

Matting films prepared from waterborne acrylic/micro-SiO₂ blends

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ABSTRACT: Acrylic resin/micro-SiO₂/polymethyl urea (AC/SiO₂/PMU) composites were prepared by physical blends of acrylic resin latex (AC), polymethyl urea resin (PMU), and modified SiO₂. The effects of SiO₂ and PMU content in the hybrid composites morphology and physical properties were investigated in detail using transmission electron microscopy (TEM), UV-Vis spectrometry (UV-Vis), scanning electron microscope (SEM), thermogravimetric analysis (TGA), and contact angle measurement. The results showed that introduction of SiO₂ into AC composites could increase the viscosity which caused by gelation and agglomeration of SiO₂. The TEM, SEM images, and TGA results indicated that hybrid membranes have phase separation. During the film formation process, a high number of PMU and SiO₂ particles of an appropriate size were stranded on the surface of the film to form matting surface. These results highlight the sensitivity of the gloss to the polymer morphology and surface. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41707.

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INTRODUCTION

Recently, a growing environmental restriction on volatile organic compound (VOC) emissions have urged both the coating industry and the consumers to develop, produce, and use less hazardous and nontoxic materials. Therefore, waterborne hybrid latex has attracted a great deal of interest in academia and industry owing to the opportunity that they bring to develop environment-friendly materials, which could combine the positive properties of both polymers in a synergistic way. In these hybrid materials, a waterborne organic/inorganic hybrid composites have been popular because their applications have dramatically improved materials properties in engineering plastics,¹ enhanced rubber, coatings, and adhesives.^{2–4} The attractive improvement includes thermal, mechanical, electronic, optical, and optoelectronic properties.^{5,6} Among the enormous number of organic/inorganic hybrid materials, acrylic polymer/silica hybrid emulsions have been widely used in many fields.⁷ The incorporation of silica into acrylic polymers can obviously improve the performances of final products and even endow some novel properties.⁸

Up to now, silica gel matting agents are widely used within the coatings for matting purposes and are considered highly

efficient in producing the type of surface roughness that is responsible for the appearance of extinction.^{9–12} Many research works have been performed regarding the preparation of acrylic/silica composite materials.¹³ But the effects of the matting agents on the morphology of the polymer latex have not yet been considered, to our knowledge. PMU is considered as an organic matting agent that could contribute strongly to form a matting surface because of its high specific surface area and pore volume. It can completely reflect the entire wavelength range of ultraviolet and visible light to create a matting effect on the material's surface.

So far, much effort has been devoted to the development of matting coatings. It is widely known that creating low gloss or matting effect is directly related to the surface roughness and refractive feature of the film.¹² In principle, a highly rough surface could cause diffuse reflection and decrease the gloss of film. On the other hand, a heterogeneous system with different morphological structures is expected to increase the roughness. The film with different refractive index allows the incident light to undergo refraction several times, leading to low reflection and reduce the visual effect of gloss. This is true to the following point: the heterogeneous system is usually caused by the

blending of a polymer which is incompatible with the matrix resin, or grafting or blocking of a copolymer into the matrix resin.

From the matting point of view, the gloss of the film depends on not only the morphology of the polymer, but also their interaction during the drying and curing process. The film shrank to form a rough surface, and matting surface is formed by means of scattering of diffuse light on the film surface.¹⁴ As it is common with the wet film stage, the matting properties of the films are strongly dependent on the solvent evaporation rate. When the system contains two or more kinds of solvents, and their solvent volatilization rates is not apparently different, it tends to make matting more difficult, whereas different solvent volatilization rate makes the surface with low gloss achieved. On the other hand, the morphology of the polymer is related to solvent volatilization rates. When the solvents in the system show different solvent volatilization rate, the certain polymer molecules tend to frizzle and precipitation. A rough surface is formed and matting surface would gain. Moreover, the polymer films usually shrink and become thinner during the drying process due to the volatilization of the solvents. In this case, the suspended particles would rearrange on the film surface. The surface is getting more rough. The gloss of the film surface reduces.

In this study, we first prepared AC/SiO₂/PMU resins based on different amount of SiO₂ and PMU by physical blending method. The structure, transmittance, thermal, and optical properties of the hybrid materials were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-Vis, thermogravimetric analysis (TGA), and gloss meter. The main purpose of this study is to probe the effects of composites structure on the hybrid membranes gloss and to obtain a matting surface.

EXPERIMENTAL

Materials

Methacrylic acid (MAA, 99%), butyl acrylate (BA, 99%), ethanol, methyl methacrylate (MMA, 98%), styrene (St, 99%), hydrochloric acid (HCl), 2-hydroxyethyl methacrylate (HEMA, 98%), potassium persulfate (KPS, 99.99%), tetraethyl orthosilicate (TEOS, >99%), triethoxyvinylsilane (VTEO, 97%), sodium dodecyl sulfate (CP), triton X-100 (Biochemical grade) were purchased from Aladdin Reagent (Shanghai). The matting agent organic thermosetting polymethyl urea resin (PERGOPAK M5) was obtained from Beijing THK sci. All these materials were used without further purification. Deionized water was used for all polymerization and treatment processes.

Preparation and Modification of SiO₂

Synthesis of SiO₂ was carried out in a 500-mL round bottom flask equipped with a mechanical stirrer, thermometer with a temperature controller, and additional funnels. The reactor flask charged with 0.15 mol of TEOS and 0.52 mol of deionized water was firstly dissolved in 1.20 mol of EtOH, and the hydrochloric acid (0.1 mol/L) was used as acid catalyst to adjust the pH to about 3. Then, the reaction proceeded at 50°C for 8 h.

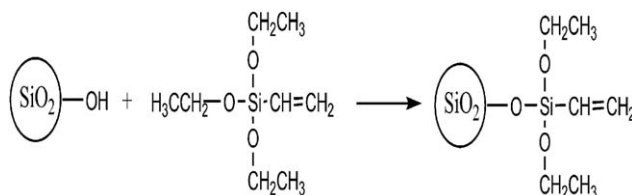


Figure 1. The grafting of VTEO onto the surface of silica particles.

After the flask was heated to 60°C, stoichiometric amount of VTEO was added to the mixture under vigorous stirring for another 2 h. A SiO₂ dispersion with a spherical particle size of about 3.5 μm was obtained, which solid content was about 15% (the reaction formula of VTEO grafting of SiO₂ was illustrated in Figure 1).

Preparation of AC/SiO₂/PMU Hybrid Materials

A 250-mL round bottom flask equipped with a mechanical stirrer, thermometer with a temperature controller, and additional funnels was charged with stoichiometric amount of surfactant dispersed in distilled water and heated to 70°C. The monomers, initiator and deionized water, as indicated in Part A in Table I, were added into the flask and heated to 80°C within 30 min under constant stirring to obtain seed latex. Then, the remaining monomers mixture and initiator solution as showed in Part B in Table I were fed through an addition funnel over the course of 3 h. After the addition of all ingredients, the reaction mixture was maintained at 80°C for 1 h to complete the reaction. Then, the reaction mixture was cooled to 45°C and stoichiometric amount of NaOH was added to neutralize the free carboxylic groups. The reaction was allowed to continue for 30 min, and then, different amount of SiO₂ was dispersed into the emulsion and stirred for 1 h. Finally, PMU was added into the flask and stirred for 30 min by mechanical agitation with 2000 r/min to obtain the final product.

Preparation of Films

The polymer films were prepared by casting the hybrid emulsion into glass molds. They were dried at room temperature for 7 days and then at 50°C for 1 day. This method of drying is used for slow drying to evaporate the water. After demolding, the films were stored in desiccators at room temperature for further study.

Table I. Typical Recipes for the Synthesis of AC Emulsions

Materials	Part A (g)	Part B (g)
HEMA	0.51	4.50
MMA	0.73	6.54
MAA	0.15	1.35
St	0.12	3.88
BA	0.13	12.51
Initiator (KPS)	0.0304	0.1217
Sodium dodecyl sulfate	0.69	0
Triton X-100	0.23	0
Deionized water	90	0

Characterization

Fourier Transform Infrared Spectroscopy (FTIR). The infrared spectra of SiO₂, AC, AC/SiO₂, and AC/SiO₂/PMU were obtained on a RFX-65 A FTIR spectrophotometer in KBr. The spectra of all dried films were collected within the range of 4000–400 cm⁻¹.

UV-Vis Spectra. A UV-Vis spectrophotometer (UV-2550) was used to measure the transmittance spectra of the AC/SiO₂ and AC/SiO₂/PMU emulsion latex within a wavelength range of 700–200 nm wavelength light. The samples were diluted to 0.2%.

Particle Size Analysis. The particle sizes of SiO₂ hybrid emulsion were measured using a laser light scattering method with a JL-1177 instrument. The samples had been diluted before the study began and were kept at 25°C during the measurement.

Viscosity. The viscosity of the hybrid latex was determined by NDJ-95 digital viscometer instrument, and No. 4 rotor was used with a speed of 60 r/s.

Morphological Properties. The morphology of the SiO₂, AC, AC/SiO₂, and AC/SiO₂/PMU latex was obtained by transmission electron microscopy (TEM, JEM-100CXII). The samples were dried on carbon-coated copper grids, and phosphotungstic acid was used to stain the sample. The morphology of the hybrid films was observed using scanning electron microscopy (SEM, JSM-6360LV), and the dried films were stained on copper grids, and gold was sprayed over the samples. Both sets of images were used to study the surface roughness of hybrid films.

Thermal Analysis. The thermal curves of thermogravimetric analysis (TGA) were recorded using a PerkinElmer analyzer. The temperature ranged from room temperature to 700°C at a heating rate of 10°C/min in a nitrogen atmosphere.

Contact Angle. A DSA 10 video contact angle measuring device was used to measure the contact angle of the hybrid films. Distilled deionized water was used as the reference liquid. About three independent measurements were made on different parts of the film, which had been dried at room temperature for 7 days by casting hybrid emulsions onto glass slides. The average contact angle was reported.

Gloss. The gloss of dried hybrid films was determined at 60° using a KGZ-60 gloss meter according to ASTM E 284. About three independent measurements were made on different parts of the film.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 2 shows the differences among the structures of micro-SiO₂, pure AC, AC/SiO₂, and AC/SiO₂/PMU. In FTIR spectra of micro-SiO₂ [Figure 2(a)], the peak at 1630 cm⁻¹ was assigned to the stretching vibration of the vinyl group.⁸ The peak at 1410 cm⁻¹ came from CH₂ deformations, while the absorption peak at 1046 and 784 cm⁻¹ corresponded to the asymmetric stretching vibration and the bending vibration of the Si-O-Si bond. The existence of vinyl groups and the disappearance of absorption in 3440–3500 cm⁻¹ and 930–950 cm⁻¹ region due to Si-OH stretching confirmed that VTEO coupling agents were

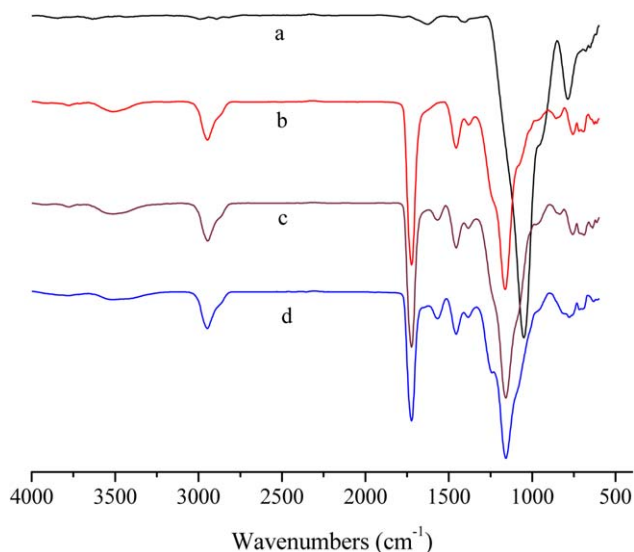


Figure 2. FTIR Spectroscopy of SiO₂ (a), pure AC (b), 5 wt. % SiO₂ (c), 5 wt. % SiO₂, 2 wt. % PMU (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemically coated onto the surface of the SiO₂ particles.^{1,6} In comparison of FTIR spectrum of AC and SiO₂, the spectra of AC/SiO₂ and AC/SiO₂/PMU exhibit strong absorption bands at 3483–3415 cm⁻¹ due to the O-H stretching vibration. The characteristic stretching peak at 2947 cm⁻¹ was ascribed to the stretching vibration of C-H (CH₃) group. The peak at 1575 and 1458 cm⁻¹ corresponded to the aromatic C-C stretch from backbone of benzene. The sharp absorption at 1160–1170 cm⁻¹ is due to the overlap of the stretching vibration of the C-O-C group. The peak in AC/SiO₂/PMU spectrum at 1160–1170 cm⁻¹, which is obviously broader than that of AC/SiO₂, can be attributed to the hydroxymethyl of PMU component. This evidence confirmed that SiO₂ and PMU have been dispersed into the AC composite during the polymerization process.

Physical Property of Composite Latex and Films

A series of composite latex and films containing SiO₂ and PMU were prepared and the physical properties were determined as shown in Table II. The data display that addition of SiO₂ can decrease the viscosity of system and leads to a high gloss surface (samples No. 1~3). The viscosity of system changed as PMU was introduced into the AC polymer. As the SiO₂ content in the polymer increased, a gradual increase in viscosity was observed and the hybrid films exhibited lower gloss. When SiO₂ content increased up to 5 wt. %, a matting surface was formed and the film became translucent. With higher concentration of SiO₂ up to 7 wt. %, a maximum viscosity of 36.3 m·Pa·s was obtained, and the gloss of film decreased to 18.9.

It is well known that emulsion viscosity shows a significant correlation with matting efficiency.⁹ High viscosity tends to make matting easier because the movement of particles was hindered. On the basis of Stoke's law [eq. (1)], the movement of the particles is related to the viscosity. At a certain point in time and within the time scale of further shrinkage, if the viscosity of

Table II. Physical Properties of AC Polymers with Increasing PMU and SiO₂

No.	SiO ₂ content (wt. %)	PMU (wt. %)	Appearance	Gloss (60°)	Viscosity (m·Pa·s)
1	0	0	Transparent	90.4	25.5
2	3	0	Transparent	92.4	17.0
3	5	0	Transparent	111.9	15.0
4	1	2	Transparent	82.7	23.7
5	3	1	Transparent	89.9	17.1
6	3	2	Transparent	87.2	17.5
7	3	3	Transparent	84.6	17.8
8	5	2	Translucent	36.3	19.8
9	7	2	opaque	18.9	36.3

system is high enough, the movement of the particles can be hindered. When the SiO₂ concentration was in a low level, chemical or physical bonding among the AC polymer, SiO₂, and PMU provided reinforcement to the hybrid materials. In contrast, appreciable agglomeration was occurred when SiO₂ content increased beyond 5 wt. %. The excess SiO₂ particles did not link with AC chains but increased the tendency toward particle growth. These particles may agglomerate together to form bigger one's. Consequently, viscosity property of the hybrid materials increases at higher concentrations of the SiO₂. And their distribution becomes irregular and nonhomogeneous, causing opaqueness and lower gloss in the hybrid films.¹⁵

$$\mu = \frac{2a^2(\rho - \rho_0)g}{9\eta} \quad (1)$$

where μ is the rate of sedimentation, a is the radius of particle, g is the acceleration of gravity, η is the viscosity of the dispersion medium, and ρ , ρ_0 are the density of particles and dispersion medium, respectively.

On the other hand, the PMU composites containing active hydroxymethyl group, which is reactive toward the functional groups (carboxyl groups) of AC and the hydroxy groups of SiO₂ and ethanol, causing some degree of gelation of the system, the viscosity of system increase. In addition, PMU particles are stranded on the surface of the wet film in the viscosity system. When effective size of the particles have been large enough, the degree of roughness developed and a matting surface was formed. It is worth noting that stable latex could not be obtained with micro-SiO₂ individually into the AC composites for matting purpose. But a stable hybrid composite latex which would form a matting surface could be obtained by the addition of PMU into acrylic composite and a lower amount of SiO₂.

UV-VIS Spectra

The UV-Vis transmittance spectra of the composite latex containing SiO₂ and PMU are shown in Figures 3 and 4, respectively. Figure 3 presents the influence of PUM content on transmittance of the hybrid emulsions. As shown in Figure 3, with increasing PMU content, the transmittance obviously decreased in the wavelength range of 290~800 nm. The reduction in transmittance in the range indicates that the film transparency become lower, which is consistent with the change in

the appearance of the film and the gloss observed. The increase in the concentration of PMU could contribute to the strong interfacial interaction between inorganic particles and AC polymer. The inorganic particles tend to agglomerate. The appearance of the composite latex containing PMU is completely opaque due to its larger particle size.² In this case, PMU particles were isolated as "dispersive" heterogeneous phase in the hybrid matrix, leading to a serious light scattering,¹⁶ and a reduction in transmittance was obtained. In contrast, the UV-Vis spectra for composites with increased SiO₂ content remained almost unchanged even up to 7 wt. % SiO₂ (Figure 4). No scattering and reflecting occurs in the visible light range. The introduction of SiO₂ into the AC polymer is less straightforward in transmittance.

The Morphology of Composite Particles

The dispersion of SiO₂ particles and PMU inside the composite polymer films observed by TEM is illustrated in Figure 5. It can be seen that SiO₂ dispersion with a spherical particle size of

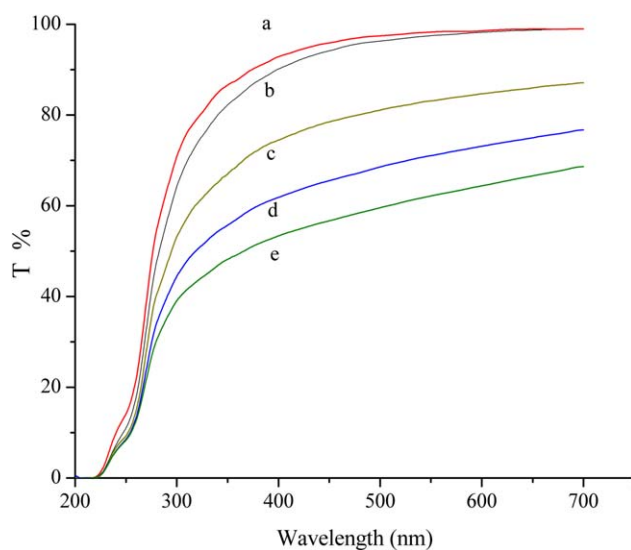


Figure 3. Transmittance spectra of AC/SiO₂ hybrid materials containing different PMU content: pure AC (a), 3 wt. % SiO₂ (b), 3 wt. % SiO₂, 1 wt. % PMU (c), 3 wt. % SiO₂, 2 wt. % PMU (d), 3 wt. % SiO₂, 3 wt. % PMU (e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

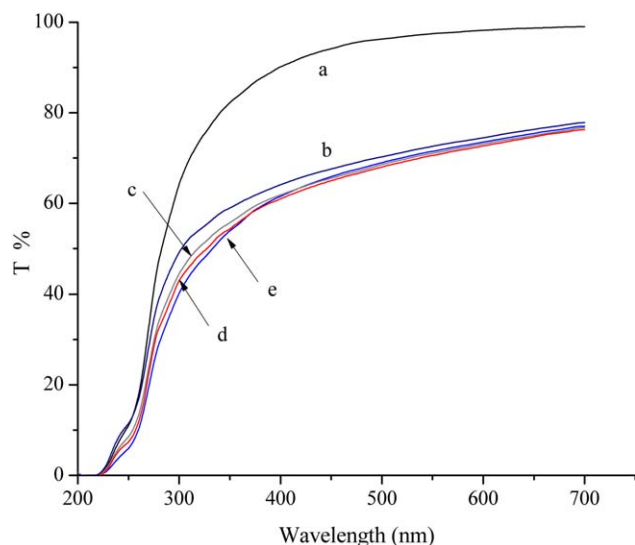


Figure 4. Transmittance spectra of AC/PMU hybrid materials containing different SiO_2 content: pure AC (a), 1 wt. % SiO_2 , 2 wt. % PMU (b), 3 wt. % SiO_2 , 2 wt. % PMU (c), 5 wt. % SiO_2 , 2 wt. % PMU (d), 7 wt. % SiO_2 , 2 wt. % PMU (e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about $3.5 \mu\text{m}$ [Figure 5(a)]. AC particles exhibit irregular spherical with a diameter about $0.7 \mu\text{m}$ [Figure 5(b)]. Figure 5(c) indicates that some SiO_2 particles were remained in aggregates and enwrapped into each latex particle. The morphology of

hybrid composite latex may be possible formed by the following mechanism: AC polymer and surfactants can be adsorbed onto the surface of hydrophobic VTEO-modified SiO_2 and act as dispersant which increases the particle surface potential to improve the intergranular static electricity rejection. A high barrier prevents the aggregation between the particles. Moreover, the polymer dispersant can form adsorption layer on the particle surface, generating strong steric hindrance between particles. On the other hand, due to higher surface energies of SiO_2 particles and smaller distance between SiO_2 particles, in fact smaller than the Van der Waals radius,⁹ VTEO-modified SiO_2 unavoidably exhibits a stronger tendency to aggregation. Moreover, when PMU was added to the system, the size of aggregates has been larger than before. The structure like leaf shape was formed [Figure 5(d)]. The morphology of hybrid composites is related to the polymer–inorganic interfacial tensions. It is clear that introduction of micro inorganic particles into AC resin increases the interfacial tensions. As a result, the free energy levels of system became lower. The leaf shape structure was formed with respect to thermodynamic equilibrium.^{17,18} Meanwhile, the morphology of hybrid material depends on the homogeneity of the inorganic particles in the organic phase. Blending is a physical method that make PMU disperse into polymer matrix, and no any chemical interaction occurs in the micro composites before the drying process. Therefore, the incompatibility with polymer matrix leads to the aggregation of SiO_2 particles. In addition, on a molecular level, the VTEO-modified SiO_2 is not soluble in the AC polymers.

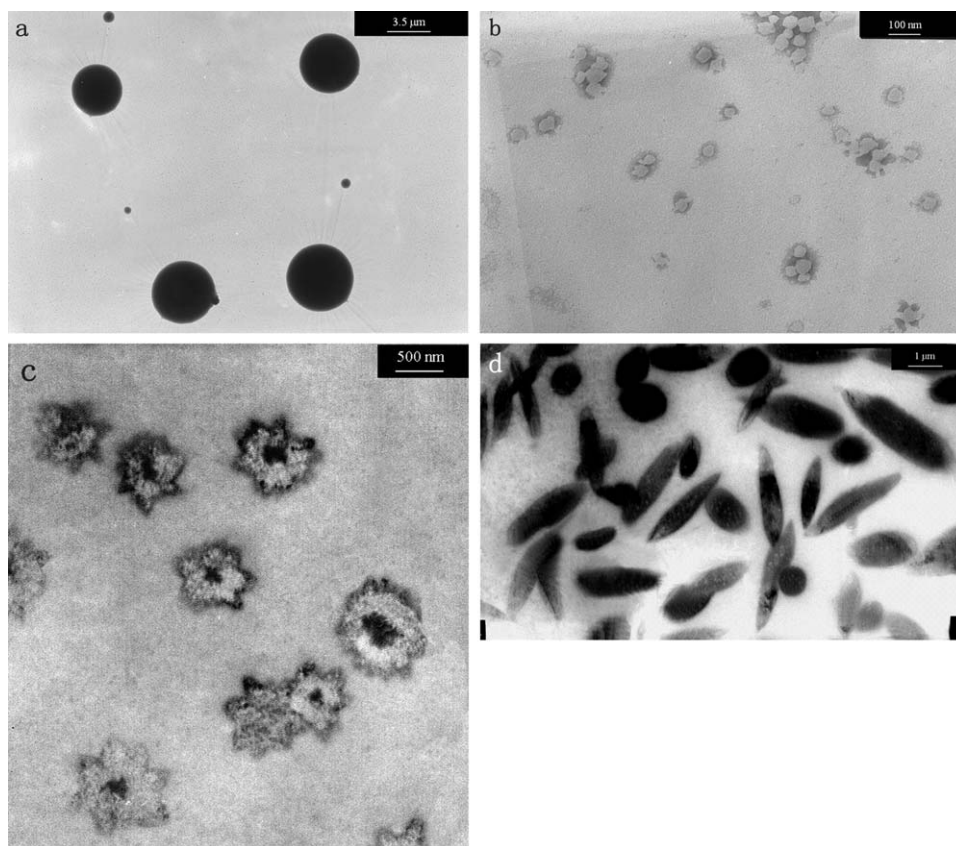


Figure 5. TEM micrographs of SiO_2 (a), pure AC (b), 5 wt. % SiO_2 (c), 5 wt. % SiO_2 , 2 wt. % PMU (d).

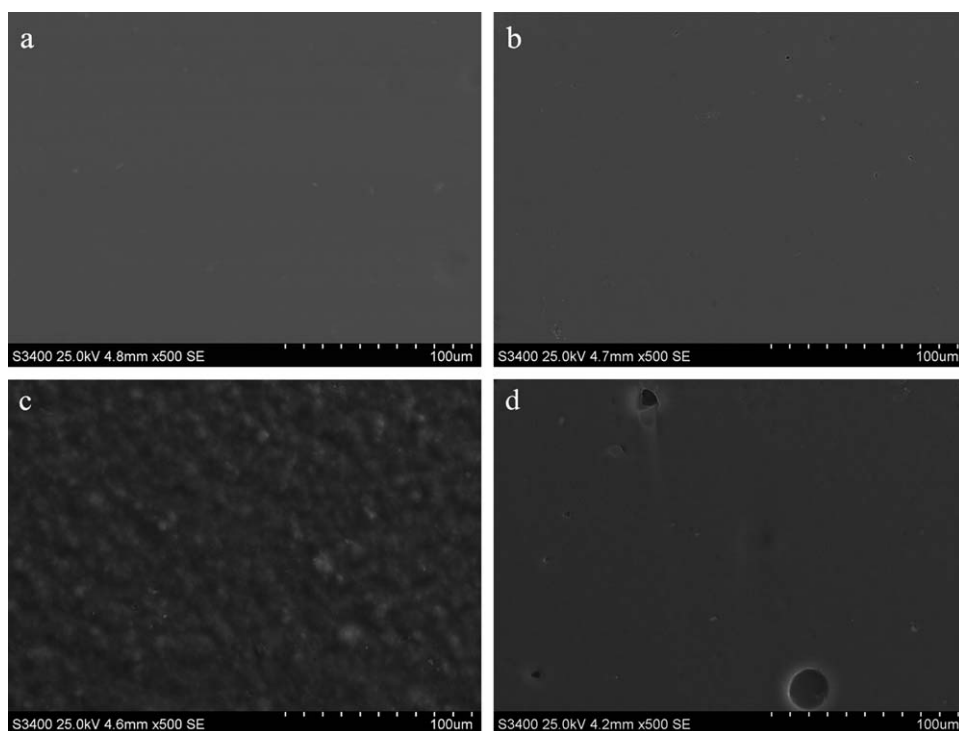


Figure 6. SEM micrographs of AC polymer (a), 5 wt. % SiO₂ (b), 5 wt. % SiO₂, 2 wt. % PMU (c), 7 wt. % SiO₂, 2 wt. % PMU (d).

Therefore, the AC–SiO₂ domains keep phase separation during film formation. The resultant discontinuous phase morphology is mainly responsible for the leaf shape structure due to high specific surface and pore volume of PMU. Finally, structures like leaf shape can be observed.

The morphology of composite films was investigated by SEM as shown in Figure 6. The SEM images in Figure 6(a,b) show that both of pure AC polymer and AC/SiO₂ hybrid membranes are homogeneous and smooth surface. The morphology is closely related to the nature of the interactions between phases.¹⁹ The morphology resulted from a competition between the cross-linking kinetics and the phase separation kinetics due to the incompatibility of SiO₂ in the AC composites.⁶ Moreover, the hybrid systems based on SiO₂ and AC polymer provides reinforcement to the hybrid materials due to strong physical links, such as hydrogen bonding, between hydroxyl functions of the SiO₂ and carbonyl groups of the AC chains. Comparing with the morphology of the pure AC polymers and AC/SiO₂ hybrid films, some irregular bulges with no clear boundary were observed when PMU was introduced into AC polymers. These irregular bulges should be a matting agent (PMU)-rich phase. On the other hand, from the visual appearance, Figure 6(c) exhibits slight agglomeration of matting agent particles, resulting in inhomogeneous distribution. The SEM micrograph of the same composite in Figure 6(d) exhibits very low matting agent concentration on the surface of the film. Due to the higher density of modified SiO₂, the viscosity of the system was high enough to make the PMU particles stay under the film. Moreover, the AC polymers have a shielding effect on the surface of these particles, which make the film less rough. In addition, a

higher SiO₂ content increases the particle size due to the gelation and agglomeration. These large domain sizes can result in the light scattering of hybrid membrane, giving opaqueness to the hybrids. The roughness and morphology of the AC/SiO₂/PMU films observed via SEM and the transmittance spectra recorded using the UV spectrum are closely consistent with the observed surface gloss.

To explain these phenomena reasonably, the film formation mechanism of hybrids emulsion is postulated as Figure 7. In the case of wetting film, PMU and SiO₂ particles showed an even distribution in hybrid emulsion. During the film shrinkage, a high number of PMU and SiO₂ particles of an appropriate size were stranded on the surface of the film by convection which resulted from the evaporation of water process. As the volume concentration increases, the viscosity of system increases and viscoelastic properties were developed. The particles tended to deform and frizzle, leading to formation of a rough surface structure related to matting film.

In hybrid systems based on AC/SiO₂/PMU, PMU shows higher value of the refractive index than that of AC polymer. According to the Fresnel's law [eq.(2)], extinction characteristics is related to the difference value of the refractive index. High difference value is highly efficient in producing the type of matting surface, as it offers the opportunity for the particles to undergo reflection, refraction, and scattering several times. The refractive index of AC polymer and SiO₂ were detected to be about 1.38 and 1.46, respectively, while the refractive index of PMU was about 1.61. The difference in refractive index was large enough to produce matting effect.

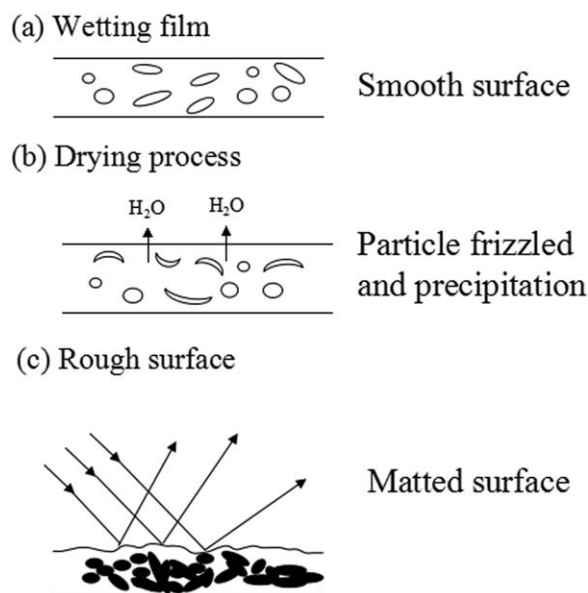


Figure 7. Film formation process of AC/SiO₂/PMU hybrid emulsions.

$$F = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \quad (2)$$

where F is the hiding power, n_1 , n_2 are the refractive index of pigment and hybrid materials, respectively.

Thermal Stability

Thermogravimetry analysis (TGA) shown in Figure 8 was carried out to examine the effect of SiO₂ and organic matting agent PMU on the thermal stability of AC hybrid polymer. The TGA curves starting at 50°C and ending at about 500°C exhibited three distinct weight loss stages. The weight loss temperature range of the first stage was from 50°C to 200°C for all samples due to the evaporation of physically absorbed water

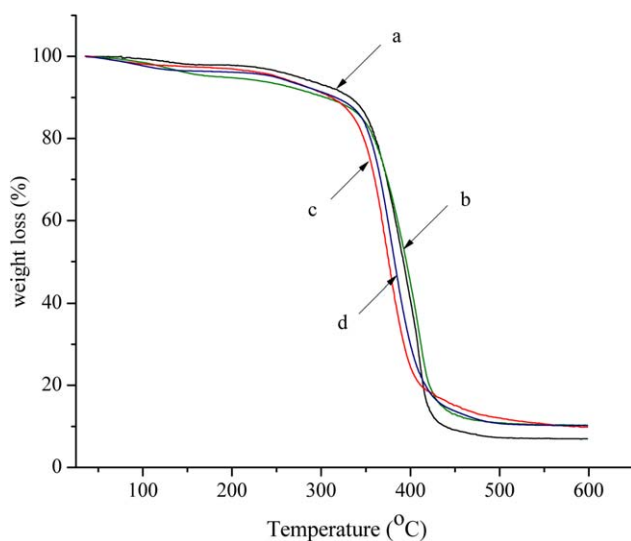


Figure 8. TGA thermograms of AC polymer (a), 5 wt. % SiO₂ (b), 5 wt. % SiO₂, 2 wt. % PMU (c), 7 wt. % SiO₂, 2 wt. % PMU (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Results of Thermogravimetric Analysis of Pure AC and Hybrid Films

Designation	$T_{0.1}$ (°C)	$T_{0.3}$ (°C)	$T_{0.5}$ (°C)	T_{max} (°C)	% Residue at T_{max}
a	332	374	392	407	6.99
b	304	374	395	374	10.23
c	312	360	376	379	9.28
d	316	367	382	380	10.18

AC polymer (a), 5 wt. % SiO₂ (b), 5 wt. % SiO₂, 2 wt. % PMU (c), 7 wt. % SiO₂, 2 wt. % PMU (d). $T_{0.1}$, $T_{0.3}$, $T_{0.5}$, T_{max} refer to the temperature at weight loss of 10%, 30%, 50%, and maximum decomposition.

and residual solvent existing in the composite films.⁶ The second stage from 200°C to 350°C originated from the decomposition of the chain from vinylidene end.⁶ In the third stage, the residues were further degraded at approximately 400°C, corresponding to the decomposition of main chain of AC. The final residues of AC, AC/SiO₂, AC/SiO₂/PMU (5 wt. % SiO₂, 2 wt. % PMU), AC/SiO₂/PMU (7 wt. % SiO₂, 2 wt. % PMU) were 6.99%, 10.23%, 9.28%, 10.18%, respectively (Table III). Consequently, the thermal stability of hybrid membranes at high temperatures exceeds that of pure AC, which suggests the successful incorporation of the SiO₂ and PMU into the hybrid membranes. This increase in the thermal stability can be attributed to the high thermal stability of SiO₂ and the existence of PMU in the polymer matrix. However, the SiO₂ and PMU loaded hybrid composites before 400°C show more weight loss as compared to pure AC polymer. Due to the aggregation of excessive SiO₂ particles, some degree of phase separation between PMU and AC was occurred. It decreased the thermal stability of hybrid composite. Additionally, simultaneous decomposition of

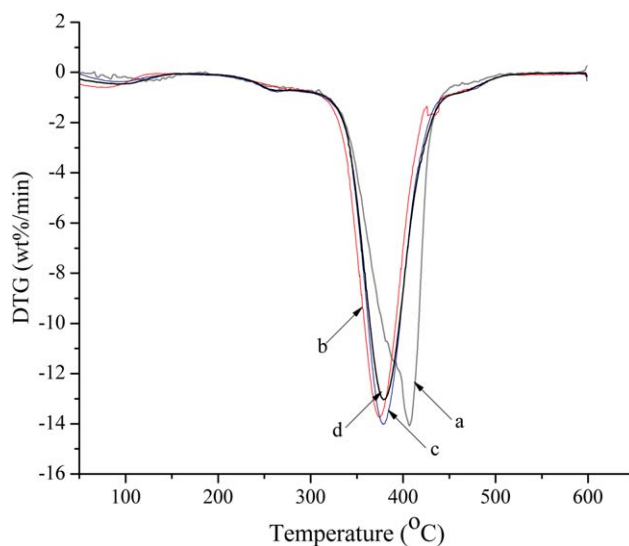


Figure 9. DTG curves of AC polymer (a), 5 wt. % SiO₂ (b), 5 wt. % SiO₂, 2 wt. % PMU (c), 7 wt. % SiO₂, 2 wt. % PMU (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Contact Angle Values of Water for Hybrid Latex

SiO ₂ content (wt. %)	0	1	3	3	3	5	7
PMU (wt. %)	0	2	1	2	3	2	2
Contact angle (°)	81.6	73.4	68.7	72.3	76.1	71.9	69.8

VTEO and PMU is also responsible for the lower thermal stability.

Figure 9 shows the DTG curves of the samples. The SiO₂ and PMU loaded hybrid composites show lower peak degradation temperature than the pure AC polymer, indicating the introduction of inorganic particles into AC could cause phase separation and decrease the thermal stability. However, the peak degradation temperature gradually increases by increasing the SiO₂ concentration when compared the samples with the same compositions. The presence of SiO₂ particles within the matrix could develop physical cross-linking, which limited the movement of AC matrix. Additionally, the Si-O bond energy existing in AC was greater than that of C-O bond which improved thermal resistance of the hybrid composites.¹⁶

Water Contact Angle

The contact angle of water on the hybrid film surface is shown in Table IV, which directly indicates surface hydrophobic property of hybrid films. The water surface contact angle on hybrid composites was found to increase continuously from 68.7 to 76.1 as PMU content increased from 1 to 3 wt. %. The PMU composites containing active hydroxymethyl group, which is reactive toward the functional groups (carboxyl groups) of AC. When cured to form films, the cross-linking reaction between PMU and AC as well as self-cross-linking reaction of PMU occurred, which decreased the water absorption. Consequently, higher contact angle value was obtained. However, the water absorption increased with the higher silica content, which may be resulted from increasing phase separation due to the aggregation of SiO₂ particles. Moreover, the surface roughness of films plays an important role on water contact angle.²⁰ The results of gloss demonstrated that the surface of hybrid films became rougher as SiO₂ content increased. A rough surface could increase the contact area of the solid-liquid, and a lower contact angle of the film was obtained.

CONCLUSIONS

Acrylic resin/micro-SiO₂/poly methyl urea composite resins were prepared by directly mixing acrylic polymer with poly-methyl urea resin and micro-SiO₂. The modified SiO₂ was synthesized via an acid-catalyzed sol-gel process by grafting of triethoxyvinylsilane on its surface. The composites latex has been stable for at least three months. FTIR indicates the structure of AC/SiO₂/PMU. The TEM images suggest that two distinct phases are formed for AC/SiO₂/PMU composites.

The morphology of hybrid films was examined by SEM. It confirmed the incorporation of the micro-SiO₂ caused higher roughness and lower gloss of the hybrid films in the presence of PMU. With higher viscosity of the hybrid system, which caused by gelation and agglomeration of SiO₂, PMU particles are stranded on the surface of the film. The effective sizes of the inorganic and organic particles are large enough to develop a rough surface. Therefore, a matting surface was developed. This study provides a new perspective on the matting material. Through the combination of AC polymer with polymethyl urea resin and micro-SiO₂ particles, a waterborne matting coating was developed.

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