Preparation and Characterization of Polysiloxane–Polyacrylates Composite Lattices by Two Seeded Emulsion Polymerization and Their Film Properties

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ABSTRACT: Gamma ray-induced seeded emulsion polymerization of methyl methacrylate and butyl acrylate was carried out in the presence of polymerizable polysiloxane seed latex, which was obtained by the ring-opening copolymerization of octamethyl cyclotetrasiloxane (D_4) and tetramethyl tetravinyl cyclotetrasiloxane(VD_4) catalyzed by dodecylbenzene sulfonic acid (DBSA). After the first seeded polymerization, 3-methacryloxylpropyltrimethoxylsilane (MPS) was added for the second seeded polymerization. The conversion–time curve showed that the first seeded polymerization rate was accelerated much by the polysiloxane seed latex. The final composite lattices also showed good storage stability, mechanical stability, and high electrolyte resistance ability. The morphology of the composite latex particles was found to be a quite uniform fine structure by transmission electron microscopy (TEM). The graft of polyacrylates onto polysiloxane and hydrolysis of MPS were confirmed by Fourier transform infrared (FT-IR) spectroscopy. The mechanical performance, water absorption ratio, surface properties, and transparency of the latex films were also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1406–1411, 2007

Key words: polysiloxane; polyacrylates; 3-methacryloxylpropyltrimethoxylsilane; seeded polymerization; composite latex

INTRODUCTION

Polyacrylics have many specific properties, such as good film forming, gloss, transparency, and mechanical properties; their corresponding products have been widely used as coatings, paints, and adhesives. However, the poor water resistance and low (or high) temperature resistance limit their application. In contrast, polysiloxane has many excellent properties, such as high flexibility and hydrophobicity, low surface tension, low glass transition temperature (T_g), weather resistance, and excellent thermal stability. But the low tensile strength and relative high costs limit its applications. Thus, the combination of polyacrylate with polysiloxane has been of importance and interest during the past few decades.[1–22] Since the polymer latex was environmentally friendly, polyacrylic lattices have been the most popular products for coatings, etc. Modification of polyacrylic lattices by polysiloxane was a convenient and effective way, so there is considerable literature on the polyacrylics/polysiloxane composite latex. As a result of the strong commercial interest, a many patents appeared.[1–6,10–16] In the above works,

however, the mechanical performance of polyacrylates was usually decreased considerably after the introduction of polysiloxane, although its water-resistant performance was improved. Generally, modification of silicon coupling agent at the surface of the latex particles does not improve water resistance of the latex films much, but strongly improves its mechanical performance. So with the combination of modification with a polysiloxane and silicon coupling agent, it was expected to obtain composite latex with good water resistance and mechanical performance for the related latex film.

Gamma ray-induced polymerization can be carried out at room temperature and under normal pressure and is hardly influenced by the change of temperature. Because there is no chemical initiator in the polymerization, the final product is not polluted. In the aqueous emulsion polymerization, the primary free radical to initiate the polymerization was produced from water and the monomer by the gamma ray irradiation. The high free radical yield produced from water results in the high initiation rate, especially for acrylates. Generally, the polymer obtained possesses higher molecular weight (MW) compared with that obtained by chemical initiator methods,[23] and higher MW is favorable to improved performance of the latex films.
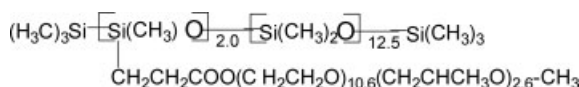
In this work, the polysiloxane seed latex was prepared by the ring-opening copolymerization of octamethyl cyclotetrasiloxane (D_4) and tetramethyl tetravinyl cyclotetrasiloxane (VD_4) catalyzed by dodecylbenzene sulfonic acid (DBSA). Gamma ray-induced seeded emulsion polymerization of methyl methacrylate and butyl acrylate was carried out in the presence of polymerizable polysiloxane seed latex. Then 3-methacryloxylpropyltrimethoxylsilane (MPS) was added for the second seeded polymerization. The consecutive seeded polymerization of acrylics induced by gamma ray irradiation was carried out at room temperature. The morphology of the latex was observed by transmission electron microscopy (TEM). The graft reaction between polymerizable polysiloxane and polyacryates and hydrolysis of MPS was confirmed by Fourier transform infrared (FT-IR) spectroscopy. The mechanical performance, water absorption ratio, surface properties and transparency of the latex films were also investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) were from Shanghai Chemical Reagent Corporation and purified with a common method. Octamethylcyclotetrasiloxane (D_4) and tetramethyltetravinylcyclotetrasiloxane (VD_4) were both purchased from the Bengbu Organic Silicon Factory. 3-Methacryloxylpropyltrimethoxylsilane (MPS), purchased from by Nanjing Shuguang Chemicals, and hexamethyldisiloxane (MM), provided by Alfa Aesar, were both used as received. Dodecylbenzene sulfate (SDBS), dodecylbenzene sulfonic acid (DBSA), poly(ethylenglycol)monooctylphenyl ether (OP-10), and silicon containing surfactant (SCS):

$$(H_3C)_3Si\text{--}[Si(CH_3)\text{--}O]_{2.0}\text{--}[Si(CH_3)_2O]_{12.5}\text{--}Si(CH_3)_3$$
$$CH_2CH_2COO(C\ H_2CH_2O)_{10.6}(CH_2CHCH_3O)_{2.6}\text{-}CH_3$$

were used without further purification. Water was distilled once.

Preparation and characterization of polysiloxane seed latex and polymerizable polysiloxane

Polymerizable polysiloxane seed latex was obtained by heating a mixture of DBSA 3 g, SCS 6 g, D_4 27.8 g, VD_4 1.7 g, MM 0.4 g, and H_2O 61.1 g for 8 h at 80°C under strong mechanical stirring ($\sim$ 1500 rpm).[24] The size of the latex particles was measured by a particle size analyzer (Zetasizer-3000HS, Malvern, UK). The vinyl content of the polymerizable polysiloxane was calculated by nuclear magnetic resonance (NMR) spectra obtained on a BRUKER Advance 300 NMR spectrometer. The viscosity average molecular weight of the polysiloxane measured by an Ubbelohde capillary viscometer according to the Mark–Houwink equation $[\eta] = KM^{\alpha}$. Here $K = 2.15 \times 10^{-2}$, $\alpha = 0.6$ when M is in the range of 2×10^4 to 1.3×10^6 and $K = 7.5 \times 10^{-2}$, $\alpha = 0.5$ when M is within the range of 2×10^3 to1×10^4.[25]

The first seeded emulsion copolymerization of MMA and BA

A certain amount of polysiloxane seed latex (10–30 wt %), acrylic monomers, surfactants (SDBS and OP-10) and water were mixed by a homogenizer at 8000 rpm for 10 mins. The mixture was shifted to a glass bottle with rubber stopper and was bubbled with nitrogen to remove oxygen. Then the polymerization initiated by ^{60}Co gamma ray irradiation was carried out at dose rate of 87 Gy/min for 1 h. For all the runs, the concentration of both MMA and BA were 20 wt %, SDBS was 1 wt % and nonionic surfactants were 2 wt % (including SCS in the seed and OP-10 added later).

Second seeded emulsion of MPS

Under strong mechanical stirring ($\sim$ 2000 rpm), 0.5 g MPS was added to 50 g composite lattices obtained by the first seeded polymerization. The mixture was then irradiated for 1 h more after oxygen was removed.

Characterization of latex properties

Monomer conversion was measured by the gravimetric method. Particle size and morphology were investigated by TEM, using an Hitachi model H-800 microscope, with phosphotungstic acid as the staining agent. The minimum film formation temperature (MFFT) of the latex was determined with a device developed by Fuhua, China. A nickel-plated steel plate is electronically cooled at one end and heated at the other. The temperature range can be varied and in this case it ranged from 0 to 25°C. Over this range, 10 thermocouples have been installed to register the temperature. Dried air was passed over the surface from the cold end to the warm end. The lattices were applied as a track on the plate. Per sample, three tracks were applied. All the samples had a solids content of $\sim$ 40%. When the films were dry, the MFFT could be determined between two thermocouples as being the temperature at which the dry film changes from white and powdery to transparent and crack free. Because the reading is a human inter-
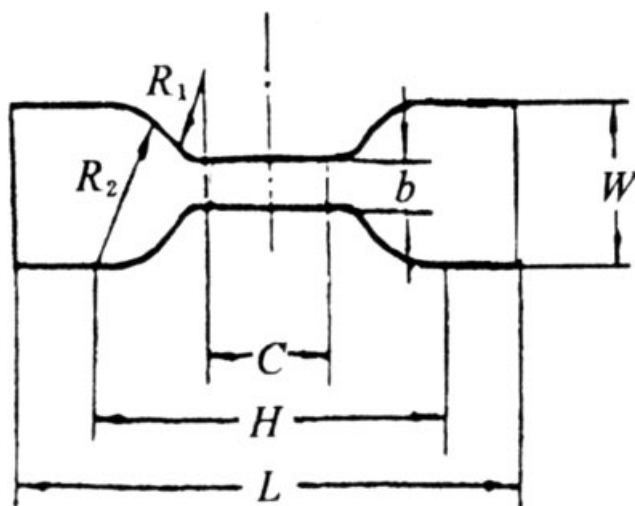
Figure 1 Shape and size of the sample for mechanical properties test. L, 110 mm; C, 25 mm; b, 6.5 mm; W, 25 mm; H, 75 mm; R_1, 14 mm; R_2, 25 mm.

pretation of the point where the film becomes clear and crack free, the MFFT could be determined with an accuracy of $\sim 0.3°C$.

Characterization of latex film properties

Latex films ($\sim$ 1.5 mm thickness) were cast from a glass mold at ambient temperature. The mechanical properties of the membranes were tested by a Shimadzu AutoGraph DCS-5000 versatile testing machine with the displacement of 25 mm/min at 15°C. The tensile stress and elongation at break were calculated according to Japanese Industry Standard, K7116-87. All the values were the average of three measurements. The sample was prepared according to GB1040-92 of China national standards (Fig. 1). Saturated water absorption (Aw) of the films was measured as method below: put a certain weight ($\sim$ 2 g) of film into water for 14 days at 20, then it was dried again. Comparing the weight of the film before drying (W1) and after drying (W2), The absorption ratio Aw (%) = (W1–W2)/W2*100. Water contact angles were determined with a JCR-10 goniometer and deionized water on thin films cast on a glass substrate. Contact angles were measured after 60 s from dropping of droplets. Volume of each water droplet was $\sim$ 20 μL. Each contact angle value given in Table I represents an average of five readings. The transparency of the films was characterized as the transmission ratio (TR) of the visible light at 500 nm per 1–mm thickness film. It was calculated by the equation $TR = 10^{(-A/d)}$. A is the absorbance at 500 nm of the latex film measured by UV-2100 photometer (Schimadzu, Japan), d (mm) is the thickness of the latex film.

TABLE I
Some properties of the latex films[a]

Polysiloxane seed latex content	W.A.R[b]		MFFT (°)		C.A (°)[c]		T.R (mm^{-1})[d]	
0	12.0	11.0	20.0	21.0	65	66	0.46	0.50
10%	5.4	5.0	12.5	13.2	95	93	0.26	0.27
20%	6.2	6.4	9.5	10.1	94	92	0.20	0.24
30%	8.5	8.8	5.0	7.0	93	94	0.16	0.18

[a] For each property there are two columns related the values before and after MPS's addition, respectively.
[b] Water absorption ratio.
[c] Water based contact angle.
[d] Transmission ratio at 500 nm.

RESULTS AND DISCUSSION

Preparation of the polysiloxane seed latex

The polymerizable polysiloxane obtained by the copolymerization of D_4 and VD_4 is a random copolymer, which had been proved by He et al.[24] The conversion was 93%. The molecular weight obtained by viscometer and the vinyl content calculated by NMR were 9701 g/mol and 5.30×10^{-4} mol/g, which were close to the theoretical values 10000 g/mol and 6.58×10^{-4} mol/g calculated by the recipe, respectively. The number-average diameter of the latex particles was $\sim$ 86 nm.

Effects of the polysiloxane seed latex to the polymerization of acrylates

The first seeded polymerization conversion-time curves of MMA and BA with different seed were shown in Figure 2. According to the classic Harkins' theory,[25] a batch emulsion polymerization process can commonly be divided into two main stages: the nucleation stage (generally conversion < 20%), par-
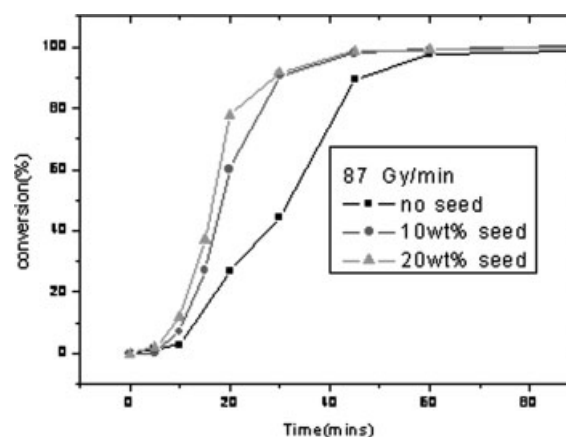

Figure 2 Conversion-time curves of MMA and BA with different seed latex content.
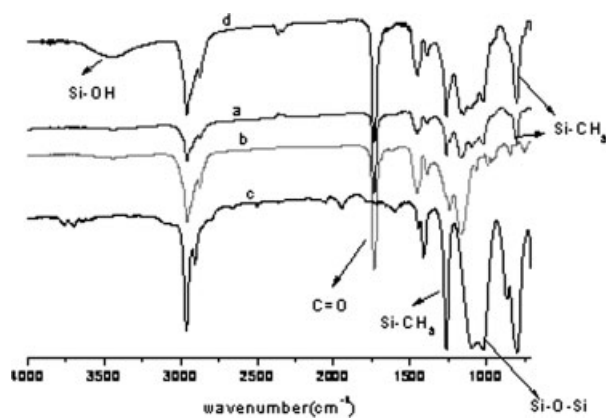
Figure 3 FT-IR spectra of (a) composite polymer (with 30 wt % polysiloxane seed latex content) extracted by *n*-hexane; (b) poly(MMA-co-BA); (c) PDMS; (d) composite polymer after addition of MPS.

ticles growth stage. If the seed were used, the first period would be a so-called "activation stage" of seed particles instead of the nucleation period. It could be seen that the presence of seed latex would accelerate the polymerization rate obviously, so activation of seed particles is easier than the new nucleation. Although some additional surfactants were added, only few of new nucleation sign corresponding to the small particles in Figure 4 could be found. It means that the added seed was the dominant polymerization place. It is also found that there was very little difference with seed latex content of 10 wt % and 20 wt %. It may be explained: as we know, the radical concentration was $\sim 10^{12}$ mL^{-1}, but the seed concentration was $\sim 10^{14}$–10^{15} mL^{-1}, so the radical concentration was the rate-determining factor after the seed concentration has reached a certain level ($\sim 10^{14}$ mL^{-1}).

To testify the occurrence of grafting between polyacrylates and polysiloxane, Soxhlet extraction with *n*-hexane as solvent was carried out for the composite polymer obtained by the first seeded polymerization. The typical IR spectrum of the extracted composite polymer is shown in Figure 3(a); the peaks at 1740 cm^{-1} are associated with C=O stretch of the polyacrylates. Polysiloxane could be characterized by Si—CH3 symmetric deformation, stretching vibration at 1260, 801 cm^{-1}, respectively; Si—O—Si asymmetric stretching within the range of 1100–1000 cm^{-1}. The IR spectra of pure poly(MMA-co-BA) and polydimethylsiloxane (PDMS) are also shown in Figure 3(b) and (c). From these spectra, it is clear that polysiloxane had been successfully grafted to poly(MMA-co-BA). After the addition of MPS, peak related to the stretch vibration of Si—OH group at 3450 cm^{-1} appeared [see Fig. 3(d)], which indicated that hydrolysis of MPS (CH$_2$=C(CH$_3$)COO(CH$_2$)$_3$ (Si—O—Me)$_3$) occurred.

Properties of the composite lattices and their films

A review of polymer latex film formation and its properties has been made by Steward et al.[27] It was concluded that the physical and mechanical properties of polymer films are affected not only by the nature of the polymers, but also by the method of both polymer and film preparation and conditioning. Some works[28–30] showed that MFFT was dependent on the number average diameter (Dn), and lower Dn tended to give lower MFFT. Peters et al.[31] used a bimodal latex blends to study the effects of the particles' size and size distribution on mechanical properties and water absorption ratio and MFFT. They found a minimum in MFFT occurred at approximately the same blend ratio ($\sim$ 80/20 large/small by weight) as the minimum in film water absorption (at short drying times) and as the maximum in tensile strength. So they attributed this effect to a packing effect with the minimum void volume being obtained at this blend ratio. The increased of transparency of latex films was observed when the annealing temperature and time were increased.[32,33]

However, in our study, as shown in Figure 4, the latex was polydispersed and the small particles was expected to fit into the interstices of larger particles. And the film annealing temperature was 35°C,
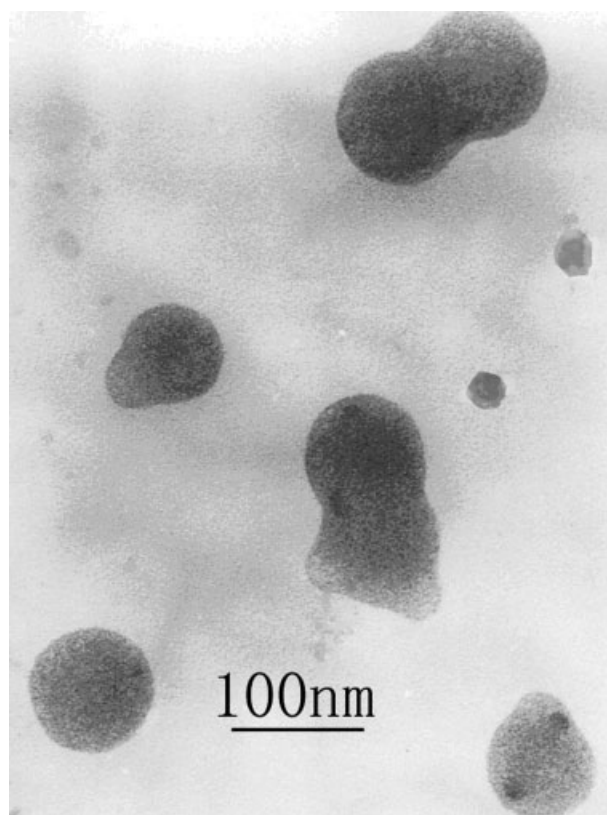

Figure 4 TEM of composite latex particles (30 wt % seed latex content).
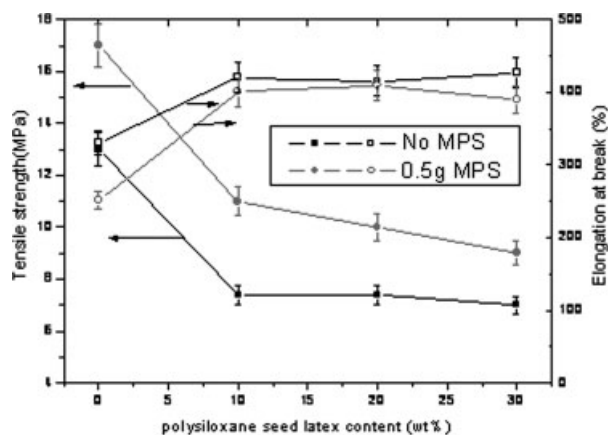
Figure 5 Mechanical properties of the composite latex films.

which was nearby the T_g of the composite polymer ($\sim 33°C$) and annealing time was long enough for polymer diffusion to fill the voids between the particles. The effects of size and size distribution of the latex on the properties of the films may be ignored, and we focus on the effects of composition on the properties of the latex films.

Stability of the latex

It has been reported by Kan et al.[9] and Huang et al.[19] that to a certain extent coagulum appeared when the batch polymerization method was used and all the obtained lattices was sensitive to the electrolyte such as NaCl and Na_2SO_4. However, in the present work, during the polymerization induced by ^{60}Co gamma ray irradiation, no coagulum appeared for all the lattices and it had been found that all the lattices were resistant to NaCl and Na_2SO_4, even up to their saturated concentrations. In this study, MPS content was limited to 2.5 wt %, and no coagulation appeared during the storage for 12 months or during the centrifugation for 1 hour with the speed $\sim 16,000$ rpm, which implied that all the latex showed good storage stability and mechanical stability. The good stability may be attributed to lower content of MPS used, nanoscale size of latex particles (~ 90 nm; see Fig. 4) and the steric and electrosteric stability offered by the combination usage of nonionic surfactant and ionic surfactant. But if the MPS content reached 5.0 wt %, coagulation occurred after 12-month storage. The coagulation may result from the Si—OH condensation between particles.

Morphology of the composite latex particles

Although the mutual solubility of polysiloxane and polyacrylates was poor, it would be improved by the graft copolymerization of polyacrylates and poly-

siloxane. The swelling with an acrylics monomer to the existing polysiloxane seed latex particles before polymerization and the vinyl groups of the seed would enhance the graft polymerization. So the morphology of the particles showed a quite uniform fine structure as shown in Figure 4 (the darker was polyacrylics and the light was polysiloxane). The few very small particles in Figure 4 could be contributed to the new nucleated copolymer of MMA and BA.

MFFT of the composite lattices

It is well known that the T_g of polydimethylsiloxane was very low ($-120°C$), so the MFFT of the composite latex decreased as expected when the content of the polysiloxane increased (see Table I). MFFT increased slightly after the addition of MPS.

Mechanical properties of the latex films

The mechanical performance of the polysiloxane rubber is very poor compared to that of the polyacrylates. So the introduction of polysiloxane will affect greatly to the performance of polyacrylates. As shown in Figure 5, after the polysiloxane seed latex was added in the system, the tensile stress of the latex films was almost reduced to one-half (from 13 MPa to 7 MPa) accompanied by an slight increase of elongation at the break.

However, with only 2.5 wt % (based on the total polymer weight) MPS' addition, the tensile strength increased from 7.4 MPa, 7.4 MPa, 7.0 MPa to 11.0 MPa, 10.1 MPa, 8.0 MPa for the composite latex films with 10 wt %, 20 wt %, 30 wt % polysiloxane seed latex content, respectively. And the elongation at break decreased little. The strong increase of tensile strength should attribute to the condensation of Si—OH groups at the surface of the particles during the film formation.

Water absorption ratio and surface properties of the latex films

The polyacrylate latex was one of the basic formulation components of the waterborne coatings and the water resistance of the waterborne coatings was mostly determined by the latex polymer hydrophobicity. The water absorption ratio and water contact angles of the latex films are two important parameters for characterization of the hydrophobicity. As listed in Table I, the absorption ratio of the latex films decreased first, which can be attributed to the excellent hydrophobicity of polysiloxane. However, it soon increased after the content exceeded 10 wt %, which could be correlated to the phase separation and the formation of large polysiloxane domain with the further increase of polysiloxane content.

Addition of the polysiloxane seed latex results in the obvious increase of the water contact angle (see Table I) because the polysiloxane tended to migrate to the air surface of the latex films due to its low surface energy in spite of the chemical linkage between the polysiloxane and polyacryates as mentioned by Oh and Kim.[34] The contact angle was found much more lower than that of the pure polysiloxane (120°) due to the influence of the surfactant used in the emulsion polymerization. The addition of 2.5 wt % MPS is found to have a slight influence on the absorption ratio and contact angle.

Transparence of the latex films

The transparence of the latex films was important in some cases. Because the large polarity difference between polysiloxane and polyacrylates, phase separation was unavoidable and transparency of the composite films was usually unsatisfied. According to the optical principle, when the disperse phase domain size was smaller than one half of wavelength of light, the light could round the disperse phase.[35,36] As listed in Table I, the transparency decreased as the polysiloxane content increased but when the seed latex content was 10 wt % the transparency was still acceptable. It is mainly because that the dispersed polysiloxane phase domain size was expected to be much smaller than the visible light wavelength (400–800 nm). And it can be seen that the addition of MPS would enhance the transparency slightly.

CONCLUSIONS

1. The conversion–time curve of the seeded polymerization of the acrylates monomer induced by gamma ray in the presence of vinyl-containing polysiloxane seed latex showed that seed latex would accelerate the polymerization rate obviously.
2. FT-IR spectra showed that polysiloxane-graft-polyacrylates existed and MPS hydrolyzed to produce Si—OH groups.
3. The final composite lattices showed good storage stability, mechanical stability, and electrolyte resistibility. The morphology of the composite latex particles was found to be quite uniform structure observed by TEM.
4. The tensile strength of the latex films increased much and the elongation at break decreased slightly after addition of MPS.
5. Addition of 2.5 wt % MPS had little influence on the water absorption ratio and water contact angle of the latex films, but 10 wt % polysiloxanes greatly reduced the water absorption ratio and increased the water contact angle.
6. Both MFFT of the composite lattices and transparency of the films reduced as the polysiloxane seed latex content increased, with a slight increase after the addition of 2.5 wt % MPS.

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