

Preparation of Nanosilica Reinforced Waterborne Silylated Polyether Adhesive with High Shear Strength

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ABSTRACT: Waterborne adhesives are extremely environment-friendly but unfortunately deficient in mechanical properties. In this article, nanosilica, stemming from tetraethyl orthosilicate (TEOS), silica sol, and/or fumed silica powder, was employed to reinforce the waterborne silylated polyether adhesives. Effects of TEOS content, silica sol content, and the type and content of fumed silica on the shear strength of the adhesive were investigated using a scanning electronic microscope and an electronic instron tester and the strengthening mechanisms of different silica source were discussed. All the shear strengths of silylated polyether adhesives first increased and then decreased as TEOS content, silica sol content or fumed silica content increased. Colloidal silica particles was less efficient than fumed silica particles for reinforcing the polyether adhesive but can increase the shear strength of hydrophobic

fumed silica embedded adhesive. Comparing the adhesives with the hydrophilic fumed silica (HS-5) or the extremely hydrophobic fumed silica (TS-720), the adhesive with moderate hydrophobic fumed silica (TS-610) had the highest shear strength. The maximal shear strength of 2.5 MPa was achieved when TEOS, silica sol, and fumed silica were combined. It seemed that TEOS, silica sol, and fumed silica played crosslinking (with polyether chain), dispersing (for fumed silica), and reinforcing roles on waterborne adhesive, respectively. This reinforcing mechanism opened a new way to fabricate waterborne adhesives (or coatings) with high performances. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2434–2441, 2008

Key words: waterborne adhesive; polyether emulsion; nanosilica sol; fumed silica

INTRODUCTION

As continuously increasing rigorous regulations and laws for environment protection are being constituted, further reduction of volatile organic compounds (VOC) poses a great challenge not only for organic coatings, inks, but also for adhesives. Similar to organic coatings, waterborne systems, for examples, waterborne polyurethane adhesive, epoxy adhesive, and acrylate copolymer adhesive, have been developed to meet the VOC restriction.^{1–4}

However, when compared with traditional solvent-based adhesives, waterborne adhesives are deficient in chemical resistance, mechanical properties, adhesive force, and so on.^{5,6} Some efforts have been made to improve the performance of waterborne adhesives. For example, nanoparticles were employed to enhance the mechanical properties of waterborne adhesives because of their unique properties.^{7–12} Of

all the inorganic nanofillers, nanosilica particles are commonly adopted.¹³ Their influences on the mechanical properties of waterborne polyurethane,^{14–17} waterborne epoxy^{18,19} have been ever reported, but no data was seen on the nanosilica-reinforced waterborne polyether adhesives.

Waterborne polyether adhesive is a newly developed adhesive with the advantages of low toxicity, low price, etc. However, because of its soft main chain, the mechanical performances of waterborne polyether adhesive are rather poor.^{20,21} Introduction of nanosilica into the adhesive is extremely necessary. Unfortunately, among the studies on the nanosilica-reinforced waterborne adhesives, the influence of nanosilica source was seldom involved, which reduced their reference value for the preparation of waterborne polyether adhesive with high performance.

In this article, based on the successful preparation of colloidal silica stabilized silylated poly(propylene oxide) emulsion using a similar process described in our previous studies,^{22–24} a way to achieve a waterborne silylated polyether adhesive with high shear strength was presented via combination of different silica sources, that is, tetraethyl orthosilicate (TEOS), silica sol, and fumed silica. Effects of TEOS content, silica sol content, and the type and content of

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fumed nanosilica particles on the shear strength of the adhesives were investigated. And, the strengthening mechanism of different silica sources was discussed.

EXPERIMENTAL

Materials

Poly(propylene oxide) capped with $\text{CH}_2=\text{CH}-$ (CH_3O) $_2\text{Si}-$ end group (M_w , 6.0×10^4 ; viscosity: 31 Pa s at 25°C, named as "silylated polyether" below) was supplied by Henkle (Düsseldorf, Germany). γ -Aminopropyltriethoxysilane (A-1100) was the product of Nanjing Shuguang Chemical Factory (Nanjing, China), and dibutyltin didodecylate (T-12) the product of Shanghai No. 1 Chemical Reagent Factory (Shanghai, China). Emulsifiers: nonylphenyl polyoxyethylene and alkyl phenyl sodium sulfonate were got from Haichuan (Shenzhen, China). Silica sol (NYACOL-9950, solid content: 40 wt %, particle size: 100 nm) was provided by Eka-Nobel (Dotterbolag, Sweden) and fumed nanosilica including HS-5 (untreated, hydrophilic), TS-610 (treated with dimethyldichlorosilane, hydrophobic), and TS-720 (treated with a dimethyl silicone fluid, extremely hydrophobic) by Cabot (Aurora, IL). TEOS was supplied by Shantou Guanghua Chemical Company (Shanton, China). All these chemicals were used as received.

Preparation of waterborne silylated polyether adhesive

The preparation of silylated polyether emulsion stabilized with colloidal silica was similar to that of aqueous organosilicone resin emulsion described elsewhere.²⁴ A SFJ-400 stirrer (Shanghai Xiandai Environment Engineering Technique, China) was used as the emulsification apparatus. Silylated polyether and emulsifiers (1 : 1 weight ratio for non-ionic/anionic) were mixed under stirring at a speed of 3000 rpm and then dropwise charged with a mixture of silica sol and deionized water over a period of 30 min, and accompanied another 30 min of stirring to get a silylated polyether emulsion (solid content: 60 wt %, silylated polyether/colloidal silica (wt/wt): 29/1). The waterborne silylated polyether adhesive was fabricated with the above emulsion. A typical formulating procedure was as follows: 1 g of fumed nanosilica powder and 1.0 g of silica sol were mixed with 40 g of silylated polyether emulsion at ambient temperature and vigorously stirred at a speed of 1000 rpm for 10 min. Subsequently, 1.0 g A-1100, 0.2 g T-12, and 2.0 g TEOS were charged into the above mixture and continuously homogenized under stirring at a speed of 500 rpm for 10 min. To investigate the effects of the contents of TEOS, silica sol, and fumed nanosilica powder on the performance of adhesives, their quantities were

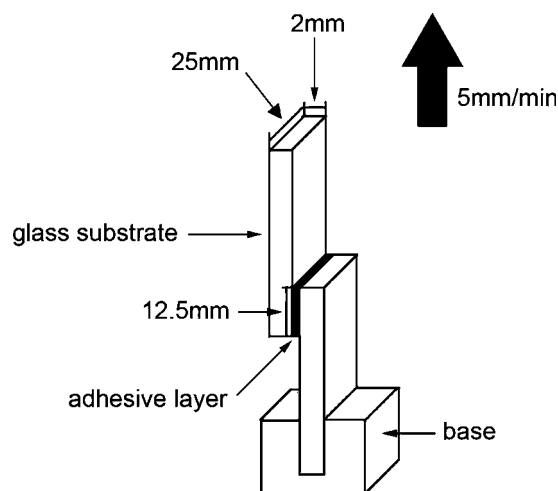


Figure 1 Schematic diagram of the sample for shear strength measurement.

controlled in the ranges of 1.0–5.0, 1.0–5.0, and 0.0–4.0 g, respectively. The obtained waterborne adhesive was cast on glass substrates and dried at room temperature for 7 days for further characterization.

Characterization

Scanning electron micrographs

Scanning electron micrograph (SEM) images of cross sections of adhesives were obtained by XL30 (Philips, Netherlands). Before SEM observations, the cured adhesives were heated at 70°C for several hours to vaporize the remaining liquid in the adhesives and broken in liquid nitrogen.

Shear strength

The shear strength of waterborne adhesive was acquired by an Instron model DXLL1000-20000 testing machine (Shanghai, China). The adhesive layer with size of $12.5 \times 25 \text{ mm}^2$ was formed between cuboids glass substrate with size of $100 \times 25 \times 2 \text{ mm}^3$, see the schematic diagram in Figure 1. The crosshead speed for tensile test was 5 mm/min according to GB 7124-86. An average of three measurements for each sample was reported.

RESULTS AND DISCUSSION

The components of curable waterborne silylated polyether adhesive

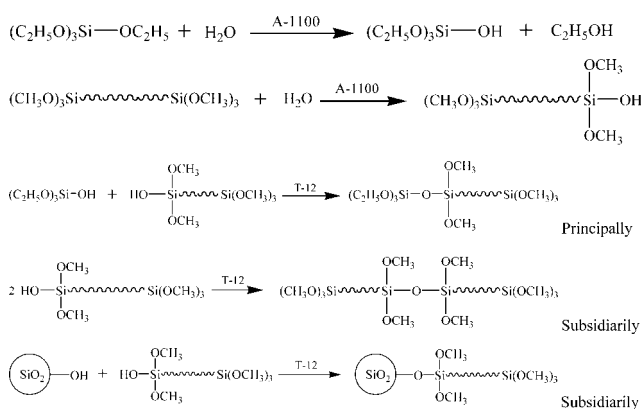
The colloidal silica stabilized silylated polyether emulsion was not curable at ambient temperature though the polyether contained alkoxyethyl groups. To endow the silylated polyether emulsion with curable property at ambient temperature, some other components had to be added. Table I summarized the qualitative curing results of these waterborne

TABLE I
The Qualitative Curing Results of Waterborne Adhesive with Different Recipes

Sample no.	Components of adhesive				Curing results at room temperature
	Silylated polyether emulsion	A-1100	T-12	TEOS	
1	+	-	+	+	Incurable
2	+	+	-	-	Incurable
3	+	+	-	+	Curable but slow
4	+	+	+	-	Curable but slow
5	+	+	+	+	Curable and quick

Note: "+" the component was included in the recipe; "-" the component was not included in the recipe.

adhesives with different recipes. The table indicated that the waterborne adhesives were not curable at all if no A-1100 (sample 1) or only A-1100 (sample 2) was included while the adhesives became curable but with low curing rate (tack-free time: more than 3 days) if T-12 (sample 3) or TEOS (sample 4) was not employed. Only A-1100, T-12, and TEOS were combined together with silylated polyether emulsion, the waterborne adhesive (sample 5) was curable with ideal curing rate (tack-free time: 4–5 h). Based on these curing results, it seemed that A-1100 acted as a catalyst for hydrolysis of alkoxy silane rather than a coupling agent (or crosslinking agent) and T-12 mainly promoted the condensation of silanol groups. Since the curing time obviously shortened when TEOS was added, the reaction of TEOS with silylated polyether should principally contribute to the curing of the adhesive. Nevertheless, deducing from the fact that the waterborne adhesive without TEOS (sample 4) was slowly curable, subsidiary contributions to the curing from the reaction between silylated polyethers themselves and the reaction of silylated polyether with colloidal silica particles were also possible. Consequently, the reactions leading to the curing of the waterborne silylated polyether adhesive can be described as follows:



Besides the components of adhesive, effect of TEOS content on the shear strength of waterborne adhesive was qualitatively investigated, as shown in Figure 2.

The figure displayed that the shear strength first increased and then decreased with TEOS content, and reaches its maximum at 10 wt % of TEOS. Figure 3 presented the SEM images of the adhesives with different TEOS content. Rather homogeneous morphology was observed for the cured adhesives with low TEOS content [Fig. 3(a,b)], whereas phase separation occurred in the sample with 12.5 wt % of TEOS [Fig. 3(c)]. Therefore, the initial increment of shear strength should be resulted from higher cross-linking degree of adhesive at higher TEOS content, and the decrease of the shear strength in the range of high TEOS level should be mainly attributed to the existence of phase separation in the adhesive. We reckoned that the phase separation was formed presumably from the condensation reaction between TEOS themselves or the aggregation of colloidal silica bridged by TEOS.²⁵ Based on the above results, appropriate TEOS content should be less than 10 wt % (based on the weight of emulsion) for the curable waterborne silylated polyether adhesive. In the following studies on nanosilica reinforced waterborne adhesive, lower TEOS content, namely 5 wt %, was

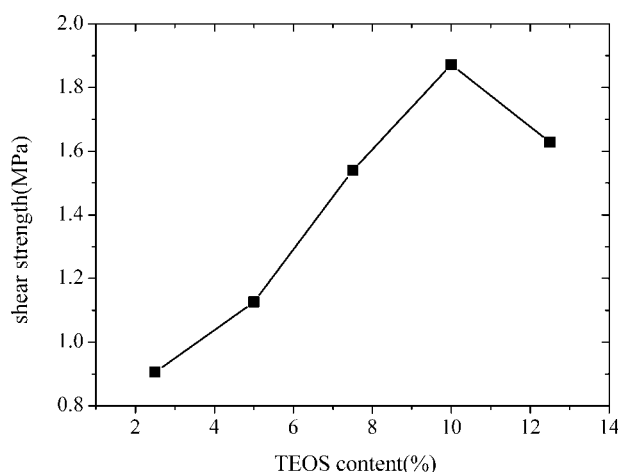


Figure 2 Effect of TEOS content on the shear strength of waterborne adhesives [A-1100: 2.5 wt % (based on the weight of emulsion)].

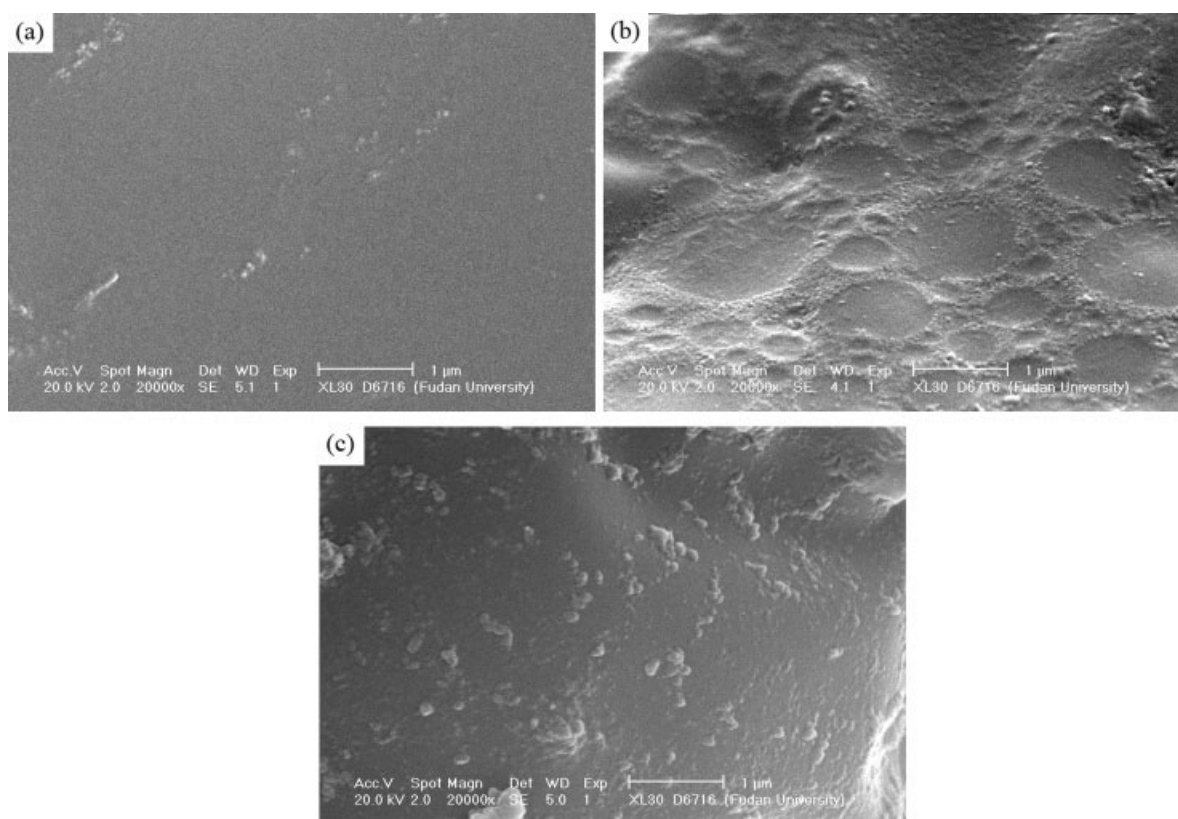


Figure 3 The SEM images of the cured adhesives with TEOS contents of (a) 2.5 wt %, (b) 7.5 wt %, and (c) 12.5 wt % [A-1100: 2.5 wt % (based on the weight of emulsion)].

selected because the nanosilica particles embedded were also possibly reacted with part of silylated polyether chains.

The shear strength of nanosilica reinforced waterborne adhesive

Effect of silica sol content

The shear strength of silylated polyether curing with TEOS was not enough. It had to be further strengthened for practical application. Herein, colloidal silica sol was first selected according to two aspects: colloidal silica particles were already one component of the silylated polyether emulsion, which offers the stabilization role for polymer particles, and secondly, reinforcing role of colloidal silica particles for polymer matrix have been demonstrated in waterborne epoxy,¹⁸ waterborne polyurethane.²⁶ Figure 4 gave the shear strength of waterborne polyether adhesive with different silica content. The shear strength slightly increased with increasing silica content at silica content no more than 5.0 wt % and decreased at silica content beyond 7.5 wt %. Serious aggregation of colloidal silica particles could be explained for the decrement of shear strength at higher silica content. The maximal shear strength, namely, 1.73 MPa, was attained at silica content of 7.5 wt %. However, it is not suffi-

ciently high for practical application. Hence, improvement of shear strength via addition of fumed silica was further investigated later.

The low efficiency of colloidal silica particles for strengthening the adhesive could be attributed to the poor miscibility of silica particles with silylated poly-

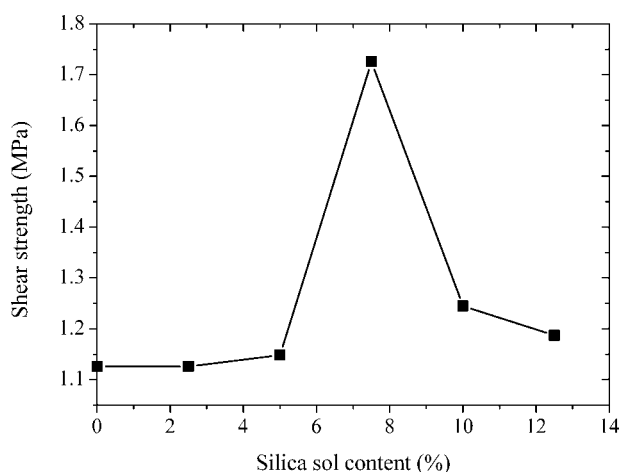


Figure 4 The shear strength of waterborne adhesives with different silica sol contents (based on the weight of emulsion) [A-1100: 2.5 wt %, TEOS: 5 wt % (based on the weight of emulsion)].

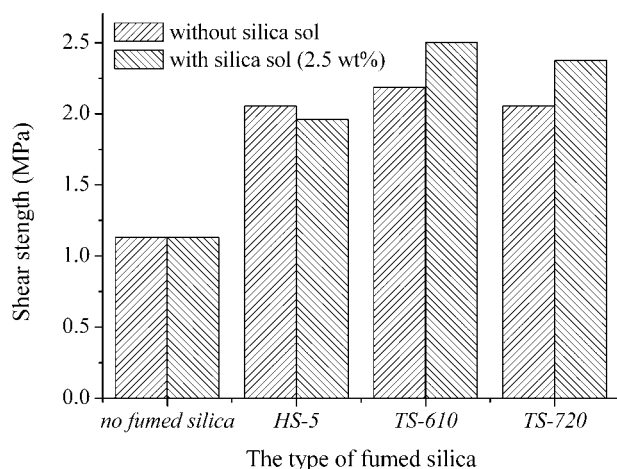


Figure 5 Effect of the type of fumed silica on the shear strength of waterborne adhesives without (left column) or with (right column) 2.5 wt % of silica sol (fumed silica content: 2.5wt%, A-1100 and TEOS contents: the same as Fig. 4).

ether chain. In our case, the silylated polyether oligomer is high hydrophobic, deducing from the fact that the silylated polyether oligomer/water mixture quickly separated into two phases once stirring was stopped. As for the colloidal silica particles in aqueous silica sol, they are extremely hydrophilic. Except for some of silica particles that attached to polymer particles via the hydrogen bond between the silanol groups of silica particles and the silanol groups hydrolyzed from $\text{CH}_2=\text{CH}-(\text{CH}_3\text{O})_2\text{Si}$ -capped groups that located at the surface of polymer particles, most of colloidal silica particles stay in aqueous phase and can not homogeneously dispersed into polymer matrix when the adhesive was dried, due to their great difference in hydrophilicity. On the contrary, colloidal silica particles tend to aggregate to form silica phase with large scale during drying, leading to poor interaction between silica particles and polymer matrix, and hence a little enhancement of shear strength in the dried adhesive.

Effect of the type of fumed silica

Three kinds of fumed silica with different surface treatment (see experimental section), namely HS-5, TS-610, and TS-720, were adopted to examine the reinforcing role of fumed nanosilica for the waterborne adhesive. Figure 5 compared their shear strengths. It was found that the shear strength considerably increased when fumed silica, regardless of its type, was introduced into the waterborne adhesive. Moreover, the adhesive containing TS-610 had the highest shear strength. This may be interpreted from the preparation process of waterborne adhesive. When fumed silica was mixed with silylated polyether emulsion, it first met with water and after-

wards merged with polymer particles during mixing and/or drying process. For HS-5, its hydrophilicity assures its good dispersion in water in mixing stage but poor compatibility with hydrophobic polymer matrix during drying, like the case with colloidal silica particles. For TS-720, its extremely hydrophobicity prevents its entrance into water phase although it possesses better compatibility with polymer matrix. However, because TS-610 possesses moderate hydrophobicity, it has better dispersion in water phase than TS-720, and better compatibility with silylated polyether in cured adhesive than HS-5. As a consequence, TS-610 has the strongest interaction with polyether matrix and thus its reinforced adhesive the highest shear strength.

Effect of coaddition of silica sol and fumed silica on the shear strength was studied too. The results were also shown in Figure 5. It was interesting to find that silica sol can enhance the shear strength of the waterborne adhesive containing TS-610 or TS-720 but not for the sample containing HS-5. To understand why silica sol has different influences for different types of fumed silica, the SEM images of the fumed silica reinforced adhesive before and after addition of silica sol were compared in Figure 6. It can be seen from Figure 6(a,b) that silica sol cannot improve the dispersion of HS-5 in adhesive because of the inherent hydrophilicity of HS-5. However, silica sol can obviously improve the dispersions of TS-610 [Fig. 6(c,d)] in adhesive. As for TS-720, for its extreme hydrophobicity, it was very difficult to embed them into waterborne adhesive during preparation and thus resulted in a seriously inhomogeneous dispersion of TS-720, which even cannot be observed in its SEM image at large magnification [Fig. 6(e)]. But when silica sol was coadded, TS-720 particles could be easily seen in its SEM image [Fig. 6(f)], suggesting the dispersion of TS-720 was also improved by silica sol. Therefore, the enhancement of the shear strength of the adhesives with TS-610 or TS-720 resulted from the improvement of the dispersion of hydrophobic fumed silica in waterborne adhesives and thus cured adhesives by silica sol. The colloidal silica actually acted as a "dispersing agent" for those hydrophobic fumed silica particles in water. The decrement of shear strength for the adhesive containing both HS-5 and colloidal silica particles should be owed to the growth of silica aggregates size after colloidal silica was coadded.

Effect of fumed silica content

Effect of fumed silica (TS-610) content on the shear strength of waterborne adhesive is shown in Figure 7. Initially, the shear strength of the adhesive quickly enhanced with the increase of fumed silica content and reached its maximum at 2.5 w% of fumed silica.

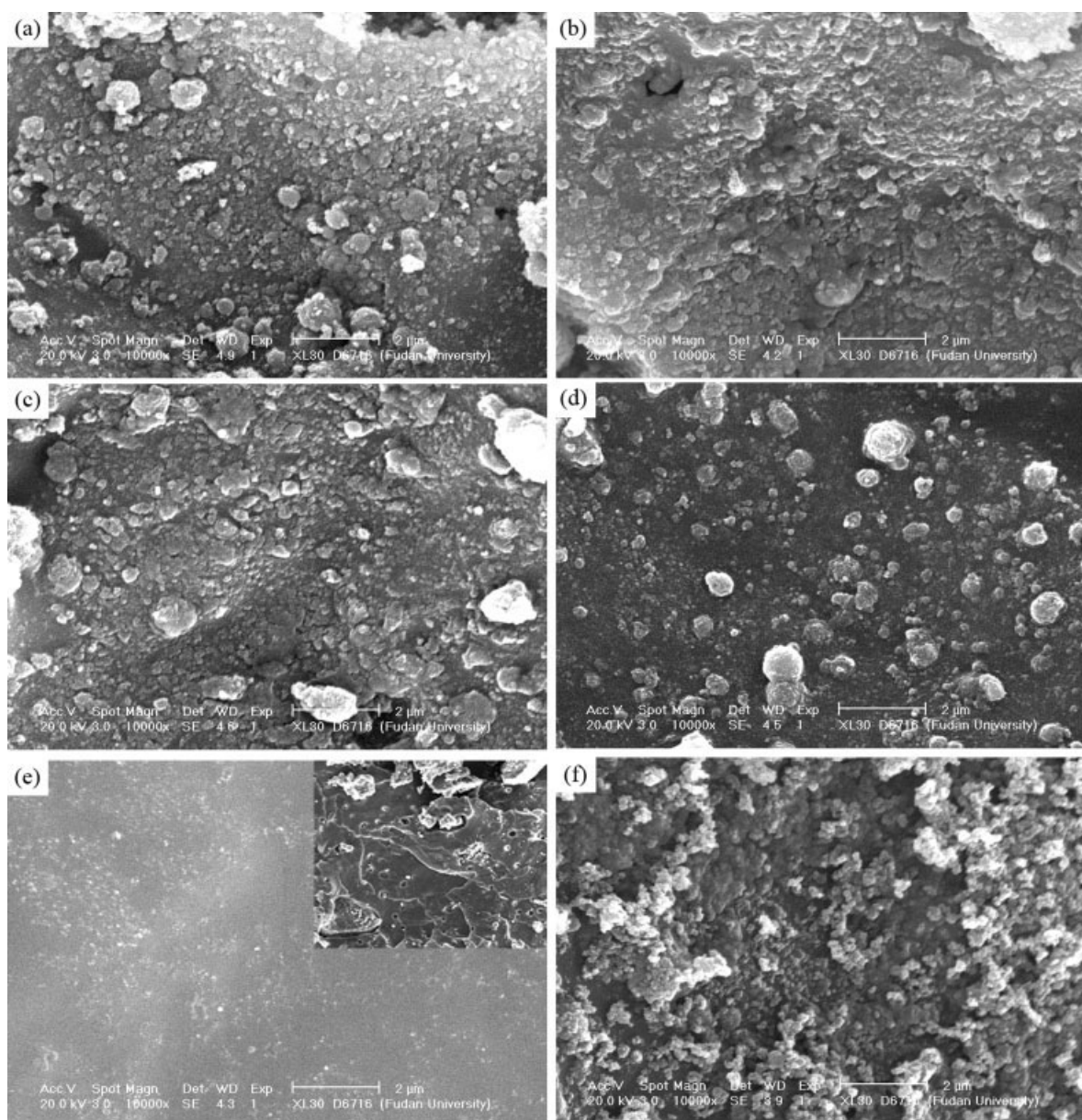


Figure 6 The SEM images of the fumed silica reinforced waterborne adhesives (a) HS-5 without silica sol, (b) HS-5 with silica sol, (c) TS-610 without silica sol, (d) TS-610 with silica sol, (e) TS-720 without silica sol (inserted picture: small magnification), and (f) TS-720 with silica sol [A-1100: 2.5 wt %, fumed silica: 2.5 wt %, TEOS: 5 wt % (based on the amount of emulsion)].

Afterward, the shear strength decreased as fumed silica further increased. The reinforcing role of fumed silica at low-fumed silica content and aggregation of fumed silica at high-fumed silica content should be responsible for the above variation of shear strength with fumed silica content, respectively.

Comparison of different silica sources

Since TEOS transformed into silica component after hydrolysis and condensation with silylated polyether or itself, the final cured adhesives were actually polyether/silica nanocomposites (or hybrids) for all

the above cases. The unique difference lied in their silica sources, namely silica from TEOS, from TEOS and silica sol, or from TEOS, silica sol, and fumed silica. To acquire some ideas on the influence of silica source, the silica content in the cured adhesive was calculated based on the assumption that TEOS completely turned into silica component and all water evaporated. The shear strengths of the cured adhesives varying with silica content are plotted in Figure 8. The figure illustrated that fumed nanosilica particles were the most efficient silica component for enhancing the shear strength of waterborne silylated polyether adhesive at the same silica content. Maxi-

mal shear strength of 2.5 MPa was obtained at silica content of 7.7 wt % (1.6, 2.2, and 3.9 wt % of silica components from TEOS, silica sol, and fumed silica, respectively). For the samples with silica components from TEOS and silica sol, their shear strengths were even lower than those containing silica component solely from TEOS at silica content less than 6 wt %, indicating colloidal silica particles can not efficiently crosslink with silylated polyether chain. However, for the silica component only stemmed from TEOS, the reinforcing role of silica appeared especially at low silica content and 1.9 MPa of maximal shear strength was obtained at 4.6 wt %. Therefore, combination of three kinds of silica sources was beneficial for preparation of waterborne silylated polyether adhesive with high shear strength. The strengthening mechanism of each silica source was just discussed in the above sections. Namely, the silica components from TEOS, silica sol, and fumed silica played crosslinking, dispersing, and reinforcing roles on the nanosilica reinforced waterborne adhesive, respectively.

CONCLUSIONS

Nanosilica-reinforced waterborne silylated polyether adhesive with ambient-curable property and high shear strength was successfully fabricated via coaddition of TEOS, silica sol, and fumed silica into silylated polyether emulsion. TEOS endowed the waterborne silylated polyether adhesive with mechanical performance through crosslinking with polyether chain. Colloidal silica particles cannot obviously enhance the shear strength for most cases, however,

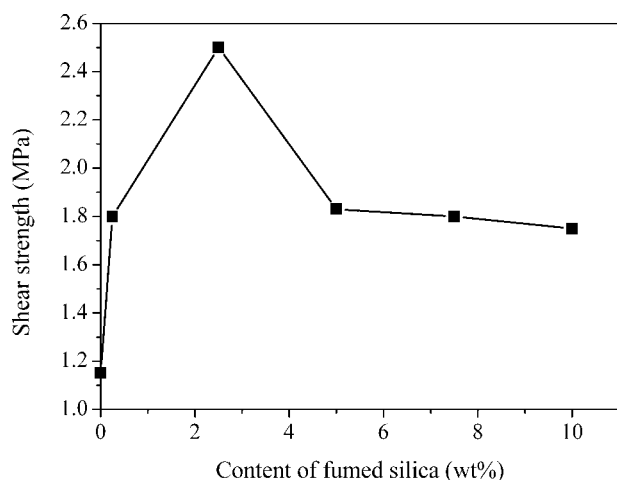


Figure 7 Effect of fumed silica (TS-610) content on the shear strength of waterborne adhesives [A-1100: 2.5 wt %, silica sol: 2.5 wt %, TEOS: 5 wt % (based on the weight of emulsion)].

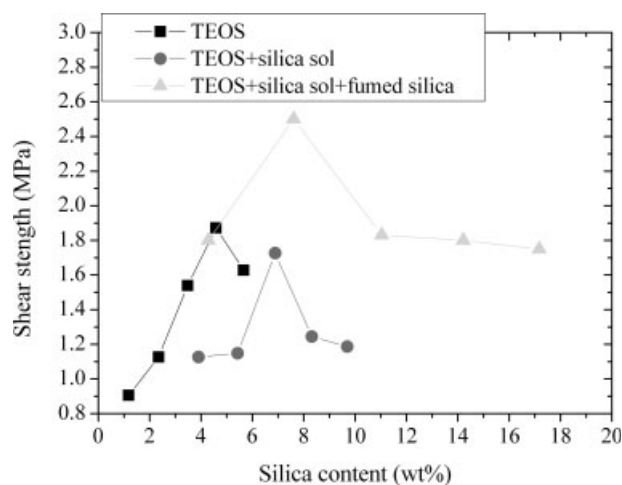


Figure 8 Comparison of the shear strength of waterborne adhesive containing silica coming from different silica source (the colloidal silica inherently existed in waterborne silylated polyether adhesive was calculated as polyether and the silica from A-1100 was not counted because it is the same for all cases).

can improve the dispersion of fumed silica in the adhesive and thus increase the shear strength. Comparing with the hydrophilic fumed silica (HS-5) and the extremely hydrophobic fumed silica (TS-720), the moderate hydrophobic fumed silica (TS-610) was more efficient on reinforcing the waterborne adhesive. Both the above results indicated that the dispersion of nanosilica particles in waterborne adhesive and the compatibility of nanosilica particles with silylated polyether chains were equally important for the preparation of waterborne adhesive with high shear strength.

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