Preparation and Characterization of the Complex Latex Formed Through Complexation of Two Polymer Latexes with Chemically Complementary Structure

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ABSTRACT: In this study, the intermacromolecular complexation of two polymers with chemically complementary structures in the latex state and the interparticle interactions were probed. Two latexes—a polydimethylsiloxane (PDMS)/poly(vinyl acetate-co-butyl acrylate) system, named PA latex, and a PDMS/poly(methacrylic acid) system, named PB latex—were prepared by seeded emulsion polymerization and the complex latexes were obtained through complexation of the PA latex with the PB latex. The properties of the obtained complex latexes were investigated using surface tension and viscosity measurements. The surface structure and composition of coatings obtained from the latexes were analyzed by X-ray photoelectron spectroscopy and scanning probe microscopy. The results confirmed that there are interactions between the $-O-\overset{O}{\overset{\|}{C}}-CH_3$ (or $-\overset{O}{\overset{\|}{C}}-O-C_4H_9$) groups in PA and the $-\overset{O}{\overset{\|}{C}}-OH$ groups in PB. The interactions result in unique properties of the polymer latex and lead to a formation of a new structure of the coatings. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1405–1411, 2003

Key words: emulsion polymerization; coatings; latices; polysiloxanes

INTRODUCTION

Intermacromolecular complexation of two polymers with chemically complementary structures is a new and effective approach to make new polymer materials and to modify the polymers, which has become more and more interesting and attractive. The studies in the literature concerned with intermacromolecular complexation are related mainly to precipitated complexes[1–3] and complex solutions.[4–8] Few works have been related to the complex latex, while it is important in making environmentally friendly polymer materials and modifying polymers. The latex complexes may have some special properties different from the original components due to the intermacromolecular complexation. In this study, the method of intermacromolecular complexation was first introduced to the latex system to prepare water-borne coatings with new structures and unique properties.

At present, organic solvents are mostly applied in the coatings field, which results in serious pollution. With increasing consciousness of the environmental protection of human beings, the research on water-borne coatings has been attached more and more importance especially for coatings with low surface energy,[9,10] and complex latex will be promising to be applied to water-borne coatings.

Copolymers containing polydimethylsiloxane (PDMS) have received considerable attention due to their unique properties, such as excellent resistance to cold, heat, water, acid and base, etc. Although in the fields of emulsion polymerization the preparation of copolymers containing PDMS have become fashionable, less work has been done in preparing and characterizing the complex latexes obtained by mixing two latexes with different functional groups. The work reported here is a primary research in this aspect. Because vinyl acetate (VAc), butyl acrylate (BA), and methacrylic acid (MAA) have functional groups ($-O-\overset{O}{\overset{\|}{C}}-CH_3$, $-\overset{O}{\overset{\|}{C}}-O-C_4H_9$, and $-\overset{O}{\overset{\|}{C}}-OH$, respectively) which can interact with each other through hydrogen bonding, we chose them as reaction monomers.

EXPERIMENTAL

Materials

Octamethylcyloteterasiloxane (D$_4$) came from the Chengdu Center of Organosilane (Chengdu, China). The silane-coupling agent (KH-570) was a product of

TABLE I
Recipes Used for Polymerization
of the PDMS Seeded Latex

Ingredients	Recipe I (g)	Recipe II (g)
DBSA	13	3
H_2O	75	57
D_4	—	40
KH-570	—	2

the Nanjing Shuguang Chemical Factory (Nanjing, China). VAc, a product of the Shanghai Sanpu Chemical Corp. (Shanghai, China), was distilled under normal pressure prior to use to remove the inhibitor. BA and MAA, from the Beijing Dong Fang Chemical Factory (Beijing, China) and the Tianjin Nankai Chemical Factory (Tianjin, China), respectively, were distilled under reduced pressure prior to use. Potassium persulfate (KPS) was product of the Beijing Chemical Factory (Beijing, China). Dodecyl benzene sulfonic acid (DBSA), a product of the Shanghai Zhongxin Chemical Factory (Shanghai, China), was used as a surfactant and catalyst. Deionized water was used for all experiments.

Preparation of the seeded latex

PDMS, a seeded latex, was prepared by polymerization of D_4 in a 500-mL three-neck flask (TNF) equipped with a mechanical stirrer and reflux condenser. First, the TNF was initially charged with recipe I (see Table I). Then, when the temperature of the mixture increased to $80 \pm 0.5°C$, recipe II was trickled slowly to the TNF by a drop funnel at a 300-rpm stirring rate and the polymerization proceeded for about 8 h. In the end, PDMS seeded latex was obtained, whose pH value was adjusted subsequently to 5–6 through a 10 mass % sodium hydroxide aqueous solution.

Preparation of PA latex (PDMS/VAc-*co*-BA)

PA latex containing $-O-\overset{\overset{\textstyle O}{\|}}{C}-CH_3$ and $-\overset{\overset{\textstyle O}{\|}}{C}-O-C_4H_9$ groups (used for the preparation of the complex latex) was synthesized by seeded emulsion polymerization in the TNF. In the beginning, 165 g PDMS seeded latex and 10 g comonomers with a 7:3 mass ratio of VAc to BA were added to the TNF. When the temperature of the mixture was increased to $80 \pm 0.5°C$, 100 g of a 0.12 mass % initiator solution was added at a rate of 20 g/h at a 300-rpm stirring rate. After 1 h, the remaining 30 g of the comonomers of VAc and BA were trickled slowly to the TNF. Four hours later, the comonomers were trickled to the TNF completely and the temperature was in-

creased to $85 \pm 0.5°C$ for about 4 h. Then, the system was cooled naturally and PA latex was obtained.

Preparation of PB latex [PDMS/poly (MAA)]

The preparation of PB latex containing $-\overset{\overset{\textstyle O}{\|}}{C}-OH$ group (used for the preparation of the complex latex) was similar to that of the PA latex. In the beginning, 65 g PDMS seeded latex and 10 g MAA were added to the TNF. When the temperature of the mixture was increased to $80 \pm 0.5°C$, 100 g of a 0.12 mass % initiator solution was added at a rate of 20 g/h at a 300-rpm stirring rate. After 1 h, 30 g MAA was trickled slowly to the TNF. During the late reaction, the viscosity of the latex increased rapidly and 90 g H_2O was added 0.5 h later; the system was cooled naturally and PB latex was obtained.

Preparation of the PA/PB complex latex

The PA/PB complex latex was obtained by mixing PA latex and PB latex in different proportions of the PA latex to the PB latex at ambient temperature.

Preparation of the coatings

The coatings were obtained by casting the polymer latexes (the PA latex, the PB latex, and the PA/PB complex latex) on a glass substrate and the evaporation of water at ambient temperature.

Measurements

Surface-tension measurements of the polymer latexes were performed on a Krüss K10ST digital tensiometer thermostat at $25 \pm 0.1°C$ using a platinum plate. Viscosity measurements of the polymer latexes were performed on an LVDV-4-type Brookfield viscometer thermostat at $25 \pm 0.1°C$ using a 18 spindle.

Surface-composition measurements of the coatings were carried out on an XSAM 800-type XPS using a MgKα X-ray (1253.6 eV) source operating at 10 kV and 7 mA with a take-off angle of 90°. All peaks were referenced to the C1s (C in C—C or C—H) peak at 284.8 eV. The surface compositions were calculated using the areas of the respective photoelectron peaks after correction with sensitivity factors. Surface-morphology measurements of the coatings were carried out on an SPA 400-type scanning probe microscope from Seiko Instruments, Inc.

RESULTS AND DISCUSSION

Analysis of surface tension of the latexes

Figure 1 shows variation of the surface tension of the complex latexes with different mass ratios of PA latex to
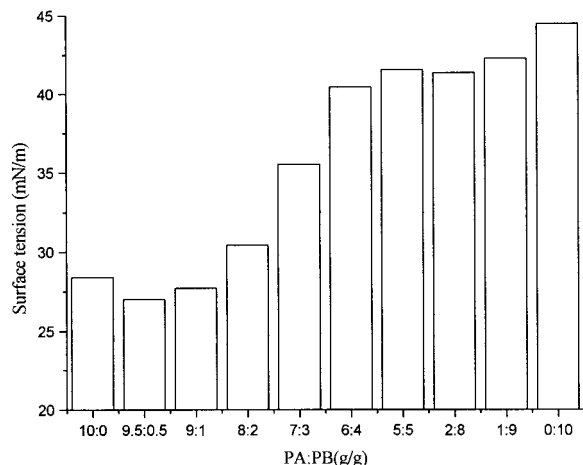
Figure 1 Surface tension of the complex latexes with different proportions of PA latex to PB latex.

PB latex. It can be seen that when the ratios PA:PB (mass ratios) are 9.5:0.5 and 9:1, the surface tension of the complex latexes are smaller than those of the component latexes; when the ratios PA:PB are 5:5 and 2:8, the surface tension of the complex latexes are nearly the same. The results indicate indirectly that there is interaction between

$$-O-\overset{\overset{O}{\|}}{C}-CH_3 \quad (or \quad -\overset{\overset{O}{\|}}{C}-O-C_4H_9) \text{ groups in PA}$$

and $-\overset{\overset{O}{\|}}{C}-OH$ groups in PB through hydrogen bonding and it gives rise to the formation of a complex (see Scheme 1).

It is well known that the surface tension of polymer latex, as an indication of intermolecular forces, is closely related to the structure of the chain units of the polymer. When the polar groups are introduced to the chain units, the surface tension of the polymer latex increases due to the stronger van der Waals forces be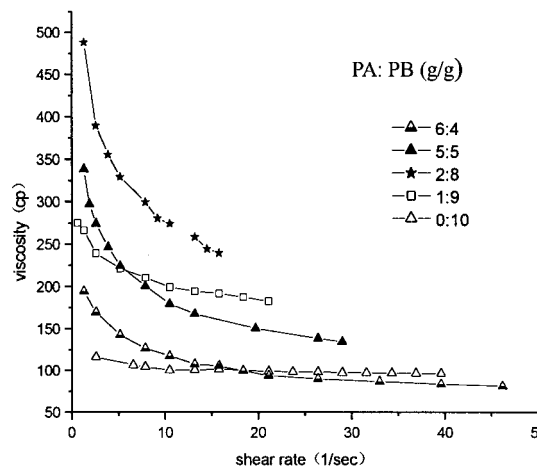tween the macromolecules. In the experiment, PA has $-O-\overset{\overset{O}{\|}}{C}-CH_3$ and $-\overset{\overset{O}{\|}}{C}-O-C_4H_9$ groups and PB

$R_1=CH_3$
$R_2=n\text{-}C_4H_9$

PA   PB
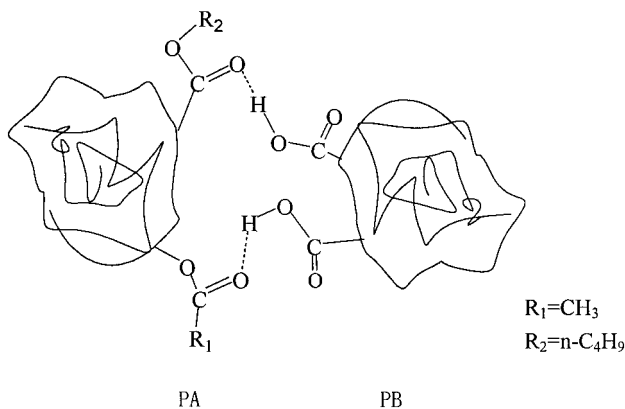
Scheme 1 Complexation of PA latex with PB latex.
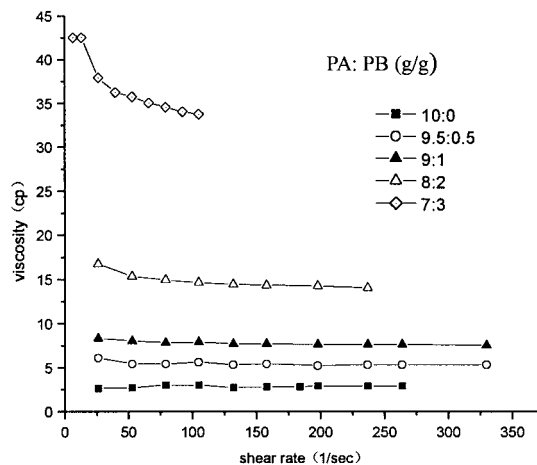
(a)

(b)

Figure 2 Shear-rate dependence of viscosities of the complex latexes with different proportions of PA latex to PB latex.

has $-\overset{\overset{O}{\|}}{C}-OH$ groups. When PB latex is mixed with PA latex, there are two effects on the surface tension of the complex latexes at the same time: The first effect is that the introduction of polar groups (especially the $-\overset{\overset{O}{\|}}{C}-OH$ group) increases the van der Waals forces between the macromolecules and makes the surface tension of the complex latex tend to increase accordingly; the second effect is that the formation of the complex by the interactions of the $-O-\overset{\overset{O}{\|}}{C}-CH_3$, $-\overset{\overset{O}{\|}}{C}-O-C_4H_9$ groups with the $-\overset{\overset{O}{\|}}{C}-OH$ group through hydrogen bonding weakens the polarity of the functional groups and makes the surface tension of
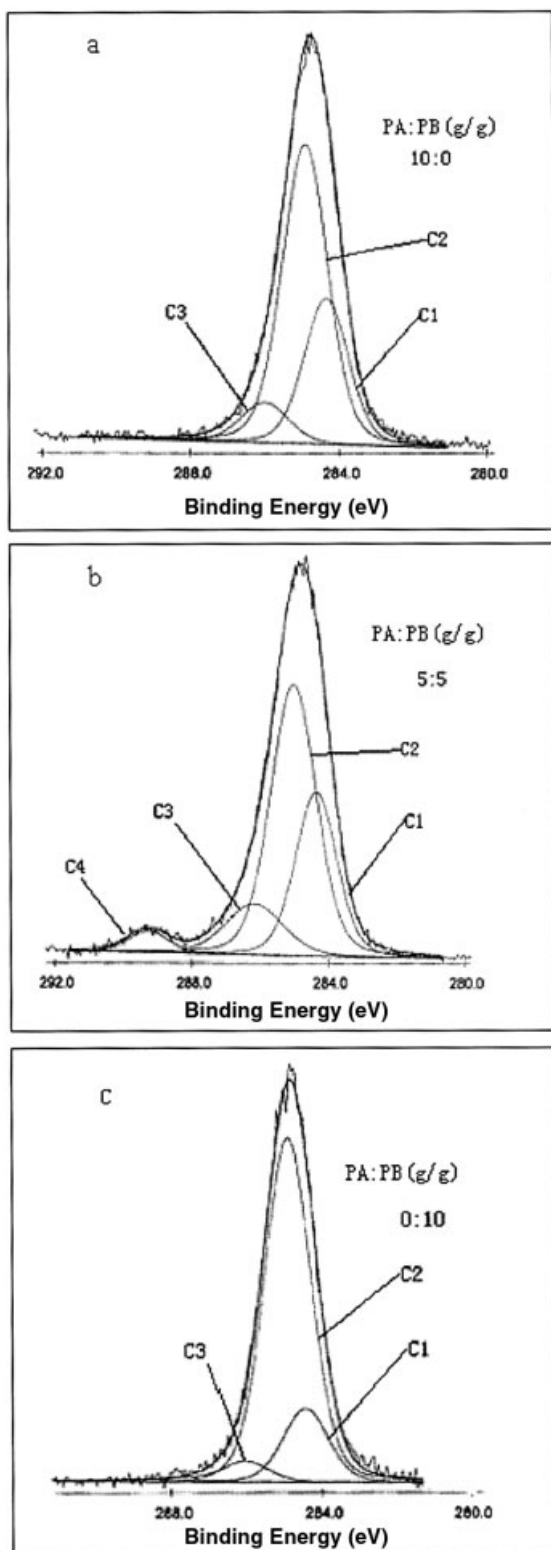
Figure 3 High-resolution XPS Cls spectra of the coatings formed from (a) PA latex, (b) PA/PB complex latex, and (c) PB latex.

the complex latex tend to decrease. Hence, when the latter effect is stronger than the former, with increase of the carboxyl group in the complex latex, the surface

tension of the complex latex does not increase accordingly.

Analysis of viscosity of the latexes

Figure 2 shows the shear rate dependence of the viscosities of the complex latexes with different proportions of the PA latex with the PB latex. From Figure 2, three results can be drawn: First, with increase of the shear rate, the viscosities of the two component latexes, that is, the PA latex (ca. 3 cP) and the PB latex (ca. 100 cP), fluctuate slightly, while those of the complex latexes decrease in different grades according to different proportions of the PA latex to the PB latex. When the content of the PB latex in the complex latex is lower, the viscosities of the complex latex decrease slightly [see Fig. 2(a)]. For example, when the shear rate is 26.4 s^{-1}, the viscosity of the complex latex with an 8:2 mass ratio of PA to PB is 16.7 cP, and when the shear rate is 264 s^{-1}, the viscosity is 14.0 cP. When the content of the PB latex increases continually [see Fig. 2(b)], with increase of the shear rate, the viscosities of the complex latexes decrease greatly, behaving as shearing thinning fluids. For example, when the shear rate is 1.3 s^{-1}, the viscosity of the complex latex with a 2:8 mass ratio of PA to PB is 488 cP, and when the shear rate is 13.2 s^{-1}, the viscosity is 258 cP. Second, when the content of PB is lower [see Fig. 2(a)], at a certain shear rate, with increase of the content of the PB latex, the viscosities of the complex latexes increase; for example, at a 105 s^{-1} shear rate, the viscosities of the complex latexes with 9.5:0.5, 9:1, 8:2, and 7:3 mass ratios of the PA latex to the PB latex are 5.6, 7.9, 14.6, and 33.7 cP, respectively. When the content of the PB latex increases to a certain degree, the viscosities of the complex latexes do not always increase with increase of the content of the PB latex [see Fig. 2(b)]; for example, at a certain shear rate, the viscosity of the

TABLE II
Relative Areas of the Peaks in the XPS Spectra (Fig. 2)
of Coatings Formed from Different Latexes

Parameter	C1	C2	C3	C4
Sample 1				
Bonding energy (eV)	284.94	284.36	286.01	—
Area (%)	61.9	29.4	8.7	0
Sample 2				
Bonding energy (eV)	285.03	284.36	286.17	289.27
Area (%)	54.1	29.5	12.7	3.7
Sample 3				
Bonding energy (eV)	284.91	284.43	286.04	—
Area (%)	78.6	16.5	4.9	0

Sample 1: coatings formed from the PA latex; sample 2: coatings formed from the PA/PB complex latex with 5:5 mass ratio of PA to PB; sample 3: coatings formed from the PB latex. C1, C2, C3, and C4 represent C in C—C, C—SI, C—O, and O—C=O, respectively.
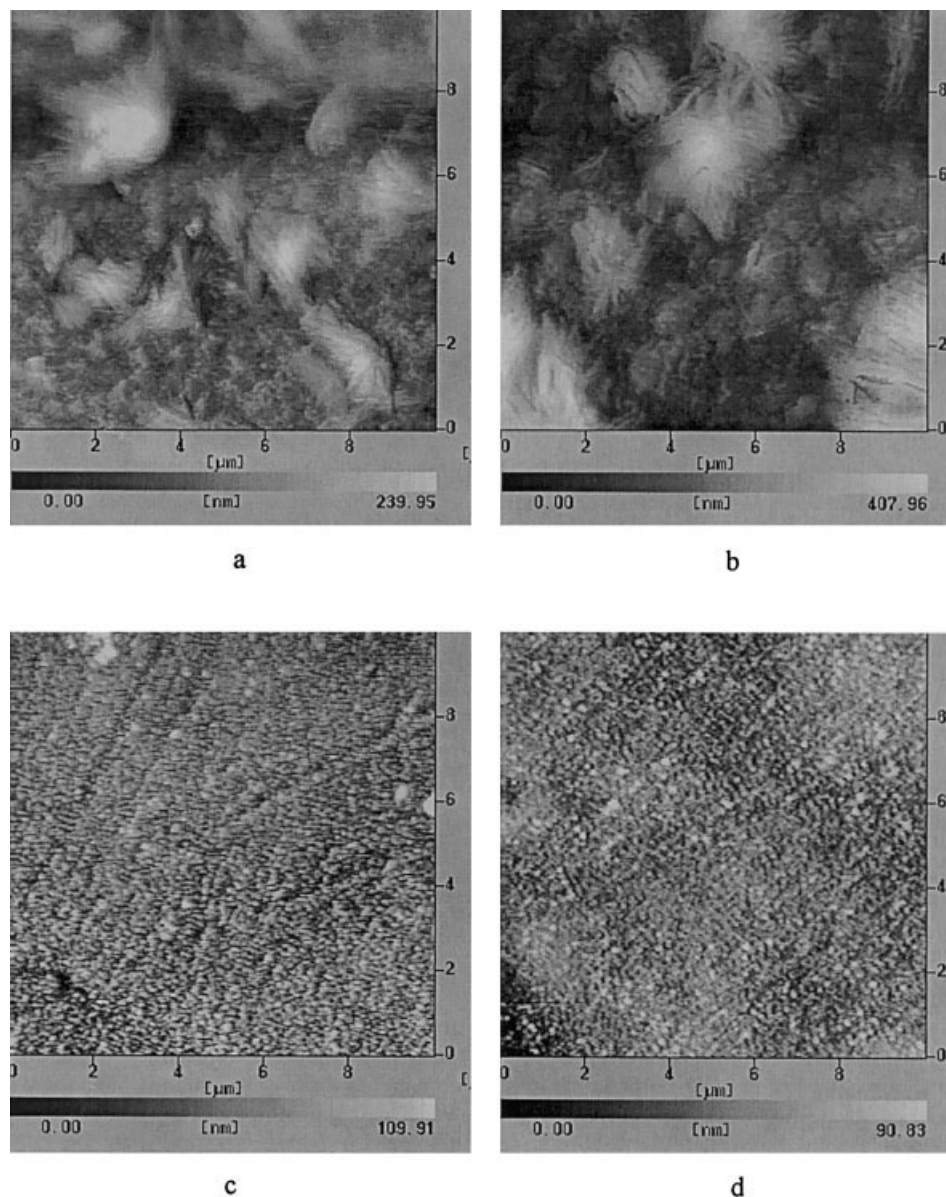
Figure 4 SPM images of the coatings formed from (a) PA latex, (b) PA/PB complex latex with 9:1 mass ratio of PA latex to PB latex, (c) PA/PB complex latex with 5:5 mass ratio of PA latex to PB latex, and (d) PB latex.

complex latex with a 2:8 mass ratio of PA latex to PB latex is higher than that of the complex latex with a 1:9 mass ratio of PA latex to PB latex. Third, it can be seen that when the ratios PA:PB are 1:9, 2:8, and 5:5, the viscosities of the complex latexes are obviously higher than those of the PA latex and the PB latex [see Fig. 2(b)].

As to the latex system, the viscosity of the latex depends mostly on the structure and size of the latex particles, and the intermolecular interactions (including interaction between the latex particles and the H_2O molecules and interactions among the latex particles). When the PA latex is mixed with the PB latex in different proportions, interactions between the parti-

cles of the PA latex with the PB latex give rise to the formation of the complex, as has been proved by the surface-tension measurement. When the interactions between particles with chemically complementary structures become stronger, the intermacromolecular complexation of the PA latex with the PB latex is to a higher degree, and the size of the complex becomes bigger, leading to an enhancement in the viscosity of the complex latex. When the content of the PB latex is lower, the complexation of the PA latex with the PB latex is weaker and cannot be shown macroscopically. With increase of the content of the PB latex, the interactions between particles with a chemically complementary structure become stronger, resulting in an
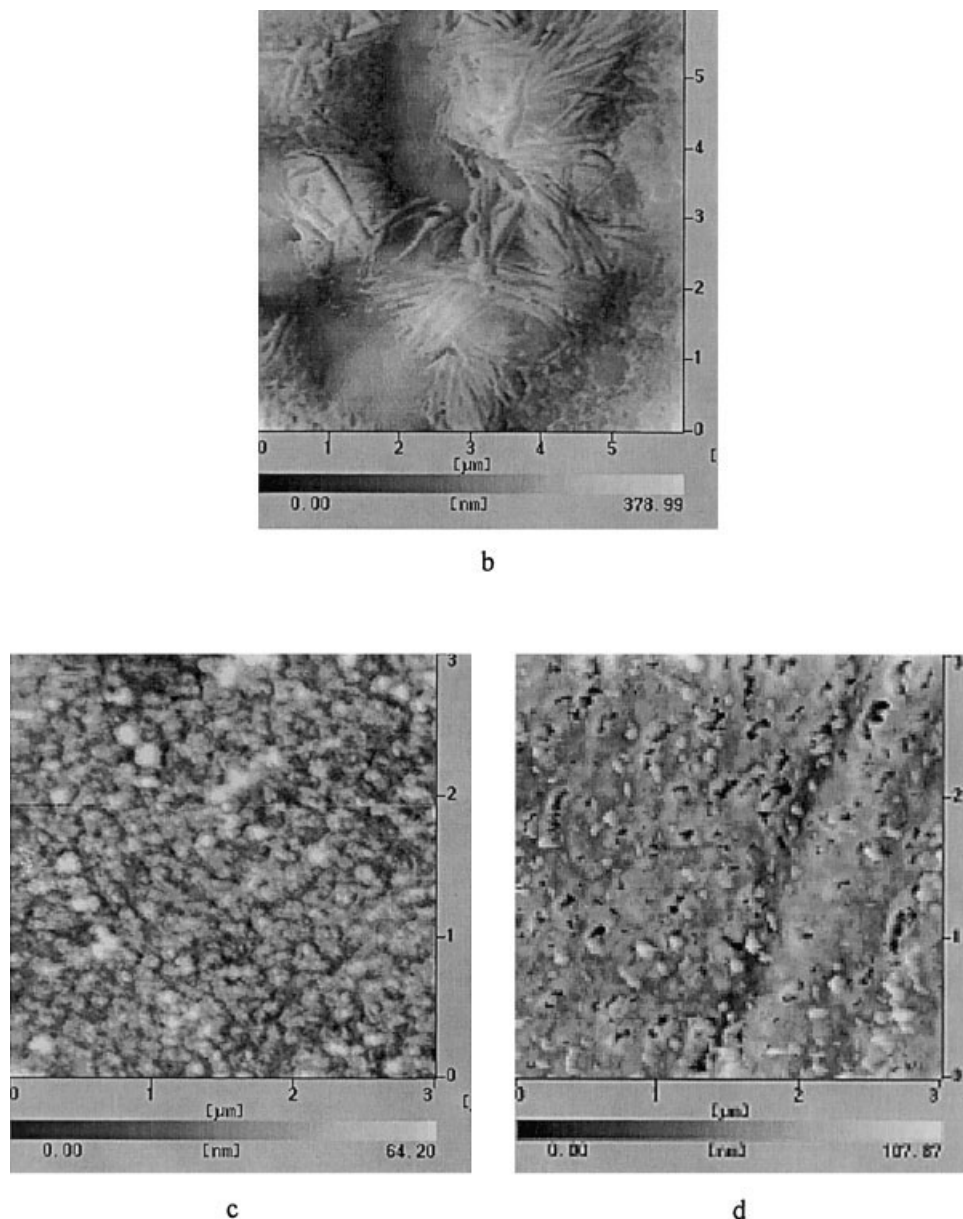
Figure 5 Enlarged SPM images of the coatings formed from (b) PA/PB complex latex with 9:1 mass ratio of PA latex to PB latex, (c) PA/PB complex latex with 5:5 mass ratio of the PA latex to the PB latex, and (d) PB latex.

increase of the complexation of PA latex with PB latex and, hence, enhancing the viscosities of the complex latexes. It can be said that the viscosity of the complex latexes depends mostly on the degree of the complexation. This phenomenon is similar to that in the case of homogeneous complexation of two polymers with chemically complementary structures in an aqueous solution reported by Dan and Wang.[8]

Analysis of surface compositions of the coatings

Figure 3 shows a high-resolution XPS spectrum of coatings formed from the PA latex [Fig. 3(a)], the PB latex [Fig. 3(c)], and the PA/PB complex latex with a 5:5 mass ratio of PA to PB [Fig. 3(b)]. Based on the compositions of coatings and the standard XPS spectra, there are three peaks in spectrum (a), four peaks in spectrum (b), and three peaks in spectrum (c). Table II shows the relative areas of the peaks in the XPS spectra of coatings formed from the PA latex, the PB latex, and the PA/PB complex latex. It can be seen from Figure 3 that C4 (C in O—C=O) can be observed in sample 2, but nearly cannot be observed in samples 1 and 3, indicating, further, the formation of a new structure in the coatings formed from the PA/PB complex latex.

The above phenomenon can be explained as follows: According to the surface theory, during the for-

mation of coatings, the polymer undergoes self-assembly in air to minimize the surface energy. The carboxyl group and ester group are polar groups and may increase the surface energy of the coatings, so they mostly move away from the coatings surface. When PA and PB was mixed, the $-\!O\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!CH_3$ and $-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!O\!-\!C_4H_9$ groups in PA and $-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!OH$ groups in PB interact with each other through hydrogen bonding, which inhibits the movement of the carboxyl group and ester group away from the surface. As a result, a new peak appeared for sample 2, which represents C4 (C in O—C=O).

Analysis of surface morphologies of the coatings

Scanning probe microscopy (SPM) was recently applied to the surface characterization and investigation of polymers with a nanometer scale without special sample treatment. In this article, SPM was employed to probe the surface structures of the coatings formed from the two-component polymer latexes and the two complex latexes with 9:1 and 5:5 mass ratios of PA latex to PB latex. Figure 4 shows SPM images of the obtained coatings. It can be seen that when the mass ratios of PA latex to PB latex are different the images of the coatings are different. Practically, the particles distributed on the surface of the coatings formed from the PA latex [see Fig. 4(a)] are larger than are the particles (about 90 nm) on the surface of the coatings formed from the PB latex [see Fig. 4(d)]; at the same time, the former is more uneven in shape and size because of the interparticle congregation. To observe the surface morphologies of the coatings more clearly, the images were enlarged [see Fig. 5(b–d)].

In comparing the coatings obtained from PA latex [Fig. 4(a)], the coatings obtained from the PB latex [Fig. 5(d)] has an apparent biphase structure. From the appearances of the SPM images, Figure 4(b) and 4(a) and Figure 4(d) and 4(c) are similar, respectively. The former two have an irregular and bigger particle shape and the latter two behave more regular and smaller particles. However, there are differences between them: In Figure 4(a), the particles are isolated, while in Figure 4(b) [especially in Fig. 5(b)], the particles are interlinked; in other words, in contrast to Figure 4(a), the morphologies of the particles from the complex latex [Fig. 5(b)] consist of intertwisting clumps. In addition, the degree of phase separation in the coatings obtained from the complex latex with a 5:5 mass ratio of PA latex to PB latex is weaker than that in the coatings obtained from the PB latex. From Figure 4(a, b)], it also can be found that a small-quantity incorporation of PB results in the SPM images of coatings formed from the PA latex and the complex latex being different.

The surface morphologies of the coatings formed from the complex latexes are obviously different from the surface morphologies of the coatings formed from the component latexes, because there are interparticle interactions in the complex latexes between $-\!O\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!CH_3$ and $-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!O\!-\!C_4H_9$ groups in PA and $-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!OH$ groups in PB. It is the interparticle interactions of the polymer latex particles with chemically complementary structures that leads to the formation of the new and unique structures of the coatings, which have been proved by the surface tension, viscosity measurements and XPS, and SPM measurements.

CONCLUSIONS

A complex latex with stronger interparticle interactions was obtained through complexation of the two-polymer latexes with chemically complementary structures. The surface composition and morphologies of the coatings formed from the complex latex are different from those of the coatings formed from the component latex. The complexation of two-polymer latexes with chemically complementary structures may be an effective approach to prepare new water-borne coatings.

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