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EXPLAINING THERMAL PROPERTY OF NANO-ZNO/PP COMPOSITE

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Abstract

In this research, firstly polyaniline-zinc oxide (PANI-ZnO) nanocomposite was successfully synthesized by chemical polymerization of aniline in the presence of ZnO nanoparticles and then, 5%, 10% and 15% solutions of PANI–ZnO nanocomposites were mixed with a solution of polystyrene (PS) in tetrahydrofurane (THF) and PANI-PS-ZnO nanocomposites were obtained. The prepared nanocomposites were used as coating on iron coupons by solution casting method and their anti corrosive performance were studied by open circuit potential (OCP) and Tafel techniques in 3.5% NaCl solution as corrosive environment. The obtained results showed that the coating of PS-[PANI-ZnO 10%] nanocomposite had superior corrosion protection effect on iron sample compared to that of pure PANI, PANI–ZnO nanocomposite, PANI-PS composite and two other PANI-PS-ZnO nanocomposite coatings. Cyclic voltammetry (CV) studies showed that the prepared PS-[PANI-ZnO 10%] nanocomposite was electroactive and this property was reversible and stable. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) techniques were used to characterize the composition and structure of PS-[PANI-ZnO 10%] nanocomposite. To study thermal stability of PS-[PANI-ZnO 10%] nanocomposite, thermogravimetric analysis (TGA) was used.

Keywords: Corrosion, Nanocomposite, Polyaniline, Polystyrene, ZnO nanoparticle.

1. INRODUCTION

Intrinsically conducting polymers (ICPs) have received considerable attention due to their similar electrical and optical properties as metals and mechanical properties and processability as polymers [1]. ICPs are used in many applications such as batteries [2], sensors [3], removal of toxic ions from water [4], antistatic coatings [5], broadband EMI (Electromagnetic_shielding) shielding [6], and anticorrosive coatings [7-9]. The undesired corrosion phenomenon is a potential problem in the world of industries that influences the economy of countries. Electrochemically active ICPs protect metals by acting as barrier layer between the metal and corrosive environment and also they are among anodic inhibitors by exhibiting some kinds of anodic protections on metals [10]. Although, a variety of ICPs have been studied as corrosion protection coatings [11,12], but polyaniline (PANI) has been the most often researched due to its high conductivity properties, environment stability, low cost and straightforward synthesis [7-10]. On the other hand, the applications of PANI are limited by its poor processability and week mechanical properties. Preparing of PANI composite with other conventional polymers is one of the most studied ways to improve processability and mechanical properties of PANI [1]. A variety of studies have been reported on the preparing of PANI composite with processiable polymers such as polystyrene [1] and PVC (polyvinyl chloride) [13].

2. EXPERIMENTAL

2.1. Chemicals

Aniline, ammonium persulfate (APS), tetrahydrofurane (THF), sodium chloride (NaCl), hydrochloric acid (HCl) 37%, were all purchased from Merck Company. Aniline monomer was distilled two times before use. ZnO nanoparticles with the average particle size of 60 nm (purity 99.9%) were used.

Polystyrene (GPPS grade) was purchased from Petrochemical Company of Tabriz.

2.2. Preparation of PANI-PS-ZnO Nanocomposite

3g aniline was dissolved in 25 ml of HCl (0.5 M) and 1.5g ZnO nanoparticles were added to aniline solution. 7.5g APS as an initiator was dissolved in 25ml HCl (0.5 M) and was dropwisely added to aniline solution in 0 ºC, under vigorous stirring. The appearance of green color indicates the formation of PANI.After the end of initiator addition, the mixture was stirred for 2 h in 0 ºC, to complete the reaction of polymerization. Finally, prepared PANI-ZnO nanocompo-site was filtered and washed with distilled water to remove oligomers and residuals, and was dried in 50˚C.To prepare PANI-PS-ZnO nanocomposite with 3 different weight percentages of ZnO nanoparticles, 0.5 g PS was dissolved in 40 ml THF. Then, 0.025g PANI-ZnO nanocomposite was added to PS solution and stirred for 2h. PANI-PS-ZnO nanocomposite with 10 and 15 weight percentages of ZnO nanoparticles were prepared by adding of 0.05 and 0.075g of PANI-ZnO nanocomposite, respectively. Pure PANI was prepared in the absence of ZnO nanoparticles.

2.3. Working Electrode Preparation

Iron coupons (1 cm ×1 cm × 0.1cm) were used as working electrode. Polyester lacquer was used to mount the behind and edges of the iron samples. Before corrosion tests, iron surfaces (with the surface area of 1 cm2) were polished using 200 to 800 grade emery papers and washed using distilled water and acetone to remove any contaminations.

The surfaces of iron coupons were coated by a thin layer (40 μm) of PANI-PS-ZnO nanocomposites by solution casting method. The solvent (THF) evaporation was performed in environment temperature for 24 h.

Coatings of PANI, PANI-ZnO nanocomposite and PANI-PS composite were prepared with similar thickness, for comparison of their anticorrosive properties with PANI-PS-ZnO nanocomposites.

2.4. Corrosion Tests

Electrochemical corrosion test methods were selected to study the anticorrosive performance of pure, composite or nanocomposite coatings.

A conventional three electrode electrochemical cell was used to record Tafel plots. Iron sample with or without coating, Pt and SCE were used as working, counter and reference electrode, respectively. Iron coupon without coating was used as a reference sample. In the absence of counter electrode, a two electrode electrochemical cell system was used for open circuit potential (OCP) measurements.

Sodium chloride solution (3.5%) was used as an electrolyte in corrosion tests. Before corrosion test, all samples were immersed in sodium chloride solution (3.5%) for 80 min to reach equilibrium.

2.5. Characterization

A galvanostat/potentiostat (Autolab/PGSTAT302N) and three-electrode electrochemical cell system included of an iron sample (coated with composite, nanocomposite or pure polyaniline) as working electrode, a platinum gauze as counter electrode and an SCE as reference electrode were used for corrosion tests.

Bruker, Tensor 27 spectrophotometer was used to record the Fourier transform infrared (FT-IR) spectra of ZnO nanoparticles, pure PANI, PS and PS-[PANI-ZnO 10%] nanocomposite.

The surface morphology of PS-[PANI-ZnO 10%] nanocomposite was studied by scanning electron microscopy (SEM) of Vegall-Tescan Company and thermogravimetry (TGA) for ZnO nanoparticles, pure PANI, PS and PS-[PANI-ZnO 10%] nanocomposite were obtained by PL-TGA (Polymer Laboratories).

Cyclic voltammetry (CV) studies were performed with a conventional three-electrode electrochemical cell by using gold film coated by PS-[PANI-ZnO 10%] nanocomposite as working electrode (area=0.25 cm2) in combination with platinum counter and Ag/AgCl reference electrodes.

3. RESULTS AND DISSCUTION

3.1. OCP measurements

Open circuit potential OCP measurements of PANI, PANI-ZnO, PANI-PS, PS-[PANI-ZnO 5%], PS-[PANI- ZnO 10%] and PS-[PANI- ZnO 15%] coated iron samples were carried out versus to time in NaCl (3.5%) electrolyte. The OCP values of coated iron coupons versus to SCE reference electrode against to time are shown in Fig. 1. According to the Fig. 1, the potential of the electrode as the corrosion potential of coated samples was decreased with the passing of time and reached to the final equilibrium values.

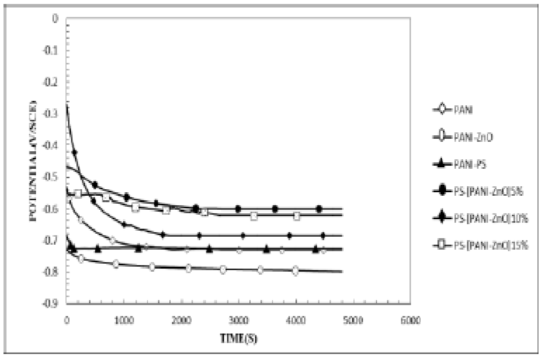

Figure 1. *OCP values of iron samples coated with PANI, PANI-ZnO, PANI-PS, PS-[PANI-ZnO 5%], PS-[PANI-ZnO 10%] and PS-[PANI-ZnO 15%] coatings in NaCl (3.5%) solution.*

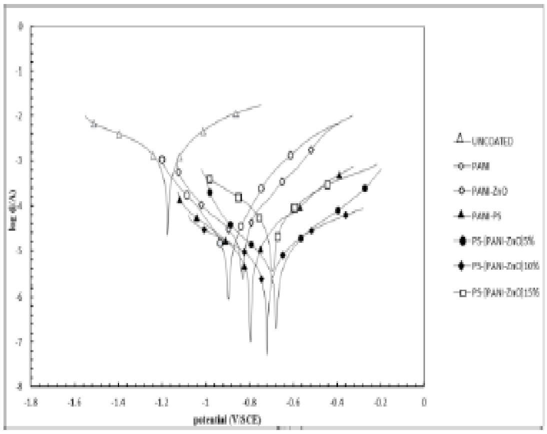

Figure 2. *Tofel plots of iron sample: (Δ) uncoated, coated with: (◇) PANI, (○) PANI-ZnO, (▲) PANI-PS, (●) PS-[PANI-ZnO 5%], (◆) PS-[PANI-ZnO 10%] and (□) PS-[PANI-ZnO 15%] coatings in NaCl (3.5%) solution.*

The values of corrosion potential, corrosion current and corrosion rate obtained from Tafel slope analysis of uncoated and coated iron samples have been shown in Table 1.

Table1. *Corrosion current and corrosion potential values of iron samples uncoated and coated with PANI, PANI-ZnO, PANI-PS, PS-[PANI-ZnO 5%], PS-[PANI-ZnO 10%] and PS-[PANI-ZnO 15%] coatings in NaCl (3.5%) solution.*

Coatings	Corrosion rate (mm/year)	E_{corr} (mV/SCE)	i_{corr} (μA)
Uncoated	7.3	1174-	631
PANI	0.46	-832	40
PANI-ZnO	0.29	-894	25
PANI-PS	0.10	-795	8.9
PS-[PANI-ZnO 5%]	0.073	-676	6.3
PS-[PANI-ZnO 10%]	0.046	-720	4
PS-[PANI-ZnO 15%]	0.45	-694	39

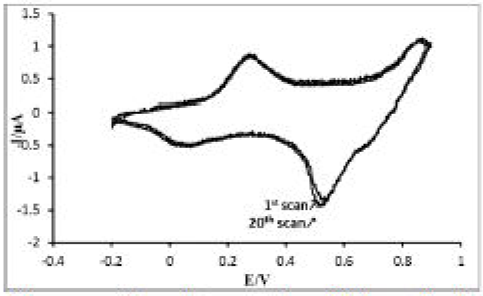

Figure 3. 1st and 20th Cyclic voltammograms of PS-[PANI-ZnO 10%] nanocomposite in 0.5 M HCl, scan rate of 50 mV/S, electrode area 0.25 cm²

3.3. FT-IR spectrum

In the FT-IR spectrum of pure PANI in curve [a] of Fig. 4 the absorption peaks at 140 cm−1 and 1580 cm−1 are attributed to the C-C stretching mode of benzonoid and quinoid rings in PANI chains respectively. The peaks at the wavenumbers of 1290 cm−1 and 3600 cm−1 are assigned to the C-N and N-H stretching bonds of the secondary amine group, respectively [7].

FT-IR spectra of ZnO (curve [b] of Fig. 4) shows three significant absorption peaks at the wavenumbers of 3500, 1500 and 400-600 cm-1. The absorption band at 400-600 cm-1 belongs to Zn-O stretching vibration. The peak near 1500 cm−1 is attributed to H-O-H bending vibration mode due to the presence of moisture [7].

The IR spectrum of PS (curve [c] of Fig. 4) showed absorption bands at 3050 and 2850 cm-1 that can be assigned to aromatic and aliphatic C-H stretchings, respectively. The peaks at 1600 and 1500 cm-1 are attributed to aromatic C=C stretchings. The C-H deformation vibration band of benzene ring hydrogen’s appeared at 950 cm-1[17].

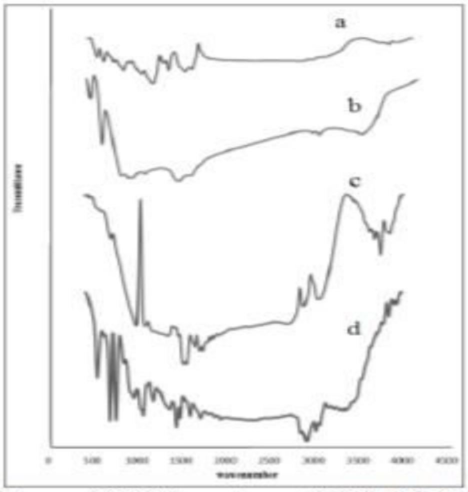

Figure 4. FT-IR spectrum of [a] PANI, [b] ZnO, [c] PS, [d] PS-[PANI-ZnO 10%] nanocomposite.

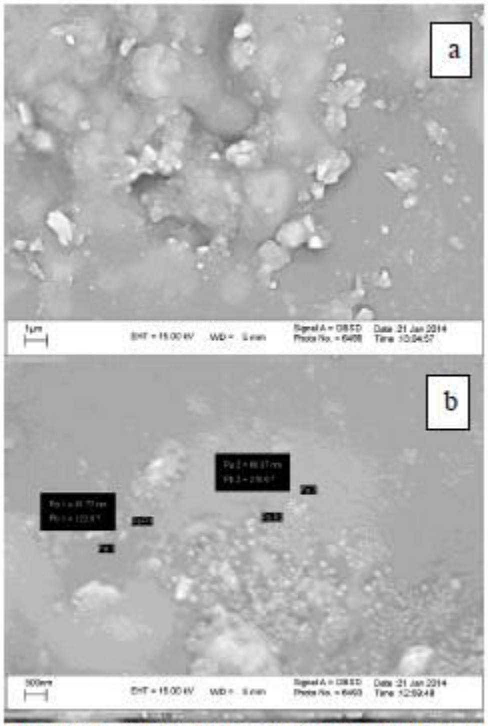

Figure 5. SEM micrographs of PS-[PANI-ZnO 10%] nanocomposite, [a] 1 μm and [b] 300 nm.

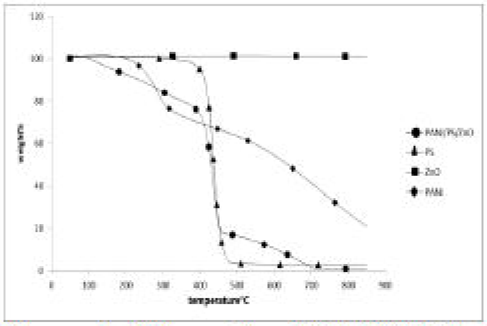

Figure 6. TGA results of (◆) PANI, (▲) PS, (■) ZnO, (●) PS-[PANI-ZnO 5%].

However, in PS-[PANI-ZnO 10%] nanocomposite, decomposition is improved in comparison to PANI at temperature ranges of about 300-400 °C and to PS at temperature ranges of about 450- 650 °C. It is probably due to the presence of a strong interaction at the interface of ZnO and PANI [23].

4. CONCLUSION

In the present work, PANI-ZnO nanocomposite was successfully synthesized by chemical polymerization of aniline in the presence of ZnO nanoparticles. 5, 10 and 15 percentages of PANI–ZnO nanocomposite were added to a solution of PS in THF to obtain PS-[PANI-ZnO 5%], PS-[PANI-ZnO 10%] and PS-[PANI-ZnO 15%] nanocomposites. The anticorrosive property of the prepared nanocomposites was studied by open circuit potential (OCP) and Tafel techniques in 3.5% NaCl solution as corrosive environment. It was demonstrated that the best corrosion protection effect belongs to the coating of PS-[PANI-ZnO 10%] nanocomposite in comparison to that of pure PANI, PANI–ZnO nanocomposite, PANI-PS composite and two other PANI-PS-ZnO nanocomposite coatings. The electroactivity of PS-[PANI-ZnO 10%] nanocomposite was studied and confirmed by CV studies. To characterize the composition and structure of PS-[PANI-ZnO 10%] nanocomposite, FTIR spectroscopy and SEM techniques were used. Also, to study of thermal stability of PS-[PANI-ZnO 10%] nanocomposite, TGA was used.

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