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SHORT COMMUNICATION

Chunmei Song
Qiaolong Yuan
Dening Wang

Effect of the content of urea groups on the particle size in water-borne polyurethane or polyurethane/polyacrylate dispersions

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C. Song · Q. Yuan · D. Wang (✉)
School of Materials Science
and Engineering, East China
University of Science and Technology,
130 Meilong Road
200237 Shanghai,
Peoples Republic of China
E-mail: wangdening@hotmail.com
Tel.: 86-21-64253037
Fax: 86-21-64253539

Abstract A series of anionic water-borne polyurethane and polyurethane/polyacrylate dispersions and their paint films was prepared. It was found by using TEM that there were three phases in the polyurethane/polyacrylate film, i.e. the hard segment-rich phase and the soft segment-rich phase of polyurethane, and the polyacrylate phase. By increasing the content of urea groups, the glass transition temperature of the soft segments and the dissociation temperature of the long-distance ordering of the hard segments were raised. This should mean that the motion of macromolecular chains was hindered by increasing the content of urea groups, and the hydrophilic carboxyl groups embedded initially in macromolecular coils could thus not transfer easily to the particle surface, which resulted in a greater average particle size in the dispersion.

Keywords Polyurethane/polyacrylate · Water-borne coating · Particle size · Urea group

Introduction

It is a general trend that solvent-borne polyurethane will gradually be substituted by water-borne polyurethane used as coatings for wooden furniture and metal articles, owing to the requirement of environmental protection [1]. The research and development work is focused mainly on polyurethanes containing anionic hydrophilic groups, especially those into which dimethylolpropionic acid (DMPA) and ethylenediamine are introduced as the hydrophilic monomer and chain extender, respectively. The study of such water-dispersible polyurethanes modified by polyacrylate has also been one of the exciting objectives in recent years, because the advantages of polyurethane and polyacrylate could thereby be combined. It is easy to understand that the dosage of the DMPA could influence the particle size of the polyurethane dispersion [2, 3, 4, 5, 6]; namely, the more the content of DMPA, the smaller the average particle size. More content of the hydrophilic monomer DMPA, however, would do harm to the water-resistance of the coating. In the present paper, the effect of the content of urea groups, resulting from the reaction of the –NCO groups of diisocyanate with the $-NH_2$ groups of amine, on the average size of the particles in the dispersion is discussed to examine if any other means could also be used to affect the dispersity of such polyurethane or polyurethane/polyacrylate particles in water.

Experimental

Materials

The main raw materials used in this study were commercial products. The diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), was supplied by Huels. The polyester diol (hydroxyl value = 56), synthesized from adipinic acid and neopentylene glycol, was obtained from Dongda Chemical Industry Company. The dimethylolpropionic acid

(DMPA) was available from Perstop Chemical Corporation. The methyl methacrylate (MMA), butyl acrylate (BA) and hydroxyethyl methacrylate (HEMA) were prepared by Gaoqiao Petrochemical Company. The *N*-methylpyrrolidone (NMP), triethylamine (TEA), tin dibutyl dilaurate (T-12), azobisisobutyronitrile (AIBN), ethylenediamine (EDA) and dihydroxyethylamine (DHEA) were all of reagent grade.

Synthesis

The polyester glycol, DMPA, and catalyst T-12, were added to a four-necked flask which was equipped with an agitator, condenser, thermometer and argon inlet and contained IPDI with very small amount of NMP as solvent The reaction was carried out at 90 °C for 5 h to obtain an NCO-terminal hydrophilic polyurethane prepolymer. After the temperature was decreased to 25 °C, a mixture of MMA and BA was added to the above prepolymer under strong stirring. The mixture of the prepolymer and these two acrylates was dispersed in deionized water before the COOH groups of DMPA attached to the backbone of the prepolymer were neutralized by TEA. EDA was then added as the chain extender for the polyurethane to form a segmented (i.e. multi-block) polyurethane containing urea groups resulting from the reaction of NCO groups with the NH_2 groups. The two terminal NCO groups of the segmented polyurethane were then capped by DHEA. Finally, HEMA and the initiator AIBN were added to the system. The latter was used for the copolymerization of MMA, BA and HEMA. The water-dispersed polyurethane/polyacrylate was obtained after the mixture was kept at 75 °C for 4 h. The solid content of the dispersion was 32%. The content of urea groups was adjusted by varying the amount of EDA, when the content of DMPA remained constant. For TEM and DSC determination, film was prepared by pouring the dispersion onto a Teflon plate and then drying for one month.

Characterization

The particle size of water-dispersed polyurethane/polyacrylate was measured by using a Malvern Autosize II instrument. A Hitachi electron microscope scanning instrument was used for observing the morphology of the film stained with RuO_4, and a Du Pont 1090A differential scanning calorimeter for determination of the transition temperatures of the film.

Results and discussion

Morphology

Figure 1 shows the TEM photograph of the film formed from the polyurethane/polyacrylate dispersion containing 1.3% (by wt.) EDA with respect to polyurethane, and Fig. 2 is the film containing 3.4% EDA. From these photographs, it could be observed that there are three phases in such films. The black and off-white regions correspond to the hard segment-rich phase and soft segment-rich phase in the polyurethane, respectively, and the white region to the polyacrylate phase. These hard segments in the polyurethane resulted from the reaction of EDA with the IPDI and contained more –NH groups which could be stained by RuO_4. The soft segments were attributed to the chain elements of the polyester diol, which could be intermixed with a few hard segments (because a thoroughgoing phase separation was not possible here) and contained smaller amount of stained –NH groups. Comparing Fig 2 with Fig. 1, it could be confirmed that the black region, i.e. the area of hard

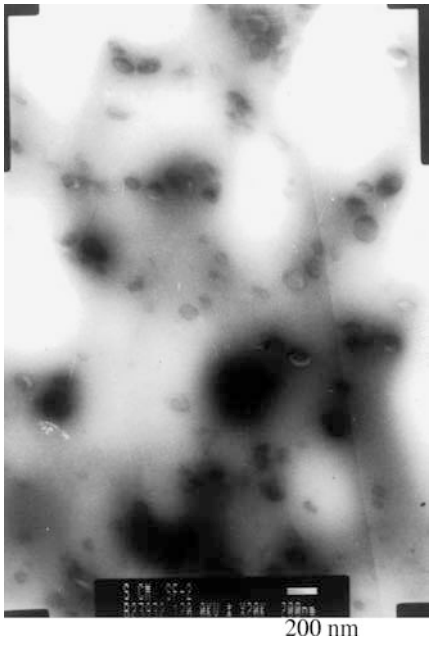

Fig. 1 TEM photograph of the film containing 1.3% EDA (×20,000)

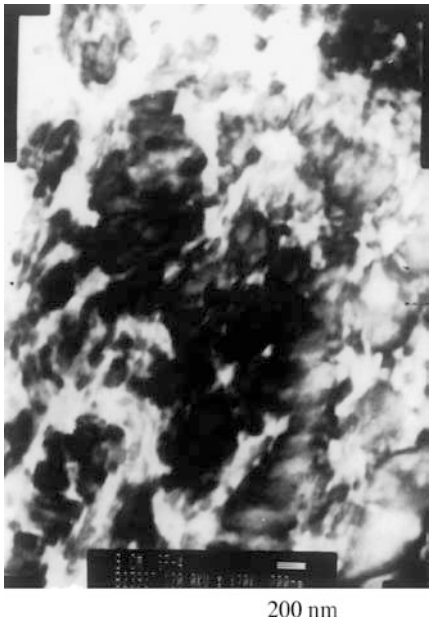

Fig. 2 TEM photograph of the film containing 3.4% EDA (×20,000)

segment-rich phase, became larger, owing to more urea groups from a higher dosage of EDA.

Influence of the content of urea groups on the average size of the dispersed particles of polyurethane

A dispersion of water-borne polyurethane was obtained, if BA, MMA, HEMA and AIBN were not added to the reaction system during the above described synthesis process. The relationship between the content of urea groups and the average particle size for such water-borne polyurethane is listed in Table 1. The amount of DMPA was fixed at 5% by weight. The results indicate that the average particle size increases with higher content of urea groups.

DHEA has only one amido group and served merely as the end-capping reagent, while EDA contains two amido groups and could form more urea groups in the backbone of the polyurethane than those resulting from DHEA.

Effect of the dosage of EDA on the particle size of water-borne polyurethane/polyacrylate

The particle size in the dispersion containing polyurethane/polyacrylate (1:1 by weight, and BA/MMA/HEMA = 3:1:1) was also determined. Table 2 also shows that the average particle size was increased with higher content of urea groups.

Changing the dosage of EDA varied the average particle size of polyurethane/polyacrylate. The results are listed in Table 3. The data reveal that the average particle size increases with increasing dosage of EDA, i.e. the content of urea groups.

Table 1 The relationship between the content of urea groups and the average particle size of water-borne polyurethane

Sample	Urea groups (wt.%)	Average particle size (nm)	Remark
PU1	0	44	Without EDA, DHEA
PU2	1.7	46	With DEHEA only
PU3	2.0	55	With EDA only
PU4	3.6	58	With EDA, DHTEA

Table 2 The relationship between the content of urea groups and the particle size in the dispersion of water-borne polyurethane/polyacrylate

Sample	Urea content (wt.%)	Average particle size (nm)	Remark
PUA1	0	50	Without DHEA, EDA
PUA2	2.2	110	With DHEA only
PUA3	6.6	174	With EDA, DHEA

Table 3 The relationship between the particle size and the dosage of EDA in the dispersion of water-borne polyurethane/polyacrylate

Sample	EDA/polyurethane (wt.%)	Average particle size (nm)	Appearance of the dispersion	NCO/OH (mol/mol)
PUA4	1.3	66	Blue, clear	1.5/1
PUA5	1.6	141	Blue	1.8/1
PUA6	2.3	231	White	2.0/1

Polyacrylate/polyurethane = 30:70 (by weight); the mole ratio of NCO to ($OH + NH_2$) was 1.34:1; the mole number of the OH groups includes those of polyester diol and DMPA; BA/MMA/HEMA = 3:1:1 (by weight); the weight ratio of DMPA to polyurethane equals to 0.0714

DSC spectra

Figure 3 shows the DSC spectra of polyurethane films with different dosage of EDA. It has been proved [7, 8, 9] that DSC spectra are helpful for segmented polyurethane, to determine the degree of microphase separation, the glass transition temperature of soft segments and the short-distance and long-distance ordering of hard segments. From Fig. 3 and Table 4, it could be observed clearly that the glass transition temperature of the soft segments and the dissociation temperature of the long-distance ordering of the hard segments increase with increasing dosage of EDA. More EDA conduced to more content of hard segments and thus the rigidity of the macromolecular chains, so that macromolecular motion became difficult. In addition, more intermolecular and intramolecular hydrogen bonds could be

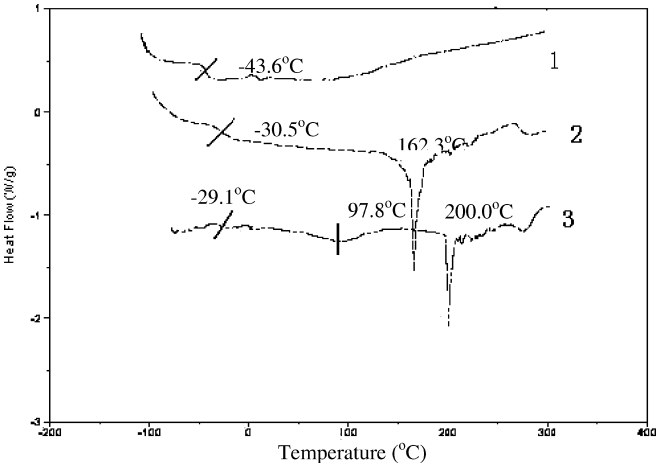

Fig. 3 DSC results of polyurethane films: curve 1, pure polyester diol; curve 2, 1.3% EDA; curve 3, 1.6% EDA

Table 4 The glass transition temperatures of the DSC spectra (°C)

Curve	Glass transition temperature	Dissociation of short-distance ordering	Dissociation of long- distance ordering
1	−43.6		
2	−30.5		∼162.3∼
3	−29.1	∼97.8∼	∼200.0∼

formed, which were also interrelated with the urea groups [10]. These hydrogen bonds also hindered the molecular motion.

According to the above results, it could be inferred why the average particle size of the water-dispersed polyurethane or polyurethane/polyacrylate could be influenced by the content of urea groups. The formation of the urea groups caused hindrance of the movement of the molecular chains, so that the hydrophilic carboxyl groups of DMPA, embedded initially in the macromolecular coils, could not transfer easily to the particle surface, and the amount of hydrophilic groups (COOH) on the particle surface decreased, which led to a larger average particle size. Moreover, DHEA is a secondary amine and existed only at the ends of the polyurethane chains, whereas EDA is a primary amine and, as chain extender, was distributed to many sites along the polyurethane chains. Therefore, the influence of the urea groups formed by DHEA on the particle size was less than that by EDA.

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