



Protonation of the polyethyleneimine and titanium particles and their effect on the electrophoretic mobility and deposition



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HIGHLIGHTS

- Protonation characteristics of polyelectrolytes and suspension particles are reported.
- The protonation characteristics explained the electrophoretic mobility and yield results.
- Adsorption mechanisms of protonated polyelectrolytes on the titanium particle is proposed.
- Hydroxyl sites on the particles link the oxide particle and the polyelectrolyte molecules.

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ABSTRACT

Proton activities of suspensions of Ti particles with added cationic polyelectrolyte as a function of acid additions have been investigated and compared in terms of the electrophoretic mobility and deposition yield. The proton activity in ethanol medium decreased with the addition of PEI polyelectrolyte and reduced further in the presence of Ti particles. The decrease in proton activity in the suspension indicates that protonation occurred on both the PEI molecules and Ti particles. It is proposed that the protonation of the amine groups of PEI and hydroxyl sites of Ti particle led to the formation of hydrogen bonding between the Ti particle and PEI molecules. Increase in the PEI and Ti with increasing acid addition translated to higher electrophoretic mobilities and deposition yield at low ranges of acetic acid addition (<0.75 vol%).

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1. Introduction

Electrophoretic deposition (EPD) is a potential coating technique for various applications, mainly because of its feasible set-up, excellent control of coating parameters of simple or complex shapes [1]. However, the EPD technique is rarely considered as an alternative to the current available surface hardening methods because of the weak mechanical properties of the produced coating [1a,1d]. Nevertheless, previous studies showed that a combination of this method with a subsequent heat treatment process is capable of increasing the bulk density, strength and coherence of the EPD coating for corrosion protection application [1d,2]. The studies also demonstrated that it is possible to obtain well-adhered coating/substrate interface through the heat treatment process.

The current study explores the deposition of titanium (Ti) particles by EPD for the application of a surface hardened layer on low-carbon steel. The application of Ti coating in this study is owing to its high corrosion resistance and easy to be transformed into hard titanium-based ceramics, such as nitride (TiN) and titanium carbide (TiC) [3]. Coarse non-colloidal Ti particles (particle size = 1–50 μm) are used in the current study owing to the advantage of lower volume ratios of the particles surface oxide layers. Although they have relatively low surface charge, they can be deposited and controlled during EPD with the addition of cationic charging agents and suitable EPD parameters [4].

EPD of the Ti particles requires charging agent to provide additional surface charge for the stabilization and electrophoretic mobility during the deposition process. Furthermore, these agents act as binders to improve the adhesion between deposited particles and substrate [1a,1d]. Polyethyleneimine (PEI), in particular is commonly used as the charging agent of suspension particles for

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EPD process due to its nontoxicity and availability [4,5]. Unlike strong charging agents such as poly(diallyldimethylammonium chloride) which maintains their strong cationic charge at wide pH range, the weak base PEI charging agent requires optimization at acidic pH range to create effective EPD of particles [6]. Nevertheless, there are continuous demands for PEI as EPD charging additive because of the absence of corrosive agent (i.e. halide) which may be harmful for the reliability of the depositing substrate. Acetic acid is preferred instead of stronger acid such as hydrochloric acid in order to minimize oxidation of the Ti particles and corrosion of substrate. Although many studies have been reported on the effect of PEI addition on EPD of suspension particles [6,7], only a number of studies went further to discuss on the adsorption interaction between the protonated PEI and the suspension particles [8,9]. Therefore, the bonding mechanism of the PEI on the suspension particles and the role of protonation, particularly on the coarse suspension particles have not been fully understood.

The aim of the present work is to investigate the protonation on PEI and Ti particles and their effects on the electrophoretic mobility and EPD of Ti coarse particles. The protonation on the PEI and Ti particles is controlled by the addition level of acetic acid. The investigation focussed in terms of: (i) proton activity of PEI-added Ti suspension particles as compared to blank medium and PEI added medium with no Ti particles, (ii) deposition coverage of Ti particles, and (iii) electrophoretic mobility of the Ti particles before deposition.

2. Experimental procedure

2.1. Liquid media preparation and pH measurement

Three suspension media samples were prepared for pH measurements: ES, PEI + ES and Ti + PEI + ES. ES was prepared by magnetic stirring of 1 mL distilled water and 19 mL anhydrous ethanol for 15 min. Whereas, PEI + ES was prepared by magnetic stirred PEI and ES for 15 min. Lastly, Ti particles + PEI + ES was prepared by magnetic stirred Ti particles, PEI and ES for 15 min, in which the addition level of PEI from Ti particles weight basis was 1 wt%. pH of each of these suspension media were measured subsequently after gradual glacial acetic acid addition and 5 min magnetic stirring. More details of the chemicals used for the samples preparations are highlighted in Table 1. pH measurement was conducted using a standard F-54 model pH meter (attached with glass electrode (model 9621-10 D), accuracy = ± 0.01 , Horiba, Ltd., Japan) at room temperature, and was priorly calibrated using pH standard solution and NIST standard.

2.2. Preparation of suspension for electrophoretic deposition and electrophoretic mobility measurement

Suspension for electrophoretic deposition was prepared by magnetically stirred 0.1 g Ti powder and 20 mL anhydrous ethanol (solids loading of 5 g L^{-1}) for 1 min. Then, small amount of PEI (i.e. addition level of 0–5 wt% from Ti particles weight basis) was added and magnetic stirred for 30 min. A longer stirring time was required due to lower PEI dissolution in anhydrous ethanol than ethanol solution. Then, small amount of glacial acetic acid (0–5 vol% from ethanol volume) was then added and then stirred for another 5 min.

For the electrophoretic mobility measurements, test volumes of 1.5 mL each of the less sedimented fraction ($\sim 1\text{--}12 \mu\text{m}$) of the prepared suspensions were placed in a 4.5 mL standard polystyrene cuvette before being used. All the EPD suspensions and electrophoretic mobility measurement samples were prepared at room temperature. The electrophoretic mobility and electrical

conductivity measurements were performed using a phase-analysis light-scattering zeta potential analyser (ZetaPALS; Brookhaven Instruments Co., USA). Details of the measurements and related sample preparation procedure have been published elsewhere [9].

2.3. EPD process

EPD set-up consisted of mutually parallel electrodes at a fixed separation, connected by alligator clips to a d. c. programmable power supply (EC2000P, E-C Apparatus Corp., USA). The cathode (working electrode or substrate) was SAE 1006-grade low-carbon steel and the anode (counter-electrode) was 304 grade stainless steel. Both electrodes (supplied by BlueScope Steel Ltd., Australia) have submerged dimensions of 10 mm H \times 10 mm W \times 1.5 mm T and electrode separation of 1 cm. Each EPD suspension was magnetically stirred for ~ 1 min following lowering of the electrodes into the suspension. Voltage was applied immediately after the stirring was stopped. Finally, the deposited cathode was removed slowly from EPD suspension at constant pulling rate of 0.2 mm s^{-1} immediately after EPD ended and was let air-dried.

2.4. Microstructural and deposit coverage characterization

Particle and deposit microstructures were assessed by scanning electron microscopy (SEM, 15 kV accelerating voltage, secondary electron emission mode, S3400 N, Hitachi High-Technologies Corporation, Japan). Surface coverage of the Ti particles deposit was measured in percentage using ImageJ software (version 1.42q). Weight gain method to determine the deposit yield was not been performed due to the very low yield value and inconsistent yield result.

3. Results and discussion

Fig. 1 shows pH of ethanol solution (ES), PEI + ES, and Ti particles + PEI + ES media as a function of acetic acid addition. Their pH measurements showed typical logarithmic decreases with the increasing acid addition, the trend is similar with the titration curve of base with acid [10]. Theoretically, pH values are derived from the logarithmic functions of hydrogen ion activities (a_{H^+}) of the studied medium and is expressed as $\text{pH} = -\log(a_{\text{H}^+})$ [10]. Thus, a_{H^+} was derived from the pH equation (i.e., $a_{\text{H}^+} = 1/10^{\text{pH}}$). The calculated a_{H^+} was plotted as a function of acetic acid level (see Fig. 2).

All the three media show their a_{H^+} increased exponentially with the increasing of acetic acid levels. Similarity of the a_{H^+} trends in the three media implies the acetic acid addition as compared to the PEI and Ti particles additions, has predominant influence on the proton formation during the increasing acid addition. The exponential increase of a_{H^+} versus acetic acid addition level was caused by the exponential increase of ion dissociation constant of acetic acid [10]. The increasing concentration of acetic acid reduced the water percentage in the ethanol-water solution, thus increased the dissociation of acetic acid into protons and anions [11].

PEI + ES medium had recorded a lower a_{H^+} increments against the acetic acid addition levels as compared to the ES medium. It is believed that the lower a_{H^+} increments for PEI + ES were due to the adsorption of some of the dissociated protons onto the amine groups of PEI [6]. A much lower a_{H^+} increment against the acetic acid addition levels was recorded in the Ti particles + PEI + ES medium, thus indicates proton adsorption also occurred on the Ti particles, presumably through the protonation of hydroxyl sites on the oxide surface of the Ti particles (see Fig. 3). Protonation of hydroxyl sites on titanium oxide surface had been reported in the

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