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Preparation and characterization of poly(trimethylolpropane triacrylate)/flaky aluminum composite particle by in situ polymerization

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ABSTRACT

Poly(trimethylolpropane triacrylate)/flaky aluminum composite particle was prepared by in situ polymerization in order to improve the corrosion resistance and adhesive property of aluminum pigments. The effect of monomer concentration, initiator concentration and feeding mode on the *conversion*, *percentage of grafting* and *grafting efficiency* in the preparation was studied. It was found that poly (trimethylolpropane triacrylate) had been successfully grafted on the surface of flaky aluminum through chemical bond, rather than the simple physical adsorption. Evolved hydrogen detection and pulling experiment showed that the corrosion resistance and adhesive property of composite particle had been markedly enhanced, implying that flaky aluminum had been compactly encapsulated with a layer of poly(trimethylolpropane triacrylate) by in situ polymerization.

1. Introduction

During the last two decades, flaky aluminum powders (also called aluminum pigments) have been widely used in automotive coatings, roof coatings, printing inks, and plastic materials for their protective and decorative functions [1–3]. The aluminum pigments are usually produced by grinding atomized aluminum powder in the ball mill together with white spirit as solvent and fatty acid as lubricant. The mill operates at a speed that allows the balls to cascade onto the fine, spherical or irregular atomized aluminum powders and finally to flatten the powders into an ultrathin flaky particles. After grinding, the subsequent filtration makes the ultrathin flaky aluminum powder in the form of paste for sale with volatile organic compounds [4–6]. However, a severe problem is the corrosion reaction of aluminum pigment in aqueous acidic or alkali painting media, which causes the evolution of hydrogen [7,8]:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow$$

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$$

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2\uparrow$$

Consequently, the corrosion reaction will change the color of aluminum pigment from silver to grey and may lead to a dangerous pressure buildup in the container [9]. Therefore it is necessary to inhibit the corrosion. At present, a lot of research has been devoted to inhibit the corrosion reaction by surface modification of aluminum pigments. Aluminum pigment was coated with SiO_2 via sol–gel method through tetraethyl orthosilicate to improve its corrosion resistance [10,11]. The corrosion inhibition by mixing aluminum pigment with commercially available styrene–maleic anhydride copolymers as an inhibitor was also investigated [12]. Al/poly(methyl methacrylate) composites containing different volume fractions of aluminum were prepared and thermal expansion and electrical behavior of the composites were investigated [13].

In our previous reports, aluminum pigment was encapsulated with styrene–maleic acid copolymer by in situ polymerization [14], and poly(methyl methacrylate)/flaky aluminum composite particle was synthesized and characterized in the presence of silane coupling agent, 3-methacryloxypropyl-trimethoxysilane [15]. In the present work, poly(trimethylolpropane triacrylate)/flaky aluminum composite particle (PTMPTA/Al) was prepared by in situ polymerization in order to improve the corrosion resistance and adhesive performance of aluminum pigments.

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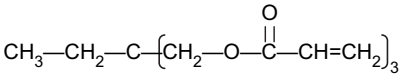

Scheme 1. The molecular structure of TMPTA.

2. Experimental

2.1. Materials and reagents

Flaky aluminum (Al, from Shanghai Weiye Co. Ltd., China) was dried in vacuum at 100 °C for 24 h to remove the volatile organic compounds, and trimethylolpropane triacrylate (TMPTA, from Nanjing Chemical factory, China) was refined to remove the antipolymerization agent before use. Azobisisobutyronitrile (AIBN, from Tianjin Chemicals Co. Ltd., China) as the initiator, 3-methacryloxypropyl-trimethoxysilane (from Wuhan University Silicone New Material Co. Ltd, China) as the coupling agent, polyvinylpyrrolidone (from Tianjin Chemicals Co. Ltd., China) as the dispersant, and toluene (from Changsha chemical factory, China) as the solvent, were all analytical grade reagents and used as received.

2.2. Preparation of PTMPTA/Al composite particle

A certain amount of flaky aluminum, toluene, TMPTA, polyvinylpyrrolidone, 3-methacryloxypropyl-trimethoxysilane, and a little acrylic acid were added into a four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a guttate funnel. Toluene solution of AIBN was slowly added into the flask by guttata funnel at 65 °C under nitrogen flowing. Then the mixture was heated to 85 °C and reacted for several hours. After the reaction, the mixture was precipitated with methanol and filtered. The cake was dried in vacuum for 24 h to obtain PTMPTA/Al composite particle.

In order to determine quantitatively grafted and non-grafted PTMPTA in PTMPTA/Al, a certain amount of PTMPTA/Al was dispersed in tetrahydrofuran with ultrasonic vibration and the non-grafted PTMPTA was dissolved in tetrahydrofuran. After the centrifugation at 10,000 rpm for 1 h, non-grafted PTMPTA was obtained by precipitating the filtrate with methanol. The cake was dried in vacuum, and PTMPTA-grafted aluminum was obtained.

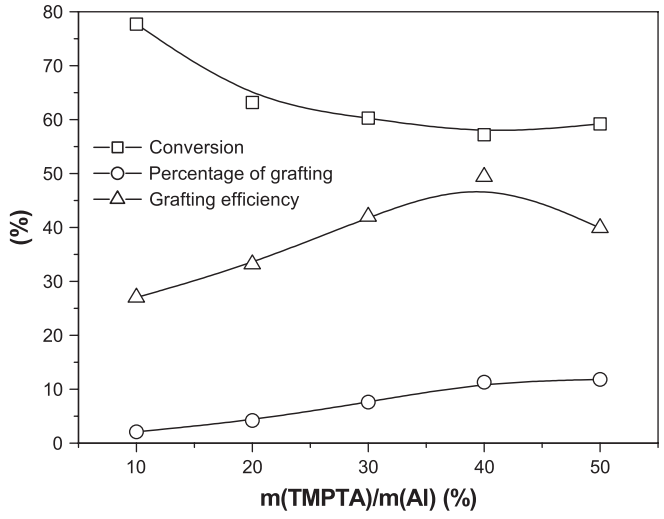

Fig. 1. The effect of monomer concentration on *conversion*, *percentage of grafting* and *grafting efficiency*.

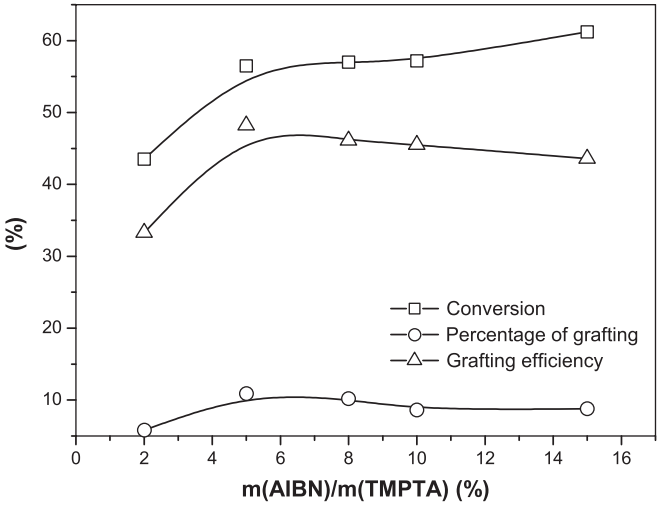

Fig. 2. The effect of initiator concentration on *conversion*, *percentage of grafting* and *grafting efficiency*.

The evolved hydrogen detection in a reaction of aqua regia with aluminum as described in literature [1] was used to measure the content of aluminum in PTMPTA-grafted aluminum. Total PTMPTA was the sum of grafted and non-grafted PTMPTA. Therefore, the *conversion*, *percentage of grafting* and *grafting efficiency* were calculated according to the following equations [16–18]:

$$\text{Conversion} = \frac{\text{total PTMPTA(g)}}{\text{TMPTA used(g)}} \times 100\%$$

$$\text{Percentage of grafting} = \frac{\text{grafted PTMPTA(g)}}{\text{flaky aluminum used(g)}} \times 100\%$$

$$\text{Grafting efficiency} = \frac{\text{grafted PTMPTA(g)}}{\text{total PTMPTA(g)}} \times 100\%$$

2.3. Characterization and testing

Fourier transform infrared (FTIR) spectroscopy patterns were recorded on a Nicolet AVATAR360 system. The surface characterization of PTMPTA/Al was accomplished by using an ESCALAB MK II Multi-functional X-ray photoelectron spectrometer (XPS) with pass energy of 29.35 eV and an Mg Kα line excitation source. The binding energy of C1s (284.6 eV) was used as a reference. Hydrogen volume was used to evaluate the corrosion resistance of samples [15], and the evolved hydrogen detection was carried out as described in the literature [19]. The adhesion of PTMPTA/Al was tested through pulling experiment [20]: the flaky aluminum or PTMPTA/Al was firstly dispersed in thinner solution, and then the mixture was sprayed onto a black plastic board, finally the plastic board was pulled by adhesive tape after air-drying.

Table 1
The effect of feeding mode on *conversion*, *percentage of grafting* and *grafting efficiency*

Feeding mode	Conversion (%)	Percentage of grafting	Grafting efficiency (%)
All reactants added together (A)	52.3	5.6	26.8
Only AIBN dropped (B)	56.5	10.9	48.3
Only TMPTA dropped (C)	62.6	9.7	38.7
AIBN and TMPTA dropped together (D)	66.8	12.1	45.3

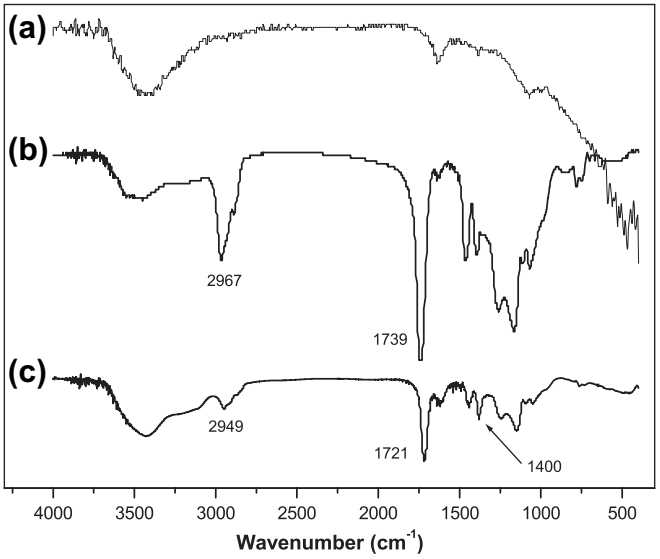

Fig. 3. FTIR spectra of flaky aluminum (a), pure PTMPTA (b) and PTMPTA/Al composite particle (c).

3. Results and discussion

3.1. Preparation of PTMPTA/Al composite particle

Firstly, the selection of TMPTA is based on the fact that there are three vinyl bonds in the molecular structure of TMPTA (Scheme 1), so the in situ polymerization of TMPTA may lead to the formation of crosslinked netty PTMPTA [21,22], which is helpful to improve the corrosion resistance and adhesive performance of flaky aluminum. Fig. 1 shows the effect of TMPTA concentration on *conversion*, *percentage of grafting* and *grafting efficiency* in the preparation of composite particle. As can be seen, *conversion* decreases with increasing *m*(TMPTA)/*m*(Al), which can be explained with the reduction of relative initiator (AIBN) concentration. It is easy to find that when *m*(TMPTA)/*m*(Al) = 40%, *percentage of grafting* remains at a plateau level of 11.3%, and *grafting efficiency* reaches the highest value of 49.4%. The increase of *m*(TMPTA)/*m*(Al) may result in the augment of TMPTA concentration around flaky aluminum, which enhances the probability of integrating between TMPTA and flaky aluminum. Nevertheless, too high TMPTA concentration may give rise to the agglomeration of flaky aluminum, which is harmful to the in situ polymerization.

Table 2
Surface elemental composition of flaky aluminum and PTMPTA/Al composite particle

Samples	Al (%)	C (%)	O (%)
Flaky aluminum	30.1	40.5	29.4
PTMPTA/Al	4.2	62.4	33.4

Secondly, the effect of initiator concentration on *conversion*, *percentage of grafting* and *grafting efficiency* is demonstrated in Fig. 2. It can be seen that *conversion* increases with the increasing *m*(AIBN)/*m*(TMPTA), which can be attributed to the increase of radical concentration. Moreover, both *percentage of grafting* and *grafting efficiency* achieve their respective culmination at *m*(AIBN)/*m*(TMPTA) = 5%. Because the amounts of radical and active chain increase with the increasing initiator concentration, the grafting between PTMPTA and flaky aluminum bears high probability. At the same time, too much initiator may lead to the formation of low-molecular-weight PTMPTA, which is unfavorable to the preparation of PTMPTA/Al composite particle with high *percentage of grafting*.

Lastly, feeding mode is of importance to the synthesis of PTMPTA/Al composite particle, and its effect on *conversion*, *percentage of grafting* and *grafting efficiency* is listed in Table 1. As shown in Table 1, mode A (all reactants added together) has the worst effect, while mode D (AIBN and TMPTA dropped together) has the best effect. The experimental result can be interpreted as follows: when AIBN and

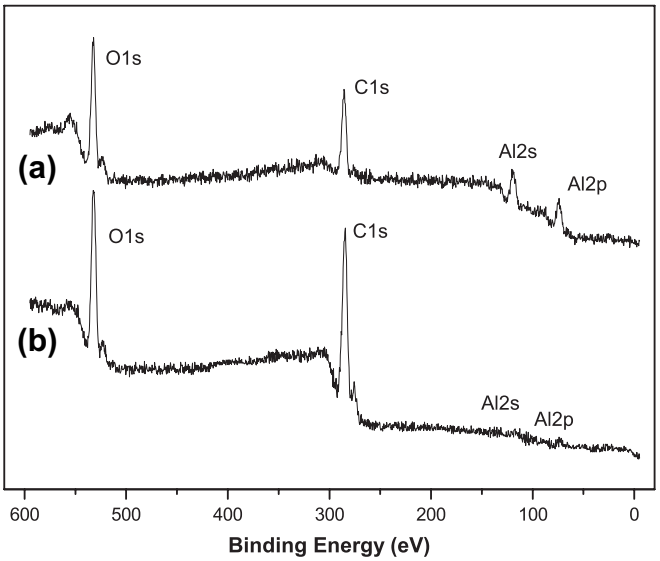

Fig. 4. XPS full-survey spectra of flaky aluminum (a) and PTMPTA/Al composite particle (b).

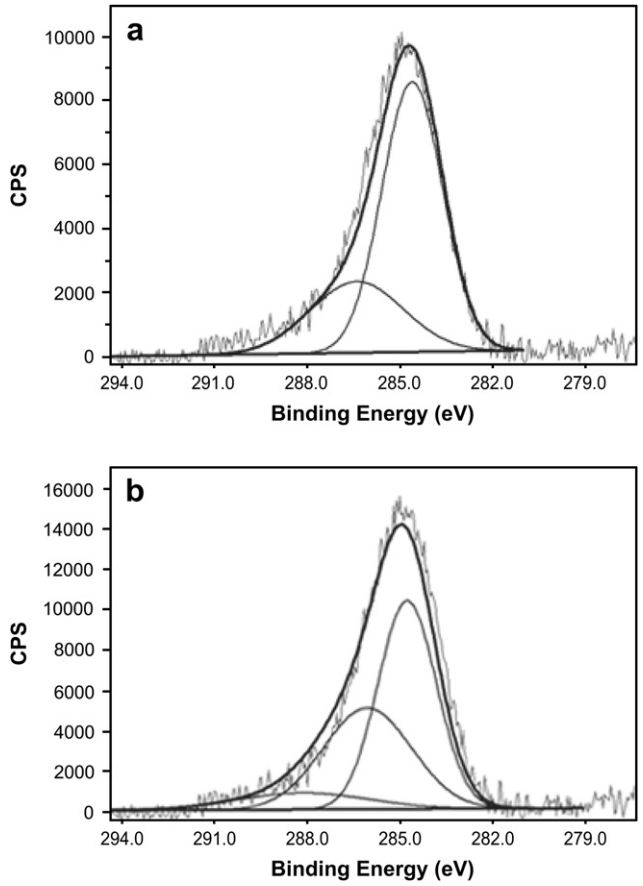

Fig. 5. High-resolution C1s XPS spectrum and curve-fitting of flaky aluminum (a) and PTMPTA/Al composite particle (b).

Table 3
C1s XPS analysis of flaky aluminum and PTMPTA/Al composite particle

Samples	Standard position (eV)	Actual position (eV)	Chemical shift (eV)	Content (%)	Attribution
Flaky aluminum	285.0	284.6	−0.4	71.1	C–C
	286.9	286.4	−0.5	28.9	C–O
PTMPTA/Al	285.0	284.7	−0.3	52.2	C–C
	286.9	286.0	−0.9	38.5	C–O
	288.6	288.1	−0.5	9.4	C═O

Table 4
O1s XPS analysis of flaky aluminum and PTMPTA/Al composite particle

Samples	Standard position (eV)	Actual position (eV)	Chemical shift (eV)	Content (%)	Attribution
Flaky aluminum	531.5	531.2	−0.3	81.3	Al–O
	533.1	533.3	+0.2	18.7	C–O
PTMPTA/Al	531.5	531.9	+0.4	54.5	Al–O
	532.0	533.3	+1.3	12.8	C═O
	533.1	533.8	+0.7	32.7	C–O

TMPTA are dropped together, the polymerizing system is actually complemented with initiator and monomer, which is beneficial to the in situ polymerization of TMPTA on the surface of flaky aluminum.

3.2. Characterization of PTMPTA/Al composite particle

Fig. 3 exhibits the FTIR spectra of flaky aluminum, pure PTMPTA, and PTMPTA/Al composite particle. Hydroxyl absorption peak at 3500 cm^{-1} in the curve of flaky aluminum attests to the existence of OH on the surface of flaky aluminum. The characteristic absorption peak corresponding to C═O stretching vibration shifts from 1739 cm^{-1} in the FTIR curve of pure PTMPTA to 1721 cm^{-1} in the curve of PTMPTA/Al, and the absorption band of $–CH_2–$ shifts from 2967 cm^{-1} in the FTIR spectrum of pure PTMPTA to 2949 cm^{-1} in the spectrum of PTMPTA/Al, which is possibly ascribed to the formation of chemical bond between PTMPTA and flaky aluminum. Furthermore, the characteristic absorption peak at 1400 cm^{-1} corresponding to AlO_2^- is also observed in the curve of PTMPTA/Al. All these results indicate that PTMPTA/Al composite particle has been successfully prepared by in situ polymerization.

XPS is generally employed to analyze the relative elemental content and chemical bond on the surface of samples. The XPS full-survey spectra of flaky aluminum and PTMPTA/Al are illustrated in Fig. 4, and the surface elemental composition is listed in Table 2. As can be seen, compared with flaky aluminum, the content of Al, C and O for PTMPTA/Al changed from 30.1%, 40.5% and 29.4% to 4.2%, 62.4% and 33.4% respectively, manifesting that PTMPTA has been grafted on the surface of flaky aluminum.

In order to clarify the status of surface chemical bond, the high-resolution XPS spectra of C1s and O1s have been scanned, and they are fitted through the software "XPSPEAKFIT" in the light of Lorentzian–Gaussian principle [23,24].

The high-resolution C1s XPS spectra and curve-fitting of flaky aluminum and PTMPTA/Al are shown in Fig. 5a and b respectively, and the binding energies and the attributions of C1s peaks are listed in Table 3. Clearly, compared with flaky aluminum, the content of C–C on the surface of PTMPTA/Al decreases while the content of C–O increases. Moreover, C═O (288.1 eV) appears in the curve-fitting spectrum of PTMPTA/Al, which can be attributed to the encapsulation of PTMPTA onto flaky aluminum. It is also found from Table 3 that the negative chemical shifts take place in the curve-fitting spectrum. Furthermore, PTMPTA/Al has more negative shift than flaky aluminum, which can be explained from the fact that the existence of PTMPTA reduces the outer electron density, weakens the shielding effect, and enhances the inner electron binding energy.

Fig. 6a and b presents the high-resolution O1s XPS spectra and curve-fitting of flaky aluminum and PTMPTA/Al respectively, and Table 4 illustrates the binding energies and the attributions of O1s peaks. Similar to C1s, the decrease of Al–O, the increase of C–O and the emergence of C═O (533.8 eV) are essentially caused by the grafted PTMPTA onto the surface of flaky aluminum. Opposite to C1s, positive chemical shifts of binding energies are found in the

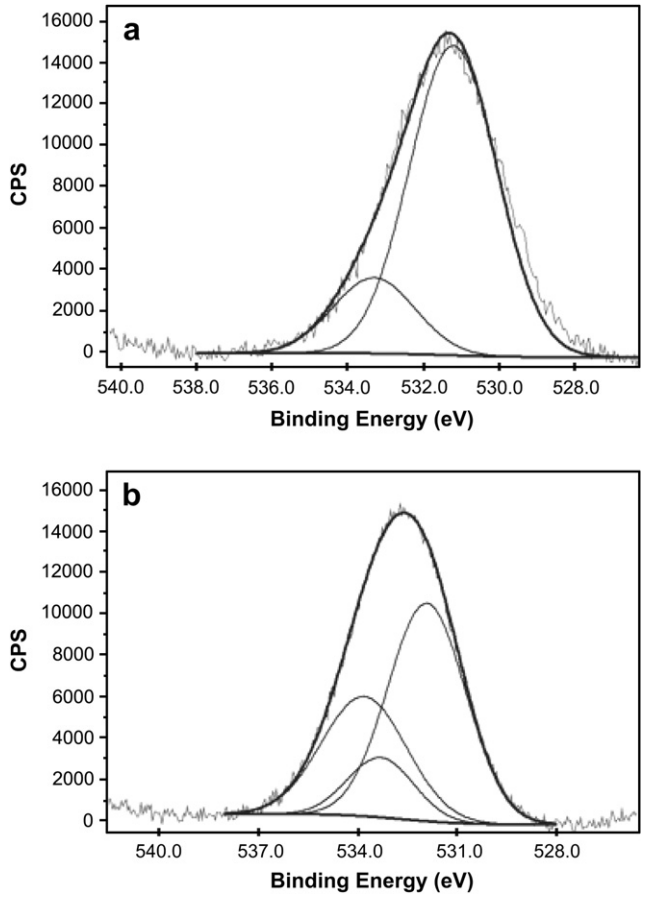

Fig. 6. High-resolution O1s XPS spectrum and curve-fitting of flaky aluminum (a) and PTMPTA/Al composite particle (b).

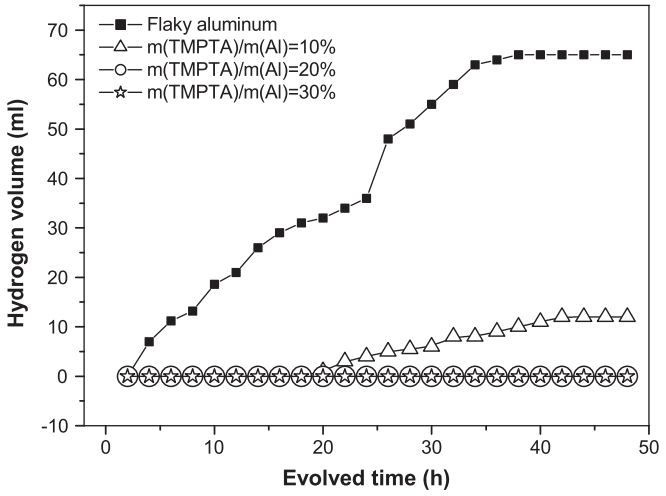

Fig. 7. Evolved hydrogen trends of flaky aluminum and PTMPTA/Al composite particle.

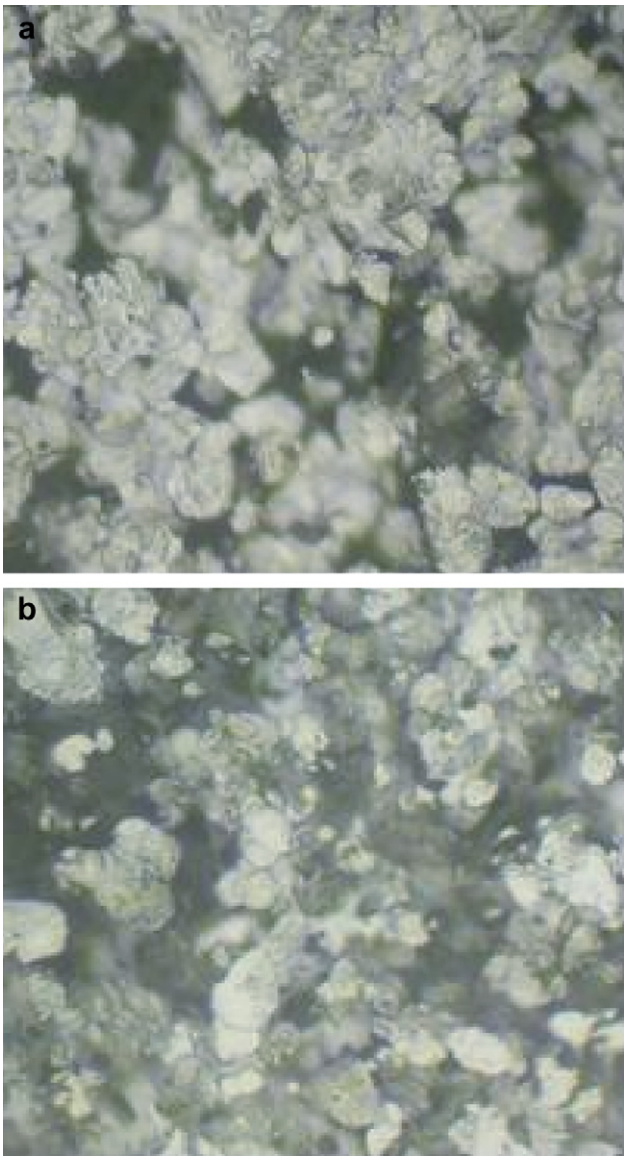

Fig. 8. The image of non-pulled board (a) and pulled board (b) of flaky aluminum.

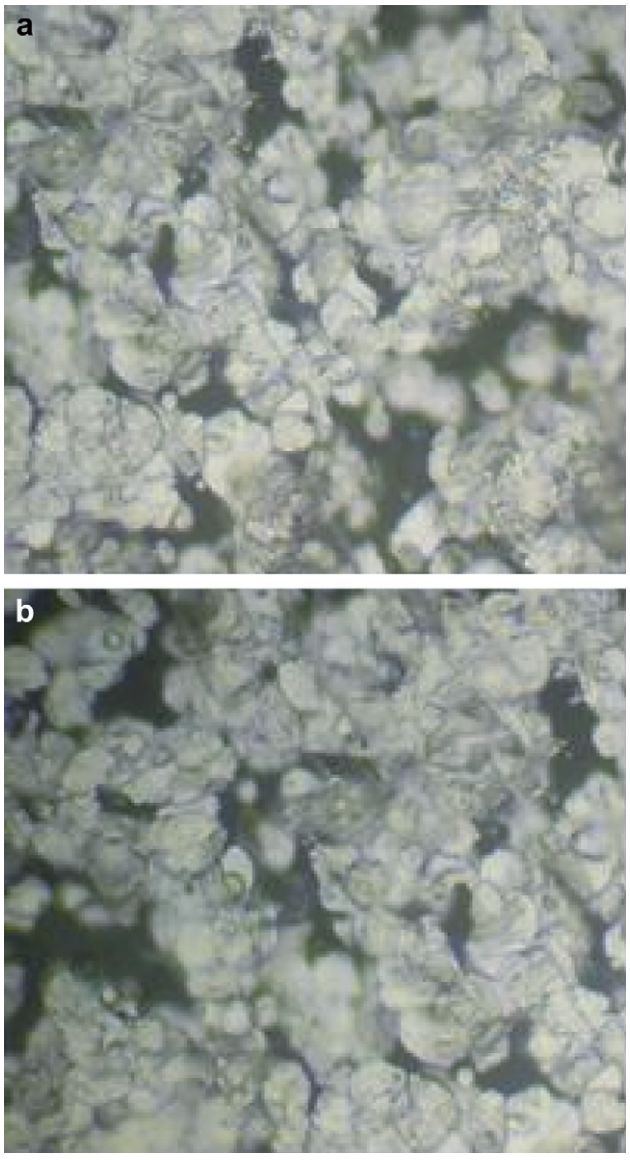

Fig. 9. The image of non-pulled board (a) and pulled board (b) of PTMPTA/Al composite particle.

O1s peaks, which is possibly relevant to the uncrystallized polymeric layer and special core–shell structure of PTMPTA/Al.

In a word, FTIR and XPS indicate that PTMPTA/Al composite particle has been successfully prepared by in situ polymerization, and PTMPTA has been grafted on the surface of flaky aluminum through chemical bond, rather than the simple physical adsorption.

3.3. Property evaluation of PTMPTA/Al composite particle

Evolved hydrogen volume is usually used to evaluate the corrosion resistance. Lesser the hydrogen volume, better the corrosion resistance [25]. Fig. 7 shows the evolved hydrogen trend of some samples in 0.1 mol L^{-1} HCl aqueous solution. As can be seen, the evolved hydrogen volume of 0.5 g flaky aluminum after 48 h is 65 ml, while PTMPTA/Al releases no hydrogen at all when m(TMPTA)/m(Al) attains 20%. Clearly, the polymeric layer on the surface of composite particle prevents aluminum from reacting with the corrosive media. A conclusion can be drawn that, compared with flaky aluminum, the corrosion resistance of PTMPTA/Al has been markedly improved, implying that flaky aluminum has been compactly encapsulated with a layer of PTMPTA by in situ polymerization.

The pulling experiment is industrially employed to assess the adhesive property of samples, and the images of some non-pulled and pulled samples are demonstrated in Fig. 8a and b, and Fig. 9a and b. It can be observed that the non-pulled board of PTMPTA/Al (Fig. 9a) is slightly denser than that of flaky aluminum (Fig. 8a). Furthermore, after pulling, there is evident desquamation on the board of flaky aluminum (Fig. 8b), while the board of PTMPTA/Al (Fig. 9b) almost keeps unchanged. There are three vinyl bonds in the molecular structure of TMPTA, so it is likely that the resulting PTMPTA is in the possession of crosslinked network structure, which is helpful to the improvement of adhesion of PTMPTA/Al. The pulling results suggest that PTMPTA/Al composite particle has much better adhesive property than flaky aluminum. It may be affirmed that a compact polymeric layer has been formed on the surface of composite particle by in situ polymerization, which is in good agreement with the analysis of corrosion resistance.

4. Conclusion

In order to improve the corrosion resistance and adhesive property of aluminum pigments, PTMPTA/Al composite particle

had been successfully prepared by in situ polymerization. It was found that both *percentage of grafting* and *grafting efficiency* could attain satisfactory results at the following conditions: m(TMPTA)/m(Al) = 40%, m(AIBN)/m(TMPTA) = 5%, and TMPTA and initiator were dropped together. Compared to flaky aluminum, the content of Al, C and O for PTMPTA/Al changed from 30.1%, 40.5% and 29.4% to 4.2%, 62.4% and 33.4% respectively, indicating that PTMPTA layer had been grafted onto the surface of flaky aluminum. Moreover, the emergence of C═O in the curve-fitting XPS spectrum of PTMPTA/Al composite particle strongly supported the fact that the driving force between PTMPTA and flaky aluminum was chemical bond, rather than the simple physical adsorption. Evolved hydrogen detection and pulling experiment indicated that the corrosion resistance and adhesive property of PTMPTA/Al composite particle had been markedly enhanced, implying that flaky aluminum had been compactly encapsulated with a layer of PTMPTA by in situ polymerization.

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