Article

Silica Nanoparticles Modified by Biphenyl Groups for Crack-Free Coating on Synthetic Paper

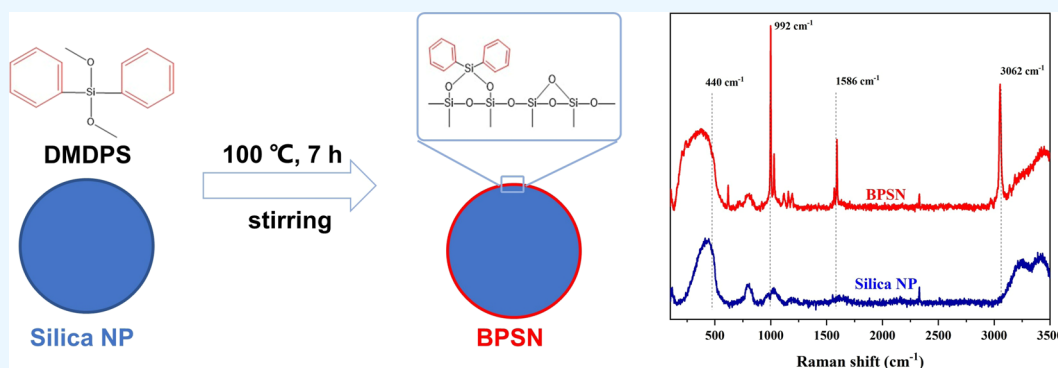Yuanqing Fan, Haifeng Lin,* Libin Kang, and Shunai Che*

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ABSTRACT: Water-based acrylic emulsions are a crucial component of water-based ink. Preventing visible cracks in emulsion coating during drying is a great challenge due to the high polarity and high surface tension of water. Herein, we propose that the cracking resistance of the coating can be enhanced through the incorporation of hydrophobic silica nanoparticles. The hydrophobic silica nanoparticles were fabricated by the modification of biphenyl groups to the surface of silica nanoparticles through postcoating using dimethoxydiphenylsilane. The presence of phenyl groups on the surface of biphenyl-modified silica nanoparticles (BPSNs) was confirmed by the Raman spectrum, Sears number, and zeta potential measurements. The formation of large cracks was significantly reduced by the incorporation of BPSN into water-based acrylic emulsion coatings. BPSN strengthens the forces of attraction between the resin particles in coatings, enabling the coating to resist the stresses caused by drying. This work provides a simple method to obtain crack-free coatings of water-based acrylic emulsion on a nonabsorbent substrate, offering a promising strategy for the printing industry to broaden the application of water-based ink.

1. INTRODUCTION

Printing ink is a key component of the printing industry. At present, the inks used in printing techniques such as flexographic printing and gravure printing are basically solvent-based inks that are formed by using polymers with a strong affinity for pigments as dispersants.[1]

Low-volatile organic compounds technology is gaining popularity in the industry due to the growing attention toward environmental issues, particularly air pollution. Water-based inks consist of pigments, additives, water, and a binder. The binder is the key component that disperses the pigments within the ink and binds them to the printing substrate. In other words, the performance of water-based inks is mainly determined by the binder. Among the explorations of binders for water-based inks, a water-based acrylic resin has garnered significant attention in recent years.[2] Compared with solvent-based inks, water-based inks with acrylic emulsions as the binders usually take longer to dry. Furthermore, because of the high polarity and high surface tension of water, water-based ink is difficult to apply on nonabsorbent printing substrates. For example, the coating may crack due to internal stresses during drying. These disadvantages limit the application of water-based inks.

The drying process of the coating involves the evaporation of the solvent inside the wet coating. The particles are tightly packed and deposited on top of the substrate, forming a solid dry film. During the drying process, the capillary force within the coating leads to internal stress in the coating, which is the direct cause of film cracking.[3−6]

To improve the performance and meet specific demands, three strategies are employed to modify the water-based acrylic resin. The first strategy involves optimizing the polymer
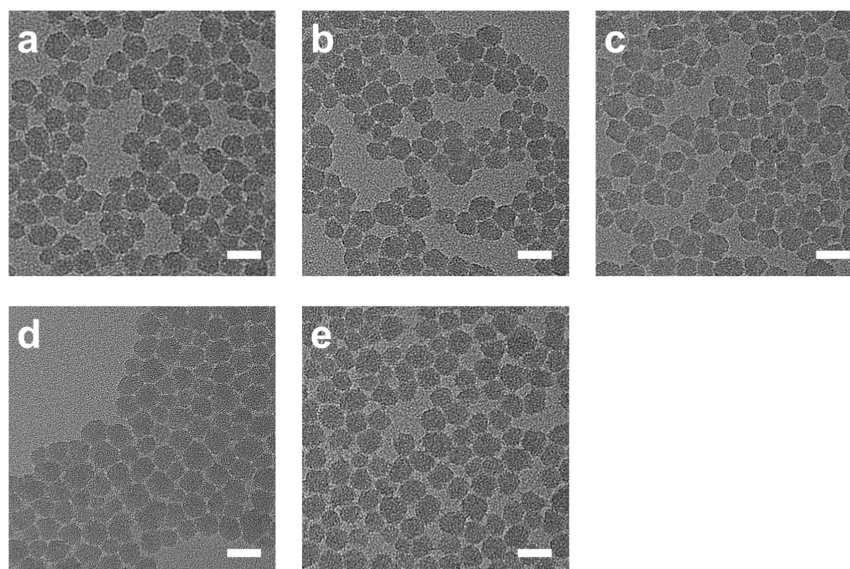
Figure 1. TEM images of silica nanoparticles before modification (a) and BPSN synthesized with different concentrations of DMDPS (b−e) (the scale bar is 20 nm). The concentrations of DMDPS in the sols were 0.116 (b), 0.154 (c), 0.460 (d), and 0.915 wt % (e).

structure at the molecular level using functional monomers, e.g., hydroxyethyl methacrylate,[7] allyl acetoacetate−hexanediamine,[8] methacrylate-terminated tetrafunctional siloxane,[9] octafluoroamyl methacrylate,[10] itaconic acid,[11] and polymerizable surfactants,[12] to enhance the performance of acrylic resin. The second strategy entails blending acrylic resin with other resin, leveraging the superior properties of resins, such as polyurethane[13] and epoxy resin,[14] to improve the corresponding characteristics of acrylic resin. The third strategy focuses on incorporating inorganic nanoparticles into the acrylic resin. The nanoparticles, e.g., SiO_2, TiO_2, ZrO_2, MgO, and ZnO, are utilized to impart specific properties to the resin, including anticorrosion,[15,16] scratch resistance,[17] weather stability,[18] superhydrophobicity,[19,20] antimicrobial resistance,[21] and high elasticity.[22]

Given the growing interest in inks made from the water-based acrylic resin due to increasing environmental awareness, a gap in research regarding the enhancement of resin performance to meet the requirements of water-based inks is becoming apparent. Inspired by these findings, we have selected silica nanoparticles to improve the properties of the water-based acrylic resin. For practical applications, silica nanoparticles should be dispersed in water in the form of a sol.

Silica nanoparticles are used to enhance the coating's resistance to internal stress due to their large surface area, well-established chemistry, and high colloidal stability.[23] The high specific surface area of nanoparticles allows for better adhesion to the coating matrix. However, the silanol groups of bare silica cause additional internal stress of coating during the drying process, which counteracts the benefits of bare silica itself for coating.

In this study, our approach is to increase the affinity of silica particles for the acrylic resin by enhancing the hydrophobicity of the surface of silica nanoparticles. The hydrophobic surface enhances the attraction between resin particles and silica nanoparticles due to the hydrophobic interaction between phenyl groups and hydrophobic groups on the resin, which increases the resistance of the coating to cracking. We synthesized biphenyl-modified silica nanoparticles (BPSNs) by using dimethoxydiphenylsilane (DMDPS) to graft phenyl

groups onto the surface of silica nanoparticles. Successful grafting was confirmed by titration experiments, Raman spectra, and increased zeta potential. Cracking of the coating is effectively suppressed by the addition of silica nanoparticles.

2. EXPERIMENTAL SECTION

2.1. Materials. Silica sol containing 30 wt % colloidal silica (the average particle size is 15 nm) was provided by Kehan Silicon Products Co., Ltd., Shandong (China). Acrylic emulsion (BCT-8200) was purchased from Shanghai Baolijia Chemical Co., Ltd., China. Dimethoxydiphenylsilane (DMDPS) (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd., China. All reagents and materials were used without further purification. The synthetic paper was purchased from Nanjing Oracle Digital Technology Co., Ltd., China.

2.2. Synthesis of BPSN with Varying Concentration of DMDPS. In a typical synthesis, 0.0933 g (0.343 mmol) of DMDPS was added into 10.10 g of silica sol. The mass concentration of DMDPS in the mixture was 0.915 wt %. Then, the mixture was heated to 100 °C for 7 h under stirring. The final pH of the sol is 9.71.

The samples were fabricated using mixtures with varying concentrations of DMDPS (0.116, 0.154, and 0.460 wt %) in the same way.

2.3. Preparation of Coating. The four-sided wet-film scraper (Huaguo Precision Instrument Co., Ltd., China) was used for the preparation of the coating layer. In a typical process, 100 g of silica sol was added to the 900 g of acrylic emulsion. Then, a film of mixture with a thickness of 50 μm was made on synthetic paper, which is made of biaxially oriented polypropylene. The film was dried at room temperature.

2.4. Characterization. Images of the silica nanoparticles were obtained by using a JEM-2100Plus transmission electron microscope (JEOL Ltd., Japan). The samples were dispersed in water and dripped onto a carbon support film on a Cu grid.

Raman spectra were obtained by using an inVia confocal Raman microscope (Renishaw, UK). The samples were prepared as freeze-dried powders.

Changes in the density of silanol groups on the silica nanoparticle surface were viewed by changes in the Sears number. The Sears numbers were determined by the titration method.[24] The Sears number corresponds to the consumption of sodium hydroxide between pH 4 and pH 9. As a simple empirical method, the Sears number determines the number of silanol groups.

Zeta potential measurements were performed with a Malvern Zetasizer Lab instrument (Malvern Instruments, UK). The samples used were not diluted or purified.

The thermogravimetric analysis (TGA) was processed by using a TGA5500 instrument (TA Instruments, USA). The analysis was performed under an air atmosphere. All samples (~mass of 25 mg) were heated from 50 to 800 °C at a heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

To synthesize hydrophobic silica nanoparticles, a conventional strategy involves grafting lipophilic groups, e.g., phenyl groups,
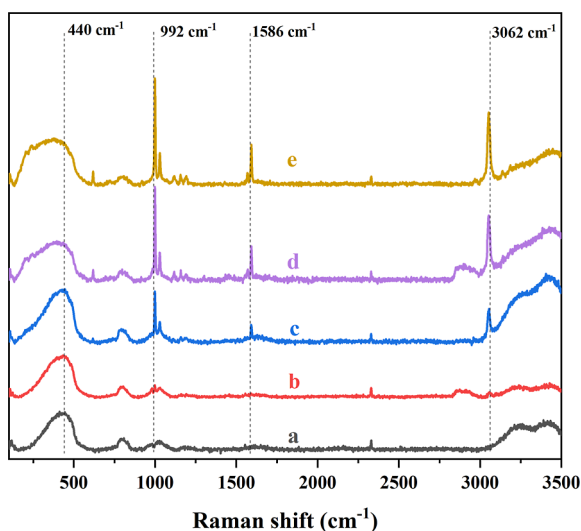

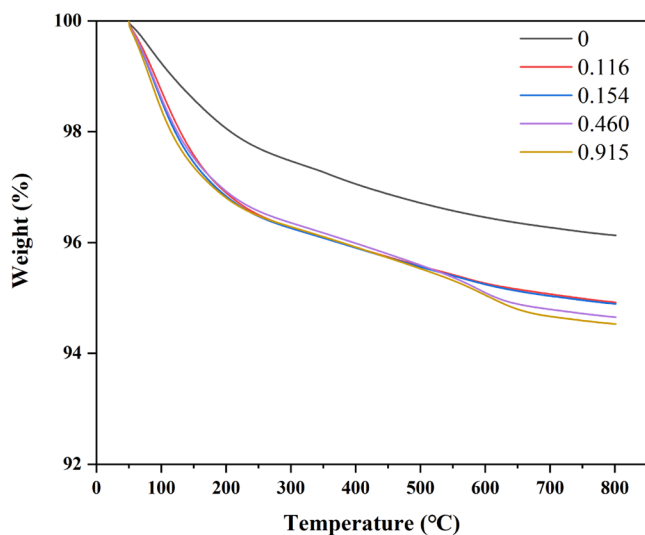**Figure 2.** Raman spectra of the samples shown in Figure 1.

Figure 3. TGA curves of unmodified silica nanoparticles and BPSN.

Table 1. Sears Number of Samples Shown in Figure 1

sample	Sears number	percentage change in Sears number/%
a	265.01	0
b	258.95	−2.29
c	258.95	−2.29
d	260.44	−1.72
e	258.95	−2.29

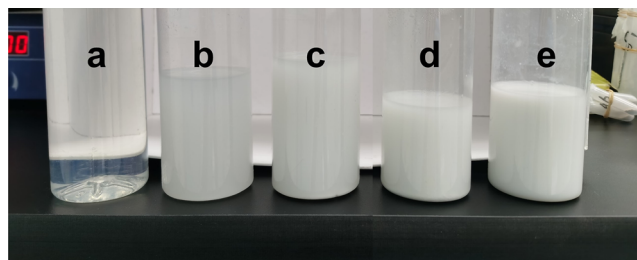**Figure 4.** Photo of the samples shown in Figure 1.

Table 2. Colloidal Stability of BPSN in Water

sample	zeta potential/mV
a	−35.86
b	−37.76
c	−36.07
d	−26.80
e	−7.04

alkyl groups, butoxy groups, mercapto groups, and calixarene, onto the surface of the particles. This conventional approach utilizes organic solvents, e.g., alcohol–water,[25] o-xylene,[26] toluene,[27] benzyl alcohol,[28] ethylene glycol–water,[29] and triethyl phosphate.[30] Additionally, for the particles in a silica sol, avoiding coagulation during the surface modification is an important challenge.[31] For the water-based acrylic resin, the addition of organic solvents increases the risk of phase separation. However, hydrophobic silica nanoparticles are typically dispersed in organic solvents. To address this issue, DMDPS was selected as the silane coupling agent. The steric effects of the phenyl groups provide sufficient hydrophobicity for applications in water-based resins, while the unreacted silanol groups maintain the colloidal stability of BPSN in water. Ultimately, an aqueous sol of BPSN suitable for a water-based acrylic resin was obtained.

To improve the cracking resistance of the coating, BPSN was used as an additive in a water-based acrylic emulsion. BPSN was synthesized via a two-step process. Initially, DMDPS underwent hydrolysis, leading to the formation of silanol groups. These reactive groups then condense with the silanol groups already present on the surface of silica nanoparticles, creating strong Si−O−Si bonds. Subsequently, biphenyl groups were grafted onto the silica nanoparticle surface, culminating in the formation of BPSN. The hydrophobic phenyl groups enhance the attraction between the silica nanoparticles and the resin particles during drying due to the hydrophobic interaction between the phenyl groups and hydrophobic groups in the resin; therefore, the distribution of phenyl groups plays an important effect on the coating performance. To control the distribution of phenyl groups on the surface of silica nanoparticles, BPSN were synthesized by varying concentrations of DMDPS (0.116, 0.154, 0.460, and 0.915 wt %), which were used to investigate the effect of
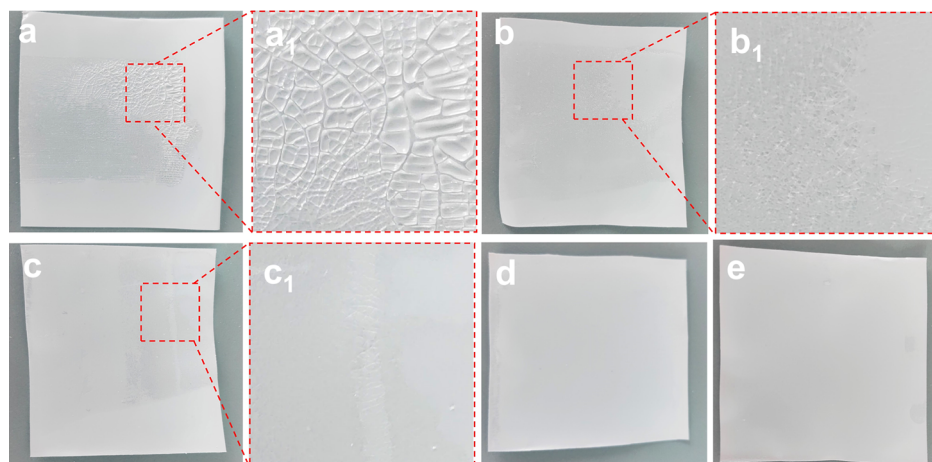
Figure 5. Surface morphologies of water-based resin composite films using samples shown in Figure 1 as additives. (a−c) Coatings with insufficient BPSN. (d,e) Coatings with sufficient BPSN. (a$_1$−c$_1$) Clearly cracked areas are marked with red squares and magnified.
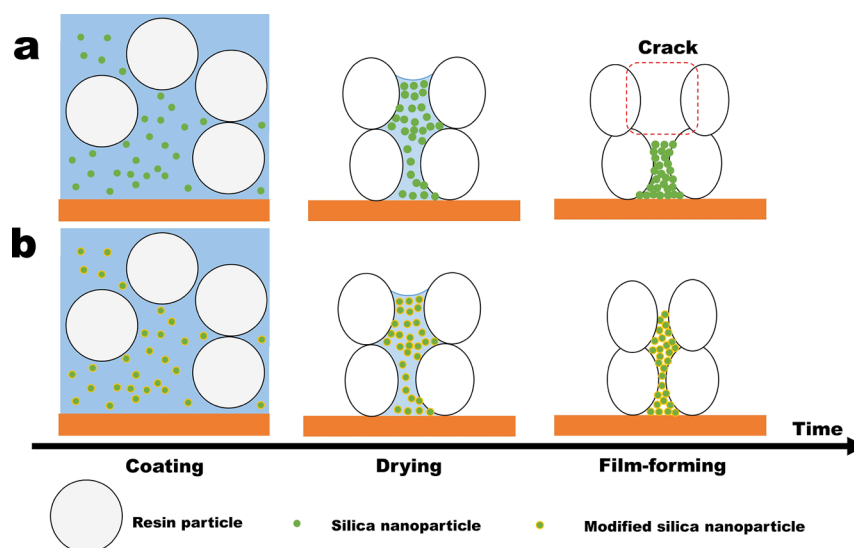

Figure 6. Schematic illustration of unmodified silica nanoparticles (a) and BPSN (b) behaviors during the drying process.

hydrophobicity on the silica nanoparticles on the coating of water-based acrylic emulsion.

3.1. Particle Size and Shape of BPSN. Compared with silica sol before modification, the silica sol after modification is not transparent. Two possible explanations for this opaque are (1) the surface of silica nanoparticles has become hydrophobic which induces a decrease in particle spacing and (2) larger solid structure, resulting from the aggregation of nanoparticles and/or the formation of larger nanoparticles, has emerged in the sol.

The size and shape of silica nanoparticles were investigated by using transmission electron microscopy (TEM). Figure 1a and b−e shows the silica nanoparticles before modification and BPSN synthesized with different concentrations of DMDPS, respectively. All samples are uniformly shaped and sized. They were nearly spherical, and the average diameter of the particles was 15 nm, and other impurities were not observed. The subtle grafting of biphenyl groups onto the surface of silica nanoparticles cannot be detected in TEM images.

3.2. Characterization of Phenyl Groups on the Surface of BPSN. Raman spectra (Figure 2) confirm the successful grafting of phenyl groups onto the silica nanoparticle surfaces. The peak around 440 cm^{-1} originates from the Si−O−Si network of silica.[32] In comparison to unmodified silica nanoparticles (Figure 2a), the grafting of biphenyl groups introduces new peaks into Raman spectra. Specifically, the peaks at 992 and 1586 cm^{-1} are attributed to the ring breathing mode, while the peak at 3062 cm^{-1} corresponds to the aromatic C−H stretch.

TGA was conducted to further confirm the modification of phenyl groups on BPSNs, as shown in Figure 3. The weight loss of samples originates from the desorption of water (<200 °C),[33] which shows a relatively fast rate of weight loss. Above 200 °C, the weight loss of samples stems from the decomposition of the silanol groups[33] (<800 °C) and the biphenyl groups[34] (400−600 °C), which show a relatively slow rate of weight loss. The TGA shows that BPSNs lose more weight than unmodified silica nanoparticles, and the total mass loss was increased with increasing DMDPS concentration of modification solution, which demonstrates the grafting of biphenyl on the surface of particles.

The titration displayed the effect of DMDPS on the surface silanol groups of the silica nanoparticles (Table 1). The decrease in the Sears number indicated a decrease of silanol

groups. The decrease originates from some silanol groups on the surface of the particles were grafted with phenyl groups.

3.3. Colloidal Stability of BPSN in the Sol.
As the amount of DMDPS increases, the hydrophobicity of the particle surface also increases, leading to a decrease in mutual repulsion between particles and a consequent decrease in the transparency of the sol (Figure 4). The difference in the colloidal stability of the silica nanoparticles was characterized by zeta potential measurements. The zeta potential of silica nanoparticles in water decreased with the reduced amount of DMDPS (Table 2) because the phenyl groups enhanced the hydrophobicity of the silica nanoparticles' surface. The phenyl groups obstruct some of the silanol groups from hydration, and the electrostatic repulsion between the silica nanoparticles decreases.

3.4. Effect of BPSN on Coating.
During the drying process, cracking of the coating originates from the film's inability to resist the stresses generated by solvent evaporation. As shown in Figure 5, BPSN effectively prevented the coating from cracking after the drying process. When the concentration of BPSN is low (5a–c), the coating cannot resist the internal stress and crack during drying; when the concentration of BPSN is high enough (5d,e), BPSN enhances the attraction between resin particles, so that the coating can resist internal stress during drying to avoid cracking.

We speculate that the coating layer's resistance to cracking is attributed to the hydrophobic nature of the modified silica nanoparticle surfaces. In the case of unmodified silica nanoparticles (Figure 6a), the hydrophilic silanol groups on their surface contribute to colloidal stability. However, as the solvent evaporates, the interparticle distance narrows, and the aggregation tendency of silica nanoparticles intensifies due to the escalating van der Waals forces. Consequently, the film structure, devoid of silica nanoparticles, cannot withstand the internal stresses, leading to cracking. In contrast, for modified silica nanoparticles (Figure 6b), the hydrophobic surfaces interact favorably with the resin surfaces. This interaction is facilitated by the affinity between the phenyl groups of BPSN and the resin surface, which promotes an even distribution of silica nanoparticles throughout the film's matrix and bolsters its structural integrity. The film remains crack-resistant because the silica nanoparticles are less prone to deformation.

4. CONCLUSIONS

Hydrophobic silica nanoparticles were synthesized by grafting phenyl groups onto their surface using DMDPS. The surface modification on silica nanoparticles was confirmed by TEM, titration, Raman spectra, TGA, and zeta potential measurements. When the mass fraction of DMDPS in the sols was between 0.460 and 0.915 wt %, no obvious cracks were observed on the surface of the dried coating. This work provides a simple method for fabricating a sol of hydrophobic silica nanoparticles. BPSN shows promise in enhancing the cracking resistance of the water-based acrylic resin.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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