

# Surface Structure and Properties of Water-Based Polymer Coating Materials Prepared by the Complexation of Two Polymer Latices with Chemically Complementary Structures

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**ABSTRACT:** In this study, water-based polymer coating materials used for the surface coating of substrates with lower surface energies were prepared by the complexation of two-component polymer latices containing polydimethylsiloxane (PDMS) and having chemically complementary structures. The film-forming performance of the polymer latices and the surface structures and properties of the coatings formed by the polymer latices were studied by means of scanning electron microscopy and by the measurement of mechanical strength, thermal performance, water absorbability, and contact angle. When the two-component polymer latices [the poly(methyl methacrylate-*co*-butyl acrylate-*co*-methyl acrylic acid)/polydimethylsiloxane system (PA latex) and the poly(methyl methacrylate-*co*-butyl acrylate-

*co*-pyrrolidone)/polydimethylsiloxane system (PB latex)] were compared, the complex polymer latex formed by the complexation of the PA latex with the PB latex had the best film-forming performance, with formed coatings that were more smooth and had fewer less cracks. Also, compared to the two coatings formed by the two-component polymer latices, the coatings formed by the complex polymer latex had a unique structure, a higher mechanical strength and elongation, a higher decomposing temperature, and better water resistance. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1748–1754, 2003

**Key words:** coatings; surfaces; structure; latices

## INTRODUCTION

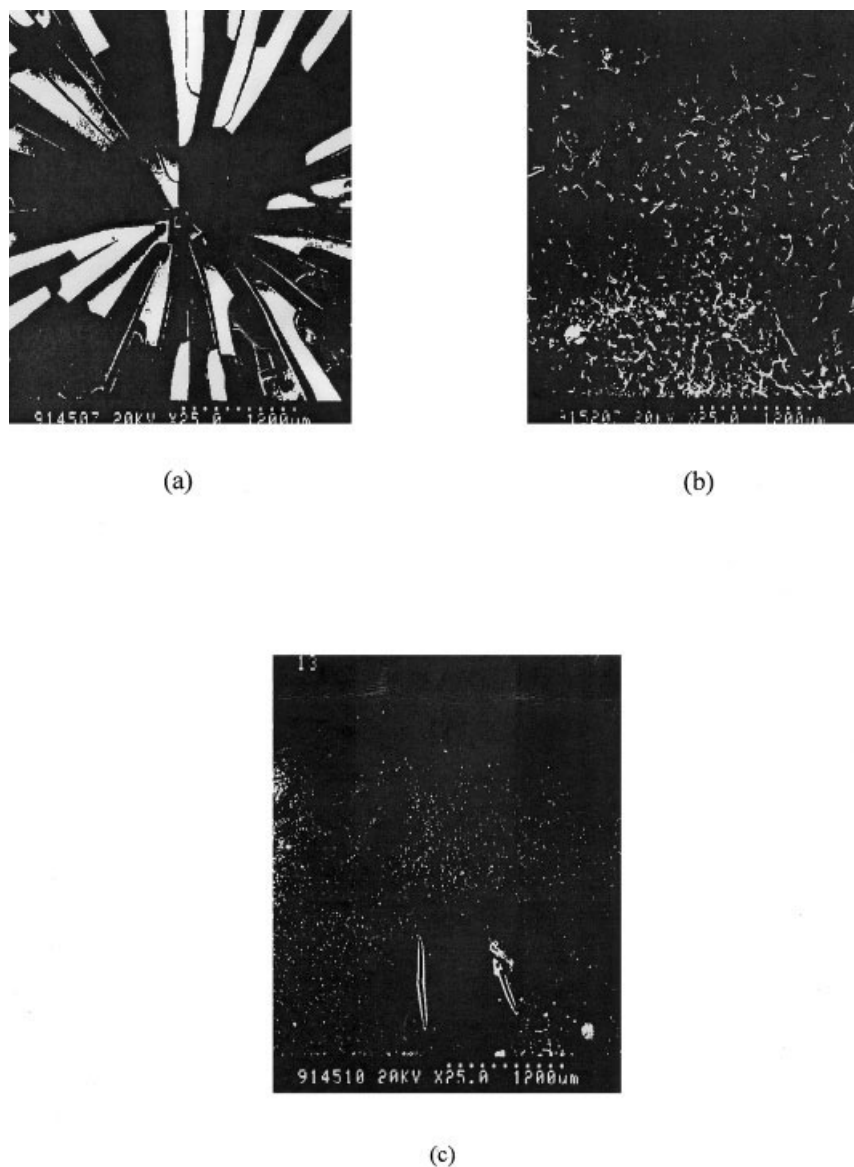
With the effects mankind has had on the environment, water-based polymer coating materials are attracting more and more attention<sup>1–2</sup> because they can replace harmful solvent-based coating materials in such areas as paints, adhesives, and ink and, hence, can reduce volatile organic compounds to a minimum. Based on the polymer–medium systems, water-based polymer coatings materials can be prepared via three approaches: (1) the dissolution of water-soluble polymers in aqueous solution or the polymerization of water-soluble monomers in aqueous solution to form a polymer solution; (2) the suspension of polymers in water to form a polymer suspension, which can also be easily obtained by suspension polymerization of the monomers; and (3) the dispersion of polymers in water to form a polymer latex or polymer dispersion, which can also be easily obtained by emulsion poly-

merization of the monomers. Usually, coating materials prepared by the first approach have poor water-resistance properties because of the dissolution of the polymer in water and cannot be used in many fields. The polymer suspension is also not appropriate for forming coatings because of the larger particle size. However, the polymer latex is widely used to form coatings because of its smaller particle size and because of the good properties of the obtained polymers; for example, they have higher molecular weights, better mechanical strengths, and better water resistance.

In general, the polymer latex can be obtained through various emulsion polymerization techniques, such as conventional emulsion polymerization, seeded emulsion polymerization, core–shell emulsion polymerization, and microemulsion polymerization, among which the conventional emulsion polymerization technique is the simplest and the easiest, but the structure and properties of the polymer latex produced by this method are not so satisfactory in some cases because of the limitations of this approach. Seeded emulsion polymerization is a effective technique for ensuring a steady process. The other techniques can produce polymers with desired structures and some unique properties, but the processes are rather difficult. In this article, a complex polymer latex

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**Figure 1** SEM pictures of coatings casted from (a) PA latex, (b) PB latex, and (c) PA/PB complex latex (with a 20/40 mass ratio of PA to PB) onto a glass substrate at 25 $\times$ .

with a desired structure and properties was first produced through the complexation of two polymer latices with chemically complementary structures, which could easily be prepared by conventional emulsion polymerization. Thus, the new approach had advantages such as (1) it was simple and easy to prepare the desired water-based coating materials, (2) the complexation ratio of the two polymer latices was adjustable, and hence, (3) the interparticle interactions were adjustable, which resulted in the ability to control the structure and properties of the coating materials.

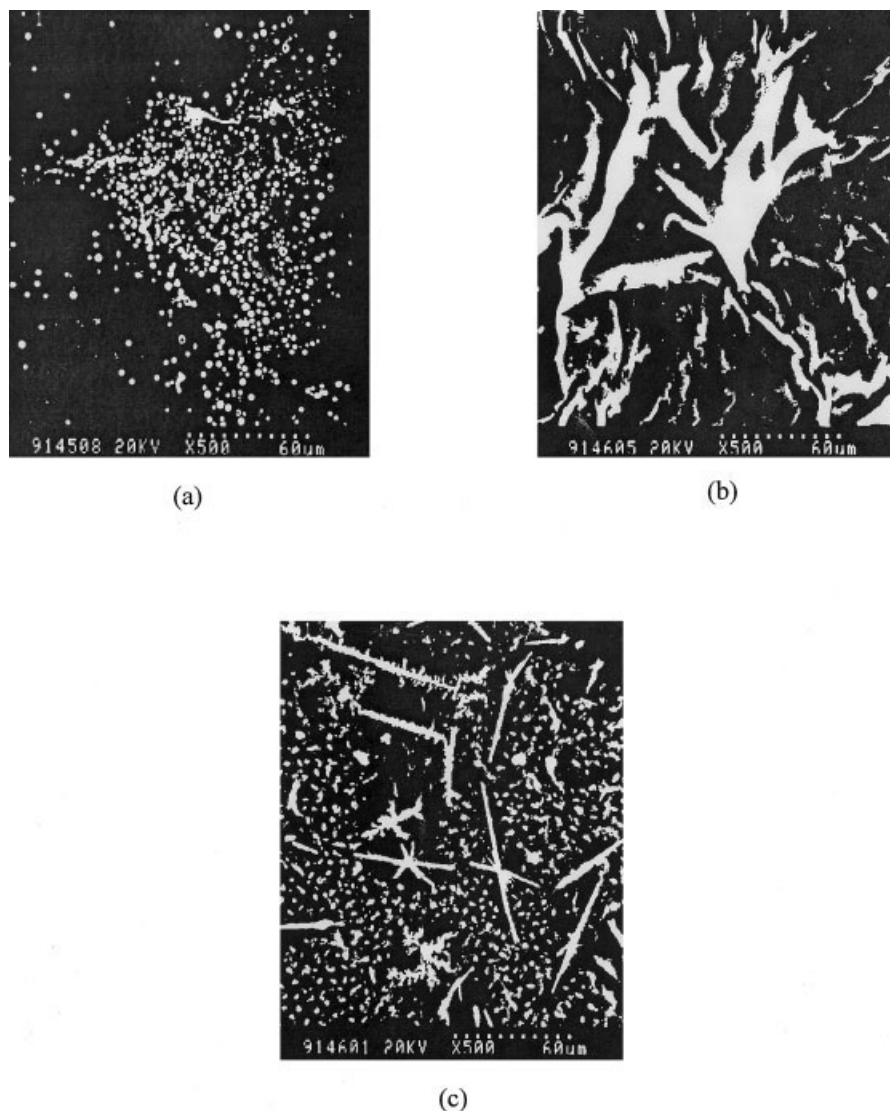
The complexation of two polymers with chemically complementary structures is an effective way to improve polymer properties; this is usually reported for intermacromolecular interactions in either polymer solution or polymer bulk.<sup>3-8</sup> The interparticle interac-

tions of two polymer latices with chemically complementary structures, however, have not been reported. This article is the first to report the preparation of a complex polymer latex and the surface structure and properties of the water-based coating materials formed through interparticle interactions.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) and methyl acrylic acid (MAA), products of the Chongqing Dong Fang Hong Chemical Factory (China), and butyl acrylate (BA), a product of the Beijing Dong Fang Chemical Factory (China), were purified by rectification. Vinyl pyrrolidone



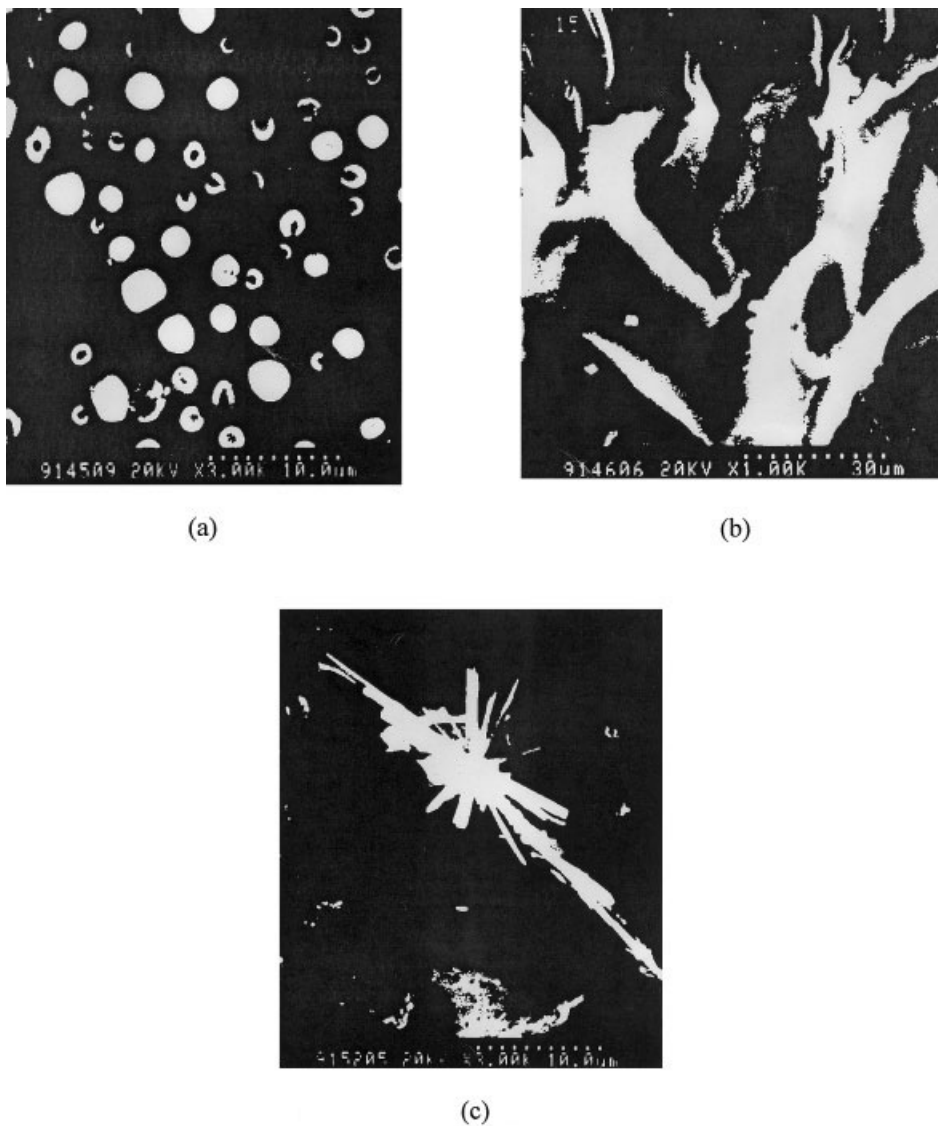
**Figure 2** SEM pictures of coatings casted from (a) PA latex, (b) PB latex, and (c) PA/PB complex latex (with a 20/40 mass ratio of PA to PB) onto a glass substrate at 500 $\times$ .

(VP), from Beijing Oilfield Chemistry Corp. (China; 99.99% content), was used without further purification. Potassium persulfate (KPS) and sodium dodecyl sulfate were products of the Beijing Chemical Factory (China) and the Wu Han Chemical Factory (China), respectively, and both chemicals were of analysis-grade purity. Octamethylcyloetrasiloxane ( $D_4$ ) came from the Chengdu Center of Organosilane. Dodecyl benzene sulfonic acid (DBSA) and its Na salt (DBSAS) were products of the Shanghai Zhongxin Chemical Factory (China) and were also of analysis-grade purity. Deionized water was used for all of the experiments.

#### Preparation of the two-component polymer latices containing polydimethylsiloxane (PDMS)

The two-component polymer latices containing PDMS were prepared through seeded emulsion polymeriza-

tion with PDMS latex as the seed. The practical method was as follows. First, the PDMS seed latex was obtained by the anionic emulsion polymerization of  $D_4$  in deionized water with DBSA as a catalyst and DBSAS as an emulsifier. The  $D_4$  content in the feed was 5–10 mass %, the reaction temperature was 70–90 $^{\circ}\text{C}$ , and the reaction time was 60–90 min. After the PDMS seed latex was obtained, the comonomers (e.g., MMA/BA/MAA and MMA/BA/VP) and initiator (KPS) were introduced gradually to the seed latex, but no new emulsifier was added in case of the formation of the new particles. At this stage, the reaction temperature was also 70–90 $^{\circ}\text{C}$ , and the reaction time was 3–5 h. At last, the two-component polymer latices containing PDMS, poly(methyl methacrylate-*co*-butyl acrylate-*co*-methyl acrylic acid)/polydimethylsiloxane latex (PA latex) and poly(methyl methacrylate-*co*-bu-



**Figure 3** SEM pictures of coatings casted from (a) PA latex, (b) PB latex, and PA/PB complex latex (with a 20/40 mass ratio of PA to PB) onto a glass substrate at (c) 3000× or (d) 1000×.

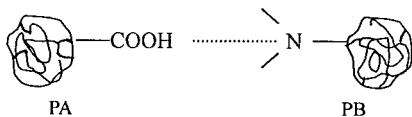
tyl acrylate-co-pyrrolidone)/polydimethylsiloxane latex (PB latex), were obtained.

**Preparation of the PA/PB complex polymer latex and the coatings**

The PA/PB complex polymer latex was produced by mixture of the PA latex and the PB latex at ambient temperature and 25 mass % polymer content. The

mixing ratio (mass ratio) of the former to the latter was from 10:50 to 50:10.

The coatings was prepared by the casting of the polymer latex (PA latex, PB latex, and PA/PB complex latex) onto glass and plastics substrates. After 3 days, the coatings were formed and dried and could then be characterized.



**Figure 4** Schematic diagram of the interparticle interactions through the hydrogen bonding of the —COOH group in PA with the N— group in PB.

**Characterization**

The surface structure and shape of the coatings were detected with a Hitachi-X650 scanning electron microscope. The thermal properties of the coatings were measured on a LCT-1 theormeter in a nitrogen atmosphere and at a heating rate of 10°C min<sup>-1</sup>.

The water resistance of the coatings was determined by a weight method. First, a 10 × 10 mm coating

**TABLE I**  
**Film-Forming Performance of the Polymer Latices and the Mechanical Properties of the Obtained Coatings**

PA/PB (g/g)	Film-forming performance of the polymer latex	$S$ (MPa)	$\epsilon$ (%)
60/0	Heaving cracking, not entire film	—	—
20/40	Entire film, only fewer cracks	2.27	178
10/50	Entire film, fewer cracks	1.94	164
0/60	Some entire film but undrying	1.31	158

sample was taken and dipped in water for a certain time (from 2 to 50 h). If the weights of the sample before and after dipping in water are  $W_1$  and  $W_2$ , respectively, the swelling ratio ( $W\%$ ) of the sample can be calculated as follows:

$$W\% = [(W_2 - W_1)/W_1] \times 100\%$$

A smaller  $W\%$  corresponds to better water resistance, whereas a greater  $W\%$  indicates poorer water resistance.

The mechanical properties of the coatings were measured on a XL-100A meter, and the mechanical strength and elongation of the coatings were calculated as follows:

$$S = F/A$$

$$\epsilon = [(L_1 - L_0)/L_0] \times 100\%$$

where  $S$  is the tensile strength (MPa),  $F$  is the force (N),  $A$  is the area ( $m^2$ ), and  $\epsilon$  is the elongation rate (%) at break of the coating sample and  $L_1$  and  $L_0$  are the

lengths (m) of the sample before and after elongation, respectively.

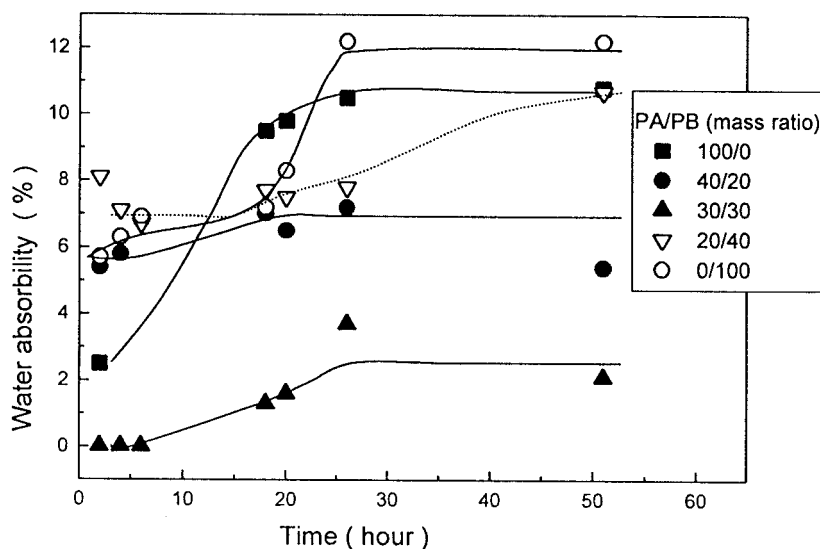
The contact angles of other liquids on the coatings were determined with a contact angle meter at 25°C.

## RESULTS AND DISCUSSION

Figures 1–3 show the scanning electron microscopy (SEM) pictures of coatings casted from the two-component polymer latices (the PA latex and the PB latex) and the PA/PB complex polymer latex with a 20:40 mass ratio of PA to PB latex onto a glass substrate at different magnifications.

At an enlargement of 25 $\times$  (Fig. 1), the whole picture of the sample is shown. As shown in Figure 1, the coatings casted from the PA latex showed many cracks that irradiated from the center of the coating to the edge, indicating that the polymer was rather brittle; coatings casted from the PB latex showed many small lines and were not dryable because of the water absorbency of the VP component and the existence of the PDMS, which was totally different from the former. The coatings casted from the complex polymer latex obtained through the mixture of the PA latex with the PB latex with a 20:40 mass ratio of PA to PB was smooth and only slightly cracked, indicating that the film-forming performance of the complex polymer latex was much better than the two-component polymer latices; that is, the complexation of two polymer latices with chemically complementary structures favored the improvement of the film-forming performance of the polymer latex.

When the SEM magnification was enlarged from 25 to 500 $\times$  (Fig. 2) and 3000 or 1000 $\times$  (Fig. 3), the surface



**Figure 5** Variation of the water absorbabilities of the coatings formed by the two-component polymer latices and the complex polymer latices with time.

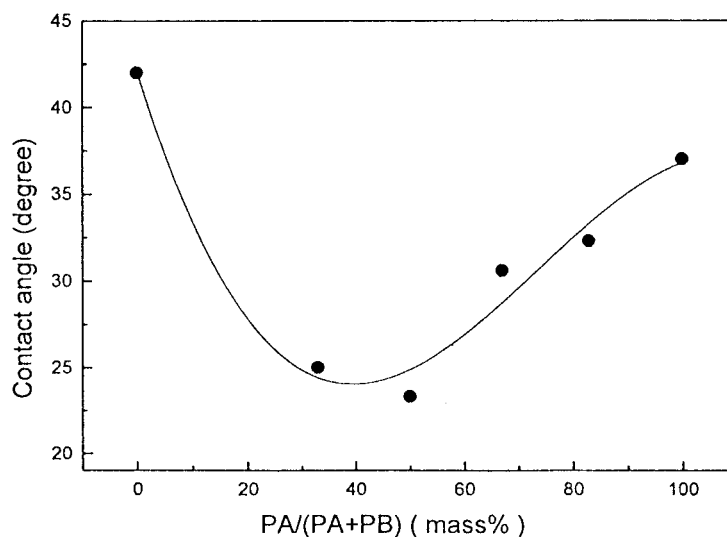


Figure 6 Variation of the contact angles of xylene on the coatings with mixing ratio of PA latex to PB latex.

structure of the coatings and the differences among the three coatings were more clear.

When the areas were locked and the magnification of the pictures was enlarged to 500, 3000, or 1000 $\times$ , many particles were visible in the picture of the coatings formed by the PA latex [Figs. 2(a) and 3(a)], indicating that the coatings was formed by coadhesion of the particles, and the shape of the particles was nearly spherical. In the PA system, the structure of the polymer was comprised of such units as MMA, MAA, and BA. According to the recipe of the system, the obtained polymer had a higher glass-transition temperature ( $T_g$ ), which made its particles exist in a single and regular shape. In the pictures of the coatings formed by the PB latex [Figs. 2(b) and (3b)], however, there were no spherical particles, but many heavier lines appeared, indicating that the latex particle was shaped during the coating formation because of the softer polymer particles. In the PB system, the obtained polymer was comprised of VP, MMA, and BA units, in which the VP unit was highly water-absorbed. The attack of water molecules on the coating or the polymer particles made the polymer particles softer and more changeable, which led to irregularly shaped particles that were not dryable. In the picture of the coatings formed by the PA/PB complex polymer latex [Figs. 2(c) and 3(c)], a very different result is shown in which not only many small particles were shaped but also many dendrenks appeared, indicating an interparticle interaction through the hydrogen bonding of  $-\text{COOH}$  groups in PA with  $\text{N}$  groups in PB (see the schematic diagram in Fig. 4) and the self-assembly of the particles with chemically complementary structures. According to the principle of intermacromolecular complexation, if the chemical structures of the macromolecules are complementary,

there will exist intermacromolecular interactions through Coulomb forces, hydrogen bonding and hydrophobic associations, and so on that are weaker than chemical bonds but much stronger than interactions between molecules with the same chemical structure. In this experiment, the intermacromolecular complexation was first introduced to interparticle interactions to prepare water-based coating materials used for coating substrates with lower surface energies. The unique shape and structure of the complex coatings certainly resulted in specific properties, examples of which follow.

Table I gives results of the mechanical strength and elongation at break measurements of the obtained coatings. The coating obtained from the complex polymer latex not only had a higher mechanical strength but also a larger elongation at brake; this offers a new approach to the production of polymer coating materials with the enhancement of both the strength and the deckle. Because the PA latex seldom form an entire film, probably because of the higher  $T_g$  of the polymer, and had many cracks in the coatings, the mechanical strength and the elongation of the obtained coatings could not be measured.

Figure 5 shows water resistance of the coatings formed by the two-component polymer latices and the complex polymer latices with 40:20, 30:30, and 20:40 mass ratios of PA to PB. It was obvious that after they were dipped in water for about 10 h, the water absorbabilities of the three coatings formed by the complex polymer latex were lower than that of the two coatings formed by the two-component polymer latices, and the water absorbability of the coating formed by the 30/30 complex polymer latex was the lowest. A lower water absorbability reflects a better water resistance. The results indicate that complexation of the

two polymer latices with chemically complementary structures enhanced the water resistance of the coatings because of interparticle interactions and intermacromolecular interactions through hydrogen bonding. The excellent water resistances of the complex coatings came from the unique surface structures of the coatings (see Figs. 1–3). As shown in Figure 5, with increasing dipping time of the coatings in water, the water absorbabilities of the all of the coatings increased, and they attained a steady state after a certain time. For different coatings, the times to reach a steady water absorbability were different. Higher contents of PB resulted in longer times to get to a steady water absorbability in the formed coatings.

Figure 6 shows the variation of the contact angles of xylene on the coatings with the mixing ratio of PA to PB. The contact angles of xylene on the coatings formed by the complex polymer latices were smaller than those on the coatings formed by the two-component polymer latices, indicating that the surface structure of the coatings formed by the complex polymer latex was different from that of the coatings formed by the two-component polymer latices. This result further proves the interparticle interactions in the complex coatings through hydrogen bonding. It was the interparticle interactions that resulted in the change in the surface structures of the coatings and the change in the surface properties.

The results in Table II show that among the three coatings, the coatings formed by the PA/PB complex latex had the highest decomposition temperature, at 514°C, further indicating interactions between —COOH groups in PA and  $\text{>N—}$  groups in PB. This result was

**TABLE II**  
**Thermal Properties of the Coatings Obtained from the PA, PB, and PA/PB Complex Latices**

Coating system	Decomposition temperature (°C)
PA	483
PA/PB	514
PB	477

consistent with the SEM and water absorbability measurements.

## CONCLUSIONS

The complexation of two polymer latices with chemically complementary structures was an effective method for the preparation of a new water-based polymer coating material. Interparticle interactions of the polymer latex particles with different groups led to the formation of coatings with unique surface structures and properties; this method is a promising new way to prepare water-based polymer coatings.

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