Dyes and Pigments 86 (2010) 155–160

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Flaky polyacrylic acid/aluminium composite particles prepared using in-situ polymerization

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ARTICLE INFO

Article history:
Received 29 June 2009
Received in revised form
28 November 2009
Accepted 28 December 2009
Available online 6 January 2010

Keywords:
Acrylic acid
In-situ polymerization
Coating
Flaky aluminium particle
Composite particle

ABSTRACT

In order to prevent corrosion of flaky aluminium particles, flaky polyacrylic acid/aluminium composite particles were prepared using *in-situ* polymerization. The influences of dosage of acrylic acid, ammonium persulphate, isopropanol and water, as well as reaction temperature and reaction time, on corrosion inhibition efficiency and gloss were investigated. Maximum corrosion inhibition efficiency was 99.7% and the gloss was 88.3 Gs. Using TGA, SEM, laser particle size analysis, FTIR and XPS, polyacrylic acid was found to be coated on the surface of clear aluminium particles.

1. Introduction

Flaky aluminium pigments have been widely used as solvent-borne automotive coatings, printing inks, and roof coatings for many years [1]. From an environmental perspective, water-borne paints and inks are being developed to reduce the emission of organic solvents [2,3]. However, aluminium can react with water and form H_2, resulting in loss of gloss as well as separation of the coating from substrates [4,5]. Much research has been carried out to inhibit such corrosion by surface modification of aluminium pigments. Nitro- and aminophenols were found to be effective inhibitors for aluminium pigments [6] as was a coating of aluminium pigments with SiO_2 via the sol–gel method using tetraethyl orthosilicate [7,8]. The anticorrosion property of aluminium pigments can be enhanced by the adsorption of corrosion inhibitors [9] as reported by Müller [10] in the case of styrene-maleic anhydride copolymers. Furthermore, flake aluminium particles coated with Fe_2O_3 or Cr_2O_3 have been synthesized as colored aluminium pigment [11].

As a means of securing cost-effective, high corrosion inhibition efficiency, water-borne aluminium pigments, flaky polyacrylic acid/aluminium (PAA/Al) composite particles were prepared using in-situ polymerization.

2. Experimental

2.1. Materials

Clear aluminium particles were prepared through washing flaky solvent-borne aluminium pigment by acetone for 6 h and then drying under vacuum at 105 °C for 6 h to remove organic compounds before encapsulation reaction and its average diameter (d_{50}) was 16.65 μm. Acrylic acid (99.5%), ammonium persulphate (>98%), isopropanol (99.7%) and hydrochloric acid (37%) were used without further purification.

2.2. Experimental process

Clear aluminium particles (2 g), acrylic acid (0.1–0.4 g), ammonium persulphate (0.1–0.4 g), isopropanol (0.5–4 g) and distilled water (50–250 g) were mixed and poured into a reactor equipped with a condenser. The mixture was heated at 65–95 °C for 0.5–2 h and then filtered and washed with water. The flaky polyacrylic acid/aluminium composite particles were dried under vacuum at 105 °C for 6 h.

2.3. Characterization

To evaluate corrosion inhibiting efficiency of PAA/Al composite particles, stability test was carried out, in which 0.5 g of composite particles and clear aluminium particles was dispersed in 0.1 M HCl

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doi:10.1016/j.dyepig.2009.12.012

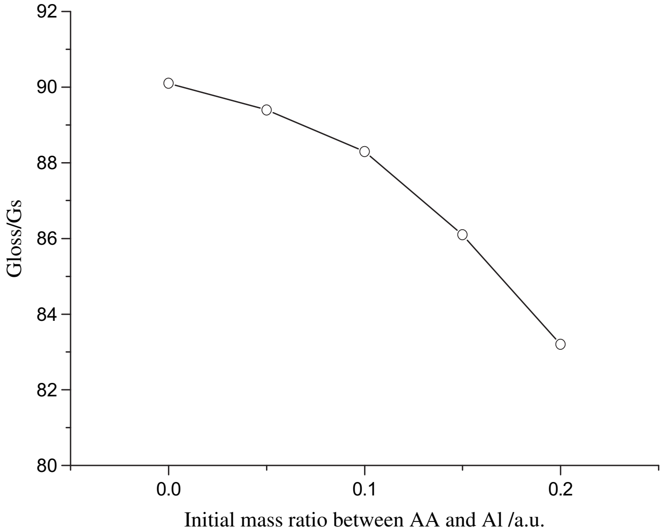

Fig. 1. Effect of AA dosage on coater gloss.

solution at RT for 24 h, respectively. And corrosion inhibiting efficiency (η) was calculated according to following formula [12]:

$$\eta = \frac{V_0 - V}{V_0} \times 100$$

Where, V_0 and V represented the volume of hydrogen gas evolved during stability test for clear aluminium particles and composite particles, respectively. Then, V_0 was 183.0 mL.

The coater gloss was measured with XGT desk-type mirror vancometer. For flaky solvent-borne aluminium pigment, the coater gloss was measured to be 90.1 Gs. Thermogravimetric analysis (TGA) of the samples was carried out with TG-209 instrument. The surface morphology was observed with field emission scanning electron microscope (SEM). The particle size distribution was tested with Mastersizer 2000 particle size analyzers. Fourier transformation infrared measurement (FTIR) was used to characterize the functional groups, for which the particles were ground with dried potassium bromide powder and then compressed into disc. X-ray photoelectron spectroscopy (XPS) was obtained through ESCALab250 photoelectron spectrophotometer.

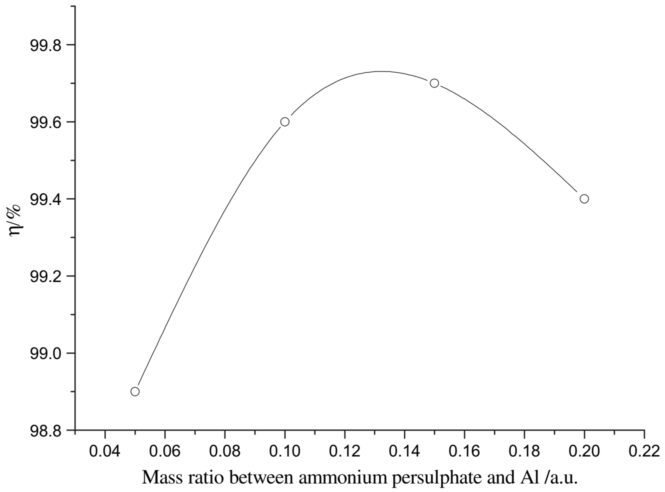

Fig. 3. Effect of ammonium persulphate dosage on corrosion inhibiting efficiency.

3. Results and discussion

3.1. Optimization of reaction conditions

3.1.1. Effect of initial mass ratio among acrylic acid, ammonium persulphate, isopropanol, water and Al

As the initial mass ratio among ammonium persulphate, isopropanol, water and Al was fixed at 0.15:0.50:50:1, reaction temperature 95 °C and reaction time 1 h, the effects of acrylic acid dosage on coater gloss and corrosion inhibiting efficiency were investigated and the results were shown in Figs. 1 and 2. It was found that with the increase of AA dosage, the coater gloss decreased, but corrosion inhibiting efficiency increased on the contrary. For composite particles prepared at initial mass ratio 0.10 showed 99.5% of corrosion inhibiting efficiency and 88.3 Gs of coater gloss.

Ammonium persulphate was used as initiator in in-situ polymerization of acrylic acid. As the initial mass ratio of acrylic acid, isopropanol, water and Al was fixed at 0.10:0.50:50:1, reaction temperature 95 °C and reaction time 1 h, the effects of ammonium persulphate on corrosion inhibiting efficiency were studied and the results was shown in Fig. 3. With the increase of ammonium persulphate dosage, polymerization rate was accelerated, which was

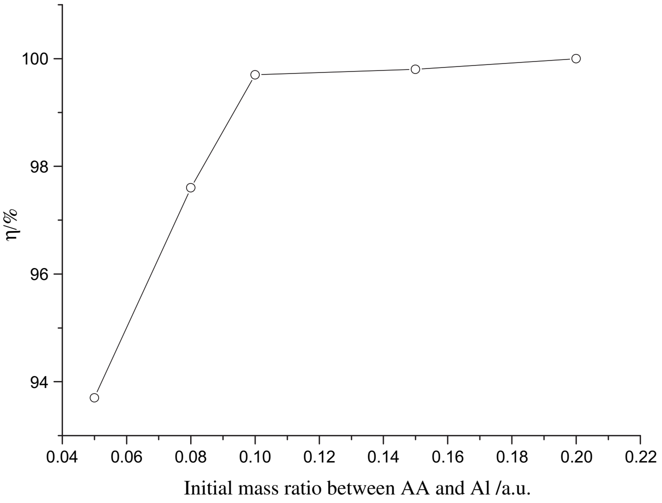

Fig. 2. Effect of AA dosage on corrosion inhibiting efficiency.

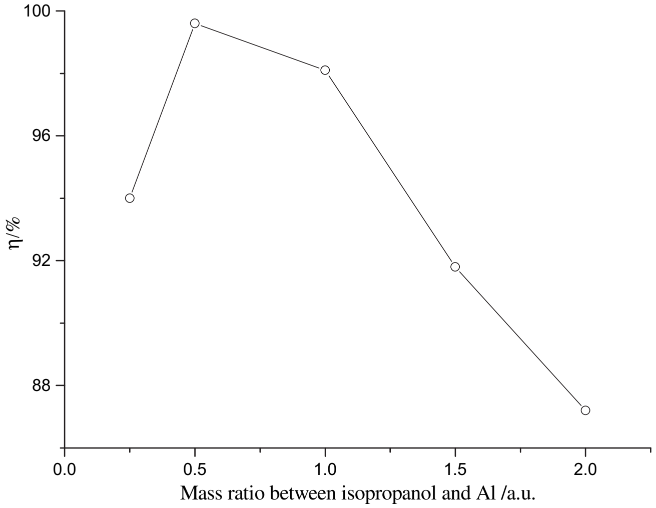

Fig. 4. Effect of isopropanol dosage on corrosion inhibiting efficiency.

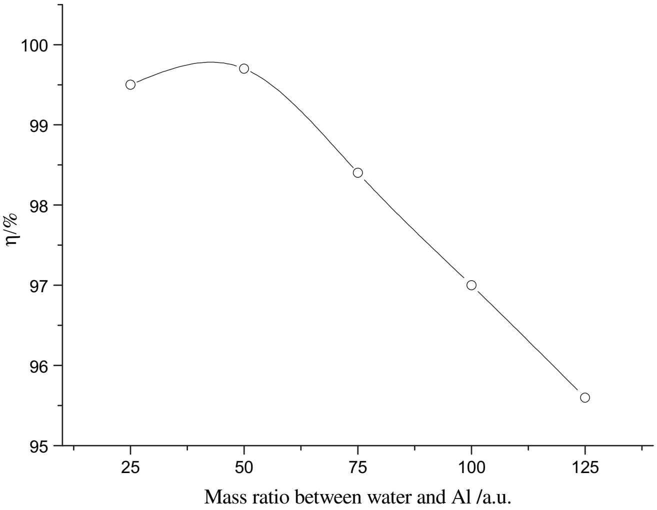

Fig. 5. Effect of water dosage on corrosion inhibiting efficiency.

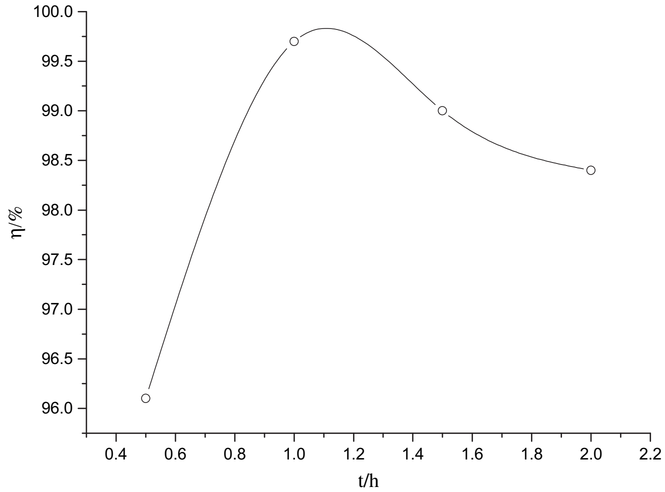

Fig. 7. Effect of reaction time on corrosion inhibiting efficiency.

favorable for preparation of PAA/Al composite particles. However, too high dosage of ammonium persulphate might result in violent reaction that affected the uniformity of encapsulation layer formed by polyacrylic acid onto aluminium particles. As the mass ratio between ammonium persulphate and Al reached to 0.15, the composite particles exhibited 99.7% of corrosion inhibiting efficiency.

Isopropanol used as dispersant played an important role in the encapsulation process of clear flaky aluminium particles. The effect of isopropanol on corrosion inhibiting efficiency was investigated as the initial mass ratio among acrylic acid, ammonium persulphate, water and Al was fixed at 0.10:0.15:50:1, reaction temperature 95 °C and reaction time 1 h, and the results were shown in Fig. 4. With the increase of isopropanol dosage, dispersibility of aluminium particles in water could be increased, which was helpful for encapsulation on clear aluminium particles. As the initial mass ratio between isopropanol and Al reached to 0.50, corrosion inhibiting efficiency was as high as 99.6%. However, too much isopropanol might generate dissociative polyacrylic acid and then affected the encapsulation process.

Water used as solvent also played an important role in the encapsulation process of clear flaky aluminium particles. The effect of water dosage on corrosion inhibiting efficiency was shown in Fig. 5 (as the initial mass ratio among acrylic acid, ammonium persulphate, isopropanol and Al was 0.10:0.15:0.50:1, reaction temperature 95 °C and reaction time 1 h). Low water dosage led to viscous slurry and then agglomeration. However, high water dosage led to thin encapsulation layer on clear aluminium particles, which meant low corrosion inhibiting efficiency. As the initial mass ratio between water and Al was fixed at 50, corrosion inhibiting efficiency was as high as 99.7%.

3.1.2. Effect of reaction temperature

The effect of reaction temperature on corrosion resistance of composite particles was shown in Fig. 6 as the initial mass ratio among acrylic acid, ammonium persulphate, isopropanol, water and Al was fixed at 0.10:0.15:0.50:50:1 and reaction time 1 h. With the increase of reaction temperature, corrosion inhibiting efficiency was steadily improved, which could be explained that both the decomposition of ammonium persulphate and in-situ polymerization of acrylic acid were improved through high reaction temperature. Taking boiling point of water into account, reaction temperature was selected as 95 °C.

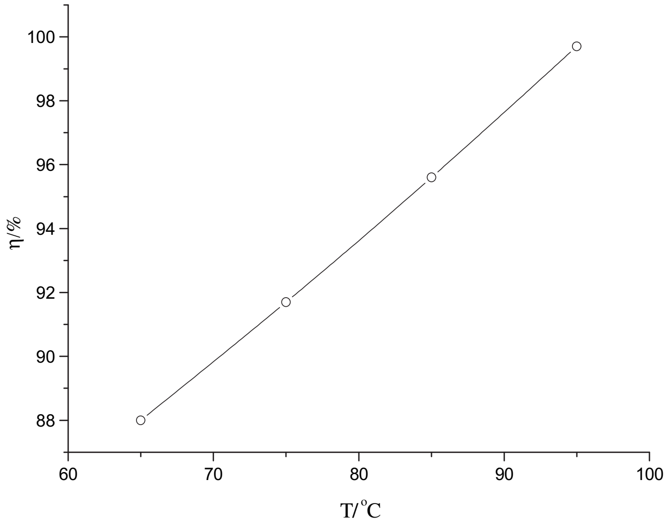

Fig. 6. Effect of reaction temperature on corrosion inhibiting efficiency.

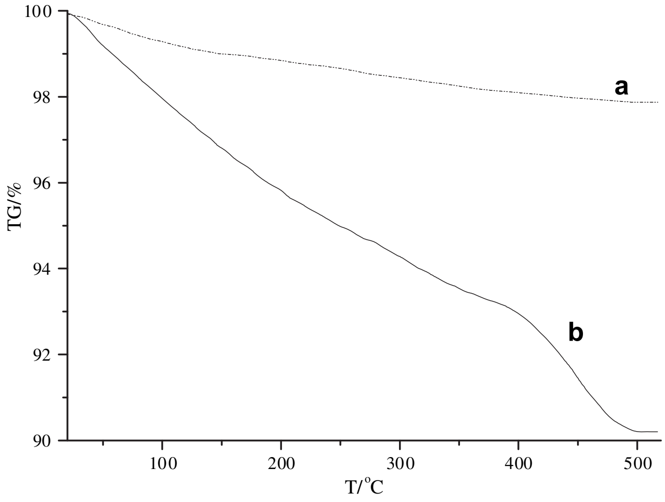

Fig. 8. TGA curves of clear aluminium particles (a) and PAA/Al composite particles (b).

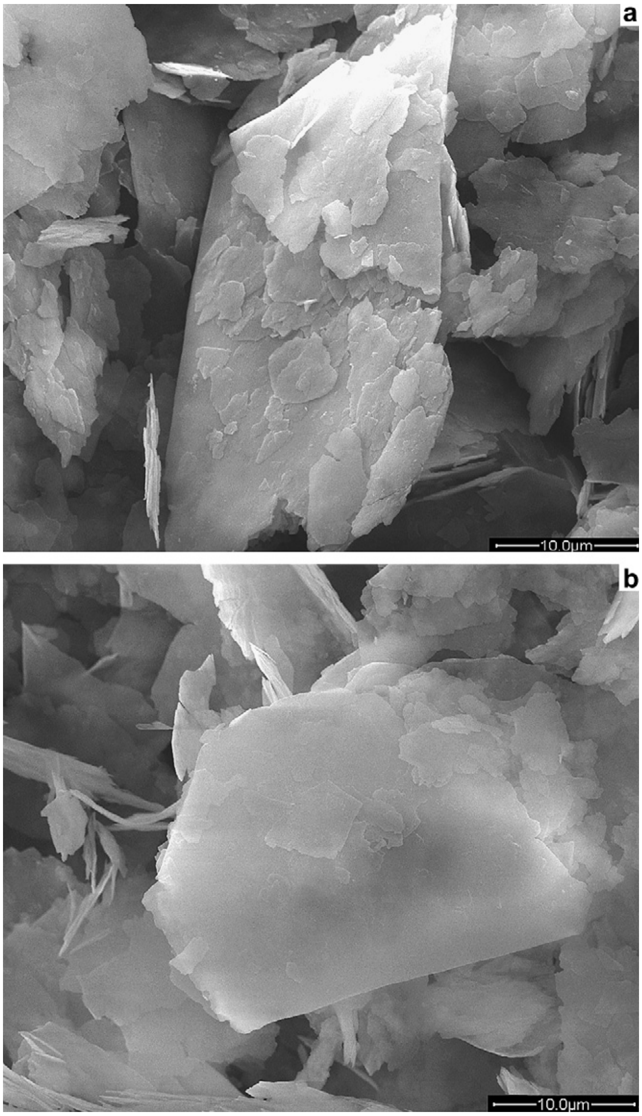

Fig. 9. Surface morphology of PAA/Al composite particles (a) and clear aluminium particles (b).

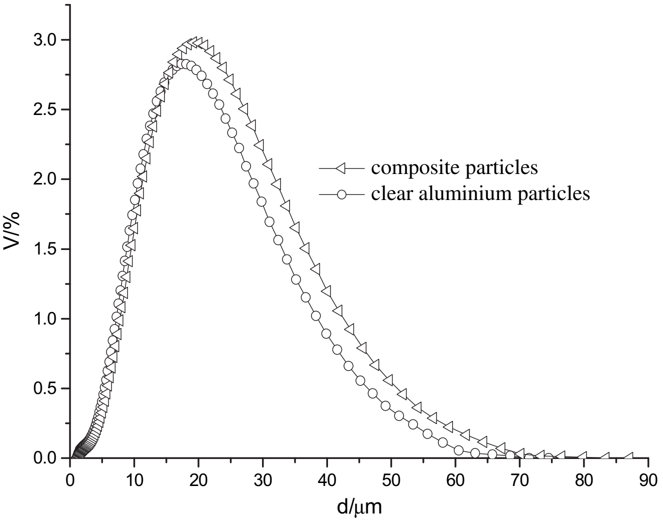

Fig. 10. Particle size distributions of PAA/Al composite particles and clear aluminium particles.

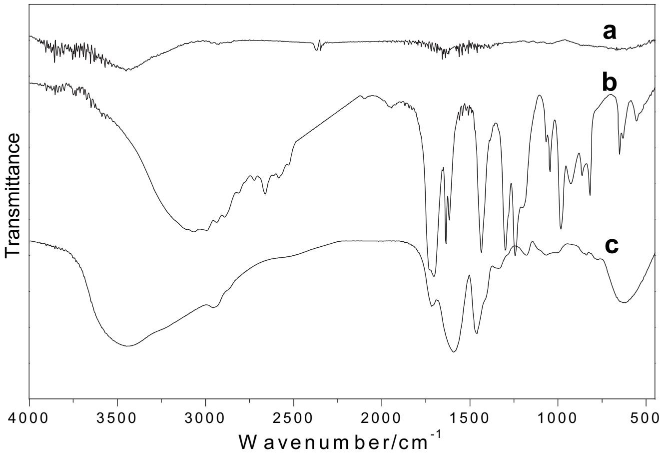

Fig. 11. FTIR spectra of clear aluminium particles (a), pure acylic acid (b) and PAA/Al composite particles (c).

3.1.3. *Effect of reaction time*

The effect of reaction time on corrosion resistance of composite particles was shown in Fig. 7 as the initial mass ratio among acrylic acid, ammonium persulphate, isopropanol, water and Al was fixed at 0.10:0.15:0.50:50:1 and reaction temperature 95 °C. When reaction time was increased to 1 h, the composite particles showed high

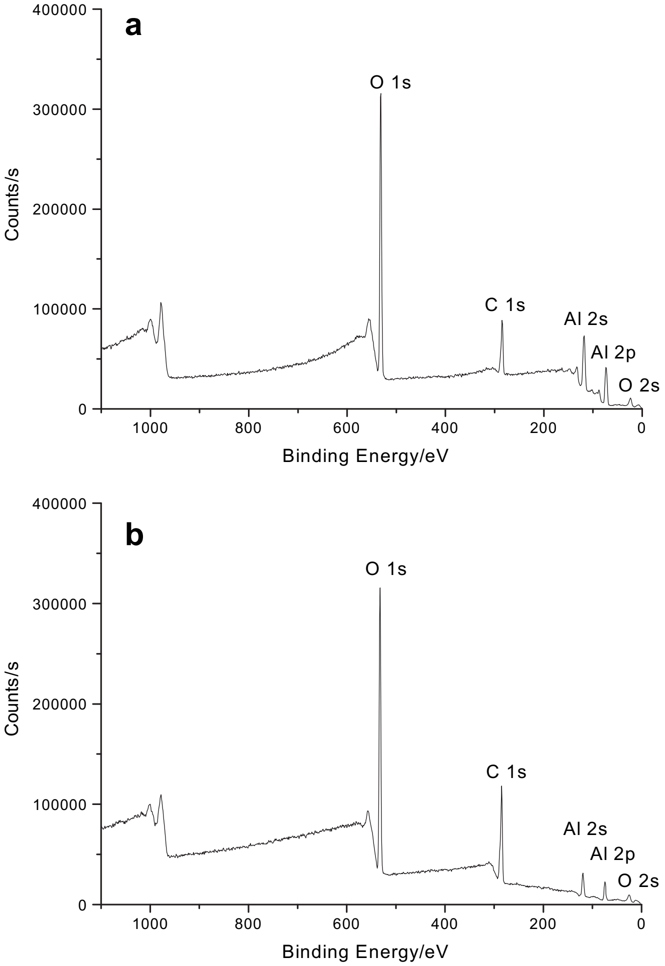

Fig. 12. XPS full-survey spectra of clear aluminium particles (a) and PAA/Al composite particles (b).

Table 1
Surface elemental composition of clear aluminium particles and PAA/Al composite particles.

Samples	Al (%)	C (%)	O (%)
PAA/Al composite particles	7.35	43.58	49.07
Clear aluminium particles	23.34	25.61	51.05

stability. However, if reaction time was further increased, corrosion inhibiting efficiency decreased on the contrary because of high viscous reaction slurry formed after a long time polymerization.

3.2. Characterization of composite particles prepared at optimum condition

The optimum condition to prepare PAA/Al composite particles was showed as follow: initial mass ratio among acrylic acid, ammonium persulphate, isopropanol, water and Al 0.10:0.15:0.50:50:1, reaction temperature 95 °C and reaction time 1 h.

The thermal stability of both PAA/Al composite particles prepared under above optimum condition and clear aluminium particles was evaluated with thermogravimetric analysis (TGA) and the result was shown in Fig. 8. For clear aluminium particles, the weight loss was only 2.129% at 500 °C. However, the weight loss of PAA/Al composite particles was as high as 9.794%. Therefore, the actual mass ratio of PAA and Al of PAA/Al composite particles was calculated to be 0.083:1, which corresponded with its initial mass ratio of 0.10:1.

The surface morphologies of both the composite particles prepared at above optimum condition and clear aluminium particles were shown in Fig. 9. Dense films were found to be formed on the surface of composite particles, while clear aluminium particles showed smooth surface.

The particle size distributions of PAA/Al composite particles and clear aluminium particles were shown in Fig. 10. The average diameter (d_{50}) of composite particles was 17.62 μm, slightly larger than that of clear aluminium particles (d_{50} 16.65 μm). It was in-situ polymerization of acrylic acid onto clear aluminium particles made the average particle size of PAA/Al composite particles 5.8% larger than that of clear aluminium particles.

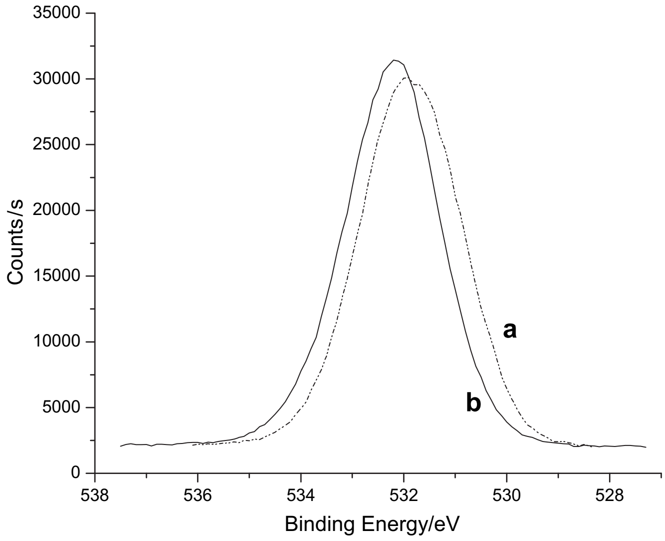

Fig. 13. High-resolution O 1s XPS of clear aluminium particles (a) and PAA/Al composite particles (b).

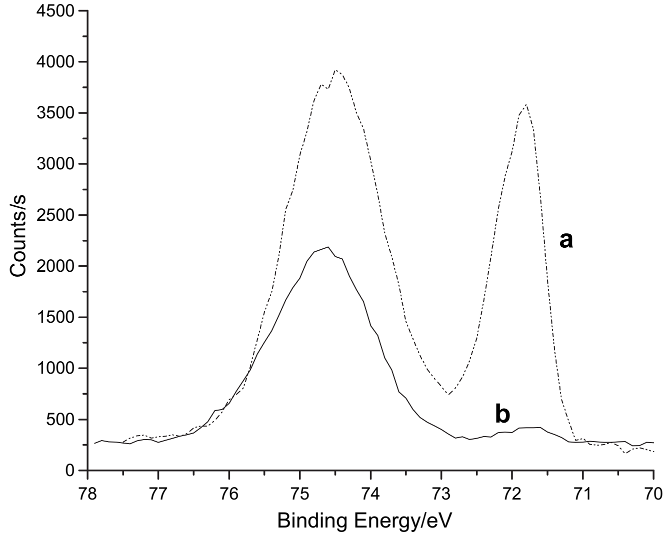

Fig. 14. High-resolution Al 2p XPS of clear aluminium particles (a) and PAA/Al composite particles (b).

The FTIR spectra of PAA/Al composite particles, acrylic acid and clear aluminium particles were shown in Fig. 11. Hydroxyl absorption peak appeared at 3400 cm^{-1} for clear aluminium particles, which indicated the existence of OH on the surface of aluminium particles. Compared with acrylic acid, the characteristic absorption peak corresponding to C═O stretching vibration of PAA/Al composite particles shifted from 1704 cm^{-1} to1720 cm^{-1}, and the absorption band of $-CH_2-$ shifted from 2940 cm^{-1} to 2960 cm^{-1}, which ascribed to the formation of chemical bond between polyacrylic acid and aluminium particle. For PAA/Al composite particles, the characteristic peak of C═C disappeared, suggesting the reaction of vinyl group.

The XPS full-survey spectra of PAA/Al composite particles and clear aluminium particles were presented in Fig. 12 and the surface elemental composition was listed in Table 1. Compared with clear aluminium particles, the content of Al, C and O of PAA/Al composite particles changed from 23.34%, 25.61% and 51.05% to 7.35%, 43.58% and 49.07%, respectively, testifying that PAA had been encapsulated on the surface of clear aluminium particles. The high-resolution XPS spectrum of the O 1s and Al 2p were showed in Figs. 13 and 14, respectively. For clear aluminium particles, O 1s peak, appeared at 531.8 eV, was induced by Al_2O_3 (Fig. 13). However, the O 1s peak of PAA/Al composite particles shifted to 532.2 eV, which mainly ascribed to the formation of chemical bond between PAA and aluminium. Compared with clear aluminium particles, the Al 2p peak of Al—O of PAA/Al composite particles shifted from 74.3 eV to 74.7 eV and the Al 2p peak of pure Al element significantly decreased, which indicated the clear aluminium particles were encapsulated through formation of C—O—Al bond.

4. Conclusion

Polyacrylic acid was encapsulated on the surface of clear aluminium particles through in-situ polymerization. The dosage of acrylic acid, ammonium persulphate, isopropanol, and water, reaction temperature and reaction time had great effect on corrosion inhibiting efficiency of as-prepared PAA/Al composite particles. The suitable condition was initial mass ratio among acrylic acid, ammonium persulphate, isopropanol, water and Al 0.10:0.15:0.50:50:1, reaction temperature 95 °C and reaction time 1 h, at which corrosion inhibiting efficiency reached to 99.7% and the coater gloss only slightly decreased from 90.1 Gs to 88.3 Gs, suggesting an excellent water-borne aluminium pigments. The analysis with TGA, SEM, laser particle size analyzer, FTIR spectra and XPS showed that polyacrylic acid was successfully encapsulated onto the surface of clear aluminium particles and PAA combined with aluminium through chemical bond.

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