Surface & Coatings Technology 204 (2010) 4075–4080

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Infrared emissivity and corrosion-resistant property of maleic anhydride grafted ethylene-propylene-diene terpolymer (EPDM-g-MAH)/Cu coatings

Chunming Shao *, Guoyue Xu, Xingmei Shen, Huijuan Yu, Xiaoxing Yan

College of Material Science & Engineering, Nanjing University of Aeronautics and Astronautics, Yu Dao Street 29, Nanjing 210016, China

ARTICLE INFO

Article history:
Received 25 September 2009
Accepted in revised form 20 May 2010
Available online 27 May 2010

Keywords:
EPDM-g-MAH
Infrared emissivity
Corrosion
Coating

ABSTRACT

Maleic anhydride grafted ethylene-propylene-diene terpolymer (EPDM-g-MAH) was prepared by grafting copolymerization method. Composite coatings with varied infrared emissivity were obtained by using copper (Cu) powder as inorganic pigments, either EPDM or EPDM-g-MAH as organic adhesive. The influences of the content of Cu powder and adhesive kinds on the infrared emissivity of the composite coatings were investigated. The as-prepared coatings were characterized by FTIR spectroscopy, infrared emissometer and SEM. The corrosion-resistant property of the coatings in aqueous 3.5 wt.% NaCl was assessed by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results have shown that the interfacial interaction between EPDM and Cu is improved due to the MAH grafting on EPDM, benefiting from the compatibility of EPDM with Cu and the low porosity of EPDM/Cu coatings, which leads to the lower infrared emissivity and better corrosion-resistant property of the coatings.

1. Introduction

With the increasing development of infrared guided weapons and infrared detection techniques, infrared low emissivity materials have been received considerable attention due to their wide applications either in military or in civil fields, such as camouflaging military equipments or vehicles, heat loss control in industry and the like [1,2]. In the past few years, extensive researches on the low infrared emissivity coatings have been reported, such as semiconductor thin-films [3,4], AlSiN and Ag-alloy multilayer films [5], composite ceramics [6,7], and organic/inorganic composite coatings [8–10]. Among them, organic/inorganic composite coatings are especially promising with advantages of low cost, good mechanical performance, flexibility to the shapes of equipments.

In general, the organic/inorganic composite coatings are composed of inorganic pigments and organic adhesives. Metals such Cu powder are usually used as pigments to reduce the infrared emissivity due to their high spectral reflection and low thermal emissivity [11,12]. For organic adhesive, Ethylene-propylene-diene terpolymer (EPDM) is widely used as adhesive materials, due to its excellent physical and durability properties [13]. However, due to the incompatibility of EPDM with inorganic pigment, the corrosion-resistant property of low infrared emissivity EPDM coating is very poor, which strongly limits their practical applications. However, noticeable improvements of above properties of EPDM can be obtained through grafting by other functional compounds. Maleic anhydride (MAH) molecule abounds in anhydride polar group having good affinity to metal or metal oxide, such as Cu, CuO, and MAH is also usually used to graft onto polymer to enhance the property [14–17].

In this paper, EPDM-g-MAH was prepared by grafting copolymerization method, and organic/inorganic composite coatings with varied infrared emissivity were obtained by using either EPDM or EPDM-g-MAH as adhesive and Cu powder as pigment. The effects of chemical composition and microstructure on the infrared emissivity and the corrosion resistance of the composite coatings were systematically discussed.

2. Experimental

2.1. Materials

Cu powder, EPDM, MAH, benzoyl peroxide (BPO) and dimethylbenzene were purchased from Nanjing Chemical Agent Limited Company, China. All reagents were analytical grade and were used as received without further treatment.

2.2. Preparation of EPDM-g-MAH

Raw EPDM (3 g) and MAH (0.15 g) were dissolved in dimethylbenzene (60 mL), then BPO solution (2.4 g/l) was slowly added. The reaction was carried out in nitrogen atmosphere at 100 °C for 2 h. Finally EPDM-g-MAH was obtained.

* Corresponding author. Tel.: +86 25 84892903; fax: +86 25 84892951.
E-mail address: shaocm2008@yahoo.com.cn (C. Shao).

0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2010.05.036

2.3. Preparation of EPDM-g-MAH/Cu coatings

Steel substrate (12 cm × 12 cm, thickness 0.3 mm), properly cleaned by ethanol and distilled water respectively, was used as the coating substrate to test the emissivity changes of various coatings. Steel substrate (3 cm × 2 cm, thickness 0.3 mm) was used as the coating substrate to test the corrosion-resistant property. Firstly, fixed amounts of EPDM-g-MAH and Cu power were mixed (19:1, 9:1, 17:3, 4:1, w/w) together under continuous ultrasonication for 10 min. Then the mixture was painted onto the substrates by spray technique (98PSI, Japan) using an accurate speed motor and appropriate pressure. The coating thickness is about 20 μm. Finally the coatings were solidified completely after curing at 50 °C for 24 h and kept for further characterization. In all cases, duplicate experiments were carried out to ensure reproducibility.

2.4. Characterization and testing

The infrared emissivity in 8–14 μm range was measured by using IR-2 Infrared Emissometer (Shanghai Institute of Technological Physics, China), with an accuracy of 0.01. The morphology and structures of samples were observed by scanning electron microscope (SEM) (FEI-Quanta200). The EPDM-g-MAH was firstly extracted with acetone to remove MAH, then Fourier transform infrared spectroscopy (FT-IR) was recorded on NEXUS-670 Fourier transform infrared spectrophotometer using KBr pellets. The thickness of coatings was measured by using a digital magnetism thickness instrument (China). The corrosion studies were performed on CHI750C electrochemical workstation at room temperature in aqueous 3.5 wt.% NaCl solution by using potentiodynamic polarization technique and EIS technique. A three-electrode cell configuration was used for the electrochemical measurements, with a saturated calomel electrode (SCE) as reference electrode, a platinum plate as counter electrode and the as-prepared coating substrate as working electrode. The NaCl solutions were purged with argon gas for 1 h prior the test. For these measurements, the edges of the coating substrate was sealed with rosin and paraffin leaving a working area of ~1 cm^2 exposed to the solution. Prior to the measurement, each sample was immersed in aqueous 3.5 wt.% NaCl solution 30 min, and the open circuit potential (OCP) was monitored until a constant value was reached. The potentiodynamic polarization measurements were performed by sweeping the potential from −0.3 V versus open circuit potential to 0.3 V at the scan rate of 0.01 V/s. The potentiodynamic polarization curves were analyzed by using the software being carried by CHI750C electrochemical workstation. This software calculates the values of the corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel constants (β_a and β_c) and polarization resistance (R_p). The EIS measurements of the EPDM/20% Cu and the EPDM-g-MAH/20% Cu coated substrates were carried out at the OCP in aqueous 3.5 wt.% NaCl solution. The frequency was varied from 0.1 Hz to 100 kHz using an ac excitation potential of 0.01 V. The analysis of impedance spectra was done by fitting the experimental results to equivalent circuits using the ZSimpWin (version 3.10) software. The quality of fitting to equivalent circuit was judged firstly by the Chi-square value (χ^2, i.e. the sum of the square of the differences between theoretical and experimental points) and secondly by limiting the relative error in the value of each element in the equivalent circuit to 5%. All the measurements were repeated at least three times and good reproducibility of the results was observed (new sample for each measurement).

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of EPDM and EPDM-g-MAH are shown in Fig. 1. It can be seen from Fig. 1a, EPDM has no obvious absorption peaks in 8–14 μm wave band (1250–715 cm^{-1}), indicating high infrared transmittance property. In the FTIR of EPDM-g-MAH (Fig. 1b), a characteristic absorption peak of C=O at 1714 cm^{-1} is observed, indicating that MAH has been successfully grafted onto EPDM. Besides, the infrared transmittance property of EPDM-g-MAH in 8–14 μm has no change after grafting copolymerization.

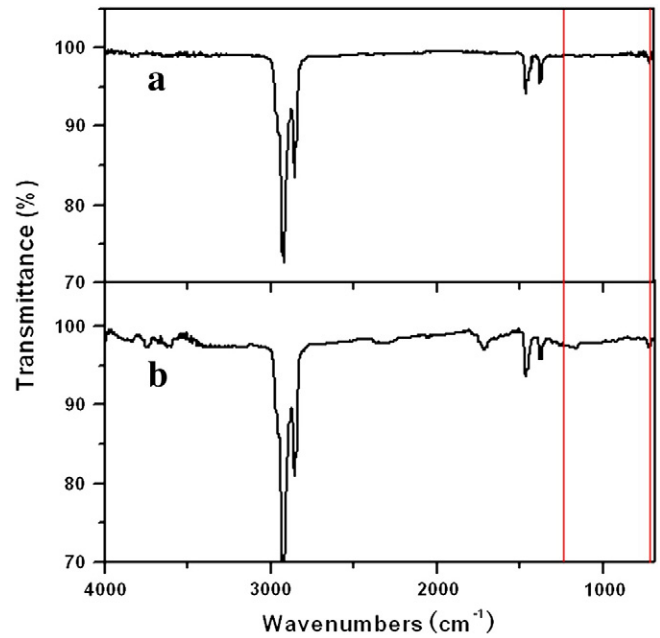

Fig. 1. FTIR spectra of (a) EPDM and (b)EPDM-g-MAH.

3.2. Infrared emissivity

Fig. 2 show the relationship curves between the content of Cu and infrared emissivity of the EPDM/Cu coatings and the EPDM-g-MAH/Cu coatings, respectively. From the curves, it can be observed that the emissivity of composite coatings decreases with the Cu content increasing from 5 wt.% to 20 wt.%. To discuss the effect of the content of Cu on the emissivity, the SEM images of the Cu powder and the EPDM-g-MAH/Cu coatings are shown in Fig. 3. It can be seen from Fig. 3a that the Cu pigments are flake particles. The image (Fig. 3b)

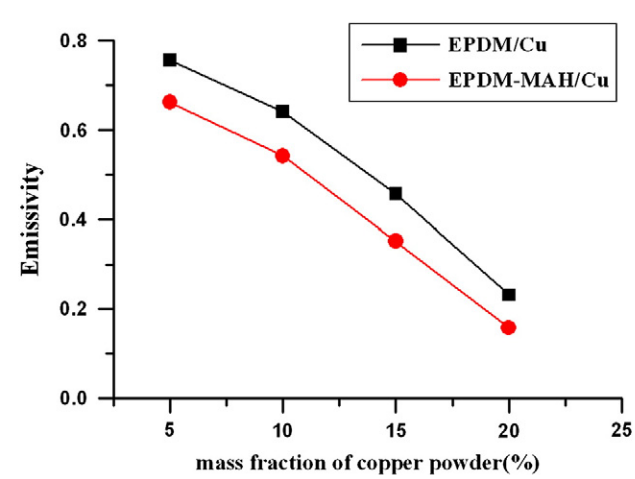

Fig. 2. The infrared emissivity of coatings vs. Cu powder content (coating thickness ≈20 μm).