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ORIGINAL CONTRIBUTION

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Structure–property study of waterborne, polyurethane acrylate dispersions based on hyperbranched aliphatic polyester for UV-curable coatings

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Abstract A series of waterborne, hyperbranched polyurethane acrylates for aqueous dispersions (WHPUDs) based on hydroxy-functionalized hyperbranched aliphatic polyester Boltorn H20 were synthesized and characterized by Fourier transform infrared spectroscopy (FTIR). The aqueous dispersions were electrostatically stabilized with carboxyl groups incorporated into their structures, which were neutralized by triethylamine (TEA). The effects of chemical structures of end groups on various properties of WHPUDs, such as particle size, interfacial tension, and rheological behavior were investigated. The average particle sizes of aqueous dispersions, 43–237 nm, were determined by laser light scattering. Owing to the enlargement of the stabilization site, the particle size decreased as the content of carboxyl group, degree of neutralization, and dielectric constant of the dispersion medium increased. Moreover, the surface tension of aqueous dispersions of WHPUDs decreased as the TEA/COOH mole ratio and degree of neutralization increased. The investigations of the rheological behavior of the WHPUDs suggested that all the dispersions belong to pseudoplastic fluids, and each of them has viscosity much lower compared with the commercial water-based resin EB 2002.

Keywords Hyperbranched polymer · Waterborne polyurethane acrylate · Aqueous dispersions · Molecular structure

Introduction

Recently, waterborne coatings using ultraviolet (UV)-curing technology have gained increasing interest because they can decrease air pollution, reduce risk of fires, improve aspects of occupational health and safety, lower energy consumption, and have high curing speed. The odor, toxicity, viscosity control, and greater ease of cleaning, especially, are all reasons given for the use of water as a diluent in UV-curing systems [1]. It is well known that waterborne polyurethane dispersions have been developed out of increasing concern over environmental and legislative pressures.

Hydrocarbon polymers are incompatible with water. Therefore, a special treatment or structural modification is necessary for the polymer to be dispersible in water. This is normally done by incorporating a small amount of ionic groups into the polymer backbone. The obtained special type of polymer is usually called an ionomer. The ionomers are more hydrophilic in nature and hence dispersible in aqueous mediums. Aqueous polyurethane dispersions have received considerable attention in the past few decades because of their applications in adhesives and coatings for various substrates including textile fabrics, plastic, wood, glass, fibers, and metals [2, 3].

The structure–property relationships of aqueous dispersions containing a fraction of ionic repeat units have been the subject of numerous articles and reviews [4, 5, 6, 7, 8]. The unique properties of aqueous polyurethane acrylate (PU) dispersion are obtained from the structure and compositions of components, preparation method, and microphase separation of incompatible soft and hard segments.

The combination of the advantages of waterborne formulations with higher crosslinking density achievable by UV curing is therefore an attractive approach towards coatings with improved properties. As a result of this, UV-curable, waterborne systems appear as a promising supplement by eliminating the use of multifunctional acrylate monomers, and water is used as the only diluent. The formulators in coating industries always balance the viscosity, cure speed, and final properties for a given UV formulation. It is a difficult compromise to achieve both rapid cure speed and lower viscosity for an oligomer by conventional techniques. New dendritic, hyperbranched polymers have provided a powerful technology in this field because of their compact, three-dimensional structures of highly branched polymers. These molecules mimic the hydrodynamic volumes of spheres, which result in low viscosity even at high molecular weight as a result of a lack of restrictive interchain entanglements.

The high-density functional terminal groups on hyperbranched polymers also offer the potential for tailoring their compatibility through conversion of end groups to chemically suitable moieties. These two properties, namely, low viscosity and tailorable compatibility, make them possible candidates to use in aqueous dispersions. In particular, the establishment of the viscosity control is very important because the suitable viscosity is different in each application method. A lot of studies on the viscosity and rheology of aqueous dispersions have been carried out [9].

It is well recognized that a minimum ionic content is required for the formation of a stable polyurethane ionomer, depending on the type of ionic species. In addition the interaction between ions and their counterions are responsible for effects on their properties. Both the degree of neutralization and content of ionic component contribute significantly to the properties of ionomers [10]. Hourston et al. reported the influence of degree of neutralization and ionic moiety on the properties of waterborne dispersions [11]. More recently, we have successfully developed a series of waterborne, hyperbranched polyesters endcapped with methacrylic and salt like groups as UV-curable, waterborne resins [12, 13].

UV-curable, waterborne dispersions can be prepared by modifying some of the hydroxyl groups of Boltorn H20 as a polyol to acidic groups and capping remaining OH groups with diisocyanate and acrylic functionality, such as isophorone diisocyanate (IPDI) and 2-hydroxyethylacrylate (HEA,) respectively. This article describes the synthesis and structure–property relationship of UV-curable, waterborne, hyperbranched ionomers based on Boltorn H20. They are different from conventional waterborne urethane acrylate ionomers having only one ionic site in the center or at the end of a molecule. The UV-curable, waterborne dispersions prepared in this study have *n* ionic sites ($n=6$, 8, 10) and $16-n$ acrylate functionality in Boltorn H20-based prepolymer.

The effects of carboxyl content, degree of neutralization, and dielectric constant of the dispersion medium on the particle size were determined. It is important to note that the particle size has a direct effect on the dispersion stability, and that the larger particle sizes ($>1{,}000$ nm) are generally unstable with respect to sedimentation. The small particle size (<200 nm) is sought after, since these dispersions are storage-stable. The rheological behaviors of the dispersions and the surface tension were investigated.

Particle size is dependent on a number of internal and external factors. The particle size distribution of WHPUDs is not only governed by the molecular weight distribution of dendritic polyester, but also strong hydrogen bonding within hyperbranched macromolecules, the compatibility of the core molecule and the ionic groups, the exact placement of ionic groups, the TEA/COOH mole ratio, the degree of ionization and the dielectric constant of the dispersion medium, which can also lead to broad particle size distribution during dispersion formation. It is reasonable to state that the presence of ionic species in WHPUDs has a considerable effect on physical properties like particle size and rheology. Liao et al. and Kim et al. also observed the broad particle size distribution during aqueous polymer dispersion formation, which is a result of competitive abovementioned factors [14, 15].

Experimental

Materials

The hyperbranched aliphatic polyester Boltorn H20 was used as a principal polyol for aqueous dispersions and was supplied by Perstorp AB, Perstorp, Sweden. Succinic anhydride was used to esterify hydroxyl groups on the polyester chains. 2-Hydroxyethylacrylate (HEA) was distilled, and a fraction was collected as a purified reactant and used after drying over 4-Å molecular sieves. Isophorone diisocyanate (IPDI) and *p*-hydroxyanisole (an inhibitor for the acrylation process) were used without any further purification. Di-*n*-butyltindilaurate (DBTDL) was used as a catalyst and was purchased from the Third Reagent Co., Beijing, China. For the neutralization process, triethylamine (TEA) was used. 1,4-Dioxane was dried over potassium hydroxide and then distilled. Butyl alcohol, methyl alcohol, and deionized water were used as dispersion mediums without any further treatment. All the chemicals for synthesis were purchased from Shanghai Reagent Co., China. The commercial, waterborne resin, EB 2002 was supplied by UCB Co., Belgium.

Synthesis

Prepolymer synthesis

The ideal molecular formula of Boltorn H20 and a schematic presentation for the reaction procedure are shown in Fig. 1. Boltorn H20 has a molecular weight of 1,747 g mol^{-1} with polydispersity of 1.3 and an average of 16 hydroxyl end groups per molecule. It is a second-generation dendritic polymer with practically 15.75 primary hydroxyl groups calculated from the molecular weight and hydroxyl number. The synthesis was carried out in a three-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and reflex condenser with a drying tube. The reaction temperature was controlled by using a constant-temperature oil bath. In the first step, 20.0 g (11.45 mmol, 180.34 mmol hydroxyl groups) hyperbranched aliphatic polyester Boltorn H20 was dissolved in 1,4-dioxane, and then 6.87 g (68.7 mmol) succinic anhydride and a catalytic amount of $SnCl_2$ were added. The reaction was conducted at 100°C, and this temperature was maintained to ensure an acceptable rate of reaction until the anhydride peak at 1,786 cm^{-1} in the FTIR spectrum disappeared, as shown in Fig. 2a. Finally, 1,4-dioxane was evaporated yielding a light yellow, highly viscous resin that has theoretically six hydroxyl groups modified to COOH groups, as described according to our previous work [12]. In the prepolymer synthesis, the chance of the transesterification reaction between the ester bonds of hyperbranched polymer and succinic anhydride has been eliminated by using stoichiometric amount of succinic anhydride for the desired extent of modification. Moreover, the first step was performed at a relatively low esterification temperature (100°C) to suppress unwanted side reactions such as etherification and transesterification.

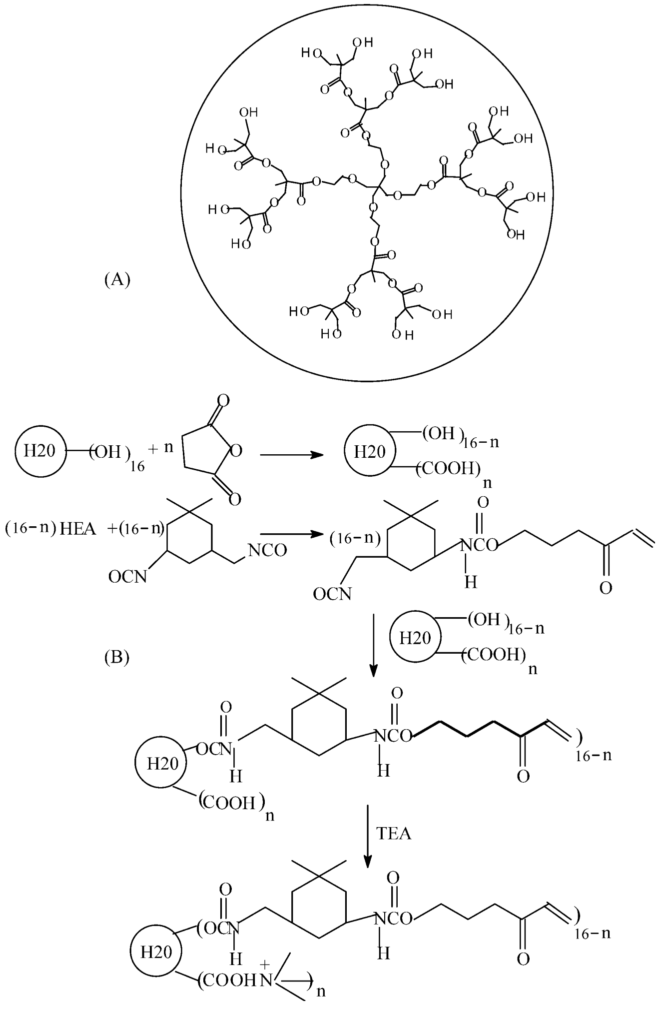

Fig. 1 *Top* Idealized formula of Boltorn H20. *Bottom* Schematic description of the synthesis for WHPUDs

In the second step, 24.45 g (11.45 mmol) IPDI and 15 mL of 1,4-dioxane were poured into clean dry glass reactor, and N_2 gas was aspirated for 10 min to eliminate residual moisture. After dissolving 0.1 wt% DBTDL (first portion of catalyst), *p*-hydroxyanisole (1,000 ppm over total amount of reactant), and 13.29 g (11.45 mmol) HEA in 10 mL dioxane, the mixture was

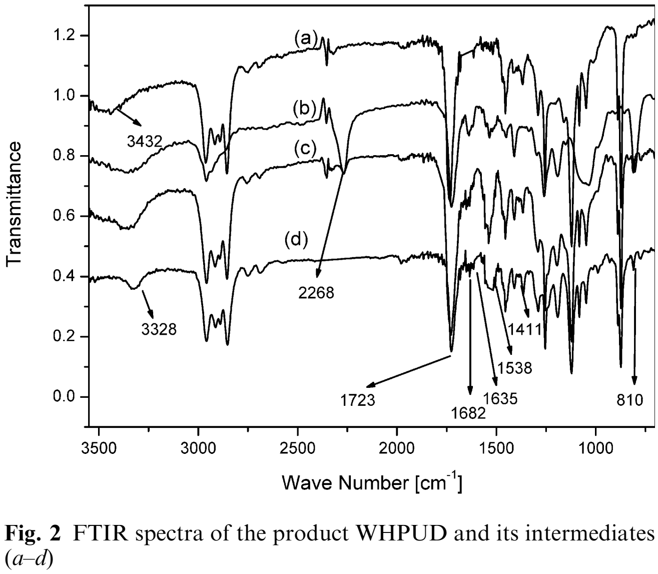

Fig. 2 FTIR spectra of the product WHPUD and its intermediates (*a–d*)

dropped slowly into the reactor under efficient stirring at 0°C and kept for another 1 h. The temperature was then increased to 30°C where it was maintained for 4 h. The relative consumption of NCO groups is shown in Fig. 2b and c. The change of isocyanate (NCO) value during the reaction was determined by the di-*n*-butylamine back titration method to find out the end point of this step [16]. Thus, the preparation of this product with a specific structure comprises one of the decisive factors for successful achievement of final products, according to the proposed reaction scheme.

In the third step, the prepolymer synthesized in first step containing the second portion of catalyst (0.1 wt% DBTDL) was added dropwise into above reaction vessel containing IPDI-terminated HEA by dropping funnel and stirred vigorously at 40°C until the peak at 2,268 cm^{-1} for NCO groups completely disappeared, which is shown in Fig. 2d. The end point was also determined by the change of NCO value by using the di-*n*-butylamine back titration method. It is difficult to consider the competitive reaction between NCO and COOH groups when using the mildest reaction conditions possible (i.e., low temperature and 0.05 wt% DBTDL catalyst). It has been reported that a significant pressure build up was observed in the reaction vessel due to elimination of CO_2 during such condensation reactions [17, 18]. However, this was not experienced in our case. In this stage the reaction conditions were carefully controlled to avoid crosslinking. As a result, neither gel formation nor much enhanced viscosity was encountered during the prepolymerization, indicating that crosslinking structures were successfully avoided.

Neutralization of prepolymer

Finally, the residual carboxylic acid groups in the ionomer (theoretically 6) were neutralized with an appropriate amount of TEA (6.93 g, 68.7 mmol). The temperature was maintained at 40°C for 2 h to ensure completion of the reaction. In Fig. 2d, a typical FTIR spectrum for the product shows the carbonyl stretching band at 1,723 cm^{-1}, an amide I band at 1,682 cm^{-1}, an amide II band (N–H bending vibration) at 1,538 cm^{-1}, and the N–H stretching vibration at 3,328 cm^{-1}. The peaks at 1,635, 1,411, and 810 cm^{-1} indicate the presence of acrylate groups.

Dispersion formation

After neutralization, the waterborne, hyperbranched polyurethane dispersion WHPUD-10.6 was obtained by evaporating the 1,4-dioxane under vacuum, dispersed by adding deionized water to the prepolymer at 35°C, and allowed to stir for a further 30 min. The dispersion was prepared at 40% solid content. From the preliminary experiments, it was found that 40% neutralization was a minimum value for forming a stable dispersion. Therefore, the degree of neutralization was varied from 40% to 100% in this study.

For comparison, a series of waterborne, hyperbranched polyurethane dispersions were prepared. Therefore, in the first step, the stoichiometry for the modification of hydroxyl groups into carboxylic acid groups and acrylate groups was adjusted in three different ratios: 10:6, 8:8, and 6:10. A stoichiometric amount of HEA was then added to obtain an NCO value of half that at the start of reaction. The reaction was continued to achieve a %NCO value close to the theoretical value and the disappearance of hydroxyl peak. The obtained products were named WHPUD-10.6, WHPUD-8.8, and WHPUD-6.10, respectively.

Measurements

The FTIR spectra were obtained with a Fourier transform IR spectrophotometer MAGNA-IR 750 (Nicolet Instrument Corporation, USA) and recorded by averaging 32 scans at a resolution of 2 cm^{-1}. The average particle sizes and the distribution of WHPUDs were measured by the laser light scattering method. A modified commercial light-scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-τ digital time correlator) was used with a solid-state laser (ADLAS DPY 425 II at $\lambda = 632.8$ nm) as a light source at 25°C. The particle concentration in the dispersion was adjusted to 0.1% by using deionized water, butyl alcohol, or methyl alcohol, and stirred well to obtain a homogeneous dispersion.

The dynamic surface tension for WHPUDs was measured by the bubble pressure method on a digital DMP-2C surface tension tester (Applied Physics Institute of Nanjing University, China) at 25°C. Thus, from the profile of a drop, software enabled the calculation of values of surface tension. The rheological behavior of final products was determined with a QNX Model Rotating Viscometer (Tianjin Instrument Co., China) with variable shear rates.

Results and discussion

Particle size

Effect of degree of neutralization of ionic groups

Figure 3 shows the effect of the degree of neutralization of carboxylic groups on the average particle size of WHPUD-8.8. It is clear from particle size distribution

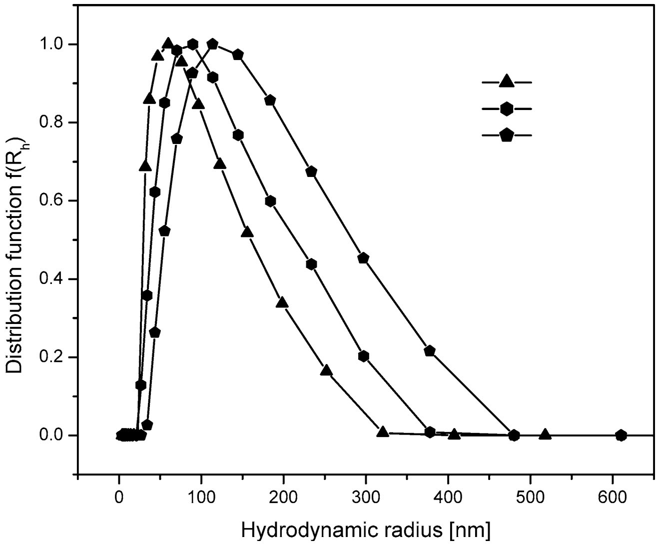

Fig. 3 Effect of degree of neutralization on the average particle sizes of WHPUD-8.8: 100% (*triangles*), 70% (*hexagons*), 40% (*pentagons*)

profiles that the particle sizes are 59.83, 89.63, and 113.82 nm, as the degree of neutralization varied from 100, 70, and 40%, respectively. The particle sizes of WHPUD-8.8 decreased as the degree of neutralization increased, because the number of dissociated carboxyl groups after neutralization increased, and these are capable of stabilization. Figure 4 illustrates the effects of TEA/COOH mole ratios on the average particle sizes of WHPUD-6.10, WHPUD-8.8, and WHPUD-10.6. It is found that the average particle sizes decrease as the mole ratio of TEA to COOH varies from 0.4 to 1.2 for three dispersions. This result was ascribed to the variation of the content of carboxylic groups that could be neutralized by TEA and which are responsible for reduction in particle sizes of aqueous dispersions. Therefore, the degree of neutralization may influence the particle formation mechanism. This is illustrated in Fig. 5, which shows the formation of smaller particles as the number of neutralized carboxylic groups increases owing to their electrostatic stabilization.

In waterborne dispersions, it is generally observed that the greater the hydrophilicity, the smaller the particle size [15]. The degree of dissociation depends on the degree of neutralization. As a result, with increasing the degree of neutralization, the surface charge density increases. Moreover, the properties of PU dispersions, such as their ability to release hydrophobic species, depend on the degree of neutralization of carboxyl groups.

Effect of acid content

The average particle size could be controlled to some extent by such emulsification conditions as stirring speed or dispersing temperature, which have an effect on the viscosity of a prepolymer, but it is mostly governed by the concentration of hydrophilic groups (i.e., carboxylic acid groups). Consequently, the average particle size

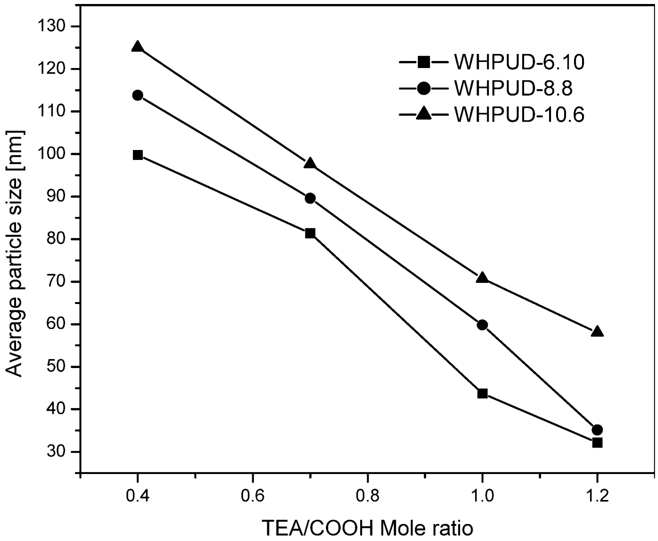

Fig. 4 Effects of TEA/COOH mole ratios on the average particle sizes of WHPUD-6.10, WHPUD-8.8, and WHPUD-10.6

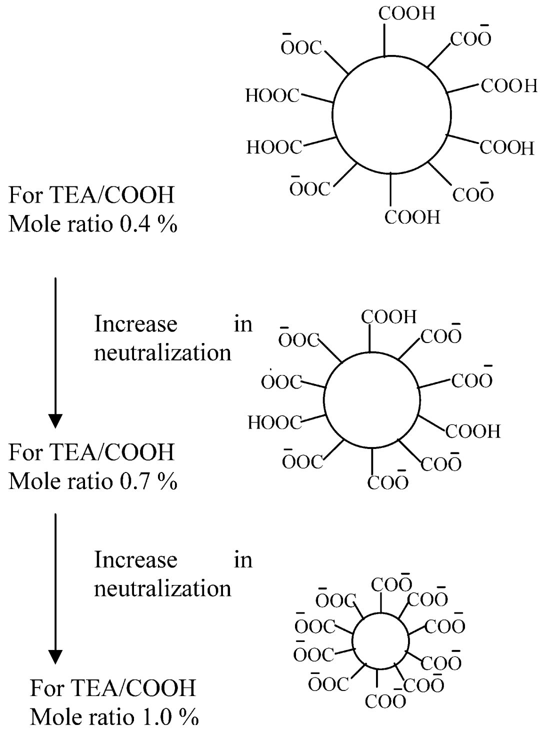

Fig. 5 Symbolic representation showing the relationship between the degree of neutralization and average particle sizes of WHPUD-6.10

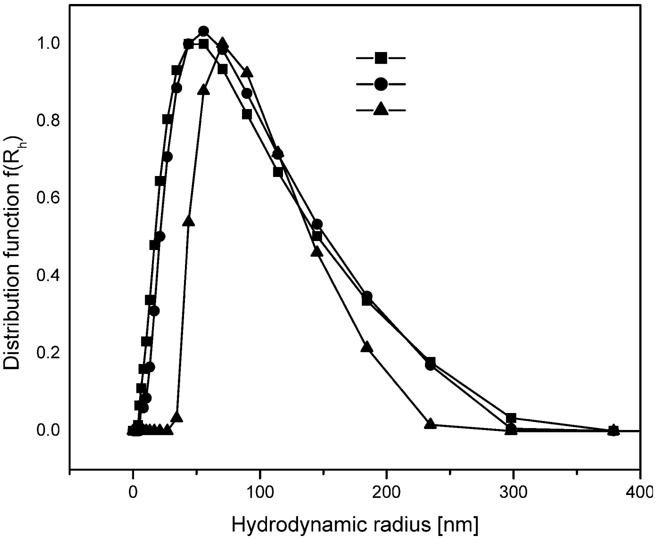

Fig. 6 Effects of carboxylic acid contents on the average particle sizes of WHPUDs at 100% neutralization of each sample

decreases as the acid content increases. It can be seen in Fig. 6 and Table 1 that the particle sizes follow the order WHPUD-10.6 > WHPUD-8.8 > WHPUD-6.10. The asymptotic decrease of particle size with increasing acid content is due to the stabilizing mechanism of ionomer dispersions. Therefore, it can be concluded that the ionic groups are located predominantly on the surfaces of particles, whereas the chain segments form the interiors of the particles. At the interface between particle and water, a double layer is formed by the dissociation of ionic groups. Hence, the electrical double layer stabilizes these dispersions in water.

Effect of dielectric constant of the dispersion medium

Deionized water, butyl alcohol, and methyl alcohol were employed as dispersion mediums for prepolymer WHPUD-10.6 to investigate the effects of their dielectric constants on the particle size with 100% degree of neutralization. It is clear from these distribution curves (Fig. 7 and the values listed in Table 1) that the average particle sizes of dispersions increase as the dielectric constants decrease. The particle size of WHPUD-10.6 in different dispersion mediums follows the order water < methanol < butanol. The higher the dielectric constant of the dispersion medium, the greater the dissociation of carboxyl groups. The average particle size is mostly governed by the concentration of dissociated groups; thus, higher dissociation is possible in high dielectric constant mediums (e.g., water). These results are in good agreement with the observation obtained by Son et al. [19].

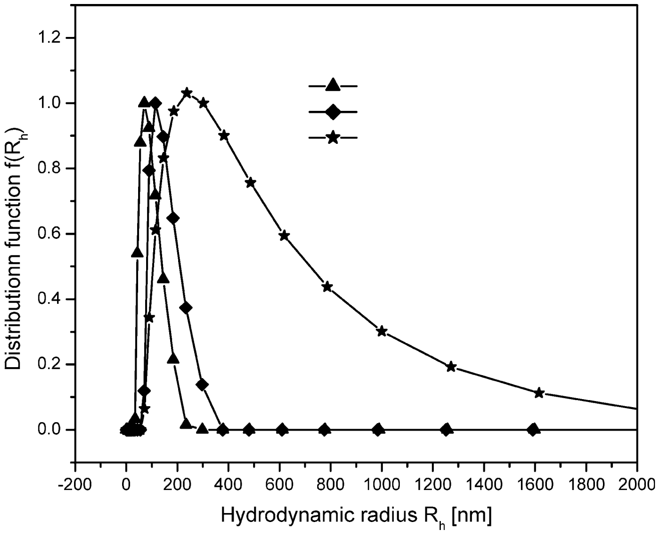

Fig. 7 Effects of dielectric constants (in parenthesis) of dispersion mediums on the average particle sizes of WHPUD-10.6 at 100% neutralization of sample: water (80.2, *triangles*), methanol (32.6, *diamonds*), butyl alcohol (15.8, *stars*)

In present study, the half widths of the distribution peaks were narrower when effects of the degree of neutralization and carboxyl content on the average particle size of WHPUDs were investigated. Broader peaks were obtained from water to methanol and butyl alcohol due to an increase of dielectric constant of the dispersion medium.

Surface tension

Sufficient substrate wetting is always important for good adhesion of waterborne dispersions for coatings. Most of the coating technologies are dynamic processes. Therefore, the dynamic surface tension gives more

Table 1 Effects of carboxyl content and degree of neutralization on the average particle sizes and surface tension

Sample	Average Particle size (nm)			Surface tension (mN m^{-1})		
	Degree of neutralization (%)			Degree of neutralization (%)		
	100	70	40	100	70	40
WHPUD-10.6	70.69 113.72[a] 237.18[b]	97.58	125.02	47.1	55.2	57.5
WHPUD-8.8	59.83	89.63	113.82	45.3	54.9	53.7
WHPUD-6.10	43.75	81.40	99.74	42.1	47.4	50.6

[a] Methyl alcohol
[b] Butyl alcohol

reliable information about the physical interactions. There are three possible interchain physical interactions within polyurethane ionomers: (a) electrostatic forces between ionic centers, (b) hydrogen bonding between urethane groups, and (c) association of hydrophobic segments. These interchain interactions control the aqueous dispersion properties, such as surface tension and rheological behavior. The effect of varying the carboxyl content on the surface tension of dispersion with the same viscosity and solid content has been studied. The surface tension values of WHPUDs with 40, 70, and 100% neutralization are summarized in Table 1. The surface tension for the prepolymer gradually decreases with increasing content of carboxylic groups. WHPUD-10.6, WHPUD-8.8, and WHPUD-6.10 at 100% neutralization have surface tension values of 47.1, 45.3, and 42.1 mN m^{-1}, respectively. It is well known that the water-solubilizing functional groups determine the hydrophilicity of a prepolymer. By increasing the carboxyl content in WHPUD-10.6 to WHPUD-6.10 may lead to the generation of strong electrostatic repulsion. As a result, the prepolymer molecular chain may assume a more extended conformation, which causes the hydrophobic segment to loosely arrange at the air–water interface; therefore, the surface tension reduces. The values listed in Table 1 also reflect the effect of degree of neutralization on the surface tension of WHPUDs. For the dispersions WHPUD-10.6, WHPUD-8.8, and WHPUD-6.10 the surface tension values decrease with increasing the TEA/COOH mole ratio from 0.4 to 1.00. This indicates that the hydrophilic functional groups neutralized by TEA could provide the polymers with sufficient aqueous dispersibility, which leads to less surface tension. It is therefore also interesting to point out that a WHPU ionomer resembling a surfactant in water could substantially lower the surface tension of water. For this reason, it is advantageous to use them for the preparation of self-emulsified, waterborne, UV-curable polymer coatings.

Rheological behaviors

The viscosity arises from the interactions between the particles of dispersions. Therefore, it is considered that there are many factors, such as molecular architecture, molecular weight, solid content, and dispersion medium, which affect the rheology of a coating. Moreover, the viscosity of a formulation is related to the dynamic extension and the segment density within the volume of a molecule and intermolecular chain entanglement. As a result of the highly branched, sphere-like structures of hyperbranched polymers, there will be few entanglements among molecular chains, thus resulting in a rather lower viscosity. In addition, the rheology of water-dispersible systems can be easily controlled by the addition of water.

In a first approach the viscosity of WHPUDs was monitored as a function of shear rate at 40% solid content . Figure 8 shows the rheological behavior of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10, and EB 2002. It has been observed that the viscosity for all dispersions decrease drastically when the shear rate increased from 0.3 s^{-1} to 6 s^{-1}, whereas it decreased gradually from 6 s^{-1} to 60 s^{-1}. When the shear rate increases, the physical crosslinks are broken down, thus leading to the drastic decrease in viscosity. This implies that WHPUDs exhibit shear thinning or pseudoplastic behavior, which arises in common polymer dispersions. The hard segment of prepolymer also plays an important role in determining the viscosity of dispersions. It seems from the results illustrated in Fig. 8 that the IPDI-based dispersions exhibit pronounced deviation from Newtonian flow behavior. The chain entanglement and hydrogen bonding between urethano and urea linkages can be more rapidly formed in the IPDI-based prepolymer because of the flexibility of the chains. Figure 8 reflects clearly that at each shear rate the viscosity of commercial, water-based resin EB 2002 is higher than those of all WHPUDs synthesized in our lab.

The effect of the carboxyl content of WHPUD on the viscosity is also illustrated in Fig. 8. The viscosity of these dispersions follow the order WHPUD-10.6 < WHPUD-8.8 < WHPUD-6.10. As the concentration of ionic groups in the prepolymer increases, the mutual repulsion of the same charges causes the expansion of chains, which may result in increasing the viscosity of dispersions. Moreover, the interchain associations resulting from hydrogen bonding between

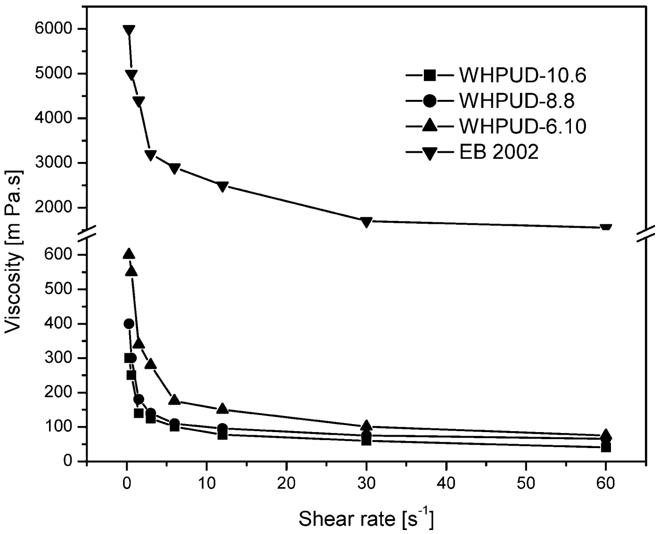

Fig. 8 Effects of carboxyl contents on rheological behavior of WHPUDs with 40% solid content

urethane groups make the chain assume a more expanded conformation, which is also responsible for increasing the viscosity.

It is important to measure the viscosity of dispersions as a function of solid content, because in the case of UV-curable aqueous resins, water must be evaporated before UV irradiation. Thus, a higher solid content with the same viscosity is beneficial in terms of energy efficiency. Figure 9 shows the viscosity profiles of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10, and EB 2002 as a function of solid content at a 60 s^{-1} shear rate. It is clear that for all samples the increase in the solid contents cause their viscosity to increase. It is important to note that the decreased solid content leads to the orientation of prepolymeric molecular chains, thus destroying the associated structures such as hydrogen bonding and chain entanglements. As a result, the flow resistance decreases and the viscosity reduce.

It is well known that the rheological behavior of a fluid can be described by the following exponential equation [17]:

$$\tau = KD^n \tag{1}$$

where τ is the shear stress, D is the shear rate, n is the flow index and equals 1 for a Newtonian fluid, and K is the viscosity coefficient. The greater the value of K, the higher the apparent viscosity of the fluid. Equation (1) is transformed into the following logarithmic form:

$$\log \tau = \log K + n \log D \tag{2}$$

where n and K can be calculated from the slope and intercept of the plot of $\log\tau$ versus $\log D$, respectively. Table 2 lists some rheological parameters of WHPUDs and EB 2002. It can be observed that all the dispersions have flow index (n) less than one, implying that all these systems exhibit pseudoplastic rheological behavior. A low viscosity coefficient (K) reflects the low apparent viscosity. As mentioned above, the low flow index and viscosity coefficients at higher shear rate imply the destruction of associated structures such as hydrogen bonding, resulting in reduction of viscosity. Moreover, WHPUDs have much low K values than EB 2002.

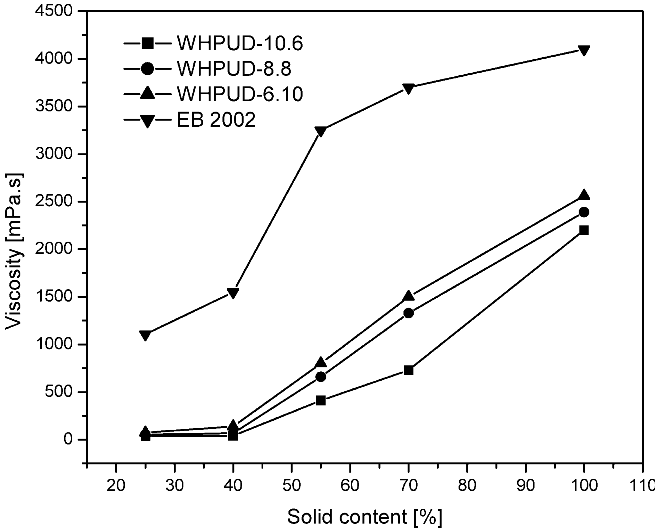

Fig. 9 Effects of solid contents on rheological behavior of WHPUDs at the shear rate of 60 s^{-1}

Table 2 Some rheological parameters of WHPUDs and EB 2002

Sample	Flow Index (n)	Viscosity coefficient (K)
WBHPD-10.6	0.658	0.189
WBHPD-8.8	0.635	0.231
WBHPD-6.10	0.592	0.403
EB 2002	0.738	0.812

It is desirable to possess such pseudoplastic behavior in terms of coating applications, especially for spraying. When coating is sprayed from the spray head at a high velocity, the greater shear rate causes a decrease in viscosity of coatings. These can then be evenly dispersed by fine spraying, thus giving a shiny and generous coat. Phase inversion is said to occur in an agitated dispersion when the dispersed phase becomes the continuous phase and vice versa, which can be monitored by viscosity variation [20]. For instance, the viscosity of PU drops slightly after initial addition of water. The viscosity then rises sharply following further water addition. After reaching a maximum, the viscosity decreases quickly and then slowly decreases until a constant viscosity is reached. Such behavior has not been observed during WHPUD formations in accordance with the rheological behavior shown in Fig. 9.

Conclusions

A new class of UV-curable, waterborne, hyperbranched polyurethane dispersions having good dispersiblity without using emulsifier have been developed by incorporating Boltorn H20, IPDI, HEA, and TEA. It was found that the presence of ionic groups in the network plays an important role in determining the final properties of prepolymer. The study of particle size using a laser light scattering method has revealed that the particle sizes of WHPUDs are sensitive to the carboxyl content, degree of neutralization, and dielectric constant of the dispersion medium. The lower the concentration of carboxyl groups per polymer, the larger the particle size of dispersion. The particle sizes decreased as the degree of neutralization increased, because the dissociated carboxyl groups are capable of stabilization. As the dielectric constant of a dispersion medium decreased, the dissociation of carboxyl groups decreased causing the particle size to increase.

The surface tension of all dispersions is much lower than that of water. The surface tension decreased as the carboxyl content and degree of neutralization increased. The rheological behavior of the WHPUDs, investigated by using a rotational viscometer, suggested that all dispersions belong to pseudoplastic fluids.

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