Synthesis and Characterisation of New Water-Based Polyurethane Dispersion via Solvent-Free Prepolymer Mixing Process

A M E Kuok, C S Sipaut and M Sundang

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia
Email: css@ums.edu.my

Abstract. A new type of water-based polyurethane dispersion (NWPUD) was synthesised from isophorone diisocyanate, polyethylene glycol (Mw = 400 g/mol and 1000 g/mol), dimethylol propionic acid, and 1,4-butanediol using the prepolymer mixing process and without the incorporation of any volatile organic solvent. The hard-/soft-segment molar ratio of NWPUD formulations was varied with higher values (i.e. 5 to 11) allowing excess diisocyanate to reduce the prepolymer viscosity. The formulation using polyethylene glycol 400 g/mol with a hard-/soft-segment molar ratio of 5 failed by solidifying upon dispersion in water. Using polyethylene glycol 1000 g/mol and varying hard segment content, successful NWPUD formulations were obtained, all with pH between 6 and 7. FT-IR spectroscopy was used for the identification of chemical structures and functional groups. The colloidal properties of NWPUD formulations such as particle size, zeta potential, and dispersion stability were investigated to demonstrate feasibility for application in industrial coatings. The size distribution of NWPUD formulations varied from heterogeneous to homogeneous when the hard-/soft-segment molar ratio was increased. It was found that formulations with hard-/soft-segment molar ratio between 7 and 11 exhibited the most desirable dispersion stability within the zeta potential range of -50 to -55 mV.

1. Introduction
Polyurethane adhesives, resins, and coatings are primarily solvent-based. Consequently, increased environmental concern has motivated the development of more environmentally-friendly polyurethane systems based on water. Research interest in water-based polyurethane dispersions (WPUDs) has increased significantly due to their versatility in various applications including adhesives, coatings, fiber sizings, and binders [1–4]. WPUDs are known generally as two-phase colloidal systems in which water-insoluble polyurethane particles are dispersed in water by incorporating an ionic moiety in the polyurethane backbone. This leads to the self-emulsification of polyurethane particles in water.

From the literatures, acetone and prepolymer mixing processes are both widely used for the synthesis of WPUDs [5–9] due to their simplicity and straightforward nature. However, each process involves the usage of either large amounts of volatile organic solvent (e.g. acetone) or high boiling point co-solvent (e.g. N-methyl-2-pyrrolidone, NMP), respectively. From an industrial point of view, the prepolymer mixing process is preferable to the acetone process since the latter requires an additional step for acetone removal which increases production costs but produces low reactor yields.
NMP is a high-boiling-point co-solvent which remains in the formulation after synthesis. Commercially available WPUDs prepared via the conventional prepolymer mixing method contain 15 to 26% NMP as co-solvent [7]. However, according to the European Commission Regulation No 1272/2008 [12], a formulation containing 5% or more NMP must be labelled as toxic due to its carcinogenic and mutagenic potential.

To overcome this drawback, several studies have reported the successful production of WPUDs using a solvent-free prepolymer mixing synthesis method by varying the types of isocyanate, the isocyanate to hydroxyl (NCO/OH) ratio, and the molecular weight of polyol [13–15]. According to Yong et al. [15], a high NCO/OH ratio corresponds to the presence of excess unreacted aliphatic disocyanate which can replace NMP as a solvent during the process of synthesis. Due to the limited literature on solvent-free prepolymer mixing systems, the colloidal properties of these WPUDs are currently poorly-understood. Colloidal properties are important parameters in predicting the dispersion stability of WPUDs to ensure the feasibility of upscaling to industrial levels. Therefore, further research must be carried out to better ascertain the colloidal properties and dispersion stability of WPUDs via the solvent-free prepolymer mixing process. In the present research, a new type of water-based polyurethane dispersion (NWPUD) was prepared from isophorone disocyanate, polyethylene glycol, dimethylpropionic acid, and 1,4-butanediol through a solvent-free prepolymer mixing process. The amount of co-solvent NMP in the NWPUD formulations was restricted to less than 5%. The effects of hard-/soft-segment molar ratio and the molecular weight of polyol on the particle size, zeta potential, and dispersion stability of the synthesised NWPUD were studied.

2. Materials and Method

2.1. Materials
The diisocyanate used was isophorone diisocyanate (IPDI, mixture of cis- and trans-isomer) and supplied by Merck, Germany. Polyethylene glycol PEG with two different molecular weights (Mw = 400 g/mol and 1000 g/mol), 1,4-butanediol 1,4-BDO, and dibutyltin dilaurate DBTDL were supplied by Merck, Germany. Dimethylpropionic acid (DMPA, 98%), N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) and triethylamine (TEA, ≥ 99.5%) were purchased from Sigma-Aldrich. Nitrogen gas was supplied by Linde, Malaysia. Sodium chloride (NaCl, ≥ 99.0%, J.T. Baker) was supplied by Avantor, USA. All chemicals were of reagent grade, and were used as received, without purification. Other materials used were distilled water and deionised water (PureLab Prima, ELGA, UK).

2.2. Synthesis of solvent-free NWPUD formulations
As shown in Table 1, five different NWPUD formulations were prepared using varying molecular weights of PEG polyol (i.e. 400 g/mol and 1000 g/mol) and varying molar ratios of isocyanate to polyol (i.e. hard-/soft-segment molar ratios from 5 to 11). The formulation were designed in this manner due to the absence of volatile organic solvent to reduce the viscosity of prepolymer. DMPA (i.e. anionic moiety) was used as the emulsifier with content fixed at 7 wt% with respect to the prepolymer. The NCO/OH molar ratio before dispersion was maintained at 1.0 to prevent the side reaction of isocyanate with water. First, PEG and DMPA (dissolved in NMP with a mass ratio of 1:2) were charged into a five-necked heating reaction flask equipped with a mechanical stirrer, nitrogen inlet, and a thermometer. The mixture was heated to 70 °C and stirred for 30 minutes to obtain a homogeneous mixture. Next, IPDI was added dropwise using a dropping funnel for 16 minutes followed by the addition of a few drops of DBTDL (as catalyst) to initiate the isocyanate-hydroxyl reaction. The reaction was allowed to proceed for four hours at 70 °C under nitrogen atmosphere to allow all hydroxyl groups of PEG to be fully reacted, forming isocyanate-terminated prepolymer. Subsequently, the prepolymer was cooled to 50 °C before TEA (DMPA mole-equivalent) was added
to neutralise the carboxylic groups in the DMPA units to facilitate the final dispersion process. Neutralisation was allowed to proceed for 30 minutes. Next, 1,4-BDO, which acted as a chain extender, was added into the neutralised prepolymer to react with the residual isocyanate. Chain extension was carried out for another 15 minutes at 50 °C. Finally, a calculated amount of distilled water (30 wt% solid content of NWPUD) was added to the reaction mixture. The dispersion process was allowed to proceed for an hour at room temperature. The NWPUD formulations obtained were stored in glass bottles and kept at room conditions without exposure to sunlight.

Table 1. NWPUD formulations based on solvent-free synthesis method.

| Sample coding | Hard-/soft- segment molar ratio | Mole equivalent | HS* [wt%] |
|---------------|---------------------------------|-----------------|-----------|
|               | IPDI [NCO]  | PEG 400 g/mol [OH] | PEG 1000 g/mol [OH] | DMPA [OH] | 1,4-BDO [OH] |
| NWPUD1        | 5          | 5                | 1                | -         | 0.85             | 3.15         | 80.0       |
| NWPUD2        | 5          | 5                | -                | 1         | 1.18             | 2.82         | 62.2       |
| NWPUD3        | 7          | 7                | -                | 1         | 1.43             | 4.57         | 69.8       |
| NWPUD4        | 9.3        | 9.3              | -                | 1         | 1.72             | 6.54         | 75.4       |
| NWPUD5        | 11         | 11               | -                | 1         | 1.93             | 8.07         | 78.4       |

*Hard segment content {HS= Mass (IPDI + DMPA + 1,4-BDO + TEA)/ Mass (IPDI + PEG + DMPA + 1,4-BDO + TEA)} [16, 17]

2.3. Preparation of NWPUD films

The corresponding films were obtained by casting the NWPUD formulations onto silicone surfaces and allowing them to dry at room temperature for seven days to ensure the complete evaporation of water. The dried NWPUD films were then removed and stored in a dessicator to avoid moisture for further characterisation.

2.4. Fourier Transform Infra-red (FT-IR) spectroscopy

FT-IR spectroscopy was used to identify and distinguish the chemical structures and functional groups of the NWPUD formulations. The IR spectra of NWPUD films were obtained using a Perkin Elmer Spectrum 100 spectrometer (Quest ATR Diamond 45°), and all measurements were recorded in the range of 4000 to 400 cm⁻¹ with an average of four scans at a resolution of 4 cm⁻¹.

2.5. pH measurement

The pH values of NWPUD formulations were measured at 25 °C using a Hanna Instruments HI 2211 bench top pH/ORP meter. An average pH value was obtained from three measurements per sample.

2.6. Particle size and zeta potential analysis

Particle size and zeta potential are two important parameters which affect the colloidal properties and dispersion stability of NWPUD formulations. Particle size was determined using a Zetasizer Nano-ZS (Malvern Instruments) via dynamic light scattering principles. The measurement angle used was 173° (Non-Invasive Back Scatter, NIBS). Similarly, zeta potential was measured using the electrophoresis principle. For both analyses, 0.1 g of each formulation was diluted with 5 mL of distilled water and measured at 25 °C. The mean particle size and zeta potential were obtained from the average of three measurements for each sample.
2.7. Electrolytic stability
Electrolytic stability of NWPUD formulations is important in order to determine dispersion stability when subjected to electrolyte resistance. An amount of 5 g of each formulation was mixed with 5 mL of deionised water in a 50 ml beaker, followed by titration with aqueous solution of 2 M NaCl using a 50 ml burette until coagulation was obtained. Electrolytic stability was indicated by the volume of 2 M NaCl required to produce coagulation.

3. Results and Discussion

3.1. NWPUD Synthesis
In this study, the conventional prepolymer mixing process, which uses no volatile organic solvent, was selected. The synthesis of NWPUD formulations began by using a molar ratio of hard-/soft-segment of 5 and DMPA content of 7 wt% (with respect to prepolymer). PEG of different molecular weights (i.e. 400 g/mol and 1000 g/mol) was used as the polyol. Using this method with PEG 400 g/mol (i.e. NWPUD1) resulted in the solidification of polyurethane (Figure 1). However, when PEG 1000 g/mol was used, NWPUD2, with a clear visual appearance, was formed. This result could be related to the different dispersion stabilities when using varying molecular weights of PEG. The dispersion stability of formulations increased when a higher molecular weight of PEG was used [18]. NWPUD1, which contained shorter chains of PEG (i.e. PEG 400 g/mol), had a higher hard segment content (Table 1). This lowered the phase separation between the hard and soft segments, making the anionic centres of DMPA unable to leave to the particle surfaces during dispersion, and led finally to the incomplete emulsification and solidification of polyurethane [19-20]. The pH of formulations synthesised from PEG 1000 g/mol were all in the range of 6 to 7, which is commercially acceptable. From Table 2, the increase in pH from NWPUD2 to NWPUD5 was probably due to the slight increase in DMPA and TEA neutraliser contents attributed to the increase in prepolymer weight with the increase in hard-/soft-segment molar ratio.

Table 2

| Formulation | Molecular Weight (g/mol) | pH  |
|--------------|-------------------------|-----|
| NWPUD1       | 400                     | 6.5 |
| NWPUD2       | 1000                    | 6.8 |
| NWPUD3       | 400                     | 6.6 |
| NWPUD4       | 1000                    | 6.9 |
| NWPUD5       | 1000                    | 7.0 |

Figure 1. New water-based polyurethane dispersion (NWPUD) formulations.
Table 2. Colloidal characteristics of NWPUD formulations with varying hard-/soft-segment molar ratio.

| Sample coding | Visual appearance | pH ± 0.01 | Difficulty in prepolymer reaction | Mean particle diameter (nm) | Polydispersity index (Pdl) ± 0.01 |
|---------------|------------------|-----------|----------------------------------|-----------------------------|----------------------------------|
|               |                  |           |                                  | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 |                |
| NWPUD2        | Clear            | 6.09      | High                             | 2.36   | 13.43  | 557.90 | 1314   | 3154   | 0.35 ± 0.02 |
|               |                  | ± 0.01    |                                  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  |
| NWPUD3        | Clear            | 6.57      | Low                              | 2.42   | 17.81  | 3664   | -      | -      | 0.33 ± 0.01 |
|               |                  | ± 0.02    |                                  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  |
| NWPUD4        | Milky white      | 6.95      | No                               | 165.53 | -      | -      | -      | -      | 0.08 ± 0.05 |
|               |                  | ± 0.01    |                                  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  |
|               |                  |           |                                  | 7.77   |       |       |       |       |       |
| NWPUD5        | Clear            | 7.06      | No                               | 47.66  | -      | -      | -      | -      | 0.26 ± 0.01 |
|               |                  | ± 0.02    |                                  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  | ± ± ±  |
|               |                  |           |                                  | 0.63   |       |       |       |       |       |

3.2. FT-IR analysis of NWPUD films

The formulated NWPUD films were characterised using FT-IR spectroscopy. All formulations prepared exhibited similar FT-IR spectra. Figure 2 shows the FT-IR spectra of IPDI, PEG 1000 g/mol, and NWPUD4 film. In the NWPUD4 spectrum, it can be observed that there was no signal at 2243.94 cm\(^{-1}\) (-NCO stretching), implying that all isocyanate (-NCO) groups were completely reacted [2, 8, 17]. The broad absorption at 3435.50 cm\(^{-1}\) (-OH stretching of PEG 1000 g/mol) shifted to 3325.83 cm\(^{-1}\) after the synthesis of NWPUD4, indicating that all hydroxyl (-OH) groups in PEG 1000 g/mol were fully reacted with the isocyanate groups to form hydrogen bonded -NH groups of urethane [3, 9]. Absorption bands corresponding to the -CH stretching of -CH\(_2\) and -CH\(_3\) of NWPUD4 can be observed at 2950.79 cm\(^{-1}\), 2908.42 cm\(^{-1}\), and 1460.28 cm\(^{-1}\), respectively [9]. The peak present at 1694.66 cm\(^{-1}\) indicated the C=O stretching vibration of urethane groups [9, 18] while the absorption bands arising at peaks 1100.42 cm\(^{-1}\) and 1041.12 cm\(^{-1}\) corresponded to the characteristics of C-O-C stretching bands of soft segment from PEG 1000 g/mol [18] (Figure 2). Based on this FT-IR evidence interpreted using the literature, the polyurethane structure was successfully synthesised.
Figure 2. FT-IR spectra of IPDI, PEG 1000 g/mol, and NWPUD4 film.

3.3. Particle size distribution

Polydispersity (Pdl) is an indicator that describes the homogeneity of the particle size distribution within a sample [21–23]. Particle size distribution is categorised as follows: highly monodisperse (Pdl ≤ 0.1), moderately monodisperse (Pdl 0.1 – 0.4), and highly polydisperse with varying particle size (Pdl ≥ 0.4 – 1) [23, 24]. The polydispersity index and mean particle size of NWPUD formulations are reported in Table 2. NWPUD2 and NWPUD3 demonstrated high polydispersity indices of 0.35 and 0.33, respectively, which reflect their heterogeneous particle size distributions in Figure 3. NWPUD4 (Pdl = 0.08; 165.53 nm) and NWPUD5 (Pdl = 0.26; 47.66 nm) exhibited a higher homogeneity (i.e. one maximum peak size).

Table 2. NWPUD2 and NWPUD3 demonstrated high polydispersity indices of 0.35 and 0.33, respectively, which reflect their heterogeneous particle size distributions in Figure 3. NWPUD4 (Pdl = 0.08; 165.53 nm) and NWPUD5 (Pdl = 0.26; 47.66 nm) exhibited a higher homogeneity (i.e. one maximum peak size).

Figure 3 shows the variation of particle size distribution with the increase in hard-/soft-segment molar ratio. The wide and multi-modal particle size distributions of NWPUD2 and NWPUD3 were attributed to the increasing viscosity of prepolymer, and this effect was greatly magnified by the solvent-free synthesis route. The particles were difficult to disperse and to fragment completely into smaller particles during the dispersion process, leading to the formation of few large particles [25–27]. The formation of clear NWPUD2 and NWPUD3 (Figure 1) was probably due to particle size variation in the dispersions.

At NWPUD4, the prepolymer mixing reaction took place smoothly as prepolymer viscosity was reduced by the excess IPDI. Therefore, the polyurethane particles in NWPUD4 were fragmented and emulsified properly during the dispersion, resulting in a single, sharp and narrow peak of mean particle size at 165.53 nm (Figure 3). The milky white appearance of NWPUD4 (Figure 1) might be
the result of its more homogeneous particle size distribution. Alternatively, the increased particle size could be due to the greater numbers of polymer chains required to stabilise the polymer micelles in water [28].

A different result was obtained for NWPUD5. From Table 2, the mean particle size of NWPUD5 decreased drastically to 47.66 nm compared to that of NWPUD4 (i.e. 165.53 nm). A reasonable explanation for this phenomenon was the effect of the distribution of DMPA units in the increasing hard segment fraction in the polyurethane chains [28]. The expected increase in series linkages of isocyanate with DMPA and 1,4-BDO led to a more homogeneous distribution of DMPA in the hard segment fraction which increased hydrophilicity and allowed the penetration of water into the hard segment to better disperse the NWPUD molecules [28-29]. As a result, the mean particle size decreased and a clear dispersion was obtained for NWPUD5 (Figure 1).

![Figure 3](image1.png)  
**Figure 3.** Particle size distribution of NWPUD formulations.

![Figure 4](image2.png)  
**Figure 4.** Zeta potential and electrolytic stability of NWPUD formulations.

### 3.4. Zeta potential and electrolytic stability of NWPUDs

Figure 4 shows the effect of hard-/soft-segment molar ratio on the zeta potential and volume of NaCl solution required to produce coagulation in NWPUD formulations (i.e. electrolytic stability). Both parameters are important in determining dispersion stability. Figure 4 shows a significant increase in the zeta potential (i.e. more negative) from NWPUD2 to NWPUD4. In general, dispersion stability increases with an increase in the zeta potential from a smaller mean particle size. A possible explanation for the increase in zeta potential with increasing mean particle size is that it was probably due to the higher strength of stabilisation of polymer micelles in water from ionic content (i.e. DMPA molecules) and polymer chains from NWPUD2 to NWPUD4.
Electrolytic stability was determined by the volume of NaCl solution required to produce coagulation. The 2 M NaCl solution prepared was a strong electrolyte and was added to make the double electrical layer of NWPUD unstable due to the interaction of electrolyte ions with NWPUD particles, hence leading to disruption of the dispersions and to coagulation [25]. From Figure 4, it is noted that the volume of NaCl required for coagulation, and hence for electrolytic stability, increased from NWPUD2 to NWPUD3. This finding is in agreement with a previous study [27].

However, an interesting finding was also obtained from NWPUD3 to NWPUD5. Zeta potential increased in magnitude (i.e. more negative) from NWPUD3 to NWPUD4 but subsequently decreased in magnitude (i.e. less negative) from NWPUD4 to NWPUD5. Despite this non-uniformity, it was found that NWPUD3 to NWPUD5 acquired a similar level of dispersion stability due to the insignificant changes in their electrolytic stabilities (Figure 4). The subsequent results were in accordance with those reported by Durrieu et al. [13]. In this study, it can be concluded that NWPUD3 to NWPUD5 exhibited the highest and most constant dispersion stability within the zeta potential range of -50 to -55 mV (Figure 4).

3.5. Initial data on the applicability of NWPUD as coatings

Figure 5 shows the different NWPUD formulations applied as coatings on stainless steel substrates. Solidified NWPUD1 could not be coated on the stainless steel substrate whereas NWPUD2 to NWPUD5 coatings were successfully formed. The coatings formed were clear, homogeneous, and uniform. However, NWPUD2 and NWPUD3 coatings were sticky and not dry, as indicated by the presence of fingerprints thereon. NWPUD4 and NWPUD5 produced dry coatings. These initial results might suggest that the minimum hard-/soft-segment molar ratio required for dry polyurethane coatings is 9.

![Figure 5. NWPUD coatings on stainless steel substrates.](image)

4. Conclusion

In this research, a new type of water-based polyurethane dispersion (NWPUD) based on a solvent-free prepolymer mixing synthesis process was successfully produced. This study provided some useful insights into the effect of hard-/soft-segment molar ratio on the particle size distribution, zeta potential, and dispersion stability of NWPUD formulations. The formulations synthesized exhibited different size distributions ranging from heterogeneous to homogeneous when hard-/soft-segment molar ratio
was increased. Formulations with hard-/soft-segment molar ratio from 7 to 11 exhibited the highest dispersion stability within the zeta potential range of -50 to -55 mV, and could be potentially useful in industrial coating applications. Research work is in progress to confirm this.

5. References

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