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Morphological Prediction and Its Application to the Synthesis of Polyacrylate/Polysiloxane Core/Shell Latex Particles

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ABSTRACT: A theoretical analysis and a morphological prediction of polyacrylate (PA)/ polysiloxane (PSi) latex particles with core/shell morphologies were first conducted based on interfacial tensions and relative volumes of the two polymers in the latex system. The results indicated that the normal core/shell morphology particles (PSi/PA), with hydrophobic polysiloxane as the core and with hydrophilic polyacrylate as the shell, can be easily formed. Although the inverted core/shell morphology particles (PA/PSi) with polyacrylate as the core could not be formed in most cases, even if the fraction volume of polysiloxane was larger than 0.872, which is the smallest value of forming a PA/PSi particle, the PSi/PA particles were unavoidably formed simultaneously with PA/PSi particle formation. The synthesis of PA/PSi particles containing equal amounts of polyacrylate and polysiloxane was then carried out using seeded emulsion polymerization. Before the cyclosiloxane cationic polymerization, 3-methacryloyloxypropyl trimethoxysilane (MATS) was introduced into the polyacrylate seed latex to form an intermediate layer and chemical bonds between the core and the shell polymers. The characterization by transmission electron microscopy (TEM) demonstrated that the perfect PA/PSi core/shell particle is successfully synthesized when both the core and the shell polymers are crosslinked. The experiments showed that both the hardness and water adsorption ratio characteristics of latex films of the PA/PSi particles are in good agreement with those of the polysiloxane film. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2251–2258, 2001

Key words: morphological prediction; polyacrylate; polysiloxane; interfacial tension; core/shell latex particle

INTRODUCTION

Latex particles with a well-controlled morphology are an extremely important class of materials used in coatings, adhesives, impact-resistance plastics, and many other materials. How to predict and control the latex particle morphology to achieve desirable physical properties has been a major subject over the past few decades.[1–7] Although most of the studies have focused on the composite latex particles prepared from methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), and vinyl acetate (VAc), only a few reports are available that investigate the system of siloxane and acrylic monomers.[8–10]

It is common knowledge that it is much easier to obtain core/shell morphology particles by seeded emulsion polymerization when the core polymer is more hydrophobic than is the shell polymer. With regard to polyacrylate and polysiloxane, their difference in polarity is very large; in addition, the former is usually synthesized through radical mechanism, whereas the latter is often prepared through ring-opening polymerization of cyclosiloxane. These considerations make the emulsion polymerization system of acrylic monomers and siloxane complicated in theoretical study. In applications, polysiloxane has many specific properties by virtue of its good water repellency, lubricity, weather resistance, high flexibility, and excellent thermal stability. In comparison to polysiloxane, polyacrylate exhibits quite different properties such as good cohesiveness, high-gloss and transparency, and excellent film-forming properties. Therefore, the combination of polyacrylate with polysiloxane has been of importance and interest during the past few decades, and various kinds of polyacrylate/polysiloxane latices concerning interpenetrating polymer networks (IPN) and graft copolymers have been synthesized by many researchers.[11–17] To date, few clear photographs with core/shell morphologies were given, although some of the latices were prepared by seeded emulsion polymerization, which is often considered as the best process for producing core/shell latex particles, and few reports on the polyacrylate (core)/polysiloxane (shell) latex particles (PA/PSi) were given except our previous work.[10]

In this study, the requisites for core/shell latex particle morphologies were first analyzed by thermodynamic consideration, then the synthesis of PA/PSi latex particles was carried out using seeded emulsion polymerization; the particle morphology was then characterized using transmission electron microscope (TEM); the phase structure and some properties of the latex films were also investigated.

EXPERIMENTAL

Materials

Octamethyl cyclotetrasiloxane (D_4) was provided by 4th Petrochemical Plant of Jinan and fractionated under reduced pressure before use. 3-Methacryloyloxypropyl trimethoxysilane (MATS) was from Aldrich (Milwaukee, WI). Chemically pure

tetraethoxy silane (TES, crosslinking agent for polysiloxane) was purchased from Beijing Chemical Reagent Plant. The analytical reagents BA, MMA, and ethylene glycol dimethacrylate (EGDMA, crosslinking agent for polyacrylate) were all from Shanghai Chemical Reagent Plant and purified before use. Dodecylbenzene sulfonic acid (DBSA, D_4 polymerization catalyst and surfactant), sodium dodecylbenzene sulfonate (SDBS, surfactant), and ammonium persulfate (APS) were analytically pure grade, and were used without further treatment. Water was deionized and distilled, the conductivity of which was below 1 μs/cm.

Measurement and Estimation of Interfacial Tensions

The interfacial tension (γ_{sw}) between water and liquid polysiloxane, which was prepared previously by emulsion polymerization of D_4 and followed by posttreatments, was determined on an autosurface tension instrument (type JYW-200; Tianjing Material Testing Machine Factory, China). The interfacial tension (γ_{as}) between polyacrylate and polysiloxane was estimated using the harmonic–mean equation method.[17a] The interfacial tension (γ_{aw}) between water and polyacrylate was obtained indirectly with the described method[17b]: polyacrylate with 2 : 1 molar ratio of BA : MMA was first synthesized through soapless emulsion polymerization and followed by posttreatments, a series of interfacial tensions between water and different concentrations of polyacrylate solutions in toluene were then determined, and the value of γ_{aw} was given by extrapolating the concentration of polyacrylate to 100% in the curve of interfacial tension–concentration.

Preparation of Polyacrylate Seed Latex

The linear polyacrylate (PAn) and crosslinked polyacrylate (PAx) seed latices were prepared using batch process at 80°C for 1.5 h in nitrogen atmosphere, respectively. The recipes are given in Table I.

Seeded Emulsion Polymerization of Siloxane

The recipe of seeded emulsion polymerization of siloxane onto the polyacrylate seed latex particles is: seed polymers, 5.0 g (about 25 g of seed latex); water, 75 g; MATS, 1.0 g; APS, 0.06 g; DBSA, 0.5 g; NaHCO₃, 0.07 g; D_4, 4.5 g; and TES, 0.5 g.

Table I   Ingredients of Polyacrylate Seed Latexes (unit: gram)

Sample	BA	MMA	SDBS	NaHCO$_3$	APS	EGDMA	H$_2$O
PAn	20	10	0.06	0.07	0.06	0	120
PAx	20	10	0.06	0.07	0.06	0.6	120

The seed latex was first diluted with 60 g of water, then NaHCO$_3$, MATS, and APS were added; after 1 h of polymerization at 80°C in nitrogen atmosphere, a solution of DBSA in 15 g of water was supplied into the reactor. The following seeded emulsion polymerization was carried out using two different processes, described next, and the latices were finally neutralized with aqueous ammonia.

1. Batch process: The siloxanes were added into the reactor and were sufficiently mixed with stirring at room temperature, after which the polymerization was conducted at 80°C for 7 h.
2. Continuous addition process: The mixture of D$_4$ and TES was continuously introduced into the reactor at 80°C for 70 min, followed by an extension of polymerization time of 6 h.

Characterization

Monomer conversion was measured by the gravimetric method. Surface tension of latices was obtained on the autosurface tension instrument. The particle diameter (D_p) and particle morphology were investigated using TEM with phosphotungstic acid as staining agent. The phase structure of latex films cast at room temperature was observed under TEM after ultrathin cross section in liquid nitrogen. The film hardness was measured using a pendulous hardometer (type QBY; Tianjing Material Testing Machine Factory, China). The water adsorption ratio (A_w) of the latex films was characterized by immersing about 2 g of film in water at 25°C for 24 h, comparing the weight of the film before (W_1) and after (W_2) immersion; A_w was defined as ($W_2 - W_1$)/W_1 × 100%.

RESULTS AND DISCUSSION

Thermodynamic Analysis of Different Latex Particle Morphologies

Morphology control in latex particles is very important, yet it is very difficult because the particle morphology is strongly influenced by thermodynamic and kinetic factors, and the particle morphology may vary greatly even if in the seeded emulsion polymerization.[2,6,7] Sundberg et al.[5,18,19] used an approach based on the change of the total interface energy at the interfaces of the three phases in a latex system to predict the final latex particle morphology in two-stage particle formation. For the composite latex system consisting of polyacrylate and polysiloxane, three possible extreme morphologies (Fig. 1) may be formed: the separate particles (Psep), the normal core/shell particle (PSi/PA) with polysiloxane as the core, and the inverted core/shell particle (PA/PSi) with polyacrylate as the core.

According to Sundberg's theory, if kinetic factors are not considered, a composite latex particle having less total interface energy (E) is more stable and easier to form than a particle having more E, and the value of E equals the sum of the products of the interfacial tensions and corresponding interfacial areas. If $E_{s/a}$, $E_{a/s}$, and E_{sep} are, respectively, denoted as the total interface energy of the PSi/PA particle, PA/PSi particle, and separated particles, then the following three equations can be established:
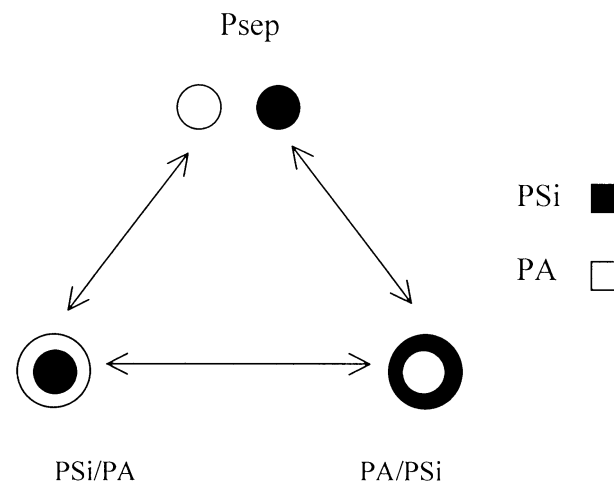
For the PSi/PA particle:

Figure 1   Three possible extreme morphologies of composite latex particles.

$$E_{s/a} = \gamma_{sa}A_{sa} + \gamma_{aw}A_{aw}$$
$$= \pi[\gamma_{sa}d_s^2 + \gamma_{aw}(d_a^3 + d_s^3)^{2/3}] \quad (1)$$

for the PA/PSi particle:

$$E_{a/s} = \gamma_{as}A_{as} + \gamma_{sw}A_{sw}$$
$$= \pi[\gamma_{as}d_a^2 + \gamma_{sw}(d_a^3 + d_s^3)^{2/3}] \quad (2)$$

for Psep particles:

$$E_{sep} = \gamma_{aw}A'_{aw} + \gamma_{sw}A'_{sw} = \pi(d_s^2\gamma_{sw} + d_a^2\gamma_{aw}) \quad (3)$$

where γ_{sa} and A_{sa} are, respectively, the interfacial tension and the interface area between the core of PSi and the shell of PA; γ_{as} and A_{as} are those between the core of PA and the shell of PSi ($\gamma_{sa} = \gamma_{as}$ in all cases, and $A_{sa} = A_{as}$ only in case that the volumes of the two polymers are equal). A'_{sw} is the interface area between PSi and water, and A'_{aw} is the interface area between PA and water in the separated particle morphology. d_a and d_s are, respectively, the diameter of PA and that of PSi particle in the separated particle morphology. d is the diameter of the core/shell particles, and $d = (d_a^3 + d_s^3)^{1/3}$.

Consider the transitions between the two of three extreme morphologies: for PA/PSi and PSi/PA, eq. (1) must be equal to eq. (2), that is, $E_{s/a} = E_{a/s}$; for PA/PSi and Psep, $E_{sep} = E_{a/s}$; for PSi/PA and Psep, $E_{sep} = E_{s/a}$.

Two morphologies coexist at the corresponding transition point. It is obvious that the PSi/PA latex particle can be formed under conditions of $E_{s/a} < E_{a/s}$ and $E_{s/a} < E_{sep}$. Therefore, the thermodynamic requisites of the PSi/PA particle formation can be expressed as follows:

$$\gamma_{sa}d_s^2 + \gamma_{aw}(d_a^3 + d_s^3)^{2/3} < \gamma_{sw}(d_a^3 + d_s^3)^{2/3} + \gamma_{sa}d_a^2 \quad (4)$$

$$\gamma_{sa}d_s^2 + \gamma_{aw}(d_a^3 + d_s^3)^{2/3} < \gamma_{sw}d_s^2 + \gamma_{aw}d_a^2 \quad (5)$$

Similarly, the PA/PSi latex particle can be obtained under conditions of $E_{a/s} < E_{s/a}$ and $E_{a/s} < E_{sep}$, and the thermodynamic requisites of its formation can be given by the following inequalities:

$$\gamma_{as}d_a^2 + \gamma_{sw}(d_a^3 + d_s^3)^{2/3} < \gamma_{aw}(d_a^3 + d_s^3)^{2/3} + \gamma_{as}d_s^2 \quad (6)$$

$$\gamma_{as}d_a^2 + \gamma_{sw}(d_a^3 + d_s^3)^{2/3} < \gamma_{sw}d_s^2 + \gamma_{aw}d_a^2 \quad (7)$$

Let V_a be the fraction volume of PA, V_s the fraction volume of PSi, and $V_a + V_s = 1$, when V is associated with d, the inequalities (4)–(7) can be simplified, respectively, to the inequalities (8)–(11) through a series of mathematical treatments: For the PSi/PA particle:

$$\frac{\gamma_{sw} - \gamma_{aw}}{\gamma_{sa}} > V_s^{2/3} - V_a^{2/3} \quad (8)$$

$$\frac{\gamma_{sw} - \gamma_{sa}}{\gamma_{aw}} > \frac{1 - V_a^{2/3}}{V_s^{2/3}} \quad (9)$$

and for the PA/PSi particle:

$$\frac{\gamma_{sw} - \gamma_{aw}}{\gamma_{sa}} < V_s^{2/3} - V_a^{2/3} \quad (10)$$

$$\frac{\gamma_{aw} - \gamma_{sa}}{\gamma_{sw}} > \frac{1 - V_s^{2/3}}{V_a^{2/3}} \quad (11)$$

The results indicated that the final morphology of a core/shell latex particle is dominated by three interfacial tensions as well as by fraction volumes of the two polymers. Thus, the core/shell latex particle with designed morphology can be prepared either by changing the interfacial tensions or by changing the relative volumes of polymers in the latex system.

Interfacial Tension and Core/Shell Particle Morphology Prediction

Under the emulsifier-free condition, the values of γ_{sw} and γ_{sa} measured at 20°C were 35.0 and 6.04 dyn/cm, respectively. The value of γ_{aw} estimated by the extrapolating method was 18.1 dyn/cm.

Substituting the values of three interfacial tensions, respectively, into inequalities (8) and (9) yields

$$2.80 > V_s^{2/3} - V_a^{2/3} \quad (12)$$

$$1.60 > \frac{1 - V_a^{2/3}}{V_s^{2/3}} \quad (13)$$

This means that the PSi/PA particle can be formed in a whole range of the value of V_s.

Substituting the values of three interfacial tensions, respectively, into inequalities (10) and (11) yields
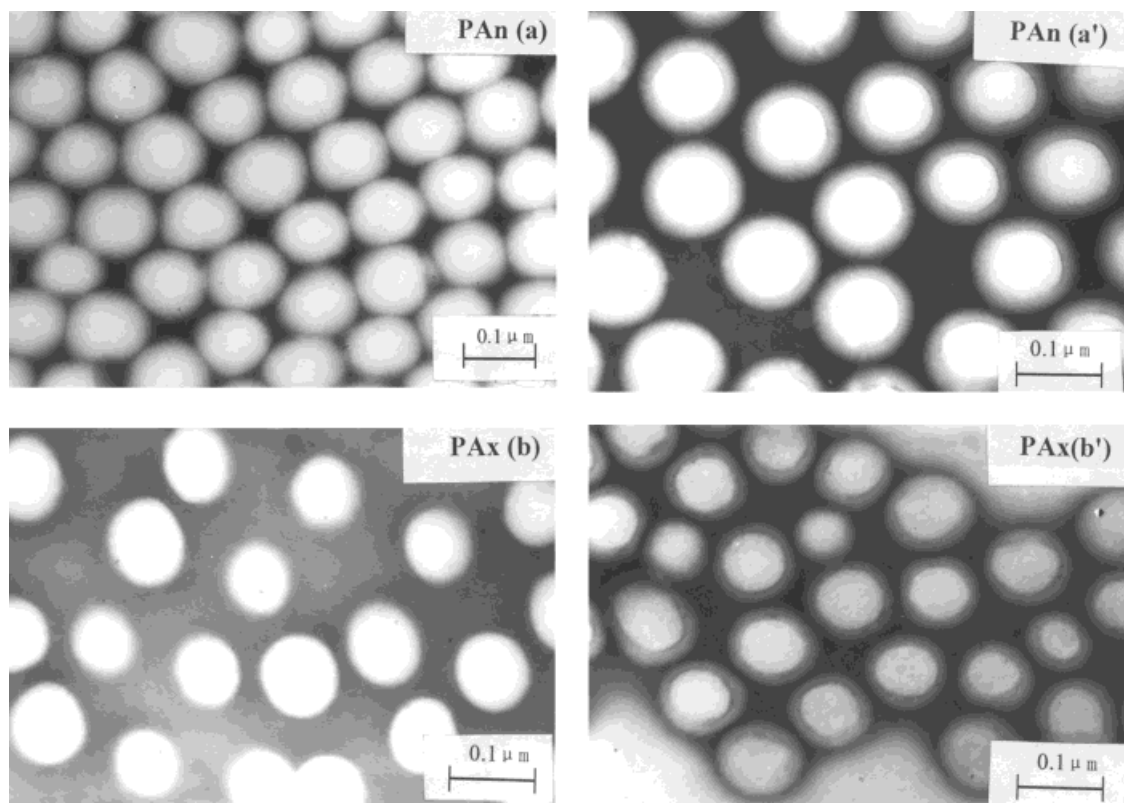
Figure 2 Micrographs of seed latices of PAn and PAx before [(a), (b)] and after [(a′), (b′)] treatment with MATS.

$$2.80 < V_s^{2/3} - V_a^{2/3} \qquad (14)$$

$$0.345 > \frac{1 - V_s^{2/3}}{V_a^{2/3}} \qquad (15)$$

From inequality (15) it can be calculated that the PA/PSi particle can be synthesized only if $V_s > 0.872$. Moreover, because the values of $(V_s^{2/3} - V_a^{2/3})$ always fell into the range -1 to 1, the illogical inequality (14) implies that the PSi/PA particle formation is not avoided in the preparation of the PA/PSi particle, even if $V_s > 0.872$.

Preparation and Characterization of the PA/PSi Latex Particles

The results of the preceding analysis indicated that, when the PA/PSi morphology particle is ex-

pected, the fraction volume of polysiloxane must be much greater than that of polyacrylate (i.e., $V_s \gg V_a$), and even if this is the case, the PSi/PA particle will be unavoidably formed simultaneously with the PA/PSi particle formation. Nevertheless, the value of V_s/V_a should be appropriate for most purposes, so that the desirable material properties can be reached, and the lesser value of V_s may be favorable because of the high cost of polysiloxane.

In view of thermodynamics, once the value of V_s is fixed, the particle morphology will be dominated only by interfacial tensions, and the PA/PSi particles with equal volumes of PA and PSi can be achieved only if the interfacial tensions are changed. In this work, to get the designed PA/PSi morphology particles, MATS was used to modify the surface of polyacrylate seed particles to in-

Table II Results of Seeded Emulsion Polymerization

Sample	Seed D_p (nm)	Conversion (wt %)	Experimental D_p (nm)	Theoretical D_p[a] (nm)	$N_p \times 10^{-17}$ (L^{-1})
PAn/PSix	100.9	84.1	121.1	104.5	0.81
PAx/PSix	83.1	86.1	110.1	104.1	1.54

[a] Calculated values obtained by assuming that all siloxane were polymerized onto the seed particles.
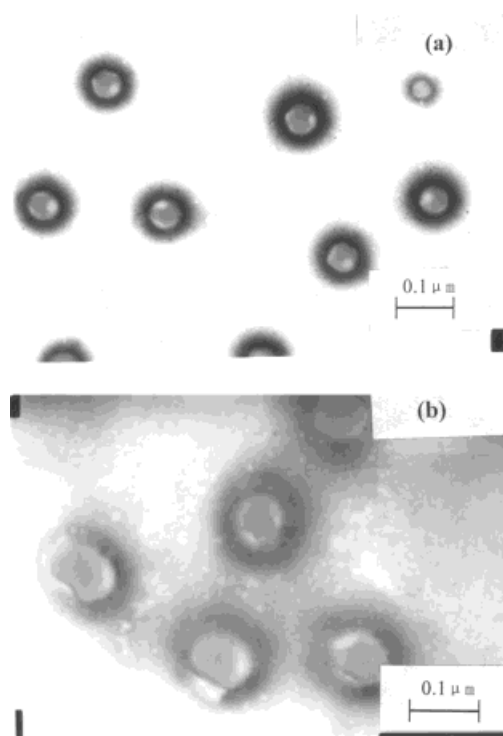
Figure 3 Micrographs of composite latices of (a) PAx/PSix and (b) PAn/PSix.

crease the compatibility of the core and the shell polymers. As a coupling agent containing one C=C and three SiOCH$_3$ groups, MATS can undergo not only radical polymerization with residual acrylic monomers in the seed particle, but also condensation with Si–OH terminal groups of polysiloxanes. MATS is therefore an ideal coupling agent, which may form an intermediate layer and chemical bonds between the core and the shell polymers.

It is worth pointing out that the addition time of MATS into the seed latex is a paramount factor for the success of the designed particle morphology. Early addition of MATS into the seed latex may allow MATS molecules to penetrate inside the seed particles and to polymerize there. If MATS is added too late, few acrylic monomers in the seed particle exist, and the radical copolymerization of MATS with acrylates would not occur. In either case, the intermediate layer surrounding the polyacrylate core would not be formed. The experiments showed that the appropriate addition time for MATS was at about 80–85% conversion of acrylic monomers in the seed latex preparation (at about 90 min of reaction time under present experimental conditions). Moreover, it is well known that the Si—O—C bond in

MATS molecules is much easier to hydrolyze both in acid and in alkali medium, which will lead to self-condensation and crosslinking reactions of MATS.[20] To prevent the emulsion polymerization process from coagulation, NaHCO$_3$ must be used as a buffer to maintain a pH value of about 6–7 before MATS is introduced into the reactor.

The TEM photos of seed latices before [Fig. 2(a) and (b)] and after [Fig. 2(a′) and (b′)] treatment with MATS indicated that the intermediate layer surrounding the seed particles was well formed.

In the seeded emulsion polymerization, two additional methods of siloxanes were used. It was found that the continuous addition process is preferable to the batch process, in which some of the new polysiloxane particles were also observed in addition to the expected PA/PSi particles. The results of seeded emulsion polymerization by the continuous addition process are listed in Table II, in which basic agreement between experimental and theoretical particle size was obtained, and no new particles of polysiloxane were created.

The TEM photos of core/shell latex particles are presented in Figure 3. The dark region of the outer layer is polysiloxane as a result of a higher electronic cloud density around silicon atoms compared to that of carbon atoms, and the lighter region in the core is a polyacrylate domain. In the PAx/PSix particles, the polyacrylate core is encapsulated by polysiloxane, as expected, whereas in the PAn/PSix particle, because the core polymer is not crosslinked, the penetration of siloxanes and polysiloxane into the polyacrylate core is not effectively prevented; therefore, the interface between the core and the shell is not clearer than that of the PAx/PSix particle, even though a core/shell morphology is also observed. Furthermore, to confirm the core/shell structure of the particle,
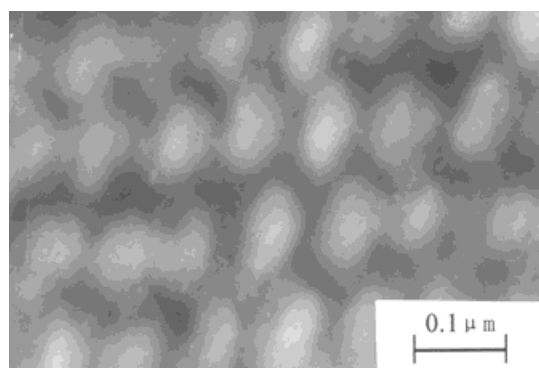

Figure 4 Micrograph of microtomed PAx/PSix latex film.

Table III   Properties of Latex Films

Property	PAn	PAx	PAn/PSix	PAx/PSix	PSix[a]
Hardness $\times 10^2$	2.73	4.09	6.82	24.32	22.50
Water adsorption ratio (wt %)	2.91	2.62	0.81	0.63	0.60

[a] Polysiloxane obtained from D_4 and TES by batch emulsion polymerization.

the TEM photograph of a microtomed slice of the PAx/PSix latex film was obtained (Fig. 4). It is clear that PA domains distributed in continuous polysiloxane phase, although the fusion of the core and the shell polymers near the interface regions partly occurred in the film-forming process; this result agrees well with the TEM observation on the latex particle morphology.

Properties of the PA/PSi Latex Films

The hardness and water adsorption ratio (A_w) of latex films are given in Table III. The PAx/PSix latex film is similar to the PSix latex film in those properties. For the PAn/PSix latex film, because the core polymer is uncrosslinked, its hardness is close to that of PAn film, whereas its A_w is similar to that of PSix film. These results reveal that the continuous phase in PAn/PSix and PAx/PSix latex films must be of crosslinked polysiloxane. These may be taken as indirect evidences that the composite latex particles with the desirable core/shell morphology are successfully synthesized.

CONCLUSIONS

1. Under emulsifier-free conditions, the thermodynamic analysis and morphological prediction indicated that the core/shell latex particle (PA/PSi), comprising a hydrophilic core of polyacrylate and a hydrophobic shell of polysiloxane, may be synthesized only when the fraction volume of polysiloxane is greater than 0.872, and even so, the formation of PSi/PA particles is unavoidable.
2. The PA/PSi latex particles containing equal amounts of polysiloxane and polyacrylate can be synthesized by continuous seeded emulsion polymerization of siloxane onto the polyacrylate seed particles, which must be modified previously with MATS. It was found that the presence of an intermediate layer to increase the chemical compatibility between the core and the shell polymers was necessary, and the perfect PA/PSi core/shell morphology was obtained when both the core and the shell polymers were crosslinked.
3. The water adsorption ratio and the hardness of PAx/PSix latex film show a good agreement with those of crosslinked polysiloxane film.

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