Effect of the particle size of nanosilica on the performance of epoxy/silica composite coatings

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Four kinds of colloidal silica particles with different size (27, 58, 79 and 173 nm, respectively) were synthesized by sol-gel process and modified with 3-glycidoxypropyltrimethoxysilicane, then homogenously dispersed into the epoxy resin and cured with alicyclic amine on aluminum alloy substrates. The results showed that the Si—O—Al bond was formed at nanocomposite coat/substrate interface, introducing nanosilica significantly enhanced the adhesive strength, scratch resistance, abrasion resistance and corrosion resistance of coats, but different particle sizes of nanosilica had various impact on these properties, which seemed to be related to the structure of the silica surface. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Epoxy/nano-silica composites have the advantages of low cost, good adhesion to most substrates, good corrosion resistance, good scratch resistance, excellent tribological properties and so on, and have many potential applications in sealants, paints, coatings, adhesives, etc. [1–5].

As it is well known, the dispersion of nanoparticles in the polymer matrix usually has a significant impact on the properties of nanocomposites. Generally, there are several methods proposed for improving the dispersion of nanoparticles into the corresponding orgainc matrix, e.g., mechanical mixing, sol-gel process, *in-situ* synthesis, ultrosonic dispersion, surface modification of nanoparticles and so on. Nevertheless, the particle size could also play a very important role in the properties of the organic-inorganic composites. There are a numbers of papers reporting the distinctive size effect between microscale inorganic particle and nanoscale inorganic particle. For examples, Zhou *et al.* [6, 7] found that nano-silica can obviously improve the UV absorbance and micro hardness of polyurethane coats while micro-silica has almost no influence on these properties. Kinloch *et al.* [8] compared the mechanical and fractural properties of epoxy/inorganic micro- and nano-composites. Ng *et al.* [9] concluded that most of thermal and mechanical properties of the nanoparticles filled epoxy composites are superior to those of the microparticles filled epoxy composites at the same weight content loading.

Up to now, however, the effect of particle size in the nano scale on the properties of nanocom-posites is scarcely involved, especially on the epoxy/nanosilica composites [10]. In this paper, the colloidal silica with different particle size are prepared by sol-gel process and further modified with 3-glycidoxypropyltrimethoxysilicane(GPTMS). The GPTMS-modified silica sols could be dispersed into epoxy resin very well. The major concern of this paper is to study how the particle sizes of colloidal silica influence the properties of nanocomposite coats on aluminum alloy substrates.

2. Experimental
2.1. Materials
Tetraethylothosilicate (TEOS) was supplied by Shanghai Huarun Chemical Company. (3-Glycidoxypropyl) trimethoxysilicane (GPTMS) was purchased from Shanghai Yaohua Chemical Company. Ammonia solution, ethanol and dibutyltin dilaurate were supplied by Shanghai Chemical Reagent Company. Diglycidylether of bisphenol-A with an epoxy equivalent weight (EEW) of 185–210 and alicyclic amine with amine value of 260–285 mg KOH/g (active hydrogen equivalent weight is about 115) acting as curing agent were supplied by Shanghai Resin Factory Co., Ltd.

2.2. Surface treatment of aluminum alloy substrates
Aluminum alloy (AA) panels with dimension of 5 × 10 × 1 mm were selected as substrates for measuring the adhesion force and salt fog resistance of the coats.

To degrease and deoxidize the AA surfaces, a cleaning process was carried out as follows: the AA panels were wiped with hexane and methanol in order and then soaked in an alkaline cleaner solution for about 60 seconds at 70°C. After taken out from the solution, it was thoroughly rinsed with deionized water for 2 min and dried in air.

2.3. Preparation of epoxy/colloidal silica composite coats

TEOS, deionized water and ethanol were charged into a 500 ml round-bottom flask equipped with a mechanical stirrer, thermometer with a temperature controller and a heating mantle and heated to 50°C then added by the mixture of ethanol and $NH_3 \cdot H_2O$ and reacted for 8 h, followed by stirring for 12 h at room temperature. Silica sols with different particle size were prepared through changing the molar ratioes of $NH_3 \cdot H_2O$ to water. The particle size was measured by particle size analyzer (Beckman, N4Plus) and the polydispersity is less than 0.5. The recipe is given in Table I.

The colloidal silica were then modified by GPTMS to improve the dispersibility and compatibility of silica particles with epoxy matrix using following procedure: the colloidal silica and catalyst were charged into a 250 ml round-bottom flask equipped with a mechanical stirrer, thermometer with a temperature controller, addition funnel, and a heating mantle and heated to 70°C, then gradually added by GPTMS (molar ratio of TEOS:GPTMS = 10:1) in 30 min. After the addition was finished, the reaction mixture was maintained at 70°C for additional 6 h to complete the reaction. Fig. 1 schematically demonstrates the chemical structure of the surfaces of the modified colloidal silica particles.

The modified silica sols were added to epoxy resin according to the weight ratio of 10/90 for silica to epoxy resin at room temperature and fully mixed under vigorous stirring. An appropriate amount of alicyclic amine was then added to the mixture to obtain a homogeneous solution, the mass ratio of the epoxy (from resin and modified silica) to the alicyclic amine is about 1.8:1. After degasification, the solution was quickly cast on AA panels by drawdown rod with the coat thickness of ~75 μm, then the coatings were placed in the room temperature for 24 h in order to make them cured completely.

2.4. Characterization
2.4.1. The grafting amount of GPTMS on nano silica
The grafting amount of GPTMS to the surfaces of colloidal silica particles is determined by the titration of epoxy group as previously described by Jay [11]. The colloidal silica particles were centrifuged from the colloidal solutions and redispersed into the ethanol, this procedure was repeated three times in order to completely remove the ungrafted GPTMS. In this method, an aliquot of the sol solution was dissolved in chloroform and titrated to a crystal violet end point with standard perchloric acid in acetic acid in the presence of an excess of tetraethylammonium bromide.

2.4.2. FT-IR analysis
FT-IR analyses of colloidal silica and modified colloid silica were carried out by a Magna-IR^{TM} 550 spectrometer (Nicolet Instruments, Madison, WI). The scan wavelength was in the range of 400–4000 cm^{-1}.

2.4.3. TEM observation
The morphologies of the nanocomposite coats were observed bya transmission electron microscope (Hitachi H-600, Hitachi Corporation, Japan). Samples were prepared by ultramicrotomy at room temperature, giving sections of nearly 100 nm in thickness. No further staining was used to improve contrast.

2.4.4. XPS analysis
A Perkin-Elmer PHI model 5000 C was used for XPS analysis. The exciting radiation was provided by an Al K$_\alpha$ X-ray source operated at a constant power of 250 W (14.0 kV). Binding energy was 93.9 eV.

2.4.5. Adhesion strength
The adhesion force of nanocomposite epoxy coat to AA substrate was measured by peel test, as indicated in Fig. 2. The nanocomposite epoxy coats on AA substrates were cured at 30°C for 24 h. Peel tests were performed at room temperature using an Instron testing machine with a cross-head speed of 30 mm/min and the peel angle of 180°. The average value of five specimens was reported.

TABLE I Typical recipes for the syntheses of silica sols with different particle size

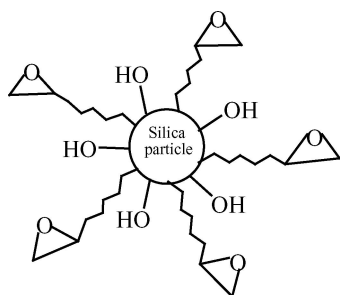| Samples	Sol-1	Sol-2	Sol-3	Sol-4
TEOS (mol)	0.60	1.20	4.80	0.04
Water (mol)	0.60	1.80	4.80	0.02
Ethanol (mol)	0.90	1.80	3.60	0.06
NH$_3$ (mol)	0.90	1.80	3.60	0.40
Particle size (nm)	27	53	79	173

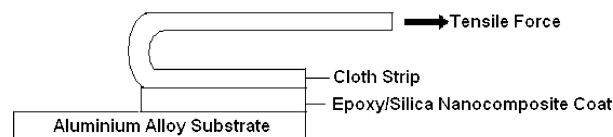*Figure 1* Chemical structure of the surface of the modified silica particles.

Figure 2 The Schematic Diagram of the Peel test on Instron testing Machine.

2.4.6. Scratch resistance

The scratch resistance of the coats on AA substrates was investigated with a C.S.E.M. automatic scratch tester (Lausanne, Switzerland), using the REVETEST technique. Rockwell type diamond tip with radius 200 μm was used and scratching tests were carried out with a speed of 10.3 mm/min, loading rate of 50 N/min, loading scale of 0–50.9 N and scratch length of 10 mm.

2.4.7. Abrasion resistance

Abrasion resistance was determined on a round glass board according to GB1768-79. The film was firstly rubbed flat for about 100 cycles then recorded the initial weight. For every 200 cycles rubbing, the abrasive wheel was renewed and the weight loss was recorded, which could be used to judge the abrasion resistance. The weight loss data was the average value of three experiments.

2.4.8. Corrosion resistance

Corrosion resistance of the coats on AA substrates was evaluated by exposing the coats to a salt fog atmosphere generated by spraying 5 wt.% aqueous NaCl solution at $35 \pm 2°C$ for 256 h in accordance with ASTM B117 specification. After removal from the salt fog chamber, all samples were rinsed with distilled water to remove any residues.

3. Results and discussion
3.1. Modification of colloidal silica with GPTMS

Fig. 3 presents the FTIR spectra of the original colloidal silica particles, sGPTMS modified silica particles and GPTMS. A peak at 911 cm^{-1} due to epoxy group, is observed in the FTIR spectrum of modified silica particles, indicating that GPTMS hasgrafted onto the surfaces of the silica particles.

The titration results are listed in Table II. The epoxy values on different silica particles are almost equal, sug-

TABLE II The grafting amount of GPTMS to silica sols with different particle size

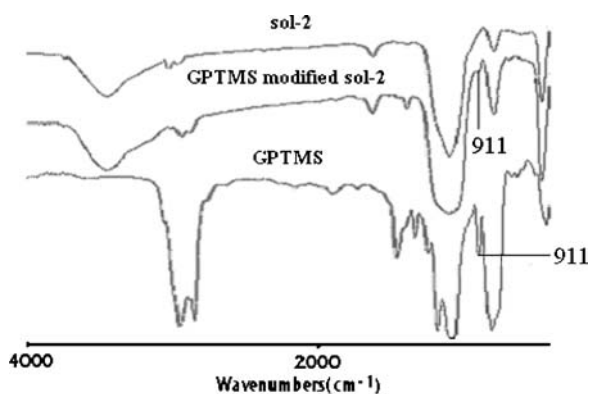| Samples	sol-1	sol-2	sol-3	sol-4
Epoxy value (mol·100 g^{-1})	0.134	0.138	0.139	0.137

Figure 3 The IR spectra of the original colloidal sillica, GPTMS modified silica and GPTMS.

TABLE III The A_{3743}/A_{800} ratios of the modified silica particles

Samples	A_{3743}	A_{800}	A_{3743}/A_{800}
sol-1	9.53	119	0.08
sol-2	20.9	64.8	0.32
sol-3	8.48	30.8	0.28
sol-4	7.27	34.2	0.21

gesting that GPTMS has the same grafting amount on different silica particles in our experimental conditions. Theoretically, if the GPTMS completely reacts with silica particles, the epoxy value of the modified silica should be around 0.167 mol/100 g. The actual grafting amount of GPTMS shown in Table II indicates less than 2 wt% of free GPTMS existing in silica sol, thus these free GPTMS can be ignored.

The FTIR spectra of the GPTMS modified silica with different particle size are illustrated in Fig. 4. The characteristic absorbing peaks of the four spectra are similar. The relative intensity of the peak at 3743 cm^{-1} belonging to Si—OH stretching vibration to the peak at 800 cm^{-1} for Si—O—Si bending mode could be used to quantitatively compare the amount of Si—OH groups [12], as summarized in Table III. The data show that the silica sol-2 and sol-3 have higher A_{3743}/A_{800} than sol-1 and sol-4, suggesting that the surfaces of the modified silica particles with 53 and 79 nm possess much more Si—OH groups than the modified silica particles with 27 and 173 nm.

3.2. Morphology observation

Fig. 5 compares the typical morphology of unmodified or modified silica dispersed in epoxy coats. It can seen that the unmodified silica particles have a strong tendency to aggregate in epoxy coat while the modified silica particles are homogeneously dispersed in polymer matrix, indicating that modification of GPTMS indeed improve the compatibility of colloidal silica with epoxy resin.

3.3. Interface analysis

The interface compositions of nanocomposite epoxy coats with AA substrates are determined by XPS and summarized in Table IV.

The data in Table IV show that Al element is not found for pure epoxy coat but observed for all epoxy/silica nanocomposite coats. The existence of Al must be caused by Si—O—Al bond formed between nanocomposite epoxy coats and AA surfaces. Since

TABLE IV The interface compositions of nanocomposite epoxy coats

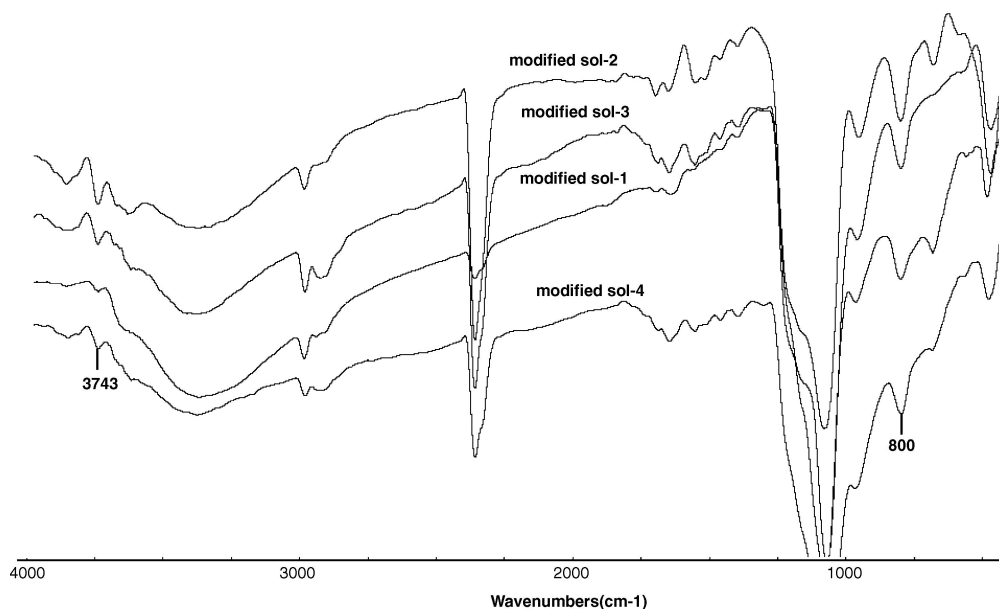| Coats	Molar content (%)				
	C	O	Si	N	Al
Pure epoxy	80.3	17.2	0.66	1.86	0.00
With sol-1	70.2	24.4	2.67	2.51	0.23
With sol-2	74.0	20.7	2.62	2.40	0.28
With sol-3	74.7	20.2	2.54	2.30	0.27
With sol-4	74.0	20.6	2.67	2.43	0.23

Figure 4 The FTIR spectra of the modified silica sols with different particle size.
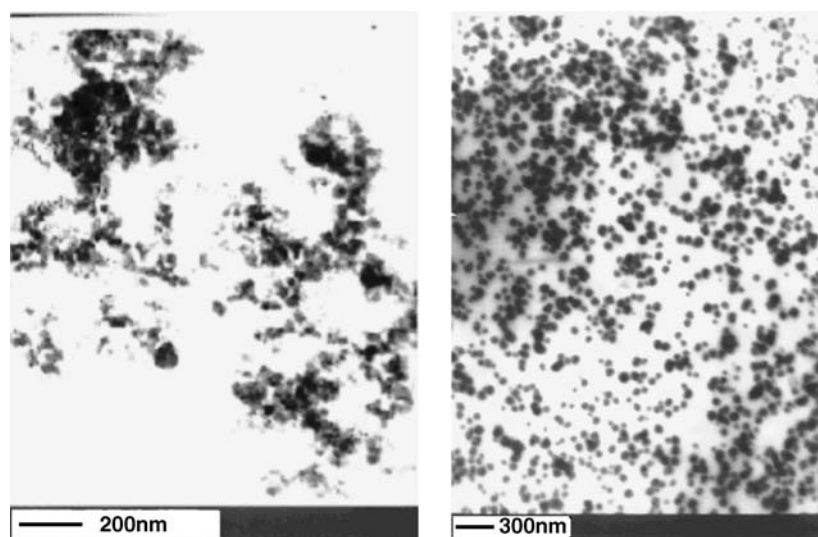

Figure 5 The TEM pictures of unmodified and modified silica dispered in epoxy matrix (a) unmodified, (b) modified.

AA panels are readily oxidized and further hydrated to form hydroxyl groups, namely Al—OH groups, at the top surface in the presence of moisture [13], the Si—O—Al bond is easily formed due to the reaction between Al—OH group and Si—OH or Si—OR group at the interfaces of nanocomposite epoxy coats with AA substrates. The more hydroxyl groups at the surfaces of silica particles, the more Al content at the interfaces of nanocomposite epoxy coats to panels are detected (see samples with sol-2 and sol-3), indicating more Si—O—Al bonds are formed due to more Si-OH reacting with Al—OH since Si—OR groups at the GPTMS modified silica are almost equal.

3.4. Adhesion strength of nanocomposite epoxy coats on AA substrates

The adhesion forces of nanocomposite epoxy coats to AA substrates are shown in Table V. The pure epoxy coat displays a very low adhesive strength, but the adhesive strength significantly increasesafter colloidal silica

is imported into epoxy matrix. The nanocomposite coat with sol-2 has the highest adhesive strength and the coat with sol-3 had second highest adhesive strength since these two coats could form more Si—O—Al bonds with AA substrates, as detected by XPS.

3.5. Scratch resistance

Fig. 6 displays the failure appearance of pure epoxy coat and the nanocomposite coats with sol-2 after scratching tests. The failure modes of other nanocomposite epoxy coats are analogous to the coat with sol-2 and thus not provided here. It can be seen from the figure that the

T A B L E V Adhesion strength of epoxy coats to AA substrates

Coats	Pure epoxy	With sol-1	With sol-2	With sol-3	With sol-4
Adhesion strength (kg cm^{-1})	0.069	0.358	1.17	1.06	0.542

(a) partial delamination   (b) total delamination

(i) pure epoxy coat

(a) partial delamination   (b) total delamination

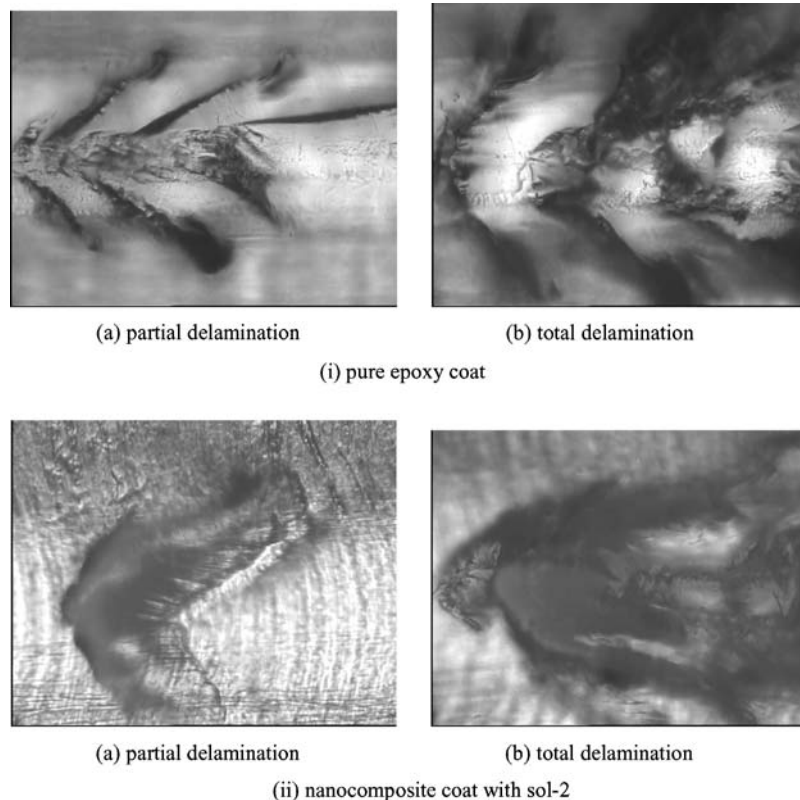(ii) nanocomposite coat with sol-2

Figure 6 The optical micrographs of pure epoxy coat and nanocomposite coat with sol-2 with the failure modes of (a) partial delamination and (b) total declamination after scatching tests.

failure mode of pure epoxy coat is quite different from that of the coat with sol-2. It seems that the pure epoxy coat is more brittle than the nanocomposite epoxy coat. In other words, GPTMS modified silica particles can enhance the toughness of epoxy coats.

The critical loads for partial and total delamination failures of different coats are summarized in Table VI. The data show that the order of critical load follows as the coats with sol-2> with sol-3> with sol-4> with sol-1> pure epoxy, indicating the nanocomposite epoxy coats containing silica particles at 53 and 79 nm have much higher adhesive force than those at 27 and 173 nm since the critical loads for total delamination correspond to the adhesive force, which is consistent with the adhesion strength determined by peel tests very well. The above results seem to suggest that the scratch resistance of the coats is also related to the interaction force between nanocomposite coats with AA substrates since the coats with sol-2 and sol-3 have much higher adhesive strength with substrates than the coats with sol-1 and sol-4, as indicated in Table V.

TABLE VI The critical loads for partial and total delaminating of different coats

Failure type	Critical load(N)				
	Pure epoxy	With sol-1	With sol-2	With sol-3	With sol-4
Partial delamination	16.5	19.9	23.7	23.4	21.7
Total delamination	21.2	21.2	25.4	25.2	22.7

3.6. Abrasion resistance

The weight losses of pure epoxy and nanocomposite epoxy coats are illustrated in Fig. 7. The weight losses of epoxy coats obviously reduce after silica particles are embedded, indicating that GPTMS modified silica can improve the abrasion resistance of epoxy coats [14]. Comparing the effect of particle size of silica on abrasion resistance demonstrates that the nanocomposite coats with sol-2 and sol-3 have relatively higher weight losses and the coats with sol-1 and sol-4, this means that the nanocomposite epoxy coats containing silica particles at 53 and 79 nm have much slightly
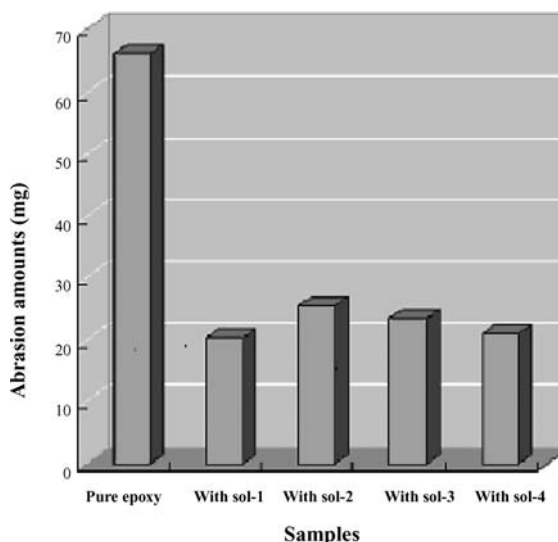

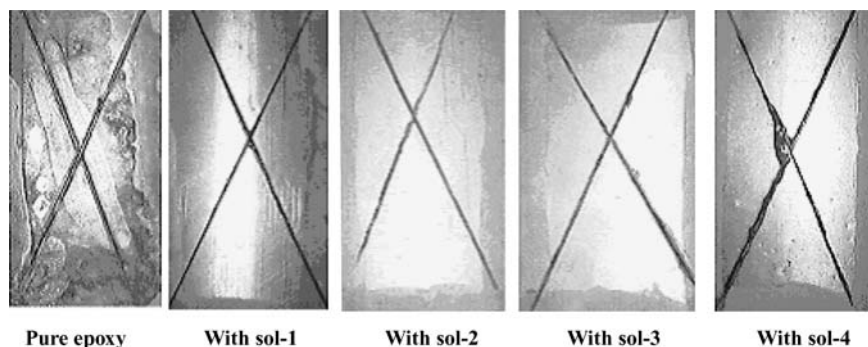*Figure 7* The abrasion resistance of pure epoxy and nanocomposite epoxy coats.

Figure 8 The appearance of the AA panels coated with pure epoxy and nanocomposite epoxy coats after 26 h salt spray test.

worse abrasion resistance than those at 27 and 173 nm, which is just contrary to the adhesion strength and scratch resistance. The reason is not very clear right now, the possible reason is the destructive mechanism by rubbing is totally different from that by stretching or scratching.

3.7. Corrosion resistance
Fig. 8 manifests the pictures of AA substrates coated with pure epoxy or nanocomposite epoxy coats after 256 h salt spray tests. Compared with nanocomposite epoxy coats, pure epoxy coats started to delaminate from AA substrates only after 35 h salt spray and severely exfoliated after 256 h salt spray test, revealing the corrosion resistance of pure epoxy coat is very bad. While for the nanocomposite epoxy coats, only a little exfoliation was observed in the nanocomposite coats with sol-1 and sol-4 and no change was seen for the nanocomposite coats with sol-2 and sol-3. This suggests that the epoxy coats embedded with nanosilica have improvement in corrosion resistance, and the nanocomposite coats with nanosilica particles at 53 and 79 nm have better corrosion resistance than those at 27 and 173 nm, this is probably because the formers have much higher adhesion strength than the latters.

4. Conclusion
From this study it can be concluded that introducing nanosilica into epoxy matrix can form Si—O—Al bond at coat/aluminum alloy substrate interface since Si-OH at nanosilica can react with Al—OH at aluminum alloy surface, significantly increasing the adhesive strength, scratch resistance, abrasion resistance and corrosion resistance of epoxy coats.

However, the degree of improvement in these properties of coats depends upon the particle sizes of nanosilica embedded. The peeling, scratching and salt spraying experiments display that the nanocomposite coats with the silica particle sizes at 53 and 79 nm have relatively higher adhesion strength, scratch resistance and corrosion resistance than those containing 27 and 173 nm silica particles while the abrasion resistance seems to be just opposite.

References
1. M. Q. ZHANG, M. Z. RONG, S. L. YU, B. WETZEL and K. FRIDRICH, *Wear.* **253** (2002) 1086.
2. B. WETZEL, F. HAUPERT and M. Q. ZHANG, *Comp. Sci. Tech.* **63** (2003) 2005.
3. A. J. KINLOCH and A. C. TAYLOR, *J. Mater. Sci. Lett.* **22** (2003)1439.
4. M. Z. R. RONG, M. Q. Z. ZHANG, G. SHI, Q. L. JI, B. WETZEL and K. FRIDRICH, *Trib. Int.* **36** (2003)697.
5. L. MATĚJKA, O. DUKH and J. KOLAŘÍK, *Poly.* **41** (2000) 1449.
6. S. X. ZHOU, L. M. WU, W. D. SHEN and G. X. GU, *J. Mater. Sci.* **39** (2004)1539.
7. S. X. ZHOU, L. M. WU, J. SUN and W. D. SHEN, *J. Appl. Polym. Sci.* **88** (2003) 189.
8. A. J. KINLOCH and A. C. TAYLOR, *J. Mater. Sci. Lett.* **22** (2003) 1439.
9. C. B. NG, L. S. SCHADLER and R. W. SIEGEL, *NanoStruct. Mater.* **12** (1999) 507.
10. T. NAGANUMA and Y. KAGAWA, *Compos. Sci. Tech.* **62** (2002) 1187.
11. R. R. JAY, *Anal. Chem.* **36** (1964) 667.
12. A. DURAN, C. SERNA, V. FORNES and J. M. FERNANDEZ NAVARRO, *J. Non-Cryst. Solids* **82** (1986) 69.
13. G. A. PARKS, *Chem. Rev.* **65** (1965) 177.
14. S. X ZHOU, L. M. WU, J. SUN and W. D. SHEN, *Prog. Org. Coat.* **45** (2002) 33.