



## Fabrication of chemically bonded polyacrylate/silica hybrid films with high silicon contents by the sol–gel method

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### ABSTRACT

Polyacrylate/silica hybrid latexes (PAES) with high silicon contents (up to 21%) were prepared by directly mixing colloidal silica with polyacrylate emulsion (PAE) modified by a silane coupling agent. Sol–gel-derived organic/inorganic thin films were obtained by addition of hydrophilic co-solvents to PAES and subsequent drying at room temperature. The effects of co-solvents and  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570) content on the properties of PAES films were investigated. Dynamic light scattering (DLS) data indicated that the average diameter of PAES (96 nm) was slightly larger than that of PAE (89 nm). TEM photo revealed that colloidal silica particles were dispersed uniformly around polyacrylate particles and that some of the colloidal silica particles were adsorbed on the surface of PAE particles. The data of crosslinking degree and FT-IR spectra confirmed that the chemical structure of the PAES changed to form Si–O–Si-polymer crosslinking networks during the film formation. AFM photos, contact angle for water, and XPS analysis showed that the polyacrylate/inorganic hybrid films with high silicon contents were formed by the co-solvent-mediated, sol–gel method and that the Si-based polymers were uniformly distributed on the surface of the dried films. TGA data demonstrated that the PAES films display much better thermal stability than the PAE counterpart.

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### 1. Introduction

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

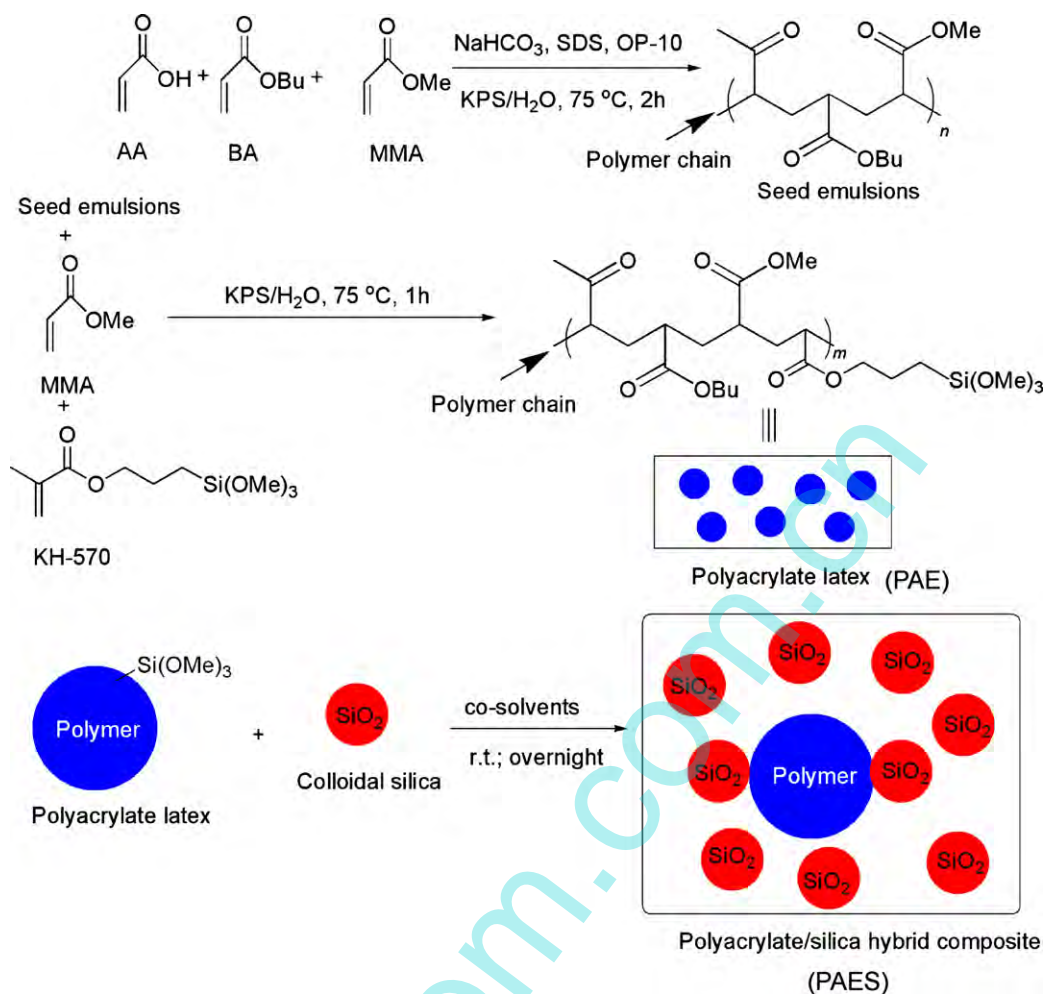
Many studies have been reported about the preparation of polymer/silica hybrid materials using organic monomers and inorganic precursors such as tetramethyloxysilane (TMOS) and tetraethyloxysilane (TEOS) through in situ emulsion polymerization and sol–gel process [7–10]. Especially, the low-temperature solution

conditions of sol–gel process enable nanoscale mixing of inorganic and organic components as precursors of hybrid solids. By this approach, multifunctional materials with homogeneous microstructures may be designed and synthesized which have an extensive range of mechanical, chemical, optical, and electronic properties. In the hybrid materials, the inorganic and organic phases are combined by the interactions including hydrogen bonds and covalent bonds. However, it is difficult to precisely control 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/silica films show poor transparency due to the phase separation between inorganic and organic phases [3,4].

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

In some studies, silane coupling agents have been used to improve properties of the organic/inorganic hybrid material by the chemical linkage between organic and inorganic components [17,18]. However, these methods have been successful only for low

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**Scheme 1.** The synthetic routes of polyacrylate/silica hybrid composites.

contents of silicon in organic/inorganic composites [3,4]. In the present study, we prepared polymer/silica hybrids with high silicon contents (Scheme 1), and revealed the morphology, chemical structure, thermal stability, and properties of the polymer/silica hybrid films.

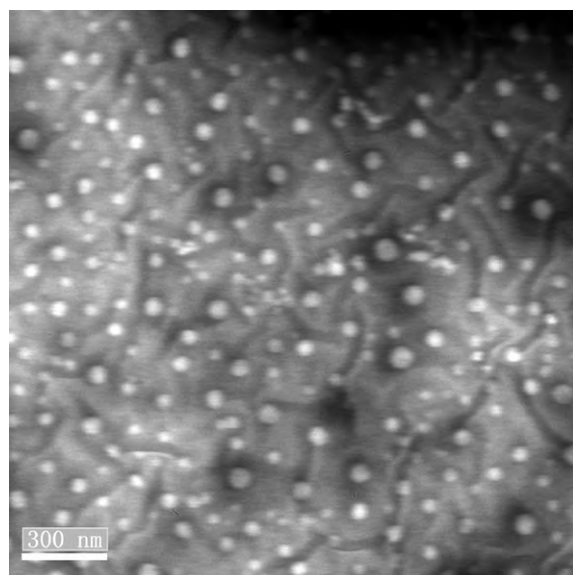
## 2. Experimental

### 2.1. Materials

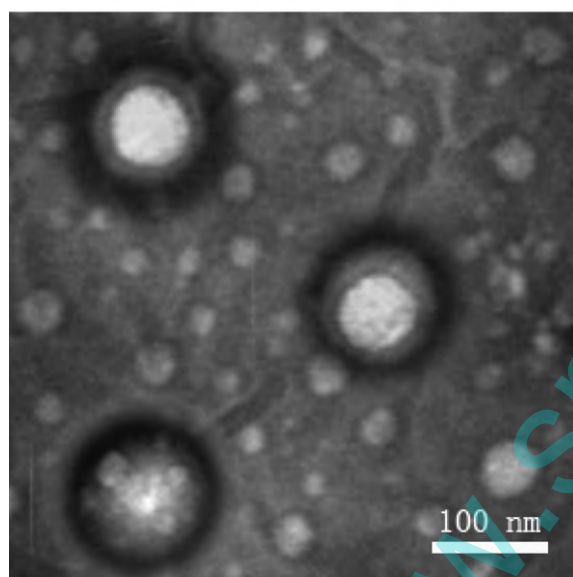
Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), diacetone acrylamide (DAAM), and adipic dihydrazide (ADH) were commercial products and used without further purification.  $\gamma$ -Methacryloxypropyltrimethoxysilane (KH570),  $\gamma$ -glycidoxypropyltrimethoxysilane (KH560), and  $\gamma$ -aminopropyltriethoxysilane (KH550) were purchased from Shanghai Yewu Chemical Co. (Shanghai, China). Colloidal silica (30 wt%, pH=11) was supplied by Foshan Nanhai Waterglass Co. (Foshan, China). Isopropanol, isobutanol, ethanol, dipropylene glycol monomethyl ether (DPM), and dipropylene glycol *n*-butyl ether (DPnB) were supplied by Guangzhou Chemical Reagent Co. (Guangzhou, China). Nonyl phenyl polyoxyethylene ether-10 (OP-10), sodium dodecyl sulphonate (SDS), sodium bicarbonate ( $\text{NaHCO}_3$ ) and potassium persulfate (KPS) were used as received. Deionized water was used for the polymerization process.

### 2.2. Preparation of polyacrylate emulsion (PAE)

Polyacrylate latexes were synthesized according to the literature [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 pre-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  $\text{NaHCO}_3$  (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 pre-emulsion. The shell monomer pre-emulsion with KH570 was prepared by the same method. Separately, a solution of ammonium persulfate (1.5 g) in deionized water (30 g) was prepared. To prepare a seed latex, the kettle contents were heated to 80–82 °C and stirred, while 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 the core monomer pre-emulsion and the initiator solution were added in 2 h with continuous stirring of the reaction flask. And then the shell monomer pre-emulsion was dropped into the reaction flask in 2 h. The initiator solution was added throughout the process at a rate of 10–15 droplet/min. The reactor temperature was maintained at 80–82 °C until 30 min after the addition was complete. During the polymerization, the pH was maintained at 7 using 5%  $\text{NaHCO}_3$  solution. The



(a) ×10 000



(b) ×40 000

Fig. 1. TEM photographs of PAES.

latex was filtered through a 200-mesh sieve. The solid content was 45%, calculated from Gravimetric Method. The monomer composition was: MMA 70–63 g, BA 40 g, MAA 1.5 g, KH570 0–7 g and DAAM 1.0 g. The KH570 contents are weight percentages based on total monomers.

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

The polyacrylate/silica hybrid latexes (PAES) were prepared by adding colloidal silica and co-solvent to PAE at room temperature, and stirred for 12 h, keeping the pH of PAES at about 8.0. The sol-gel-derived films were prepared by the casting PAES onto Polytetrafluoroethylene (PTFE,  $\Phi = 7$  mm,) plate and drying it at room temperature for 48 h, and annealing at 80 °C for 12 h. The PTFE plate was washed by ethanol before use, and the thickness of dried film is 0.1 mm. The PAE film was prepared by the same method as PAES.

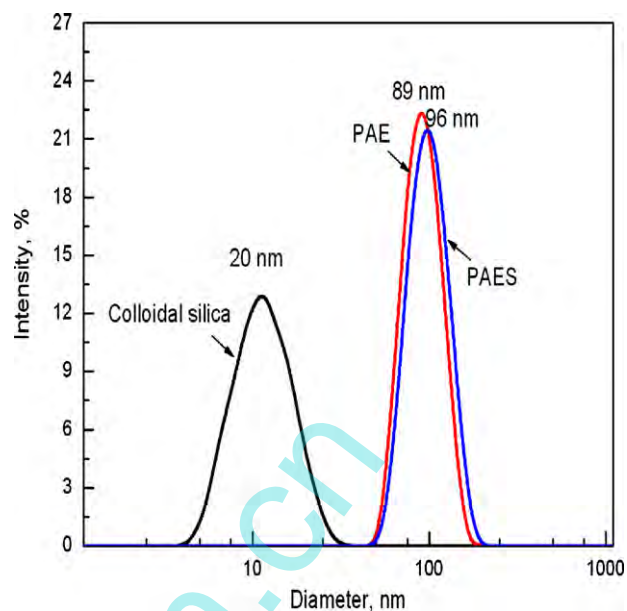


Fig. 2. The particle sizes and distributions of colloidal silica, PAE and PAES.

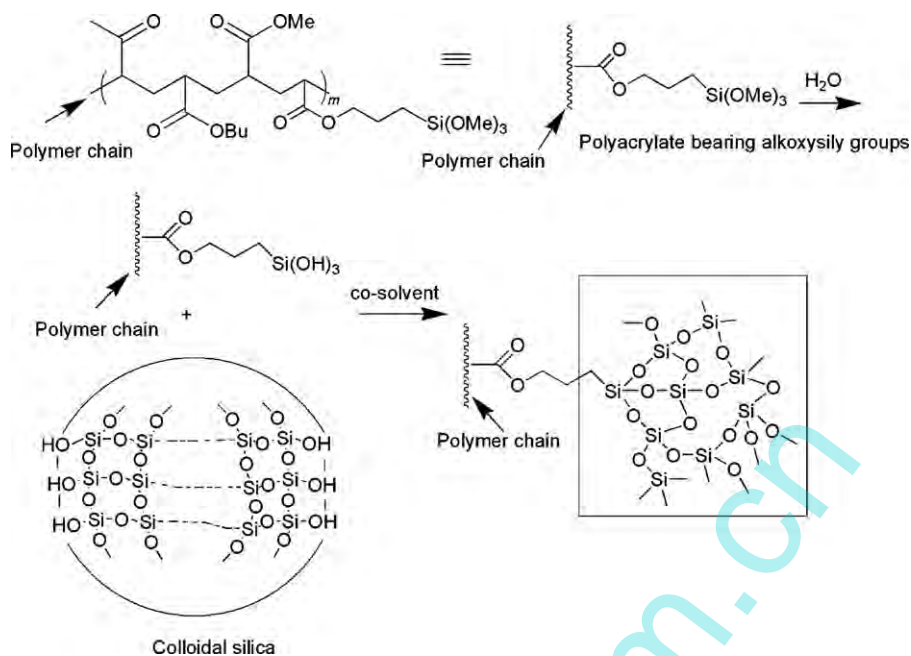
### 2.4. Measurements

The latex particle size and its distribution were determined with a granularity analyzer (ZS Nano S) from Malvern Co. (England). Fourier transform infrared (FT-IR) spectra (Spectnm2000, Perkin Elmer Co. USA) were measured to elucidate the chemical structures of PAE and PAES. The morphologies were directly observed by using a JEM-100 CX II transmission electron microscope (TEM) (JEOL Ltd., Japan) with an acceleration voltage of 60 kV. The samples were diluted and stained with 1% phosphato-tungstic acid ( $H_3[P(W_3O_{10})_4] \cdot 14H_2O$ ). The surface morphology of composite films was studied by scanning probe microscopy (cspm-3000, Benyuan Nano Co.). The thermal stability and silica content of dried films were determined by the thermogravimetric analyzer (TG/DSC, STA449C) (Netzsch Co. Germany) by heating the sample (8–10 mg) from 40 to 700 °C at 10 °C/min and at an air flow rate of 30 mL/min. In order to remove the water and solvent inside the films, the temperature was kept at 100 °C for 3 min. The TGA samples were prepared by the method described in the film preparation. The residual weight content was calculated by following equation

$$\text{residual weigh}(\%) = \frac{W_2 \times S_2}{W_1 \times S_1 + W_2 \times S_2}$$

$W_1$  is the mass of the PAE,  $S_1$  is the solid content of PAE,  $W_2$  is the mass of the colloidal silica (40 wt% PAE), and  $S_2$  is the solid content of colloidal silica.

A known weight 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 constant weight ( $W_1$ ). The gel content (wt%) 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 (weight  $W_2$ , dimensions 25 mm × 25 mm × 1 mm) were immersed in water/ethanol at room temperature for 8 days, removed from the water/ethanol, and weighed ( $W_3$ ). Then the film samples were dried to constant weight ( $W_4$ ) at room temperature. The percentage of the water absorption ( $W_A$ , %), the ethanol absorption ( $W_E$ , %), the weight loss of polymer films in water ( $W_x$ , %) and ethanol ( $W_y$ , %) were calculated according



**Scheme 2.** The mechanism of how KH570 improves the properties of PAES films.

to the following formula [3,20].

$$W_A \text{ or } W_E = \frac{W_3 - W_2}{W_2} \times 100\% \quad (1)$$

$$W_x \text{ or } W_y = \frac{W_2 - W_4}{W_2} \times 100\% \quad (2)$$

Solid contents or polymer or polymer/SiO<sub>2</sub> contents were determined by weight loss method at 120 °C for 1 h. The QBY type pendulum durometer was employed to measure the film hardness [21]. The gloss of film was measured with a glossmeter (60°). The contact angle for water (WCA) was measured with an OCA15 contact angle goniometer of Dataphysics Co., Germany, and data were collected for five drops across the surface. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra DLD system equipped with Al K $\alpha$  source and operating at 150 W; the scanning scope was 700  $\mu$ m  $\times$  300  $\mu$ m.

### 3. Results and discussion

#### 3.1. The preparation of the PAES

PAE was prepared from MMA, BA, AA, DAAM and KH570 by the free radical emulsion polymerization, as illustrated in Scheme 1. Since KH570 can co-polymerize with acrylic monomers and afford -Si(OMe)<sub>3</sub> groups in polymer side chains, the hydrolysis and condensation between -Si(OMe)<sub>3</sub> and Si-OH groups of the colloidal silica may combine silica with acrylic polymers [13]. Fig. 1 shows the TEM micrographs of the PAES. It demonstrates that colloidal silica particles are dispersed uniformly around the polyacrylate latexes, which shown in Fig. 1(a), it can be observed that the polyacrylate latex possesses clear core-shell structure and some colloidal silica particles are adsorbed on the surface of PAE particles when the magnification times is 40,000 in Fig. 1(b). The average diameter of colloidal silica particles and that of polyacrylate latex are about 20 nm and 100 nm, respectively, according to the TEM.

Fig. 2 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 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 -Si(OMe)<sub>3</sub> groups on polymer side chains, as shown in Scheme 2. The results are consistent with those of the TEM.

#### 3.2. Co-solvent-induced, sol-gel reaction and film formation

With addition of 10 wt% (based on polymers) co-solvents into the PAES with 3% KH570, the PAES films were prepared and their properties were examined. Table 1 shows results for the effects of co-solvents on the properties of PAES. As is obvious from Table 1, the addition of co-solvents increased the film gloss and gel contents. A probable reason is as follows: as water and the neutralizing agent evaporate during the drying process of PAES, the concentrations of colloidal silica 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-connected polymers [22], which is distributed on the film surface. This was inspected by AFM, and the AFM topographic images of PAES without and with isobutanol are shown in Fig. 3.

Fig. 3 demonstrates that the average roughness ( $R_a$ ) and root mean square roughness ( $R_q$ ) of the PAES film (sample 2) without isobutanol are 13.6 and 18.2 nm, respectively, while those of the PAES film (sample 4) with isobutanol are 1.61 and 2.15 nm, as shown in Table 1. The PAES film with isobutanol is uniform, and the boundaries between the silica and polyacrylate are ambiguous, while the film surface of PAES without isobutanol exhibits silica particles on an array of polyacrylate latex particles. Thus, when isobutanol is used, the 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 examined isopropanol, isobutanol, ethanol and dipropylene glycol monomethyl ether (DPM) and dipropylene glycol *n*-butyl ether (DPnB) as co-solvents to find that the kind of co-solvents greatly affects both the film formation of PAES and the surface appearance of PAES film. The mechanism of sol-gel-derived film formation in the presence of co-solvents is currently under study.

The contact angle for water (WCA) on film surface is dependent on chemical composition and surface structure of the film [23], and

**Table 1**  
Effect of co-solvents on the properties of PAES.<sup>a</sup>

Sample	Co-solvent	$R_a$ (nm) <sup>c</sup>	$R_q$ (nm)	$W_A$ <sup>d</sup> (%)	$W_x$ (%)	Gel content (%)	Hardness	Gloss (%)	WCA (°) <sup>e</sup>	$T_d$ (°C) <sup>f</sup>
1 <sup>b</sup>	Isobutanol	1.67	2.01	32.8	14.1	32	0.43	89	53	187
2	No	13.6	18.2	17.4	9.0	40	0.79	69	60	183
3	Isopropanol	2.53	3.22	11.2	5.8	89	0.86	95	74	234
4	Isobutanol	1.61	2.15	12.3	6.1	88	0.85	97	76	268
5	Ethanol	5.43	7.86	15.7	7.5	83	0.75	82	63	191
6	Methanol	4.67	6.06	14.5	6.9	85	0.80	84	65	196

<sup>a</sup> Colloidal silica/PAE = 20 wt%.

<sup>b</sup> Sample 1 is pure PAE.

<sup>c</sup> The average roughness ( $R_a$ ) and root mean square roughness ( $R_q$ ) of the PAE and PAES films were determined by AFM.

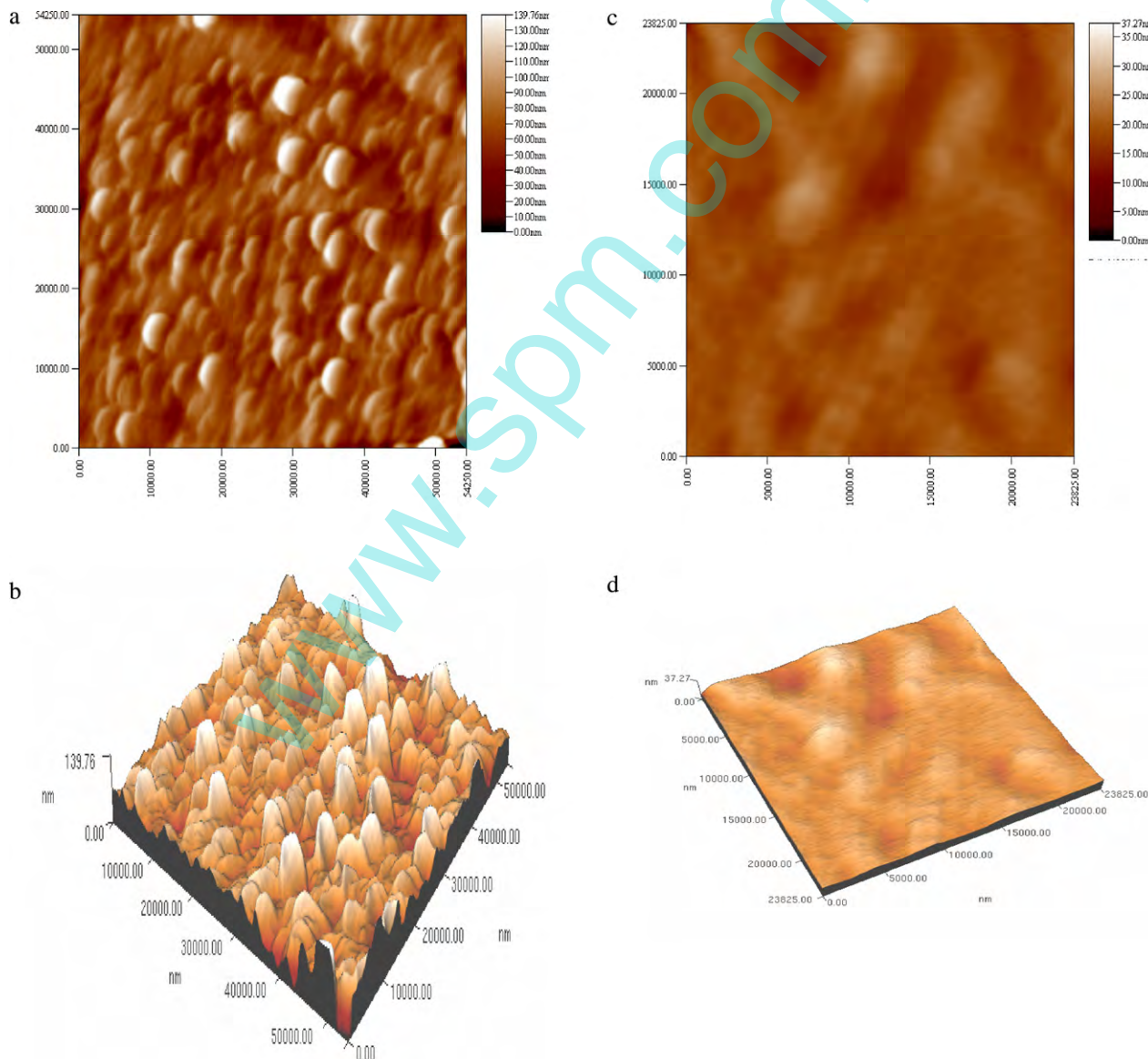
<sup>d</sup> Determined by Eqs. (1) and (2).

<sup>e</sup> Measured with an OCA15 contact angle goniometer.

<sup>f</sup> Determined by TGA.

films with higher WCA generally display good hydrophobic and water-resistance. The WCA values of PAES with co-solvents are given in Table 1. The WCA value of sample 1 is about 53°, indicating that the PAE film was somewhat hydrophilic due to the existence of hydrophilic groups including carboxyl groups. The PAES film with-

out co-solvent exhibits slightly higher WCA value (60°) than that of PAE, which is attributable to addition of colloidal silica to the PAE; silica particles in hybrid latexes will migrate to the surface of hybrid film due to their low surface energy to increase the WCA value of PAES during film formation [24,25]. By addition of co-solvents,



**Fig. 3.** The AFM images of sample 2 (a, two dimensional; b, three dimensional) and sample 4 (c, two dimensional; d, three dimensional) measured in scanning sizes of 50  $\mu\text{m} \times 50 \mu\text{m}$  and 24  $\mu\text{m} \times 24 \mu\text{m}$ , respectively.

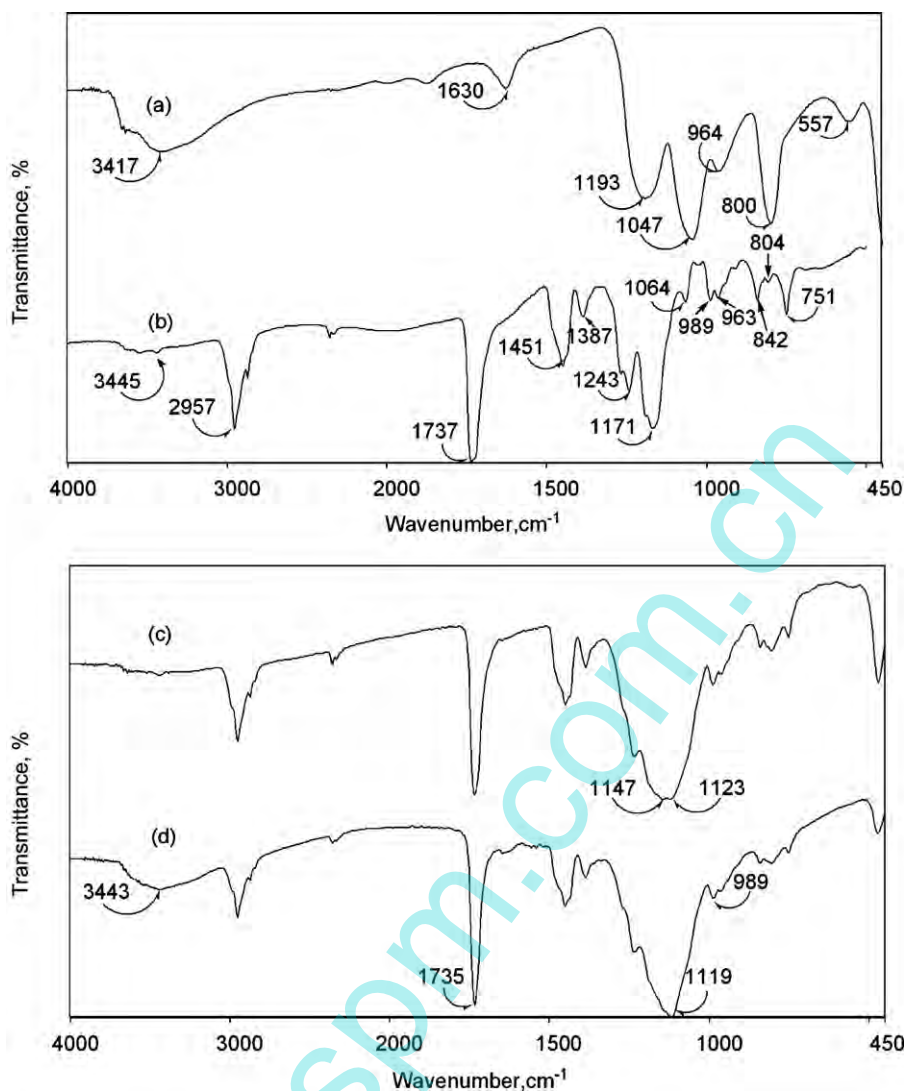


Fig. 4. FT-IR spectra of colloidal silica and samples 1, 2, and 4 measured in the range 450–4000  $\text{cm}^{-1}$ .

the WCA values of PAES increased up to 63–76°, which means that the co-solvents induced the hydrolysis and condensation reaction of the colloidal silica and PAE, and a large number of the Si–O–Si groups were formed on the film surface. It is especially important that isobutanol is the best co-solvent to improve the physical and chemical properties of PAES in terms of WCA as well as  $R_a$  and  $R_q$ .

### 3.3. Effect of KH570

Table 2 shows the influences of KH570 content on the properties of PAES films. The KH570-modified PAE is expected to increase the miscibility between the hydrophilic inorganic silica phase and the hydrophobic organic phase, and a probable mechanism is given in Scheme 2. As KH570 content was increased up to 3%, the gel content (or crosslinking degree), hardness of PAES films, and the water/alcohol-resistance increased. However, when KH570 content exceeded 3%, the overabundant bridge bonds between the inorganic and organic materials brought about the brittleness of the polymer, and consequently the mechanical properties rather deteriorated. Serious coagulation occurred in the latex in the reaction with 7% of KH570. We also investigated the effects of silane coupling agents on the stability of PAES to find that the silane coupling agents with epoxy or amino groups such as KH560 and KH550 may react

with carboxy groups in the PAE to decrease the storage stability, while KH570 with C=C group hardly affected the polymerization and storage stability at the content up to 3.0%.

### 3.4. FT-IR analysis

Fig. 4 shows the FT-IR spectra of colloidal silica, PAE, and PAES. In Fig. 4(a), the absorption peaks around 3417 and 964  $\text{cm}^{-1}$  are associated with the stretching vibrations of Si–OH group, while 1193 and 800  $\text{cm}^{-1}$  are attributed to the stretching vibrations of Si–O–Si group. In Fig. 4(b), the characteristic stretching peaks of  $-\text{CH}_3$  and  $-\text{CH}_2$  groups are at 2957 and 2869  $\text{cm}^{-1}$ , respectively. The stretching vibration of C=O group at 1737  $\text{cm}^{-1}$  is attributed to the carboxy of polyacrylate, the stretching vibrations of C–O–C at 1243, 1171, and 1064  $\text{cm}^{-1}$  are related to the MMA and BA moieties [26]. Peaks of 804, 963, and 3445  $\text{cm}^{-1}$  in Fig. 4(b) are attributed to Si–OH and Si–O–Si groups of KH570. No distinct change is observed between the FT-IR spectra of PAE [Fig. 4(b)] and PASE except the band of 1064  $\text{cm}^{-1}$ , which may be affected by minimal formation of Si–O–Si groups in emulsion states. When the PAES was dried to form a film, the absorption peak at 1119  $\text{cm}^{-1}$  attributable to the stretching vibrations of C–O group shifts to 1123  $\text{cm}^{-1}$ , and a new absorption peak at 1147  $\text{cm}^{-1}$  appeared in the spectra

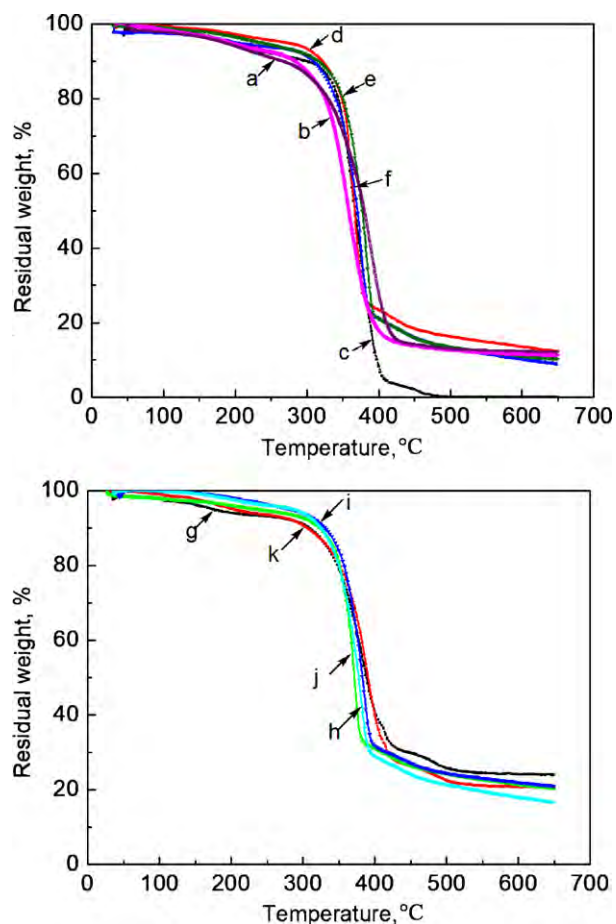


Fig. 5. TGA curves of PAES film with co-solvent (a–f, samples 1–6) and KH570 (g–k, samples 7–11) measured at a heating rate of 10 °C/min in air.

of Fig. 4(c). At the same time, the stretching vibration of Si–OH groups at  $3443\text{ cm}^{-1}$  almost disappeared, and the signatures of uncondensed Si–OH groups at  $964\text{ cm}^{-1}$  also disappeared [10]. It is reasonably assumed that the sol–gel processes of colloidal silica occurred to form Si–O–Si crosslinking bonds during the drying process of PAES.

### 3.5. TGA analysis

The thermal decomposition behavior of dried PAES films was investigated at a heating rate 10 °C/min under air flow, as illustrated in Fig. 5. The temperature corresponding to 5 wt% loss was defined as the initial degradation temperature of polymer ( $T_d$ ) [8,9]. It is seen from Tables 1 and 2 that the highest  $T_d$  of the sample was attained with isobutanol as a co-solvent and 3% of the KH570. The  $T_d$  value of pure PAE (sample 1), sample 4, and sample 9 was 187, 268, and 287 °C, respectively, and hence it can be said that the ther-

Table 2  
The effect of KH570 on the properties of PAES.<sup>a</sup>

Sample	KH570 (%)	$W_A^b$ (%)	$W_x$ (%)	$W_E$ (%)	$W_y$ (%)	Gel content (%)	Hardness	Gloss (%)	WCA (°) <sup>c</sup>	$T_d$ (°C) <sup>d</sup>
7	0	25.4	12.3	50.7	23.1	56	0.60	78	61	175
8	1	14.5	8.4	42.6	16.7	75	0.66	82	69	282
9	3	7.3	6.9	38.7	13.4	89	0.82	85	76	287
10	5	8.4	7.4	41.8	14.5	85	0.74	88	63	235
11	7	8.6	7.3	40.7	13.6	81	0.71	88	63	202

<sup>a</sup> Colloidal silica/PAE = 40 wt%, and the co-solvent is isobutanol.

<sup>b</sup> Determined by Eqs. (1) and (2).

<sup>c</sup> Measured with an OCA15 contact angle goniometer.

<sup>d</sup> Determined by TGA.

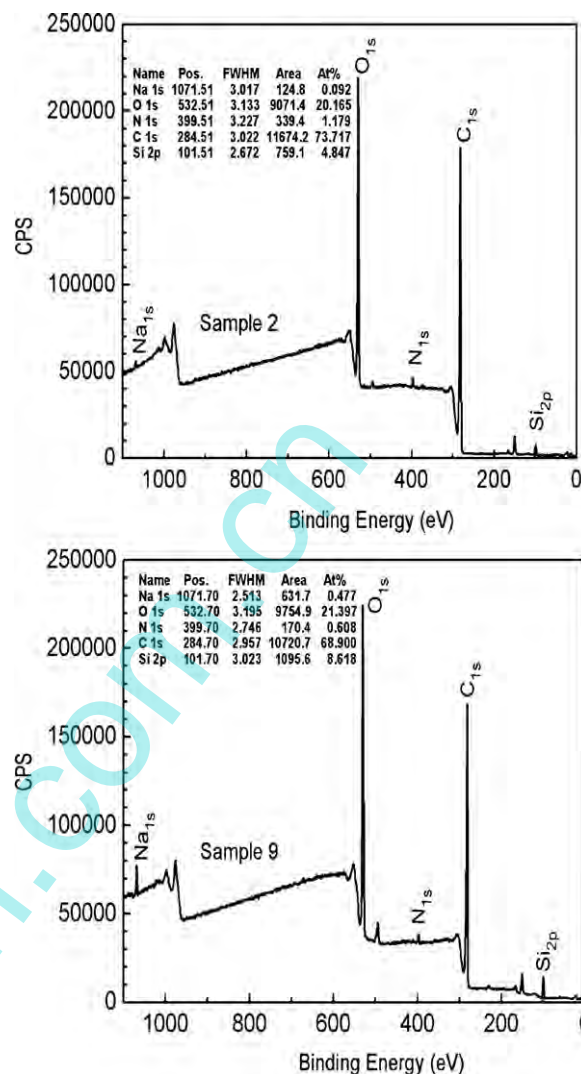


Fig. 6. XPS survey spectra of samples 2 and 9.

mal stability of PAES film is much better than that of PAE. This is explicable in terms of both the formation of Si–O–Si-polymer bonds with high bond energy on the film surface to improve the thermal stability and the increase of thermal stability with increasing silica content of PAES films. The residual weight of PAES (sample 9) is 21%, while that of PAE is about 0%, indicating that the amount of SiO<sub>2</sub> is about 21%.

### 3.6. XPS analysis

Fig. 6 depicts the XPS spectra of samples 2 and 4. The peaks at 532, 399, 284, and 102 eV can be attributed to oxygen (1s), nitro-

gen (1s), carbon (1s), and silicon (2p), respectively [24]. The overall percent contents of Si in samples 2 and 9 were 5.45 and 9.81%, respectively, which were calculated from the SiO<sub>2</sub> contents determined by TGA data. According to XPS data, the Si contents on the film surface of samples 2 and 9 were 4.85% and 8.62%, respectively. Thus the actual Si content on the film surface of sample 2 is about 89% of the average Si content, while that of sample 9 is about 88%. In general, the silica particles (or silica-based polymers) with low surface energy tend to migrate to the air–interface during film formation. However, the co-solvent induced the sol–gel reactions during the film formation of sample 9 to generate Si–O–Si-polymer covalent bonds, which made more silica particles remain in the internal part of film.

#### 4. Conclusions

The polymer/silica hybrid emulsions (PAES) with high silicon contents (up to 21%) were prepared by direct mixing of colloidal silica with PAE modified with KH570. DLS data indicated that the average diameter of PAES (96 nm) was slightly larger than that of the PAE (89 nm). TEM photos revealed that the colloidal silica was uniformly dispersed around the polyacrylate particles and some colloidal silica particles were adsorbed on the surface of PAE particles. FT-IR spectra confirmed the variations of chemical structure and the formation of Si–O–Si crosslinked network. The polyacrylate/silica hybrid emulsions with 3 wt% KH570 displayed excellent film properties. AFM photos showed that the co-solvents promoted the sol–gel process of colloidal silica and the self-assembly on the film surface upon drying of emulsions. TGA curves demonstrated that the PAES film with 3 wt% KH570 and isobutanol as co-solvent displayed the best thermal stability. WCA results confirmed that Si–O–Si crosslinking was produced during PAES film formation to improve the hybrid film properties. XPS analysis provided further evidence that co-solvents induced sol–gel reaction during the film formation.

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