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Preparation and Characterization of Water Dispersion Polyurethane

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Abstract: A series of water dispersion polyurethanes (PUD) were prepared by polyaddition reaction using isophorone diisocyanate (IPDI), poly(oxytetramethylene) glycol (PTMG) and dimethylol propionic acid (DMPA). IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. Various formulations were designed to investigate the effects of process variables such as NCO/OH ratio on the physico-mechanical properties of PUD. The effect of NCO/OH molar ratio on the structure and properties o f these polyurethanes were characterized by particle size analyzer, DSC, viscosity and tensile tester, etc. Particle size distribution becomes broader and the average particle diameter increases as NCO/OH molar ratio increases, which is mainly attributed to the decrease in chain flexibility and decrease in viscosity of the dispersed particles. DSC Results identify that the phase mixing increases when some ionic groups were incorporated in soft segments and phase separation increases as NCO/OH molar ratio increases. The tensile strength, tear strength and hardness increase and elongation at break decrease with increase of NCO/OH molar ratios. The increase of tensile strength and tear strength properties are interpreted in terms of increasing hard segments in structure of polyurethane.

Key words: Polyurethanes · Dispersions · Mechanical properties · Physical properties · Ionomers

INTRODUCTION

The continuous reduction in costs and the control of volatile organic compound emissions are increasing the use of aqueous based resins, motivating the development of polyurethanes dispersed (PU) in water [1, 2]. These products present many of the features related to conventional solvent borne coatings with the advantage of presenting low viscosity at high molecular weight and good applicability.

Polyurethanes (PU) are segmented polymers comprising of alternating sequences of soft segments and hard segments that constitute a unique microphase-separated structure. Ions can be readily introduced into either hard or soft segments of polyurethanes to yield a wide range of polyurethane ionomers with prescribed properties [3, 4]. The distributions and contents of hard and soft segments and the NCO/OH molar ratio of prepolymer are main factors to affect the structure and organization of PU and the sequential microphase separation and properties [5-7]. There has been extensive work done in the field of synthesis and characterization of various kinds of polyurethanes and polyurethane ionomers [8-10]. Ionomer type PU dispersion is made by the dispersion of amphiphilic prepolymers prepared by the addition of diisocyanates, polyols and dimethylolpropionic acid (DMPA) and subsequent chain extension [11-13]. As in the case of conventional segmented polyurethanes, polyurethane ionomers contain low-polarity flexible segments and urethane groups that are polar and capable of interaction via hydrogen bonds. Ionic groups in polyurethane tend to interact with each other and aggregate but are attached to the 'alien' hydrophobic neighborhood. As will be demonstrated later, by varying the structure, molecular weight of the segments and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained. The materials can be hard and brittle, soft and tacky, or anywhere in between. Various types of diisocyanates can be used to synthesize PU. The diisocyanates can be either aromatic or aliphatic with different chemical reactivities. The aromatic diisocyanates are more reactive than aliphatic ones, which can only be utilized if their reactivities match the specific polymer reaction and

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special properties desired in the final product. For example, polyurethane coatings made from aliphatic isocyanates are light stable [14-17], while coatings made from an aromatic isocyanate will undergo photodegradation [18, 19].

In this paper, we describe a new series of waterborne PU dispersions where the ionic groups are incorporated in both soft and hard segments using isophorone diisocyanate (IPDI), poly(oxytetramethylene) glycol (PTMG) and dimethylol propionic acid (DMPA) as main materials according to prepolymer mixing process. The effect of NCO/OH molar ratio on the dispersion characteristics and properties of dispersion casting films are studied.

MATERIALS AND METHODS

Materials: Poly(oxytetramethylene) glycol (PTMG, M_w = 2000, OH number = 55 mg/g, Korea PTG, Korea) was dried and degassed at 80°C, 1 - 2 mm Hg for 2 h before use. Dimethylol propionic acid (DMPA, M_w = 134.13, Aldrich) was dried at 50°C for 48 h, while isophorone diisocyanate (IPDI, M_w = 222.29, Bayer) was used as received. Triethylamine (TEA, M_w = 101.19, Merck) was dried over molecular sieves (Å), ethylenediamine (EDA, M_w=60.1, Merck), N-methyl-2-pyrrolidinone (NMP, Fluka) and deionized (DI) water was used throughout the reaction.

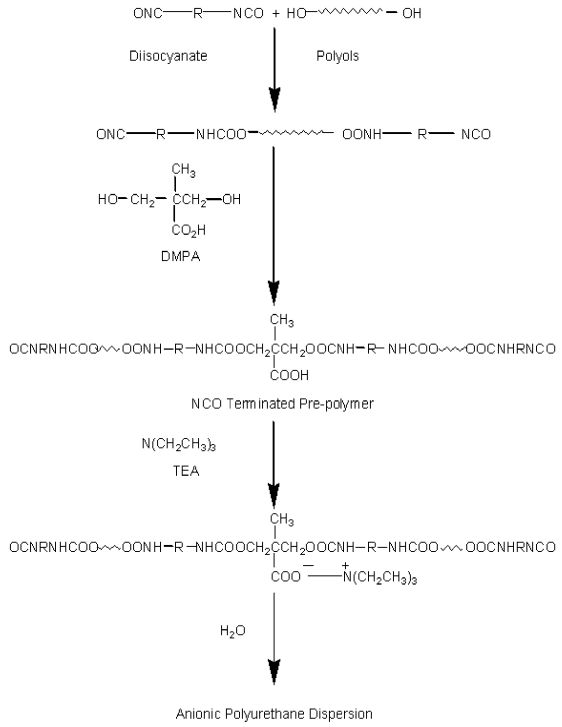
Preparation of Pre-Polymer: The polyurethane dispersions were prepared as previously described in the literature [20-23]. Polymerization was performed in a 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube. Reaction was carried out in an N_2 atmosphere in a constant-temperature oil bath. IPDI and polyol were charged into the reactor and the mixture was heated at 100°C for 1 h. After that, DMPA and NMP were added to the mixture and the reaction proceeded at the same temperature until the theoretical NCO value was reached, as determined by the di-n-butylamine titration method [24, 25]. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in scheme 1. Samples were prepared by different NCO/OH molar ratios are shown in Table 1.

Neutralization and Dispersion of the Prepolymer: After the prepolymer temperature dropped to 40°C, the carboxylic acid groups were neutralized by the addition of triethylamine (TEA) and the degree of neutralization is 100%. The mixture was stirred for further 20 min to ensure the reaction was completed. Then, the prepolymers were dispersed by adding distilled water to the prepolymer solution which was stirred vigorously. The addition rate was controlled carefully using a tubing pump with a calibrated flow rate [26]. Finally 10 wt% ethylenediamine aqueous solution was added to extend the chain at room temperature. The emulsion was stable for more than 6 months after preparation at room temperature.

Film Preparation: Films were prepared by casting the aqueous dispersions on leveled surfaces and allowing them to dry at room temperature for 7 days and then at 60°C, for 12 h[27-29]. The films were stored in a desiccator at room temperature for further characterization and measurements.

Table 1: Feed compositions of dispersion polyurethanes synthesized with variable contents of polyol and isocyanate

	M1		M2		M3	
	Polyols, OH					
Samples	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)
PTMG	140	24.9	140	21.4	140	18.3
DMPA	7	1.24	9.8	1.5	12.6	1.7
Mole of OH (gm/mole)	0.1222		0.1431		0.1639	
	Isocyanates, NCO					
IPDI	40.75	7.3	63.62	9.7	91.09	11.9
Mole of NCO (gm/mole)	0.1833		0.2862		0.40978	
NCO/OH Molar ratio	1.5		2.0		2.5	
NMP	14	2.5	19.6	2.99	25.2	3.3
TEA	5.28	0.93	7.4	1.12	9.5	1.2
EDA	3.67	0.65	8.6	1.31	14.77	1.92
Water	351.3	62.5	406.5	62.01	472.44	61.7



Scheme 1: Formation of PU dispersion having anionic centre

Measurements: Particle size and distribution were measured by laser light scattering (Sema Tech, SEM-633, He-Ne laser). The samples were diluted to the required concentration with distilled water before the measurement. FTIR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer. The viscosity (η) of the dispersions were measured using a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100 S^{-1} at 25°C. The tensile properties of the emulsion cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least 4 measurements was taken and the 1-kN load cell was used. Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N_2 flow at 20 mL min^{-1}. The measurements were carried out between -150°C and +100°C at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

FT-IR Analysis: IR spectrum obtained from the cast film is shown in Table 2. This analysis was used to check the end of polymerization reaction,

Table 2: FT-IR data of the aqueous polyurethane dispersion

cm^{-1}	Vibration assignment
--	NCO
3291	N - H
2795-2938	C - H stretching - aliphatic
1730	C = O stretching
1550	N - H bending
1000-1150	C - O - C stretching

verifying the disappearance of the ν NCO at 2265 cm^{-1} and the appearance of ν N - H at 3291 cm^{-1}. The presence of expected peaks implies that the reaction was completed and the predesigned PU was formed. IR spectra also contains all the related information on the primarily structure of the final polymer. An absorption band of the N - H stretching mode at 3291 cm^{-1} was observed. Aliphatic C - H stretching mode of 2795-2938 cm^{-1} and carbonyl (C = O) stretching absorption band at 1730 cm^{-1} were observed. N - H bending vibrations at 1550 cm^{-1}, C - O - C stretching absorption band corresponding to the ether oxygen of the soft-segment at 1000-1150 cm^{-1} were also observed. These vibrations are strong evidence for the formation of PU. The N - H group in polyurethane could form hard segment H - bonding with the carbonyl oxygen and hard-soft H - bonding with the ether oxygen. The stronger hard-hard segment H - bonding acts as physical cross-links leading to difficult segmental motion of the polymer chain which results in a more significant phase separation between the hard and soft segments. The phase separation improves the mechanical properties of polyurethanes but reduces the flexibility and solubility [30, 31].

Physical Properties: The physical properties of the polyurethane films depend on the molecular structure. They also depend on the content of functional groups and on the molar ratio of NCO/OH. The isocyanates used in this work were IPDI and TDI, which has good thermal stability, low vapour pressure, low toxicity and relatively high stability. DMPA, a carboxylic group containing diol, was used to form a water-dispersible urethane prepolymer without any significant reaction between the carboxylic group and isocyanate group because the hydroxyl group is much more reactive relative to the aliphatic isocyanate component. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in Scheme 1. Samples were prepared by changing the NCO/OH ratios are shown in Table 1.

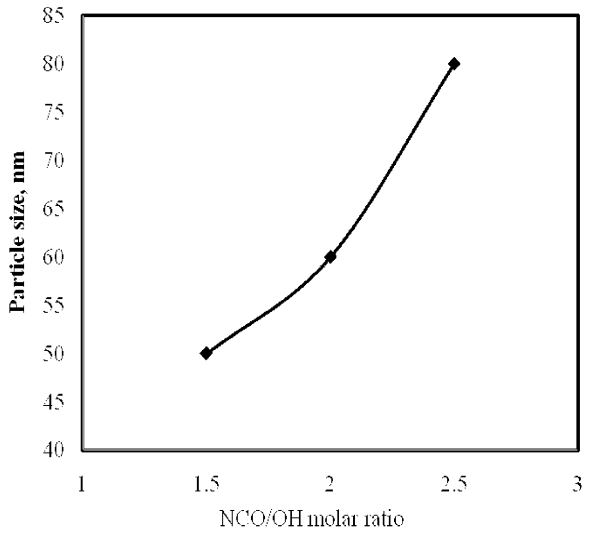


Fig. 1: Particle size of PU dispersion as a function of NCO/OH molar ratio

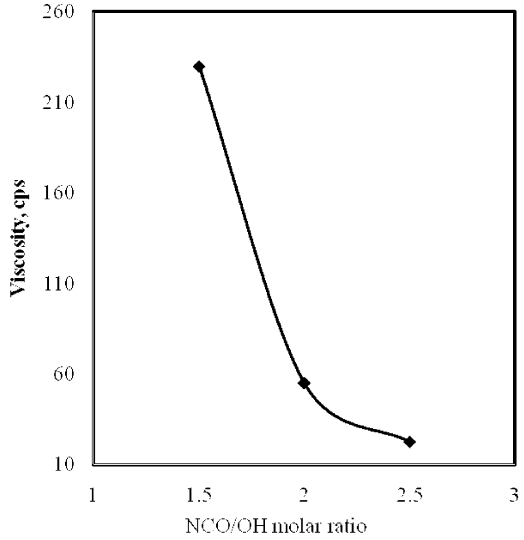


Fig. 2: Viscosity of PU dispersion as a function of NCO/OH molar ratio

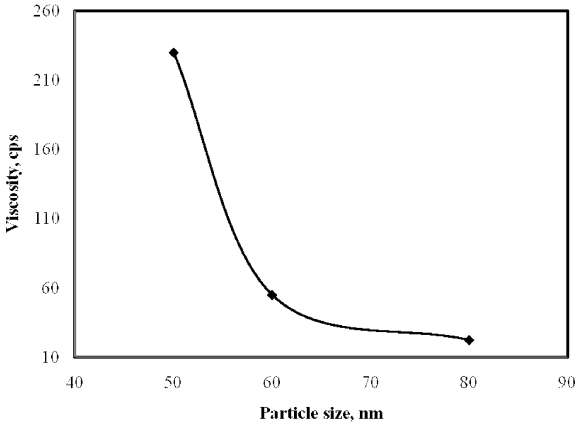


Fig. 3: Particle size of PU dispersion as a function of viscosity

Aqueous PUDs are mainly used in coatings. In PU dispersions, particle size and viscosity are important parameters. For example, in many surface coatings, relatively large particles are preferred to facilitate fast drying and relatively small particles are preferable when deep penetration of the dispersion into the substrate is an essential requirement. A suitable viscosity range is required to avoid sagging (in case of low viscosity) and practical difficulty in application (encountered with high viscosity).

The variations of particle size for three different PUDs are given as a function of NCO/OH molar ratio in Figure 1. The result exhibits that particle size of PUD increases with increasing NCO/OH molar ratio. In PUDs, the particle size is mainly governed by the hydrophilicity of PU [32, 33]. However, the hydrophilicity decreases with the increase in NCO/OH molar ratio may be related to two parameters. First, as NCO/OH molar ratio increases, the residue of NCO group increases and therefore, they react with water during dispersion process, resulting in carbamido and sequentially decrease the flexibility of polymer chain. Second, the carbamido groups are very polar and they distribute in the surface of the particles and cause the reaction heat to increase, which can heighten the viscosity of the particles and make them easy to stick together and hard to disperse under shear force, resulting in bigger size particles [34]. With increased particle size, the number of dispersion particles decreases and lower dispersion viscosity results. Figure 2 shows the decreasing in emulsion viscosity with the increasing amount of NCO/OH molar ratio, which also led to the decrease in the total ionic content. In PU dispersion, the ionic groups are located predominantly on the surface of droplets and stabilized by the electrical double layers. With the increase of the polymer particle size, the relative size of the water layer to total particle size decreases. In addition, with the particle size increasing, there is a decrease in the number of particles [35-37]. Hence, the effective hydrodynamic volume of the dispersed phase decreases and the force of friction among particles decrease, resulting in a decrease of viscosty.

Particle size of the PU dispersion depends on many factors, such as type of isocyanates, polyols and viscosity of the prepolymer [38]. Figure 3 shows that the particle size increases and the viscosity decreases with increasing NCO/OH molar ratios in the pre-polymer.

Table 3: Mechanical properties of the PU emulsion cast films

Samples	M1	M2	M3
Tensile strength (kgf/cm^2)	255.5	306.91	480.75
Elongation (%)	1262.0	1060.00	397.83
Tear strength (kgf/cm^2)	54.3	83.40	89.04
Hardness (shore A)	65.0	73.00	98.00
Tg, °C	-80.5	-76.20	-66.70

The decrease in viscosity is mainly due to decrease in chain flexibility of the polyurethane with the increasing NCO/OH. The results also reveal that particle size and viscosity are directly related to NCO/OH molar ratio.

Mechanical Properties: The NCO/OH molar ratio is important for the properties of emulsions and films. As shown in Table 3, elongation at break of polyurethane films decreased, tensile and tear strength increased as the NCO/OH ratio increases. Because increasing the NCO/OH molar ratio enriched residual NCO groups that react with water while emulsification. The reaction produced urea linkages that contribute to hard segments of polyurethane. This indicates that the more hard segments allow more effective hydrogen bonds. Therefore, mechanical property increased with the increase of the hard segment. However, increase of the NCO/OH molar ratio will lead to the increase of emulsion particle size and decrease of gloss of emulsion cast films, the NCO/OH molar ratio should be determined to a appropriate value.

Similarly, hardness was found to increase with increasing NCO/OH molar ratio.

The glass transition temperature (Tg) of PU moves toward the lower temperatures as the NCO/OH ratio decreases as shown in Table 2. The tan δ peak located at about -66.7°C is shifted to about - 80.5°C as the NCO/OH molar ratio decreases from 2.5 to 1.5. The decrease of Tg with decrease of NCO/OH molar ratio due to decreased chain flexibility and phase separation in PU structure.

CONCLUSION

Aqueous polyurethane dispersions were synthesized from IPDI, PTMG and DMPA with different NCO/OH molar ratios. The effect of NCO/OH molar ratios on the particle size distribution, viscosity and mechanical properties are studied. Average particle size of the prepared polyurethane emulsions increases and the viscosity decreases with the increasing NCO/OH. Tensile strength, tear strength and hardness increase with the increasing of the NCO/OH. The increase in tensile properties is interpreted in terms of increasing hard segments in the polyurethane structure.

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