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Castor Oil Based Polyurethanes: Synthesis and Characterization

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Abstract. In this study, polyurethanes based on castor oil and 1,6-hexamethylene diisocyanate (HMDI) were synthesized with varying weight ratio of the castor oil and HMDI. The formation of urethane linkages was verified through the use of a fourier transform infrared spectroscopy (FTIR). The hydrophilicity of the films was evaluated through the use of a contact angle meter and it was found that the contact angle of all the films were below 90 degrees which confirms their hydrophilicity. The thermal stability of the PU films were studies through the use of a thermal gravimetric analyzer and found that all of the polyurethane films exhibited two weight loss events at elevated temperatures wherein the first weight loss event was observed to occur at 285°C to 384°C while the second weight loss event was observed at around 521°C to 551°C. The hardness, elastic modulus, and tensile elongation of the PU films were determined by using a universal testing machine (UTM) where it was found out that the hardness and the elastic modulus of the film is directly proportional with HMDI loading while the tensile elongation is inversely proportional to it. Lastly, it was known through the swelling studies of the PU films that it does not swell, this is due to the presence of unreacted triglycerides in the material, which prevents water from permeating to the films.

1. Introduction

Bio-based materials are now receiving considerable attention in the promotion of sustainable chemistry in the production of materials by its replacement of petroleum-derived raw materials in the production of different products needed in various industries [1]. The shift to a more green way of chemistry is due to the increasing concerns about the environment and a shift to a more sustainable engineering are pushing scientist and engineers to research new ways to better understand renewable resources and how can they be used efficiently in the conversion of raw materials to products [2]. Polyurethanes, which are usually produced using diisocyanate is one of the materials receiving intensive studies today due to their potential in being used in different fields such as biomedical engineering and tissue engineering. These new polyurethanes which uses materials derived from vegetable oils like canola oil, castor oil, etc. can be used as a scaffold in which isolated cells may be seeded into which allows the cells to grow and proliferate until it forms a tissue construct which can then be implanted back to the patient [3]. These new polyurethanes may exhibit the ability to biodegrade, has excellent mechanical, chemical, and thermal properties, and has high wear resistance



and good blood and tissue compatibility [4]. Thus, the goal for the next generation development of bio-based polyurethanes is to develop a material which minimizes the side effect of diisocyanate which is toxic and to enhance traits which can improve the efficiency of the produced product. Another goal for this is to lessen the consumption of petroleum derived polymers which may contribute to the promotion of green chemistry and sustainable engineering. Polyurethanes mainly consist of a flexible soft segment and a hard segment derived from diisocyanate [1]. The effects of modifying the chemical structure of polyurethane is also not widely known, it may exhibit specific traits like it being rigid or flexible, or they can exhibit biodegradation or biostability when its chemical structure is modified which can be exploited to fit the traits of polyurethane to the needs of a specific industry. The main objective of this study is to synthesize polyurethanes using castor oil (with ricinoleic acid) and 1,6-hexamethylene diisocyanate. The second objective of this study is to characterize and compare the chemical, mechanical, and thermal properties of the synthesized polymer with different weight ratios of the hard and soft segments using different apparatuses. Its swelling study is also studied. This study will focus on synthesizing bio-based polymer and characterizing its properties that can be used in polymer production as an alternative source of raw material.

2. Methodology

2.1. Synthesis of castor oil based polyurethane films

Different weight ratios of castor oil and HMDI (95:5, 90:10, 85:15, 80:20, 70:30, 60:40, and 50:50) is added in a 50 mL beaker. Then, the mixtures are heated at 55 degrees Celsius and stirred at 220 rpm until the mixture is deemed to be viscous and also free from air bubbles. The mixture is then poured into glass slides and allowed to settle for 3 to 4 days until the reaction is complete after which the resulting polymer film is removed from the glass slide and then stored at a cabinet for characterization.

2.2. Characterization of the polyurethane films

The formation of urethane linkage for the PUs will be determined using Shimadzu IR Prestige 21 Fourier-Transform infrared spectrophotometer (FTIR). The thermal stability of the sample was determined by thermal gravimetric analysis using a Mettler Toledo TGA/SDTA 851e. The heating range set was from 30°C to 1000°C at a heating rate of 10°C per minute. The sample will be scanned for 32 times with a scan rate of 8 cm⁻¹ from 4000 to 600 cm⁻¹. Culture plates with bacteria were then incubated at 35 °C for 24 hours. Surface topography of the polymers was determined by shell electron microscopy using JEOL JSM5310. The polarity of a polyurethane film was tested by using a Theta Life Optical Tensiometer. First, the sample was affixed in the glass slide to make sure that the sample was flat for better results. Then, the sample was placed on the instrument. The volume of water drop used was 5±0.1 microliter for every trial and allowed to settle for 1 minute. The effect of varying the weight ratio of castor oil and HMDI on the mechanical properties of the PUs will be evaluated using an Instron Single Column Universal Testing Machine 3343 (UTM) equipped with an Instron 2519-103 Force Transducer with a 100N capacity. The samples were cut into 40 mm x 10 mm strips and were mounted onto the UTM. The mechanical properties of the PU samples such as elastic modulus, tensile strength and maximum tensile extension will then be determined. Stress-strain curves will be collected at a strain rate of 10 mm/min.

3. Results and Discussion

3.1. Synthesis of PU based on castor oil and 1, 6-hexamethylene diisocyanate

Polyurethanes (PU) films were successfully prepared by the coupling of 1,6-hexamethylene diisocyanate (HMDI) with castor oil, which is a polyhydroxylated triglyceride. The coupling reaction may facilitate the covalent linking between of triglyceride molecules. The proposed molecular structures of PUs with varying degrees of cross-linking are shown in Figure 1. Adding excess

amounts of HMDI facilitates the formation of urethane linkages between triglyceride molecules and then inter and intrachain crosslinking bridges are formed.

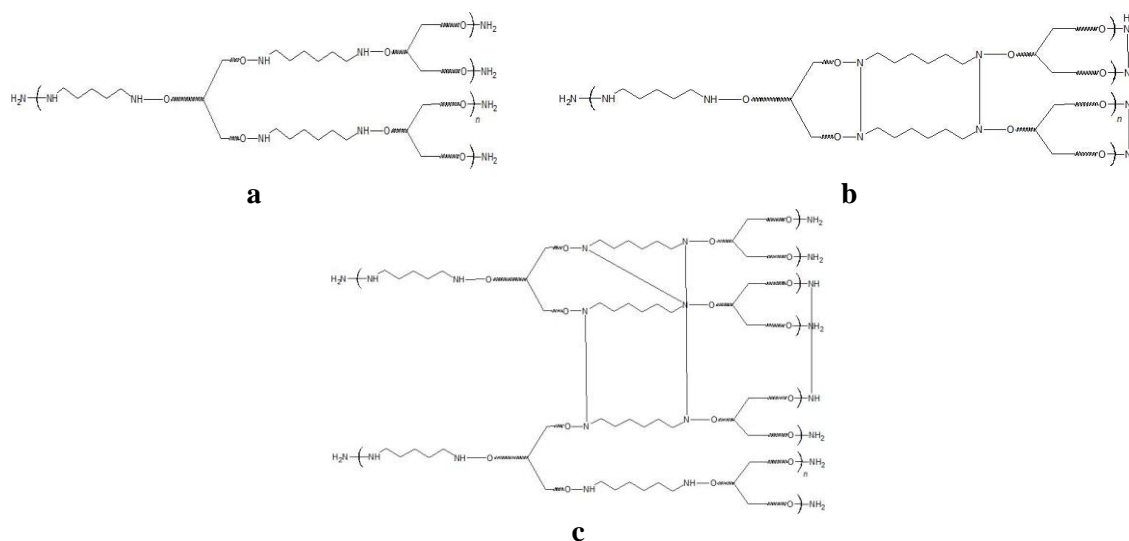


Figure 1. Proposed structure of castor oil and HMDI based PU: (a) uncrosslinked PU, (b) lightly crosslinked and (c) highly crosslinked PU structures

3.2. Molecular structure of the PU materials

The occurrence of urethane bond between HMDI and castor was determined by Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra of the of the pristine HMDI, castor oil and PU films are shown in Figure 2. The peaks at the wavenumber around 1535 cm^{-1} is indicative of urethane linkage (C-N-H) formation in all of the synthesized PU samples. In addition, vibration peak found at 3342 cm^{-1} corresponds to the amide N-H stretching in urethane. These two peaks are absent to the IR spectra of HMDI; while, pristine HMDI exhibited peaks at 2254 cm^{-1} to 2310 cm^{-1} , a unique peak which is attributed to the unreacted isocyanate group $\text{O}=\text{C}=\text{N}$. The peak at 1743 cm^{-1} which is attributed to the ester carbonyl ($\text{C}=\text{O}$) stretching of castor oil and urethane carbonyl. The bands between 2854 cm^{-1} and 2927 cm^{-1} are attributed to the methylene (CH_2) asymmetric and symmetric stretching vibration of the hydrocarbon chain of castor oil and HMDI. The peaks at 3008 cm^{-1} to 3014 cm^{-1} in the spectra of the PU films and castor oil is attributed to the methyl group (CH_3) stretching.

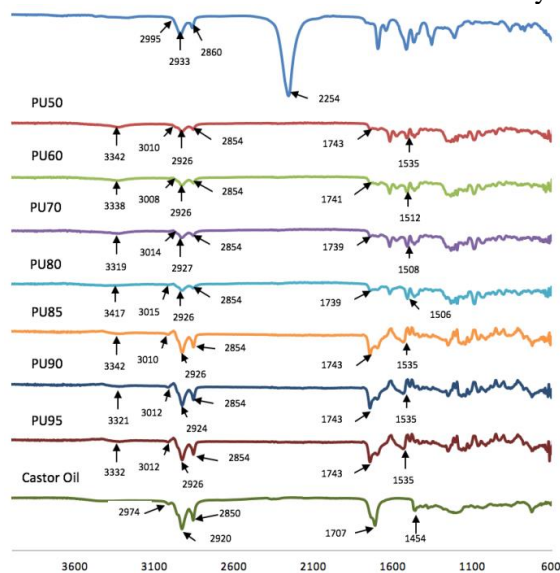


Figure 2. FTIR spectra of the PU materials

3.3. Thermal stability of PU materials

The thermograms of PU films and their derivatives are shown in Figures 3a and 3b respectively. All PUs exhibited two weight loss events at elevated temperatures. The first and the major weight loss event was observed to occur at 285°C to 384°C, which might be attributed to the thermal degradation or thermolysis of the ester linkage between the ricinoleic fatty acid to the glycerol backbone of castor oil. In addition, the first stage of decomposition is known to be dominated by urethane bond decomposition. The correlation of the amount of residue with the amount of unreacted isocyanate in polymers have found that even though the first stage of decomposition is subjected to urethane bond decomposition, the weight loss at higher conversion was possibly affected by polymer component. In addition, it can be observed that as the HMDI content is increasing, a shoulder peak becomes more prominent and is shifting from higher temperature 325°C (PU95) to 285°C (PU50). These shoulder peaks are quite near to the degradation temperature of pristine HMDI, thus it can be inferred that this shoulder peak is in fact the degradation temperature of HMDI. A second weight loss event is observed at around 521°C to 551°C and this peak is observed to shift to higher temperature with increasing HMDI loading. This weight loss event can be attributed to the decomposition of the hard segments of the PU films. The high amount of HMDI during the reaction promotes formation of allophanate bonds between urethane linkages. In the presence of excess of HMDI, almost all of the hydroxyl groups of castor reacts with HMDI; however, the same condition promotes the side reaction where excess HMDI reacts with the urethane linkage forming an allophanate. PU50 and PU60 are highly crosslinked because of allophanate bridges resulting to a more apparent second degradation event occurring at higher temperature. PU with lower HMDI content exhibited this second weight loss event but it occurs at a lower temperature relative to crosslinked PUs.

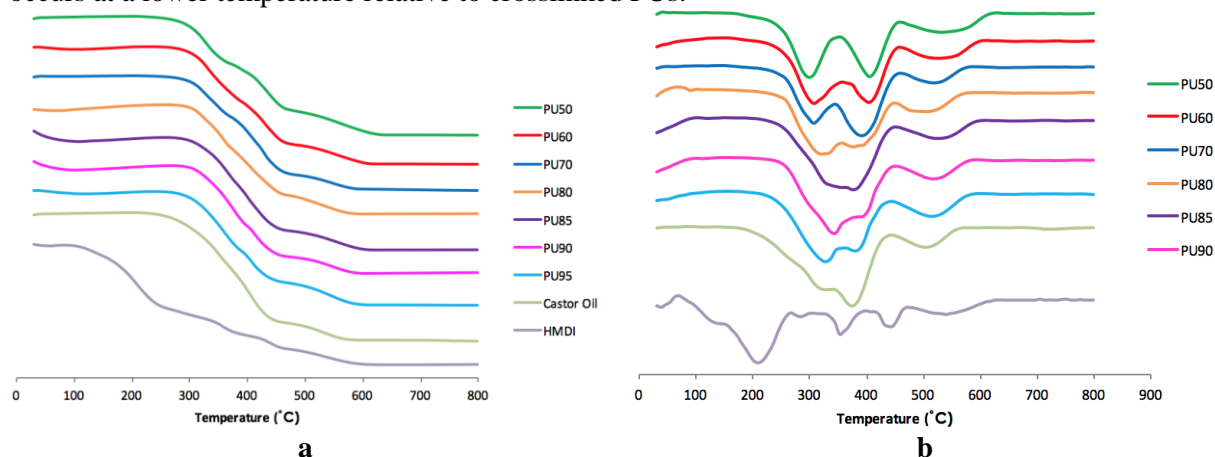


Figure 3. (a) Thermograms and (b) derivative of thermograms of the PU materials

3.4. Tensile properties of the PU materials

Stress strain curves of the polyurethanes (PU50, PU60, PU70, PU80) are separately shown in Figure 4 and the corresponding tensile properties of the PU materials are shown in Table 1. All of the polyurethanes have been found to be flexible. Since castor oil represents the soft segment part of the PU, the flexibility of the PU increases as the castor oil content increases. Based on stress-strain curve of all of the PU's, it was found that PU50 is least flexible because it has the least amount of castor oil content among the PU's. As the PU50 is the least flexible, it followed by PU60, PU70, PU80 to PU95 as PU95 is the most flexible among the PU due to its castor oil content. Regarding with the tensile strength, it was found the PU50 has the highest value of tensile strength among the PU's. Tensile strength of the PU was found directly proportional to the HMDI content of the PU since HMDI represent the hard segment part of the PU which is responsible for its hardness. Following the trend, PU50 has the highest value of tensile strength followed by PU60, PU70, PU80 to PU95 as PU95 has

the least value of the tensile strength due to its HMDI content. In addition, the elasticity of PU's varies significantly as the castor oil to HMDI weight ratio change.

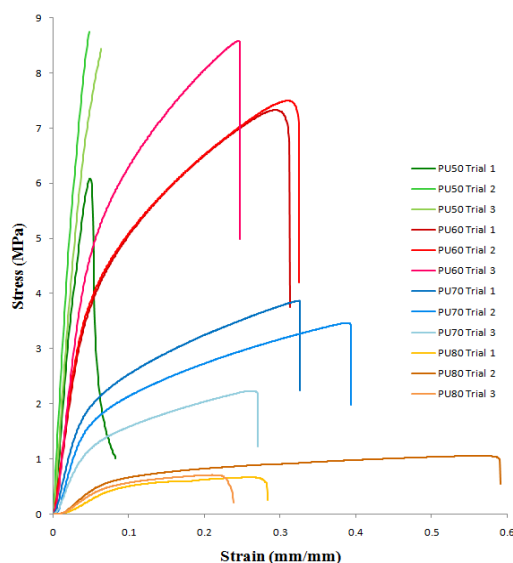


Figure 4. Stress-strain curves of the PU materials

Table 1. Elastic Modulus and Tensile elongation of Polyurethane

Polyurethane Code	Elastic Modulus (MPa)	Tensile Elongation (mm)
PU50	208.37804	2.57917
PU60	88.55964	11.78859
PU70	30.78883	13.20859
PU80	7.877735	14.83083
PU85	2.64017	5.58287
PU90	2.05394	5.77198
PU95	0.19691	4.58656

3.5. Surface properties of the PU materials

The surface morphology of the PU films was observed and recorded by scanning electron microscopy and the micrographs are shown in Figure 5. The surface of the films with high HMDI content, PU50 and PU60, showed the highest surface roughness at high magnification (15,000X), with the presence of peaks and valleys. These features were not so apparent at lower magnification. The roughness of the PU's surface might be due to the shrinkage of the polymer chains after covalent crosslinking. The surface morphology of the PUs with intermediate amount of HMDI exhibited a smoother surface morphology than those that have high HMDI content and this might be due to the less extensive crosslinking of the polymer matrices. PUs with the lowest HMDI content, PU85, PU90 and PU95, did not completely dry up allowing the samples to react for 4 days which makes it unsuitable for electron microscopy. It might be due to presence of completely or partially unreacted triglycerides.

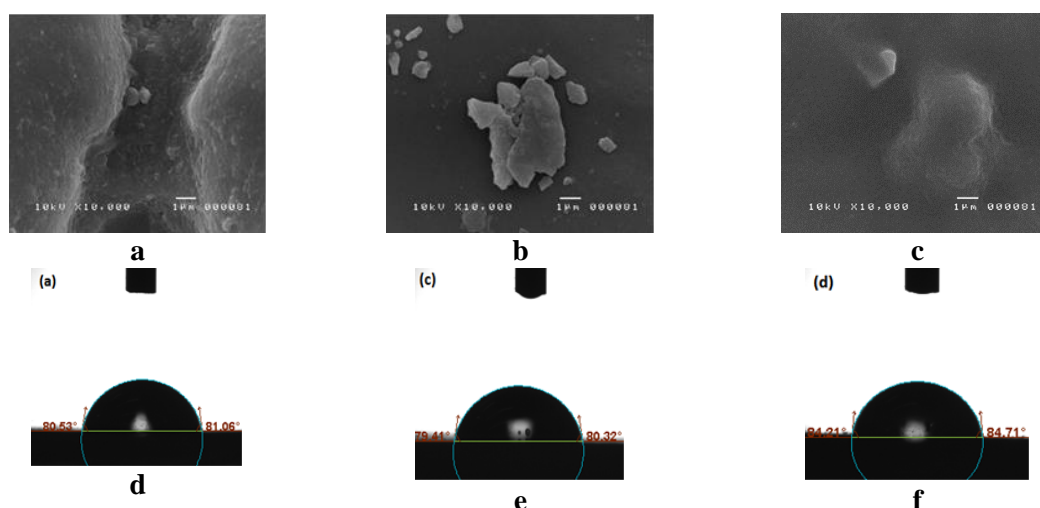


Figure 5. Electron micrographs of (a) PU50, (b) PU70 and (c) PU80. Water contact angle of (d) PU50, (e) PU70 and (f) PU80

The hydrophilicity of the polyester urethane films is evaluated through the measurement of the contact angle formed as water is dropped onto the surface of the films via a contact angle meter. Coatings can be described by their measured contact angle, a coating with contact angle below 90 degrees is considered to be hydrophilic, between 90 to 150 degrees is considered to be hydrophobic, and above 150 degrees is considered as ultra-hydrophobic. As seen on the figures above, the contact angle in all of the PEU film samples is lower than 90 degrees, which indicates that the film is hydrophilic in nature. Although vegetable oils are hydrophobic in nature due to the hydrophobicity of triglycerides, the use of a hydrophilic isocyanate such as HMDI together with changes in the surface roughness of the PEU films should make a PEU film hydrophilic. As such, this type of PEU can be used as biomaterials, filter membranes, biosensors, water permeable materials, etc. [5], [6].

4. Conclusion

Polyurethanes films were prepared by the coupling reaction of castor oil and HMDI. The polyurethane films exhibited the formation urethane linkage (C-N-H) formation, amide N-H stretching, ester carbonyl (C=O) stretching between castor oil and urethane carbonyl based on FTIR spectroscopy. The PU films were found to be thermally stable by thermogravimetry with degradation temperature greater than 300°C. The surface morphology of the PU films was observed to increase in surface roughness with increasing HMDI content due to the formation of highly crosslinked polymer network. The PU films were found to be slightly non polar by water contact angle meter. The tensile properties of the PU films varied with the HMDI content; where PUs with high HMDI content were rigid and inelastic while PUs with low HMDI content were soft and pliable. The present study demonstrated a facile method of preparing PUs with a wide range of physical properties.

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