

Effect of Oleic Acid Content and Chemical Crosslinking on the Properties of Palm Oil-Based Polyurethane Coatings

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ABSTRACT: Polyurethanes (PU) were prepared by reacting palm oil-based polyols and aromatic diisocyanate (toluene 2, 4 diisocyanates). The content of oleic acid was varied in the polyester polyols and the hydroxyl value was fixed to be 140 mg KOH g⁻¹. The NCO/OH ratios were varied to 1.2, 1.4, and 1.6. Crosslinking density of the PU was measured by swelling in toluene at room temperature. It was found that the crosslinking increased with decreasing oleic acid content and increasing NCO/OH ratio. The samples were assessed by thermogravimetric analysis, differential scanning calorimetric, and short-term creep measurements. The highest rupture strength of the PU films was 36 MPa and thermostability improved as the oleic acid content and the NCO/OH ratios were increased in the sample. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 415–421, 2013

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INTRODUCTION

Many researchers have recently refocused their attention on renewable resources as substitutes for petrochemical derivatives because of increasing price of crude oil and the limited success in finding new crude oil reservoirs.^{1,2} Many of the objects that we use in our daily lives are coated for protection, decoration, or signal-enhancing. However, most of today's coatings are produced using nonrenewable resources. For instance, researchers have been developing numerous different types of polyurethane (PU) from synthetic chemicals for the past few decades.^{3,4} Nonetheless, raw materials from vegetable oils can be an important source for green polyols. In fact, literature reveals that some vegetable oils such as nahar,⁵ linseed,⁶ soya,^{7–9} amaranth,¹⁰ castor,^{11–13} sunflower,¹⁴ cashew nuts,^{15,16} and palm oil^{17,18} have been used for the production of renewable PU.

In this study, we report on PU coatings prepared using polyols made of native palm oil. The chemical diversity of the starting material allowed evaluation on the effect of dangling oleic acid chains and the NCO/OH ratio on the properties of the coatings. It is well known that the thermal and mechanical properties closely related to several structural parameter including chemical composition, formulation, crosslinking structure, and other morphological structure. Hitherto, we had conducted systematic studies on these polyols and corresponding PU, which include synthesis and characterization,¹⁹ physical and mechanical properties.²⁰ In continuation of the previ-

ous study, this investigation discusses the correlation of oleic acid content and NCO/OH ratio of the PU with the crosslinking, thermal, and creep properties of the material. We discovered that the ability of controlling the physical properties of the PU coating helps to maximize the performance of the coatings.

EXPERIMENTAL SECTION

Materials

Oleic acid (purity 99.5%) and glycerol (purity 99.5%) were obtained from Cognis Oleochemical (M) Sdn. Bhd. (Malaysia). Phthalic anhydride, PA (P.T. Petrowidada, Indonesia) and toluene diisocyanate, TDI (Aldrich, USA) (an 80 : 20 mixture of two isomers: 2,4-toluene diisocyanate and 2,6-toluene diisocyanate) were used as received. Toluene (JT Baker, USA) was used as the solvent and was dried overnight with activated molecular sieves before use. We used L6900 silicone surfactant (Air Products, USA) and BYK-088 defoamer (BYK Chemie, Germany).

Synthesis of Polyester Polyol and Polyurethane

Polyols were prepared using oleic acid, glycerol, and PA. The synthesis of polyols from oleic acid and polyurethane has been described previously.^{19,20} Three different formulations of alkyd polyols were synthesized by using 28, 40, and 65% oleic acid and were named Alk28, Alk40, and Alk65, respectively. These polyesters were formulated to have similar hydroxyl value, which was 140 mg KOH g⁻¹. The polyols were reacted with TDI in the presence of solvent (toluene), surfactant, and

Table I. Glass Transition Temperatures, T_g (°C), of PU samples

Samples	NCO/OH = 1.2	NCO/OH = 1.4	NCO/OH = 1.6
PUalk28	122.8	122.5	122.9
PUalk40	122.8	123.7	123.2
PUalk65	123.1	123.0	122.7

defoamer at 80°C over 3 hours with continuous stirring. Three different NCO/OH ratios were tested (1.2, 1.4, and 1.6). Partially reacted sample formed a viscous solution and was transferred into a square 12 × 12 cm² mold and cured at ambient temperature overnight into a 0.5-mm thick film. The film was then left for 2 days in an oven at 60°C to evaporate off the solvent. For the creep measurement, the test specimens conforming to the dimensions stated in the ASTM D638 type IV standard and the specimens were prepared by die cutting.

Characterization

Calorimetric measurements were carried out using differential scanning calorimetry (DSC 6, Perkin Elmer) from 35°C to 150°C at 20°C min⁻¹. The sample size was ~ 10 mg. The thermal stability of the polymer film after curing was studied in an N₂ environment using a thermogravimetric analysis (TGA) instrument (Rheometric Scientific, Model 1000+) at a heating rate of 20°C/min from room temperature to 900°C. The densities of the polyurethane were measured by immersing the sam-

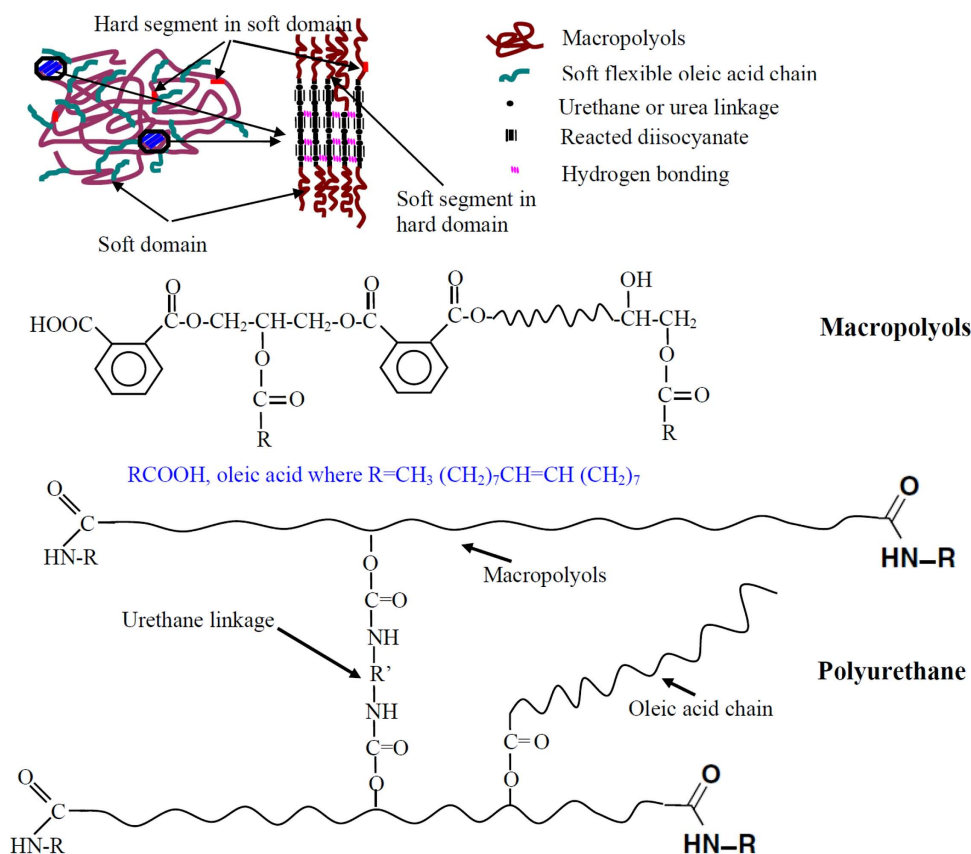
ple in water as specified by ASTM 792. Swelling experiments were performed on rectangular (20 × 20 × 2 mm³) samples of the PU in toluene for 1 week. Swelling time of 1 week was chosen as the basis of the test results on several samples, which showed no significant changes after a week of immersion in toluene. Crosslink density was calculated and expressed as moles of crosslink per kg of insoluble network.

The apparatus used for the creep measurement is as described previously.²¹ A grip was attached to a panel that was fixed. A second grip capable of perpendicular movement with minimum friction was attached to a weight pan. The testing specimens were clamped between the grips. For each sample, at least five specimens were tested and the results were found to be reproducible with 5% uncertainty, provided that the applied load was greater than 50 g and the extension exceeded 25% strain.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry Analysis

A single broad T_g was observed in each of the PU samples synthesized and analyzed in this work (Table I). The existence of a single T_g for each sample suggests that there were less visible phase separations between the soft and hard domains. There were no visible endothermic peaks in the scans, indicating that crystalline regions did not exist in our samples as confirmed by the XRD result reported in Ref. ¹⁹. A schematic drawing of the structure of PU in this system is shown in Scheme 1.



Scheme 1. A schematic diagram of PU synthesized by palm oil-based polyol and TDI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

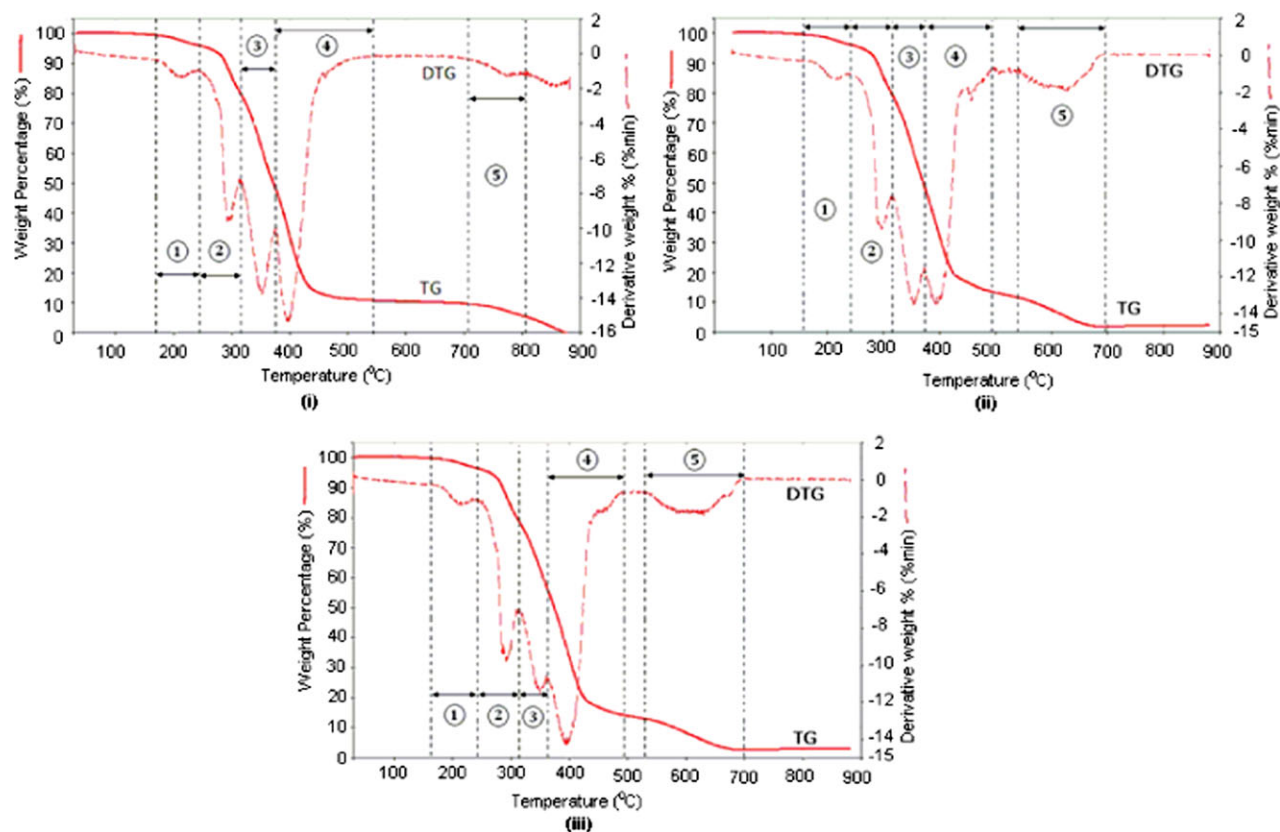


Figure 1. TGA and DTG curves of PUalk28 for NCO/OH ratios of (i) 1.2, (ii) 1.4, and (iii) 1.6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Oleic acid chains were grafted as flexible side chain at the backbone of PU as shown in the Scheme 1. This fact further confirmed by X-ray diffractogram (XRD) results, the amorphous nature of the PU, as discussed in Ref. ²⁰.

Apparently, the oleic acid content in the polyol and the NCO/OH ratio did not influence the T_g , which was around 123°C. The T_g is controlled by structure of the main chain of the polymer, which is similar for all the PU samples in this study due to the fact that the polyols have identical hydroxyl value. The only difference in the structure of the PU chain is the number of side branch of the oleic acid. In this case, the side chain obviously did not contribute to the T_g of the sample.

Thermogravimetric Analysis

A representative thermogravimetry (TG) and derivative thermogravimetry (DTG) curve of PUalk28 is shown in Figure 1. The rest of the TG results on PUalk40 and PUalk65 are tabulated in Table II, which shows the decomposition temperature at various weight loss percentages for all the degradation stages. Three to five degradation stages were observed for the nine PU samples. The polymers were stable up to 170°C. Rapid weight loss occurred between ~ 170 and 700°C. For PUalk28, five stages of degradation were observed (Figure 1). During the first decomposition phase, the polymer remained mostly intact and only the flexible oleic acid ester link decomposed. Rapid weight loss started approximately between 240 and 700°C. The second

stage of weight loss (temperature ranging from 260 to 360°C) was mainly due to decomposition of polyols and urethane links. These decompositions preceded the formation of CO₂, alcohols, amines, aldehydes, CO, and other compounds.^{22–24} During the third stage (at ~ 360°C), isocyanates in the urethane decomposed, which is consistent with a prior report on isocyanates decomposition of urethane elastomer by Long et al. (1976)²⁵ for temperature ranging from 290 to 370°C. The fourth stage of the degradation occurs in the range of 370–500°C, which is related to rupture of ester compound.²⁶ Complete degradation of the polymer carbon backbone²⁷ occurs in the region between 500 and 700°C.

Results of the investigation (tabulated in Table II) shows that the thermal stability of the PU films during the second stage increased as the NCO/OH ratio increased. Isocyanate-based polymers provide thermostability in the following order: isocyanurate > urea > urethane > biuret > allophanate.^{28,29} In this investigation, the excess isocyanate in higher NCO/OH ratio led to the formation of urea; thus, the thermostability of the polymer increased.

Thermostability of the films was also correlated with the decomposition of oleic acid fragments in the films. Literature³⁰ reported that thermal desorption of extra oleic acid layers occurs approximately at 200°C. Thus, the increase in the contribution of oleic acid to the PU network formation resulted in

Table II. Thermal Behavior of PU in a Nitrogen Atmosphere

Sample	Stages	Decomposition	Temperature T ± 5 (°C)		Weight (%)
			T ₁	T ₂	
PUalk28 (1.2)	1	170	241		3.31
	2	241	316		16.43
	3	316	375		31.51
	4	376	533		37.17
	5	699	878		10.10
PUalk28 (1.4)	1	172	243		3.33
	2	243	316		6.82
	3	316	372		30.00
	4	372	507		36.42
	5	541	690		9.60
PUalk28 (1.6)	1	178	244		3.17
	2	244	313		17.30
	3	313	364		23.26
	4	365	510		41.49
	5	538	701		10.06
PUalk40 (1.2)	1	171	236		1.89
	2	236	311		13.54
	3	311	375		31.76
	4	375	541		41.37
	1	198	238		1.85
PUalk40 (1.4)	2	238	311		17.44
	3	311	503		16.55
	4	537	698		9.73
	1	199	244		1.48
	2	245	310		18.04
PUalk40 (1.6)	3	311	523		67.11
	4	539	689		9.57
	1	201	288		8.95
	2	288	499		77.44
	3	499	677		10.90
PUalk65 (1.2)	1	201	289		9.08
	2	289	514		81.57
	3	801	871		3.11
	1	213	219		13.74
	2	301	392		40.86
PUalk65 (1.6)	3	396	598		37.89
	4	526	749		10.12

higher thermostability. For NCO/OH ratio of 1.4, the initial degradation temperatures were 172, 198, and 201°C for PUalk28, PUalk40, and PUalk65, respectively.

In summary, the analysis suggests that PU containing higher oleic acid percentage and higher NCO/OH ratios were more stable where the initial degradation temperatures were above 200°C. The thermostability of the PU sample is almost equivalence with commercially available polyether-urethane coating as reported in literature where most polyurethane decompose within 2–4% weight in the temperature range of 0–200°C.^{30–32}

Swelling of Networks

Crosslinking density of polyurethane network can be extracted from swelling data. The degree of swelling is dependent on the crosslink density of polymer network; the greater the degree of swelling the lesser the crosslink density. The thermodynamics of swollen polymer network are based on Frenkel-Flory-Rehner model [eq. (1)] where the number average molecular weight between crosslinks, M_c , and concentration of elastically active network chains can be calculated.

$$M_c = \frac{[\rho V_1 (V_2^{1/3} - V_{r/2})]}{[-\ln(1 - V_2) + V_2 + \chi_{12} V_2^2]} \quad (1)$$

where ρ is the density of the dry polymer, V_1 is the molar volume of the solvent, V_2 is the volume fraction of the swollen sample, and χ_{12} is the polymer solvent interaction parameter. The volume fraction of polymer V_2 can be calculated from eq. (2).

$$V_2 = \frac{m_1 d_s}{m_1 (d_s - d_2) + m_2 d_2} \quad (2)$$

where m_1 is the weight of polymer before swelling, m_2 is the weight of polymer after swelling, d_s is the density of solvent, and d_2 is the density of polymer. Furthermore, in order to determine M_c , identifying the interaction parameters is very important. The polymer-solvent interaction parameter, χ_{12} can be calculated from the eq. (3).

$$\chi_{12} = \frac{(\delta_1 - \delta_2)^2 V_1}{RT} \quad (3)$$

where δ_1 and δ_2 are the solubility parameters for the solvent and polymer network, respectively. The solubility parameter of polyurethane networks were calculated using group contribution method to the molar attraction constant,³³ F (Hoy) and the solvent molar volume, V_1 and the solubility parameter for toluene³³ were 106.2 cm³mol⁻¹ and 18.3 J^{1/2}/cm^{3/2}, respectively. The results of swelling tests for the PU are given in Table III.

The results indicate that the crosslink density values of the PU significantly increased with increasing amounts of excess isocyanate in the PU prepolymer. The swelling capacity of the PU with toluene decreases with increasing degree of crosslinking. The swelling degree of PU increased with the oleic acid content. More crosslinks were formed with lower oleic acid content in the polyols and higher excess diisocyanate in the PU prepolymers. The incorporation of higher percentages of oleic acid

Table III. Crosslink Density and Swollen Degree of the Polyurethanes

Sample	Density (g cm ⁻³)	Swelling degree (%)	Crosslink density (mol kg ⁻¹)
PUalk28 (1.2)	1.080	95.01	0.709
PUalk28 (1.4)	1.089	80.85	0.714
PUalk28 (1.6)	1.130	78.03	0.729
PUalk40 (1.2)	1.051	98.10	0.673
PUalk40 (1.4)	1.069	96.75	0.692
PUalk40 (1.6)	1.074	96.58	0.698
PUalk65 (1.4)	1.005	99.30	0.601
PUalk65 (1.6)	1.048	98.90	0.615

content in the polyols apparently hinders chemical crosslinking in the PU system.

Short-Term Creep and Recovery Analysis

The results of the experimental short-term creep for PU are tabulated in Table IV. Fracture stress was tested, and then the

loads smaller than the value were selected and applied to samples within the first 15 min. Summary of the material characteristics during the creep tests are reported in Table IV. Results of PUalk65 (1.2) were purposely omitted in the table because of the inept nature of the sample to perform creep test.

The results from creep and subsequent strain recovery curves were found to have a general form showing an instantaneous elastic strain on loading that was followed by a period of slow linear deformation [exemplify creep result is shown in of Figure 2(a) for PUalk40(1.2)]. These two regions were separated by a transition zone (at $t = 15$ min) that was more pronounced at higher load levels. The results tabulated in Table IV indicate that the PUalk28 showing almost full recovery after removal of creep loads of 0.5 to 35 MPa thus can be concluded as perfectly elastic. In contrast, PUalk40 (1.2) shows a strain of $\sim 50\%$ and PUalk40 (1.4) and PUalk40 (1.6) display strain of $\sim 6\text{--}8\%$. There is a dramatic change in the creep strain between PUalk40 (1.2) and PUalk40 (1.4), although the change in NCO/OH ratio is not that different. Besides, PUalk65 shows a strain of more than 50% and demonstrate less plasticity (irreversible strain becomes prominent when higher loading is employed)

Table IV. Material Characteristics and Percentage Recovery During Creep Tests

Samples	Material characteristic	Stress applied	Percentage recovery
		($\sigma \pm 0.3$) MPa	($E_r \pm 0.5$) %
PUalk28(1.2)	Very hard, brittle, elongated $\sim 1.5\%$	0.5–26.0	100.0
		27.0	F
PUalk28(1.4)	Very tough and brittle, elongated $\sim 1.5\%$	0.5–32.0	100.0
		33.0	F
PUalk28(1.6)	Very tough, brittle, elongated $\sim 1.5\%$	0.5–35.0	100.0
		36.0	F
PUalk40 (1.2) $\sim (10\text{--}90)\%$	Elastic, elongated	0.5–8.0	100.0
		8.5	65.7
		9.0	44.6
		10.0	48.3
PUalk40(1.4)	Tough, elongated $\sim 3\%$	0.5–15.0	100.0
		16.0	F
PUalk40(1.6)	Tough, brittle, elongated $\sim 3\%$	0.5–18.0	100.0
		19.0	F
		0.5	24.3
		2.0	59.8
PUalk65 (1.4) elongated $\sim (5\text{--}140)\%$	Soft, elastic	1.0	74.9
		1.5	63.6
		2.0	59.8
		2.5	F
		0.5–1.5	100.0
PUalk65 (1.6) elongated $\sim (5\text{--}43)\%$	Soft,	2.0	76.9
		2.5	72.7
		3.0	64.3
		3.5	F

F, Fractured; Er, recovery strength.

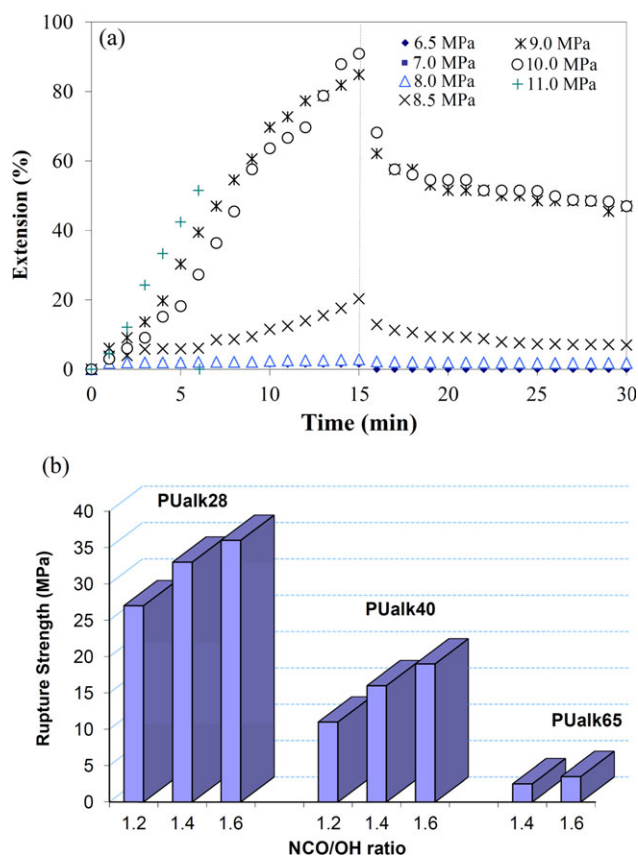


Figure 2. (a) The results from creep and subsequent strain recovery curves for PUalk40 (1.2) showing an instantaneous elastic strain on loading followed by a period of slow linear deformation. (b) Rupture Strength of PUalk28, PUalk40, and PUalk65 at various NCO/OH ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared with the rest of the PU. These results explained are as follows.

The three polyols contain same amount of hydroxyl group and significant amount of carboxylic group. It is understood that isocyanates react with H-activated groups, thus likely to react with both OH and COOH groups to form urethane linkages. Plausibly, the polyols with higher oleic acid content have same amount of available OH to react (as the OH value is controlled in the system) with additional COOH groups due to oleic acid chain to form crosslinking. Available isocyanates during moisture cure were higher for lower oleic acid content polyol (PUalk28) compared with PUalk65, because most of the isocyanates terminated by COOH group and has less available NCO to react with moisture. As polyols react with isocyanates forming polyurethane, flexible oleic acid chain increases the inter-chain molecular distance and liberate motion of soft segment. PUalk28 (with 28% oleic acid content) have reduced interchain molecular distance, which restrain molecular motion, thus, explains the rigidity and toughness of the samples.²⁰ In contrast, PUalk40 and PUalk65 were resilience and able to withstand stretch to a certain extend and exhibit plasticity.

The crosslinking density results support the fact that as the NCO/OH ratio increased more percentage of isocyanate reacts with hydroxyl and carboxylic group causing crosslinking and network formation. At higher degree of crosslinking, the polymer molecules are almost immobilized and enormously rigid. Concurrently, oleic acid dangling chain may function as plasticizers²⁶ especially for polyols with 40 and 65% oleic acid content; thus, the material to exhibit less plasticity although the NCO/OH ratio increased.

Rupture strength from creep is represented in Figure 2. The highest rupture strength of the coating was 36 MPa (refer to Figure 2), which was higher than the values reported in literature³⁴ for lithium polyurethane pipeline coatings (i.e., 25–35 MPa). The rupture strength increased as the oleic acid content decreased and NCO/OH ratio increased, mostly due to higher degree of crosslinking.

Through understanding of the insights of coatings on physical, thermal, and creep strain properties of the PU, designing of coating materials becomes simple. In general, PUalk28 coatings were considered adequate and potential to become highly robust coating material through molecular structure of the cross linking network. PUalk40 coatings may possibly withstand regular stress situation and could applied as a primary coatings. In contrast, PUalk65 was soft coating and special precautions must be taken to incorporate the property of good modulus strength, otherwise, the pitfall of developing deterioration of performance is a possible risk. Thus, PUalk65 was improved by increasing the NCO/OH ratios.

CONCLUSIONS

In summary, the TGA results demonstrated that degradation of PU started at 170°C and quite stable up to 170–200°C and mostly this temperature is adequate as generally organic coatings cannot withstand temperature above 150°C. The highest thermal stability recorded was 213°C for PUalk65 (1.6). The absence of endothermic peaks in the DSC scans indicated that both phase separation and crystalline formation may have been inhibited by the presence of chemical crosslinks. Thus, the T_g values of PU remained constant, regardless of the NCO/OH ratio increment. From the measurement of crosslink density on PU it was found that the crosslinking density significantly increased with an increase amount of excess isocyanate and reduced amount of oleic acid content in the polyols. Furthermore, creep tests demonstrated that PUalk28 may be a highly robust coating with the highest rupture strength of 36 MPa and by varying the oleic acid content and NCO/OH ratios a carefully designed high quality coating system could be formulated for premium performance and reliable in the long term. Thus, it can be concluded that the palm-oil based PU coatings are promising replacement for petroleum based PU.

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