

Upcycled Polyurethane Products Based Waterborne Polyurethane Dispersions

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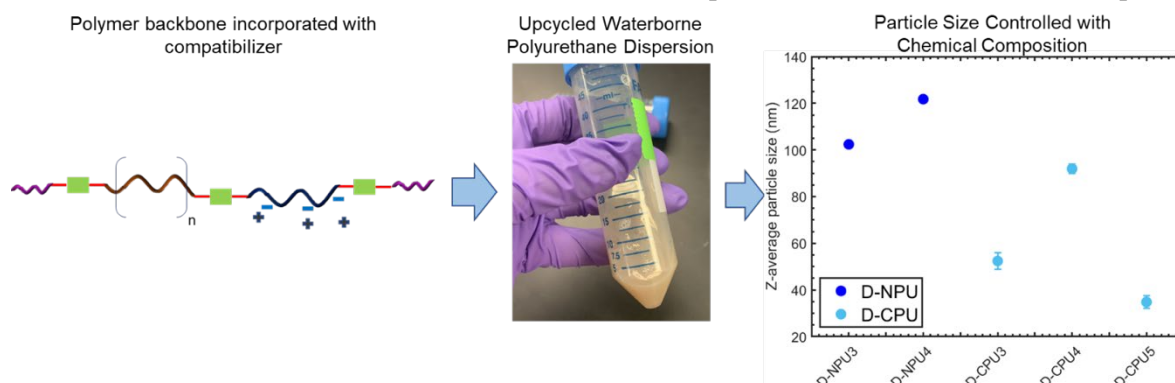
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EXECUTIVE SUMMARY

In 2020, the Mattress Recycling Council California, LLC (MRC) recovered approximately 13 million pounds of flexible polyurethane foam in California. Volume in future years is expected to grow due to several factors some of which include increased popularity of all foam mattresses, improved collection and logistics processes and recycling rate improvements. MRC's research team supports new and innovative end of life solutions for post-consumer polyurethane foam. A research contract was established with UCLA to evaluate the conversion of upcycled polyurethane foam into waterborne polyurethane dispersions.

This report summarizes the key findings of the research on the production of waterborne polyurethane dispersions (WPUDs) from upcycled polyols. The major accomplishments of this project are as follows:

- We have established a protocol for the synthesis of cationic and anionic WPUDs using upcycled polyols. Thus, we have demonstrated the viability of upcycled polyurethane products (suitable as partial replacement for virgin polyol in foam production) as raw materials for synthesis of stable WPUDs with properties commensurate to commercially available dispersions.
- WPUD characteristics (surface charge, particle size, and stability) are tuned through optimization of the compatibilizer content, isocyanate:hydroxyl (NCO:OH) ratio and the extent of neutralization. Alterations in chemical composition of the polymer backbone significantly affect the surface charge and consequently, the particle size distribution in the dispersions.
- The synthesized WPUDs have typical particle sizes in the range of 60 nm–100 nm and zeta potentials ranging from 40 mV–80 mV (sign changing with the cationic/anionic nature of the WPUDs), which are commensurate with literature reports and with commercial samples.



Summary of this work: Stable cationic and anionic upcycled waterborne polyurethane dispersions utilizing only upcycled polyol and properties commensurate with commercial products.

INTRODUCTION

Polyurethane, despite being predominantly hydrophobic in nature, can be dispersed in water when incorporated with suitable compatibilizers.^[1-3] Waterborne polyurethane dispersions (WPUDs) exhibit compatibility with multiple substrates and offer good tunability, while also mitigating the shortcomings of organic solvent-based dispersion, including their environmental toxicity, flammability, and high costs.^[1,3] Hydrophilicity in PU can be imparted by cationic,^[4-6] anionic,^[7,8] or non-ionic^[9,10] compatibilizers, which are incorporated into the polymer backbone during polymerization. These waterborne dispersions are employed as adhesives, coatings, and membranes.

Strategies for WPUD synthesis differ in the method of incorporating the compatibilizer and the subsequent dispersion in water. The initial step – formation of an NCO-terminated pre-polymer – is common to all processes. For example, in the acetone process, the prepolymer is dissolved in acetone to reduce viscosity,^[2] while in the melt-mixing process, the NCO-terminated pre-polymer is heated to a high temperature, thus eliminating the solvent requirement.^[3] Other processes include ketimine & ketazine process and the pre-polymer mixing process.^[2,3] The latter has been adopted in this study due to its relatively low solvent requirement, moderate reaction conditions (60 °C, 2 hours). Additionally, the pre-polymer mixing process is known to result in stable dispersions with particle sizes between 100 nm and 500 nm.^[2]

In the pre-polymer mixing process, an NCO (diisocyanate):OH (polyol) > 1 is typically maintained. The diisocyanate, polyol, and compatibilizer (cationic, anionic, or non-ionic) are reacted in the presence of a catalyst (typically organometallic) to form a compatibilizer-incorporated NCO-terminated pre-polymer. The compatibilizer groups are then neutralized (resulting in charge groups in the polymer backbone), followed by dispersion in water. Finally, the pre-polymer is then chain extended with a diamine (e.g., hexamethylene diamine, ethylene diamine) or a diol (1,3-butane diol), resulting in a high molecular weight dispersion stable in water.^[11]

In addition to the chemical composition (NCO:OH, solid content, compatibilizer content), diisocyanate structure (aliphatic, aromatic), chain extender (diamines, diols) and type of compatibilizer, the WPUD synthesis process is especially sensitive to the nature of the polyol (degree of branching, molecular weight, structure). Post-chemolysis upcycled polyols are often highly branched and polydisperse; a lack of effective control over these factors limits their incorporation in WPUDs. In this work, we establish a protocol for synthesis of anionic and cationic WPUD using virgin polyols and demonstrate the tunability of dispersion characteristics (e.g., particle size, stability, and zeta potential) by altering their chemical composition. Further, we characterize the upcycled polyol (Infigreen-300, obtained by glycolysis of post-industrial scrap foam) and utilize it to synthesize stable upcycled cationic and anionic WPUDs. We note that systematic changes in chemical composition – compatibilizer content, extent of neutralization, NCO:OH ratio – allow the successful replacement of virgin polyols by these high hydroxyl value upcycled polyols in the synthesis of cationic and anionic WPUDs. Additionally, we compare the properties of the synthesized virgin and upcycled WPUDs with commercially available dispersions and present perspectives for their use as suitable candidates for coatings, adhesives, elastomer films, and membranes.

RESULTS AND DISCUSSION

Characterization of Virgin and Upcycled Polyols

Fourier transform infrared (FT-IR) (**Figure 1a**) and thermogravimetric analysis (TGA) (**Figure 1b**) studies were performed on the virgin (polypropylene glycol; PPG) and upcycled (Infigreen-300) polyols to investigate their chemical structures and inform the WPUD synthesis protocols. As shown in **Figure 1a**, the spectra for PPG and Infigreen-300 were similar; ether groups (C-O-C), aliphatic (CH₂ and CH) and hydroxyl (O-H) were recorded in both polyols. The Infigreen-300 spectrum, however, had an additional distinct ester carbonyl (C=O) peak. This confirmed the polyether-polyester structure of Infigreen-300, as opposed to the purely polyether backbone of PPG. Further confirmation of the differences in chemical structures of virgin and upcycled polyols was sought from thermal degradation studies as shown in **Figure 1b**. Thermal stability of Infigreen-300 was significantly higher as compared to PPG (**Figure 1b**) but compared well with thermal stability profiles for polyester polyols.^[19]

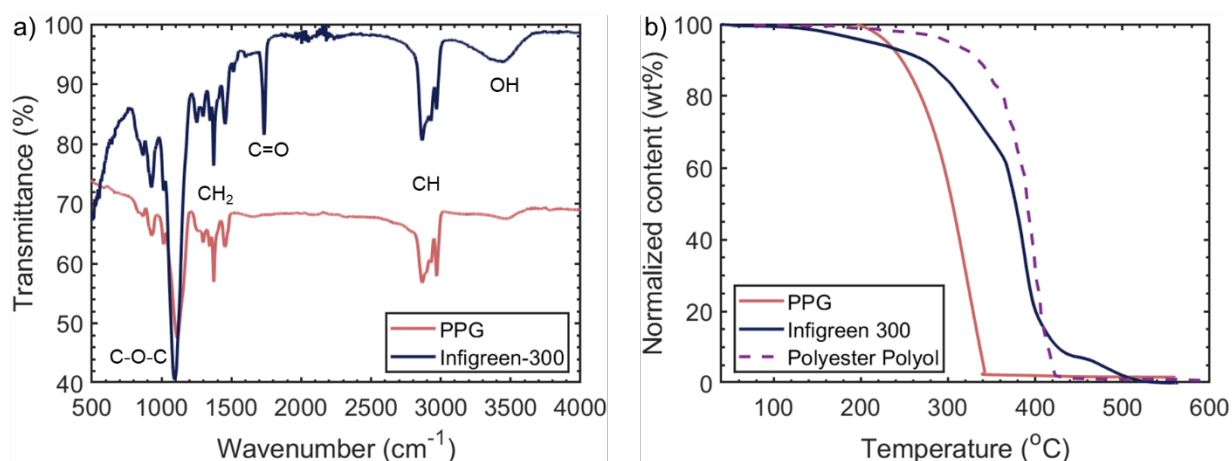


Figure 1 a) FT-IR spectra of PPG and Infigreen-300 confirmed the presence of ether (C-O-C), aliphatic (CH₂, CH) and hydroxyl (OH) groups in both. Carbonyl ester (C=O) group was detected in Infigreen-300 but not in PPG b) Infigreen-300 remained resisted thermal degradation until 420°C, as opposed to PPG which decomposed at 340°C. The distinct thermal behavior of Infigreen-300 is characteristic of polyester polyols, as reported in literature.^[19]

Anionic and Cationic WPUD: Synthesis and Characterization

Anionic and cationic WPUDs were synthesized by the pre-polymer process.^[2,4,5,7,11] A low-molecular weight NCO-terminated prepolymer comprising polyols (PPG or Infigreen-300), diisocyanate (isophorone diisocyanate; IPDI), and compatibilizer (anionic dimethylol propionic acid: DMPA, or cationic N-methyl diethanolamine: NMDA) was synthesized in the presence of catalyst dibutyltin dilaurate (DBTDL). The NCO-termination was confirmed by the dibutylamine back titration method.^[12] Subsequently, the compatibilizer groups were neutralized with triethylamine (TEA; for anionic) or acetic acid (AcAc; for cationic). The neutralized pre-polymer was then dispersed in water under high-speed mechanical mixing (900 rpm) using a dissolver type impeller. Chain extension with hexamethylene diamine (HDA) was carried out as the final step to obtain high molecular weight WPUDs with solid contents ranging between 25–30 wt% (reaction scheme in **Figure 2**). NMP was used in calculated amounts (8–15 wt% of dispersion) to aid dispersion of compatibilizer in polyol and maintain a workable viscosity. Dispersions with

different compositions – polyol type (virgin vs upcycled), NCO:OH (0.97–1.6), compatibilizer content (8–15 wt%) and extent of neutralization (100–300 mol%) – resulted in changes in WPUD stability, particle size and zeta potential. A higher extent of neutralization (300 mol%) was required for cationic dispersions to maintain stability of the acid neutralized charged particles against the alkaline hexamethylene diamine chain extender.

WPUDs based on Virgin Polyols: Size of the PU particles in the anionic WPUDs based on virgin polyol (PPG) (NPU3–NPU17; sample details in **Table A1**) mostly varied between 100–300 nm (**Figure 3a**), rendering colloidal stability to the dispersions. The particle sizes of the synthesized WPUDs compared well with the commercial dispersions (UD108, UD135), and were also in agreement with literature (**Figure 3a**).^[2,7,13–15] Some samples had larger particles (NPU3, NPU5 and NPU13); the large particle sizes and the variations thereof in these samples can be attributed to the lack of stability and the consequent aggregation and settling of

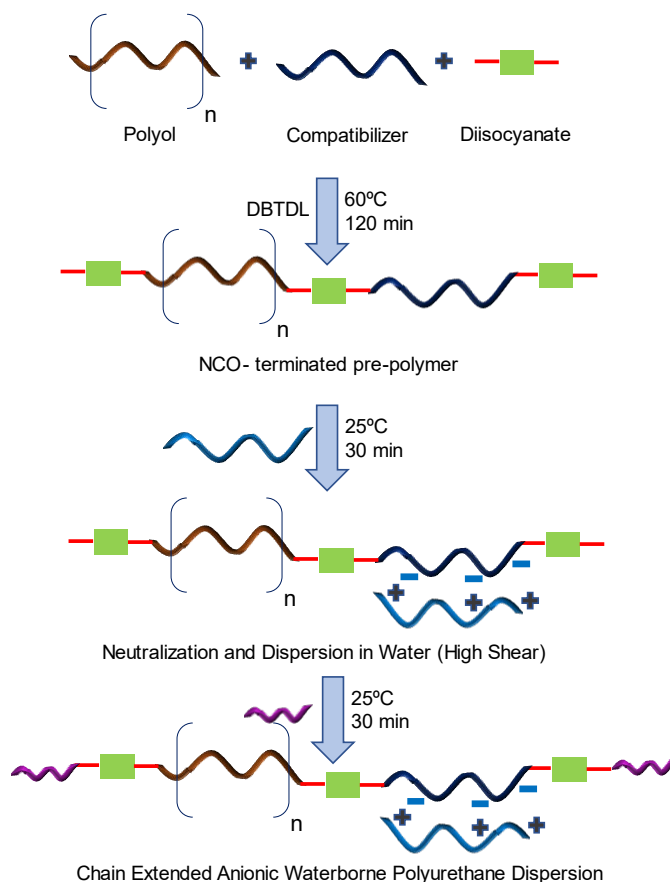


Figure 2: Synthesis of Anionic WPUD by pre-polymer mixing process. An NCO-terminated pre-polymer, consisting of a polyol, compatibilizer and diisocyanate is formed in the presence of a catalyst at 60 °C. The compatibilizer functional groups are then neutralized at room temperature, followed by dispersion in water and subsequent chain extension

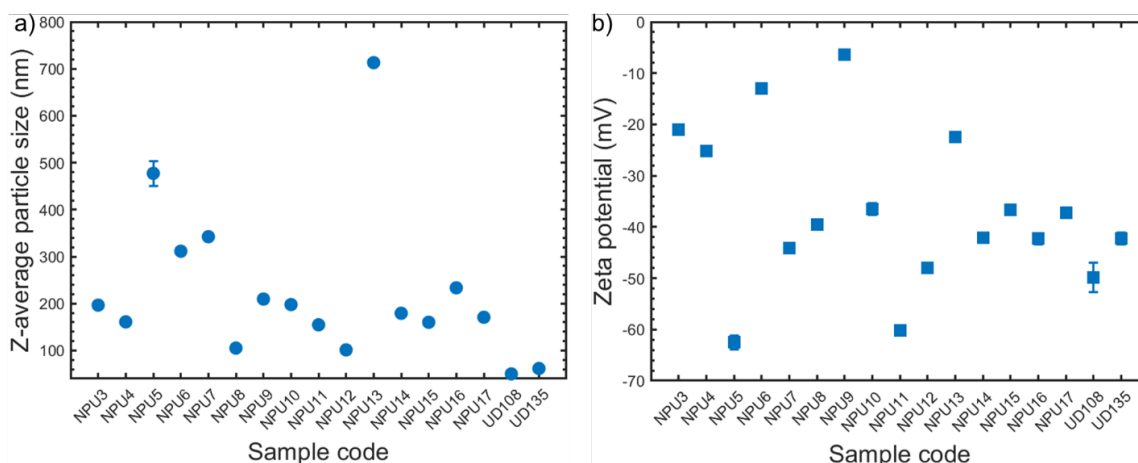


Figure 3 a) The average particle sizes (100–300 nm) of synthesized anionic WPUDs (NPU3–NPU17) compared well with commercial dispersions (UD108, UD135). The particle sizes evolved with changes in chemical composition. b) The negative zeta potential values (-5mV to -60mV) of synthesized anionic dispersions confirmed the incorporation of the anionic compatibilizer and lay in the same range as UD108 and UD135. Data represents average of triplicate measurements.

particles. The incorporation of anionic DMPA into the polyurethane chain renders particles with negatively charged surfaces, leading to the negative zeta potentials of the particles (-20 – -50 mV) (**Figure 3b**). The negative surface charge is expected to impart stability to the PU particles in water. No specific trends were noted for the zeta potential values.

Systematic changes in the chemical composition – NCO:OH ratio (1.6, 2), DMPA content (5–10 wt%), and extent of neutralization (75–125 mol%, basis DMPA) – resulted in changes in particle size and stability of the dispersions (**Figure 4a and 4b**). The particle size decreased with an increase in NCO:OH, irrespective of DMPA content (**Figure 4a**) or extent of neutralization (**Figure 4b**). This is ascribed to the dominant aliphatic nature of residual IPDI (at higher NCO:OH) resulting in reduced viscosity of the pre-polymer which allows a greater reduction in particle size during high shear dispersion in water.^[16,17] Additionally, an increase in the compatibilizer content (at 100 mol% neutralization) led to an increase in the particle size of anionic dispersions (**Figure 4a**). Particle size of WPUDs is also influenced by the extent to which the compatibilizer groups (here, DMPA) are neutralized.^[13] As the extent of neutralization increased from 70 to 100 mol%, the particle size increased (**Figure 4b**). However, as the neutralization was increased to 125 mol%, the particle size decreased for both NCO:OH (1.6, 2) and DMPA contents (8, 10 wt%) (**Figure 4b**).

These trends contradict previous studies that have suggested that increased hydrophilicity (due to higher compatibilizer content and higher extent of neutralization) would lead to lower particle sizes.^[7,8,18] However, our observations for DMPA (at 100 mol% neutralization) (**Figure 4a**) are likely due to the increased viscosity and ‘stickiness’ at higher DMPA contents thereby impeding the reduction of particle size during mixing. Additionally, as seen in **Figure 4b**, an optimum amount of TEA is required to completely neutralize and ionize the compatibilizer groups for the formation of low particle-size stable dispersions.

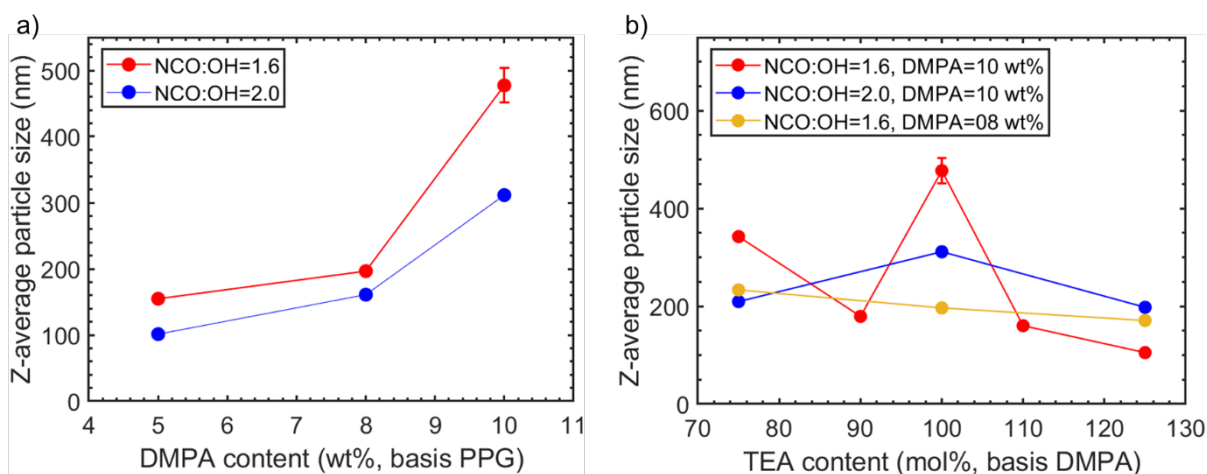


Figure 4 a) The average particle sizes of synthesized anionic WPUDs increased from 160nm to 500 nm and 100nm to 300 nm for NCO:OH 1.6 and 2 respectively, with an increase in compatibilizer (DMPA) content (5–10 wt%) at 100 mol% neutralization. The particle sizes for NCO:OH 1.6 remained consistently higher than NCO:OH 2. b) As the extent of neutralization increased, the particle sizes increased until 100 mol% neutralization, irrespective of DMPA content or NCO:OH. However, at >100 neutralization, the particle size decreased for all dispersions. Data represents average of triplicate measurements

The WPUD synthesis strategy was extended to cationic WPUDs (sample details in **Table A2**), albeit with a few modifications to achieve stable dispersions. Higher NCO:OH values (>1.55) resulted in agglomeration of particles leading to a polymer dense phase, separated from the aqueous medium. Additionally, neutralization below 300 mol% also caused dispersion instability. Thus, cationic WPUDs with NCO:OH ranging between 1–1.55 were synthesized with 300 mol% neutralization. Modifications in the synthesis strategy resulted in particle sizes between 60–100 nm, varying with chemical composition (CPU2–CPU9; **Figure 5**). The particle sizes were lower than anionic WPUDs (**Figure 3a**) but were comparable to commercial dispersions (UD108, UD135; **Figure 5**). Additionally, the zeta potential values for all cationic dispersions were positive and ranged from 20–60 mV.

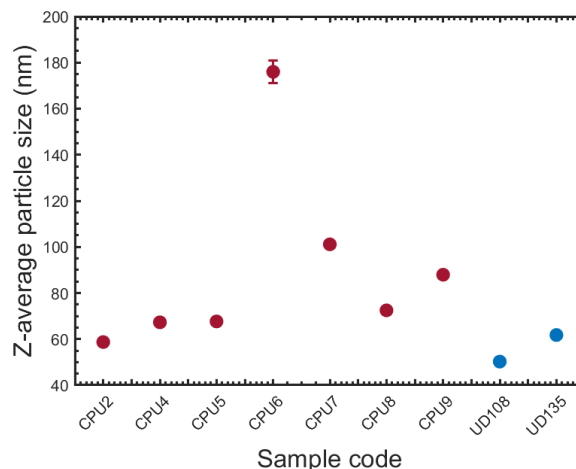


Figure 5 Particle sizes of cationic WPUDs with different compositions mostly ranged between 60–100 nm and were similar to commercial anionic WPUDs (UD108, UD135). Data represents average of triplicate measurements.

Stable Upcycled Anionic and Cationic Dispersions based on Upcycled Polyols: Infigreen-300 was used as a complete replacement to virgin polyols in the synthesis of anionic and cationic upcycled WPUDs. For the anionic WPUDs (D-NPU3, D-NPU4) an NCO:OH = 1.6 was maintained while for the cationic dispersions (D-CPU3, D-CPU4, D-CPU5), the NCO:OH was reduced to 0.97. In both sets of upcycled dispersions, the NCO:OH ratio had to be reduced due to the high hydroxyl value of Infigreen-300 (290 mg/g KOH), as opposed to PPG (56 mg/g KOH); a higher NCO:OH led to formation of unstable dispersions likely due to a robust network formation impeding

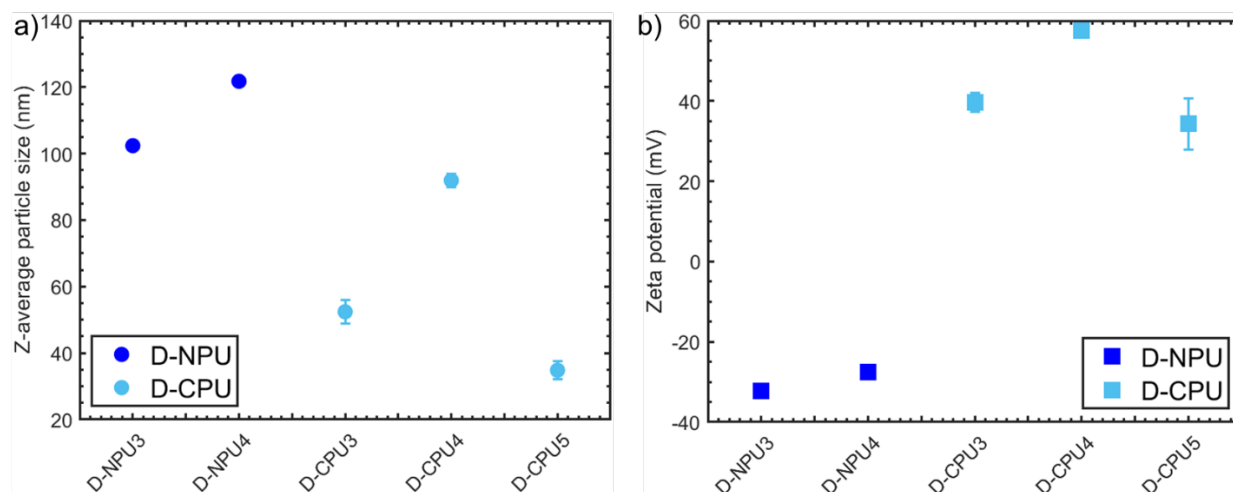


Figure 6 a) The particle sizes of upcycled anionic (D-NPU) and cationic (D-CPU) dispersions varied with a change in chemical composition. They ranged between 40nm and 120 nm. b) The zeta potential values corroborated well with the type of compatibilizer incorporated into the polymer backbone. D-NPU3 and D-NPU4 had negative zeta potentials (-30mV) while D-CPU3, D-CPU4 and D-CPU5 had values between 40 mV and 60 mV. Data represents average of triplicate measurements.

dispersion of particles in water. Due to NCO:OH being <1 for cationic dispersions, the chain extension step was eliminated.

With systematic modifications to the synthesis procedure and chemical composition, upcycled cationic and anionic dispersions were synthesized using Infigreen-300. The particle sizes of D-NPU3 and D-NPU4 were 100 nm and 120 nm respectively, while D-CPU3, D-CPU4 and D-CPU5 had particle sizes between 40 nm and 100nm (**Figure 6a**) and remained consistently comparable to commercial anionic dispersions (**Figure 3a**). The zeta potential values of the anionic and cationic dispersions were negative (-30 mV) and positive (40–60 mV), respectively (**Figure 6b**), thereby confirming the incorporation of compatibilizers and their subsequent stability in aqueous medium. These findings suggest the tunability of dispersion properties with chemical composition and underscore the role of the nature of polyol in dispersion stability. Additionally, by utilizing polyols that are generally utilized in smaller quantities (10–25 wt%) as a replacement for virgin polyol in foam production, we have presented avenues for upcycled dispersion synthesis.

CONCLUSION AND FUTURE WORK

We established a protocol for the synthesis of stable anionic and cationic WPUDs and demonstrated the tunability of their particle size and zeta potential values by changing the chemical composition. Upcycled polyol, Infigreen-300 received from Emery Oleochemicals, is determined to possess a polyether-polyester backbone, inferred from infrared spectroscopy and thermal degradation studies. The WPUD synthesis protocol was altered to account for the high hydroxyl value of Infigreen-300; a lower NCO:OH ratio for cationic and anionic dispersions and a higher extent of neutralization for the cationic dispersions were pursued. These systematic changes resulted in stable upcycled anionic and cationic dispersions with particle sizes between 40 nm–130 nm, depending on the chemical composition. These values corroborated well with the particle sizes of commercial dispersions UD108 and UD135.

These findings present opportunities for synthesis of greener and stable dispersions that can then be applied as membranes (for separation processes), coatings for surface protection, and barrier films for packaging. To address some challenges faced in this study – dispersion instabilities, opaque appearance of dispersions, counterintuitive trends in particle size – and to inform the design of well-tuned waterborne dispersions, further investigations using optical microscopy (particle size distribution, impurity detection), and gel permeation chromatography (pre-polymer molecular weight estimation) are recommended.

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APPENDIX A

Materials and Methods

Chemicals & Equipment

Polypropylene glycol (PPG; polyol) with $M_n \sim 2000$, Isophorone diisocyanate (IPDI), Dibutyltin dilaurate (DBTDL; catalyst), 2,2-bis(hydroxymethyl)propionic acid (DMPA; anionic compatibilizer), triethylamine (TEA; neutralizing agent for DMPA), N-methyl diethanolamine (NMDA; cationic compatibilizer), acetic acid (AcAc; neutralizing agent for NMDA), N-methylpyrrolidone (NMP; co-solvent), Hexamethylene diamine (HDA; chain extender), Dibutylamine (DBA; reagent for titration), Tetrahydrofuran (THF; solvent for titration), Sodium hydroxide (NaOH; reagent for titration), Hydrochloric acid (HCl; reagent for titration) and Bromophenol blue (indicator) were procured from Sigma Aldrich (Millipore Sigma) and used in the synthesis process. Commercial waterborne polyurethane samples (UD108 and UD135) were provided by Bond Polymers International LLC and Infigreen-300 was provided by Emery Oleochemicals. A dissolver type mechanical mixing apparatus was purchased and used.

WPUD Synthesis

Waterborne polyurethane was synthesized by the pre-polymer process [27]; the first step involved synthesizing a low-molecular weight compound (the pre-polymer) consisting of polyol (PPG), diisocyanate (IPDI), the compatibilizer (DMPA or NMDA) and the neutralizing agent (TEA or AcAc). The endpoint, in terms of the residual NCO groups, was determined and confirmed by the dibutylamine back titration method [12]. The pre-polymer was then dispersed in water, under high-speed mechanical mixing (900 rpm), using a dissolver type impeller and subsequently chain extended with HDA to obtain a high molecular weight aqueous dispersion of polyurethane. NMP was used in small amounts to help disperse DMPA in the polyol and to maintain a workable viscosity. Dispersions with solid contents of 25-30 wt% were synthesized. The sample details are given in **Table A1, A2**.

WPUD Characterization

The particle size and zeta potential of the synthesized and commercial dispersions were studied using Dynamic Light Scattering technique (Malvern Zetasizer Nano ZS). The samples were diluted to ~1 wt.% with DI water and vortex mixed, prior to analysis. The WPUD samples were also characterized for their thermal stability using Thermogravimetric Analysis (Perkin Elmer Diamond Thermogravimetric/ Differential Thermal Analyzer) by heating the samples to 550 °C at 20 °C/min and holding at that temperature for 3min.

	UD 108	UD 135	NPU 3	NPU 4	NPU 5	NPU 6	NPU 7	NPU 8	NPU 9	NPU 10	NPU 11	NPU 12	NPU 13	NPU 14	NPU 15	NPU 16	NPU 17
NCO: OH	UD108: aliphatic/ polyether waterborne polyurethane UD135: aliphatic/ polyester waterborne polyurethane		1.6	2.0	1.6	2.0	1.6	1.6	2.0	2.0	1.6	2.0	1.6	1.6	1.6	1.6	1.6
DMPA (wt% basis polyol)			8	8	10	10	10	10	10	10	5	5	15	10	10	8	8
TEA (mol% basis DMPA)			100	100	100	100	75	125	75	125	100	100	100	90	110	75	125
Solid content (wt%)	~40		~25	~25	~30		~30	~30									

Table A1: Details of waterborne polyurethane synthesis with different chemical compositions achieved by varying the NCO: OH ratio, DMPA content and TEA content

	UD108	UD135	CPU2	CPU4	CPU5	CPU6	CPU7	CPU8	CPU9	D-NPU3 [†]	D-NPU4 [†]	D-CPU3 [*]	D-CPU4 [*]	D-CPU5 [*]
NCO: OH	UD108: aliphatic/ polyether waterborne polyurethane UD135: aliphatic/ polyester waterborne polyurethane		1.55	1	1	1.2	1.2	1.2	1.2	1.2	1.2	0.97	0.97	0.97
NMDA (wt.% basis polyol)			8	10	15	8	8	10	10	15	10	10	15	20
AcAc (mol% basis DMPA)			150	100	100	150	200	150	200	100	100	300	300	300
Solid content (wt.%)	~40		~30	~30	~30	~30	~30	~30	~30	~30	~30	~30	~30	~40

Table A2: Details of waterborne polyurethane synthesis with different chemical compositions achieved by varying the NCO: OH ratio, compatibilizer content and extent of neutralization

†: Upcycled anionic WPUDs; *: Upcycled cationic WPUDs