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Preparation and Shelf-Life Stability of Aqueous Polyurethane Dispersion

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Summary: A series of aqueous polyurethane dispersion were prepared by the reaction of hydroxyl-terminated poly(ethylene adipate), dimethylol propionic acid, 4,4'-diphenylmethane diisocyanate, and ethylene glycol. Formation of the dispersion was achieved by phase inversion of an acetone solution of the polyurethane with water, utilizing carboxylate anion groups as the internal emulsifying sites. The amount of acetone added has a large effect on the particle diameter (0.08 µm to 8.61 µm) and particle size distribution of the polyurethane emulsion. The storage stability was evaluated in terms of particle size and particle size distribution. The aqueous emulsion obtained with no use of acetone was sufficiently stable in storage at least over six months.

Keywords: particle size; particle size distribution; phase inversion; polyurethanes; shelf life stability

Introduction

From the view points of inherently environmental friendly process, workers' health and hygiene, and legislative requirements, polluting organic solvents (e.g., volatile organic compounds (VOCs)) that evaporate during the formulations of coatings cause a wide variety of air quality problems. In order to reduce or eliminate organic solvents from the formulations, organic solvents should be partially or completely replaced with an environmentally benign solvent (e.g., water), in the coating formulations to achieve small or no VOC content.[1] Polyurethane is widely used in the coating industry due to their excellent performance. The organic solvent-based (e.g., *N,N'*-dimethylformamide (DMF) and *N,N'*-dimethylacetamide (DMAc)) polyurethane (PU) will be

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restricted in their traditional applications sooner or later because of the demands of environmental regulations. In contrast, aqueous PU dispersion would be one of candidates promising to replace them. An aqueous PU dispersion is a binary colloidal system in which PU particles are dispersed in an aqueous medium.

Aqueous-dispersible PU was introduced in open literature in late 1960s.[2] In order to produce high-molecular-weight aqueous PU dispersions, it is necessary to reduce the viscosity of mixing system. Various processes have been developed for the preparation of aqueous PU dispersions.[3–5] Among these processes, the acetone process represents one of the most popular processes,[6] in that acetone is inserted with respect to the PU formation, freely miscible with water, and a low boiling point solvent can be removed with ease. The addition of water to an acetone solution of PU ionomer followed by removal of the acetone results in aqueous PU dispersions.

A typical PU is produed by polyaddition of diisocyanates and diols so that urethane linkage occur in the polymer chain. An approach to making an aqueous-dispersible PUs is to incoporate hydrophilic segments into PU backbones by replacing a small portion of the aforementioned diols with component that contains aqueous-solubilizing functional groups such as carboxylate or sulfonate groups in its molecular structure. These components are often called internal emulsifiers or hydrophilic monomers.[7–8] Many research groups[9–13] have used the carboxylic acid containing low molecular weight diol dimethylol propionic acid (DMPA) as an internal emulsifier. The degree of hydrophilicity is one of the important factors determining the particle size of the PU particles. [10–13] In general, smaller particles result with increasing in hydrophilicity. In practice, PU emulsion is stored for a while prior use, therefore, storage stability is an important characteristic of an emulsion. In dilute emulsion systems, creaming velocity (v_{Stokes}) was described in Stokes terminal velocity equation[14–15]

$$v_{\mathrm{Stokes}}=\frac{d_{\mathrm{p}}^{2}\left|\rho-\rho_{\mathrm{o}}\right|g}{18\mu_{\mathrm{c}}} \qquad (1)$$

where d_{p} is the diameter of emulsion particle, ρ and ρ_{o} are the density of water and emulsion, μ_{c} is the viscosity of water and g is the gravity acceleration velocity. Obviously, in the dilute emulsion system, diameter of emulsion particle has a significant effect on the creaming velocity. That is the smaller particle, the slower creaming velocity. The creaming velocity of an emulsion as defined by Stokes terminal velocity equation (Eq.1) gives only the rate of creaming of a single droplet. However, in a polydisperse system consisting of n_i droplets of radius r_i, the mass creaming rate ($\bar{u}$), has been defined as[16]

$$\bar{u} = \sum_i \frac{8\pi}{27\mu_o V} g n_i r_i^5 \left| \rho - \rho_o \right| \qquad (2)$$

where V is the total volume of the disperse phase, μ_o is the viscosity of emulsion.

Consequently, the shelf life colloidal stability of aqueous dispersion PUs is influenced by their particle size distribution.

Here, we describe the synthesis of PU having built-in carboxylic (COOH) groups as an internal emulsifier and the preparation of aqueous PU emulsions using a two-step process. Since, the shelf life stability is an important characteristic of an emulsion, the study focuses on the colloidal stability properties of aqueous dispersion PU. The effect of acetone content on the shelf life stability of the resulting emulsions was also investigated in terms of particle size, particle size distribution (PSD).

Experimental

Materials

Hydroxyl-terminated poly(ethylene adipate) (EGAA, M_n = 1000, Asahi Denka Kogyou) was dried by azeotropic distillation with toluene. The distillation was continued until no further distillate was collected. The moisture content of EGAA was determined by Karl Fisher titration (< 0.03 wt%). Ethylene glycol (EG, Nacalai Tesque), and triethylamine (TEA, Wako Pure Chem. Ind.) was dried according to standard methods just before use. *N*-Methyl-2-pyrrolidinone (NMP, Wako Pure Chem. Ind.) and acetone (Wako Pure Chem. Ind.) were dried over 4 Å molecular sieves. Dimethylol propionic acid (DMPA, Tokyo Kasei Kogyo) and 4,4'-diphenylmethane diisocyanate (MDI, Nippon Polyurethane Ind.) were used as received.

Preparation of Aqueous PU Dispersions

A series of aqueous PU dispersions were prepared with varying the amount of acetone. Their formulations are presented in Table 1. DMPA (ca. 3 wt% based on total solid PU) was dissolved in a minimum amount of NMP in a round bottom flask equipped with a stirrer, a thermometer, and an inlet of dry nitrogen. Molten EGAA and solid MDI (1.5 equiv) were added to the flask on a heating oil bath. Pre-polyaddition was carried out with mechanical stirring at 40 °C under a nitrogen atmosphere until the consumption of isocyanate (NCO) groups reached a theoretical amount estimated by assuming an equimolar reaction of the NCO and OH groups. This temperature and atmosphere was maintained to avoid any competitive side reactions, such as the formation of allophanates. The unreacted NCO groups were determined by a back-titration using di-*n*-butylamine. After the resulting viscous prepolymer was diluted with a given amount of acetone, EG (an equiv amount to the unreacted NCO groups) was added. The chain-extension reaction was continued at 50 °C until the IR spectra showed no stretching band due to the NCO groups at 2270 cm^{-1}. The COOH groups in the resulting chain-extended PUs were neutralized with TEA (1.2 equiv) in acetone at 50 °C for 1 h, and then water was gradually added with vigorous stirring (750 rpm) at 50 °C. The dispersion was stirred for further 30 min. Removal of acetone by a rotary vacuum evaporator gave a milky white aqueous PU emulsion or suspension, which contained about 30 wt% PU.

Table 1. Formulation for PU Dispersions.

Formulation	PUD1	PUD2	PUD3	PUD4
$[\mathrm{NCO}]/[\mathrm{OH}]_{\mathrm{EGAA}}/[\mathrm{OH}]_{\mathrm{DMPA}}/[\mathrm{OH}]_{\mathrm{EG}}$	1/0.49/0.17/0.34	1/0.49/0.17/0.34	1/0.47/0.20/0.33	1/0.48/0.18/0.34
DMPA (w/w% solid PU)	3	3	3	3
Neutralization (%)	120	120	120	120
Soft Segment (%)	60.88	61.11	59.06	60.21
Acetone (w/w% dispersion)	0	12	24	30

Characterizations

Infrared spectra were recorded on a JASCO model FT/IR-3 or A-202 infrared spectrometer. The particle size and particle size distribution (PSD) of PU emulsions were measured using of a laser diffraction particle size analyzer (Shimadzu Model SALD 2001) at ambient temperature. Because the PU emulsions exhibited in a skewed distribution function, the lognormal distribution was used for describing the particle size of PU emulsion. On the basis of the lognormal distribution, the geometric mean diameter (d_g) and geometric standard deviation (σ_g) were calculated according to eqs. (3) and (4), respectively.[17]

$$d_g = \exp\left(\frac{\Sigma(n_i \ln d_i)}{N}\right) \tag{3}$$

$$\sigma_g = \exp\left(\frac{\Sigma n_i (\ln d_i - \ln d_g)^2}{N-1}\right)^{1/2} \tag{4}$$

where n_i is the number of particles in group i, having a midpoint of size d_i, and where $N = \Sigma n_i$, that is, the total number of particles.

Results and Discussion

Preparation of Aqueous PU Anionomer Dispersions

Aqueous PU dispersions were prepared by two-step process, prepolymerization and chain extension, followed by subsequent neutralization of the carboxyl groups of DMPA with base. PU prepolymer with terminal isocyanate groups was prepared by the polyaddition of hydroxyl-terminated EGAA with an excess amount of MDI incorporating 3 wt% of DMPA. It is accepted that a minimum ionic content is required for the formation of stable aqueous PU dispersions, the actual amount depends on the type of ionic species and countercations (neutralizing agents) employed. Chen and Chen[9] found that fully neutralized PU anionomer with a minimum of about 0.8 wt% of COOH groups is required to form stable dispersions for at least 1 month. It has been reported that the average weight percentage of hydrophilic ionic site, rather than the average number of DMPA per polymer, is the critical factor for good dispersion.[18] The COOH content is defined as follows:

$$\text{COOH content (wt\%)} = \frac{\text{weight of COOH in solid PU}}{\text{total weight of solid PU}} \times 100 \tag{5}$$

Because of the high melting point of DMPA (181–185 °C), minimum amount of water miscible cosolvent NMP was introduced to carry out a homogeneous reaction at 40 °C. NMP is often the preferred cosolvent because it acts as a process aid in film formation.[8] To test the stability of MDI in cosolvent NMP, blank runs were carried out in the reaction temperature. The results obtained for three hours reaction time are shown in Table 2.

No CO_2 gas bubbles were observed in prepolymerization of MDI, EGAA and DMPA, suggesting that no significant amount of water reacts with NCO groups and no reaction takes place between NCO groups and COOH groups in DMPA. The main advantage of DMPA is that the carboxylic acid is sterically hindered and so preferentially reacts into the backbone through the hydroxyl groups. It has been reported that in reaction of one equivalent of isocyanate with a hydroxy aliphatic acid, having carboxylic group, gives preferential reaction with the hydroxyl group.[19] Moreover, in prepolymerization stage, esterification would not take place because a higher temperature is required.[12,20] Therefore, the NCO groups of MDI react preferentially with the hydroxyl groups of EGAA and DMPA.

Table 2. Stability test of MDI in dried NMP at 40 °C.

Time (h)	[NCO] (mmol/g)	NCO unreacted (%)
0	5.157	100.0
0.5	5.157	100.0
3.0	5.136	99.6

The PU prepolymer was diluted with a given amount of acetone, and then chain-extended by the coupling between the unreacted NCO groups and EG. The post-polymerization PU thus obtained was composed of ternary diOH segments, such as EGAA, EG, and DMPA units. The DMPA unit has a potentially ionizable COOH group, which can act as an internal emulsifying agent. Since the average particle sizes decrease asymtotically as the TEA/DMPA mole ratio increase, because the carboxyl groups can become more dissociate. In addition, a TEA/DMPA mole ratio greater than 1.0 (more than 100% neutralization) is not affect the particle size.[11] Consequently, in order to secure a fully neutralization, the 1.2 times stoichiometric amount TEA was added to neutralize the built-in COOH groups of DMPA. As the ionomers formed, an increase of viscosity was attributed to the formation of microionic latices.[13] Lorenz et al.[21] have prove that in PU ionomer dispersions, the ionic sites COO^- is located substantially on the particle surfaces, while the hydrophobic chain segments form the interior of the particles. Thus, the aqueous PU emulsion was prepared by catastrophic phase inversion from the acetone solution to an aqueous emulsion by addition of water. The hydrophilic groups facilitated mutual repulsion between the particles provide particle stability. From the experiments, it was observed that the initial addition of water produced local turbidity that quickly disappeared with vigorous stirring. More addition of water made the bulk turbid, which was an indication of the formation of a dispersed phase. As water was continually added to a certain content, the phase inversion process was achieved. Particle stabilization from this structure can be described by the well known model of the diffuse electrical double layer.

Effect of Acetone on Particle Size

Addition of acetone to the prepolymer was suitable for reducing the viscosity and, in special, facilitating to disperse PU in water. The different aqueous PU emulsions were prepared with varying amounts of acetone from 0 to 30 wt% based on the total weight of the PU emulsion (30 wt% of PU in 70 wt% of water and NMP after removal of acetone). Figure 1 shows the particle size of the emulsions left for one day after the removal of acetone. Similar effect of the acetone content on the particle size was also visually observed as a transition from a bluish-white emulsion at 0 wt% of acetone to a milky white dispersion at high content of acetone. Apparently, the particle size increased with increasing the acetone content. A similar phenomenon has also been reported by other researchers.[6, 22-23] One possible explanation for this phenomenon lies in the retained acetone among the chains, even after the process of evaporation. Such acetone is probably adsorbed by the hydrophobic part of PU chain resulting in swelling of particle.

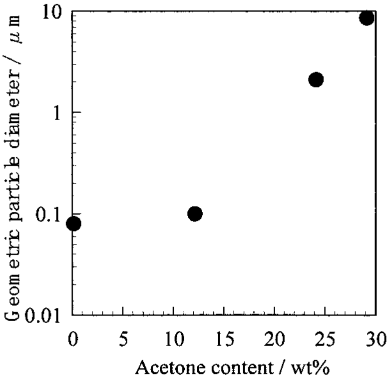

Figure 1. Effect of acetone content on the geometric particle diameter after 1-day storage.

The effect of acetone can be explained in terms of solubility parameter. According to the Hildebrand theory, the solvate power of a polymer-solvent medium can be estimated from $(\delta_1\text{-}\delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and polymer, respectively. The solubility of a polymer in a solvent is favored when $(\delta_1\text{-}\delta_2)^2$ is minimized, that is, when the solubility parameters of the two components are most closely matched. In this case the lower the difference between the solubility parameters of the hydrophobic part and the acetone, the higher the affinity between these two components. Literature data indicate that the solubility parameter for acetone[24] is 20.3 $\text{MPa}^{1/2}$ and that for polyurethane[25-26] ranges from 19.4 to 21.5 $\text{MPa}^{1/2}$. Thus, the affinity between the hydrophobic chain and acetone is high, so that the polyurethane chain configuration was easily to spread out in the presence of acetone in reaction process. Scaling arguments[27] can be used to interpret the dependence of the polymer size on the concentration of acetone. If $c >> c^*$ the chain is ideal, and $R_g \propto c^{-1/8}$ (where c^* is the overlap concentration, c is the number of segment per unit volume and R_g is the radius of gyration of the polymer), therefore, a higher amount of acetone causes more swelling of the PU polymer.

Shelf Life of Aqueous PU Dispersions

Even though the pendant COOH-built-in PUs was capable of forming aqueous emulsions just after the preparation, some emulsions aggregated during storage at room temperature, resulting in a cream or precipitates. These phenomena seemed to associate closely with the amount of acetone used for preparing the emulsion. Recently, Keyvani[28] reported that distribution data, rather than average particle size numbers, can give a better indication of shelf life stability. Therefore, the storage stability of the PU emulsions prepared in 0 to 30 wt% of the acetone content was evaluated in terms of particle size distribution (PSD) change during the storage. In the case of a labile emulsion, the PSD should broaden and shift toward a larger particle size due to aggregation of the particles.[29] After one-day storage, the geometric particle diameter of the emulsion particle prepared with no use of acetone was 0.08 μm, and the size rarely changed even over six-month storage. Moreover, the emulsion showed almost no change of unimodal PSD during the storage, as shown in Figure 2(a). This indicates the high storage stability of this emulsion. However, the system was rather difficult to mix and disperse with water because of extremely high viscosity. To facilitate the mixing and dispersing process, acetone was added to the reaction system during the chain extension process. The particle size of the genetic emulsion particle prepared in 12 wt% of the acetone content was increased from 0.10 to 0.54 μm by about 4.4 times after one-month storage, resulting in a cream. Figure 2(b) shows the PSDs of emulsion prepared in 12 wt% of acetone, indicating a remarkable shift to a larger size during the storage. This phenomenon should be studied in further.

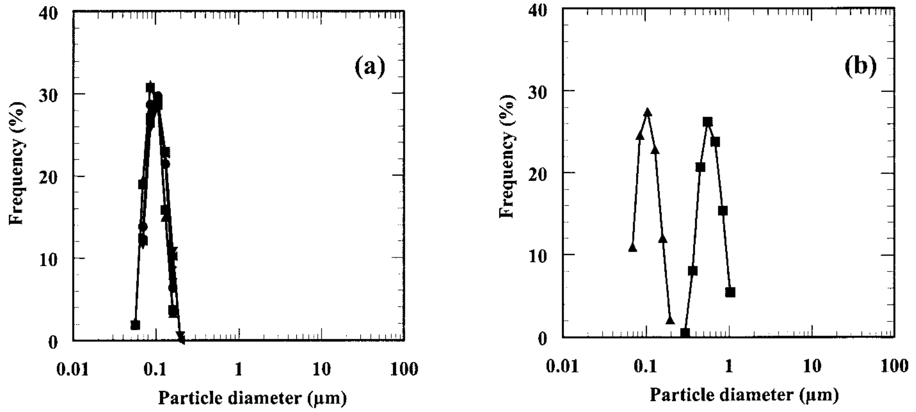

Figure 2. Time-dependence of the PSD for the aqueous PU emulsions; ▲ = after 1 day, ■ = after 1 month, ● = after 2 months, ♦ = after 3 months, ▼ = after 4 month, ◀ = after 5 months, ▶ = after 6 months; (**a**) 0 wt% of acetone, (**b**) 12 wt% of acetone.

On the other hand, the particle size of the emulsion particle prepared in 24 wt% of acetone was 2.11 μm after one-day storage. The appearances of second and third peaks of PSD were seen in storage for one month and later as shown in Figure 3. Similarly, the particle size of emulsion obtained in 30 wt% of acetone was 8.48 μm in unimodal PSD. However, second and third peaks of PSD were observed after one-month storage. Moreover, after two-month storage, the fourth peak was observed resulting in low stability.

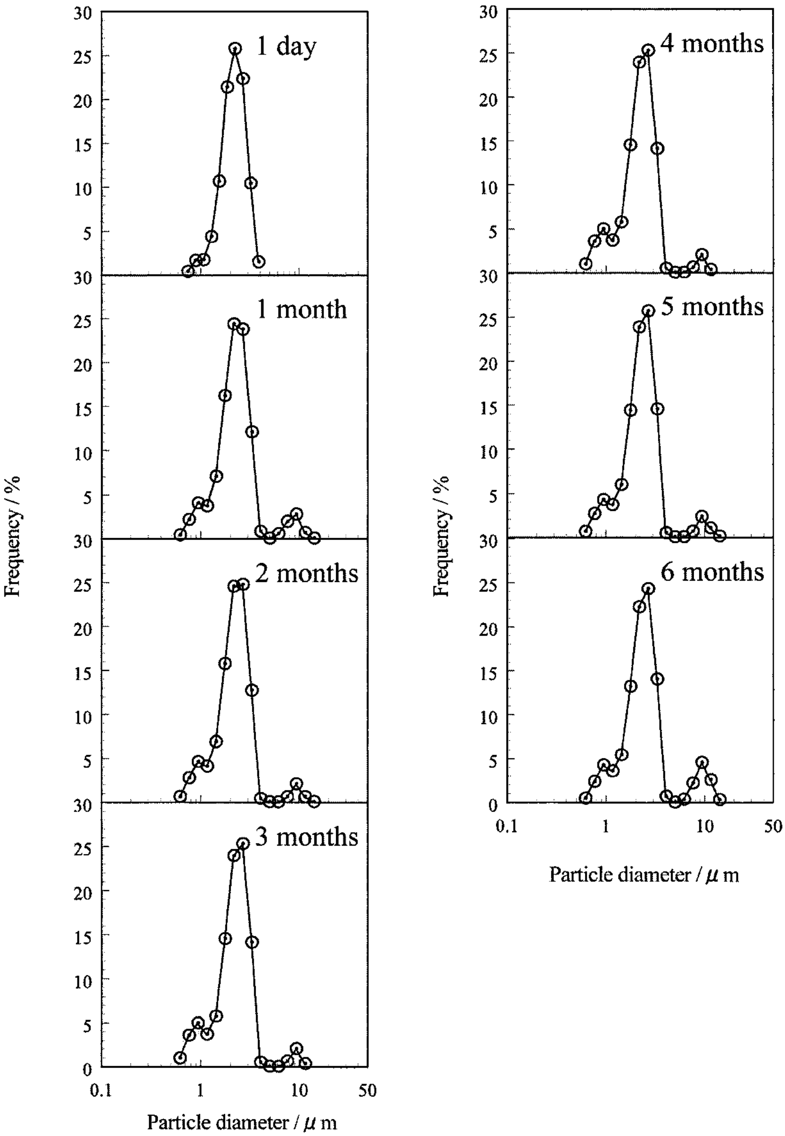

Figure 3. Time-dependence of the PSD for the aqueous PU emulsions; 24 wt% of acetone.

Conclusion

The COOH-built-in PU has been prepared using 3 wt% of DMPA, which is one of the diol components and acts as an internal emulsifying agent. The aqueous emulsion is prepared by neutralization all of the COOH groups with TEA, followed by phase inversion of an acetone solution of the PU with water. The particle size of the PU emulsion increases with increasing the acetone content. The PU emulsion prepared with no use of acetone reveals the highest storage stability at room temperature over than six months with almost no change of unimodal PSD.

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