

Preparation of Aqueous Polyurethane Dispersions Using Aromatic Diisocyanate

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Summary: Aqueous polyurethane dispersions were prepared by the reaction of hydroxyl-terminated poly(ethylene adipate), ethylene glycol, dimethylol propionic acid and aromatic diisocyanate, 4,4'-diphenylmethane diisocyanate. The influence of molecular weight of oligoester and molar ratio between isocyanate and hydroxyl groups (NCO/OH) in the prepolymerization step were investigated. Molecular weight, particle size and particle size distribution were measured and compared. It was verified that the molecular weight increases with increasing in NCO/OH molar ratio. The results suggest that the hard segment content plays an important role in particle size and particle size distribution of the dispersions.

Keywords: aqueous dispersions; aromatic diisocyanate; hard segment content; particle size dispersion; polyurethanes

Introduction

Polyurethane (PU)-based coating materials are of commercial interest in many applications because of their excellent properties such as abrasion resistance, chemical resistance, as well as toughness combined with good low-temperature flexibility. There are various ways of combining a wide variety of polyols and diisocyanates to produce tailored PU products. These properties, in addition to the environmentally benign characteristics of water-borne systems, make aqueous PU dispersions continue to show growth in commercial applications.^{[1–}

^{3]} The deleterious solvent-based [e.g., *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc)] PUs will be restricted in their traditional applications

sooner or later because of the demands of environmental regulations. In contrast, aqueous PU dispersions would be a candidate with promise to replace the traditional solvent-based PU.

In practice, PU emulsion is stored for a while prior use. In many areas of the coating industry, coating materials are often required to be storage stability for six months or more.^[4] In addition, the emulsions with small particle size have a better curing performance. The smaller of particle size leads to coatings with better gloss, hardness and resistance to chemicals.^[5] It has been reported that in the ionic content,^[6–8] the degree of neutralization,^[9–12] the type of ionic component,^[12] the counterion used,^[6,11–13] the molecular weight of soft segment,^[10,14] and the amount of cosolvent,^[15–17] each gives a considerable effect on the particle size of aqueous dispersion of polymer.

Basically, segmented PUs, which generally consist of high T_g hard segment and low T_g soft segment,^[18] can be produced by two-step method that is composed of prepolymerization and chain extension steps. In prepolymerization step, the NCO-terminated prepolymers can be

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formed by the reaction between OH and excess amount of NCO groups. The prepolymers are then chain extended with low-molecular weight diol. Aqueous PU dispersions can be prepared by incorporating ionic groups into the PU backbone. These ionic PUs usually contain pendant acid groups or tertiary amine groups.^[3,19–21] Water-dispersible anionomer PU is obtained by neutralization of the acid groups. The dispersion of neutralized ionic PU with water results in an aqueous PU dispersion.

The depletion of free NCO because of side reaction with water during dispersion, resulting in a decrease of the molecular weight, seems to be inevitable, especially, when the aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate (MDI) are employed.^[22–24] For this reason, the majority of PU dispersions have been made with aliphatic diisocyanates, such as isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI), having low reactivity toward water molecules. Because of the high price of aliphatic diisocyanates, therefore, the use of aromatic diisocyanates would provide cost benefits for which oxidative discoloration is not an issue for the applications.

In this work, PU dispersions were prepared with aromatic diisocyanate. The study that follows was intended to describe how the properties of aqueous PU dispersions would depend on the stoichiometry in the prepolymerization and on the molecular weight of polyol. The effect of hard segment content upon the particle size of PU dispersions were investigated and compared.

Experimental

Materials

4,4'-Diphenylmethane diisocyanate (MDI, Nippon Polyurethane Ind., Japan) was stored at -22°C to prevent the dimerization. Hydroxyl-terminated poly(ethylene adipate) (EGAA, $M_n = 629, 1018, \text{ and } 2007$) was used as received. The moisture

content of EGAA was determined by Karl Fisher titration ($<0.03 \text{ wt}\%$). *N*-Methyl-2-pyrrolidinone (NMP, Wako Pure Chem. Ind., Japan) and acetone (Wako Pure Chem. Ind., Japan) were dried over 4 \AA molecular sieves. Dimethylol propionic acid (DMPA, Tokyo Kasei Kogyo, Japan), ethylene glycol (EG), and triethylamine (TEA, Wako Pure Chem. Ind., Japan) were used as received.

Characterizations

Isocyanate content during the experiment was determined by the potentiometric titration on a potentiometric automatic titrator (Kyoto Electronics, model AT-420, Japan) equipped with auto piston burette (Kyoyo Electronics, model APB-510, Japan). Infrared spectra were recorded on a FTIR spectrometer (Perkin Elmer model Spectrum One). Molecular weights of PU films were measured on a gel permeation chromatography system (Tosoh, model HLC-8220GPC, Japan) equipped with a differential refractometer, using tetrahydrofuran as an eluent with a flow rate of 1.0 mL min^{-1} at room temperature. The molecular weight calibration curve was obtained using polystyrene standards. The particle sizes and particle size distributions (PSD) of PU emulsions were measured by the dynamic light scattering technique using of a High Performance Particle Sizer (HPPS, Malvern, UK) at 25°C . Because the PU emulsions exhibited in a skewed distribution function, the lognormal distribution was used for describing the particle size of PU emulsion.

Preparation of Aqueous PU Dispersions

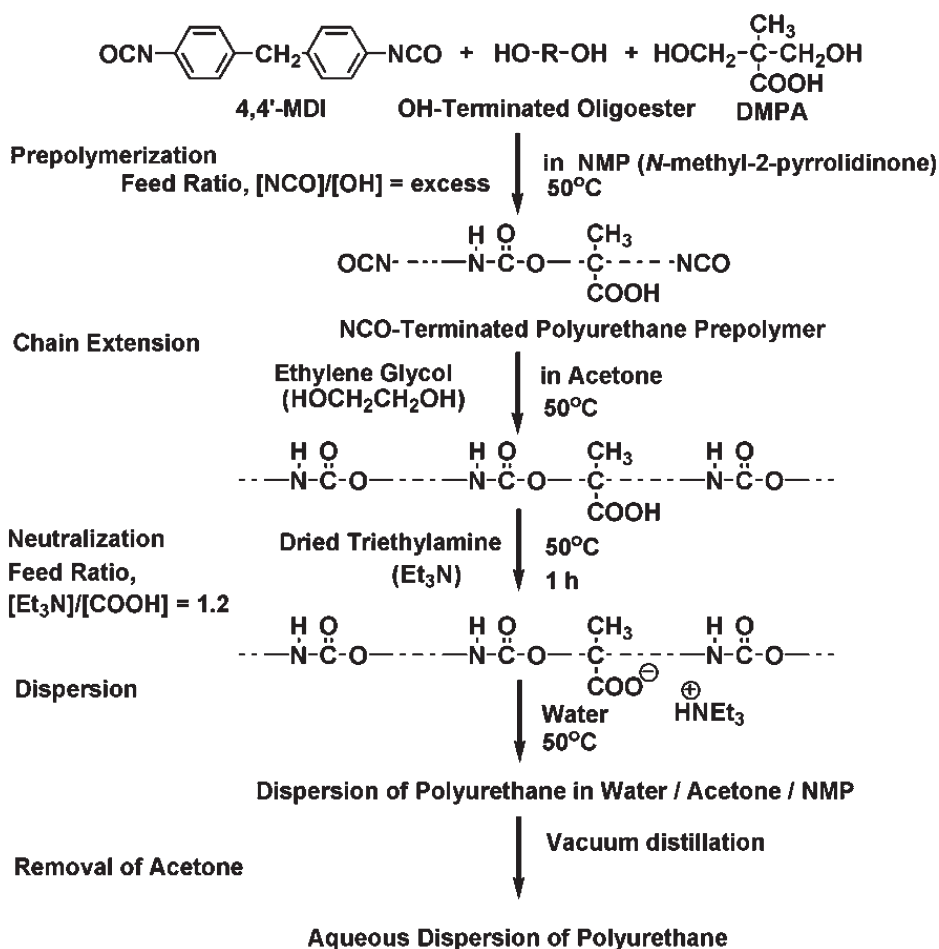
A series of aqueous PU dispersions were prepared with varying the molecular weight of polyol and stoichiometric molar ratio of NCO and OH in prepolymerization step. Their formulations are presented in Table 1 and a typical preparation procedure is shown in Figure 1. DMPA was dissolved in a minimum amount of NMP in a 1000-mL four-necked round bottom flask equipped with a stirrer, a thermometer, and an

Table 1.

Formulation for PU dispersions with varying molecular weight of polyol and [NCO]/[OH] ratio.

Sample ^a	[NCO]/[DMPA]/ [EGAA]/[EG]	DMPA Content (mmol/g solid PU)	M _n of EGAA	Prepolymer [NCO]/[OH] ratio	Total [NCO]/[OH] ratio
P3M06k1.3	1/0.16/0.63/0.17	0.23	629	1.27	1.04
P3M06k1.6	1/0.12/0.50/0.34	0.20	629	1.63	1.05
P2M06k2.0	1/0.10/0.40/0.50	0.18	629	2.00	1.00
P3M10k1.2	1/0.21/0.62/0.14	0.23	1018	1.20	1.03
P3M10k1.6	1/0.15/0.46/0.33	0.20	1018	1.63	1.05
P2M10k2.0	1/0.12/0.38/0.44	0.18	1018	2.00	1.07
P2M20k2.0	1/0.17/0.33/0.44	0.18	2007	2.00	1.06

^a The first pair of letter and number in the sample code denotes the DMPA and content used, the second the number-average molecular weight of EGAA polyol divided by hundred and the third the [MDI]/([DMPA] + [EGAA]) molar ratio feed, k, in prepolymerization step.

**Figure 1.**

General preparation procedure used.

inlet of dry nitrogen. Molten EGAA and solid MDI were added to the flask on a heating water bath. Pre-polyaddition was carried out with mechanical stirring at 50 °C under a nitrogen atmosphere until the consumption of 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 with potentiometric titrator. After the resulting viscous prepolymer was diluted with acetone, EG (stoichiometric amount to the unreacted NCO groups) was added. The chain-extension reaction was continued at 50 °C until the NCO content approached to zero as evidenced by titration (<0.1%) or when the IR spectra showed no stretching band due to the NCO groups about 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 by a peristaltic pump with stirring at 50 °C. The dispersion was stirred for further 30 min. Removal of acetone by distillation gave an aqueous PU emulsion or suspension, which contained about 30 wt% PU.

Results and Discussion

Effect on the Molecular Weight of PU Emulsions

The preparation of PU by diisocyanate-diol route was conducted as a two-step process. The first step is to form a NCO-terminated PU prepolymer by reacting excess amount of diisocyanate, MDI, with hydroxyl-terminated polyol, EGAA, and ionic component, DMPA. Afterwards, in the second step, the prepolymers were chain extended with diol, EG. In this work, the different aqueous PU dispersions were prepared with varying molar ratio of NCO and OH in the first step, prepolymerization. The results of GPC experiments are summarized in

Table 2. A polydispersity index around two is typical for condensation polymerization.^[25–26] In case of non-polar polymers with limited number of charged groups (–COO⁻ etc.) such as the ionomers, the polymers are absorbed on the surface of the microgels as they pass through the columns, thus offering somewhat enhanced resistance to elution as a consequence.^[27] Such a phenomenon would lead to larger elution volumes and to relatively low molecular weight than usual.

It is obvious that the weight-average molecular weight of PU emulsion increases with increasing in NCO/OH molar ratio, as shown in Fig. 2. This increase is attributable to the increasing of free NCO content in prepolymers. That is, as free NCO content in prepolymerization step is higher (i.e., higher NCO/OH molar ratio), this prepolymer will have a higher degree of chain extension in the second step of the synthesis reaction, giving a final PU with higher molecular weight. In other words, high degree of chain extension corresponds to high content of hard segment. From the results discussed above, it is worthy to note that in this series of experiments, which the content of hard segment content was higher than 31%, the chain extension step is essential to determine the molecular weight of PU. This reason, together with reasons mentioned earlier, provides a better understanding to describe the same tendency in literature, where hard segment content is higher than 16% (calculated number from a literature^[28]) for MDI, poly(ϵ -caprolactone) ($M_n=3000$), 1,4-butanediol system. Harris et al.^[29] also reported that the molecular weight of polyurethanes increase with increasing of hard segment content from 31.9% to 43.5%.

As shown in Table 2, it is important to note that the content of hard segment is related to the size of soft segment (i.e., molecular weight of polyol), that is a longer soft segment will dilute the concentration of hard segment. Therefore, at the same NCO/OH molar ratio, content of hard segment can be high or low if the size of soft segment is low or high, respectively.

Table 2.

The molecular weight and particle size^a of the aqueous PU dispersions with varying molecular weight of polyol and [NCO]/[OH] ratio.

Sample	Hard segment content (wt%) ^b	M_w of PU film ($\times 10^{-4}$)	M_w/M_n	d_g^c (nm)	σ_g^d
P3M06k1.3	41.39	4.52	2.15	118	1.29
P3M06k1.6	48.05	5.20	2.10	132	1.23
P2M06k2.0	53.82	— ^e	— ^e	— ^e	— ^e
P3M10k1.2	31.16	3.24	2.42	97	1.40
P3M10k1.6	38.18	4.34	2.22	129	1.18
P2M10k2.0	43.30	4.87	2.31	145	1.31
P2M20k2.0	31.33	4.68	2.30	119	1.18

^a From dynamic light scattering.

^b Hard Segment Content = $\frac{(MDI+DMPA+EG)(g)}{(MDI+EGAA+DMPA+EG)(g)} \times 100$

^c Geometric mean diameter of the fresh PU emulsion particle.

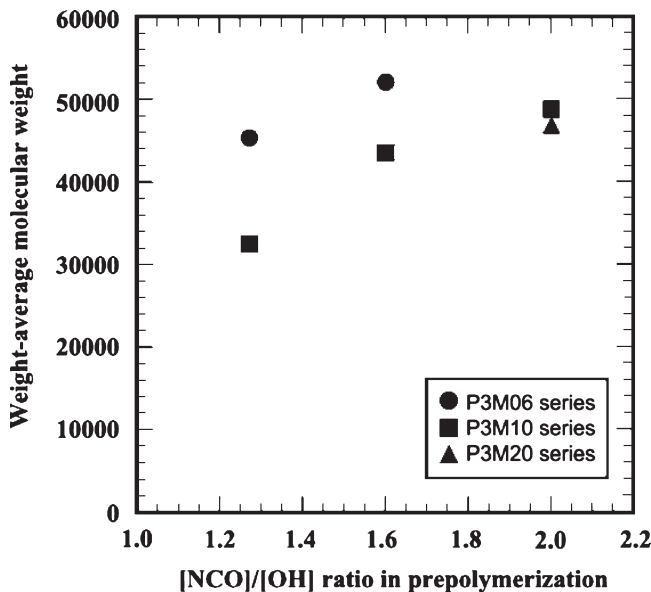
^d Geometric standard deviation.

^e Not available because of stable emulsion was not possible to prepare. Reproducibility of sample P2M06k2.0 was checked five times.

Effect on the Particle Size and Particle Size Distributions

It has been reported that a minimum ionic content is required for the formation of stable aqueous PU dispersions. When DMPA was employed to provide anionic sites on PU backbone, Mequanint and Sanderson^[30] extrapolated a minimum ionic content of about 2.5 mmol COOH/g

of PU from a plot between number of latex particles and concentration of bound COOH groups. Satguru et al.^[31] also reported this value as 0.25 mmol COOH/g PU, below this concentration a stable dispersion could not be formed. Chen and Chen^[13] found that a minimum value of 0.178 mmol COOH/g PU with fully neutralization is required to form a stable

**Figure 2.**

Effect of [NCO]/[OH] molar ratio in prepolymerization on weight-average molecular weight for cast films of polyurethane emulsion prepared by varying molecular weight of EGAA polyol: (●) $M_{n,EGAA} = 629$, (■) $M_{n,EGAA} = 1018$, (▲) $M_{n,EGAA} = 2007$.

dispersion for at least 1 month. From the experimental result, it is surprising that the emulsions were stable more than 6 months with DMPA content lower than the minimum required from the literatures. This indicates that structure of PU have a significant influence on particle size of emulsion. The hydrogen bonding between hard-hard segment attribution to N–H group in urethane linkage could resist the segmental motion of the polymer chain. This leads to decrease chain flexibility and results in the increase of particle size of emulsion. From Figure 3 and Table 2, at the same content of DMPA in PU backbone, the particle size increases with increasing of hard segment content. Incidentally, the particle size distributions of PU emulsions are generally broaden than the conventional latexes.^[32] Since PU emulsions are

dispersed mechanically, the emulsification process contributes to broader size distribution due to area of non-uniform mixing.

Storage Stability of PU Emulsions

It is well known that the storage stability of emulsion is influenced by particle size and its distribution. That is the smaller particle and sharper in particle size distribution, the slower creaming velocity.

Table 2 show the particle size distribution of PU emulsions. From the experiment, it was clearly shown that all samples have storage stability over 6 months except P2M06K20, which has the highest hard segment content (54%, see Table 2) and precipitated just after preparation. It has been reported in the literature^[33] that to obtain sufficient storage stability, the particle diameters for the 50th ($d_{50\%}$) and 90th

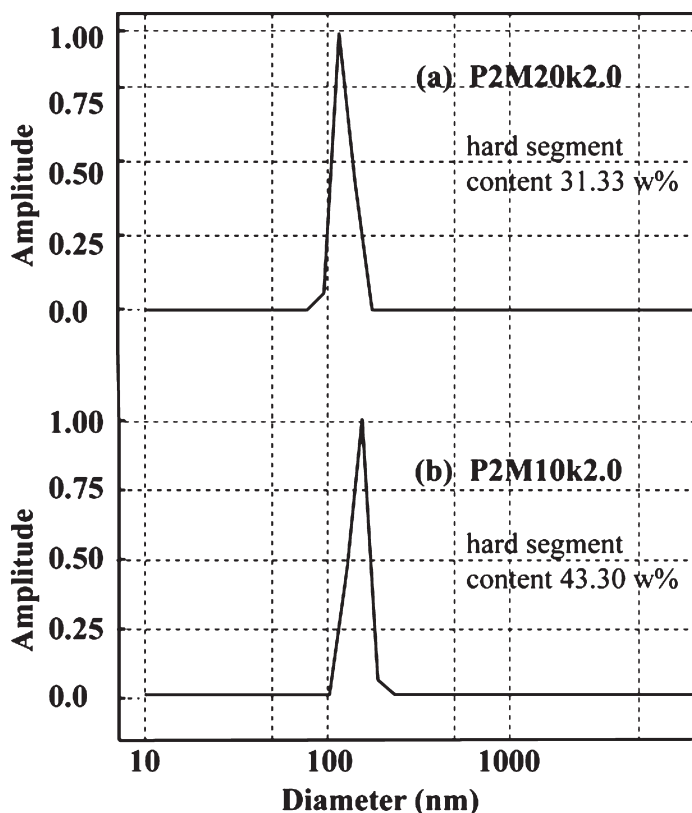


Figure 3.

Particle size distributions of PU emulsions after storage for six months which prepared at the same content of DMPA (0.18 mmol/g solid PU); (a) P2M20k2.0, (b) P2M10k2.0.

($d_{90\%}$) cumulative mass percentile of less than 750 nm and 1000 nm, respectively, is required. It is confirmed that sample P2M06K20 is located outside the stable vicinity as mentioned earlier. This indicates that, at a certain content of ionic component, there is an upper limit of hard segment content that a stable emulsion cannot be prepared, because the PU chains lose their flexibility to form a sufficiently small size of particles.

Conclusion

This study provides some useful alternative way to prepare aqueous PU dispersions using a commercially cheap and high reactive aromatic diisocyanate, MDI. Hard segment content, in term of NCO/OH molar ratio, plays an important role on molecular weight of the final PU film and particle size of PU emulsions. Because of the increasing of free NCO content in prepolymers, the weight-average molecular weight of PU emulsions increases with increasing in NCO/OH molar ratio in prepolymerization step. The stable PU emulsions were prepared with remarkable storage stability more than six months. Besides the ionic group content, the stiffness of PU structure that is the hard segment content is also significant to control the particle size. The particle size of the emulsions increases with increasing of hard segment content. At a certain ionic content, however, there is a maximum content of hard segment that a stable emulsion cannot be prepared.

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