JOURNAL OF Applied Polymer SCIENCE

Performance of palm oil-based dihydroxystearic acid as ionizable molecule in waterborne polyurethane dispersions

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ABSTRACT: Waterborne polyurethane dispersions (WPUDs) containing a renewable palm oil-based 9,10-dihydroxystearic acid (DHSA) as an isocyanate-reactive compound bearing ionizable carboxylic group to incorporate hydrophilic groups into the polymer chain have been successfully prepared. The WPUDs were prepared by using polyether and polyester polyols of 2000 molecular weight, DHSA and its traditional petroleum-based counterpart 2,2-bis(hydroxymethyl)-propionic acid (DMPA), and an aliphatic diisocyanate (isophorone diisocyanate, IPDI). A comparison was made between the properties of WPUDs obtained using blends of DHSA and DMPA at different molar ratios and a reference WPUD based on DMPA. The particle size of polyester type WPUDs containing DHSA was reduced at a 0.5 to 0.5 molar ratio of DMPA to DHSA. A lower initial temperature was used in the preparation of NCO-prepolymers with DHSA as compared to DMPA and this eased the preparation of WPUDs. The effect of molar ratio of DMPA to DHSA on the properties of films and coatings prepared with WPUDs was evaluated. The best properties were obtained with WPUDs prepared with a 0.5 to 0.5 molar ratio of DMPA to DHSA. The incorporation of renewable palm oil-based DHSA into WPUDs improved water resistance (lower water uptake) and exhibited good combination of properties including hardness, adhesion strength, tensile strength, and elasticity. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43614.

KEYWORDS: applications; biopolymers & renewable polymers; polyurethanes

Received 22 November 2015; accepted 6 March 2016

DOI: 10.1002/app.43614

INTRODUCTION

The global interest for utilizing crop-based feedstock as bio-renewable alternatives to petroleum-based feedstock has been stimulated due to the rapid depletion of crude oil reserves and the concern over climate changes. It is a challenge for scientists and engineers in finding ways to improve and overcome the limitations of natural oils so that they have wider industrial applications for niche markets.[1] One of them is polyurethanes (PUs), which is one of the most common polymers in many modern technologies. Considerable amount of research has been focused on the replacement of petroleum-based starting materials for PUs with bio-renewable-based materials.[2–6] PU coatings are known to contain a significant amount of organic solvents, which is hazardous to human health and the environment. Increasing concern on these issues has pressured the PU industry to move toward waterborne systems with renewable content. The waterborne PU dispersion (WPUD) is a rapidly growing segment of the PU coatings and adhesives industry.[4,7–9] Polymeric structure of WPUD consists of building blocks that include diisocyanates, polyols, amines, catalysts, and additives. It is not possible to directly synthesize PU ionomer in water due to the undesired reactivity of diisocyanates with water. Several methods have been developed to synthesize WPUDs, including the acetone process, the NCO-prepolymer process (which is used in this study), the melt dispersion process, and the ketamine/ketazine process.[10–12] Commonly, the first step for its preparation involves synthesis of medium molecular weight oligomer known as NCO-prepolymer, which can be formed by reaction between suitable diols or polyols, usually macrodiols such as polyesters, polyethers, or polycarbonates and with excess diisocyanates or polyisocyanates.

PUs are basically hydrophobic and require the use of emulsifiers to disperse them in water. Introduction of internal emulsifiers in the polymer was found to be more advantageous than using external emulsifiers.[13] Thus, the introduction of hydrophilic groups of ionic or non-ionic nature during the synthesis of the

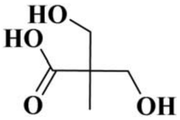

Figure 1. Molecular structure of 2,2-bis(hydroxymethyl)-propionic acid (DMPA).

polymer and subsequently becoming part of the main chain of the polymer is more desirable.[12,14] One of the most preferred hydrophilic chemical to be incorporated in the preparation of anionic type of WPUDs is 2,2-bis(hydroxymethyl)-propionic acid (DMPA), which is a dihydroxycarboxylic acid.[6,11,15–17] The main advantage of DMPA is that the carboxylic acid group is much less reactive than its primary hydroxyl groups which preferentially reacts with the isocyanate in forming PU backbone.[12] The carboxylic group of DMPA is neutralized with a tertiary amine forming ammonium salt group that facilitates the dispersing of the hydrophobic PUs in water.

However, there are certain process-related disadvantages of DMPA in the production of the WPUDs. The main reason is that DMPA has relatively high melting temperature (185–190 °C) and needs to be homogenized with polyol at relatively high temperature (~140 °C). After homogenization, the blend of polyol and DMPA needs to be slowly cooled to 70–80 °C (temperature of NCO-prepolymer synthesis) under continuous agitation to prevent precipitation of DMPA. This leads to a prolonged reaction time in the synthesis of WPUD. Other undesirable property is that DMPA is a small molecule and in the blend with high molecular weight polyol it will react faster with isocyanate, forming longer hard segment. The hydroxyl groups of the polyol will react at slower rate prolonging the reaction with isocyanate in the prepolymer synthesis. This causes the carboxyl groups to be non-uniformly distributed throughout the PU backbone and contributes to relatively high viscosity of PU NCO-prepolymer.[13]

Klauck and Daute reported a process for production of carboxyl functional PU from dihydroxyfatty acids and dihydroxypolyfatty acids as isocyanate-reactive compound bearing an ionizable group in WPUDs.[13] In 1998, palm oil-based dihydroxystearic acid (DHSA) was successfully produced from palm oil-based oleic acid by Malaysian Palm Oil Board (MPOB Selangor, Malaysia.) as described in Malaysian Patent PI 9,804,456.[18–22] Both DMPA and DHSA are molecules with three functional groups namely two hydroxyl groups and one carboxylic group. The difference between both molecules is the carbon chain length, where DMPA (Figure 1) has a shorter carbon length of C_5 whereas DHSA (Figure 2) has a longer carbon chain length of C_{18}. In addition, DHSA has secondary and DMPA primary hydroxyl groups.[20] Due to longer hydrocarbon chain, it is expected that DHSA will increase hydrophobicity of polymer backbone and lower water uptake of WPUD coatings and films.

This opens an opportunity for DHSA to be used as an internal emulsifier for the preparation of WPUDs and great opportunity for DHSA to address the disadvantages of DMPA while being able to perform the same function as DMPA. In addition, DHSA is obtained from a renewable source such as palm oil.

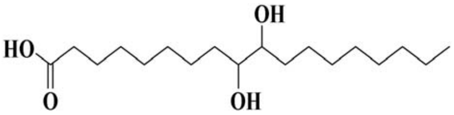

Figure 2. Molecular structure of 9,10-dihydoxystearic acid (DHSA).

The properties of DMPA and DHSA are tabulated in Table I. To our best knowledge, there have been no reports in literature of WPUDs using palm oil-based DHSA as isocyanate-reactive compound bearing ionizable group for production of WPUDs.

In this study, DHSA was introduced as a potential internal emulsifier or ionizable molecule that could fully or partially replace DMPA for the preparation of WPUDs. The developments of WPUDs in this study are based on the NCO-prepolymer process, which has the advantage of avoiding the use of large amount of organic solvent.[11,12,17]

EXPERIMENTAL

Materials

The raw materials used in this study were used as received without any further purification. Polyols were de-moisturized under vacuum at 80 °C for overnight prior to use if the moisture content was above 0.05%. All the polyols used in the study were 2000 molecular weight (MW) diols. Polyether polyol (Poly-G 20-56) with a hydroxyl equivalent weight of 1000 was supplied by Arch Chemicals, Inc (Monument Chemical Kentucky LLC, Brandenburg, Kentucky, USA). Dimer acid-based polyester polyol (Priplast 3192) with a hydroxyl equivalent weight of 984 was supplied by Croda (Edison, New Jersey, USA). Polyester diol polyol (Diexter G 4400-57) with a hydroxyl equivalent weight of 984 was supplied by Coim USA Inc (West Deptford, New Jersey, USA). 2,2-bis(hydroxymethyl)-propionic acid (DMPA) with a hydroxyl equivalent weight of 67 was supplied by Perstorp Specialty Chemical AB. Palm oil-based DHSA from palm oil-based oleic acid with an equivalent weight of 158 was supplied by MPOB. Isophorone diisocyanate (IPDI) with an isocyanate equivalent weight of 112 was supplied by Rhodia (Le-Pont-de-Claix, France). Dibutyltin dilaurate (DBTL) was supplied by Merck (Schuchardt OHG, Hohenbrunn, Germany). Triethylamine (TEA) was supplied by Fisher Scientific (Leicestershire LE11 5RG, United Kingdom) and was used after dehydration with 4 Å molecular sieves for a week. Ethylene diamine (EDA) was supplied by Dow Chemical (Sdn. Bhd., Selangor, Malaysia).

Table I. Properties of DMPA and DHSA

Properties	DMPA	DHSA
CAS number	4767-03-7	120-87-6
Molecular formula	$C_5H_{10}O_4$	$C_{18}H_{36}O_4$
Molecular weight, g mol^{-1}	134.13	316.48
Hydroxyl value, mg KOH g^{-1}	834	230-310
Melting point, °C	185-190[a]	85-90[b]
Physical appearance	White crystal	White powder

Note: Reproduced from [a]ref. 23 and [b]ref. 22.

Synthesis of Prepolymer and Preparation of WPUDs

The WPUDs were synthesized via prepolymer process. Polyols were dried prior to use to ensure the moisture content of the polyols was less than 0.05%. It was done by heating the polyol at ∼80 °C under steering and vacuum of 1 to 3 mm Hg. The NCO-prepolymers were synthesized in a 500-mL four necked round flask equipped with a stirrer, a thermometer, an inlet and outlet of nitrogen and wrapped with a heating jacket. Nitrogen purge and constant agitation were applied throughout the course of the reaction. At first, the polyols and ionizable molecule either DMPA or DHSA or mixtures of both were added into the reaction flask to homogenize under heat and mixing. In the case of DHSA or combinations of DHSA and DMPA as ionizable molecules, their mixtures with a polyol were heated to 90 to 100 °C and homogenized for 45 min. In the case of DMPA as sole ionizing molecule, the mixture with polyol was homogenized at 135 °C, which was significantly lower temperature than the melting temperature of DMPA (Table I) due to the DMA solubility in the polyol. The homogenous mixture of polyol and chain extender was cooled down to 70 to 80 °C under continuous mixing followed by the addition of IPDI and catalyst (DBTL). Upon completion of the additions, reaction mixture was heated at 75–80 °C and the reaction was allowed to proceed until the percentage of free isocyanate (NCO %) was close to its theoretical value. The changes in the NCO % during the reaction were determined with the standard di-butylamine back titration method according to ASTM D 2572. Subsequently, the NCO-terminated prepolymer (NCO-prepolymer) was cooled to 60 °C to proceed with neutralization of the carboxyl group of the ionizable molecule by addition of TEA. After 30 min of neutralization reaction, distilled water (55–60% weight percentages of NCO-prepolymer depending on the targeted solid content) was added dropwise under vigorous stirring at 1500 rpm, forming dispersion in water. The neutralized NCO-prepolymer dispersed in water was chain extended at room temperature with EDA solution which was added dropwise in the period of 10 min under vigorous stirring. Upon addition of EDA the mixing was continued for 30 min to complete the polymerization reaction. The WPUDs prepared with 40 ± 5% of solid content were kept in air tight bottles for analyses as described.

Characterization of Waterborne Polyurethane Dispersions

Viscosity of Waterborne Polyurethane Dispersions. The viscosity at room temperature around 23 °C was determined by using Brookfield Model DV-III Ultra (Brookfield VF viscometer according to ASTM D2369-10.

pH Value Measurement of Waterborne Polyurethane Dispersions. The pH values of the WPUD were measured at 25 °C with a pH meter (Mettler Toledo, Switzerland). The pH reported was calculated as the average of three experimental determinations.

Particle Size Distribution of Waterborne Polyurethane Dispersions. The particle size of the WPUD was measured with Mastersizer 3000 equipped with Hydro EV (Malvern Instruments Ltd, UK) provided with laser diffraction that measures the intensity of the scattered light over a range of angles, from an ensemble of particles of unknown size. A small amount of WPUD was diluted to the required concentration with distilled water before measurement. The mean particle size was calculated as the average of three experimental determinations.

Solid Content of Waterborne Polyurethane Dispersions. Test method ASTM D2369-10 was used to determine the weight percent of solid content of WPUDs. Approximately 1.00 g of WPUD was weighed in an aluminum weighing dish and heated at 110 ± 5 °C for 60 min and measured the solid content. The solid content of the WPUD was calculated based on the formula below:

$$\text{Solid content}[\%]=1-\frac{(W_i-W_f)}{W_i}\times 100$$

W_i is the initial weight of the sample and W_f is the final weight of the sample after exposure to 110 ± 5 °C for 60 min.

Preparation of Thin Film from Waterborne Polyurethane Dispersion

Some properties of the WPUDs were evaluated as solid films prepared by casting the WPUDs using Dr. Blade on various substrates such as Q-panel cold roll steel (CRS), glass panel, and polypropylene panel and allowing them to dry at room temperature for 24 h. Then, WPUD films were subsequently heated at 60 °C for 24 h to allow complete removal of water. The dry thickness of the films obtained was about from 20 to 30 μm. The films were conditioned at room temperature for a week before characterizing and measuring the properties of the films. The films coated on CRS and glass substrates were evaluated for film hardness and adhesion strength and films coated on polypropylene substrates were tested for tensile strength and water absorption.

Characterization of Films Based on Waterborne Polyurethane Dispersions

Fourier Transform Infrared with Attenuated Total Reflectance Analysis of Films Based on Waterborne Polyurethane Dispersion Films. A Fourier transform infrared spectrometer (FTIR) Spectrum 100 equipped with universal attenuated total reflectance (ATR) (Perkin Elmer, UK) was used to analyze the functional groups presence in the WPUD films. The films were prepared by coating the WPUDs onto polypropylene substrates resulting in dried films of thickness ∼20–30 μm. Each FTIR measurement consists of 32 scans at 4.0 cm^{-1} resolution.

Water Absorption of Films Based on Waterborne Polyurethane Dispersions. The WPUD films were immersed in water for 24 h at 25 °C and the swelling weigh percentage was determined from weight increase:

$$\text{Swelling (\%)} = (W-W_0\times 100)/W_0$$

where the W_0 is the weight of the dried film prior to immersion in water and W is the weight of the film after swelling.

Adhesion Properties of Films Based on Waterborne Polyurethane Dispersions. Adhesion strength of WPUD films was determined by measuring the adhesion of the film on CRS and glass substrates by tape test according to ASTM D 3359-97. Once the films are ready to be tested, two cuts on the film were made with each 40 mm long that intersect near their middle

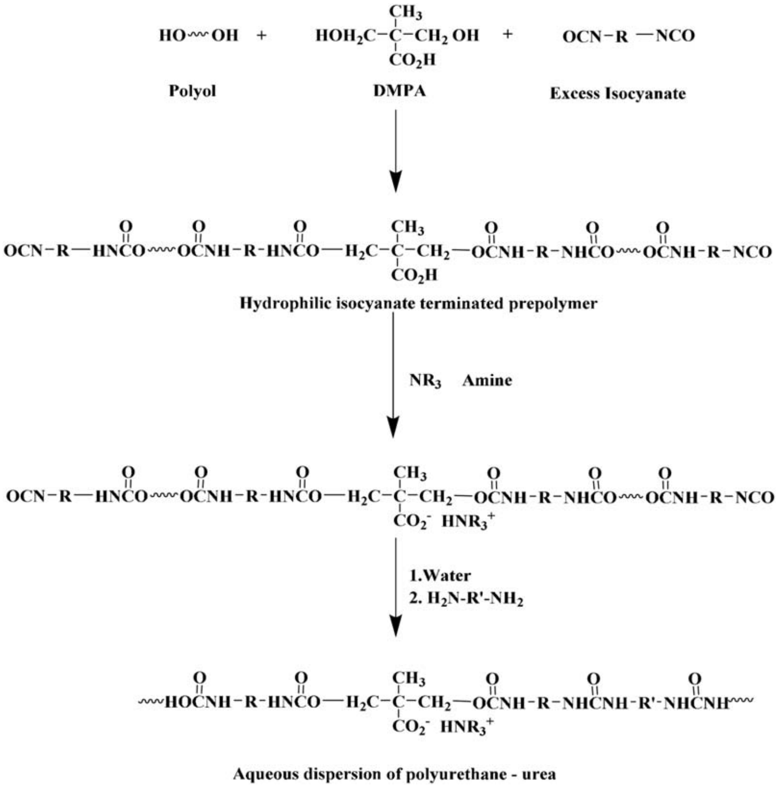

Figure 3. Synthesis procedure for preparation of anionic type WPUD *via* prepolymer process.

with a smaller angle between 30° and 45°. A piece about 75 mm long adhesion tape was cut and the center of the tape was placed at the intersection of the cuts with the tape running in the same direction as the smaller angles. The tape was smoothed into place with finger in the area of the incisions and then rubbed firmly with eraser on the end of a pencil. Within 30–90 s of application, the tape was removed by seizing the free and pulling it off rapidly without jerked back upon itself as close to an angle of 180° as possible. The X-cut area was inspected for removal of coating from the substrate or previous coating and the adhesion was rated.

Pencil Hardness Test of Films Based on Waterborne Polyurethane Dispersions. Test Method ASTM D 3363 was used to determine the hardness of the WPUD film coated on CRS and glass panels by drawing pencil leads of known hardness. The test was carried out at 25 ± 2 °C. Coated substrate was placed on a firm horizontal surface and pencil was held firmly against the film at 45° angle (point away from the operator). The pencil was then pushed away from the operator. The test was started using the hardest pencil and continued down the scale of the hardness to determine the two end points: (i) the pencil that did not cut or gouge the film and (ii) the pencil that did not scratch the film.

Tensile Strength of Films Based on Waterborne Polyurethane Dispersions. The tensile strength of the WPUD films was tested according to ASTM D 412 (modified) by using Zwick-Single Column testing machine manufactured by Zwick Roell, Germany. The films were prepared by casting WPUDs on polypropylene substrates. The films were conditioned for a week before testing. The specimens of the test were prepared by cutting the films into dumb-bell shape using dumb-bell dice. The crosshead speed was 77 mm min^{-1} with 20 N load-cells. The stress and strain measurement data were analyzed for tensile strength and elongation at break. The values were reported as the average of minimum five measurements for each sample. The measurement was carried out at 25 °C and 50% relative humidity.

RESULTS AND DISCUSSION

WPUDs consist of basic chemical components that include diisocyanates, polyols, and ionizable molecules as the building blocks. The two key classes of polyols used for PUD are polyethers and polyesters. Polyester polyols have been largely used in PUD paints as they exhibit outstanding adhesion, resistance to light and aging. The main classes of polyester polyols are linear or lightly branched aliphatic polyesters, low molecular weight aromatic polyesters, polycaprolactones, and polycarbonates. Meanwhile, polyether polyols are hydrophobic, have lower viscosity that facilitate preparation of dispersion and give chain flexibility.

Several important reactions take place during the preparation of WPUD. In the initial stage, the reaction between polyols and diisocyanates (in excess amount) would lead to formation of NCO-prepolymer. The subsequent reaction involves neutralization of carboxylic acid group of NCO-prepolymer with tertiary amine to yield ammonium carboxylate ionic site. Meanwhile, in a third reaction the remaining isocyanate groups react with diamine forming urea groups and completing polymerization (Figure 3). Since the reaction takes place in water, a fourth side

Table II. Compositions of NCO-Prepolymers and Their NCO %

Type of polyol	Molar ratio of Polyol/DMPA/ DHSA/IPDI	Carboxyl groups weight (%)	Theoretical NCO (%)	Experimental NCO (%)	Difference in NCO (%)	Duration of reaction (min)
Poly-G 20-56	1/1/0/4	1.52	5.92	6.19	+4.56	90
	1/0.75/0.25/4	1.50	5.93	5.92	−0.17	150
	1/0.5/0.5/4	1.48	5.75	5.50	−4.35	120
	1/0.25/0.75/4	1.45	5.67	5.94	+4.76	120
	1/0/1/4	1.43	5.59	5.68	+1.61	120
Diexter G 4400-57	1:1:0:4	1.54	5.92	5.79	−2.20	90
	1:0.75:0.25:4	1.52	5.84	5.79	−0.86	90
	1:0.5:0.5:4	1.49	5.75	5.68	−1.22	90
	1:0.25:0.75:4	1.47	5.67	5.68	+0.17	90
	1:0:1:4	1.45	5.60	5.67	+1.25	90
Priplast 3192	1:1:0:4	1.54	5.99	5.83	−2.67	90
	1:0.75:0.25:4	1.52	5.89	5.75	−2.78	90
	1:0.5:0.5:4	1.49	5.81	5.85	+0.69	90
	1:0.25:0.75:4	1.47	5.74	5.75	+0.17	90
	1:0:1:4	1.45	5.64	5.70	+1.06	90

reaction between the isocyanate and water might take place which gives unstable carbamic acids that decompose rapidly to amine and carbon dioxide. The resulted amines react with isocyanate to form urea group.[10,17] In order to minimize this reaction, that can affect stability of WPUDs, the NCO-prepolymer containing ionic site dispersed in the water should be kept at room temperature for minimum time before reaction with EDA. The preparation of WPUD, compared to solvent-based PUD is more challenging because it involves dispersing relatively hydrophobic polymer in the aqueous phase. Knowing the challenges involved, preparation of stable WPUDs was established as a benchmark protocol via NCO-prepolymer process as illustrated in Figure 3. In this study, polyester polyols namely Diexter G 4400-57 (based on adipic acid) and Priplast 3192 (based on dimer acid) and polyether polyol namely Poly-G 20-56 were used as soft segments and IPDI as hard segment of PU. DMPA and DHSA were used as ionizable molecules. The molar ratio of DMPA/DHSA were varied in order to study the effect of DHSA in combination with commonly used soft segments on the physical and mechanical properties of WPUD's films as well as its adhesive strength.

The compositions of NCO-prepolymers prepared with their theoretical NCO % compared to experimental NCO % and reaction time are shown in Table II. During the synthesis of the NCO-prepolymer, the change in the content of NCO % was measured as a function of reaction time. The result shows that the experimental NCO % was close to the theoretical NCO % with less than 5% differences for all the NCO-prepolymers prepared. The theoretical NCO % for NCO-prepolymers based on polyester polyols was achieved within 90 min. The NCO-prepolymers prepared from polyether polyol took longer time to reach the theoretical NCO % than the NCO-prepolymers prepared from polyester polyols (Table II). This is due to lower polarity of polyether polyols as compared to polyester polyols and a nature of hydroxyl groups in the polyols. Polyether polyol

Table III. Compositions and Properties of the WPUDs

Type of polyol	Molar ratio of DMPA/DHSA	Solid content (%)	pH at 25 °C	Particle size (μm)	Viscosity at 25 °C (mPa s)
Poly-G 20-56	1/0	41	9.5	0.5	18
	0.75/0.25	41	9.5	22.5	58
	0.5/0.5	41	9.3	7.1	28
Diexter G 4400-57	1/0	45	9.2	17.2	104
	0.75/0.25	41	9.4	4.2	52
	0.5/0.5	40	9.6	3.3	20
Priplast 3192	1/0	42	9.0	9.3	26
	0.75/0.25	40	9.6	13.4	80
	0.5/0.5	41	9.3	2.0	52

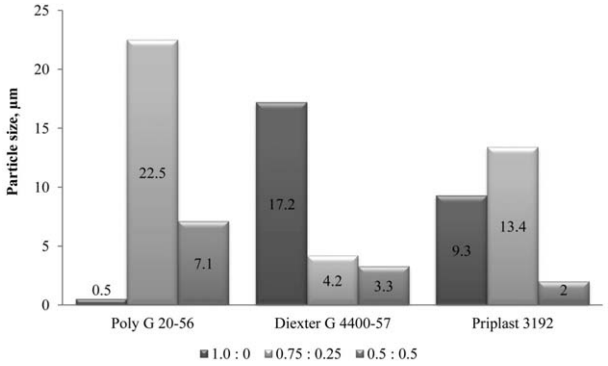

Figure 4. Effect of the molar ratio of DMPA to DHSA on the particle size of WPUDs.

has secondary hydroxyl groups which are less reactive than the primary hydroxyl groups in polyester polyols.

Since the melting point of DHSA is around 85–90 °C, the mixture of polyol with either DHSA or combination of DHSA and DMPA was homogenized at 90–100 °C. The melting point of DMPA is 185–190 °C, thus higher temperature (135 °C) was required to homogenize the mixture of polyol and DMPA when used as a sole ionizing molecule. Therefore, with the introduction of DHSA, less time and energy were required in the initial stage to homogenize (dissolve) the ionizable molecules and the polyol.

The compositions and properties of the WPUDs are shown in Table III. WPUDs with solid content of 40 ± 5% were targeted. The solid content of most of the WPUDs prepared was around 41%. The NCO-prepolymers synthesized from all the polyols with molar ratio 0.25/0.75 and 0/1 of DMPA/DHSA tend to agglomerate during the preparation of the dispersion due to the presence of higher amount of DHSA with longer carbon chain (C_{18}) and those WPUDs were excluded for further testing. The change in concentration of carboxylic groups in the NCO-prepolymers was small with increase in DHSA amount (Table II) and thus the effect of DHSA on stability of WPUDs cannot be ascribed to the change in concentration of ionic sites but to their more hydrophobic and less polar nature. The lower ionic strength of DHSA ionizing site leads to lower electrostatic repulsive force between the particles in the WPUDs system and this is not sufficient to stabilize the particles and they start to agglomerate.[24] Otherwise, DHSA was successfully incorporated as ionizable molecule up to 50% in the NCO-prepolymers used to prepare the WPUDs. All the WPUDs prepared at 1/0, 0.75/0.25, and 0.5/0.5 of DMPA/DHSA were stable at room conditions. The pH of the WPUDs was alkaline in the range of 9.2–9.6, which could be expected.

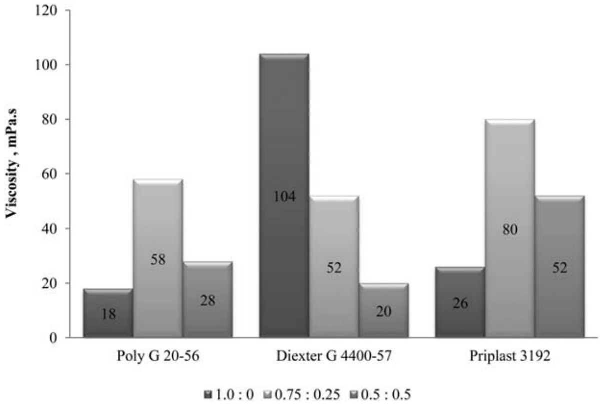

Figure 5. Effect of the molar ratio of DMPA to DHSA on the viscosity of WPUDs.

The incorporation of DHSA into WPUDs has significant effect on the particle size (Figure 4) and viscosity (Figure 5) of WPUDs. For WPUDs based on PolyG 20-56 and Priplast 3192 (Figure 5), the viscosity of WPUDs increased with incorporation of DHSA and the highest increase in viscosity was observed when the molar ratio of DMPA/DHSA was 0.75/0.25. However, for

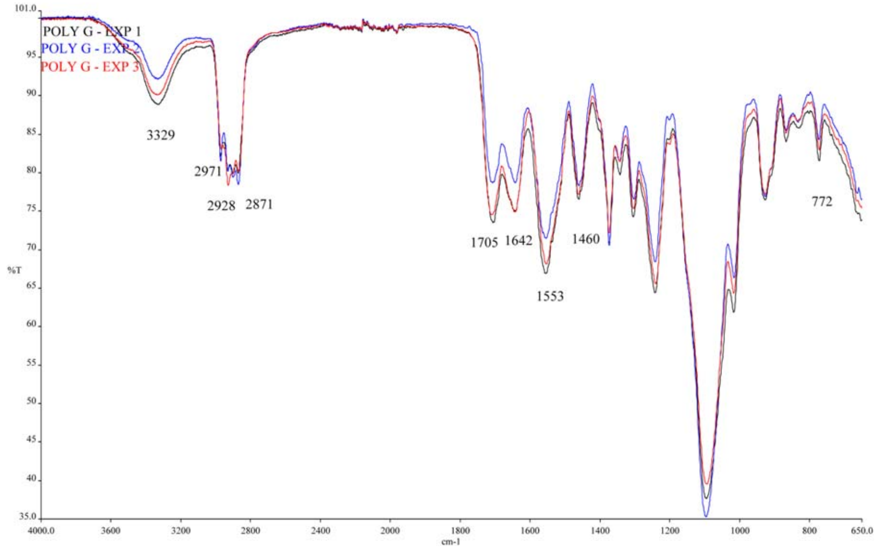

Figure 6. FTIR spectra of films casted from WPUD based on Poly-G 20-56 polyol (DMPA/DHSA molar ratio of 1/0, 0.75/0.25, and 0.5/0.5, respectively in EXP 1, EXP 2, and EXP 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

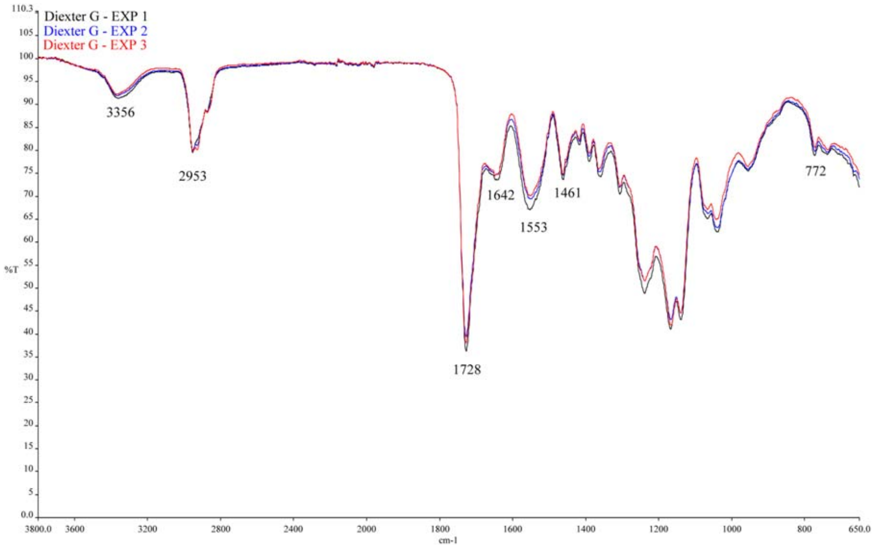

Figure 7. FTIR spectra of films casted from WPUD based on Diexter G 4400-57 polyol (DMPA/DHSA molar ratio of 1/0, 0.75/0.25, and 0.5/0.5, respectively in EXP 1, EXP 2, and EXP 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

WPUDs based on Diexter G 4400-57, the incorporation of DHSA reduced the viscosity of WPUDs and the largest reduction of viscosity was observed with equimolar ratio of DMPA/DHSA.

Nanda *et al.* (2005) reported that WPUD with higher concentration of the DMPA unit have smaller particle size and viscosity of WPUD is expected to increase with decrease in particle size but increase in the number of the particles. This increases relative size of the water layer to the total particle size. Hence, effective volume of the dispersed phase increases, resulting in an increase in viscosity.[25] However, most of these observations were reported based on studies using DMPA solely as ionizable molecules. In this study, the presence of DHSA as ionizable molecule, which has longer carbon chain and more hydrophobic than DMPA had changed the above observation on particle and viscosity of WPUDs. When 25% of DHSA was introduced as the ionizable molecules in WPUDs having Poly-G 20-56 and Priplast 3192, the viscosity and particle size of WPUDs increased (Figures 4 and 5). However, when more DHSA was introduced, up to 50%, the particle size and viscosity decreased further for these WPUDs prepared with different types of polyols. This might be due some synergic effect between DHSA and DMPA, which caused the viscosity and particle size of WPUDs to increase and decrease in the same trend, unlike as reported previously using DMPA.

FTIR spectra of WPUD films obtained from the films casted on polypropylene substrates are shown in Figures 6–8. This analysis was done to check the end of polymerization reaction by verifying the disappearance of the NCO group at wave number 2270 cm^{-1}. The appearance of absorption band at 3329 cm^{-1} for Poly-G 20-56 and 3356 cm^{-1} for Diexter G 4400-57 and

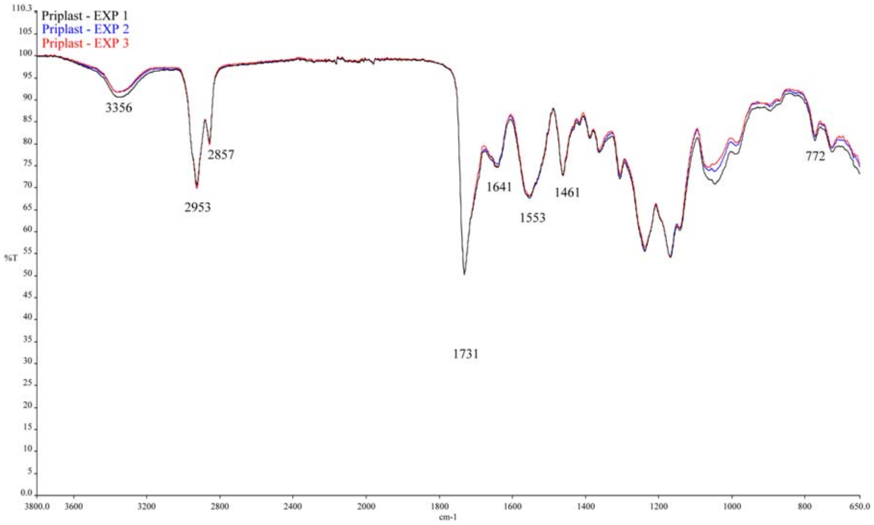

Figure 8. FTIR spectra of films casted from WPUD based on Priplast 3192 Polyol (DMPA/DHSA molar ratio of 1/0, 0.75/0.25, and 0.5/0.5, respectively in EXP 1, EXP 2, and EXP 3).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

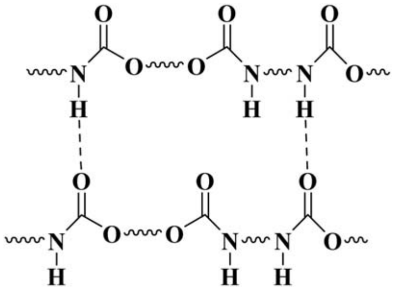

Figure 9. Hydrogen bond formation in PUs.[12]

Priplast 3192 indicates N—H stretching vibration, which relates to hydrogen bonded N—H groups of urethane formed in the reaction of isocyanate and polyols (NCO-prepolymers synthesis). In addition, the absorption band corresponding to hydrogen bonded C=O of urethane linkage is observed at 1705 cm^{-1} in WPUD films based on Poly-G 20-56. Meanwhile, the absorption band at 1728 cm^{-1} overlapped the stretching vibration of the carbonyl group C=O of urethane and the ester groups for WPUDs based on Diexter G 4400-57 (Figure 7). The absorption bands at 2928 cm^{-1}, 2871 cm^{-1}, and 1460 cm^{-1} correspond to the C—H stretching of the $–CH_2$ and CH_3 groups. The C—O—C stretching absorption band corresponding to the ether oxygen of the polyether soft segment at 1005–1152 cm^{-1} were observed with the films based on Poly-G 20-56 as it is a polyether polyol (Figure 6). The N—H group in PU could form hydrogen bonding with the carbonyl oxygen in hard segment and also with carbonyl groups in soft segment of polyester polyols or with ether oxygen in polyether polyols. FTIR spectra of films based on Poly-G 20-56 polyol exhibit absorption band of 1705 cm^{-1} which is in part due to hydrogen bonded groups between urethane and soft segment. Theoretically, there is a significant hydrogen bonding as shown in Figure 9, between adjacent chain due to urethane, urea, and ester functional groups. In the hard segment, hydrogen bonding acts as physical cross-links and reinforces hard segment. This results in a phase separation between the hard and soft segments. The phase separation improves the mechanical properties of PU but reduces the flexibility and solubility.[26]

Referring to analysis results shown in Table IV, the Diexter G 4400-57 films casted on CRS were found to be harder than the Poly-G 20-56 films. In general, polyether PUs are more flexible and less hard than polyester PUs. ATR-FTIR spectra indicate also significant presence of phase mixing via hydrogen bonding in films based on Poly-G 20-56, thus less organized hard segment and lower hardness. More significant phase separation between the hard and soft segments takes place in polyester polyols-based films and this improves the mechanical properties of PU but reduces the flexibility.[26] However, the hardness of the films casted from WPUDs based on Priplast 3192 was similar to those based on Poly-G 20-56. This might be due to the longer carbon chain of the dimer acid based polyol that has relatively less ester group moiety than Diexter G 4400-57. Thus, there is less interaction between flexible chains, which contribute to lower hardness of the film. The hardness of the films coated on glass substrates for Poly-G 20-56 and Diexter G 4400-57 were similar to films coated on CRS. But the hardness of films made from Priplast 3192 casted on the glass was slightly harder than films coated on CRS. This might be due to effect of the surface tension of the substrates used. Films prepared from WPUDs with higher amount of DMPA have higher hardness value than those films containing DHSA. DMPA is well known for its hard property because of its small molecule size compared to DHSA, which is a bigger molecule due its C_{18} carbon chain length. The long carbon chain of DHSA gives the flexibility and softness to the films. Therefore, as the amount of DHSA increased, the hardness of film was reduced, as could be expected. The adhesion strength for all the films produced from WPUDs of Poly-G 20-56, Diexter G 4400-57, and Priplast 3192 coated on CRS and glass surface were found to be similar.

Table IV. Compositions and Properties of the Films Casted from WPUDs

		Scratch resistant - Pencil test, (ASTM D3363)		Adhesion by tape test (ASTM-D3359-97)	
Type of polyol	Molar ratio of DMPA/DHSA	Cold roll steel	Glass surface	Cold roll steel	Glass surface
Poly-G 20-56	1/0	3H	3H	5A	4A
	0.75/0.25	3H	3H	5A	5A
	0.5/0.5	2H	2H	5A	5A
Diexter G 4400-57	1/0	5H	5H	5A	3A
	0.75/0.25	5H	5H	5A	3A
	0.5/0.5	4H	4H	5A	5A
Priplast 3192	1/0	3H	4H	5A	5A
	0.75/0.25	3H	4H	5A	5A
	0.5/0.5	2H	4H	5A	5A

Hard to soft →

Pencil Hardness: 6H, 5H, 4H, 3H, 2H, H, HB, F, B, 2B, 3B, 4B, 5B

Adhesion: 5A – No peeling or removal

3A – Jagged removal along most incisions up to 1.6 mm on either side

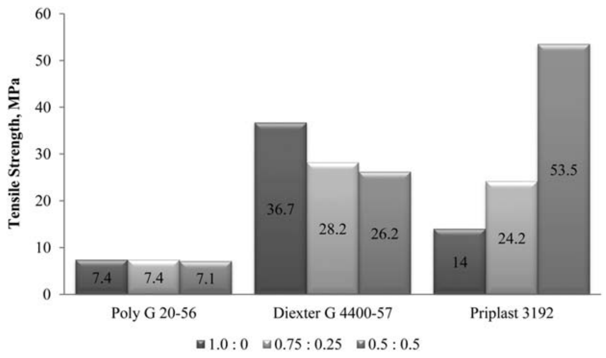

Figure 10. Effect of different types of polyols and ratio of ionizable molecules on the tensile strength of films based on WPUDs.

The tensile strength of films prepared from polyether polyol, Poly-G 20-56 based WPUDs were lower than films based on polyester polyols (Diexter G 4400-57 and Priplast 3192) as shown in Figure 10. The films prepared with WPUD based on Priplast 3192 in combination with DMPA/DHSA molar ratio of 0.5/0.5 exhibited excellent tensile strength of 53.5 MPa. Meanwhile, comparison between the polyester polyols showed the tensile strength of the Diexter G 4400-57 films were higher than the Priplast 3192 films, except for the film with molar ratio of DMPA/DHSA of 0.5/0.5, Figure 11. The films based on Poly G 20-56 exhibited the highest elasticity as measured by the elongation at break which was ~300%, Figure 11. The elasticity of films based on polyester Diexter G 4400-57 and Priplast 3192 was between 100 and 200%. The results showed that the films with lower tensile strength were elongated more compared to the films with higher tensile strength. In 2011, Sendijeravic reported on the properties of PUs based on different types of polyols. PU based on polyether polyol have lower tensile strength but high flexibility compared to PU based on polyester polyol, which has high tensile strength but lower flexibility. It was further reported the natural oil-based polyols have similar properties as the polyether polyols.[27] Similar trend was observed in this study in which films prepared with Diexter G 4400-57, Poly-G 20-56, and Priplast 3192 exhibited the anticipated properties.

The effects of ionizable molecules and the amount used were observed on the tensile strength and elongation at break of the films prepared. The incorporation of DHSA as ionizable molecule in the films prepared with Poly-G 20-56 did not have significant effect on the tensile strength and elongation at break.

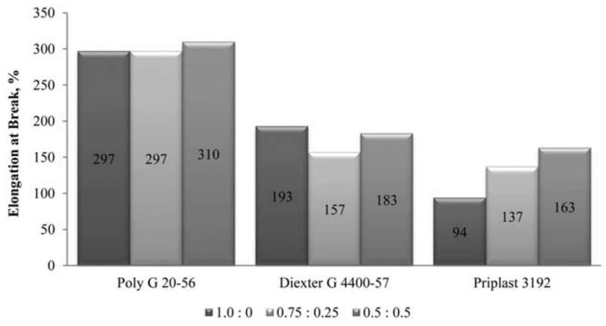

Figure 11. Effect of different types of polyols and ratio of ionizable molecules on the elongation at break of films based on WPUDs.

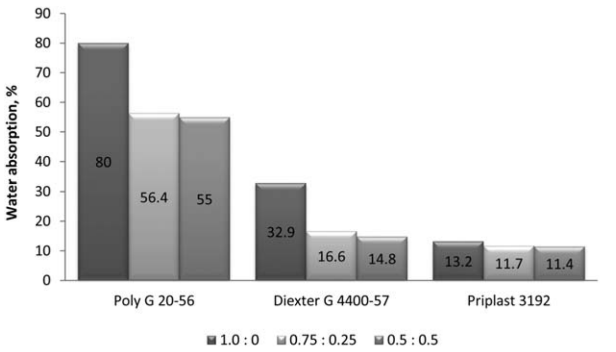

Figure 12. Effect of different types of polyols and molar ratio of ionizable molecules on the water absorption of films based on WPUDs.

The tensile strength of the films prepared with Diexter G 4400-57 decreased somewhat when DHSA was introduced as an ionizing molecule (Figure 10). Besides, the elongation at break increased slightly when the molar ratio of DMPA/DHSA was 0.5/0.5. The tensile strength of the films prepared with Priplast 3192 increased with the introduction of DHSA (Figure 10).

The water absorption of films prepared using polyether polyol were much higher than the films prepared using polyester polyols as shown in Figure 12. Films prepared with Priplast 3192 absorbed least amount of water because of the presence of long carbon chain, C_{36}, which imparts the hydrophobicity of the dimer acid-based polyol. The water absorption decreased as the amount of DHSA was increased in the films, regardless on the type of polyol. The presence of DHSA in the film decreased the water absorption of the film due to C_{18} carbon chain in the DHSA molecule compared to only C_5 carbon chain in DMPA molecule.

CONCLUSIONS

A number of stable anionic types of WPUD were prepared using commercial polyether and polyester polyols as the soft segments. These WPUDs were produced via the prepolymer process. Palm oil-based DHSA prepared from palm oil-based oleic acid was successfully introduced, in combination with DMPA, as ionizable molecule in the preparation of WPUDs. WPUDs prepared at 0.5/0.5 molar ratio of DMPA/DHSA appears to have beneficial properties such as lowered particle size and low viscosity regardless of type of polyol. At 0.75/0.25 molar ratio of DHSA/DMPA, WPUD were not stable. Due to lower melting temperature, DHSA lowered the reaction temperature and time at initial stage of the synthesis, which involves making homogenous blend with polyol. The films based on WPUDs with DHSA exhibited better water resistance and flexibility as compared to the reference WPUD based on DMPA as sole ionizing molecule preserving good adhesion properties. It appears that most of films and coatings exhibited very good properties at 0.5/0.5 of DMPA/DHSA in all WPUDs such as hardness, tensile strength, elongation at break, and water absorption. The best improvement in properties with introduction of DHSA were observed with WPUDs based on Priplast 3192 dimer-acid polyester polyol, which could be ascribed to good compatibility of long aliphatic chains in DHSA and the polyol. The significance of this WPUD is its biobased content of 67% originating from the polyol and DHSA ionising site. The reported work is the first attempt to introduce DHSA into WPUDs. The objective of follow-up research is to maximize the concentration of DHSA in WPUDs including variations of types and molecular weights of polyols, solid content, addition of surfactants, and mode of dispersing the NCO-prepolymers in water. The evaluation of these novel WPUDs as one component adhesives to various substrates will also be studied.

ACKNOWLEDGMENTS

The authors would like to thank Director General of Malaysian Palm Oil Board for her permission to publish this paper and funding this project. The authors would like to thank Mrs. Zulina Abd Maurad for providing the DHSA for this study. The authors also thank the laboratory staff of Polymer and Composite group of AOTD, for their assistances especially for Mrs. Norhidayah Ahmad Yusoff.

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