ELSEVIER

International Journal of Adhesion & Adhesives 28 (2007) 23–28

International Journal of Adhesion & Adhesives

www.elsevier.com/locate/ijadhadh

Effect of nano-Al_2O_3 on adhesion strength of epoxy adhesive and steel

L.L. Zhai, G.P. Ling*, Y.W. Wang

College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Accepted 5 March 2007
Available online 23 March 2007

Abstract

Nanosized Al_2O_3 particles were introduced into an epoxy adhesive to improve the adhesion strength of bonded steel utilizing both modified and unmodified epoxy adhesive. The adhesion strength was measured by pull-off adhesion test as a function of nano-Al_2O_3 amount and interface roughness. The results indicated that the adhesion strength was increased dramatically by addition of nano-Al_2O_3 into the epoxy adhesive compared with that of pure epoxy adhesive. The highest adhesion strength was obtained with 2 wt% nano-Al_2O_3 in epoxy adhesive, being almost four times higher than that of the unmodified. As the adhesion strength increased, the locus of failure changed from interfacial to the mixture of interfacial and cohesive.

Scanning electron microscopy (SEM), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDX), and X-ray photoelectron spectroscopy (XPS) were used to investigate the interface morphology and chemical composition of steel and epoxy adhesive. TEM proved that nano-Al_2O_3 was finely dispersed in the epoxy adhesive. The results of SEM and EDX showed little difference between unmodified and modified samples. The XPS results showed that a new chemical group, identified as a carboxyl group, was formed at the interface between the steel and epoxy adhesive after modification by nano-Al_2O_3. Thus, the enhancement in adhesion strength was correlated with the introduction of this new polar group.

Keywords: Epoxy adhesive; Steel; adhesion; Nano-Al_2O_3

1. Introduction

Epoxy resins have a wide range of excellent physical and chemical properties, which makes them essential for the current technologies and for the development of new technologies. Owing to their strong adhesion to a variety of treated or untreated metal surfaces [1], epoxy-based adhesives are extensively employed in many industries, in order to bond different materials substrates [2,3].

In spite of their high initial adhesion to several common metals such as steels, adhesion is rather weak after exposure in humid and hot environment. So it is very important to improve the adhesion between epoxy adhesives and steels. However, the adhesion-promoting treatments [4–6], such as chromating, coupling agents [7], and other surface treatment [8] are relatively expensive, harmful and complicated.

Recently, it has been found that nanoparticles incorporation into the adhesive is an economical and environmentally friendly way to modify the physical and chemical properties of polymer. Nanoparticles possess unique properties such as increased chemical activity and physical properties [9,10]. So many researches [11–13] have shown great promise for obtaining much increased performance, such as mechanical and thermal properties with adding low concentrations of nanoparticles into epoxy. However, a systematic study of the influence of nanoparticles addition on the interfacial adhesion between an epoxy and steel is not available and only a few papers have reported the influence of nanoparticles addition on adhesion [14]. Therefore, it is very interesting to consider the influence of nanoparticles additive on the adhesion and understand the interface in the metal–polymer system and the adhesion mechanism. In this paper, we proved that an increase in adhesion is achieved by nanoparticles

---

*Corresponding author. Tel.: +86 571 87952648; fax: + 86 571 87952358.
E-mail address: linggp@zju.edu.cn (G.P. Ling).

0143-7496/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijadhadh.2007.03.005

addition in an epoxy adhesive and discussed the adhesion mechanisms.

2. Experimental

2.1. Preparation of adhesives and samples

Dollies (20 mm diameters) and sheets (34 mm × 34 mm × 1.7 mm) of low carbon steel (0.15%C, 0.56%Mn, 0.015%S, 0.011%P) were used as substrates. To remove oxidation and contaminants and to roughen the surfaces, first they were abraded with silicon carbide paper of 60 (60#) and 150 (150#), or polished to an optical flatness. Then these substrates were degreased with acetone to remove any moisture or dust and blown dry using compressed clean air.

A commercially available Pattex® Kraft-Mix adhesive from Henkel Adhesives Ltd. was used, which is a two-component system (an epoxy resin and a hardening agent). The SEM image of applied Al_2O_3 nanoparticles with an average diameter of 80 nm is shown in Fig. 1. Different quantities of Al_2O_3 were added into the epoxy resin on the tray, and thoroughly ground with a spatula for 5 min to disperse evenly. Then the equal amount of hardening agent was added into the mixture and mixed mechanically. Fig. 2 showed that 2% nano-Al_2O_3 was well dispersed in epoxy adhesive by mechanical dispersion, with a typical diameter of about 60–100 nm, consistent with the size of original nano-Al_2O_3 particles. In contrast to pure epoxy adhesive, epoxy adhesive without nano-Al_2O_3 was also prepared, equal amount of resin and hardener (1:1) were mixed up homogeneously. Thin adhesive layers were then applied onto the surfaces of the steel dollies and the sheets, and joints were stuck together and held in place with “cellotape”. Finally, the coated substrates were cured for 2 h at 50 °C in a dust-free cabinet. The thickness of the adhesive layers after cure was about 0.3 mm.

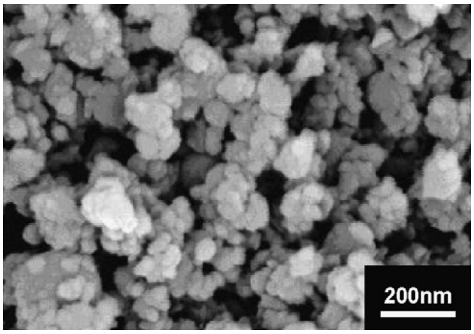

Fig. 1. SEM image of nano-Al_2O_3.

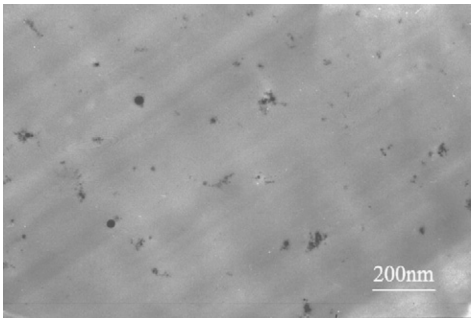

Fig. 2. TEM image of 2% nano-Al_2O_3 in epoxy adhesive.

2.2. Adhesion strength tests

The pull-off adhesion tests were performed with a PosiTest® pull-off adhesion tester (DeFelsko Corporation, New York) in accordance with ISO 4624. Before testing, the adhesive around the edges of the dolly was cut through with a 20 mm cutting tool, and any excess adhesive was removed. Then, the dolly was pulled vertically away from its steel substrate using hydraulic pressure at room temperature. The experiment value was obtained from the average of at least four measurements that were performed.

2.3. Surface characterization

The cross-section like sandwich of the metallographic specimen was abraded and polished, then cleaned with ethanol and coated with gold. Interface morphology was observed by field emission scanning electronic microscope (FESEM, FEI SIRION, Netherlands), and an energy dispersive X-ray (EDX) analyzer coupled to the SEM instrument was used to monitor the chemical composition of the interface. The dispersion of nano-Al_2O_3 in epoxy adhesive was characterized by transmission electron microscope (TEM, JEOL 1200, Japan). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific) was used to investigate the chemical states of the adhesive. The spectra were recorded with monochromatized Al Kα radiation (1486.6 eV) as the excitation source with a base pressure of 1.3×10^{-9} mbar, at a constant power of 150 W(15 kV, 10 mA). The pass energy was 20 eV for the high-resolution spectra.

3. Results and discussion

3.1. Effect of nano-Al_2O_3 particles addition on adhesion strength

The adhesion strength of tensile-tested joints as a function of different surface treatments and Al_2O_3 addition was summarized in Table 1. With pure epoxy adhesive, the adhesion strength changed little, whatever the surface roughness. Modified by 2% nano-Al_2O_3, the strength on the surface abraded with 150# was visibly improved by about 5 times. While the strength multiplication on the surfaces both polished and abraded with 60# was 2 times.

Evenly dispersed nano-Al_2O_3 may have some effect on the physical and chemical properties of the adhesion to the epoxy adhesive. The rough surface would increase adhesion strength by enlarging the interaction area [15,16]. While nano-Al_2O_3 perhaps enlarged the interaction area or/and enhanced the adhesion strength per interaction area to increase the adhesion strength. When the surface was very smooth, as the case of optical flatness, the interaction area was less than that of the joints abraded with 150#, so the increase of adhesion strength was not high.

The surface of the epoxy added in 2% Al_2O_3 peeled from the steel substrates with two different roughnesses were investigated. As shown in Fig. 3, some voids were observed on the much rougher surface. These voids were the result of air being entrapped in the valleys (corresponding to the peaks on the surface of epoxy adhesive) created by the surface roughness [17], during coating the epoxy adhesive. As the interaction area decreased, the adhesion strength of the joints abraded with 60# was similar to that of the polished joints. If these voids were eliminated, the average adhesion strength of the joints abraded with 60# probably would have increased [18].

Fig. 4 showed the adhesion strength of modified epoxy adhesive and steel abraded with 150# as a function of different weight percentages of nano-Al_2O_3 in the epoxy adhesive. All the adhesion strength values of the nano-modified were higher than the unmodified which was 3.8 MPa. When the content was 2%, the adhesion strength was the highest, 18.4 MPa, about four times increase in the adhesion strength as compared with the unmodified. However, with the increased addition of nano-Al_2O_3 in epoxy adhesive, the surface wetting ability of the adhesive reduced because of its increased viscosity, which went against the adhesion strength.

Table 1
The adhesion strength of tensile tested joints as a function of different surface treatments and Al_2O_3 addition

Surface roughness	0% nano-Al_2O_3 (Mpa)	2% nano-Al_2O_3 (Mpa)
60#	3.6	7.8
150#	3.8	18.4
Polished	3.0	6.3

3.2. Failure modes

The failure modes were investigated as they correlated with the adhesion mechanisms. A mixed failure mode (cohesive and interfacial) was observed for the samples incorporating 2% nano-Al_2O_3, as illustrated by Fig. 5(b) and (d).

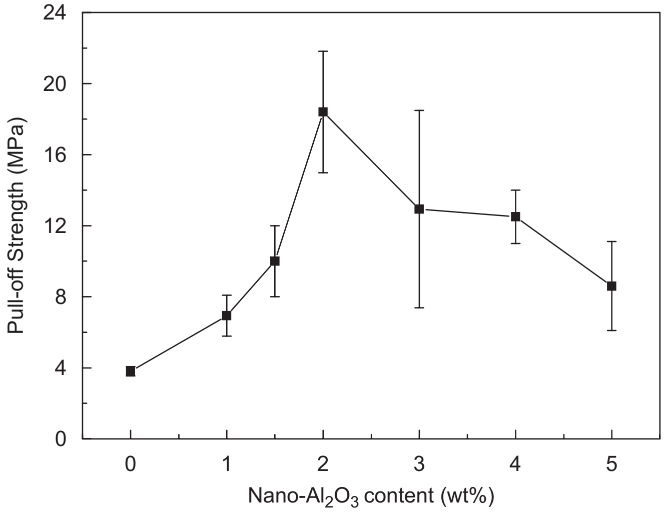

Fig. 4. Effect of nano-Al_2O_3 additive content on the adhesion strength.

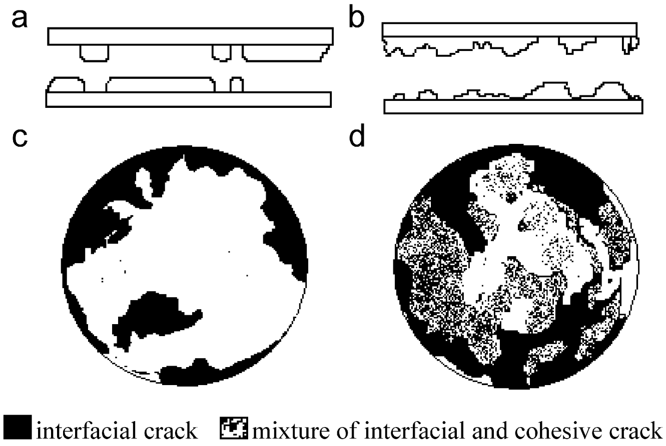

Fig. 5. Schematic illustration of interfacial crack ((a) and (c)) and the mixture of interfacial and cohesive crack ((b) and (d)).

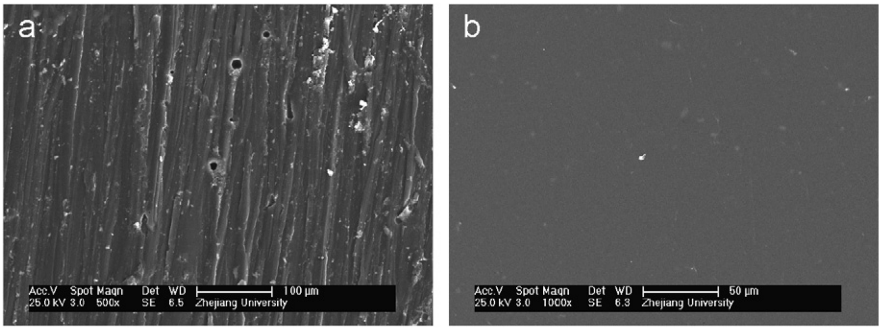

Fig. 3. SEM photographs of the epoxy surface added in 2% nano-Al_2O_3 peeled from the steel substrate (a) abraded with 60# and (b) polished.

In contrast, interfacial failure occurred for the samples without nano-Al_2O_3, as illustrated by Fig. 5(a) and (c). The stronger the observed adhesion was, the more cohesive the crack.

Different interface bond failure mechanisms suggested different bond strengths. The active cohesive and interfacial forces in epoxy adhesive were responsible for its strength (Fig. 6). An interfacial crack occurs and the adhesive–steel connection failed when the interfacial forces of interaction are exceeded due to the applied forces. Therefore, for unmodified joints system, failure was at the interfaces because these forces were weaker than the cohesive forces and did not stand the applied forces. While for nano-modified joints system, the addition of nano-Al_2O_3 may reinforce the interfacial forces in some way, which can compare with cohesive forces. In the modified case the observed failure mode was due to the occurrence of cohesive and interfacial cracks at the same time. The cohesive crack was more visible than others when the content of nano-Al_2O_3 additive was 2%, showing that a stronger bond was formed between the adhesive and the substrate. It can be said that epoxy adhesive had strong interaction with steel substrate due to nano-Al_2O_3, indicating that nano-Al_2O_3 can enhance adhesion at the interface.

3.3. *Effect of nano-Al_2O_3 addition on interface morphology*

The interface morphology was examined by SEM, of samples with different surface roughness and nano-Al_2O_3 content. Seen from Figs. 7 and 8, there was little difference of interface morphology between the samples, and the surfaces of steel and epoxy adhesive contacted fairly closely. It meant surface roughness was not the essential factor increasing adhesion strength and the amount of nano-Al_2O_3 did not affect the morphology of contact surface. Thus, it was presumably thought that nano-Al_2O_3 at the interface had chemical effects on the adhesion property of epoxy adhesive. EDX spectra of the interface (Fig. 9), demonstrated the presence of element Al at the boundary layer of the adhesive interface, which did not exist in unmodified epoxy adhesive. For the adhesive was made up of C, O, S, they were absent in the steel substrate but present at the adhesive. It was considered that nano-Al_2O_3 at the boundary layer of the interface probably inspired epoxy adhesive to give rise to polar functional groups, which can react with steel, and form some chemical bonds with it.

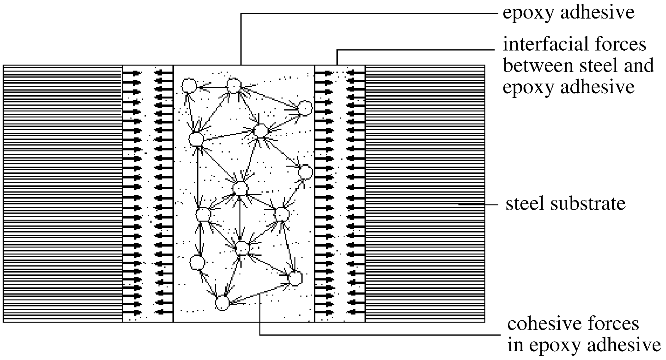

Fig. 6. Schematic illustration of cohesive and interfacial forces in steel and epoxy adhesive.

3.4. *XPS analysis*

High-resolution spectra of C (1s), and O (1s) were analyzed on the steel side pulled off epoxy adhesive, in order to better determine the chemical effect of nano-Al_2O_3 at the interface on the adhesive property of epoxy adhesive.

Fig. 10 was XPS spectra of C (1s) for the steel side. In Fig. 10(a), there were three peaks, with binding energy at 284.6, 285.9 and 287.4 eV, attributed to C–C, C–OH and C=O [19,20]. In Fig. 10(b), a drastic change of a large new peak at 288.5 eV was present. It was identified as carboxyl group [21]. Meanwhile, the new appearance was accompanied by the relative loss of peaks at 285.9 and 287.4 eV compared with 284.6 eV (in Fig. 10(b)), corresponding to the high transition of the C–OH and C=O. Accordingly, it was speculated that carboxyl group was transformed from the disappeared C–OH and C=O and the new peak resulted in the relative loss of the two peaks.

Fig. 11 exhibited the O (1s) spectra collected from the steel side. There were peaks near 529.6 eV and 530.7 eV in Fig. 11(a) and (b), which were assigned to Fe_2O_3 [22,23] and C=O [24,25]. However, the width and intensity of the

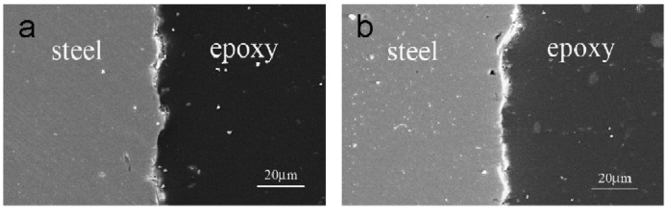

Fig. 8. SEM interface micrographs of steel whose surface abraded with150# and modified epoxy (a) 0% nano-Al_2O_3 and (b) 5% nano-Al_2O_3.

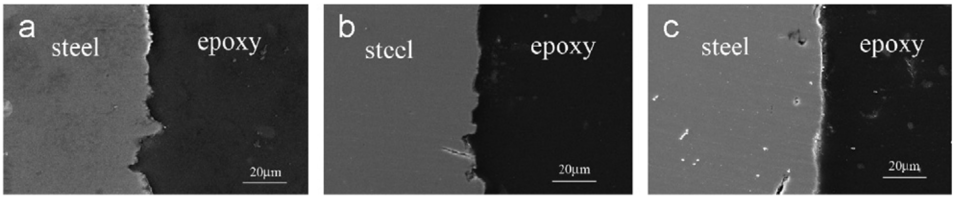

Fig. 7. SEM interface micrographs of 2% nano-Al_2O_3 modified epoxy/steel with different surface roughness. (a) 60#, (b) 150# and (c) polished.

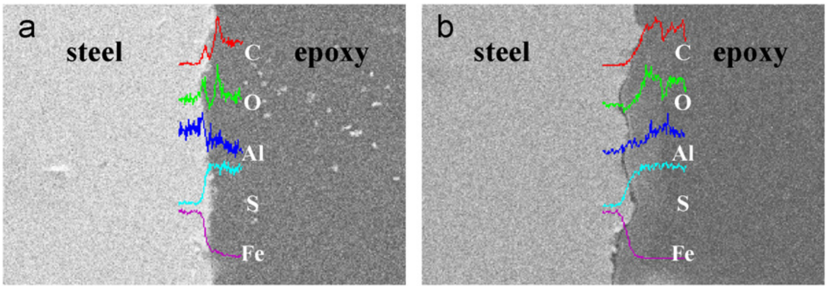

Fig. 9. EDX spectra of the steel surface abraded with 150# (a) 0% nano-Al_2O_3 and (b) 2% nano-Al_2O_3.

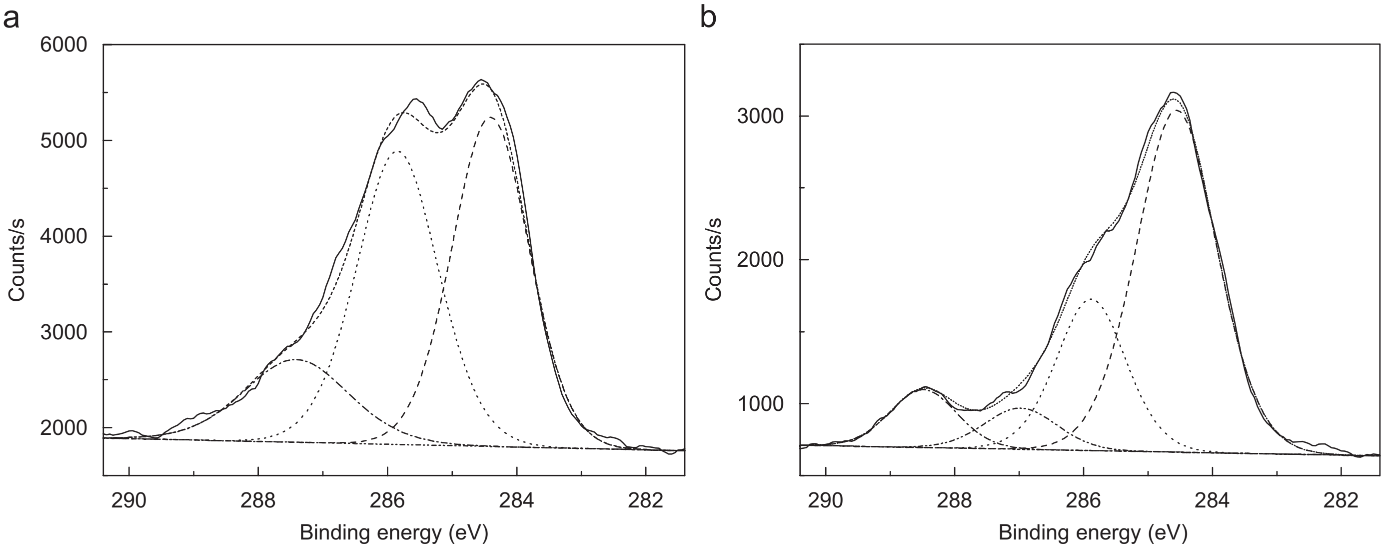

Fig. 10. C (1s) spectra of the steel side with (a) pure epoxy adhesive pulled off and (b) epoxy adhesive added in 2% nano-Al_2O_3 pulled off.

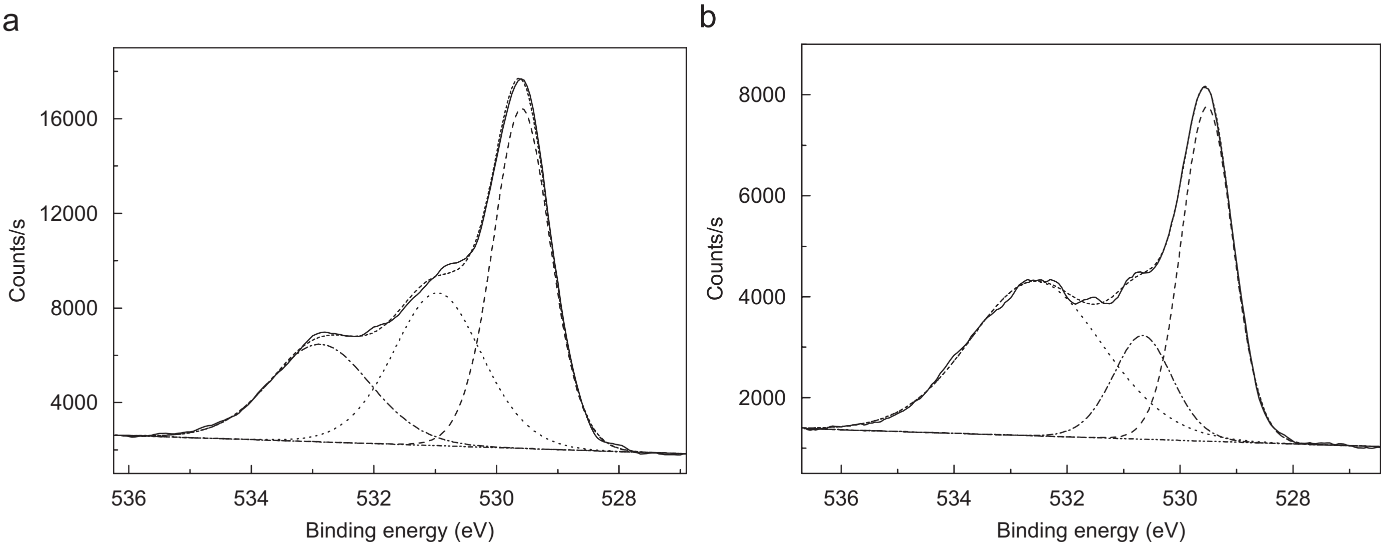

Fig. 11. O (1s) spectra of the steel side with (a) pure epoxy adhesive pulled off and (b) epoxy adhesive added in 2% nano-Al_2O_3 pulled off.

peak near 530.7 eV in Fig. 11(b) decreased, compared with that in Fig. 11(a). Moreover, the peak at 532.8 eV (Fig. 11(a)), characteristic of H_2O [26], shifted to 532.5 eV, which was ascribed to carboxyl functional group [27]. So, it can be considered that the formation of carboxylic group was accompanied by the consumption of some C=O bonds and the transformation of H_2O. These observations were consistent with the C (1s) spectra shown in Fig. 10.

Also, the O atoms of nano-Al_2O_3, which were lack of electrons, might strongly attracted or snatched the electrons of C atoms of C=O and C–O after the adsorption of nano-Al_2O_3 on the molecule chains of epoxy adhesive. When the O atoms of nano-Al_2O_3 shared duplet with C of C=O and C–O, carboxyl was formed in epoxy adhesive.

These results indicated that the addition of nano-Al_2O_3 into epoxy adhesive had changed its chemical property, resulting in carboxyl groups. Carboxyl group, which was used to improve the adhesion of a commonly used epoxy coating [28], showed the highest interaction with metal than other functional groups [29,30]. So, the new polar functional group was the most important factor for adhesion improvement. Moreover, rough surface may enlarge interaction area of epoxy and steel, thus amplify the effect of the adhesion strength enhancement by nano-modification, because of the numbers increase of chemical bond coming from carboxyl groups and steel.

On the other hand, interfacial crack of the failure modes, as discussed in Section 3, implied that tensile strength of epoxy adhesive matrix would be related with the adhesion strength.

4. Conclusion

Well-dispersed nano-Al_2O_3 in epoxy adhesive can distinctly increase its adhesion strength. Both rough surface and nano-Al_2O_3 can enhance the adhesion strength of epoxy adhesive on steel, while the effect of nano-Al_2O_3 was much more remarkable.

Modified by 2% nano-Al_2O_3, the adhesion strength of epoxy adhesive on the surface abraded with 150# was 18.4 MPa, visibly improved by about 5 times. Interfacial crack usually happened for joints without nano-Al_2O_3 additive, and a mixed failure mode for nano-modified joints. Besides, the stronger the adhesion was, the more cohesive the crack. XPS spectra indicated that nano-Al_2O_3 in epoxy adhesive at the interface had chemical effects on adhesive property of epoxy adhesive, resulting in a new polar functional group.

The mechanisms responsible for the adhesion were highly complex because they depended upon simultaneous action of different factors. In this paper, it was found that the new polar functional group was one of the most important factors for adhesion improvement. Other influences of nano-Al_2O_3 about intrinsic stress, cohesive force and tensile strength of epoxy adhesive matrix were still on the study.

Acknowledgements

This research is financially supported by the National Natural Science Foundation of China (No. 50371077).

References

[1] Kozma L, Olefjord I. Mater Sci Technol 1987;3:954–62.
[2] Lapique F, Redford K. Int J Adhes Adhes 2002;22(4):337–46.
[3] Abraham G, Packirisamy S, Vijayan TM, Ramaswamy R. J Appl Polym Sci 2003;88(7):1737–46.
[4] Bullet TR, Rudram ATS. J Oil Col Chem Assoc 1959;11:789.
[5] Santágata DM, Seré PR, Elsner CI, Di Sarli AR. Prog Org Coat 1998;33(1):44–54.
[6] Kirmann J, Roizard X, Pagetti J, Halut J. J Adhes Sci Technol 1998; 12(4):383–97.
[7] Walker P. J Adhes Sci Technol 1991;5(4):251–348.
[8] Weikart CM, Miyama M, Yasuda HK. J Colloid Interf Sci 1999; 211(1):28–38.
[9] Service RF. Science 2001;294(5546):1448–9.
[10] Auer S, Frenkel D. Nature 2001;413(6857):711–3.
[11] Kinloch AJ, Lee JH. J Adhes 2003;79(8/9):867–73.
[12] Kim JK, Him HS. J Adhes Sci Technol 2003;17(3):329–52.
[13] Naganuma T, Kagawa Y. Compos Sci Technol 2002;62(9):1187–9.
[14] Meguid SA, Sun Y. Mater Design 2004;25(4):289–96.
[15] Kalnins M, Sirmacs A, Malers L. Int J Adhes Adhes 1997;17:365–72.
[16] Krongauz VV, Schmid SR, Vandeberg JT. Prog Org Coat 1995;26: 145–62.
[17] Kinloch AJ, Little M SG, Watts JF. Acta Mater 2000;48:4543–53.
[18] Ajayan PM, Stephan O, Colliex C, Trauth D. Science 1994;265: 1212–4.
[19] Beamson G, Briggs D. High resolution XPS of organic polymers: the Scienta ESCA300 Database, 1992.
[20] Hong SG. Polym Degrad Stabil 1995;48:211–8.
[21] Laoharojanaphand P, Lin TJ, Stoffer JO. J Appl Polym Sci 1990; 40:369–84.
[22] Nefedov VI, Salyn YV, Leonhardt G, Scheibe R. J Electron Spectrosc Relat Phenom 1977;10(2):121–4.
[23] McIntyre NS, Zetaruk DG. Anal Chem 1977;49:1521–9.
[24] Chehimi MM, Delamar M. J Electron Spectrosc Relat Phemon 1990; 50:C25–32.
[25] Gervais M, Douy A, Gallot B, Erre R. Polymer 1986;27:1513–20.
[26] Martensson N, Malmquist PA, Svensson S, Basilier E, Pireaux JJ, Gelius U, et al. Nouveau J Chim 1977;1:191.
[27] Sugama T, KuKacka LE, Carciello N, Hocker NJ. Cement Concrete Res 1989;19:857–67.
[28] van den Brand J, Van Gils S, Beentjes PCJ, Terryn H, Sivel V, de Wit JHW. Prog Org Coat 2004;51:339–50.
[29] Friedrich J, Kühn G, Mix R, Fritz A, Schönhals A. J Adhes Sci Technol 2003;17(12):1591–617.
[30] Hjertberg T, Lakso JE. J Appl Polym Sci 1989;37:1287–97.