Structure-Property Studies of Thermoplastic and Thermosetting Polyurethanes Using Palm and Soya Oils-Based Polyols

Issam Ahmed Mohammed1*, Emad Abbas Jaffar Al-Mulla2, Nurul Khizien Abdul Kadar3 and Mazlan Ibrahim3

1 Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
2 Department of Chemistry, College of Science, University of Kufa, P.O. Box 21, An-Najaf, 54001, Iraq
3 School of Industrial Technology, University Sains Malaysia, 11800 Penang, Malaysia

Abstract: Palm and soya oils were converted to monoglycerides via transesterification of triglycerides with glycerol by one step process to produce renewable polyols. Thermoplastic polyurethanes (TPPUs) were prepared from the reaction of the monoglycerides which act as polyol with 4,4′-methylene diphenyl diisocyanate (MDI) whereas, thermosetting polyurethanes (TSPUs) were prepared from the reaction of glycerol, MDI and monoglycerides in one pot. Characterization of the polyurethanes was carried out by FT-IR, ¹H NMR, and iodine value and sol-gel fraction. The TSPUs showed good thermal properties compared to TPPUs as well as TSPUs exhibits good properties in pencil hardness and adhesion, however poorer in flexural and impact strength compared to TPPUs. The higher percentage of cross linked fraction, the higher degree of cross linking occurred, which is due to the higher number of double bond presents in the TSPUs. These were reflected in iodine value test as the highest iodine value of the soya-based thermosetting polyurethanes confirmed the highest degree of cross linking. Polyurethanes based on soya oil showed better properties compared to palm oil. This study is a breakthrough development of polyurethane resins using palm and soya oils as one of the raw materials.

Key words: monoglyceride, palm oil, soya oil, polyurethane, thermoplastic, thermosetting

1 INTRODUCTION

Polyurethane is a versatile polymer which had been found an increasingly outstanding position among the most important organic polymers in coating industries, elastomeric items, and materials for engineering, biomaterials in implants, electronic and technological applications as their structure can be tailor-made to suit specific requirements due to the vast variety of raw materials available of polyols and isocyanates.

Thermoplastic polyurethane is a linear segmented block copolymer composed of hard and soft segments that can be deformed plastically under the influence of heat and returns to solid when cooled. On the other hand, thermosetting polyurethane which is highly cross-linked polymer behaves differently as they cannot be melted after curing process. Both thermoplastic and thermosetting polyurethanes are usually consumed petroleum as their raw material in products such as coated fabrics, wire coatings, shoe soles and sporting goods for thermoplastic, while the tough and durable with high temperature of thermosetting polyurethane is found in some polymeric coatings, electronic chips and composites.

As worldwide demands for replacing petroleum derived raw materials because of fluctuating price of petroleum and stringent environmental rules have driven the utilization of the natural renewable resources. Thus, vegetable oils also can be one of the important raw materials as the general chemical composition of vegetable oils is triglycerides. It is an ester derived from glycerol and fatty acids that mostly composed of saturated and unsaturated compounds. In Malaysia, palm oil that produced from oil palm, Elaeis guineensis is largely cultivated that the industry forms the economic backbone of Malaysia and makes up the major part of the stocks in the world. Furthermore, soybean also cultivated in Malaysia that producing soya oil and other products with growing demands.

*Correspondence to: Issam Ahmed Mohammed, Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
E-mail: issam@upm.edu.my, and Emad A. Jaffar Al-Mulla, E-mail: almullaemad@gmail.com
Accepted June 19, 2013 (received for review April 30, 2013)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/ http://mc.manuscriptcentral.com/jjocs
In recent years, enormous research and development works on vegetable oil utilization have been carried out due to the global economy and environmental friendly alternative to petroleum resources. Most studies of vegetable oils were focused on polyurethanes preparation as polyurethane foams and elastomers. However, studies on vegetable oil based polyurethane coatings are still progressing while for palm oil-based polyurethane, there has not been published yet. Besides that, the polyol derived from vegetable oils were usually achieved by two steps processes namely: (1) epoxidization of vegetable oils and followed by alcoholysis, (2) hydroformylation of vegetable oils followed by hydrogenation or ozonolysis and hydrogenation of vegetable oils. Whereas in this research, green polyols based on palm and soya oils would undergo one step process which would replace the petroleum-based polyols for polyurethane coatings and considered environmental friendly and low in cost.

2 EXPERIMENTAL
2.1 Materials
All chemicals used in this study were obtained from commercial sources and used either further purification or distillation before used. Palm and soybean oils were purchased from commercial market from Malaysia and used as received. Glycerol and calcium oxide were purchased from Fluka Chemicals, USA and used as received. 4,4'-methylenebis(phenylisocyanate) (MDI) was purchased from Sigma-Aldrich, USA. N,N-dimethylformamide (DMF) was purchased from Fluka Chemicals, USA and distilled with CaH₂. Chemicals used for testing such as sodium hydroxide, (NaOH) and potassium hydrogen phthalate, (KHP) were purchased from Fisher Chemicals, UK whereas sodium chloride was purchased from Systerm, USA.

2.2 Polyol (monomer) preparation
This section described the synthesis of the vegetable oil-based polyol where 200 g of palm and soya oils were first reacted separately with glycerol (143.70 g for PO and 125.60 g for SO) in the presence of 0.1% calcium oxide as a catalyst (based on oil) and heated to 235°C for 3 hours until monoglyceride formed, a small portion of the reaction mixture was taken out to test the solubility in ethanol. The reaction continued until no emulsion or white spots were observed and finally the polyol was left to cool and poured into the beaker for further experiment. The properties of the polyols are listed in Table 1. Scheme 1 depicts the structure of palm and soybean-oil monoglycerides.

2.3 Determination of Hydroxyl Content
The hydroxyl value of the polyols was determined according to ASTM titration method D 1957-86 using a hydroxyl number reagent (a mixture of phthalic anhydride and pyridine) and potassium hydroxide as the titrant. The hydroxyl value, hydroxyl content and equivalent weight of polyols were calculated by using the following equations:

$$\text{Hydroxyl value} = \frac{5.61 \times N \times (m_{L_{\text{blank}}} - m_{L_{\text{sample}}})}{\text{sample weight (g)}}$$

$$\text{Hydroxyl content (\%)} = \frac{\text{Hydroxyl value}}{33}$$

Table 1 Properties of palm and soya-oil polyols.

<table>
<thead>
<tr>
<th>Type of polyols</th>
<th>Hydroxyl value, mg KOH/g</th>
<th>Viscosity, cps</th>
<th>Equivalent Weight</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm Oil</td>
<td>233</td>
<td>3186</td>
<td>24.03</td>
<td>Dark Brown</td>
</tr>
<tr>
<td>Soya Oil</td>
<td>251</td>
<td>3290</td>
<td>22.31</td>
<td>Pale Yellow</td>
</tr>
</tbody>
</table>

Scheme 1 Synthetic route of the monoglycerides by one step reaction.

R = Fatty acid of oils
-(CH₂)₇CH=CH(CH₂)₇CH₃ (Oleic)
-(CH₂)₇CH=CHCH₂CH=CH(CH₂)₆CH₃

2.4 Synthesis of thermoplastic and thermosetting polyurethanes

Thermoplastic polyurethanes (TPPUs) were synthesized by a one-pot polymerization process as illustrated in Scheme 2. The monoglycerides of palm (0.030 mol) or soybean oils (0.028 mol) were transferred separately into a three-neck round bottom flask which was equipped with a nitrogen gas inlet, mechanical stirrer and a dropping funnel. By means of 1:1 ratio of polyol and isocyanate, MDI (0.030 mol for PO and 0.028 mol for SO) was added into the flask with appropriate amount of DMF, and the reaction was allowed to stir in inert atmosphere for 2 hours at temperature of 70°C with vigorous stirring. The temperature of the reaction was increased to 110°C and continued for 10 hours for completion of reaction.

Thermosetting polyurethanes (TSPUs) were synthesized by a one-pot polymerization as illustrated in Scheme 3 with 1:3:2 ratio of glycerol, isocyanate and polyol. First, the 0.54 mol of glycerol was reacted with MDI (1.62 mol) into the flask for 2 hours at temperature of 70°C. Then, the polyols (1.08 mol) were added gradually into the flask and stirred for an hour, after that the temperature of the reaction was raised to 110°C for 10 hours for completion of reaction.

The experimental yields of TPPUs and TSPUs were approximately around 77–79%. The polyurethane products were divided to equivalent amount for analyses. The thermoplastic and thermosetting polyurethanes were coated onto the flat surfaces of glass and aluminum substrates with 90 μm of aperture coated by SHEEN Hand Coater and furthermore, they were transferred into an oven and heated at 70°C for 2 hours to remove solvent residues. The thermosetting polyurethanes then were post-cured at 120°C for 10 hours.

2.5 Testing

The Infrared spectra for palm and soya oil-polyols and synthesized thermoplastic and thermosetting polyurethanes were analyzed on a Nicolet FT-IR Avatar Model 360 spectrometer. All the spectra were recorded within the wavenumber range of 4000-400 cm⁻¹. ¹H NMR spectra were recorded by a Bruker 400 MHz NMR spectrophotometer using dimethyl sulfoxide (DMSO-d₆) as a solvent, and tetramethylsilane (TMS) as the internal reference. The morphology study of the polyurethanes' coats was investigated with a field-emission scanning electron microscope (FE-SEM) Leo Supra 50VP and the specimens were sputter coated with a thin layer of gold.

Iodine value test was used to determine the amount of unsaturated groups present in synthesized TPPUs and TSPUs.
TSPUs according to Lubrizol Standard AATM 112-01\textsuperscript{21}. Weight of 0.25 g (for TPPU-PO) and 0.16 g (for TPPU-SO and TSPUs) was dissolved respectively in ten milliliter of chloroform and Twenty five milliliter of Hanus solution, mixed thoroughly by swirling and placed in the dark for 1 hour. Twenty milliliter of 10\% potassium iodine solution was added followed by titration to an end point of yellow color with the standardized 0.1 N sodium thiosulfate. three milliliter of starch solution was added and the titration was continued until a clear and colorless solution. The volume of sodium thiosulfate was recorded and the iodine number was calculated using the equation as shown below:

\[
\text{Iodine Value} = \frac{(mL_{\text{blank}} - mL_{\text{sample}}) \times N \times \text{Na}_2\text{S}_2\text{O}_3 \times 12.69}{\text{Sample Weight}} \tag{3}
\]

Sol-gel analysis was performed to determine cross linking degree\textsuperscript{20}. About 0.05 g of 1 cm x 4 cm of TSPU was placed in a 20 mL of chloroform and was allowed to remain in the solvent for 24 hours at room temperature. The swollen gel was taken from the solvent and dried in a vacuum oven at 20\textdegree C. The remaining solution was evaporated and the polymer residue was dried in a vacuum oven at 20\textdegree C. Cross linked fraction in the sample was calculated as shown below:

\[
\text{Cross linked fraction, wt} = \frac{\text{Sample Weight} - \text{Polymer Residue Weight}}{\text{Sample Weight}} \times 100 \tag{4}
\]

Thermogravimetric analyses (TGA) were performed using a Perkin Elmer Pyris Series 6 thermal analyzer. The measurements were performed in nitrogen atmosphere with a heating rate of 20\textdegree C min\textsuperscript{-1} from room temperature to 800\textdegree C and the weight loss of the sample was measured as a function of temperature. Differential Scanning Calorimetry (DSC) was conducted using Perkin-Elmer Pyris Series 7 thermal analyzer under a nitrogen purge at 20\textdegree C min\textsuperscript{-1}.

Impact strength tests were carried out by SHEEN Tubular Impact Tester. The coated aluminum panels were placed on the base and a standard falling load of 1 kg was impacted on the panels until crack were formed on the coating.

Aluminum panels were used as substrates for the Mandrel Bend Test according to ASTM D 522 Method B. The panels were bent over approximately 180\textdegree angle around the mandrel and the resistance to crack of the coating was determined. The panels were bent over to various number of cyndrical mandrel until a crack is visible starting from largest to smallest diameter. The total elongations of coatings were determined by formula:

\[
E = e_1 + tc_1 \tag{5}
\]

where \(E\) = total elongation, \(\%\), \(e_1\) = elongation, \(t\) = thickness, and \(c_1\) = correction factor.

Pencil hardness test done according to ASTM D 3363-92 standard method. Two types of substrates are used which is aluminum plate and glass. A set of 14 pencils with differ-
ent hardness ranging from 6B to 6H were used to carry out this test. The test procedure started with the hardest pencil to be held at a 45° angle while being pushed firmly across the surface of the coating and continues using progressively softer pencils until the hardest pencil that does not scratch, rupture or permanently indent the surface of the coating has been established.

The cross-hatch adhesion test was performed according to the cross-hatch adhesion test method ASTM D3359-97. A lattice pattern of cuts at right angle with similar spacing was made on the surface of plates with the cross-hatch cutter and commercial cellophane tape was applied over the lattice. The adhesion of the coating was classified according to 0B (90-100% of coating are detached), 1B (35-65% of coating are detached), 2B (15-35% of coating are detached), 3B (5-15% of coating are detached), 4B (5% of coating are detached) and 5B (0% of coating are detached).

The water and chemical resistance was determined on coated glass plates that had been allowed to dry for three days. The plates were immersed vertically in distilled water (according to ASTM D1647-89), alkali solution (10% NaOH), salt solution (25% NaCl), acid solution (10% HCl), alcohol (ethanol), ketone (acetone), or hydrocarbon solvent (xylene). Any changes in appearance were observed after 48 hours.

3 RESULTS AND DISCUSSION

3.1 Characterization

FT-IR spectra performed in vegetable oils-based polyols, diisocyanate, TPPUs and TSPUs were shown in Fig. 1. In palm oil polyol (PO-polyol) and soya oil polyol (SO-polyol), two broad stretching bands at 3460-3480 cm⁻¹ were assigned to the presence of hydroxyl groups. The absorption bands at 2850-2930 cm⁻¹ were attributed to the symmetric and non-symmetric stretching of the aliphatic C-H of polyols, whereas a small absorption peak was observed at 3008 cm⁻¹ (soya-polyol) and 3010 cm⁻¹ (palm-polyol) indicates the presence of the alkene = C-H stretching vibrations in the polyols. Ester group in the polyols exhibit their carbonyl C=O stretch at 1739 cm⁻¹ and 1736 cm⁻¹, and also the absorption bands at 1047-1241 cm⁻¹ from the couplings of C-O and C-C. The appearance of absorption band at 721 cm⁻¹ exhibits cis-isomer of alkene C=C in both polyols.

The absorption peak of isocyanate groups for MDI was observed at 2430 cm⁻¹ and this peak had been proven to disappear for the polyurethanes. N-H stretching vibrations.
of TPPUs and TSPUs’ urethane groups were observed at 3310-3345 cm\(^{-1}\). It was secondary amine exhibits in the polyurethanes as there was one band spotted in the spectra. The N-H bending bands were observed at lower wavenumbers (1590-1645 cm\(^{-1}\)) proposed hydrogen bonding between hard and soft segments or either the hard segments\(^{25}\). Another characteristic of amine presented in the polyurethanes is multiple C-N stretching vibrations at 1176-1307 cm\(^{-1}\). The absorption peaks for C = O of the urethane linkage in the TPPUs and TSPUs were spotted at 1740-1783 cm\(^{-1}\). These peaks suggest that urethane groups are formed by the reaction of MDI with polyols\(^{18}\).

Aromatic compounds contain delocalized π electrons from the resonance-stabilized double bonds (C=C) and C-C within the ring showing skeletal vibrations at 1597-1405 cm\(^{-1}\), whereas the absorption bands at 3000-3006 cm\(^{-1}\) were contributed by the stretching of aromatic C-H. Furthermore, the presence of absorption bands of 650-910 cm\(^{-1}\) in the region usually indicates the aromatic characters\(^{26}\). In addition, the appearance of absorption bands at 755-757 cm\(^{-1}\) commonly exhibits cis-isomer of alkene C=C.

The structure of the polyol was supported by \(^{1}H\) NMR spectrometer as shown in Fig. 2. The triplet peak at δ = 0.86 ppm was due to the terminal methyl group and the strong multiplet peaks at δ = 1.24 ppm and δ = 1.51 ppm were due to the protons in the methylene –CH\(_2\) groups and the proton attached next to the terminal methyl group of the fatty acid chains, respectively. The proton of the C = C-H vinylic groups of the monoglyceride was observed at δ = 4.00 ppm (multiplet) and δ = 5.33 ppm. The –CH\(_2\) protons adjacent to –OH groups and the proton of –OH groups were appeared at δ = 4.85 ppm and δ = 4.86 ppm, respectively. As there were no aromatic groups present in the compound, the peaks were observed below δ = 7.00 ppm.

The \(^{1}H\) NMR study for thermoplastic polyurethanes (TPPUs) and thermosetting polyurethanes (TSPUs) were shown in Fig. 3 and 4, respectively. The peaks ranged at δ = 0.86 ppm to δ = 5.33 ppm (as assigned as a-e and j-l) were the backbone of polyol as shown in Fig. 2. The peaks at δ = 3.80 ppm showed the –CH\(_2\) adjacent to the aromatic group. The peak at δ = 3.46 ppm confirmed the –CH\(_2\) protons of glycerol moiety attached to the urethane linkages\(^{27}\) and the –CH proton adjacent to ester groups are found at δ = 3.62 ppm. The proton for –CH of glycerol, unsaturation of fatty acid and hydroxyl group showed at δ = 7.11 ppm and δ = 7.40 ppm were assigned to the protons of aromatic ring\(^{27}\). The proton of –NH of the urethane linkage was observed at δ = 8.50 ppm. Thus, the spectra analyses confirmed the formation of vegetable oil polyol based polyurethanes.

The number of double bonds present in the polyurethanes was determined by iodine value test as iodine compounds react with the double bond. According to the results in Table 2, soya oil based polyurethanes showed the highest iodine value than palm oil based polyurethanes. Thus, it shows that higher the iodine value, the higher the double bond for cross linking in the composition.

Cross linked fraction in sol-gel analysis refers to the degree of cross linking occurred in TSPUs as shown in Table 2. Both TSPUs have high percentage of more than 90% which TSPU-SO showed the highest fraction (93.87% with STDEV ± 0.17) whilst 91.25% with STDEV ± 0.22 of TSPU-PO. The higher percentage of cross linked fraction, the higher degree of cross linking occurred, which was due
Structure-Property Studies of Thermoplastic and Thermo-setting Polyurethanes Using Palm and Soya Oils-Based Polyols

Fig. 3 $^1$H NMR spectrum of TPPU in DMSO-d$_6$.

Fig. 4 $^1$H NMR spectrum of TSPU in DMSO-d$_6$ by heating.

Table 2  Iodine value, sol-gel fraction, pencil hardness and adhesion of TPPUs and TSPUs.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Thermoplastic PU</th>
<th>Thermoset PU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Palm Oil</td>
<td>Soya Oil</td>
</tr>
<tr>
<td>Iodine Value (g/100 g)</td>
<td>58.17</td>
<td>103.12</td>
</tr>
<tr>
<td>Sol-Gel Fraction, %</td>
<td></td>
<td>91.25%</td>
</tr>
<tr>
<td>(± 0.22)</td>
<td></td>
<td>(± 0.17)</td>
</tr>
<tr>
<td>Hardness</td>
<td>H</td>
<td>2H</td>
</tr>
<tr>
<td>Adhesion</td>
<td>3B</td>
<td>4B</td>
</tr>
<tr>
<td>Glass</td>
<td>3B</td>
<td>4B</td>
</tr>
<tr>
<td>Aluminum</td>
<td>3B</td>
<td>4B</td>
</tr>
</tbody>
</table>

* 6B 5B 4B 3B 2B B HB F H 2H 3H 4H 5H 6H
Slofter Harder
** Cross-hatch adhesion
3B= 5-15% detached coating, 4B= 1-5% detached coating

3.2 Morphological study

The morphological study of thermoplastic and thermosetting polyurethanes (TPPUs and TSPUs) would assist us to study the molecular shapes and the way of molecules is arranged in the polymers. The study was carried out by scanning electron micrographs as shown in Fig. 5 and 6.

Fig. 5  SEM micrographs of surface of TPPUs and TSPUs.

to the higher number of double bonds present in the TSPUs. These were reflected in iodine value test as the highest iodine value of TSPU-SO confirmed the highest degree of crosslinking.
respectively. Figure 5 displayed the TPPUs and TSPUs of both palm oil and soya oil and a uniform matrix with small whitish speckled was discovered protruding from the polymer surface of the TPPUs.

The TSPUs showed some branching-like structure and some spheres located randomly with clear whitish speckled protruding from the surface. Xu et al. (2008)\textsuperscript{25} was reported to found a protruding "spherulitic-like" structure in his study of castor oil based polyurethane cast film which he believed it was attributed to the hard segment contents. From my observation in both TPPUs and TSPUs for palm oil and soya oil, they demonstrate several similarities with the surface morphology in terms of whitish speckled protruding from the polymer surface.

In comparison of the palm and soya oils based TSPUs as shown above in Fig. 5, TSPU-SO possessed more protruding "spherulitic-like" structure of the hard segment contents than TSPU-PO. This can be reflected with the cross-linking fraction of TSPUs shown in Table 2 where TSPU-SO proved to have the highest percentage of cross-linking fraction indicated more cross-linking in the composition occurred. However, there is no much difference in terms of molecular shapes and arrangement between palm and soya oils based TSPUs.

The surface of hard segment contents found from the polyurethanes’ surface was observed at higher magnification as shown in Fig. 6 to discover their further structures where it was observed to exhibit a large number of granular structures. Coarse-grained structure of TPPUs was displayed whereas a smooth-grained structure was observed in TSPUs. By comparing the micrographs of TPPUs and TSPUs, it can be seen enhancement in phase distribution of the hard segment contents in TSPUs.

3.3 Thermal properties

Figure 7 showed TGA curves of the thermoplastic (TPPUs) and thermosetting (TSPUs) polyurethanes where two steps of degradation were occurred and the shapes of the weight loss curves for all polyurethanes were almost identical. TGA curves provide the information about the decomposition behavior, the temperature up to which the coating can work without appreciable degradation of the coating\textsuperscript{28}. In general, the thermo-stability of polyurethanes depends on the number of aromatic moieties and the urethane linkages, as they can withstand an suitable amount of heat\textsuperscript{27}. As shown in the figure, the first step thermal degradation of TPPUs and TSPUs were due to the decomposition of the urethane group which start around 200 to
The second degradation occurred around 400 to 500°C was due to the decomposition of aromatic rings in the backbone of the polyurethanes.

The temperature required for 10% and 20% degradation and the percentage of char at 600°C were outlined in Table 3. At 10% and 20% weight loss temperature, the soya oil-based polyurethanes exhibit higher degradation temperature than the palm oil-based polyurethanes. The thermal properties of both TPPUs were to be lower than TSPUs, this may due to the different secondary interactions as TSPUs are compact structures and stronger. The weight residue for all polyurethanes at 600°C was around 4-5% weight loss.

The DSC thermograms of polyurethanes (Fig. 8 and 9) are usually characterized for determining phase separation between the soft and hard segments. The DSC thermograms usually undergo three typical transitions; the glass transition of the soft segment, the glass transition of the amorphous portion of hard segments and melting of the hard segments if the hard segment symmetry exists along with suitable thermal history to allow crystallization to occur.

As can be seen in Table 4, TPPUs had lower glass transition temperature, T_g compared to TSPUs. The incorporation of glycerol into TSPUs obviously enhances the glass transition temperature, T_g of TSPU-PO as well as for TSPU-SO. Two inflectional points were observed for each sample due to the glass transition \( T_g \) of the sample during heating, which was due to an enhancement of molecular motion in the polymer. They also suggested that glass transition at \( T_{g1} \) might be attributed to long alkyl carboxyls from the polyol molecules. They also assumed that the carboxyl groups are to be sticking out from the backbone. Enhancement of molecular motion at \( T_{g2} \) as suggested by Tanaka et al. might be due to the backbone of polyurethanes.

### Table 3  Thermal decomposition temperature of TPPUs and TSPUs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thermal decomposition temperature (°C)</th>
<th>Residue yield at 600°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 wt % loss</td>
<td>20 wt % loss</td>
</tr>
<tr>
<td>TPPU-PO</td>
<td>270</td>
<td>304</td>
</tr>
<tr>
<td>TPPU-SO</td>
<td>283</td>
<td>310</td>
</tr>
<tr>
<td>TSPU-PO</td>
<td>347</td>
<td>367</td>
</tr>
<tr>
<td>TSPU-SO</td>
<td>360</td>
<td>388</td>
</tr>
</tbody>
</table>

### 3.4 Mechanical properties

The graph of impact strength was illustrated in Fig. 10 showed TPPUs had higher impact than TSPUs as TPPUs could deform and ductile when impact was applied. Thus it was able to absorb high energy therefore difficult to break it to fracture. TSPUs was highly cross-linked thus, literally...
brittle in room temperature and it was easy to break when impact was applied. As the TSPUs act as rigid solid, therefore the impact resistance was hugely decreased. Guo et al. (2006)\(^7\) affirms that the addition of glycerol which served as a trifunctional crosslinker enhances the rigidity of the polyurethanes.

As shown in Fig. 11, TPPUs showed higher flexibility compared to TSPUs because TPPUs able to deform when force is applied. The high flexibility of TPPUs contributed to its high impact strength. The flexibility of ester linkages.


The long hydrocarbon chain of the oil attributed the coating flexibility. From the Fig. 11, palm oil-polyurethanes showed greater flexibility than soya oil-polyurethanes due to highly saturated compounds exhibits in palm oil-polyol.

Furthermore, two tests were carried out to investigate the adhesion properties, which are pencil hardness and cross-hatch adhesion where the results of the polyurethanes were presented in Table 1. It was revealed that both of the palm oil and soya oil based thermosetting polyurethanes possessed higher hardness properties than the thermoplastic polyurethanes and this was due to the high degree of cross-linking of the TSPUs. Soya-oil polyurethanes showed greater hardness compared to palm-oil polyurethanes due to surface roughness of soya-oil poly-

3.5 Corrosion resistances

The coated substrates in Table 4 showed no change in gloss within 48 hours was rated as excellent resistance, whilst slight changed in the gloss and chalking was rated as good. Both of the polyurethanes showed excellent result and resistance in water. In alkali solution, the result for TSPUs showed poor results whilst TSPUs showed good results and this due to the presence of the alkali hydrolysable ester groups of monoglyceride segments.

Velayutham et al. (2009) affirmed that alkali had greater detrimental effect or destructive on the coating than acid.

From the acid resistance test, TPPUs showed good resistance, however in TSPU showed excellent resistance. Moreover, in polar solvents such as alcohol and ketone and non-polar solvent of xylene, both of the TPPUs and TSPUs showed excellent chemical resistance. In a nutshell, TSPUs had better chemical resistance TPPU due to higher extend of crosslinking reactions which form a stable physical network.

4 CONCLUSIONS

Monoglycerides were successfully synthesized from palm and soybean oils via transesterification of the triglycerides...
by one step process. From this study, it can be concluded that thermoplastic and thermosetting polyurethanes can be prepared lucratively from palm oil and soya oil too. From the morphology study, it is confirmed that the uniform phase distribution of the polymers. The thermo-setting polyurethanes (TSPUs) showed good thermal properties compared to thermoplastic polyurethanes (TPPUS) due to highly cross-link exhibits in TSPUs, whilst TSPUs exhibits good properties in pencil hardness and adhesion, however poorer in flexural and impact strength compared to TPPUs. Soya oil-based PU shows good properties in thermal, impact strength and pencil hardness than palm oil-based PU, whilst palm oil-based PU is shown flexible. However both oils show similar properties in physical resistance and adhesion test.

REFERENCES


