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Effect of DMPA Content on Colloidal Stability of Jatropha Oil-based waterborne Polyurethane Dispersion

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Abstract. Driven by the increase of oil price in the market as well as environmental concerns by the society, a renewable raw material such as vegetable oil becomes the alternative to produce bio-based polyol to replace non-renewable polyols in polyurethane production. The recent development of aqueous polyurethane dispersion proves that environmentally waterborne PUD offers an efficient alternative to the solvent-borne PUD for the application in ink, adhesives, and coatings. In this study, the jatropha oil has been successfully functionalized to polyol (JOL) by epoxidation and oxirane ring opening steps. Jatropha oil-based waterborne polyurethane (JPU) dispersions were produced by polymerizing the JOL with isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA). The colloidal stability of JPU dispersions was studied in terms of particle size and zeta potential. Varying DMPA content from 5.0-7.0 wt.% resulted in small average particle size of dispersion from 39.40 nm to 133.2 nm. High zeta potential obtained in a range of -52 mV to -65 mV indicates the particles in the dispersion are sufficiently separated and therefore stable. Eventually, the study provides an overview of vegetable oil-based waterborne polyurethane dispersion with good stability for surface coating application.

1. Introduction

The production of bio-based materials is creating worldwide interest in economic, energy and environmental concern to the society. A renewable raw material such as vegetable oil becomes the alternative due to its low cost, and readily available for polyol synthesis [1][2]. Moreover, this vegetable oil also has been growing as an interesting sustainability platform to develop eco- friendly functional polymers which can replace the existing petroleum-based polymers on a cost and property performance basis[3]. Thus, there is a growing demand to replaced petroleum-based polyol in polyurethane (PU) production which is nonrenewable.

Presently, polyol produced from jatropha oil has been utilized as feedstock for polyurethane adhesives and coatings [4–6]. As mentioned by [7], jatropha oil is a popular feedstock for biodiesel production. Jatropha oil contains a high concentration of toxic ingredients of phorbol esters, which renders it being inedible [4,8–11]. As such, it is beneficial to use jatropha oil since its usage does not affect the market for edible vegetable oil negatively, which in turn will decrease the usage of other edible oils for chemical purposes [8,10,11]. Jatropha oil is an excellent contender amongst vegetable-based oils to be marketed in polyurethane dispersions manufacturing as its price is not influenced by the growth in food industry. Hence, jatropha oil can be a great alternative to petroleum in terms of sustainability in the synthesis of polyurethane dispersion.

Polyurethanes are one of the important class of polymers that are used widely for application in ink, adhesives, and coatings. In particular, waterborne PUD has sparked much interest in research as environmentally-friendly coatings in the past year. In fact, waterborne PUD are one of the most rapidly developing and active branches of polyurethane chemistry [12]. Moreover, water is the best choice to be used as a medium to synthesize and produce chemical products as water was regarded as a cheap, safe, non-toxic and environmentally benign solvent, which may enhance the rates and efficiencies of a wide variety of organic reactions [13].

Polyols made from jatropha oil can then be incorporated into PUs by reacting with diisocyanates during the PU synthesis to yield eco-friendly PUs. The presence of triglyceride units in the PUs may improve the physical and chemical properties such as hydrolytic biodegradability and thermal stability [14]. Up to the present time, the synthesis of jatropha oil-based polyurethane dispersions used polyols made from epoxidation using methanol [4,10,11]. To date, no study relating to the usage of another ring-opening agent other than methanol to synthesis jatropha oil-based polyol has been done. In this study, ethanol is used as the ring-opening agent to prepare the Jatropha oil-based polyol.

The environment-friendly characteristics of waterborne PUD are usually achieved by the introduction of the emulsifiers and employing water as a dispersant. Jatropha oil-based PUDs will be synthesized by varying the emulsifier content (DMPA) using the prepared polyol. Since there is insufficient information regarding this matter, the amount of emulsifier required needs to be investigated to produce PUDs that have high storage stability and potential to be used as coatings. Moreover, jatropha oil has a high unsaturation percentage in its structure, therefore it has the potential to be modified chemically.

The stability of the polyurethane dispersions is generally determined by the particle size, by which according to [15,16], smaller particle size will produce a more stable polyurethane dispersion. Hence, polyurethane dispersions with smaller particle size can be utilized to produce coatings with better gloss, hardness, and resistance to chemicals [17]. In their study, [16] concluded that the size of particle is influenced by the modifications in polyol hydroxyl number and the amounts of hard segment and DMPA content.

In this study, Jatropha oil will be used to prepare a bio-based polyol by using epoxidation and oxirane ring-opening process. The prepared polyol will then be used to produce waterborne PUDs which will then be studied based on its particle size, Zeta potential, and viscosity. This novel material can be applied in surface coating application.

2. Experimental

2.1 Materials

Crude Jatropha oil was acquired from BATC Development Berhad, Malaysia. Hydrogen peroxide, sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (NaOH), ethyl methyl ketone (MEK), pyridine, and acetone were supplied by Merck, Germany. Formic acid and ethanol were obtained from Systerm. Magnesium sulphate ($MgSO_4$) was purchased from Sigma Aldrich. Dimethyl propionic acid (DMPA), dibutyltin dilaurate (DBTDL) and isophrene diisocyanate (IPDI) were supplied by Aldrich.

2.2 Synthesis of jatropha oil-based polyol

2.2.1 Epoxidation. The reactions were carried out in a 1000-mL beaker equipped with a mechanical stirrer, isobaric funnel, and thermometer. The beaker was placed inside a water bath to maintain the reaction temperature.

Jatropha oil and formic acid were added into the beaker and heated until the temperature was 40 ^{o}C. After the mixture has reached 40 ^{o}C, hydrogen peroxide was added drop by drop using the isobaric funnel for 30 minutes. The molar ratio of Jatropha oil to formic acid to hydrogen peroxide used was 1:0.6:1.7 [10]. The temperature of the reaction was then increased and maintained at 60°C for 4 hours. The reaction was quenched after 4 hours by cooling the reaction mixture to room temperature. The mixture was then transferred to a 1000-mL separating funnel to allow phase separation. The aqueous phase was removed and the remaining acid was removed by washing the oil layer using distilled water. Magnesium sulphate was added into the mixture and left overnight to remove the remaining aqueous phase.

2.2.1 Oxirane Ring Opening. The reactions were conducted in a 1000-mL beaker equipped with a magnetic stirrer and a thermometer. In this reaction, ethanol was used as to ring-opened the epoxidized Jatropha oil (EJO).

Generally, a calculated amount of ethanol, sulphuric acid, and water were added to the beaker and the mixture was stirred continuously and heated until it reached ethanol boiling point. Then, the EJO was added to the mixture and was kept at ethanol boiling point for 30 minutes. Sodium bicarbonate was added to quench the reaction. The mixture was then transferred into a separating funnel and distilled water was added. The funnel was shaken and left aside for 30 minutes for the polyol to separate from the reactant mixture. The excess water and ethanol were removed using rotary evaporator. Then, the resulted jatropha oil-based polyol was analyzed for OH number according to ASTM D4274-99 (Test Method C-Reflux Phtalation).

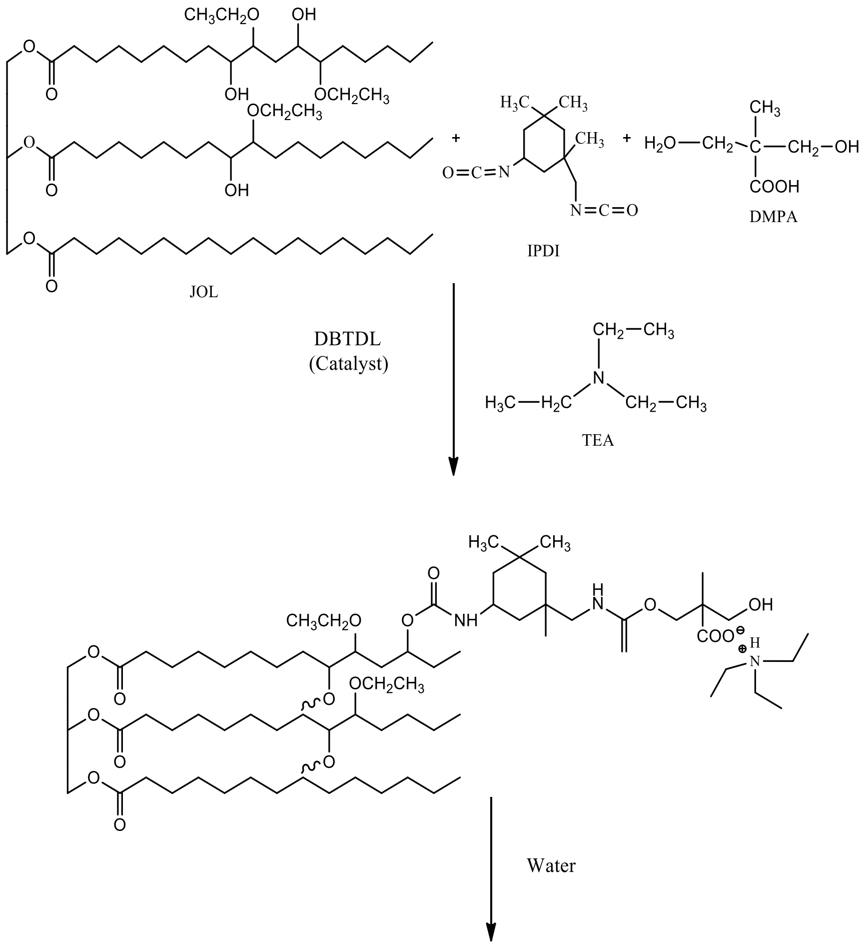
2.3 Synthesis of waterborne jatropha oil-based polyurethane dispersions

For the synthesis of JPU dispersions, the DMPA content (wt.%) were varied 5.0, 5.5, 6.0, 6.5 and 7.0 wt. % while the ratio of NCO/OH = 1. The formulation of JPU dispersions is shown in Table 1. Synthesis of JPU dispersions were performed according to a method described by Saalah et al., (2018) with some modification. Briefly, the calculated amount of dimethylol propionic acid (DMPA) was dissolved in of n-methyl pyrrolidone (NMP) in a 200-mL beaker and stirred at a temperature of 50.0 °C. After the DMPA has dissolved, the prepared Jatropha oil-based polyol, JOL183 (OH number = 183 mg/KOH) was added into the mixture and stirred 30 minutes at 60 °C. Isophrene diisocyanate (IPDI) was added drop by drop into the mixture and one drop of dibutyltin dilaurate (DBTDL) was added into the mixture as a catalyst. Methyl ethyl ketone (MEK) was added batch by batch to decrease the viscosity of the mixture. The reaction was conducted at a temperature range of 70.0 – 80.0 °C for 3 hours. The mixture was then cooled after a 3-hour reaction and triethylamine (TEA) was added to neutralized the mixture. Finally, the PU solution was dispersed in distilled water at high stiring speed. The reaction was followed by dispersion at high speed using distilled water. The synthesis scheme of the JPU dispersion is shown in Figure 1. A Waterborne JPU dispersion was successfully synthesised after the removal of the solvent.

Table 1: The Formulation of Jatropha oil-based polyurethanes (JPU) dispersion.

DMPA wt.% for JPU183 formulation (wt.%)	Amount (g)			[a]Hard segment (wt%)
	JOL183	DMPA	IPDI	
5.0	1	0.38	1.38	39.67
5.5	1	0.43	1.43	40.98
6.0	1	0.47	1.47	42.27
6.5	1	0.53	1.53	43.59
7.0	1	0.58	1.58	44.88

[a] Hard segment content [HS= Mass (IPDI+DMPA+TEA)/ Mass (Polyol+DMPA+IPDI+TEA)].



Jatropha oil-based, waterborne PU dispersion (JPU)

Figure 1: Reaction scheme for synthesis of water-borne polyurethane dispersion.

2.4 Characterizations of JPU dispersion

2.4.1 FTIR Spectra. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the functional groups in the Jatropha oil-based polyol and polyurethane dispersion. The equipment used was diamond crystal tip-equipped Perkin-Elmer Spectrum 100 spectrometer by using range of 4000 - 500 cm$_{-1}$ with a nominal resolution of 4 cm$_{-1}$.

2.4.2 Particle size and zeta potential. A Zetasizer Nano-S (Malvern Instruments) was used to determine the size of particle of the polyurethane dispersions. 3 mL of distilled water was used to dilute approximately 0.1 mL of the polyurethane dispersion before and after removal of solvent. The diluted dispersion was then measured at 25 °C. The Zeta potential was determined by electrophoresis principle using a Zetasizer Nano ZS.

2.4.3 Rheology. A TA Instruments AR1500ex rheometer was used to determine the viscosity of JO, JOL183 and JPU183 as a function of shear rate at 25 °C. The rheometer was equipped with a 40 mm 2^{o} cone and the gap between the truncated tip of the cone and bottom Peltier plate was kept at 56 μm.

3. Result and Discussion

3.1 FTIR analysis

Figure 2 shows the comparison of FTIR spectra for the waterborne PUDs with different DMPA content in comparison with the polyol. The successful formation of polyurethane in all samples were confirmed by appearance of essential functional essential functional groups that the samples exhibited. In the range of 3325 to 3360 cm$_{-1}$, there are broad absorbance peaks corresponds to the —NH bending. There were peaks at the range between 2270 and 2300 cm$_{-1}$ for some samples which were an evidence of —NCO groups. This showed that the polyol has not reacted completely with DMPA and IPDI. Other than that, the peaks at 1710 and 1540 cm$_{-1}$ indicated the C=O bonds of urethane linkage and —NH deformations respectively [16].

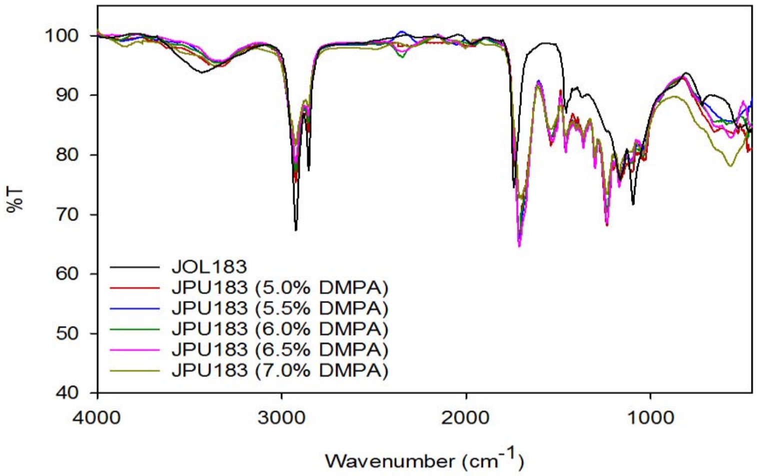


Figure 2: FTIR spectra of all JPU183 samples with varying DMPA content.

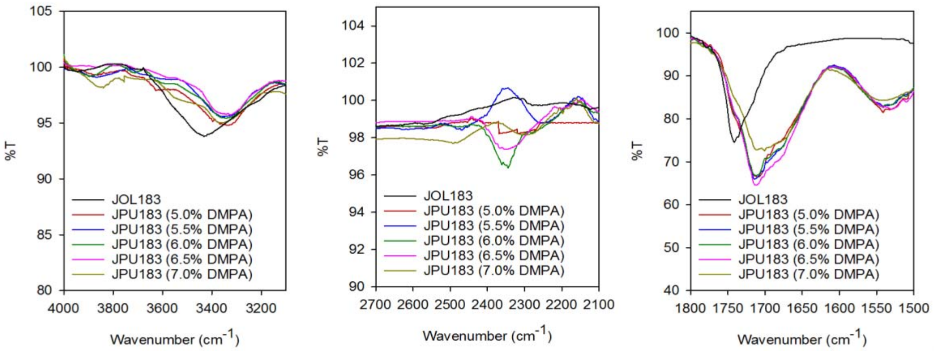


Figure 3: Essential functional groups in JPU183 samples.

3.2 Particle size and zeta potential analysis

The stability of a dispersion can be projected by using particle size and zeta potential analysis. Generally, a stable dispersion has smaller particle size and high zeta potential value. The ideal particle size to produce a stable colloid as proposed by [18] is around or below 100 nm. Different particle sizes are employed in different applications, where smaller sizes are used for surface coatings while larger sizes are applied for rapid drying of the coatings. On one hand, large values of zeta potential (positive and negative) are more stable as the particles tend to repel each other. A stable dispersion generally has an absolute zeta potential value higher than 30 mV [19].

It is generally recognized that the particle size will decrease as the amount of hard segment increases. The dispersions in this study have decreasing particle sizes with increasing hard segment content. However, JPU183 5.5% DMPA exhibited the smallest particle size among all the dispersions. The value does not correlate to the trend of decreasing particle size with increasing DMPA content. Table 2 shows the particle size and its deviation for all dispersions before and after the removal of solvent. The values for the particle size were taken at the Z-average. We can conclude that removal of solvent (MEK) after evaporation by application of heat was not affect the particle sizes for all dispersions. The small particle size for all dispersion indicates good stability of JPU dispersion for surface coating.

Table 2: Physico-chemical characteristics, particle size, and Zeta potential of JPU183 samples with varying DMPA content.

JPU183 DMPA (wt%)	Solid content (wt.%)	Colour/ Appearance	Before removing solvent (MEK)		After removing solvent (MEK)	
			Particle size (nm)	Zeta potential (mV)	Particle size (nm)	Zeta potential (mV)
5.0	35.7	Pinkish, opaque	134.3 ± 0.61	-63.53 ± 2.37	130.77 ± 0.87	-54.47 ± 2.47
5.5	34.3	Yellowish, transparent	35.98 ± 0.09	-49.23 ± 2.42	34.68 ± 0.40	-62.15 ± 4.55
6.0	31.7	Yellowish, transparent	56.22 ± 2.45	-60.70 ± 1.18	53.6 ± 0.60	-64.85 ± 2.15
6.5	31.7	Yellowish, transparent	50.13 ± 3.06	-47.43 ± 1.02	49.8 ± 1.41	-50.6 ± 6.2
7.0	31.0	Yellowish, transparent	25.81 ± 0.01	-39.77 ± 1.96	40.02 ± 0.91	-64.9 ± 5.7

All the dispersion samples exhibited high zeta potential values, which were in a range from -56.5 mV to -66.4 mV. This indicates that the samples repel each other successfully, showing that they are stable colloidally. The results obtained correlate with studies done by [11,16].

3.3 Rheology

Figure 4 illustrates the viscosity curve of JO, JOL183 and JPU183 dispersions against shear rate. All samples display flow behaviour that ranges from nearly-Newtonian to shear-thinning fluid. JPU183 with DMPA contents of 5.0 and 5.5% behaved as shear thinning fluids at a constant temperature of 25 ^{o}C. The viscosity of both the samples decreases with increasing shear rate as the structure of the material breaks down and they flow more readily. On the other hand, JO, JOL183 and JPU183 with DMPA contents of 6.0, 6.5, and 7.0% showed an almost Newtonian fluid behaviour as their viscosities maintained through the range of applied shear rate.

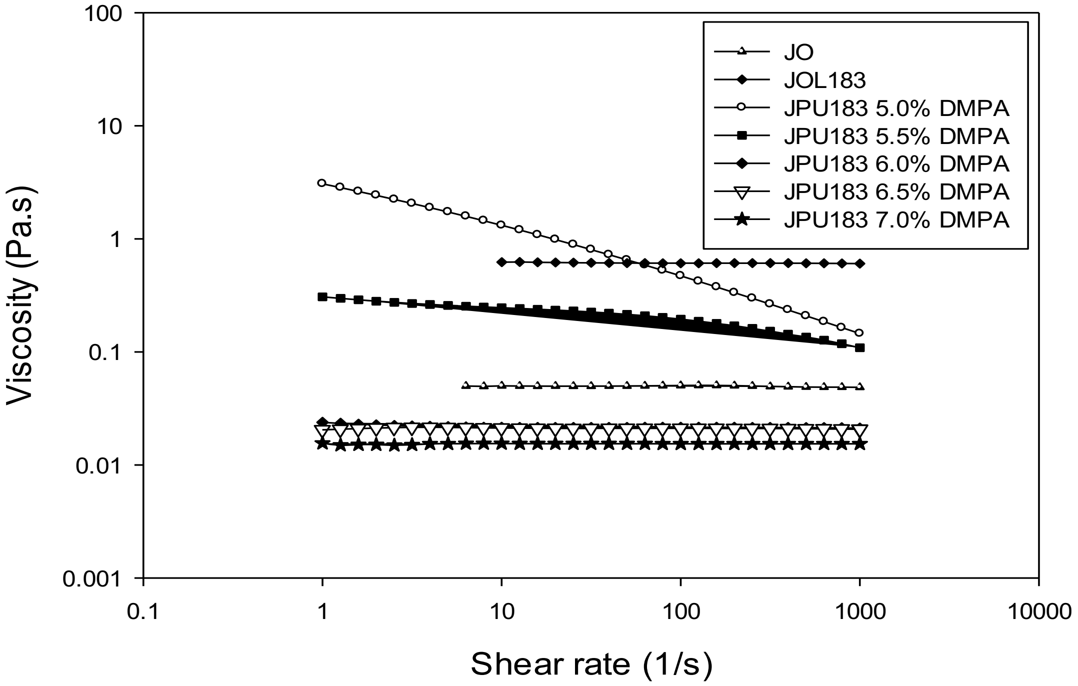


Figure 4: Viscosity of JPU183 dispersions as a function of shear rate at 25 °C.

Table 3 shows the viscosities and the zero-shear viscosities obtained for JPU183 dispersions for DMPA content 5.0 and 5.5% shows higher viscosity which were 7962 and 300 mPa.s respectively. Zero shear viscosity was obtained by fitting the experimental data with Cross equation available in the software used for the rheometer [20]. Zero-shear rate viscosity indicates the storage stability of the dispersions. During storage, the dispersions are only affected by gravity as they are under a low stress state. Dispersions which have high viscosity under a low shear rate are very stable as they can resist settling. Besides, the coatings produced from high zero-shear dispersions will have a smooth finish as they are less likely to clump on the coating substrate. On the other hand, coatings from lower viscosity dispersions produces an evenly-distributed finish on the coating substrate [16]. Hence, JPU183 dispersions with DMPA content 5.0 and 5.5% are beneficial as they have the high zero-shear viscosity required for stability and smooth finish. For JPU183 dispersions with DMPA content 6.0, 6.5, and 7.0%, their Newtonian properties can be modified to shear-thinning properties by increasing the solid content of the dispersions.

Table 3: Viscosity and Zero shear viscosity of JO, JOL183 and JPU183 with various DMPA content at temperature 25°C.

Samples	Zero shear viscosity (mPa.s)	Viscosity (at shear rate of 100s-1)
JO	500	503
JOL183	600	600
JPU183 5.0 wt%	7962	471
JPU183 5.5 wt%	300	212
JPU183 6.0 wt%	20	21
JPU183 6.5 wt%	20	21
JPU183 7.0 wt%	10	15

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4. Conclusion

In conclusion, Jatropha oil-based polyol (JOL) was successfully synthesised by the two-step method, epoxidation and oxirane ring opening, using ethanol as the ring-opening agent. Five samples of polyurethane dispersions (JPU) with varying DMPA contents were synthesised from the prepared JOL, by maintaining the molar ratio of NCO/OH to 1. The increasing DMPA content used from 5.0 to 7.0% produced dispersions with decreasing particle sizes, which was in a range of 40.0 to 130.0 nm. The high absolute value of Zeta potentials of all dispersions, ranging from 50.6 to 64.9 mV showed that the dispersions were stable. This investigation indicates that the amount of DMPA content also plays an important role to the stability of JPU dispersion. Finally, JO, JOL183 and JPU183 dispersion for DMPA content 6.0, 6.5 and 7.0% showed an almost Newtonian fluid behaviour, while for the JPU183 5.0 and 5.5 shows higher viscosities which were 7962 and 300 mPa.s respectively proves that the dispersions are stable and suitable for coating application.

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