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Studies on the Particle Morphology of Waterborne Cationic Polyurethane/Polyacrylate Microemulsions

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Polyurethane containing tertiary nitrogen atoms was synthesized from polyol, diphenylmethane diisoccyanate (MDI) and N-methyl diethanolamine. The polymer was converted into cationomers by quarternizing with methacrylic acid (MAA) and then dispersed in water. In this reaction, methyl methacrylate (MMA) was used to decrease viscosity; at the same time, it was the monomer in the later reaction. Finally the cationic polyurethane dispersions were further polymerized with an oil-soluble initiator, azobisisobutyronitrile (AIBN), water-soluble initiator, $K_2S_2O_8$ *(KPS) and the mixture of AIBN and KPS. The different emulsion particles with shell-core structure, "invert" shell-core structure and "irregular" sandwich structure were obtained; the morphological structures were characterized by TEM observation, FT-IR and particle size analysis.*

Keywords polyurethane, cationomers, compound emulsions, shell-core structure, "invert" shell-core structure, "irregular" sandwich structure

Introduction

Due to their excellent chemical, solvent and abrasion resistance, as well as outstanding hardness and toughness combined with low temperature flexibility, polyurethanes (PU) are suitable for many coating applications (1, 2). During the raw material stage, volatile organic solvents had to be used in the preparation due to the fact that di or poly-isocyanate were highly moisture sensitive. The effects of volatile organic solvents in the environment are detrimental; there has been a growing concern about the development of water-borne coatings (3). During recent years, anionic polyurethane dispersions have become commercially predominant while little literature is available on cationic dispersions. The reason behind this is because cationic polyurethane has poor water resistance and lack of hardness and toughness (4, 5). However, cationic PU has unusually good adhesion to various ionic substrates, especially to anionic substrates like leather and glass (6, 7).

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They also have been proven useful in special applications, such as additives in the coagulation process which is used to make poromerics (8–10). Polyacrylate emulsions possess good mechanical properties and outstanding climate and water resistance, except for the defect of hot-viscidity and cold-brittleness. The composite emulsion of polyurethane/polyacrylate combines the excellent properties of polyurethane dispersion and polyacrylate emulsion, which improves the properties of coatings greatly (11, 12).

Recently, there has much research conducted on waterborne polyurethane/polyacrylate emulsions. A series of core-shell type polymer hybrid emulsions with different properties have been obtained by a combination of polyurethane and polyacrylate. The polymerizing process, different core-shell ratio, cross-linking structures, the relationship between particle morphology and reaction parameters, and the glass transition behavior have been carefully studied (13–16). However, most of the work about core-shell emulsions concentrated on anionic polyurethane, and the morphological structures of the particles were merely core-shell type and interpenetrating polymer networks (17–19). The traditional method of water-borne polyurethane preparation usually makes use of an organic solvent, such as acetone, etc, which has to be eliminated from the final products (20, 21). Hence, it is of interest to study the particle morphology of cationic polyurethane/polyacrylate emulsions. In this article, a novel method of polymerization of cationic polyurethane emulsions is given. Cationic polyurethane emulsion was prepared using a non-organic solvent. Three morphological structures of cationic polyurethane/polyacrylate have been synthesized. A picture of the mechanism of the reaction process is given. The morphological structure of the compound emulsions were characterized by the average particle diameters and transmission electron microscopy.

Experimental

Materials

Polytetrahydrofuran 2000 (PTMG) and poly(ethylene glycol) 2000 (PEG) were supplied by Wanhua Co., Yantai, China, and were vacuum dried at 110°C for 1 h as a soft segment composite. 4,4′-Diphenylmethane diisocyanate (MDI) was also supplied by Wanhua Co. N-Methyl diethanolamine (N-MDEA) was supplied by Fluda Chemie, Buchs, as a chain extender. It was distilled under reduced pressure and the middle portion was stored in nitrogen atmosphere. Methyl methacrylate (MMA) was supplied by Shanghai Chemical Co., China; it was used to decrease the viscosity and was the monomer in the seeded emulsion polymerization. Methacrylic acid (MAA) was a neutralizing agent. KPS and AIBN were initiators supplied by Shanghai Chemical Co., China.

Sample Preparation

The Synthesis of Cationic Polyurethane Emulsion. The polyaddition reaction was conducted in a 250 ml four-necked flask, equipped with a mechanical stirrer, a nitrogen gas inlet, and a condenser. Polyol (PEG : PTMG = 1:1) was dried at 110°C under vacuum to eliminate water. Blends of MDI with polyol were reacted at an NCO/OH equivalent ratio of 2:1, heated to 80°C with mild agitation. While keeping the temperature at 80°C, NMDEA dissolved in MMA was added to the mixture. The weight ratio of PU/MMA was 1:2. The NCO group content reached a given value that was calculated based on the assumption that all the hydroxyl groups were consumed by NCO groups, as determined by the dibutylamine back titration. The product was then neutralized by MAA at

40°C, and then emulsified in double-distilled and deionized water with a high–torque stirrer. The solid content of the emulsion was about 30%.

Synthesis of Compound Emulsions

The polyaddition reaction was conducted in a 250 ml four-necked flask, equipped with a mechanical stirrer, a nitrogen gas inlet, and a condenser. Cationic polyurethane emulsion was diluted by deionized water. The MMA and MAA in the cationic polyurethane emulsion were initiated at 60°C for 2 h by (a) AIBN: 5% of monomer, (b) KPS: 1%–2% of monomer, and (c) AIBN: 4% of monomer and 2 h later, KPS: 1% of monomer. Polyurethane/polyacrylate composite emulsions were obtained. Solid contents of the emulsions were about 25%.

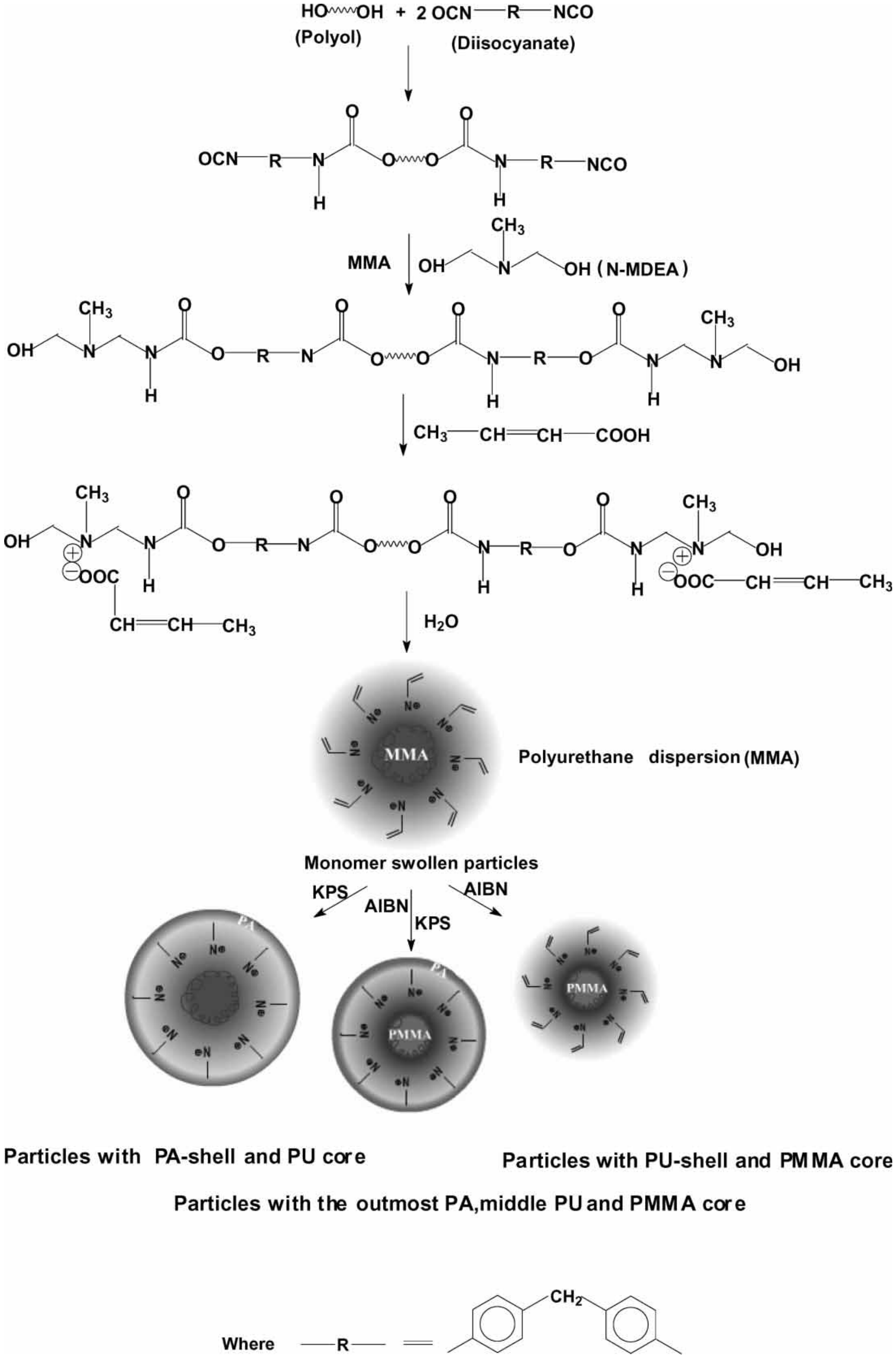
Characterizations

The average particle diameter was determined by a particle size analyzer (Nano-ZS, Malvern Company, U.K.). The transmission electron microscopy (TEM) specimens of the microemulsions were diluted to 1% with deionized water, and then dropped on copper grids whose surface was covered by a carbon film. The samples were dried for observation. The transmission electron micrographs were obtained using a Hitachi-800 instrument with a voltage of 175 kv. The PMMA appears as the dark phase of the images. The FT-IR spectra were recorded using a FT-IR Nicolet NEXUS-670 spectrometer (Nicolet Company, USA) at a resolution of 2 cm^{-1}, scanning from 4000 cm^{-1} to 400 cm^{-1}. The sample for infrared analysis was a dry film of the microemulsions. Scans were made at room temperature (18 ± 2°C).

Results and Discussion

Reaction Mechanism

Scheme 1 illustrates the reaction process. A blend of PTMG and PEG (weight ratio = 1:1) were reacted with MDI to form the PU pre-polymer. MMA was used as a solvent to lower the viscosity of the pre-polymer. The pre-polymer was then extended by N-MDEA. By adding MAA, reactions were created with the tertiary ammonium of the PU chain, forming hydrophilic ionic groups, which were then self-emulsified by the use of double-distilled and deionized water. Due to its hydrophobic property, MMA was enwrapped by the hydrophilic segments of PU, forming MMA swollen particles. In the polymerization of the composite emulsions, oil-soluble initiator (AIBN), which is soluble in the MMA phase, initiated MMA polymerization to form particles with PU-shell and PMMA core. When the water-soluble initiator (KPS) was used, it opened the double-bonds of MAA, which was on the surface of the PU particles. Due to there being only a little MAA in the polymerization system, MMA from the core diffused to the surface of the particle to supply the reacting monomer; thus, the subsequent particles with PMAA/PMMA-shell and PU core were gained. When AIBN was used to first initiate MMA, KPS added later initiated the double-bonds of MAA; an “irregular” sandwich structure of particles with PMAA/PMMA-shell, PMMA core and PU interlayer were obtained.



Scheme 1. The polymerization reaction scheme exhibiting the reaction process and resulting particle structure.

FT-IR Analysis

FT-IR spectrum of the cationic polyurethane is shown in Figure 1. The spectrum shows characteristic bands of urethane >NH at 3300 cm^{-1} and >C=O stretching of the urethane linkage at 1730 cm^{-1}. The symmetric and asymmetric stretching of -C-H- were observed between 3000 and 2840 cm^{-1}. The aromatic >C=C< band of MDI was observed around 1600 cm^{-1}. The band at 1540 cm^{-1} was due to the C-N stretching and NH deformation. The >C-O-C< stretching of the polyurethane results in the broad band at 1100 cm^{-1}. When the block copolymers were converted to their cationomers, the tertiary nitrogen atoms were converted to quaternary ammonium groups, which increased the peaks up to 980-930 cm^{-1}, characteristic of aliphatic quaternary ammonium salts. Thus, the anticipated structure of cationic polyurethane was obtained.

The Average Particle Diameters. Figure 2 illustrates the particle diameter; distributions with the average sizes are listed in Table 1. The particle size of cationic PU dispersion is about 266 nm, while the size of particles initiated by AIBN is significantly lowered, to about 96 nm. The reason is that the density of PMMA is larger than that of the monomer and some MMA volatilized. Therefore, the volume of particles after polymerization is reduced. When initiating by AIBN first, then by KPS, a surface layer of PMAA/PMMA can be formed. Therefore, the particle size is increased to about 146.4 nm. When KPS is used, the particle size is about 201.3 nm. This is because the polymerization mainly occurred on the surface of particles. MMA from the inner part of the particle diffuses to the surface to take part in polymerization; thus the particles become hollow, and the particle size is only slightly smaller than that of particles before initiation.

TEM observations of the composite emulsions give consistent results. Figure 3 illustrates the images of the emulsion particles with different structures. The PMMA appears as the dark phase in the images, the PMAA or the mixture of PMMA and PMAA appears as

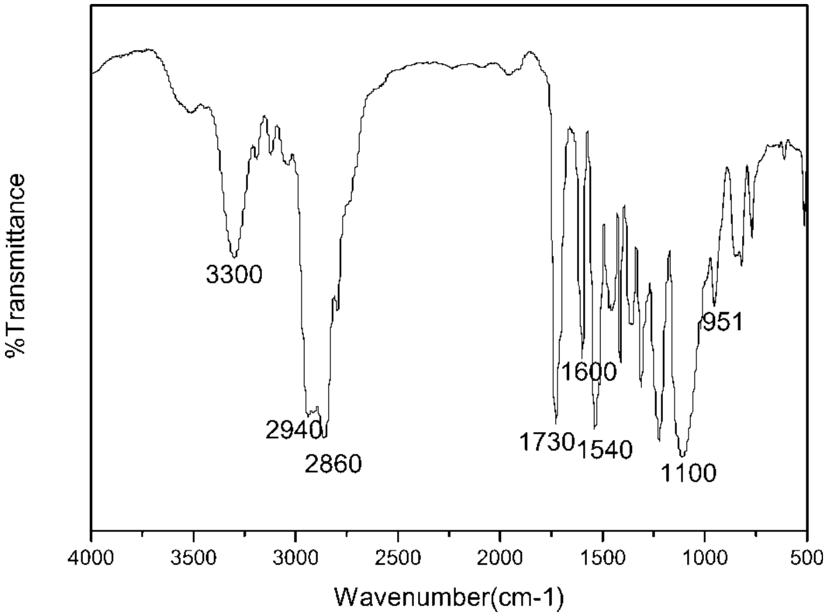


Figure 1. FT-IR spectra of cationic polyurethane.

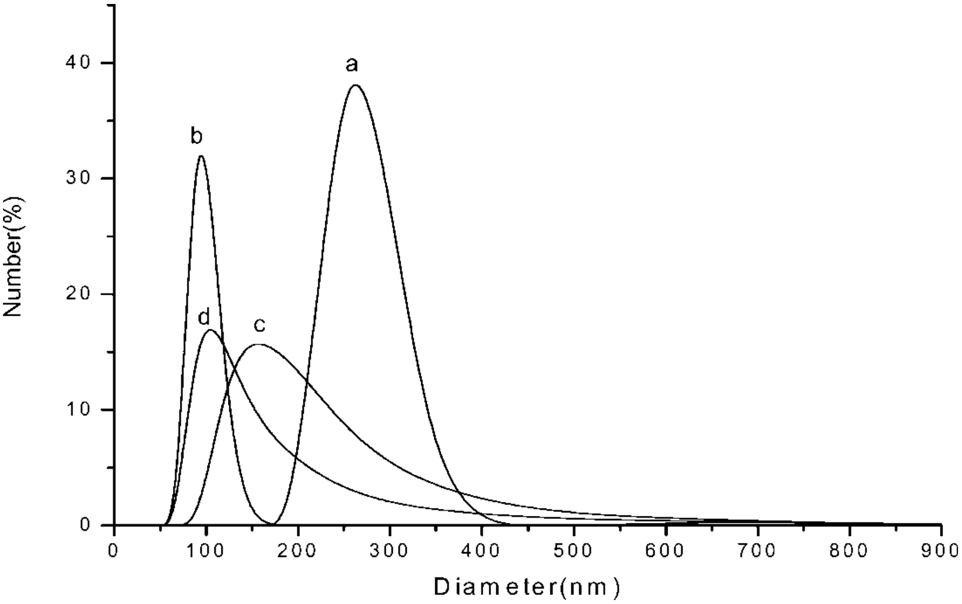


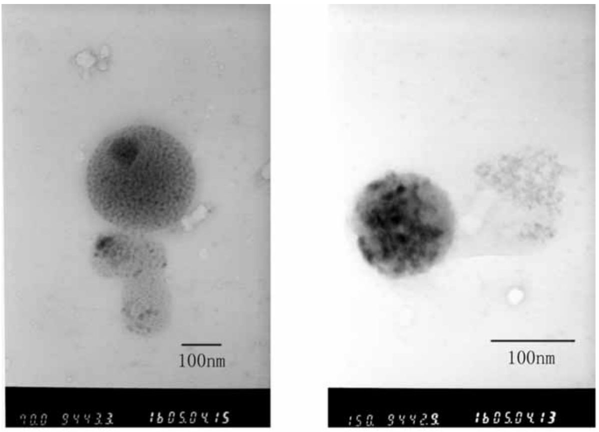
Figure 2. Particle diameter distributions of (a) cationic polyurethane emulsions; (b) AIBN initiation; (c) KPS initiation; (d) the mixture of AIBN and KPS initiation.

the light grey phase in the images and the PU appears as the grey phase in the images. From picture “a”, due to its hydrophobic property, MMA is enwrapped by the hydrophilic segments PU, forming MMA swollen particles. The black granules are MMA, they do not disperse evenly within the particle of PU. The size is about 300 nm. In picture “b”, core MMA is initiated into PMMA by AIBN, but the reaction is not very complete and regular. Thus, particles with PU-shell and granular PMMA core are obtained, its size is ca.100 nm. In picture “c”, the shell-core structure can be clearly seen. The light grey phase is the PMMA/PMAA surface layer, and the darker gray phase may be the mixture of PU and PMMA. As mentioned above, when KPS initiates the reaction in a water environment, the polymerization mainly occurred on the surface of the particles. MMA from the inner part of the particle diffuses to the surface to take part in polymerization, thus, the particles become hollow to some extent. The inner part of the particle should be composed of PU and PMMA. The size is about 280 nm. From picture “d”, particles with “irregular” sandwich structure are suggested. The dark area in the core is PMMA, the grey area in the middle is PU, the PMMA/PMAA surface layer appears as

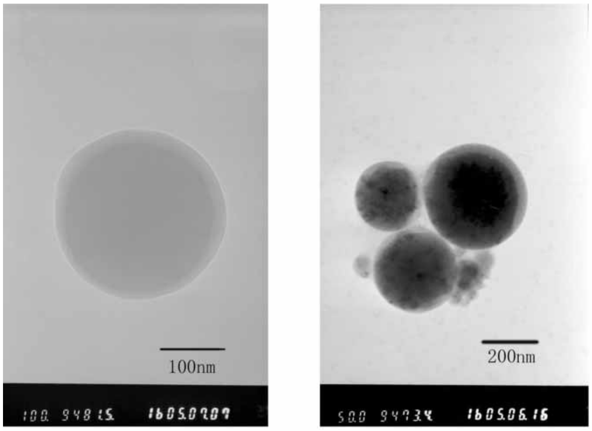
Table 1

Average particle diameters of cationic polyurethane and the different structure compound emulsions: a) cationic polyurethane emulsions; b) AIBN initiation; c) KPS initiation; d) the mixture of AIBN and KPS initiation

	a	b	c	d
The average diameters (nm)	266.3	96.45	201.3	146.4



(a) cationic polyurethane (b) AIBN initiation



(c) KPS initiation (d) the mixture of AIBN and KPS initiation

Figure 3. TEM picture of different emulsions.

the light grey phase of the images. From Figure 3(d), the structure of the three layers still can be seen. The size of the particle is about 250 nm. Hence, the observations are consistent with the above reaction mechanism.

Conclusions

In the preparation process of the composite emulsions, MMA is both the solvent for the synthesis of polyurethane and the monomer for composite emulsions. Emulsion particles with three morphological structures can be obtained using AIBN, KPS and the mixture of AIBN and KPS as initiators. They are emulsion particles with shell-core structure, "invert" shell-core structure and "irregular" sandwich structure, respectively. The proposed reaction mechanism clearly explains the reaction process and the morphology of the particles; at the same time, the results of average particle diameters and the TEM micrographs also can confirm the reaction mechanism.

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