

Preparation of Organic/Inorganic Hybrid Polymer Emulsions with High Silicon Content and Sol-gel-derived Thin Films^{*}

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Abstract A novel polymer/SiO₂ hybrid emulsion (PAES) was prepared by directly mixing colloidal silica with polyacrylate emulsion (PAE) modified by a saline coupling agent. The sol-gel-derived thin films were obtained by addition of co-solvents into the PAES. The effects of γ -methacryloxypropyltrimethoxysilane (KH-570) content and co-solvent on the properties of PAES films were investigated. Dynamic laser scattering (DLS) data indicate that the average diameter of PAES (96 nm) is slightly larger than that of PAE (89 nm). Transmission electron microscopy (TEM) photo discloses that colloidal silica particles are dispersed uniformly around polyacrylate particles and some of the colloidal silica particles are adsorbed on the surface of PAE particles. The crosslinking degree data and Fourier transform infrared (FT-IR) spectra confirm that the chemical structure of the PAES is changed to form Si-O-Si-polymer crosslinking networks during the film formation. Atomic force microscope (AFM) photos show the solvent induced sol-gel process of colloidal silica and the Si-based polymer distribution on the film surface of the dried PAES. Thermogravimetric analysis (TGA) curves demonstrate that the PAES films display much better thermal stability than PAE.

Keywords colloidal silica, polymer/SiO₂ hybrid emulsions, sol-gel process, water resistance

1 INTRODUCTION

Acrylate polymer emulsions used for waterborne wood coatings are typical low volatility organic compound (VOC) content coatings with many excellent properties including good film appearance, high gloss, and good mechanical properties. However, they also exhibit poor water-/solvent- resistance and low hardness [1, 2]. One of the methods to improve their properties is to combine of inorganic nanometer materials to form organic/inorganic composite coatings [3, 4]. Polymer/SiO₂ nano-composites have been received much attention in recent years and employed in a variety of applications, such as coatings and optical-electric materials. The nano-SiO₂ acts as a reinforcing agent to improve the hardness, strength, and thermal stability of the polymers [5, 6].

Many studies have been reported about the preparation of polymers/silica hybrid materials with organic monomers and inorganic precursors such as tetramethyloxysilane (TMOS) and tetraethyloxysilane (TEOS) through *in situ* emulsion polymerization and sol-gel processes [7–10]. In the hybrid materials, the inorganic and organic phases are combined by the interactions including hydrogen bonds and chemical covalent bonds. However, it is difficult to control precisely the simultaneous hydrolysis and condensation of alkoxysilyl groups during the sol-gel process. Therefore, high concentrations of inorganic precursors in polymer emulsions greatly decrease the stability of hybrid emulsions in sol-gel and storage process [11–13]. Most of the polymer/SiO₂ films show poor transpar-

ence due to the phase separation between inorganic and organic phases [3, 4].

An alternative way is the direct mix of inorganic colloidal silica and polymer emulsion, to prepare the organic/inorganic hybrid emulsion with high silicon content and improve storage stability in sol-gel process. However, it is difficult to uniformly disperse inorganic colloidal particles in the polymer emulsion and film to obtain high gloss films [14–16].

In some studies, saline coupling agents have been used to improve the properties of the organic/inorganic hybrid material as well as the chemical interaction between organic and inorganic components [17, 18]. However, these methods are suitable only for low contents of silicon in organic/inorganic composites [3, 4]. In present paper, we demonstrate the preparation of the polymer/silica hybrid with high content silicon (Fig. 1). The morphology, chemical structure, thermal stability, and properties of polymer/silica hybrid films are illustrated.

2 EXPERIMENTAL

2.1 Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), diacetone acrylamide (DAAM), and adipic dihydrazide (ADH) were commercial products and used without further purification. γ -methacryloxypropyltrimethoxysilane (KH570), γ -glycidoxypropyltrimethoxysilane (KH560), and γ -aminopropyltriethoxysilane (KH550) were purchased

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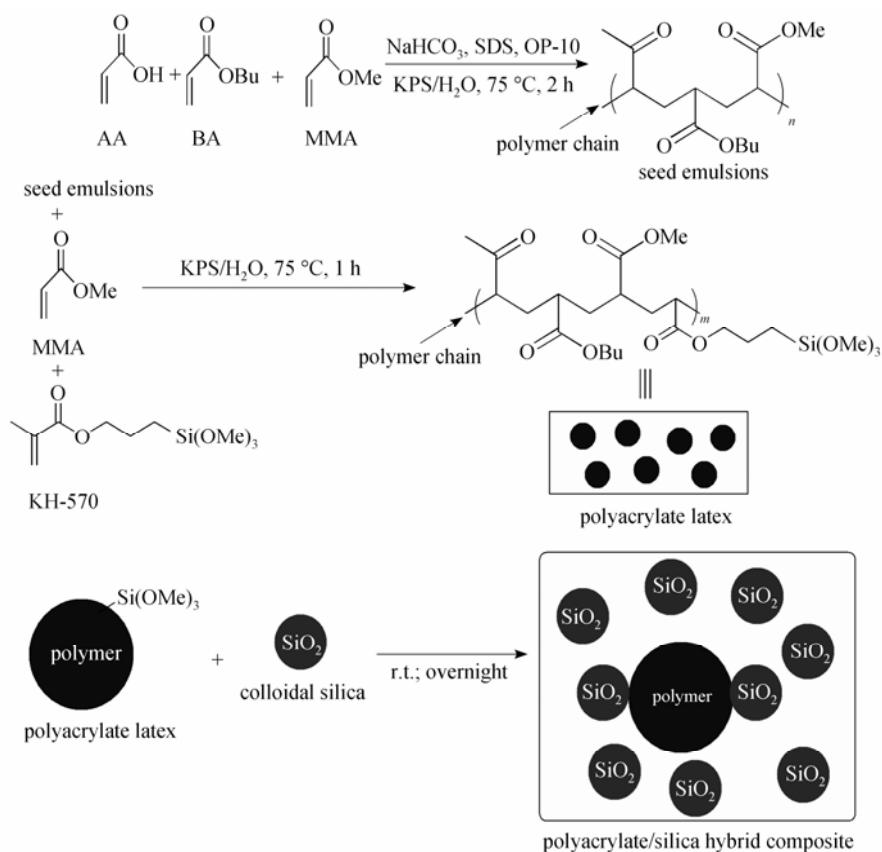


Figure 1 The synthetic route of polyacrylate/SiO₂ hybrid composites

from Shanghai Yewu Chemical Co. Colloidal silica [30% (by mass), pH=11] was supplied by Foshan Nanhai Waterglass Co. Isopropanol, isobutanol, ethanol, dipropylene glycol monomethyl ether (DPM), and dipropylene glycol *n*-butyl ether (DPnB) were supplied by Guangzhou Chemical Reagent Co. Nonyl phenyl polyoxyethylene ether-10 (OP-10), sodium dodecyl sulphonate (SDS), sodium bicarbonate (NaHCO₃) and potassium persulfate (KPS) were used as received. Deionized water was applied for the polymerization process.

2.2 Preparation of polyacrylate emulsion (PAE)

The polyacrylate emulsions were synthesized according to Ref. [19]. Polymerization was performed under a nitrogen atmosphere in a 500 ml, 4-neck flask equipped with a mechanical stirrer (fitted with a crescent Teflon blade), a temperature control system, an inlet for feeding monomer emulsion, an inlet for feeding initiator solution and a reflux condenser. The kettle was charged with deionized water (60 g), SDS (2.0 g), OP-10 (1.0 g) and NaHCO₃ (0.25 g). Deionized water, SDS, BA, MMA, DAAM and MAA were placed in a graduated beaker with a magnetic stirrer and stirred to give a white monomer emulsion. The shell monomer emulsion with KH570 was prepared by the same method. Separately, a solution with 1.5 g of

ammonium persulfate in 30 g of deionized water was prepared. To make a seed latex, the kettle contents were heated to 80–82 °C and stirred as the following ingredients were added sequentially: (a) 1/4 of the core monomer emulsion, (b) a solution of ammonium persulfate. The mixture was stirred at 80–82 °C for 20 min. The rest of core monomer emulsion and the initiator solution were added in 2 h with continuous stirring of the reaction flask. After 30 min, the shell monomer emulsion was added in 120 min. The initiator solution was added throughout the process at a rate of 10–15 droplet per minute. The reactor temperature was maintained at 80–82 °C until 30 min after the addition was complete. Then the latex in the kettle was cooled to about 60 °C, and a 50/50 (mass ratio) solution of dimethylethanolamine in deionized water was added with continuous stirring to adjust the pH to 9.2–9.5 along with an ADH solution was added to the latex. The kettle temperature was reduced to about 40 °C. The latex was filtered through a 100 μm filter (200-mesh sieve). The monomer composition was: MMA 70 g, BA 40 g, MAA 1.5 g, KH570 0–7 g, DAAM 1.0 g and ADH 0.5 g.

2.3 Preparation of polyacrylate/silica hybrid composite (PAES) films

The colloidal silica (50 g) and co-solvent (10 g)

were added to PAE (100 g) and stirred for 12 h, keeping the pH of PAES at about 8.0.

The sol-gel derived films were prepared by dip-coating to form the PAES, and then dried at room temperature for 48 h and annealed at 80 °C for 12 h. The PAE film was prepared by the same method as PAES.

2.4 Characterization

The latex particle size and its distribution were determined by granularity measured instrument (ZS Nano S) from Malvern Co. (England). Fourier transform infrared (FTIR) spectra (Spectnlm2000, PERKIN ELMER Co. USA) were obtained to determine the chemical structures of PAE and PAES. The morphologies were directly observed by using a JEM-100 CX II transmission electron microscopy (TEM) (Electron Co. Japan) with an acceleration voltage of 60 kV. The samples were diluted and stained with 1% phosphotungstic acid ($\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4] \cdot 14\text{H}_2\text{O}$). The surface morphology of composite films was studied by a scanning probe microscopy (cspm-3000, Benyuan Nano Co.). Thermal stability and silica content of dried films were determined by the Thermo gravimetric analyzer (TG/DSC, STA449C) (NETZSCH Co. Germany) by heating the sample (8–10 mg) from 40 to 650 °C at 15 °C·min⁻¹ at an air flowrate of 40 ml·min⁻¹. The TGA samples were prepared by the method described in the film preparation. A known mass of an oven-dried film (W_0) was placed in a Soxhlet extractor for continuous extraction with THF for 24 h, and the polymer gel after extraction was dried to a constant mass (W_1). The gel mass content (%) was calculated from $W_1/W_0 \times 100$. The water- and solvent-resistance of the film was characterized by water/solvent absorption. Film samples (mass W_0 , dimensions 25 mm×25 mm×1 mm) were immersed in water/ethanol at room temperature for 8 days, removed from the water/ethanol, and weighted (W_1). Then the film samples were dried to a constant mass (W_2) at room temperature. The percentage of the water absorption (W_A), the ethanol absorption (W_E), the mass loss of polymer films in water (W_x) and ethanol (W_y) were calculated according to the following formulas [3, 20].

$$W_A = \frac{w_1 - w_2}{w_2} \times 100\% \quad (1)$$

$$W_x = \frac{w_0 - w_2}{w_0} \times 100\% \quad (2)$$

$$W_E = \frac{w_1 - w_2}{w_2} \times 100\% \quad (3)$$

$$W_y = \frac{w_0 - w_2}{w_2} \times 100\% \quad (4)$$

Solid contents of PAE and PAES were determined by the weight loss method. The QBY type pendulum durometer was employed to measure the

film hardness. The gloss of film was measured by glossmeter (60°).

3 RESULTS AND DISCUSSION

3.1 PAES hybrid composite

PAE was prepared with MMA, BA, AA, DAAM and KH-570 by the free radical emulsion polymerization, as illustrated in Fig. 1. Since KH-570 can co-polymerize with acrylic monomers and afford $-\text{Si}(\text{OMe})_3$ groups in polymer side chains, the hydrolysis and condensation between $-\text{Si}(\text{OMe})_3$ groups and $\text{Si}-\text{OH}$ groups of the colloidal silica may combine SiO_2 with polyacrylic polymers [13]. Fig. 2 shows the TEM micrograph of the PAES. It demonstrates that the polyacrylate emulsion possesses clear core-shell structure and colloidal silica particles are dispersed uniformly around the polyacrylate particles. In addition, some colloidal silica particles are adsorbed on the surface of PAE particles. The average diameter of colloidal silica particles and that of polyacrylate latex are about 20 nm and 100 nm, respectively, according to the TEM.

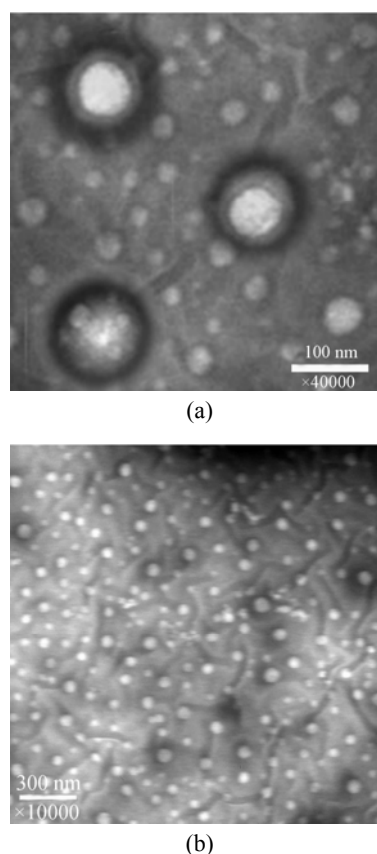


Figure 2 TEM photograph of PAES emulsion

Figure 3 illustrates the particle size distributions of the colloidal silica, PAE, and PAES. The average diameter of colloidal silica is about 20 nm, and that of

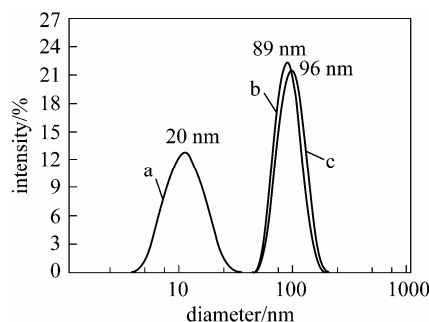


Figure 3 Particle size and size distribution of colloidal silica (a), PAE (b) and PAES (c)

PAES is 96 nm. The mean diameter of PAES is slightly larger than that of PAE (89 nm), which is probably attributed to the hydrolysis and condensation between colloidal silica and $-\text{Si}(\text{OMe})_3$ groups on polymer side chains, as shown in Fig. 4. The results are consistent with those by the TEM.

Figures 5 and 6 show the FTIR spectra of colloidal silica, PAE, and PAES. In Fig. 5 (a), the absorption peaks around 3417 and 964 cm^{-1} are associated with $\text{Si}-\text{OH}$ group stretching vibrations, while 1193 and 800 cm^{-1} are attributed to $\text{Si}-\text{O}-\text{Si}$ group stretching vibrations. In Fig. 5 (b), the characteristic stretching peaks of $-\text{CH}_3$ and $-\text{CH}_2$ groups are at 2957 and 2869 cm^{-1} , respectively. The stretching vibration of $\text{C}=\text{O}$ group at 1737 cm^{-1} is attributed to the carboxyl of polyacrylate, the stretching vibrations of $\text{C}-\text{O}-\text{C}$ at 1243 , 1171 and 1064 cm^{-1} are referred to the MMA and BA moieties [21]. Absorption peaks of 804 , 963

and 3445 cm^{-1} in Fig. 5 (b) are attributed to $\text{Si}-\text{OH}$ and $\text{Si}-\text{O}-\text{Si}$ groups of KH570, which provides evidence that KH570 is copolymerized with acrylate monomers. No distinct change is observed between the FT-IR spectra of PAE [Fig. 5 (b)] and PAES emulsions [Fig. 6 (b)] except at 1064 cm^{-1} , which may be affected by minimal formation of $\text{Si}-\text{O}-\text{Si}$ groups in emulsion states. When the PAES emulsion is dried to form films, the absorption peak at 1119 cm^{-1} attributed to $-\text{C}-\text{O}$ group stretching vibrations shifts to 1123 cm^{-1} , and a new absorption peak at 1147 cm^{-1} appears in spectra of Fig. 6 (a). At the same time, the stretching vibration of $\text{Si}-\text{OH}$ groups at 3443 cm^{-1} almost disappears, and the signatures of uncondensed $\text{Si}-\text{OH}$ groups at 946 cm^{-1} also disappear [10]. It is assumed that sol-gel processes of colloidal silica occur to form $\text{Si}-\text{O}-\text{Si}$ crosslinking bonds during the drying process of PAES.

3.2 Effect of KH570

The influences of KH570 content on the properties of PAES films are shown in Table 1. The KH570 modified PAE increase the miscibility between the hydrophilic inorganic silica phase and the hydrophobic organic phase, and the mechanism is shown in Fig. 4. As KH570 content increases, the gel content, crosslinking degree, hardness of PAES films and the water/alcohol-resistance increases, but when KH570 content is higher than 3.0%, the overabundant bridge bonds between the inorganic and organic materials increases the brittleness of the polymer, so that the

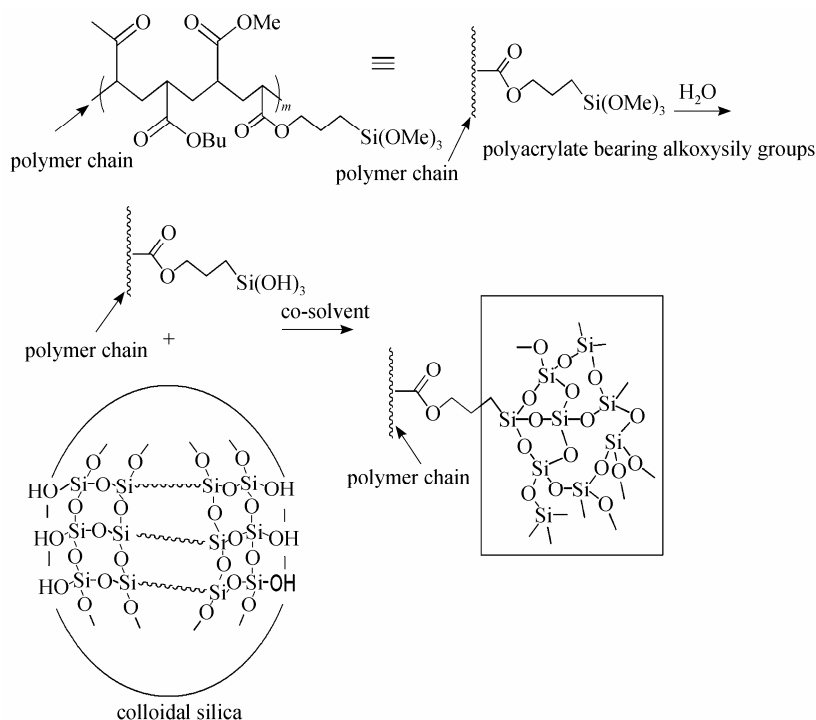


Figure 4 The mechanism for improving the properties of PAES films by KH570

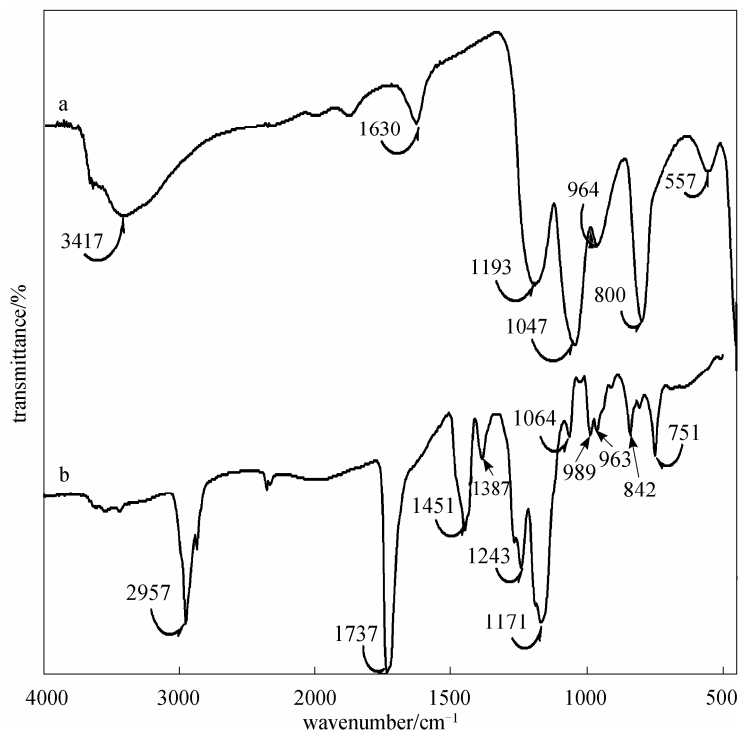


Figure 5 FT-IR spectra of colloidal silica (a) and PAE (b)

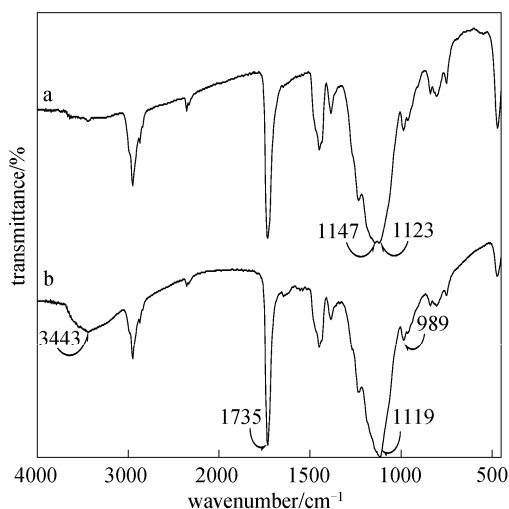


Figure 6 FT-IR spectra of PAES film (a) and PAES emulsion (b)

mechanical properties can not be improved further. Serious coagulation occurred in the emulsion in the reaction with 7% of KH570. We also investigated the effects of saline coupling agents on the stability of PAES and found that the saline coupling agents with epoxy or amino groups such as KH560 and KH550 may react with carboxy groups in the PA and decrease the storage stability, while KH570 with C=C group hardly affect the polymerization and storage stability at the content up to 3.0%.

Table 1 Effects of KH570 content on properties of PAES films

KH570/% (by mass)	W_N / %	W_S / %	W_E / %	W_Y / %	Gel content/%	Hardness	Gloss 60°/%
0	25.4	12.3	50.7	23.1	56.2	0.60	78
1	14.5	8.4	42.6	16.7	75.3	0.66	82
3	7.3	6.9	38.7	13.4	88.6	0.82	85
5	8.4	7.4	41.8	14.5	84.9	0.74	88
7	8.6	7.3	40.7	13.6	81.4	0.71	88

3.3 Sol-gel derived films

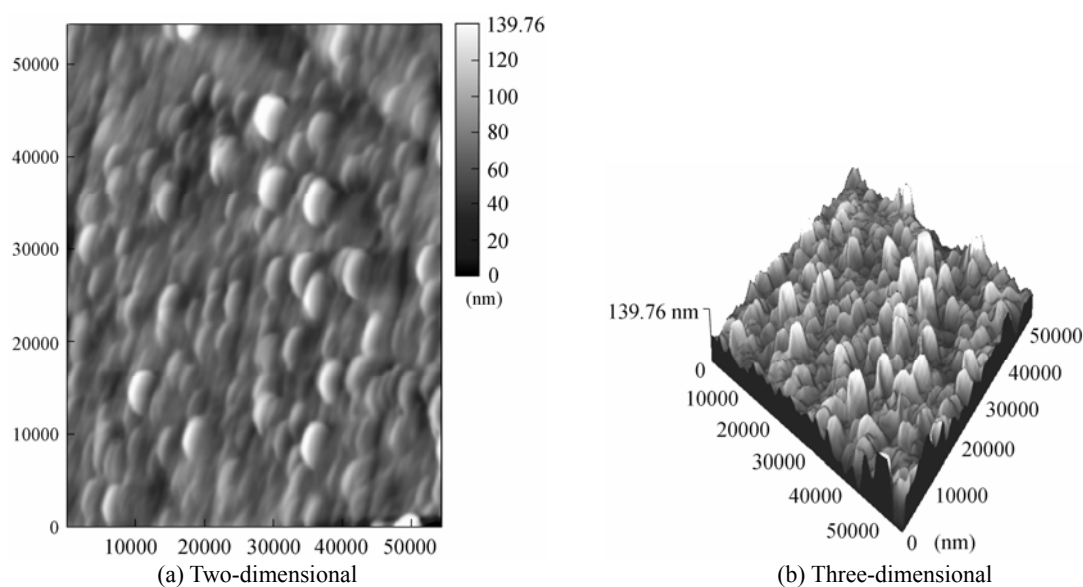
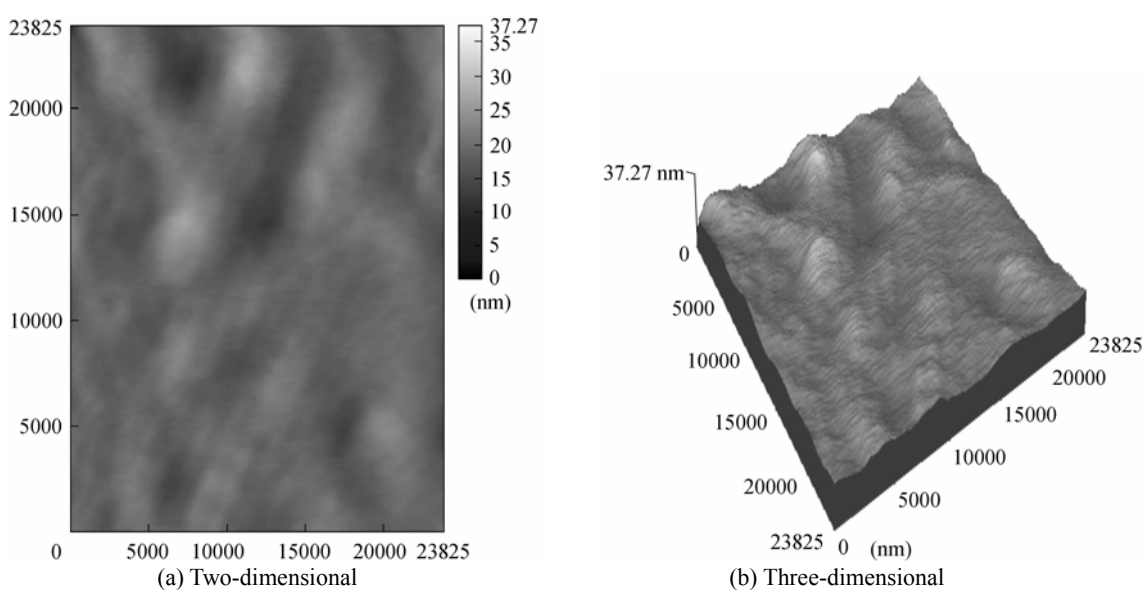
With the addition of 10% (polymers mass content) co-solvent into the PAES with 3% KH570, the PAES films were prepared and their properties were tested. The effects of solvent on the properties of PAES are listed in Table 2. The addition of solvent increases the film gloss and gel contents. During the drying process of PAES, as the water and neutralizing agent evaporate, the concentration of silica colloidal and polymer increase and the pH value of PAES decreases. The rest of the solvent induces the hydrolysis and condensation reaction of the colloidal silica, namely, the sol-gel process occurs to form Si-based polymers [22], which is distributed on the film surface and tested by the AFM photos. The AFM topographic images of PAES without and with isobutanol are shown in Figs. 7 and 8, respectively.

Table 2 Solvents induced in sol-gel process and properties of PAES films

Solvents	W_A /%	W_x /%	Gel content /%	Hardness	Gloss (60°) /%
no solvents	17.4	9.0	40.2	0.79	69
isopropanol	11.2	5.8	89.2	0.86	95
isobutanol	12.3	6.1	88.3	0.85	97
ethanol	15.7	7.5	83.4	0.75	82
methanol	14.5	6.9	85.3	0.80	84

Figure 7 demonstrates that the average roughness (Ra) and root mean square roughness (Rq) of the PAES film without isobutanol are 13.6 and 18.2 nm,

respectively, while those values are 1.61 and 2.15 nm of the PAES film with isobutanol shown in Fig. 8. The PAES film with isobutanol is uniform, and the boundaries between the silica and polyacrylate are ambiguous, while the film surface PAES without isobutanol exhibits silica particles on an array of polyacrylate latex particles. Thus with isobutanol sol-gel process occurs in the PAES emulsion and re-distribution occurs on the film surface to form a film with high gloss and excellent performance. We also studied the effects of solubility of solvent in water on the surface appearance of PAES film, which includes isopropanol, isobutanol, ethanol and dipropylene glycol monomethyl ether (DPM) and dipropylene glycol *n*-butyl ether (DPnB), and found that the

**Figure 7** AFM images of PAES film without isobutanol**Figure 8** AFM images of PAES film with isobutanol

solubility greatly affects the film formation of PAES and sol-gel-derived silicon sol. The mechanism of sol-gel derived film formation by solvent is being studied.

3.4 TGA analysis

The thermal decomposition of dried PAES films was investigated at a heating rate of $15\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in an air flow, as illustrated in Fig. 9. The temperature corresponding to 5% loss is defined as the initial degraded temperature of polymer (T_d). The T_d values of the curves a and b are 269 and $311\text{ }^{\circ}\text{C}$, respectively, so that the thermal stability of PAES film is much better than that of PAE. The phenomenon is due to the formation of Si—O—Si— polymer bonds with high bond energy on the film surface, which improves the thermal stability. On the other hand, more silica component in PAES films will increase the thermal stability. The residual weight of PAES is 27% while that of PAE is about 0%, indicating the amount of SiO_2 is about 27%.

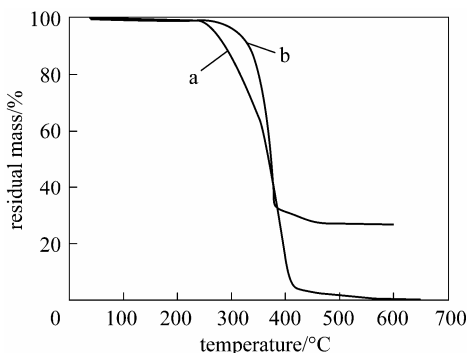


Figure 9 TGA curves of PAE film (a) and PAES film (b)

3.5 Properties of PAES films

Table 3 lists the properties of PAE and PAES films. PAES film exhibits better properties including water-/ethanol resistance, hardness and gloss.

Table 3 The properties of PAE and PAES films

Items	PAE	PAES
appearance	bluish	bluish
$W_N/\%$	32.8	11.2
$W_E/\%$	14.1	5.8
$W_H/\%$	soluble	38.7
$W_S/\%$	soluble	13.4
crosslinkage/%	0	89.2
hardness	0.43	0.86
gloss (60°)/%	89	95
stability	+	+
surface drying time/h	1	0.5
solid content/%	45	42.5
inorganic materials content/%	0	27.0

4 CONCLUSIONS

The polymer/silica hybrid emulsions (PAES) with high silicon contents (up to 27%) were prepared by directly mixing colloidal silica with PAE modified with KH570. DLS data indicates that the average diameter of PAES (96 nm) is slightly larger than that of PAE (89 nm). TEM photos disclose that colloidal silica particles are dispersed uniformly around polyacrylate particles and some colloidal silica particles are adsorbed on the surface of PAE particles. FT-IR spectra confirm the chemical structure change and the formation of Si—O—Si crosslinking network. The polyacrylic/ SiO_2 hybrid emulsions with 3% KH570 (based polymer) display excellent film properties. AFM photos show that the solvent induces the sol-gel process of colloidal silica and self-assembly on the film surface during drying of emulsion. TGA curves demonstrate that the PAES film displays much better thermal stability than PAE.

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