



Investigation of corrosion behavior of aluminum flakes coated by polymeric nanolayer: Effect of polymer type



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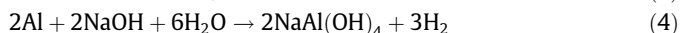
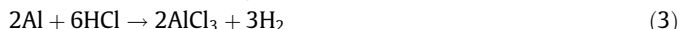
ABSTRACT

Protection of aluminum pigments from corrosion phenomenon has been extended by an encapsulating polystyrene (PS) and poly(acrylic acid) (PAA) nanolayers. Flakes were first coupled with 3-methacryloxypropyltrimethoxysilane (MPS) and in situ polymerizations of styrene and acrylic acid, initiating with Azobisisobutyronitrile (AIBN) were performed. The encapsulated flakes were characterized by Fourier transform infrared (FTIR), energy-dispersive X-ray spectroscopy (EDX), and transmission electron microscope (TEM). Also, polymer chains were analyzed by gel permeation chromatography (GPC). Subsequently the chemical stability of the pigments in alkaline and acidic aqueous media was examined. Results indicated that polystyrene coating remarkably improved flakes' anticorrosion property while PAA evolved hydrogen.

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1. Introduction

Plate-like aluminum pigments (aluminum flakes) have been widely applied in the fields of paints, inks and plastic industries as silver bronze pigments due to their low price, metallic appearance and “flop-effect” [1–4]. However, when they contact with water, acid and alkali media, they are attacked because of their high surface area and their corrosion causes evolution of hydrogen according to the following equations [5–11]:



Abbreviations: PS, polystyrene; PAA, poly(acrylic acid); MPS, 3-methacryloxypropyltrimethoxysilane; AIBN, Azobisisobutyronitrile; FTIR, Fourier transform infrared; EDX, energy-dispersive X-ray spectroscopy; TEM, transmission electron microscope; GPC, gel permeation chromatography; DMF, dimethylformamide; DMP, 2,6-dimethylpyridine; Al, pristine aluminum flake; Al/MPS, MPS-modified Al flakes; Al/PS, PS-encapsulated Al flakes; Al/PAA, PAA-encapsulated Al flakes.

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These results in severe deterioration of metallic luster and dangerous pressure build up in the storage vessels [1,9]. Therefore, inhibition of this corrosion reaction is necessary. The methods adopted for aluminum pigments stabilization in aqueous media can be divided into two principal categories [1–3]: the adsorption of corrosion inhibitors on the surface such as phosphorus-containing compounds, molybdates or vanadates [5], chromium (VI) complexes or other heavy metal based compounds [6] and the encapsulation of the pigment by organic or inorganic materials [7–8,12–15].

Recent investigations reported that the encapsulation method is more promising since the protective layer can insulate the aluminum pigments from the corrosion medium [3]. This can be done by organic polymer layers resulted from in situ polymerization [1,7–8,12–15]. However, there is no report about the effect of polymer type on corrosion behavior of aluminum flakes.

In this work, aluminum pigments were encapsulated by PS and PAA nanolayers. At first, aluminum flakes were modified using MPS; then, in situ polymerization of styrene and acrylic acid were performed to prepare an organic layer. The structure of the encapsulating nanolayers was characterized by means of FTIR, EDX, TEM and GPC. Also, the hydrophilicity and hydrophobicity of the flakes were examined by contact angle test. Furthermore, the stability of the coated aluminum pigments in acid media of pH 1 and alkaline media of pH 12 was also measured and effect of polymer type was investigated.

2. Experimental methods

2.1. Materials

Blitz Aluminum paste with average particle size of 12 μm (Benda Lutz, Batch number 2100552-2) was washed with dimethylformamide (DMF) several times to remove the organic compounds and then it was dried under vacuum at 100 °C for 24 h. Styrene (St, Tabriz petrochemical company, Iran) and acrylic acid (Merck, 99%) was purified by passing through a column packed with aluminum oxide to remove the polymerization inhibitor by adsorption. Azobisisobutyronitrile (AIBN) as an initiator was recrystallized from methanol prior to use, 2,6-dimethylpyridine (DMP) as a catalyst, 3-methacryloxypropyltrimetoxysilane (MPS, Merck, 98%), maleic anhydride (Merck, 99.9%), toluene (Merck, 99%), acetone (Merck, 99.8%) and ammonia solution (Merck, 25%) were used directly without further purification.

2.2. Modification of Al flakes with MPS

Briefly, 3 g Al flakes were firstly dispersed in 100 mL acetone in a three-necked flask equipped with a magnetic stirrer and a reflux condenser. Then 3 mL MPS was added followed by 3 drops of DMP. The mixture was boiled in 56 °C under a nitrogen atmosphere. After 2 h, 0.03 g maleic anhydride diluted in 0.2 mL distilled water and 30 mL acetone was complemented into flask and the mixture was further refluxed in 56 °C under nitrogen atmosphere for 3 additional hours. After the reaction, the resulting product was filtered and washed several times with acetone, and finally placed in vacuum oven at 40 °C for 12 h to obtain Al/MPS flakes.

2.3. In situ polymerization of styrene and acrylic acid

To attach polymeric chains to the surface of MPS-grafted Al flakes, 1 g of flakes, 22 mL toluene (or 19 mL ethanol) and 22 mL styrene (or 19 mL acrylic acid) were added into the reaction flask. After a certain time, when all reactants had dissolved under stirring, AIBN was added to start the polymerization at 60 (or 45) °C. The mixture was refluxed and stirred for 24 h under a nitrogen atmosphere. After the reaction, the resulting product filtered and the residue washed with toluene (or ethanol) to remove unreacted

monomer and freely-produced polymer chains. The resulting pigments (Al/PS or Al/PAA) were dried under vacuum at 40 °C for 12 h.

2.4. Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FTIR-spectrophotometer, within a range of 500–4000 cm^{-1} using a resolution of 4 cm^{-1} . An average of 24 scans has been carried out for each sample. The samples were prepared on a KBr pellet in vacuum desiccators under a pressure of 0.01 torr. Transmission electron microscope (TEM), Tescan Mira, with an accelerating voltage of 100 kV was used to study the morphology of the nanocomposites; the samples of 70 nm thickness

Table 1
Results of EDX analysis of different particles.

Samples	Element (wt.%)			
	Al	C	O	Si
Al	90.41	3.68	5.91	–
Al/MPS	85.62	6.58	6.77	1.03
Al/PS	67.64	26.20	5.35	0.81
Al/PAA	70.20	14.94	14.01	0.85

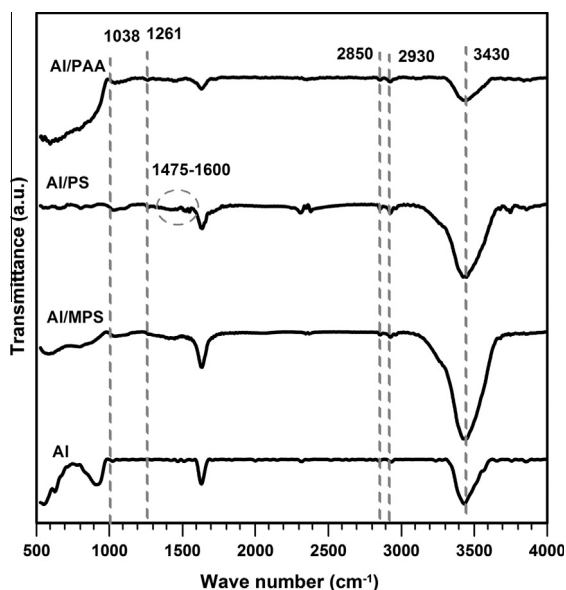


Fig. 1. FTIR spectra of Al, Al/MPS, Al/PS and Al/PAA.

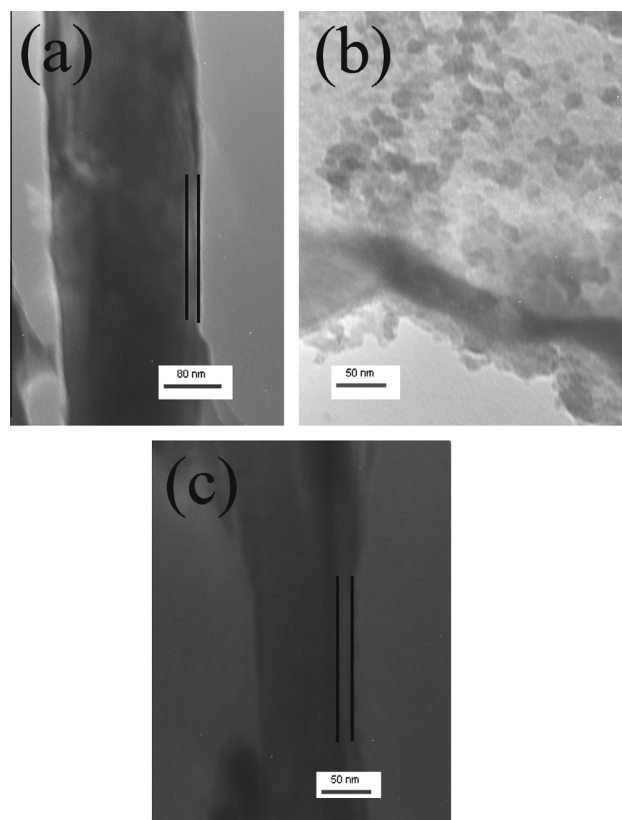


Fig. 2. TEM image of (a and b) Al/PS flakes and (c) Al/PAA flakes.

Table 2
Average contact angles (over 10 samples) of test liquids on the films and samples (the standard deviation is shown in parentheses).

Sample	Distilled water	Diiodomethane
Al	80.9 (8.6)	11.2 (8.0)
Al/MPS	72.3 (7.0)	20.6 (9.0)
Al/PS	126.4 (8.9)	0.0 (0.0)
Al/PAA	61.9 (6.7)	24.3 (7.9)

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