

Film-formation of polyacrylate/silica composite latexes by sol-gel process

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ABSTRACT: The polyacrylate/silica composite latexes were prepared by directly mixing silica particles with polyacrylate modified by γ -methacryloxypropyltrimethoxysilane (MPS). Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS) analysis of polyacrylate/silica composite films confirmed the sol-gel processes occurred to form Si–O–Si crosslinking bonds during the process of film-formation. Transmission electron microscope (TEM) images revealed that the polyacrylate latexes were in contact with silica particles while some silica particles stayed together. Atomic force microscope (AFM) photos showed that organic and inorganic phases were strictly connected with each other and silica particles were embedded in the polymeric matrix with a size range of 20–50 nm. Differential scanning calorimetry (DSC) curves demonstrated that the composite film with 3% MPS has higher T_g than those of pure polyacrylate films. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42417.

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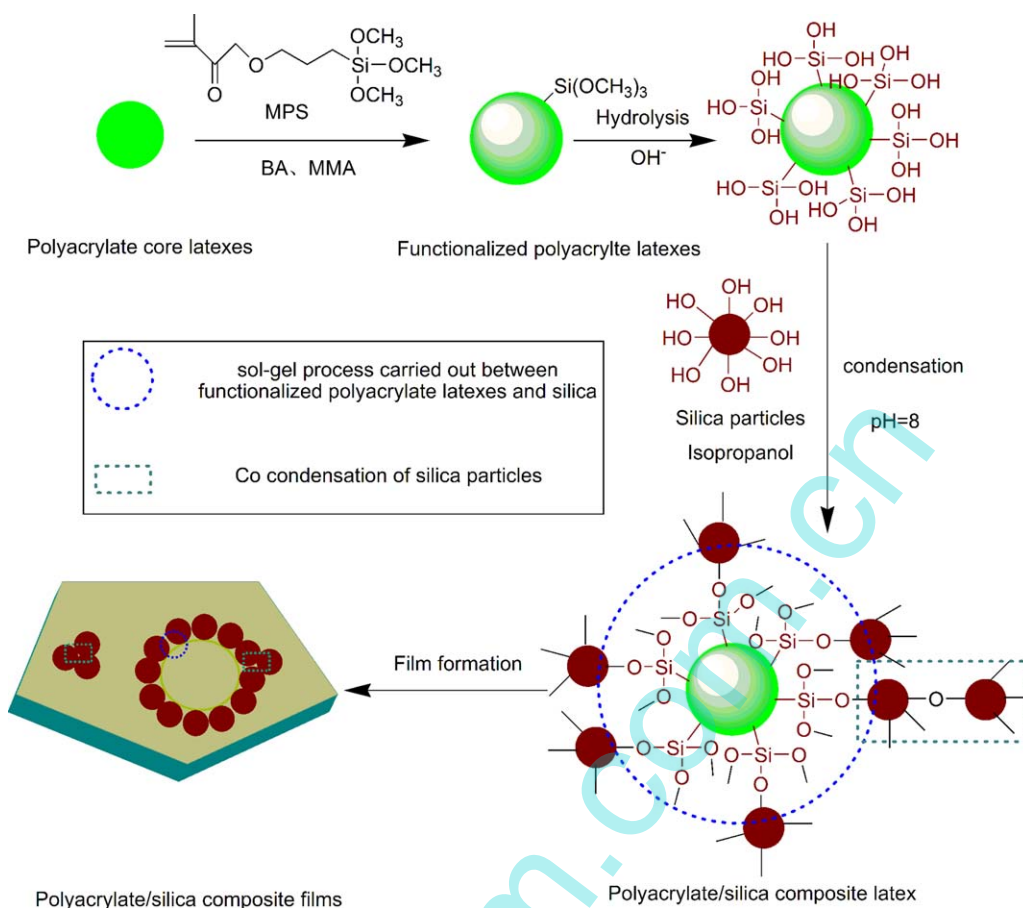
INTRODUCTION

Recently, much attention has been focused on development of new organic-inorganic composite materials of prospective use in many areas because of their combined features of inorganic nanoparticles and organic polymer matrix.^{1–8} A lot of studies show that introducing nanosilica into polymers obviously improves some properties such as tensile strength, abrasion resistance, scratch resistance, hardness, etc., and finds wide range of potential application in areas as coating, plastic, fibers, photocatalysis, optics, biotechnology, and so on.⁹ The nano-sized silica acts as a reinforcing agent to improve the hardness, strength, and thermal stability of the polymers.^{10–12}

Several strategies have been reported for the preparation of polymer/silica hybrid materials according to the starting materials and processing techniques: blending (direct mixing of the silica nanoparticles into the polymer), sol-gel process, and in situ emulsion, which involves the dispersion of nanosilica in the monomers first and then curing of the resulting mixture.^{1,13} Properties of nanocomposites are strongly influenced by the silica dispersion on the hybrid films and interactions between inorganic and organic phases.¹⁴ Nanocomposites with high silicon content prepared from blending method exhibited poor gloss owing to the aggregation of silica particles.^{15,16} In some studies, silane coupling agents have been used to improve properties of the organic/inorganic hybrid material by the covalent

bonds between organic and inorganic components.^{17–21} For example, the surface of silica particles was firstly modified by a silane coupling agent with vinyl terminal groups then copolymerized with monomers. Similarly, some authors have synthesized acrylic polymer-silica organic-inorganic hybrid emulsions by sol-gel reactions using a silane coupling agent containing acrylic polymer emulsion and tetraethoxysilane (TEOS). However, it is difficult to precisely control the simultaneous hydrolysis and condensation of alkoxy-silyl 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.^{4,22–24}

Till now, most previous works on polymer/silica hybrid material reported so far were involved in the synthetic method, properties, and surface morphology, little attention has been paid to the film-formation of these hybrid colloidal particles.¹⁵ Recently, Armes *et al.* investigated the film-forming properties of raspberry-like polymer/silica colloidal nanocomposites particles prepared by aqueous emulsion polymerization,^{14,25} and found that the silica embedded could reach around 40%. In our previous jobs, polymer/silica hybrid latexes with high silicon contents were prepared by directly mixing colloidal silica with polyacrylate emulsion modified by MPS.^{26,27} The results showed that Si–O–Si-polymer crosslinking networks were formed by the co-solvent-mediated and sol-gel method, meanwhile, more silica



Scheme 1. The synthetic routes of polyacrylate/silica hybrid composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles remain in the internal part of film. However, it has not yet been known when the sol-gel processes take place to form Si–O–Si–polymer crosslinking networks. In the present study, we investigate the formation of polyacrylate/silica composite particles by monitoring the change of chemical structure, and propose the sol-gel processes mechanism in the presence of co-solvent-mediated.

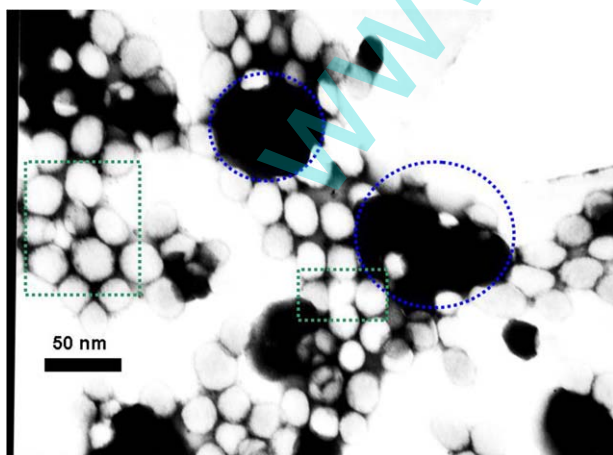


Figure 1. TEM photographs of polyacrylate/silica composite latexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), and diacetone acrylamide (DAAM) were commercial products which were purchased from Shanghai Lingfeng Chemical Co. (Shanghai, China) and used without further purification. γ -methacryloxypropyltrimethoxysilane (MPS) was purchased from Shanghai Yewu Chemical Co. (Shanghai, China). Colloidal silica (30 wt %, pH = 11) was supplied by Foshan Nanhai Waterglass Co. (Foshan, China), the diameter of the silica particles are in the range of 10–50 nm. Isopropanol was supplied by Guangzhou Chemical Reagent Co. (Guangzhou, China). Nonyl phenyl polyoxyethylene ether-10 (OP-10), sodium dodecyl sulfonate (SDS), sodium bicarbonate (NaHCO_3), and potassium persulfate (KPS) were used as received. Deionized water was used for the polymerization process.

Preparation of Polyacrylate/Silica Composite Latexes

MPS modified polyacrylate latexes were synthesized by emulsion polymerization as follows: The mixture of BA (24 g), MMA (43 g), DAAM (1 g), and AA (2 g) was added to the SDS and OP-10 aqueous solution (0.6 g SDS and 0.3 g OP-10 dissolved in 30 g deionized water) under a magnetic stirrer and pre-emulsified for 0.5 h. In a typical synthesis formulation: deionized water (40 g), SDS (1.0 g), OP-10 (0.5 g), KPS (0.17 g), and NaHCO_3 (0.25 g) were charged into a 500 mL four-neck

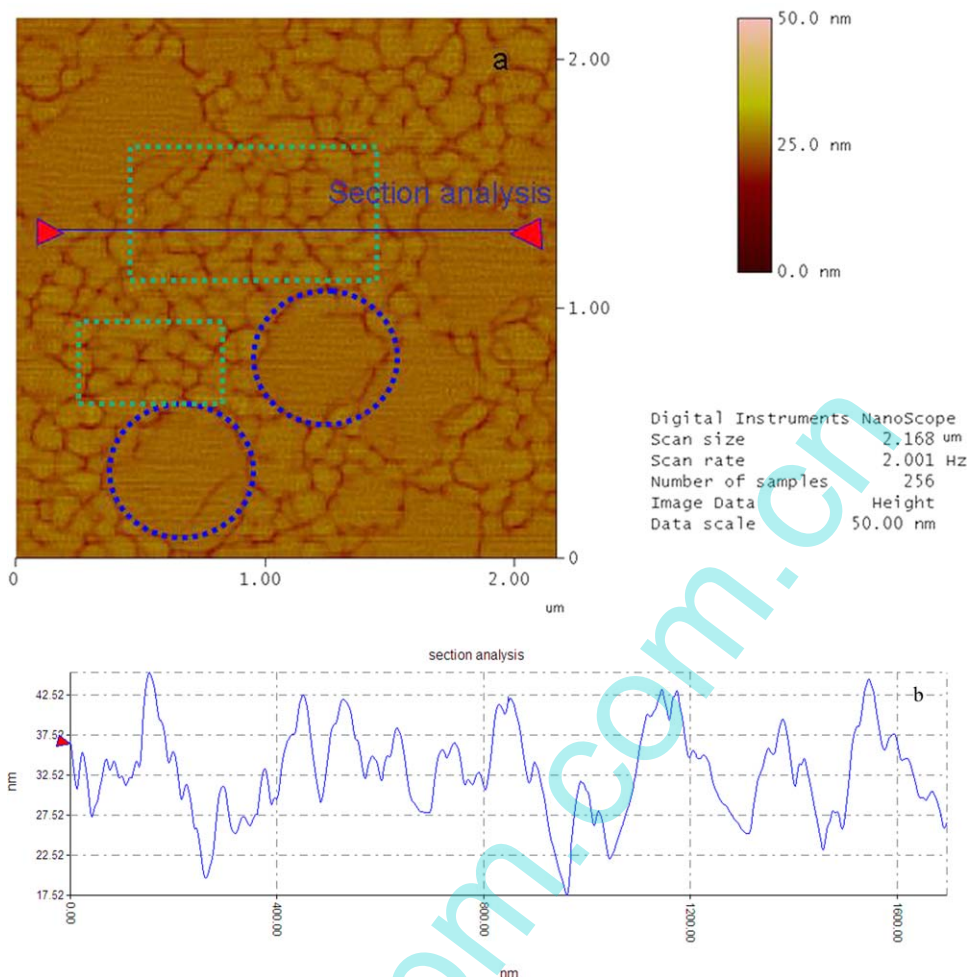


Figure 2. The AFM topography (a) and section analysis (b) of polyacrylate/silica composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

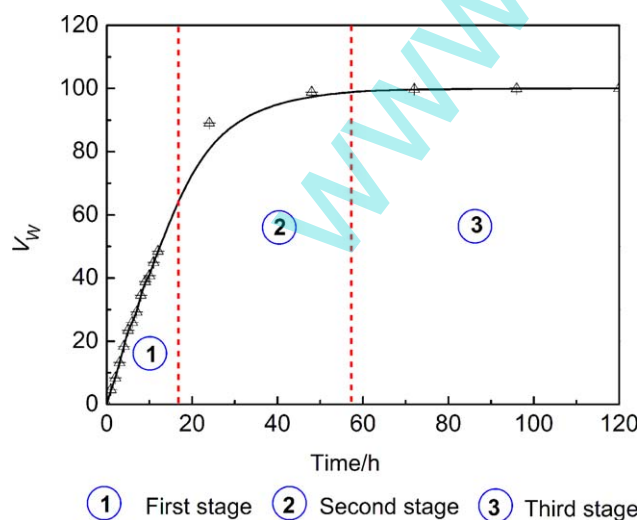


Figure 3. The water evaporation rate of polyacrylate/SiO₂ composite latexes at constant temperature and humidity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flask with a machine stirring, and heated to 80–82°C under nitrogen atmosphere. Then 25 g of pre-emulsion was dropped into the mixture and processed for 20 min to prepare the seed latex, the rest of the core monomer pre-emulsion and initiator solution (0.17 g KPS dissolved in 20 g deionized water) were added in 2 h with continuous stirring. The system was kept temperature at 80–82°C for 0.5 h after finishing dropping core shell monomer pre-emulsion, and then the shell monomer pre-emulsion with MPS (prepared by the same process, the ratio of monomers: 10 g BA, 17 g MMA, 3 g MPS) was added to system in 1 h. The initiator solution (0.17 g KPS dissolved in 10 g deionized water) 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% NaHCO₃ solution. The latex was filtered through a 200-mesh sieve.

The polyacrylate/silica composite latexes were prepared by adding colloidal silica and co-solvent (Isopropanol) to MPS modified polyacrylate latexes at room temperature, and stirred for 12 h, keeping the pH at about 8.0.

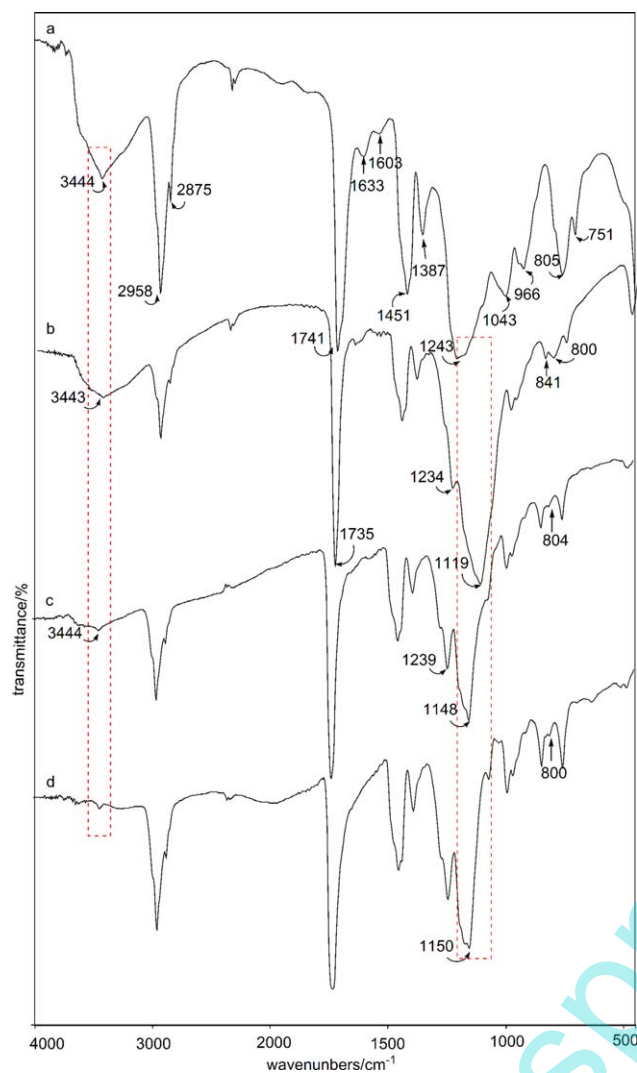


Figure 4. FTIR spectra of polyacrylate/silica composite latexes (a) and films (b, c, d are the three stages of film-formation process which was a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of Polyacrylate/Silica Composite Films

Polyacrylate/silica composite films were produced by casting the resulting latex onto Polytetrafluoroethene (PTFE, $\Phi=7$ cm) plate and allowing the water to evaporate at room temperature. The PTFE plate was washing by ethanol before use, and the thickness of film is about 0.10 mm by controlling the solid content of composite emulsions.

Characterization

The morphology and structure were directly observed by using a JEM-100 CX II transmission electron microscope (TEM) (JEOL, Japan) with an acceleration voltage of 60 kV. The samples were diluted and stained with 1% phospho-tungstic acid ($H_3[P(W_3O_{10})_4] \cdot 14H_2O$). The surface morphology of composite films was studied by atomic force microscope (AFM, cspm-3000, Benyuan Nano Co.). Fourier transform infrared (FTIR) spectra (Spectrum 2000, Perkin Elmer Co. USA) were monitoring the change of chemical structure of composites during film-

formation. Differential scanning calorimetry (DSC) were performed under a nitrogen flow at a heating rate of $10^\circ C/min$. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra DLD system equipped with Al K α source and operating at 150 W; the scanning scope was $700 \times 300 \mu m$.

RESULTS AND DISCUSSION

The Preparation of the Polyacrylate/Silica Composite

Since MPS can co-polymerize with acrylic monomers by the free radical emulsion polymerization, and afford $-Si(OMe)_3$ groups at the surface of polyacrylate latexes, the hydrolysis and condensation of alkoxy silyl groups are inhibited by controlling $pH=7$; however, the basic condition would promote the progress of the condensation reaction.^{28,29} The sol-gel process was carried out between silica particles and MPS modified polyacrylate latex as co-condensation of silica particles to build Si-O-Si crosslinking bonds, as illustrated in Scheme 1. Figure 1 shows the TEM micrographs of the polyacrylate/silica composite. It can be observed that the polyacrylate latexes were in contact with silica particles, while some silica particles were together. However, accumulation of silica particles was not found according to the TEM.

In Figure 2, the AFM topography and section analysis of polyacrylate/silica composite films were reported. It can be found that the organic and inorganic phases are strictly connected with each other, silica particles are embedded in the polymeric matrix with a size range of 20–50 nm. Furthermore, the image of section analysis indicated that the maximum height of composite particles was 50 nm, which is similar with the diameter of silica particles. The results of AFM showed that sol-gel process was carried out to build strong interactions between inorganic-organic networks had reduced the phase separation. This phenomenon is consistent with the TEM result, and provides further evidence for the sol-gel process which were carried out between silica particles and MPS polyacrylate latexes, as discussed in Scheme 1.

FTIR Analysis

The water evaporation rate of polyacrylate/SiO₂ composite latexes at constant temperature and humidity were calculated by weight loss method, as illustrated in Figure 3. It was found that the mechanism of polyacrylate/SiO₂ composite film formation was accord with Vanderhoff's laws.³⁰ And then the changes of chemical structure during film formation were monitored by FTIR spectroscopy.

Figure 4 shows the FTIR spectra of polyacrylate/silica composite latexes and films. In Figure 4(a), the absorption peak around 3444 cm^{-1} is associated with the stretching vibrations of OH groups, which becomes weaken and almost disappears at last during film-formation process. The characteristic stretching peaks of $-CH_3$ and $-CH_2$ groups are at 2958 and 2875 cm^{-1} . The stretching vibration of C=O group at 1741 cm^{-1} is attributed to the carboxy of polyacrylate, while the absorption peak at 1633 cm^{-1} is attributed to the intra-molecular hydrogen bonds between OH groups from silica particles and OH, C=O from MPS modified polyacrylate. The bending vibration peaks of $-CH_3$ and $-CH_2$ groups are at 1387 and 1451 cm^{-1} . The stretching vibrations of $-O-C$ at 1243 , 1043 , and 966 cm^{-1} are

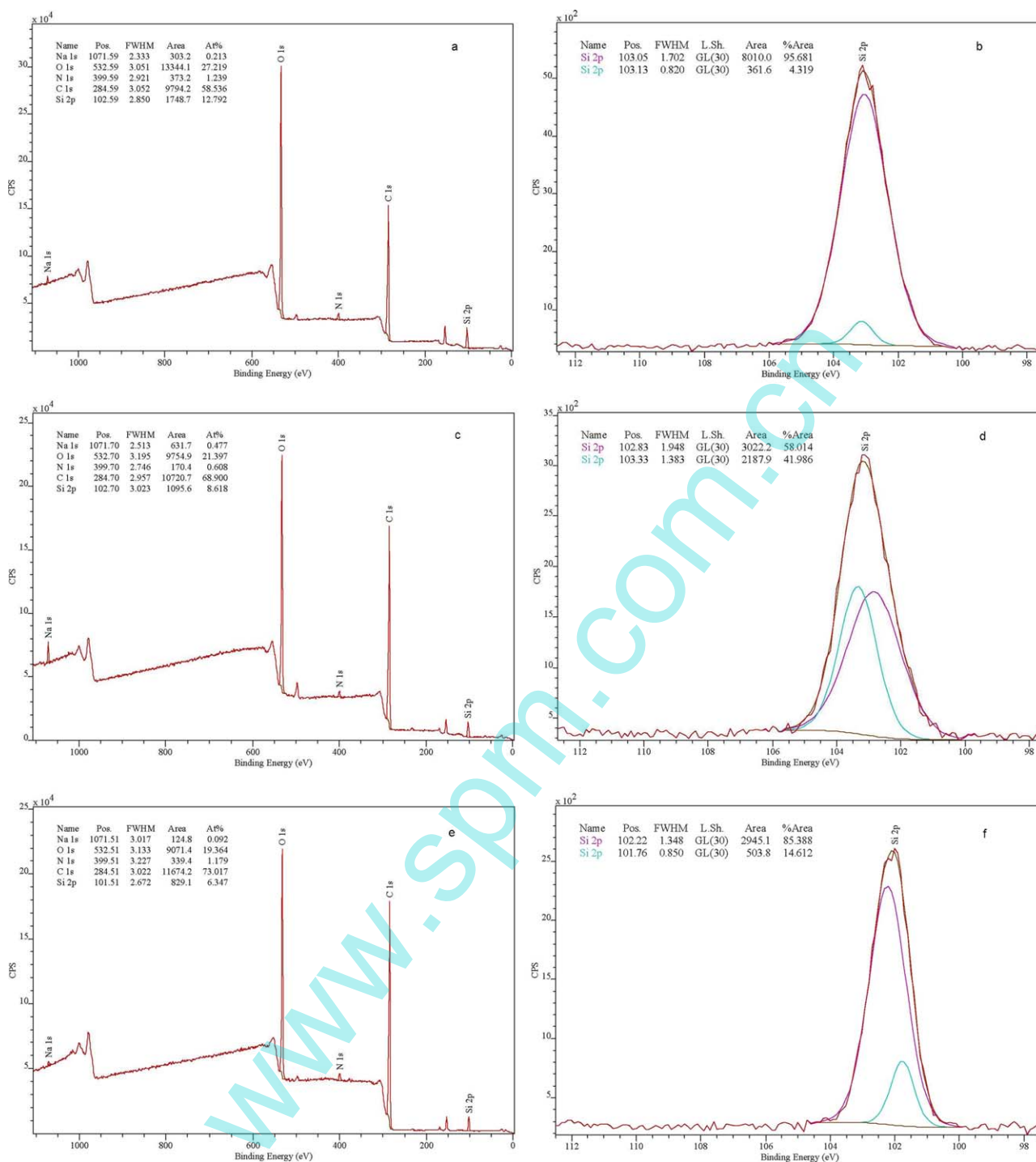


Figure 5. XPS spectra of polyacrylate/silica composite films: (a) survey and (b) Si_{2p} spectrum with MPS=0 wt %, (c) survey and (d) Si_{2p} spectrum with MPS=1 wt %, (e) survey and (f) Si_{2p} spectrum with MPS=3 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

related to the MMA and BA moieties, while peak of Si–O–Si from sol-gel process is at 805 cm^{-1} . The peak of the C=O stretching vibration shifts from 1741 cm^{-1} in the initial latexes to 1735 cm^{-1} in the first stage because of the damage of intramolecular hydrogen bonds. At the same time, a new absorption peak at 1119 cm^{-1} appeared in the spectra of Figure 4(b), which was attributed to the Si–O–Si group, and moved to 1148

and 1150 cm^{-1} in the spectra of Figure 4(c,d). It is reasonably assumed that the sol-gel processes occurred to form Si–O–Si crosslinking bonds during the entire process of film-formation.

XPS Analysis

The XPS was carried out to determine the chemical structure of polyacrylate/silica composite films.³¹ The survey and Si spectra are

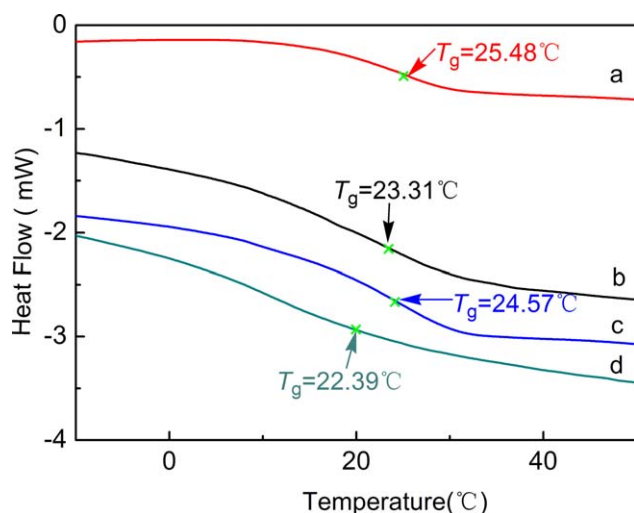


Figure 6. DSC curves of polyacrylate/silica composite films ((a) MPS=3 wt %, (b) MPS modified polyacrylate, (c) MPS=1 wt %, and (d) pure polyacrylate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

given in Figure 5(a–f) with MPS=0, 1, 3 wt %, respectively. The peaks at 532.59 ± 0.1 eV, 399.59 ± 0.1 eV, and 284.59 ± 0.1 eV can be attributed to oxygen (1s), nitrogen (1s), and carbon (1s). There are also peaks of silicon (2p) corresponds to Si–O at 102.59, 102.71, and 101.51 eV with MPS=0, 1% and 3%, respectively. According to XPS data, the Si contents on the film surface decreased with increasing MPS content. In Figure 5(b), two kinds of Si–O bonds were found in Si_{2p} spectrum, the peaks located at 103.05 eV and 103.13 eV are related to the Si–O groups of silica particles and Si–O–Si groups formed by sol-gel processes. As MPS content increases from 0 to 3 wt %, the peak area of Si–O groups which belonged to silica particles decrease from 95.681% to 14.612%, while Si–O–Si groups formed by sol-gel processes increase from 4.319% to 85.388%. The XPS results confirmed that sol-gel processes occurred to form Si–O–Si group and then more silica particles embedded in polymeric matrix, which is consistent with the AFM results.

DSC Analysis

Figure 6 shows DSC curves of pure polyacrylate, MPS modified polyacrylate and polyacrylate/silica composite films, respectively. The glass transition temperature (T_g) of pure polyacrylate is around 22°C, which accorded with the Fox equation. The T_g are slightly higher than that of pure polyacrylate because of introducing $-\text{Si}(\text{OMe})_3$ groups at the surface of polyacrylate latexes. As discussed above, the sol-gel processes were promoted to form Si–O–Si groups by increasing MPS content, the Si–O–Si groups can restrict the segmental motion of the polymeric chains and increase the crosslinking density in the polymer network.³² Therefore, the T_g of polyacrylate/silica composite film is increasing to around 25°C when the content of MPS was 3 wt %.

CONCLUSIONS

The polyacrylate/silica composite latexes were prepared by directly mixing silica particles with polyacrylate modified by

MPS. FT-IR spectra and XPS analysis of polyacrylate/silica composite films confirmed the sol-gel processes occurred to form Si–O–Si crosslinking bonds during the process of film-formation. TEM images revealed that the polyacrylate latexes were in contact with silica particles while some silica particles stayed together. AFM photos showed that organic and inorganic phases were strictly connected with each other and silica particles were embedded in the polymeric matrix with a size range of 20–50 nm. DSC curves demonstrated that the composite film with 3% MPS has higher T_g values than those of pure polyacrylate films.

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