

Palm Oil Based Water-Resistant Coating using Pre-Polymer Method

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DOI: <https://doi.org/10.30880/jst.2021.13.02.001>

Received 19 May 2021; Accepted 3 August 2021; Available online 2 Disember 2021

Abstract: The paper presents some results on the ability of palm oil polyol to replace the petroleum-based polyol in polyurethane (PU) synthesis. In this study, palm oil polyol with amine functionality with hydroxyl value (OH value) between 240 - 253 mg KOH/g was used as the polyol component to replace the conventional petroleum-based polyol. Four different formulations of polyurethane coating have been prepared using pre-polymer process namely PU1, PU2, PU3 and PU4 with the polyol to isophorone diisocyanate ratio (OH:NCO) of 1:0.6 and 1:0.5 and acetone within 25-50 wt %. PU1 (1:0.6) and PU2 (1:0.5) result in brittle film, while PU3 (1:0.6) and PU4 (1:0.5) has a soft and flexible film with better transparency. This finding establishes that the acetone content effect the final properties of the polyurethane formed. The polymerization reaction was monitored using the fourier transform infra-red spectroscopy and it was found that the peak corresponds to NH (3302 cm^{-1}), CO (1627 cm^{-1}) and CN (1543 cm^{-1}) stretching of urethane linkage appearing in all the PU films. The water uptake test was done on the films and it was found that the percentage of water uptake is less than 5% within 24 hours of immersion. The surface morphology of the PU films shows that homogeneity was achieved in 1:0.6 of OH:NCO ratio with 25 wt% of acetone. The PU films have the potential to be developed for water resistant coating.

Keywords: Polyurethane thin film, palm oil polyol, transparent film, water resistant

1. Introduction

Polyurethane as one of the superior polymeric materials that can be used as foams, elastomers, coating, adhesive, sealant and plastics are extremely one of the important materials nowadays. This polymeric material was produced from the reaction of polyol and isocyanate that is derived from petroleum-based feedstock. However, the diminishing store of petroleum has led to an extensive research on the utilization of vegetable oils and their fatty acids as the raw materials in synthesizing these polymeric materials (Paraskar, Prabhudesai, & Kulkarni, 2020). Literature revealed that the inclusion of fatty acids into the polymeric resins provide superior properties like increased mechanical properties, increased hydrophobicity, flexibility, low melting point, improved handling, better degradation to polymers in comparison to the simple physical mixing of fatty acids with polymers as well as limited toxicity (Prociak, Malewska, Kurańska, Bąk, & Budny, 2018; Stirna, Fridrihsone, Lazdiņa, Misane, & Vilsone, 2013; Dai et al., 2020; Rajput, Hundiwale, Mahulikar, & Gite, 2014; Siti Munira, Ahmad Faiza, & Rahmah, 2013). Malaysia is one of the largest producers and exporters of palm oil in the world with a yield capacity of about 4-6 tons of oil per hectare per year for the best commercial plantation (Arniza et al., 2015; Sarjadi, Aziz, & Rahman, 2018). A locally available palm oil has undergone some extensive studies to convert the oil into palm oil-based polyols (POP) via a few reaction routes such as epoxidation (Gan, Goh, & Ooi, 1992; Prociak et al., 2018), transamidation (Lee, Ooi, Chuah, & Ahmad, 2007) and transesterification (Badri, Ahmad, & Zakaria, 2001), and the ability of the POP as monomer in polyurethane film (Zulkifli, Badri, Nor, & Amin, 2017), polyurethane foam (Augu, Prociak, & Ryszkowska, 2021; Badri, Othman, &

Ahmad, 2004; Chavarro, Zakaria, & Min, 2020) and polyurethane adhesive (Ang, Lee, Cheng, & Cheng Hock, 2014) has been demonstrated. Due to the increasing awareness of the social community towards environmentally friendly products, it is desirable to study the ability of palm oil to replace the petroleum-based polyols. In this study, polyurethane films with isocyanate to polyol ratio of 1:0.6 and 1:0.5 were prepared using palm oil polyol prepared in a previous study (Soloi, Majid, & Rahmat, 2018). The amine-based palm polyol has an OH value range between 240-253 mg KOH/g and molecular weight around 450 Da. This study aims to investigate the applicability of the palm oil polyol with amine functionality to be used as a polyol component in preparation for the polyurethane thin film.

2. Experimental Section

2.1 Materials

The materials used were palm oil polyol obtained from the previous study (Soloi et al., 2018), isophorone diisocyanate (98% purity, Sigma, US), hydrazine hydrate (50-60% purity, Sigma, US), and acetone (99.5% purity, ACS).

2.2 Instrumentation

Instruments used were ShimadzuIRTracer-100, mechanical testing machine GOTECH AL-7000M, Brookfield Viscometer and Bruker SEM S-3400N.

2.3 Preparation of Polyurethane Coating

PU films were prepared using the pre-polymer process as described by (Zulkifli et al., 2017). Palm oil polyol (POP) used in this study was obtained from the previous study (Soloi et al., 2018). Initially, all formulation was prepared in the ratio of 1:0.6 with 50 wt% acetone; however, when brittle film was obtained, the ratio and acetone content was reduced as tabulated in table 1. In the first step, POP and hydrazine hydrate as the chain extender was stirred in a small amount of acetone at 40°C - 50°C for 30 minutes at 100 rpm. Isophorone diisocyanate (IPDI) was separately dissolved in the remaining acetone at room temperature to form urethane pre-polymer. The amount of acetone in table 1 is the sum of acetone used in the POP mixture and IPDI pre-polymer. The IPDI pre-polymer was then added into the POP solution drop wise and the mixtures were stirred for 5 min at 100 rpm at room temperature. The mixtures were then casted onto a petri dish and dried in a humidity chamber (37 °C, 50% ± 5 relative humidity) for 24 hours to evaporate the solvent and was oven-dried for curing at 50°C until it became completely dry.

Table 1 - The formulation of IPDI to POP with acetone as solvent

| Sample | [(POP:hydrazine hydrate) : IPDI] = [OH: NCO] | Acetone (wt%) |
|--------|--|---------------|
| PU1 | 1:0.1 : 0.6 | 50% |
| PU2 | 1:0.1 : 0.5 | 30% |
| PU3 | 1:0.1 : 0.6 | 25% |
| PU4 | 1:0.1 : 0.5 | 25% |

2.4 FTIR Spectroscopy Analysis

The detection of the main functional groups of polyurethane (PU) in the FTIR was carried out using ShimadzuIRTracer-100 spectrometer via the Attenuation Total Reflectance (ATR) method and all spectra were corrected by the Shimadzu IRTracer-100 software.

2.5 Mechanical Properties

Stress-strain measurements were obtained using GOTECH AL-7000M with ±10kN grips and cross speed set at 10 mm/min. The PU film dimension was cut by 40 mm × 1.5 mm. Film thickness (2.0 cm x 6.0 cm) was measured by a hand-held micrometer (Mitutoyo). The tensile strength, modulus of elasticity and elongation of break were measured during the test.

2.6 Water Uptake

The water uptake experiment was conducted based on the method by (Yeganeh & Hojati-Talemi, 2007) using ASTM D-570. The water uptake was measured by weighing the dried PU films (W_{dry}) with the dimension of 10 mm × 10 mm prior to the immersion in water bath (37 °C). The films were removed after 24 hours, wiped gently with a filter paper to expel the surface solution, and then weighed (W_{wet}). Water uptake was then determined from the equilibrium-swelling ratio $[(W_{wet} - W_{dry})/W_{dry}] \times 100$.

2.7 Viscosity Test

The viscosity of the PU films was measured using Brookfield Viscometer at room temperature using chloroform as the solvent.

2.8 Surface Morphology

The surface morphology of the films was observed under 100× magnification using SEM S-3400N with a voltage range from 0.5 to 30 kV. All the PU films were platinum-coated prior to examination.

3. Results and Discussions

3.1 Physical Observation

PU1, PU2, PU3 and PU4 were physically checked for curing before and after being oven-dried and the observations were tabulated in table 2. All samples were sticky before the curing process. After all the samples were dry, PU1 and PU2 resulted in brittle films while PU3 and PU4 showed flexible properties, respectively. The brittleness and flexibility of the PU film were assured based on an observation on the naked eye. Since PU 1 and PU2 can easily crack and PU3 and PU4 can be bent without cracking, the terms ‘brittle’ and ‘flexible’ were used to describe their physical appearance, respectively. Figure 1 shows the physical appearance of the PU films and the transparency of PU3. Acetone is a polar solvent that most likely will increase the solubility of the polar hard segment (urethane linkage) and decrease the solubility of the non-polar soft segment (polyol). As shown in table 2 PU derived from the same NCO:OH ratio show a significant difference in the physical properties when the amount of acetone is increasing or decreasing. As the amount of acetone increases, more of the hard segment will dissolve reducing the intramolecular and intermolecular hydrogen bonding in the polyurethane obtained (Sikder & Jana, 2018). Hence, a weak network structure was formed in PU1 and PU2 that makes them brittle and easily crack.

Table 2 - Physical state of the PU films at different NCO:OH ratios

| Sample | NCO:OH ratio | Physical observation | | Acetone (wt%) |
|--------|--------------|----------------------|--------------|---------------|
| | | Before curing | After curing | |
| PU1 | 0.6 :1 | Tacky | Brittle | 50 |
| PU2 | 0.5 :1 | Tacky | Brittle | 30 |
| PU3 | 0.6:1 | Tacky | Flexible | 25 |
| PU4 | 0.5 :1 | Tacky | Flexible | 25 |

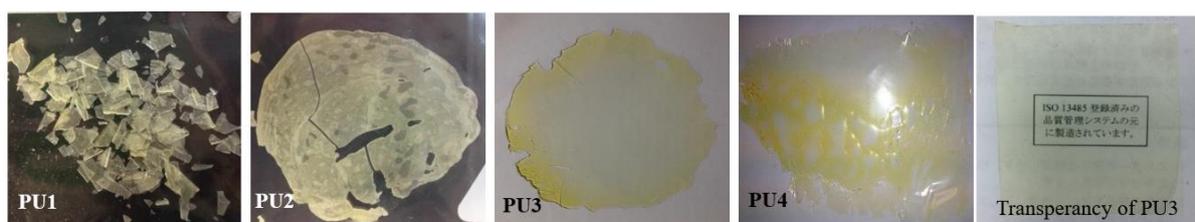


Fig. 1 - Physical appearance of the polyurethane film

3.2 FTIR Spectroscopy Analysis

The reaction between polyol and isocyanate to form a thin film polyurethane is a type of condensation polymerization resulting in urethane linkage. The palm oil polyol (POP) used in this study was synthesized in our previous study (Soloi et al., 2018). Isophorone diisocyanate (IPDI) as a source of isocyanate component was used since IPDI is easily soluble and expected to give a better transparency to the thin film obtained (More et al., 2013). From the previous study, the POP contains amine functional group as well as fatty acid chain of the triglyceride. The chemical structure of the POP is shown in figure 2. As the polymerization proceeds, the urethane linkage was formed between the polyol and isocyanate as shown in figure 2. The FTIR analysis can be used to identify the presence of urethane linkage in the polymer. Based on the FTIR spectra of the PU in figure 3, the most prominent peak which resonated at 1543 cm^{-1} and 1627 cm^{-1} was attributed to the presence of $\nu(\text{-CN})$ and $\nu(\text{-CO})$ stretching of urethane group respectively. The disappearance of the peak attributed to $\nu(\text{C-OH})$ and $\nu(\text{C-C-O})$ symmetric stretching in polyol at 1172 cm^{-1} 835 cm^{-1} proves that the alcohol group in the polyol has reacted with -NCO group of isocyanates. The $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ stretching at 2915 and 2842 cm^{-1} was present in all the samples since the PU films contain the fatty acid chain from the POP. The broad absorbance at 3406 cm^{-1} in the polyol shifted to 3302 cm^{-1} in the PU implying that the OH group was converted to a hydrogen-bonded NH group.

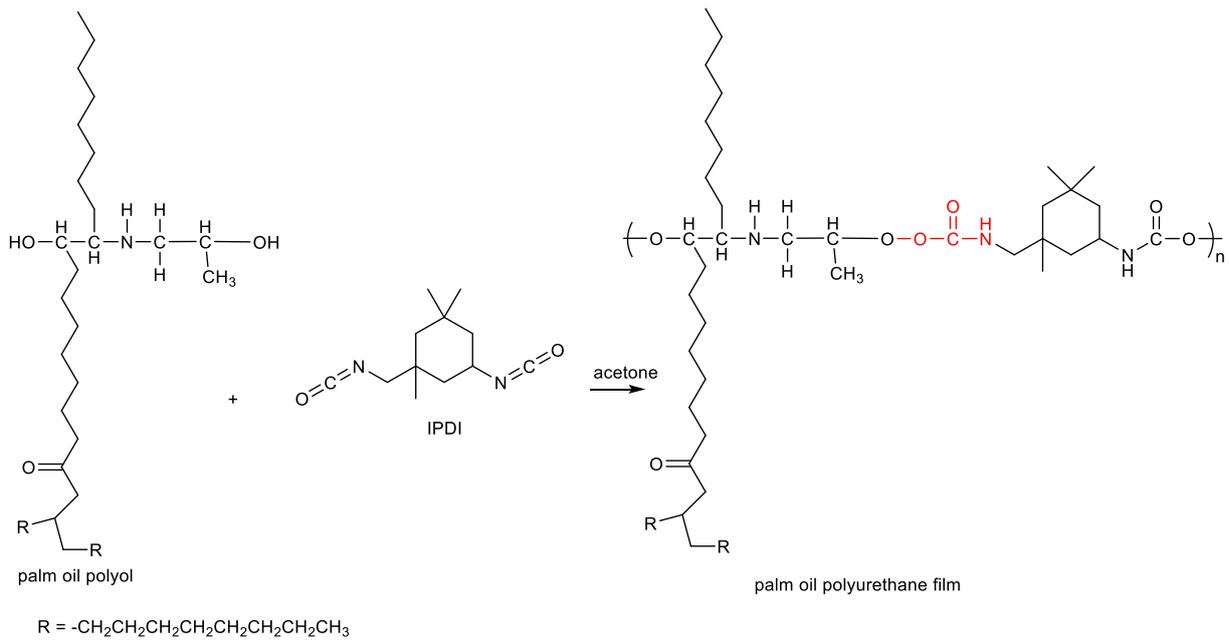


Fig. 2 - The urethane linkage formed between the palm oil polyol (POP) with IPDI during the polymerization to produce palm oil polyurethane film

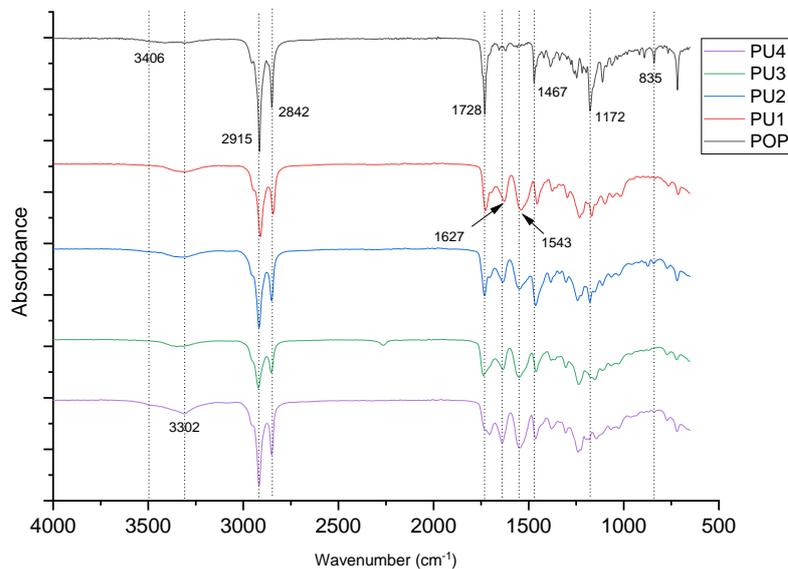


Fig. 3 - FTIR Spectra of palm oil polyol (POP) and polyurethane thin film (PU1, PU2, PU3 and PU4) obtained in this study

3.3 Mechanical Analysis

Due to the limitation of the sample, only PU3 and PU4 had undergone the tensile analysis since PU1 and PU2 were brittle and cannot be cut into the size as needed by the standard testing. Based on the tensile analysis in table 3, the mechanical properties of PU3 are better than PU4. As we can see in figure 1, the physical appearance of PU3 is smooth with good transparency. This indicates that the degree of polymerization was higher in PU3 compared to PU4. Higher degree of polymerization means a longer chain that contains a urethane linkage and results in the formation of a strong hydrogen bonding between the polymer chain thus increasing the ability of the polymer to sustain the external force (Saalah et al., 2015). Meanwhile, low degree of polymerization means shorter chains with end groups or dangling chains that increase the free volume and molecular mobility. Dangling chains represent imperfections in the network structure since they do not support external force (Zlatanić, Petrović, & Dušek, 2002). Therefore, the strength and

modulus are lower in PU4. Meanwhile, the type and amount of solvent are believed to affect the mechanical properties of the same polymer (Kim, Song, & Suj, 1998; Sikder & Jana, 2018).

Table 3 - Mechanical performance of PU3 and PU4

| PU Samples | Maximum Load (N) | Tensile Strength (N/mm ²) | Modulus of Elasticity (N/mm ²) | Elongation at Break |
|------------|------------------|---------------------------------------|--|---------------------|
| PU3 | 4.940 ±0.79 | 2.003 ±0.46 | 22.937 ±2.55 | 7.170 ±2.08 |
| PU4 | 1.228 ±0.33 | 0.170 ±0.01 | 16.877 ±2.30 | 4.402 ±2.45 |

3.3 Water Uptake

One of the applications of this PU coating in this study was intended to be developed for water resistance coating. Therefore, the water uptake analysis was done to measure the percentage of water uptake by the PU film. The water uptake analysis was done for 24 hours. Based on figure 4 the percentage of water uptake within 24 hours of immersion shows that PU3 films have the properties of water resistance. It is believed that the incorporation of plant oil polyol increases the hydrophobicity due to the existence of long chain fatty acid in their chemical structure (Stirna et al., 2013). In this study, as film formation in PU3 is better, the polymer network that forms between the palm oil polyol and isophorone diisocyanate contributes to the presence of more of the fatty acid chain that is non-polar, hence inhibiting the water uptake.

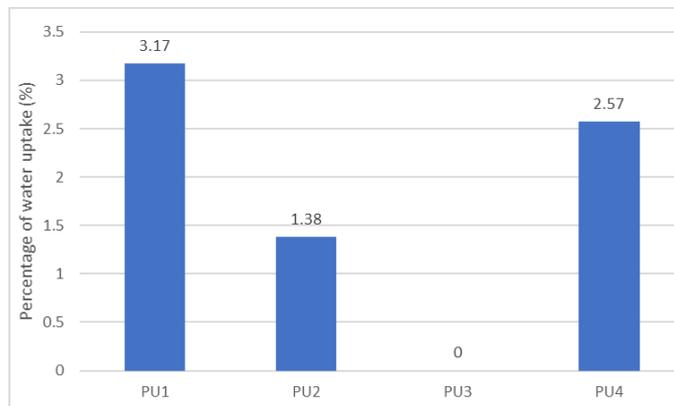


Fig. 4 - Percentage of water uptake for PU films within 24 hours of immersion

3.4 Viscosity Test

Generally, the viscosity of the PU films is related to the molecular weight of the polymer (Miao et al., 2014). Increasing the chain length would increase the polymer viscosity due to the increasing intermolecular interactions. Based on figure 5 below, the highest viscosity by PU3 indicates that the polymerization rate occurs better in PU3 formulation since higher viscosity means that more polymer network was formed. However, the viscosity of the PU films obtained in this study was lower compared to other studies (Zlatanić et al., 2002) probably because the palm oil polyol used in this study consists of a shorter fatty acid chain (Soloi, 2018). Hence, it produced polyurethane films at low molecular weight.

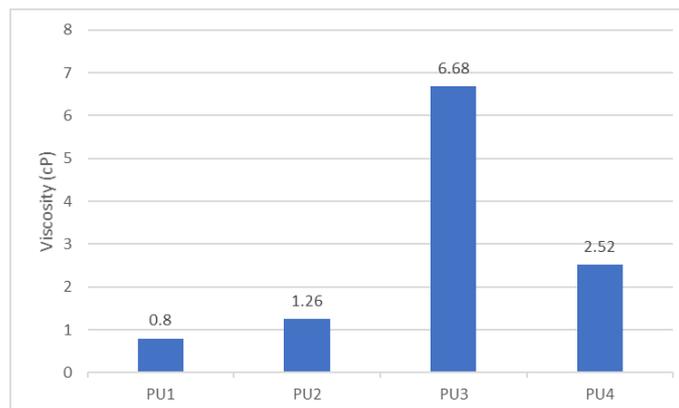


Fig. 5 - Viscosity of PU films in chloroform

3.5 Surface Morphology

The surface morphology of the films is shown in figure 6. Based on this figure, PU1 and PU2 exhibit a rough-like and non-homogeneity surface. Meanwhile, PU3 and PU4 exhibit better smoothness and homogeneity. However, the smoothness surface of PU3 is much better compared to PU4. This SEM image supports that the polymerization reaction occurs better in PU3. The better smooth surface of PU3 also contributes to the flexibility of the film.

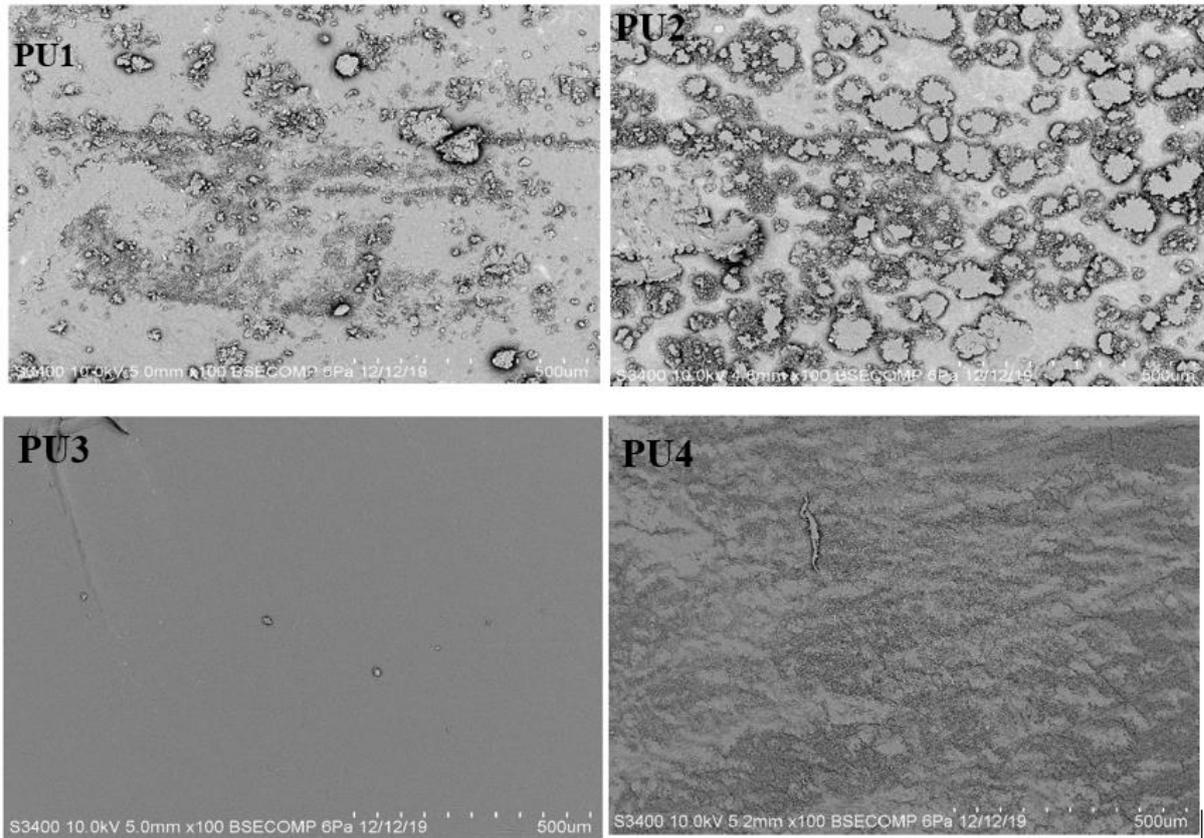


Fig. 6 - Scanning Electron Microscope (SEM) image of PU1, PU2, PU3 and PU4 films at 100×

4. Conclusion

The study shows that palm oil polyol (POP) exhibits the ability to replace the petroleum-based polyol. Flexible polyurethane films which exhibit water resistant properties have been successfully prepared at NCO:OH ratio of 0.6:1 in 25 wt% of acetone.

Acknowledgement

Authors would like to acknowledge the Faculty of Science and Natural Resources for lab facility in conducting this study and Universiti Malaysia Sabah for SLB0161-2017 research grant.

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