



Cathodic delamination of polyurethane/multiwalled carbon nanotube composite coatings from steel substrates



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ABSTRACT

Polyurethane composite coatings with different multiwalled carbon nanotube (MWCNT) contents were prepared on steel substrates to study the effect of MWCNT content on the cathodic delamination of the polyurethane composite coatings. The cathodic delamination of the polyurethane composite coatings was measured using a Scanning Kelvin Probe (SKP). An increase in MWCNT content to 0.5 wt% significantly reduced the cathodic delamination of the polyurethane composite coatings because the high density of MWCNTs blocked the transport pathways of water and oxygen molecules through the coating. It could be concluded that the incorporation of MWCNTs was a possible way to lessen the cathodic delamination of the polyurethane coatings.

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1. Introduction

Steel is widely used for structural applications but corrodes in many media including most outdoor atmospheres. Organic based coatings are extensively applied to retard the corrosion degradation of steel structures. Properly applied anticorrosive coatings can effectively prevent steel substrates from corrosion in various aqueous solutions for long periods. However, organic coatings often fail upon exposure to an electrolyte because degradation of coating adhesion allows subsequent exposure of the underlying steel substrate to the electrolyte [1–3]. In addition, the physical damage of anticorrosive coatings caused by impact, scratch or wear during service allows direct contact of underlying steel substrates to aggressive environments and electrochemical reactions taking place at coating/substrate interfaces. As a result, anodic dissolution of steel substrates in defect areas ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) releases electrons to cathodic sites beneath coatings where oxygen is reduced by the released electrons to produce hydroxide ions ($\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$) [4,5]. An increase in hydroxide ions concentration under coatings results in alkalization, which in turn weakens the adhesion between coatings and steel substrates. The corrosion circuit is closed by the transport of cations (such as Na^+) along the interface between the anodic defect and the cathode at the end of the delaminated region. This cathodic delamination pro-

cess is one of the primary mechanisms of coating failure on steel [4,6,7].

It is known that transport of water and oxygen molecules through organic coatings can play a critical role in the oxygen reduction process while the transport of cations along the interface can be a controlling factor in the cathodic delamination of the coatings [4,6,7]. Therefore, improvements in the physical properties (e.g. density) of organic coatings can impact cathodic delamination of the coatings by changing transport pathways of the molecules [6]. Carbon nanotubes (CNTs) are considered to be an ideal reinforcing agent for high-strength polymer composites because of their ultrahigh tensile strength, high density, high aspect ratio, and high thermal stability and conductivity [8–10]. However, the dispersion of CNTs in polymer matrices is difficult because the high surface energy, high aspect ratio and strong Van der Waals interaction of CNTs promote self-agglomeration [8–10]. Nevertheless, it has been reported [11–14] that incorporation of multiwalled CNTs (MWCNTs) in epoxy matrices improved the wear resistance of the epoxy composites by improving the mechanical strength and reducing the friction of the composites. MWCNTs have also been studied in metal matrices. Hu and co-workers [15] found that incorporation of MWCNTs in electroplated lead-tin coatings improved the corrosion resistance. The opposite effect has also been observed, however, as micro-galvanic interaction has been found to degrade corrosion resistance when CNTs are incorporated in metal matrixes [16–19]. The cathodic and catalytic activity of the CNTs could accelerate oxygen reduction and thereby increase corrosion rates [16–19]. In spite of these findings, several researchers have reported success-

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ful improvements of corrosion protective performance of organic coatings associated with incorporation of CNTs [15,16,20,21]. It is possible that incorporation of MWCNTs in organic coatings would improve the cathodic delamination of the coatings by hindering the transport of water and oxygen molecules in addition to improving the tribological performance of the coatings.

In this study, polyurethane composite coatings with different MWCNT contents were prepared on steel substrates to investigate the effect of MWCNT content on the cathodic delamination of the coatings. The presence of MWCNTs in the polyurethane composite coatings was evaluated using field emission scanning electron microscopy (FE-SEM). The pore resistance of the polyurethane composite coated steel samples was examined using electrochemical impedance spectroscopy (EIS). The cathodic delamination of the polyurethane composite coatings from their steel substrates was studied using a Scanning Kelvin Probe (SKP).

2. Experimental details

Commercially available polyurethane (PPG) was used for this study. The polyurethane resins ultrasonically mixed with MWCNTs at different contents of 0, 0.1 and 0.5 wt% were applied on low carbon steel substrates (UNS G10180; 0.6–0.9 Mn%, 0.15–0.2C%, 0.05 S%, 0.04 P%, and balance Fe). The best dispersion of MWCNTs in the polyurethane resins was found up to the MWCNT content of 0.5 wt%. The polyurethane coatings with a thickness of about 100–150 μm were prepared on the steel substrates with a draw-down bar. Before the coating, the steel substrates were mechanically abraded using 1200 grit SiC papers and cleaned in an ultrasonic bath with ethylene alcohol. The MWCNTs (Baytubes C 150HP) were purchased from Bayer Materials Science, Germany. The diameter, length, number of walls, and bulk density of the MWCNTs according to the manufacturer's specifications were 5–20 nm, 1–10 μm , 3–15, and 140–230 kg m^{-3} , respectively.

The surface morphology and topography of the samples were studied using FE-SEM (JEOL-JSM-5800) and optical profilometry (Veeco). An average root-mean-squared surface roughness (R_q) was determined from three measurements per sample.

The corrosion resistance of the samples was measured in a 0.5 M NaCl solution using an electrochemical workstation (Gamry Reference 600) with a three-electrode cell at room temperature (RT \sim 22–24 $^{\circ}\text{C}$). The tested area on the samples was a circle of 1 cm in diameter. A saturated standard calomel reference electrode (SCE) and a platinum mesh counter electrode were used. Nyquist plots of the samples were acquired at their relevant open circuit potentials in the frequency range of 10^5 – 10^{-2} Hz with an AC excitation signal of 10 mV after an immersion period of 42 h.

The SKP measurement was carried out using a height-regulated SKP in air with >95% relative humidity (RH) [4]. The sample preparation and the measurement procedure were based on the works reported previously [4,22,23]. Detected interface potentials were reported with respect to the standard hydrogen electrode (SHE) after calibration against a Cu/CuSO₄ electrode. Prior to the SKP measurement, the coated samples were exposed in humid air for 2 h to reduce electrostatic charging on the polymer coatings. Then cathodic delamination was initiated by filling an artificial defect (uncoated region isolated on three sides by a dam made of epoxy) with a 0.5 M NaCl solution. The cathodic delamination of the coatings was measured by repeatedly scanning a line extending from the defect region over the coating using SKP. All of the coated sample sets were exposed in the SKP chamber at the same time and measured sequentially to avoid any interfering fluctuation in exposure condition, and thus improve the comparison. The results were confirmed by two measurements per sample.

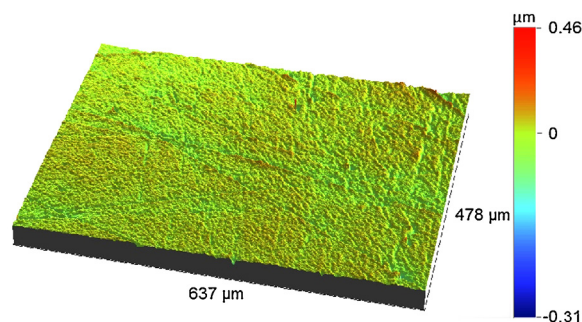


Fig. 1. Surface topography of polished steel substrate using 1200 grit SiC paper.

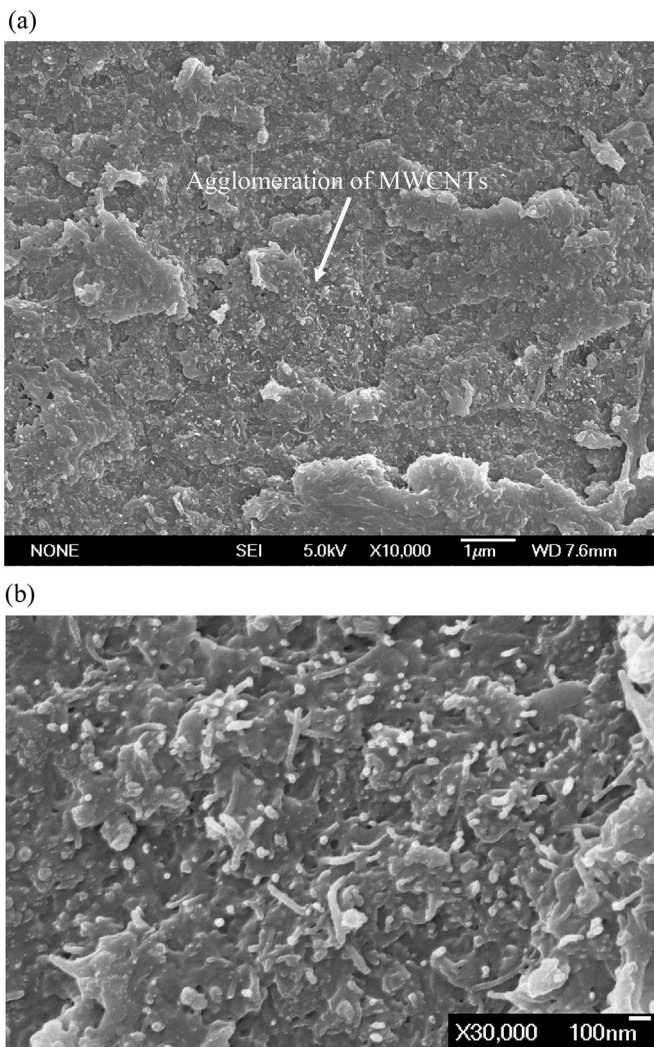


Fig. 2. SEM micrograph showing dispersion of MWCNTs in fractured polyurethane matrix with 0.5 wt% MWCNTs at (a) low and (b) high magnifications.

3. Results and discussion

Fig. 1 shows the surface topography of the abraded steel substrate determined by optical profilometry. The surface of the steel substrate was quite smooth, which is confirmed by the small R_q of 28.3 ± 1.3 nm.

SEM images of the fracture surface of a broken polyurethane composite coating with 0.5 wt% MWCNTs are shown in Fig. 2. Although agglomerations of MWCNTs are found at some places over the fracture surface at low magnification (Fig. 2a), the rela-

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