

Complexation of Poly(dimethylsiloxane)/Poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) Latex with Poly(dimethylsiloxane)/Poly(vinyl acetate-*co*-butyl acrylate) Latex

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ABSTRACT: Two latices—the poly(dimethylsiloxane) (PDMS)/poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) system (PA latex) and the PDMS/poly(vinyl acetate-*co*-butyl acrylate) system (PB latex)—were prepared by seeded emulsion polymerization, and PA/PB complex latices were obtained through the interparticle complexation of the PA latex with the PB latex. In addition, for the further study of the interparticle complexation of the PA latex with the PB latex, copolymer latices [PDMS/methyl methacrylate-*co*-butyl acrylate-*co*-vinyl acetate-*co*-methacrylic acid) (PC)] were prepared according to the monomer recipe of the complex latices and the polymerization process of the component latices. The properties of the obtained polymer latices and complex latices were investigated with surface-tension, contact-angle, and viscosity

measurements. The mechanical properties of the coatings obtained from the latices were investigated with tensile-strength measurements. The results showed that, in comparison with the two component latices (PA latex and PB latex) and the corresponding copolymer latices (PC latices), the PA/PB complex latices had lower surface tension, lower viscosities, and better wettability to different substrates. The tensile strengths of the coatings obtained from the complex latices were higher than the tensile strengths of the coatings from the two component latices and copolymer latices. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2522–2527, 2004

Key words: latices; emulsion polymerization; polysiloxanes; mixing; coatings

INTRODUCTION

The intermacromolecular complexation of two polymers with chemically complementary structures is a new and effective approach to making new polymer materials and to modifying the polymers, which have become more and more interesting and attractive. The studies in the literature concerning intermacromolecular complexation are primarily focused on precipitated complexes^{1–3} and complex solutions.^{4–8} As for complex latices, related studies are mostly focused on the performance combination of two polymer latices;^{9–11} few works concern complexation in chemically complementary structures.

A combination of two latices with chemically complementary structures may result in some special properties different from those of original components because of intermacromolecular complexation.^{12,13} In this study, a method of intermacromolecular complexation with chemically complementary structures

was used with a latex system to prepare water-borne coatings with new and unique structural properties.

People's increasing environmental consciousness has inspired the use of water as a partial or total replacement of solvents. Research on water-borne coatings, especially those with low surface energy, is more and more important,^{14,15} and complex latices are promising for applications in water-borne coatings.

In this study, two latices—the poly(dimethylsiloxane) (PDMS)/poly(methyl methacrylate-*co*-butyl acrylate-*co*-methacrylic acid) system (PA latex) and the PDMS/poly(vinyl acetate-*co*-butyl acrylate) system (PB latex)—were prepared by seeded emulsion polymerization, and complex PA/PB latices were obtained through the complexation of the PA latex with the PB latex. The wettability of the complex latices on the substrates, the rheological properties of the complex latices, and the mechanical properties of the coatings from the latices were investigated.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D₄) came from the Chengdu Center of Organosilane (Chengdu, China). The silane coupling agent (KH-570) was a product of

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Nanjing Shuguang Chemical Factory (Nanjing, China). Vinyl acetate (VAc), a product of Shanghai Sanpu Chemical Corp. (Shanghai, China), was distilled under normal pressure before it was used for the removal of the inhibitor. *n*-Butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA), supplied by Beijing Dong Fang Chemical Factory (Beijing, China), Rongfeng Chemical Reagents Factory (Chengdu, China), and Tianjin Nankai Chemical Factory (Tianjin, China), respectively, were distilled under reduced pressure before they were used. Potassium persulfate was a product of Beijing Chemical Factory (Beijing, China). Dodecyl benzene sulfonic acid (DBSA), a product of Shanghai Zhongxin Chemical Factory (Shanghai, China), was used as a surfactant and catalyst. Sodium bicarbonate, used as a pH regulator, came from Shanghai Waigang Chemical Factory (Shanghai, China). Sodium hydroxide, used as a pH regulator, was a product of Chengdu Chemical Reagent Factory (Chengdu, China). Deionized water was used for all the experiments.

Preparation of the seeded latex

PDMS (seeded latex) was prepared by the polymerization of D_4 in a 500-mL, three-necked flask (TNF) equipped with a mechanical stirrer and a reflux condenser. First, 26 g of DBSA and 150 g of H_2O were added to the TNF; when the temperature of the mixture rose to $80 \pm 0.5^\circ\text{C}$, the mixture emulsion, obtained from 6 g of DBSA, 114 g of H_2O , 80 g of D_4 , and 4 g of KH-570, trickled slowly into the TNF through a drop funnel at a stirring rate of 300 rpm, and the polymerization proceeded for about 8 h. In the end, the PDMS seeded latex was obtained, the pH value of which was subsequently adjusted to 5–6 with a 10 mass % sodium hydroxide aqueous solution.

Preparation of the PA latex

The PA latex, used for the preparation of the complex latex, was synthesized by seeded emulsion polymerization in a TNF equipped with a mechanical stirrer and a reflux condenser. In the beginning, 59 g of the PDMS seeded latex, 48 g of deionized water, and 17 g of the comonomers in a 8 : 12 : 1 mass ratio of MMA to BA to MAA were added to the TNF. When the temperature of the mixture rose to $50 \pm 0.5^\circ\text{C}$, the temperature was kept constant for 0.5 h, and then the temperature was increased to $80 \pm 0.5^\circ\text{C}$. A 0.143 mass % initiator solution (28 g) was added at a rate of 7 g/h at a stirring rate of 300 rpm. After 1 h, 67 g of the remaining comonomers trickled slowly into the TNF; at the same time, 16 g of a 2.5 mass % sodium bicarbonate solution was added at regular intervals. Three to four hours later, the comonomers began to trickle to the TNF completely, and the temperature was in-

creased to $85 \pm 0.5^\circ\text{C}$ for about 2 h. Then, the system was cooled naturally, and the PA latex was obtained. The solid content of the PA latex was 39.9 mass %.

Preparation of the PB latex

The preparation of the PB latex was similar to that of the PA latex. In the beginning, 47.2 g of the PDMS seeded latex, 48 g of deionized water, and 16 g of the comonomers in a 12 : 8 mass ratio of VAc to BA were added to a TNF. When the temperature of the mixture rose to $50 \pm 0.5^\circ\text{C}$, the temperature was kept constant for 0.5 h, then the temperature was increased to $75 \pm 0.5^\circ\text{C}$. A 0.143 mass % initiator solution (28 g) was added at a rate of 7 g/h at a stirring rate of 300 rpm. After 1 h, 64 g of the remaining comonomers began to trickle slowly into the TNF; at the same time, 16 g of a 2.5 mass % sodium bicarbonate solution was added at regular intervals. Three to four hours later, the comonomers trickled into the TNF completely, and the temperature was promoted to $80 \pm 0.5^\circ\text{C}$ for about 2 h. Then, the system was cooled naturally, and the PB latex was obtained. The solid content of the PB latex was 39.7 mass %.

Preparation of the PA/PB complex latices

The solid content of PA was adjusted to 39.7 mass % with deionized water. The PA/PB complex latex was obtained by the mixing of the PA latex and the PB latex in different proportions of the PA latex and the PB latex at the ambient temperature. The mass ratio of the PA latex to the PB latex ranged from 1 : 9 to 9 : 1.

Preparation of the copolymer latices [PDMS/methyl methacrylate-*co*-butyl acrylate-*co*-vinyl acetate-*co*-methacrylic acid) (PC)]

The copolymer latices were prepared according to the monomer recipe of the complex latices and the polymerization process of the component latices (here, the prepared latices are called copolymer latices to distinguish them from the complex latices). For example, the main monomer recipe of the copolymer latex with a 4.86 molar content of MAA (based on the content of the monomers added to the total polymer latex), corresponding to the complex latex with a 2 : 8 mass ratio, was 35.8 g of the PDMS seeded latex, 16 g of MMA, 28.3 g of BA, 2 g of MAA, and 6.4 g of VAc. Copolymer latices with 1.11, 1.75, and 3.53 molar contents were also prepared. The corresponding relationship of the —COOH content of the copolymer latices with the PA/PB ratio of the complex latices is shown in Table I.

Preparation of the coatings

The coatings were obtained through the casting of the polymer latices onto glass vessels paved with polyeth-

TABLE I
Relationship Between the —COOH Content of the Copolymer Latices and the PA/PB Ratio of the Complex Latices

	PA/PB (complex latices)			
	2 : 8	4 : 6	6 : 4	8 : 2
—COOH content (copolymer latices; mol)	1.11	1.75	3.53	4.86

ylene (PE) film and the evaporation of water at the ambient temperature.

Surface tension measurements

These measurements of the polymer latices were performed on a Krüss K10 ST digital tensiometer (Germany) at $25 \pm 0.1^\circ\text{C}$ with a platinum plate.

Viscosity measurements

These measurements of the polymer latices were performed on a Brookfield LVDV-4 viscometer (USA) at $25 \pm 0.1^\circ\text{C}$ with a #0 spindle.

Contact-angle measurements

These measurements of the polymer latices were performed on a contact-angle apparatus (Optionbutton, Japan) at $10 \pm 0.5^\circ\text{C}$. The contact angle was made through the placement of polymer latex droplets (ca. 5 μL) on the solid specimens [glass, PE, polyester (PU), etc.] with a 1-mL pipette. The reported results of the measurements are the average values of 10 tests.

Tensile-strength measurements

These measurements for the coatings formed by polymer latices were performed on an XL-100A tensile test machine (Guangzhou, China) at $10 \pm 0.5^\circ\text{C}$. The tensile rate was 200 mm/min. The samples for the tensile strength were obtained according to the literature.¹⁶

RESULTS AND DISCUSSIONS

Analysis of the surface tension of the latices

Figure 1 shows the variation of the surface tension of the complex latices with different mass ratios of the PA latex to the PB latex. The surface tensions of the complex latices with the different mass ratios are lower than that of the component latex PA; when the PA/PB ratio is 1 : 9, the surface tension of the complex latex is smaller than that of the two component latices (PA and PB). The results indicate that interparticle complexation can make the surface tension of the latex

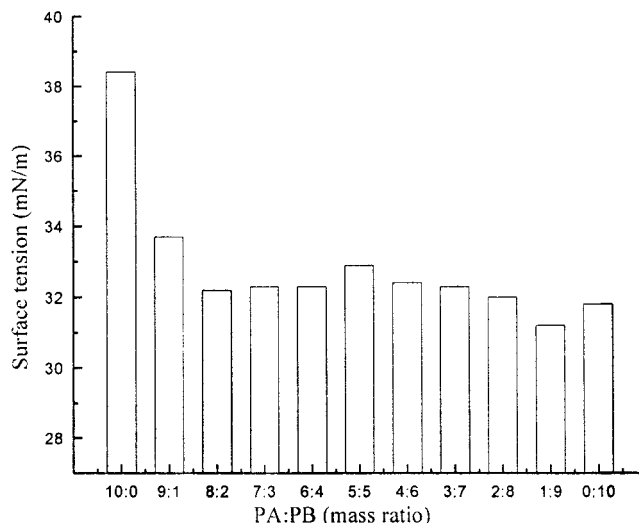


Figure 1 Surface tension of the complex latices with different proportions of the PA latex and the PB latex.

lower; this agrees with the conclusion drawn from a previous experiment.¹⁴

Furthermore, to investigate the interactions between different functional groups of the complex latex particles, we also prepared the copolymer latices according to the monomer recipes of the complex latices and the polymerization process of the component latices; they were differentiated by different —COOH molar contents. A comparison of the surface tensions of the complex latices and the copolymer latices is shown in Figure 2. With an increase in the —COOH molar content, the surface tensions of the complex latices do not vary obviously, whereas those of the copolymer latices increase distinctly, and the surface tensions of the complex latices are lower than those of the corre-

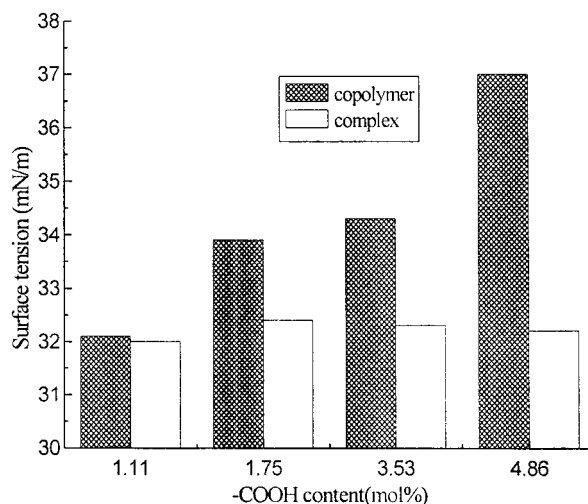


Figure 2 —COOH content dependence of the surface tension of the PA/PB complex latices and the copolymer latices.

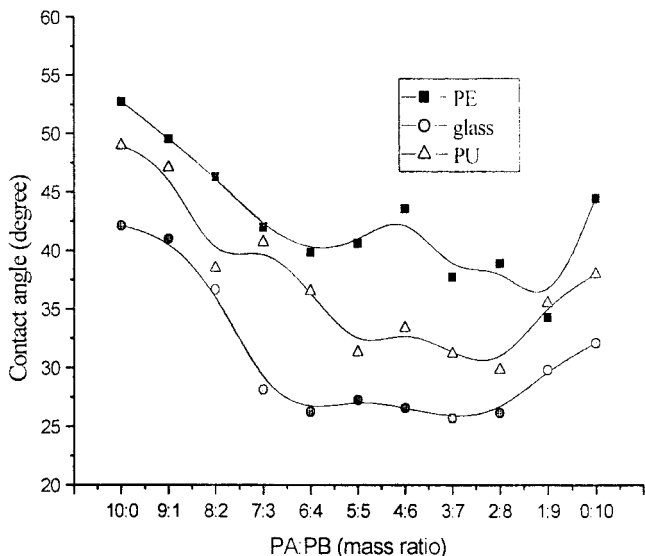


Figure 3 Contact angle of the complex latices with different proportions of the PA latex and the PB latex.

sponding copolymer latices. The results indicate that interparticle interactions between different functional groups can reduce the surface tension of the polymer latex.

Analysis of the contact-angle measurements of the complex latices

The contact angles of the polymer latices on three substrates (glass, PE, and PU) are shown in Figure 3. For a certain latex, the contact angle of the latex on the PE substrate is the largest, whereas that on the glass substrate is the smallest. However, for a certain substrate, when the mass ratio of the PA latex to the PB latex is 7 : 3 to 1 : 9, the contact angle of the complex latices is smaller than that of the component latices. To further study the contact angles of the complex latices on the substrates, we compared the contact angles of the complex latices and the corresponding copolymer latices with the same —COOH molar contents on the same substrates; the results are shown in Figure 4. With respect to a certain substrate (PE, glass, or PU), the contact angle of the complex latex is always lower than that of the copolymer latex, and this indicates that interparticle complexation can make the contact angles of the latices on the substrates smaller.

The contact angle is useful in indicating the extent to which a liquid will spread on a given solid. When the contact angle is greater than 90°, wettability is poor; when the contact angle is less than 90°, however, wettability is good but not perfect. The smaller the contact angle is, the better the wettability is. According to wettability theory,¹⁷ the wettability of a liquid on a solid is related to the surface tension of the solid and that of the liquid. The lower the surface tension of

the liquid is with respect to that of the solid, the smaller the contact angle is of the liquid on the solid, and the better the wettability is of the liquid on the solid. Among the PE, PU, and glass substrates, the surface energy of PE is the lowest, whereas that of the glass is the highest. Correspondingly, the contact angle of a certain latex on the PE substrate is the largest, whereas that on the glass substrate is the smallest. Because the surface tensions of the complex latices are lower than those of the component latices and the corresponding copolymer latices, as confirmed in the surface-tension section, the contact angles of the complex latices on a certain substrate are lower than those of the component latices and the corresponding copolymer latices on the same substrate.

Interparticle interactions between different functional groups make the surface tension of the complex latex lower, resulting in smaller contact angles of the complex latices on the substrates; that is, the wettability of the complex latices on the substrate is better.

Analysis of the viscosity of the latices

The shear-rate dependence of the viscosities of the complex latices with different proportions of the PA latex and the PB latex is shown in Figure 5. For a certain latex, with the variation of the shear rate, the viscosity does not obviously change; the viscosity of a complex latex with a 9 : 1 mass ratio of PA to PB is obviously lower than that of the component latex PA. With an increase in the content of the PB latex, there is a slight fluctuation among the viscosities of the other complex latices. The viscosities of the complex latices with 3 : 7, 2 : 8, and 1 : 9 mass ratios of PA to PB are a little lower than that of the component latex PB.

The viscosities of the complex latices and the corresponding copolymer latices measured at a shear rate of 24.4 s⁻¹ are compared in Figure 6. With an increase

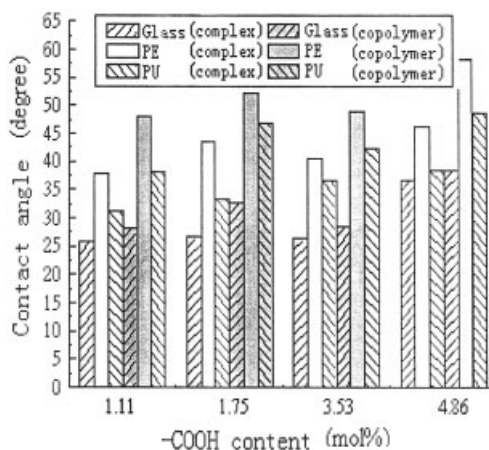


Figure 4 —COOH content dependence of the contact angle of the PA/PB complex latices and the copolymer latices.

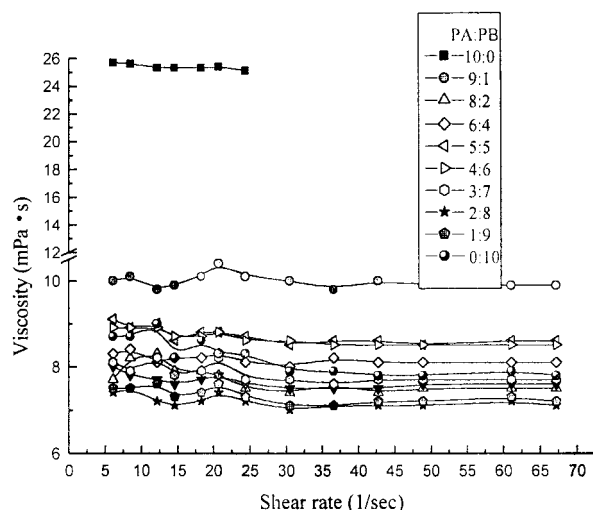


Figure 5 Shear-rate dependence of the viscosities of the complex latices with different proportions of the PA latex and the PB latex.

in the —COOH molar content, the viscosities of the complex latices do not change obviously, whereas those of the copolymer latices increase greatly.

The viscosity of latex is mostly related to such factors as the structure and size of the latex particles, interactions between the latex particles, and interactions between the latex particles and continuous phase. Concretely, in this study the viscosity of the complex latices exhibits complex trends; the latices may exhibit decreasing viscosity after mixing, remain relatively constant with respect to their viscosity, or exhibit increasing viscosity. This depends greatly on the interactions between the latex particles and interactions between the latex particles and continuous phase. Interactions between the latex particles cause two simultaneous effects. First, interparticle interactions make the polarity of the surface groups of the

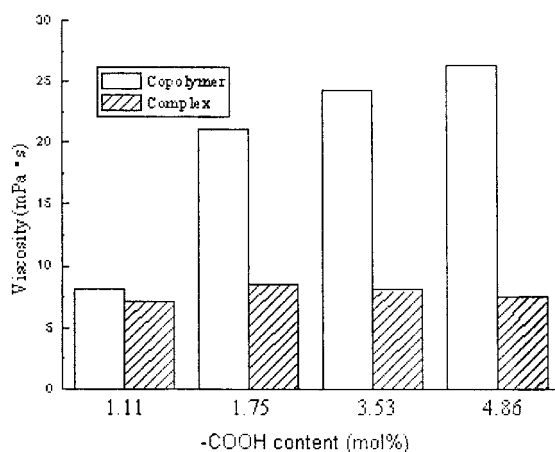


Figure 6 Comparison of the viscosities of the complex and copolymer latices at a shear rate of 24.4 s^{-1} .

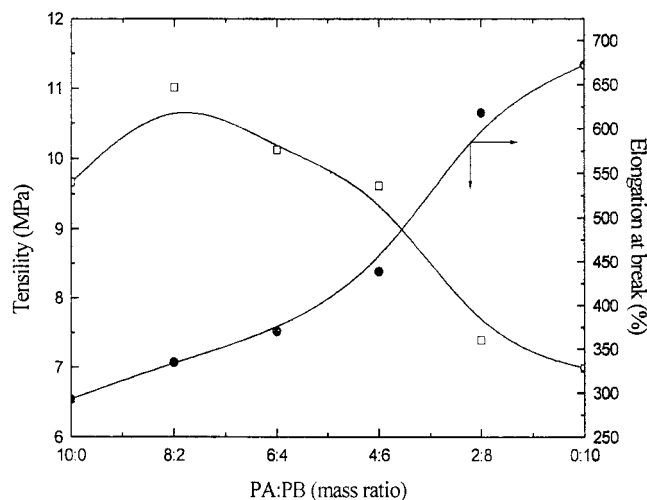


Figure 7 Tensile strength of the coatings obtained from the PA/PB complex latices with different proportions of the PA latex and the PB latex.

latex particles decrease, as confirmed by surface-tension measurements of the complex latices, and this further weakens the interactions between the latex particles and continuous phase, resulting in a decrease in the viscosity of the complex latices. Second, interparticle interactions make the particles larger, and this results in an increase in the viscosities of the complex latices. When the latter effect is the primary one, the viscosities of the complex latices increase; this also occurred in our previous study.¹⁴ When the former is the primary one, however, the viscosities of the complex latices decrease. On the basis of these experimental results, the interactions between the latex particles reduce the polarity of the surface groups, and this results in a decrease in the viscosities of the complex latices.

Analysis of the mechanical strength of the coatings formed by the complex latices

Figure 7 shows the results of the tensile-strength measurements of the coatings formed by the complex latices with different proportions of the PA latex and PB latex. With an increase in the content of the component latex PB, the tensile strength of the obtained coatings from the complex latices increases first and then decreases. The tensile strengths of the coatings formed by the complex latices with 8 : 2 and 6 : 4 mass ratios of the PA latex to the PB latex are higher than those of the coatings formed by the component latices. Concretely, the tensile strength of the coatings formed by the component latex PA is 9.7 MPa, whereas that of the coatings formed by the complex latex with an 8 : 2 mass ratio of the PA latex to the PB latex is 11.0 MPa, and that from the complex latex with a 6 : 4 mass ratio of the PA latex to the PB latex is 10.1 MPa. In addition,

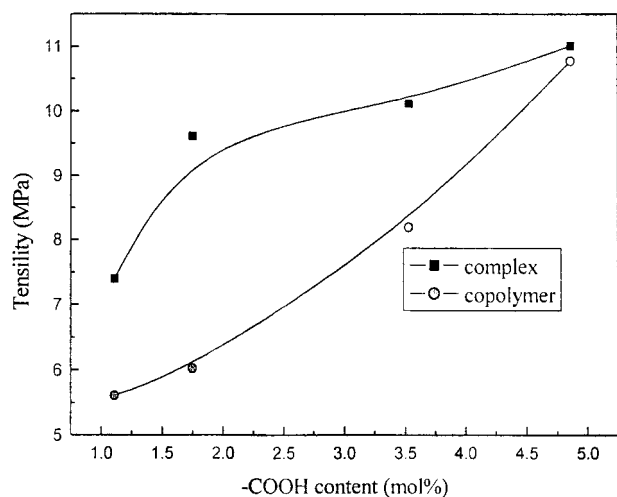


Figure 8 Comparison of the tensility of the coatings obtained from the complex and copolymer latices.

the tensile breaking elongation of the coatings increases with an increase in the content of the component latex PB. The results for the tensile strengths of the coatings formed from the complex latices and the corresponding copolymer latices with the same monomer recipe are shown in Figure 8. Obviously, the tensile strength of the former is higher than that of the latter.

From this research, it can be concluded that the complex latices have lower surface tension, lower viscosities, and better wettability to different substrates than the two component latices. The tensile strength of the coatings obtained from the complex latices with an 8 : 2 mass ratio of the PA latex to the PB latex is higher than that of the coatings obtained from the component latices. The tensile strength of the coatings obtained from the complex latices is greater than that of the

coatings obtained from the corresponding copolymer latices.

CONCLUSIONS

On the basis of intermacromolecular complexation, the interparticle complexation of polymer particles with chemically complementary structures has been found in this study and a previous study, and a novel approach has been proposed for preparing new polymer latices with unique characteristics and properties.

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