STUDIES ON PPY-TiO_2 COMPOSITE-EPOXY POLYAMIDE COATINGS FOR CORROSION PROTECTION

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Abstract

The semi conducting polymer and inorganic metal oxide composites composed of polypyrrole /titanium dioxide (PPy/TiO_2) were synthesized by sol-gel techniques. The products were characterized by FT-IR, Scanning electron microscopy (SEM), thermo gravimetry, differential thermal analysis (TG-DTA) and XRD (X-ray diffraction) techniques. The corrosion performance of polypyrrole-titanium dioxide composite incorporated epoxy-polyamide coatings on mild steel was evaluated by salt spray test and electrochemical impedance spectroscopy (EIS). The results showed that 2% PPy-TiO_2 composite incorporated epoxy-polyamide coating exhibits better corrosion protection than other systems. The glass transition and decomposition temperature of PPy-TiO_2 composites were found.

Key words: Sol-gel technique, TG-DTA, XRD, Salt spray testing, EIS.

I. INTRODUCTION

One of the current challenges of anticorrosive paint industries is to produce environmentally stable products. Polypyrrole (PPy) as a typical conducting polymer has attracted more attention because of their unique electrical, optical and photo electronic properties as molecular wires and molecular devices (1-3). On the other hand titania (TiO_2) has unique electrical properties as well as extensive applications in environmental protection and catalytic operations.

The development of conducting PPy–TiO_2 composites and incorporation of such composites into the epoxy-polyamide coatings for corrosion evaluation studies are reported in this paper.

II. EXPERIMENTAL METHOD

Pyrrole monomer, Titanium tetra isopropoxide, Ferric chloride tetra hydrate, isopropyl alcohol, nitric acid, dodecyl benzene sulphonic acid sodium salt, acetone and other commercial grade pigments were used in this study.

A. Synthesis of PPy-TiO_2 composite

Titanium isopropoxide (0.05 M) was dispersed in pyrrole followed by the addition of isopropyl alcohol under cold condition for complete dissolution and acidified with nitric acid. The molar ratios of Titanium isopropoxide, H_2O, IPA and HNO_3 were 1:3:20:8. Then the mixure of ferric chloride (0.1 M) and sodium dodecyl benzene sulphonic acid (0.01 M) was dissolved in 100 ml of water and added to the reaction vessel stirred at a speed of 800 rpm for 4 hours at room temperature. The gels were dried under vacuum for 12 hours.

B. Paint formulation

Paint formulation was done with various weight percentages (2%, 4%, and 6%) of PPy-TiO_2 composite pigment incorporated in epoxy polyamide coating for corrosion evaluation. The PVC and volume of solid in the coating was fixed as 30% and 50% respectively. The paints developed were applied on steel substrate for corrosion evaluation studies.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The peak at 2θ values of 24° (Fig 1) is assigned to stacking and ordering of PPy chains due to a strong

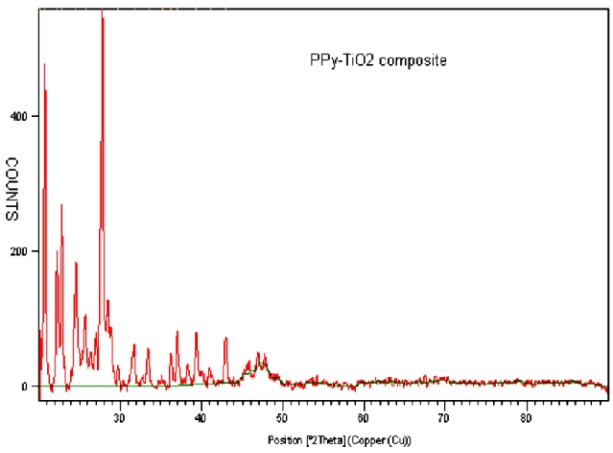

Fig. 1. XRD pattern of PPy-TiO_2 composite

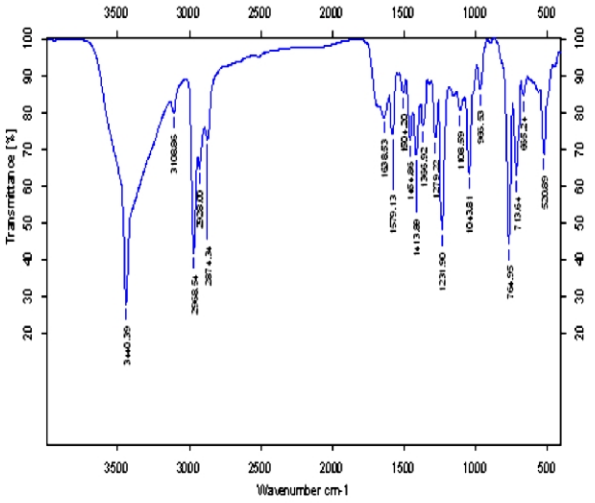

Fig. 2 FTIR spectrum of PPy-TiO_2 composite.

repulsion between the two adjacent pyrrole rings and the result shows that PPy-TiO_2 composites have higher degree of crystallinity. The 2θ values for PPy-TiO_2 composite were 20.7575, 27.294, and 22.8923 with d values of 4.2793, 3.8848 and 3.2078 clearly indicate the presence of Ti-O linkages in the composite.

IV. FT-IR SPECTRUM

In fig. 2, A broad peak observed at 3440 cm^{-1} is attributed to N-H stretching. The absorption band at 1232 cm^{-1} corresponds to N-H in the plane mode and it is characteristic band for PPy. The peak at 1108 cm^{-1} corresponds to symmetric C-H in the plane mode. The stretching modes of polypyrrole are shown in the region 1600-1400 cm^{-1}. The absorption observed at 1579 cm^{-1} corresponds to C-C stretching mode of PPy. The C=C Stretching vibration at 1638 cm^{-1} and 1455 cm^{-1} indicate the presence of PPy polymer in the composites. The spectrum of PPy-TiO_2 composite shows that all the characteristic bands of PPy are present and obviously shifted to the lower wave numbers.

V. THERMOGRAVIMETRIC ANALYSIS (TGA)

Fig.3. shows the TG-DTA diagram of the PPy-TiO_2 composite. It is observed from the DTA diagram that the glass transition temperature of the composite is 353 Kand reaches the steady value of 423 K.

The weight loss of 3.08% at 493.83 K corresponds to the evaporation of water molecules in the polymer. The weight loss (15%) changes occurs at 532.4 K is attributed to the elimination of organic impurities. At the temperature of 572.73 K the weight loss changes to 72.17%, due to the decomposition of PPy in the composites.

With further increase in temperature up to 931.89 K, the stable residue of TiO_2 (4.5%) due to phase transition was obtained.

Similar to the TGA, two exothermic peaks are observed in the DTA, at the temperature of 662.09 K and 931.89 K, corresponds to the decomposition of PPy and the phase transition of TiO_2 occurs.

VI. SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs of PPy-TiO_2 composites and pure polypyrrole are shown in Figs. 4 (a) & 4 (b). Scanning electron micrograph of PPy-TiO_2 composite shows that the TiO_2 particles are embedded in the PPy chains and form a true composite but in the case of polypyrrole spongy like structure with large cavities were obtained It is spherical in nature.

VII. CORROSION EVALUATION STUDIES

A. Salt spray test

4 different coated specimens (2%, 4%, 6% and PPy alone coated) were subjected to salt spray tests for corrosion evaluation. The results indicated that 2% PPy-TiO_2 composite exhibit better corrosion protection than others and with stood 212 hours in the salt spray. PPy alone coated samples with stood 195 hours in the salt spray.

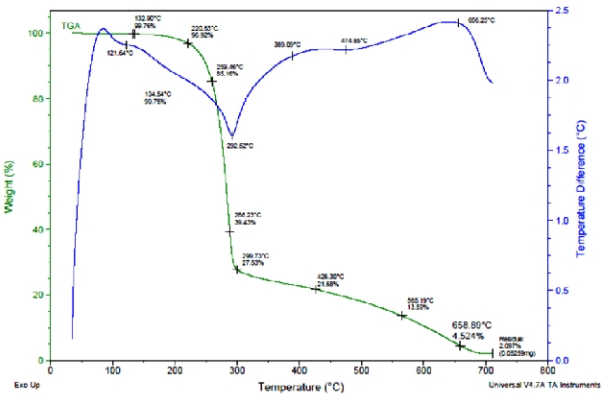

Fig. 3. TG-DTA curves for PPy-TiO_2 composite

Table 1: Corrosion protection of different specimens

System	Charge transfer resistance R_{ct} (Ωcm^2)			Double layer capacitance C_{dl} ($F\ cm^{-2}$)		
	0 day	1 day	7 days	0 day	1 day	7 days
S_1 (2%)	8.129×10^7	4.886×10^5	4.022×10^5	1.138×10^{-10}	4.009×10^{-10}	5.23×10^{-10}
S_2 (4%)	5.299×10^6	5.137×10^3	2.795×10^3	1.889×10^{-10}	9.270×10^{-10}	1.510×10^{-9}
S_3 (6%)	8.547×10^7	1.899×10^5	1.009×10^4	1.110×10^{-10}	3.232×10^{-10}	7.302×10^{-10}
S_4 (PPy)	6.893×10^7	1.751×10^5	9.027×10^4	9.474×10^{-11}	3.001×10^{-10}	6.637×10^{-10}

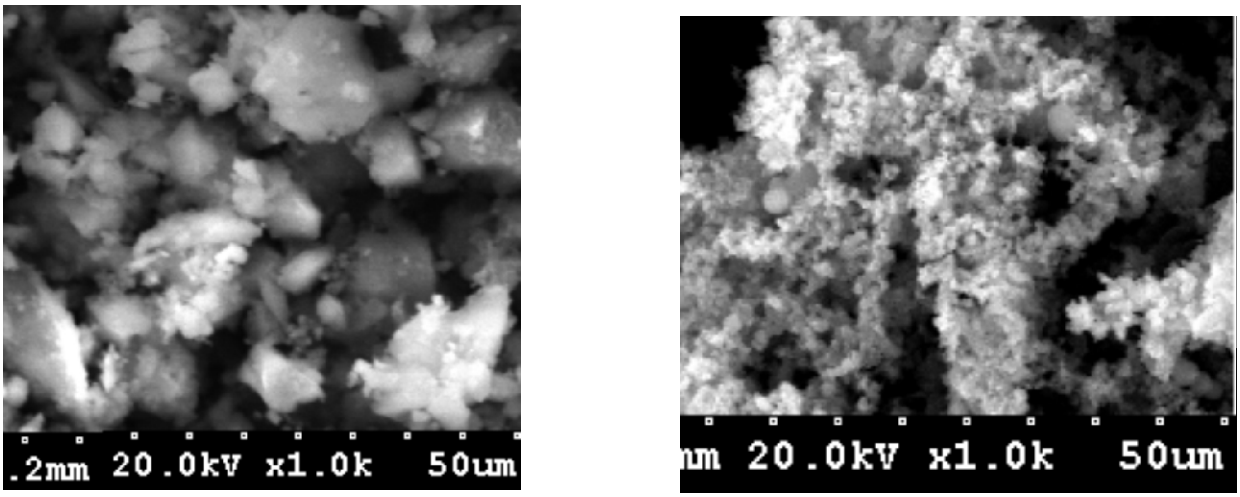

Fig. 4. (a) SEM image of PPy-TiO_2 (b) SEM image of PPy

B. EIS study

The study shows that the R_{ct} values increased initially due to the formation of protective oxide layer on the metal surfaces. After 24 hours, the resistance value decreases due to the water diffusion on to the metal surface.

After 7 days of exposure, 2% PPy-TiO_2 coated sample exhibited steady resistance values of 4.022×10^5 ohm.cm^2 due to less porous nature of the coatings, but all other coated specimens show decreasing trend of resistance because of more porosity in the coating system. The capacitance values show the higher order in the range of 5.23×10^{-10}. The resistance and capacitance values of 2% PPy-TiO_2 composite incorporated coating protect the metal surface to a considerable extent from corrosion in the aggressive environment.

VIII. CONCLUSION

XRD studies indicate the presence of Ti-O linkages in the composite and more crystalline than PPy particles. FT-IR spectra indicate that the absence of characteristic bands of TiO_2. From the TGA-DTA studies the glass transition temperature of PPy-TiO_2 was found to be 353 K, the decomposition temperature of PPy was 573 K. The phase transformations occurred at the temperature of 931.89 K. SEM studies indicate that the prepared composites are agglomerated and it is spherical in nature.

Salt spray test and EIS measurement shows that the 2% composite coatings exhibited better corrosion protection than that of other systems.

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