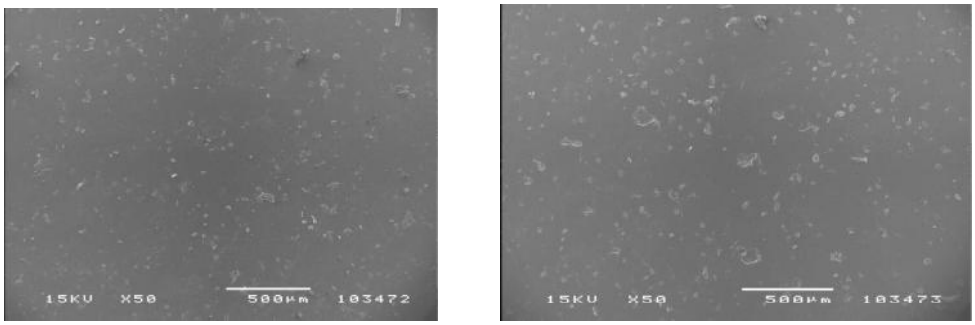
Figure 2 Rejection factor vs pressure on reverse osmosis process

From figure 1 dan figure 2 can be seen that optimum performance at reverse osmosis process resulted by PU membrane with protection process i.e flux was 29.61 L/m^2 h and rejection factor was 44.3 %. This showed

that there was a less performance membrane producted by non protected free fatty acid, so it was resulted minimum flux and maximum rejection factor. The higher the pressure applied

he higher flux and rejection factor resulted. From this experiment concluded that the membrane properties not maximum yet, so we have to find out the alternative ways of PU membrane preparation.

Analysis of membrane morphology by SEM instrument showed that the homogenous surface at Figure 3, before and after applied at reverse osmosis process. This fact indicated that this membrane has streght and can be used for a long time.



(a) (b)

Figure 3 Morphology of PU membrane from free fatty acid (a) before and (b) after reverse osmosis process

4. CONCLUSION

The present result indicated that:

1. Acetylation protected process affected PU membrane properties from free fatty acid of castor oil.
2. Optimum condition on PU membrane synthesis were –OH/-NCO 1.2 : 0,41 (mole/mole) for hydrated membrane without protected, and 1.2 : 0,52 (mole/mole) for acetylation protected membrane.
3. Membrane performance from protected free fatty acid on reverse osmosis process was flux 29.61 L/m^2 h and rejection factor 44.3 %. Membrane properties are homogenous, elastic and strenght.

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