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The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process

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Abstract

There are many variables in the preparation of aqueous polyurethane (PU) dispersions. Chemical and compositional variables such as carboxylic acid concentration, concentration of the polymer, degree of pre/post-neutralization of the carboxylic acids and chain extension that all impact solution properties such as particle size and viscosity. Another variable is the method by which the dispersion is prepared; two primary methods are currently employed in industrial manufacture, the prepolymer mixing process and the acetone process. This study evaluates the impact of the chemical variables on a given PU dispersion formulation prepared by the acetone process. Changes in carboxylic acid concentration, degree of pre/post-neutralization and chain extension were found to have the expected impacts on dispersion solution properties. Increased ionic concentration, and degree of pre-neutralization led to lower particle size and higher viscosity, increased degree of chain extension led to larger particle size and lower viscosity, increased post-neutralization increased both particle size and viscosity, and increased concentration of the polymer led to a viscosity increase without any change in particle size.

Keywords: Polyurethane dispersion; Acetone process; Compositional variations

1. Introduction

The evaporation of volatile organic compounds (VOCs) during the formulations of coatings, inks, and paints cause a wide variety of air quality problems. Consequently, governmental organizations such as the Environmental Protection Agency (EPA) in the United States and Local Air Quality Regulators have stepped up their efforts to limit the amounts of VOCs released to the atmosphere. These regulations and consumer demands are forcing industries to develop environmentally friendly products [1–4]. Among several options to develop technology, water is the best choice to use as a medium in formulating coating systems. To reduce or eliminate organic solvents from the formulations, solvents should be partially or completely replaced with environmentally benign solvents (e.g. water), in the coating formulations to achieve little or no VOC content [5–13].

Polyurethanes are widely used in the coatings and adhesives applications because of their excellent performance. Organic solvent based polyurethanes [14,15] are increasingly restricted in their traditional applications because of the demands of environmental regulations, abatement costs and safety. In contrast, aqueous PU dispersions prepared with low levels of organic solvent seeing ever wider use.

Several processes have been developed for the synthesis of polyurethane dispersions. The preparation of polyurethane dispersions by the prepolymer mixing process has received some attention in the literature [16–26]. In this process, a medium molecular weight polymer (the prepolymer) is synthesized by the reaction of suitable diols or polyols (usually polyether or polyester macrodiols) with a molar excess of diisocyanates or polyisocyanates. In this reaction mixture, an internal emulsifier is added to allow the dispersion of the polymer in water; this emulsifier is usually a diol with ionic groups (carboxylate, sulfonate, or quaternary ammonium salt) or non-ionic groups [poly(ethylene oxide)]. The internal emulsifier becomes part of the main chain of the polymer. Approximately, 15% organic solvent, typically *N*-methyl pyrrolidinone (NMP), is used to reduce the viscosity of the medium as well as to dissolve the internal surfactant. The final

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step is the dispersion of the prepolymer in water followed by chain extension with a water soluble diamine to buildup the molecular weight of the polymer.

Recently, we reported a thorough study of the effects of ionic concentration, concentration of the polymer, degree of pre/post-neutralization and chain extension on the properties of polyurethane dispersions prepared by prepolymer mixing process [24]. The prepolymer was made from poly(hexylene adipate–isophthalate)diol, isophorone diisocyanate (IPDI) and dimethylol propionic acid (DMPA) in presence of 12% NMP. The prepolymer was then neutralized with triethyl amine (TEA), dispersed in water and chain extended with hexamethylene diamine (HMDA). In the pre-neutralization process, the prepolymer was partially/fully neutralized with TEA, dispersed in water and chain extended with HMDA. The partially pre-neutralized PU dispersion has both free carboxylic acid groups and carboxylate ions. In the post-neutralization process, partially pre-neutralized PU dispersion was fully neutralized with additional TEA. Our observations as to the impact of ionic concentration, degree of pre-neutralization and chain extension were expected, and very similar to previous reports on prepolymer mixing process. However, unexpectedly there was a large increase in the particle size and viscosity with an increase in the degree of post-neutralization or concentration of the polymer. The explanation for unexpected results in the post-neutralization/concentration of the polymer in prepolymer mixing process was attributed to the role of surfactant in the presence of NMP in the dispersion. Additional work is in progress to understand the effect of surfactant/NMP in the prepolymer mixing process.

An alternative route to prepare PU dispersions is available. Industrially, a large number of products are prepared using the acetone process [1–3,27–34]. After the prepolymer process for making PU dispersions, the acetone process is the most widely used [34]. The main differences are in the chain extension and dispersion steps. Initially the prepolymer is prepared in the same way as described for the prepolymer mixing process, however, instead of NMP the solvent is acetone and is used at a much higher relative level than if NMP was used. The prepolymer is chain extended with diol/diamine, the dispersing groups neutralized and dispersion effected by the slow addition of water to the polymer solution. Following the dispersion step, the acetone is removed by distillation yielding a product containing either very low or no VOCs. Despite this advantage there are very few Refs. [35–40] related to this process in the open literature. Within these detailed investigations a modified acetone process was used in which acetone replaced some, but not all, of the NMP in the PU dispersion.

We describe here the preparation of polyurethane dispersions by a true acetone process. Using acetone by itself allows for the polymerization solvent to be completely removed by distillation, yielding an organic solvent free PU dispersion. The effect of the variables, such as ionic concentration, concentration of the polymer, degree of pre and post-neutralization and chain extension on the particle size and viscosity are carried out, and compared with the prepolymer mixing process published earlier [24].

2. Experimental

2.1. Materials

Poly(hexylene adipate-isophthalate)polyester diol (Desmophen 1019-55—OH# 55 and Acid# 2), and isophorone diisocyanate (IPDI) (Desmodur-I) were supplied by Bayer MaterialScience, Pittsburgh, PA. Dimethylol propionic acid (DMPA), dibutyltin dilaurate (DBTDL), triethylamine (TEA), 1,4-butane diol (BD), 1-butanol, dibutyl amine, 0.4 wt% aqueous solution of bromophenol blue and 1.0 N aqueous solution of HCl were received from Aldrich Chemical Co. Acetone (99.5%), toluene (99.5%) and isopropanol (99%) were received from Fluka. All materials were used as received.

The films used for GPC analyses were prepared by casting onto a polypropylene plate and drying in a vacuum oven at 120 °C for 3 days. The concentration of polymer is verified by heating 1 g of dispersion in a glass vial in a vacuum oven at 120 °C for 6 h.

2.2. Measurements

Dispersion particle sizes (PS) were determined on a Microtrac UPA 250 light scattering ultrafine particle analyzer. The samples were diluted to the required concentration with distilled water before measurement. The analysis was carried out with estimated solution parameters as follows: refractive index of 1.81, particle density at 1 gm/cm^3 and viscosity between 0.797 and 1.002 mPa s. The time for each analysis was fixed at 360 s, and minimum two runs were carried out to verify a reproducibility of ±2 nm.

GPC measurements in THF were performed using a Polymer Laboratories, model PL-ELS 1000 equipped with a PL gel 5 μm mixed C, 300×7.5 m^2 column and a Waters 590 HPLC pump at a flow rate of 1 ml/min. The GPC was calibrated with monodisperse poly(methyl methacrylate) (PMMA) standards with PDI's <1.04. Nine different PMMA standards of $M_n=1000$, 1800, 6500, 14,000, 30,000, 62,000, 148,000, 242,000, and 550,000 were used for the calibration curve.

Solution viscosity was determined at 25 °C using a Brookfield DV-I viscometer with No. 2 spindle at a shear rate of 100 s^{-1}.

The NCO content of the prepolymer was determined by pipetting 4.0 g of the prepolymer solution into a 250 ml conical flask. Fifty grams of toluene and 10 g standard solution of 2 M dibutyl amine in toluene were added, and the flask was stirred until the prepolymer dissolved completely. One hundred grams of isopropanol was then added and the solution titrated against 1.0 N HCl (aq) using bromophenol blue as the pH indicator. A blank titration was carried out using the above procedure without any sample. The percentage of NCO was calculated using the following equation:

$$\%\mathrm{NCO}=\frac{[(\text{ml HCl for blank}-\text{ml HCl for sample})\times 4.2]}{\text{sample wt}}$$

Table 1
Compositions for variation in carboxylic acid content—g (equiv.)

Reagent	PU1	PU2	PU3	PU4	PU5	PU6	PU7
DMPA	2.1 (0.031)	3.1 (0.046)	4.0 (0.060)	5.0 (0.075)	5.5 (0.083)	6.0 (0.089)	7.0 (0.104)
Polyester diol	75.2 (0.073)	71.3 (0.069)	67.5 (0.066)	63.6 (0.062)	61.6 (0.060)	60.2 (0.058)	55.7 (0.054)
IPDI	18.6 (0.167)	20.6 (0.185)	22.4 (0.201)	24.4 (0.219)	25.4 (0.228)	26.0 (0.234)	28.3 (0.255)
BD	2.5 (0.055)	2.7 (0.060)	3.0 (0.065)	3.2 (0.071)	3.3 (0.074)	3.4 (0.074)	3.7 (0.082)
TEA	1.6 (0.016)	2.3 (0.023)	3.0 (0.033)	3.8 (0.037)	4.2 (0.041)	4.4 (0.044)	5.3 (0.052)
Acetone	80	80	80	80	80	80	80
Water	212	212	212	212	212	212	212

2.3. Representative PU dispersion preparation (PU2)

A 500 ml round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser with nitrogen in/out let and a pipette outlet was charged with the polyester diol (71.3 g, 0.069 hydroxyl equiv.) and DMPA (3.1 g, 0.046 hydroxyl equiv, 0.023 acid equiv). While stirring, acetone (80 g, (41 wt% in the prepolymer mixture)) was added and stirring was continued until a homogeneous mixture was obtained. IPDI (20.6 g, 0.185 isocyanate equiv.) and DBTDL were added drop wise and stirring was continued for 30 min at 60 °C. Upon reaching the theoretical NCO value (2.0% NCO), the prepolymer was chain extended by the addition of 2.7 g of BD (0.060 hydroxyl equiv.), and allowed to react for 2 h at 60 °C to make the PU polymer. The final polymer was neutralized by the addition of 2.3 g of TEA (0.023 mol) over 30 min while maintaining the temperature at 55 °C. Dispersion was accomplished by slowly adding water (212 g) to the neutralized PU solution at 45–50 °C over 30 min with agitation speed of 600 rpm. The stirring was continued at the same temperature for additional 30 min. The acetone was removed at 35 °C on a rotary evaporator.

2.4. Additional preparations

The compositions of additional samples are given in Tables 1 and 2. Formulations PU1 through PU7 represent a systematic variation in DMPA content. For experiments (PU8 and PU9, Table 2) requiring control of the molecular weight, 1-butanol was added as a chain terminator with the ratio of isocyanate groups to chain extender/terminator hydroxyl groups maintained at 1.1:1. For the extent of neutralization and variation of concentration of polymer studies, formulation PU2 was used as the basis with only the content of TEA or water varied to meet the conditions given in the text.

3. Results and discussion

The preparation of PU dispersions by the acetone process is shown in Scheme 1. The entire polymerization is carried out in presence of a low boiling solvent acetone. In contrast to the prepolymer process, the prepolymer is chain extended before the dispersion step. Finishing the polymerization in the absence of water gives control over stoichiometry and uniform chemical reaction. The addition of water to the PU solution causes the formation of a dispersed polymer phase as the polymer becomes insoluble in the acetone water mixture.

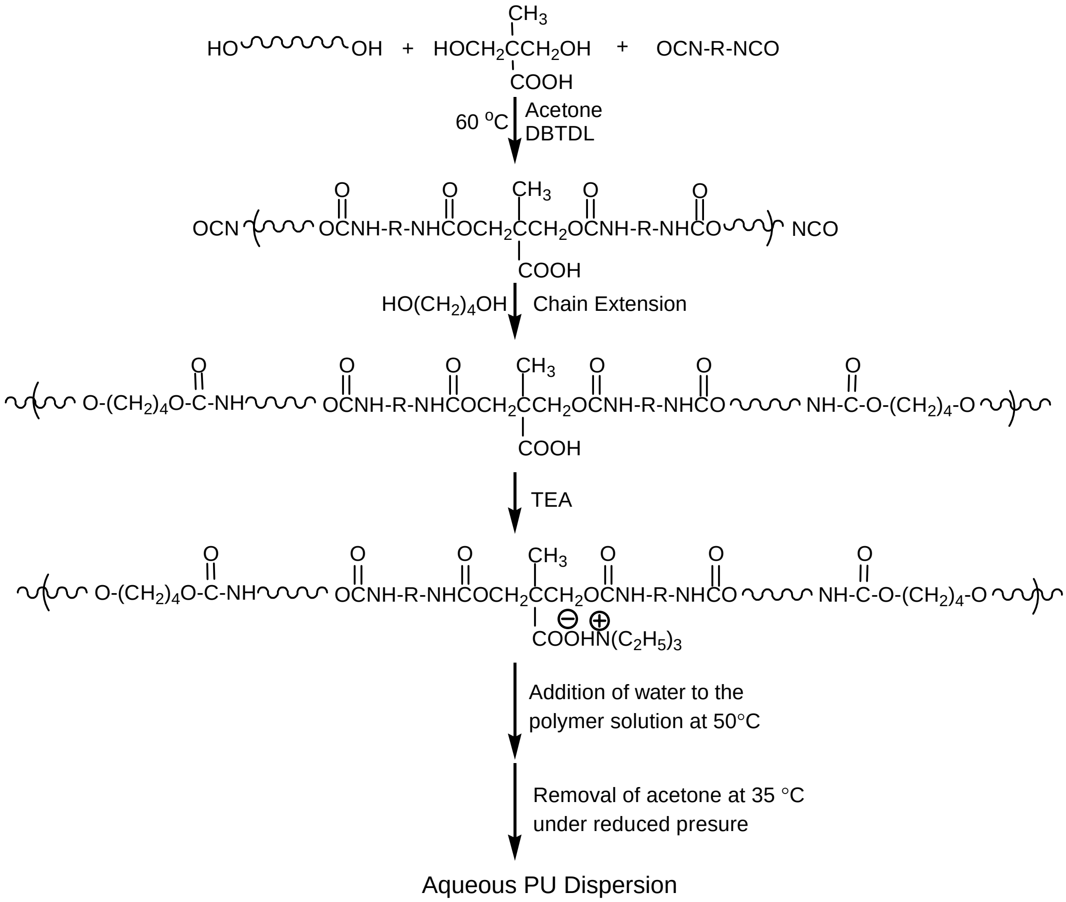
3.1. DMPA concentration

In PU dispersions, the average particle size is important. The average particle size can be controlled to some extent by emulsification conditions such as impeller speed and temperature. However, it is primarily governed by the concentration of dispersing groups. In the present polyurethane dispersions these are typically ionic salts, for example ammonium carboxylate anions [–$COO^-HN^+(C_2H_5)_3$].

To probe the effect of changing the amount dispersing groups attached to the polymer backbone, the DMPA content was varied from 2 to 7 wt% based on total concentration (PU1–PU7). For this portion of the study the polymer concentrations were maintained at 32 wt% and chain extension at 90% and the neutralizing amine (TEA) content was adjusted to keep a 1:1 ratio of COOH to $N(C_2H_5)_3$ (100% neutralization). The impact of dispersing group concentration on dispersion solution properties is shown in Fig. 1. The particle size decreases with increased DMPA concentration as the overall surface area of the dispersed phase increasing to accommodate the additional salt groups at the interface (Fig. 1). Concurrently there is an increase in the number of particles [41,42] and an increase in viscosity even though polymer content itself has not changed. The relative amount of water associated with the particle ionic surface increases relative to the total dispersed phase content augmenting the effective volume of the particles. For DMPA concentration above 5 wt% there was no additional lowering of particle size, perhaps due to inability of the system to effectively structure itself to accommodate the additional surface active groups.

Table 2
Compositions for variation in molecular weight—g (equiv.)

Reagent	PU2	PU8	PU9
DMPA	3.1 (0.046)	3.1 (0.046)	3.1 (0.046)
Polyester diol	71.3 (0.069)	71.1 (0.069)	71.0 (0.069)
IPDI	20.6 (0.185)	20.4 (0.184)	20.2 (0.183)
BD	2.7 (0.060)	1.5 (0.033)	0
1-Butanol		2.0 (0.027)	4.4 (0.060)
TEA	2.3 (0.023)	2.3 (0.023)	2.3 (0.023)
Acetone	80	80	80
Water	212	212	212



Scheme 1. Elementary steps for the preparation of PU dispersions by acetone process.

3.2. Degree of chain extension

Our previous work with the prepolymer mixing process showed that a minimum 4 wt% of DMPA was required to make stable dispersions [24]. Here, using the acetone process a stable dispersion could be obtained with only 2 wt% of DMPA. The higher concentration of DMPA needed for the prepolymer process could be due to (1) a decrease in surface activity of the carboxylate groups on the surface of PU particles caused by NMP or (2) a decrease in the stability of the particles resulting from the low molecular weight prepolymers.

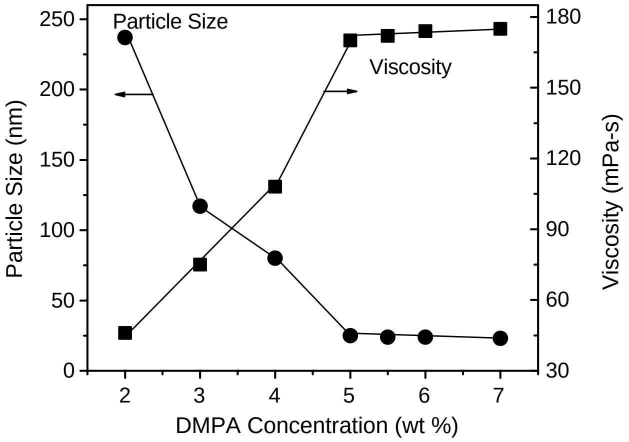


Fig. 1. Effect of DMPA concentration on particle size and η (chain extension, 90%; pre-neutralization, 100%).

The effect of lower molecular weight on the particle size and viscosity was investigated by reducing the butane diol chain extender and replacing it with a chain terminator, 1-butanol (PU8 and PU9). The samples for this portion of the study were prepared at 32 wt% of the concentration of the polymer, with 3 wt% DMPA and neutralized to 100% with TEA. As shown in Table 3, the addition of 1-butanol in place of all the butane diol (BD) results in a 90% reduction in the anticipated molecular weight that would be found at the time of dispersion.

The particle size decreased from 107 to 95 nm with a corresponding increase in viscosity from 75 to 82 mPa s as the chain extension was reduced from 90 to 0% (Fig. 2). This was opposite of what was expected and most likely represents the fact that at higher polymer viscosity, the stress increases at the interface during phase inversion. Having the dispersed phase (polymer phase) viscosity as it forms much higher than the

Table 3
Effect of chain extension on molecular weight

Sample	Chain extension (%)	M_n (g/mol) (calculated)	M_n (g/mol) (GPC)
PU9	0	2800	3000
PU8	50	5900	5000
PU2	90	29,000	23,000

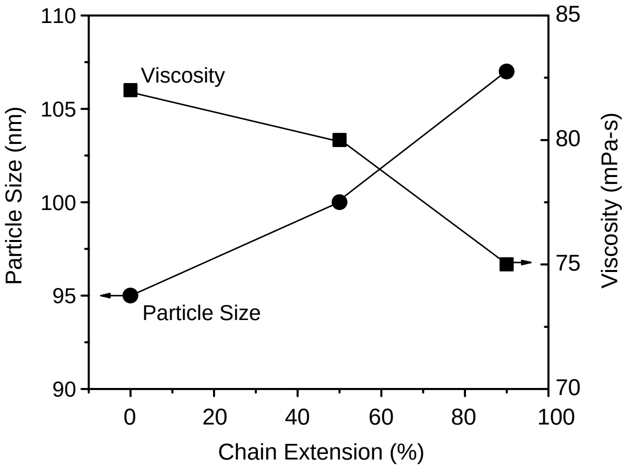


Fig. 2. Effect of chain extension on particle size and η of dispersion (pre-neutralization, 100%; DMPA, 3 wt%).

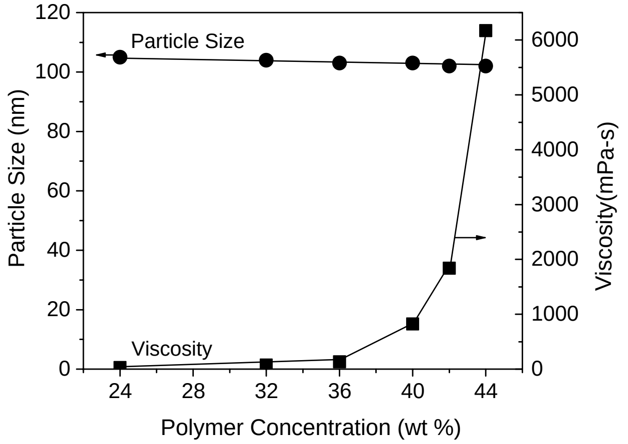


Fig. 3. Effect of polymer concentration on particle size and η of dispersions (chain extension, 90%; DMPA, 3 wt%; pre-neutralization, 100%).

continuous phase (acetone plus water) results in lower phase deformation with increase in molecular weight and hence larger particles [19].

In the prepolymer mixing process, the particle size and viscosity remained nearly constant with an increase in the degree of chain extension [24]. This was due to the addition of prepolymer to the water followed by chain extension after the dispersion. Hence, chain extension step did not affect the formation of particles.

3.3. Concentration of the polymer

In the formation of dispersion using the prepolymer mixing method, an unexpected dependence of particle size on final dispersion solids was found. Higher the final solids in the dispersion resulted in larger particle sizes with broader distributions [24]. A similar study was run here using the acetone process and the formulation of PU2. In stark contrast to the prepolymer process the particle size remained essentially constant as the concentration of the polymer of the resulting dispersions was raised from 24 to 44 wt% (Fig. 3).

In the acetone process, the dispersion particles are formed early in the inversion step as the addition of water causes the polyurethane polymer to phase separate from the acetone water mixture. At this point the ionic concentration of each particle and the number of particles are fixed, continued addition of water only dilute the particles. The slight reduction of particle size with increased solids is probably due to increased ionic concentration.

This manner of particle formation is very different than that in the prepolymer process where the isocyanate terminated prepolymer solution is added with vigorous agitation to the water. Early in the dispersion step particles are forming in an environment low in NMP and ionic concentration, as the prepolymer addition continues the particle formation is taking place with increasing NMP and ionic concentration.

The viscosity increases as expected with the concentration of the polymer and is higher than found with the prepolymer process (Fig. 3).

3.4. Degree of neutralization

Neutralization of the carboxylic acids can take place either before the dispersion step or afterwards (designated here as pre-neutralization and post-neutralization, respectively). Often during final product formulation in making an adhesive or coating the degree of neutralization is varied by adjusting the pH to change the rheology but there has not been a systematic

	Equivalent % of TEA vs DMPA				
Preneutralization	60	70	80		100
Particle Size (nm)					107
η(mPa-s)					75
Particle Size (nm)			178	20% →	234
η(mPa-s)			50	Post	95
Particle Size (nm)		223	30% →		280
η(mPa-s)		28	Post		115
Particle Size (nm)	153, 4	40% →			1108, 225
η(mPa-s)	25	Post			185

Fig. 4. Effect of post-neutralization on particle size and η (chain extension, 90%; DMPA, 3 wt%).

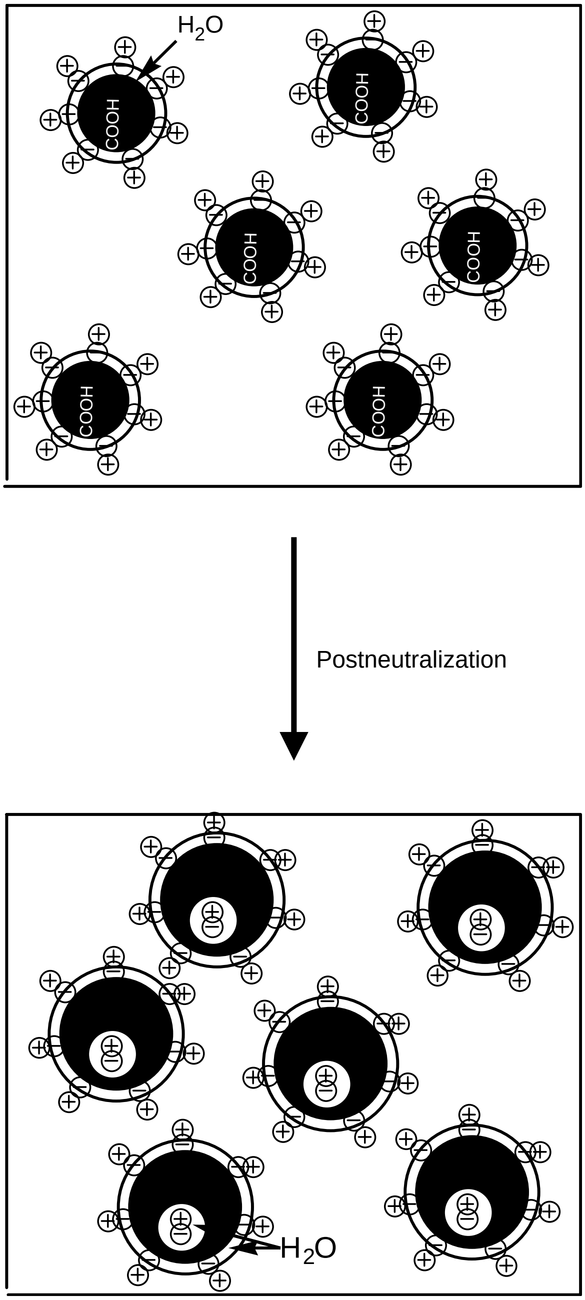


Fig. 5. Effect of post-neutralization on particle size.

study of this for PU dispersions. To study the impact of neutralization two series of experiments were performed off of the base formulation of PU2. The first focusing solely on the degree of pre-neutralization and the second on the post-neutralization of dispersions formed with less than a 1:1 TEA:COOH content. The results for these experiments are given in Figs. 4 and 5.

With simple pre-neutralization, the particle size increased from 108 to 223 nm as the TEA equivalents were decreased from 100 to 70% based on DMPA. The smaller particle size at increased pre-neutralization is due to the increase in the ionic content due to the transformation of hydrophobic carboxylic acid groups to hydrophilic amine salts. For the dispersion made with 60% pre-neutralization, bimodal particle size distributions (153 nm (65%) and 4 nm (35%)) were obtained. At this level of neutralization there are not sufficient ionic groups to stabilize dispersions prepared with 3 wt% DMPA. This situation would be the same as 1.8% fully neutralized DMPA dispersion, below the level found to be required. A similar trend was observed for the effect of degree of pre-neutralization on particle size and viscosity for the PU dispersion made by prepolymer mixing process [24].

To evaluate post-neutralization, additional TEA was added to the dispersions made with different levels of pre-neutralization. For all the dispersions the particle size and the viscosity increased following the post-neutralization to a 1:1 ratio of TEA to COOH (100%). Post-neutralizing the PU dispersion made with 70% pre-neutralization resulted in changes in particle size and viscosity of 223–280 nm, and from 28 to 115 mPa s, respectively. As prepared, the 70% preneutralized PU dispersion has a maximum of 70% of the carboxylic acids as ions [–COO$^-$HN$^+$(C$_2$H$_5$)$_3$]. The remaining 30% of the carboxylic acid groups are hydrophobic, and trapped inside the core of the particle. Subsequently, the residual acid groups are to some extent converted to –COO$^-$HN$^+$(C$_2$H$_5$)$_3$ ions by the additional TEA in the post-neutralization step. Some ion pairs may come out to stabilize the surface of the particle while others may be trapped inside and pulling water to the inside of the particle. As a result, the size of the particles increases resulting in an increase size of effective volume of the dispersed phase (Fig. 5). A similar phenomenon was observed by the post-neutralization of the dispersion made by 80% pre-neutralization (Fig. 4). For 40% post-neutralization, the particle size increased and the distribution was bimodal (1108 nm (37%), 225 nm (63%)) as was found for the parent dispersion supporting the assumption that number of polymer particles did not change in this step.

The increase in viscosity was not as dramatic for the post-neutralization of the acetone dispersions (Fig. 4) compared to that reported for the prepolymer mixing process [24]. A 70-fold increase in η was found for the prepolymer process compared to 7-fold increase found here for the acetone process at 40% post-neutralization.

4. Conclusions

The current study details the effect of the DMPA concentration, concentration of the polymer, degree of pre/post-neutralization and extent of chain extension on particle size and viscosity of a given formulation prepared by the acetone process. A number of key differences were identified when comparing earlier findings for dispersions made with the prepolymer mixing process [24].

First, the acetone process afforded stable PU dispersions at a lower concentration of DMPA (2 wt%), the prepolymer process required a minimum of 4 wt% DMPA to make a stable dispersion of similar composition. This reflects a higher effectiveness of the incorporated dispersing groups, a point also reflected in the small particle size.

Second, the method of dispersion used for the acetone process (water to polymer solution) the particle size obtained was basically independent of polymer concentration in the final dispersion, a result of all particle formation taking place at once after enough water is added to make the polymer insoluble.

Lastly, under-neutralized dispersions prepared using the acetone process do not exhibit the very large changes in viscosity found with the prepolymer process.

Overall, it has been seen that the acetone process is more robust for generating reproducible results with a lower sensitivity to process variables. Additional work is required to understand why the efficiency of the dispersing groups appears to be higher and to deconvolute what maybe contradictory effects of viscosity at the time of dispersion and molecular weight.

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