PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 6(2013), 119-128

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Effects of Nano Silica on the Anticorrosive Properties of Epoxy Coatings

Z. Ranjbar[1*], Sh. Ashhari[2], A. Jannesari[3] and Sh. Montazeri[4]

[1.] Associate Professor, (a) Center of Excellence for Color Science and Technology and (b) Department of Surface Coatings and Corrosion, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

[2.] M. Sc., Department of Surface Coatings and Corrosion, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

[3.] Assistant Professor, Department of Resins and Additives, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

[4.] Ph.D. Student, Department of Surface Coatings and Corrosion, Institute for Color Science and Technology(ICST), P.O. Box: 16765-654, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 12-01-2013
Final Revised: 16-05-2013
Accepted: 21-05-2013
Available online: 21-05-2013

Keywords:
Corrosion
Coating
Nano silica
Epoxy

ABSTRACT

In this study, a series of epoxy/silica nanocomposites were prepared by using nano silica particles which had different surface modifications. The morphology of the nanocomposite coatings was characterized by scanning electron microscopy (SEM). The effects of the hydrophilic and hydrophobic feature of the nano particles on the T_g and anticorrosive properties of nanocomposite coatings were evaluated by DSC and EIS instruments. It was observed that the presence of the hydrophobic nano silica particles affected the curing and cross linking density of the organic coatings and consequently reduction in corrosion resistance of nanocomposite coatings. On the other hand, hydrophilic nano composite coatings showed better corrosion resistance even after 60 days immersion in 3.5% NaCl solution in comparison to pure epoxy coating. Prog. Color Colorants Coat. 6(2013), 119-128. © Institute for Color Science and Technology.

1. Introduction

Using organic coatings as corrosion protectors on the metallic structures is a common way that is used widely in the world [1-6]. For increasing the corrosion protection efficiency of these coatings, they are mostly reinforced by some pigments and extenders like Zn, Fe_2O_3 and mica [6, 7]. In recent years, polymer nanocomposites have received significant attention by emerging the nano technology. Nano particles can improve the physical, mechanical and chemical properties of organic coating because of their structure or surface energy in comparison to pure polymers. There are several nano particles like nano silica, clay, ZnO, Fe_2O_3 and TiO_2that are used in organic coatings for improving the corrosion resistance [8-12].

Due to its structure, nano silica causes some unique mechanical, thermal and chemical properties in nanocomposites. There are some researches on the corrosion protection properties of silica based nanocomposites [13, 14]. Lu [14] showed that surface modification of silica can lead to better dispersion of

*Corresponding author: ranjbar@icrc.ac.ir

particles and less agglomerates that causes better corrosion resistance in composite.

In this study, hydrophilic and hydrophobic nanosilica particles were dispersed into epoxy matrix by grinding and milling. The effects of nanosilicas with different surface characteristics in different amounts of loadings were evaluated by electrochemical impedance spectroscopy (EIS) during 60 days immersion in 3.5% NaCl solution.

2. Experimental

2.1. Materials

Epoxy resin (EPIKOTE 828) and aromatic amine hardener were purchased from Momentive Co (EPIKURE F205). Nanosize hydrophilic silica (AEROSIL 200) and hydrophobic silica (AEROSIL R 972 V) were obtained from Degussa (Hanau, Germany) with the specifications given in Table 1.

2.2. Sample preparation

Different amounts of nano particles (2.5, 5 and 7.5 wt%) were gradually poured into the epoxy resin with stirring for 2 hr with a high-shear mixer and then milling by 1 mm zirconium pearls for 30 min.

For preparing the coatings, steel panels were degreased chemically by acetone and then polished mechanically with 600, 800, and 1000 emery papers. The stoichiometric amount of the hardener was added to the epoxy resin-containing nanoparticles. The mixtures were applied by a film applicator (ZEHNTNER 2000.1000 universal applicator) on steel panels with 30µ wet thickness.

After curing, the dry film thickness was about 25 µm. For better evaluation, three panels were coated by each coating composition.

2.3. Methods

The Tg of nanocomposite coatings with different amounts of nano particles were measured by differential scanning calorimetry (DSC) (DSC Pyris6, Perkin-Elmer).

Morphology of the nanocomposites was evaluated by scanning electron microscopy (SEM).

Corrosion protection effects of nano composites were investigated by electrochemical impedance spectroscopy (EIS) in a three electrode system made by Ivium Compactstat Company (Eindhoven, The Netherlands). A saturated calomel electrode and graphite rod was used as a reference electrode and auxiliary electrode, respectively. About 1 cm^2 of the coated metals were exposed to 3.5% NaCl electrolyte, and the rest was covered with a 75/25 beeswax–colophony mixture. The frequency range used was 100 kHz to 10 mHz, and the perturbation was 10 mV.

3. Results and discussion

3.1. Morphology investigations by SEM

Figure 1 shows the SEM images of the epoxy/ hydrophilic silica and epoxy/silica 972 nanocomposities with 7.5 wt% nano silica.

Table1: Nanosilica specification.

Type	pH	Average particle size
Hydrophilic silica	3.7-4.7	12 nm
Hydrophobic silica	3.6 - 4.4	16 nm

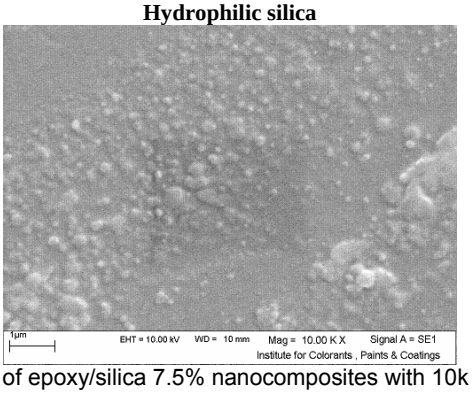

Figure 1: SEM of epoxy/silica 7.5% nanocomposites with 10k magnification.

Hydrophobic silica

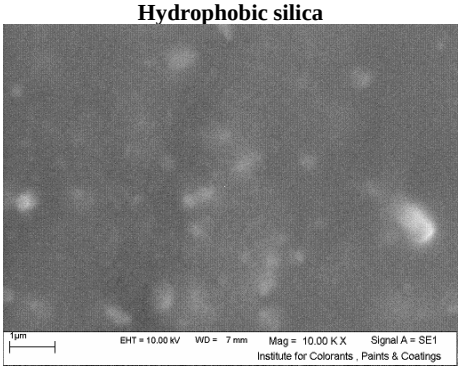

Figure 1: Continued.

It can be seen that the epoxy/ hydrophilic silica shows more aggregations, while epoxy/ hydrophobic silica shows better dispersion of nano particles with less aggregations.

Both of the samples are very homogeneous and free from any localization of matrix and micro cracks.

3.2. Measuring the Tg of nanocomposites by DSC

The glass transition temperatures (Tg) of epoxy/silica nanocomposites can be measured by using DSC instrument. Table 2 shows the DSC thermo gram curves. It can be seen that by increasing the amount of hydrophobic silica, Tg values reduces from 70 to 63 ^{0}C. So adding the hydrophobic nano silica particles to the epoxy matrix can affect the crosslink density of the nanocomposite coatings and reduce it and prevent the coating from complete curing. On the other hand, adding hydrophilic nano particles to the epoxy matrix does not have any remarkable effect on the Tg and consequently crosslink density of the nanocomposite coatings. Since the hydrophilic silica has more –OH groups on its surface, the interaction of this nanoparticle with epoxy macromolecular chains via hydrogen bonding between -OH groups of silanol and ethylene oxide groups from resin molecules can be occur.

3.3. Corrosion protection evaluation by EIS

The corrosion-protection properties of the epoxy–silica nanocomposite films were evaluated by measuring the coating resistance (Rpor) values and coating capacitance during different times of immersion in a 3.5% NaCl solution.

For obtaining the values of coating resistance and capacitance, Bode and Nyquist diagrams were fitted by the equivalent circuits, which are shown in Figure 2. In these circuits, Rsol, Rpor, and Ccoat are the resistance of the electrolyte, pore resistance and the capacitance of the coating, respectively.

Table2: DSC results.

	Hydrophobic silica	Hydrophilic silica
2.5%	63.44	68.98
5%	66.6	63.85
7.5%	63.72	67.89
blank	70.13	70.13

The Nyquist and Bode plots of the samples during different immersion times in 3.5% NaCl solution are shown in Figures 3 and 4. The obtained parameters after fitting the diagrams are listed in Tables 3,4,5 and 6.

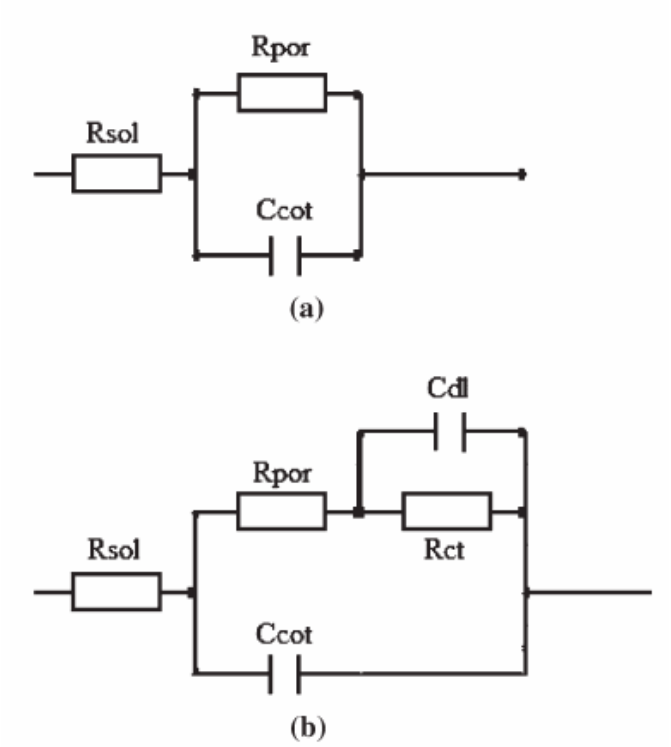

Figure 2: Equivalent circuits used to simulate the results of the EIS tests.

Table 3: Fitted parameters of epoxy/ hydrophilic silica nanocomposites.

Immersion day	2.5%		5%		7.5%	
	C(nF)	R (Gohm)	C(nF)	R (Gohm)	C(nF)	R (Gohm)
1	0.1495	54.98	0.1592	49.78	0.1829	20.50
30	0.1474	1.205E	0.1468	2.499	0.1782	5.034
60	0.1401	1.140	0.1707	1.642	0.1839	2.046

Table 4: Fitted parameters of epoxy/ hydrophobic silica nanocomposites.

Immersion day	2.5%		5%		7.5%	
	C(n F)	R (Gohm)	C(nF)	R (Gohm)	C(nF)	R (Gohm)
1	0.1093	10.76	0.1762	5.470	0.2040	8.010
30	0.1531	0.1201	0.2000	0.004	0.1534	0.002
60	0.1391	0.05859	0.2133	0.007	-	0.008E-02

Table 5: Fitted parameters of blank epoxy coatings.

Immersion day	Blank	
	C(nF)	R (Gohm)
1	0.2227	1.346
30	0.1093	0.0693
60	0.1500	0.0250

When a capacitor and a resistor are parallel in the circuit, phase difference between current and voltage is a criterion for current flow through either capacitor or resistor. The coating is capacitive if the resistance and/or capacitance are high, and the phase angle would be near 900. The coating is resistive if the resistance and/or capacitance are low, and the phase angle would be near 0. According to the Table 6, hydrophilic nanocomposites show capacitive behavior during immersion time while hydrophobic nanocomposite is more resistive.

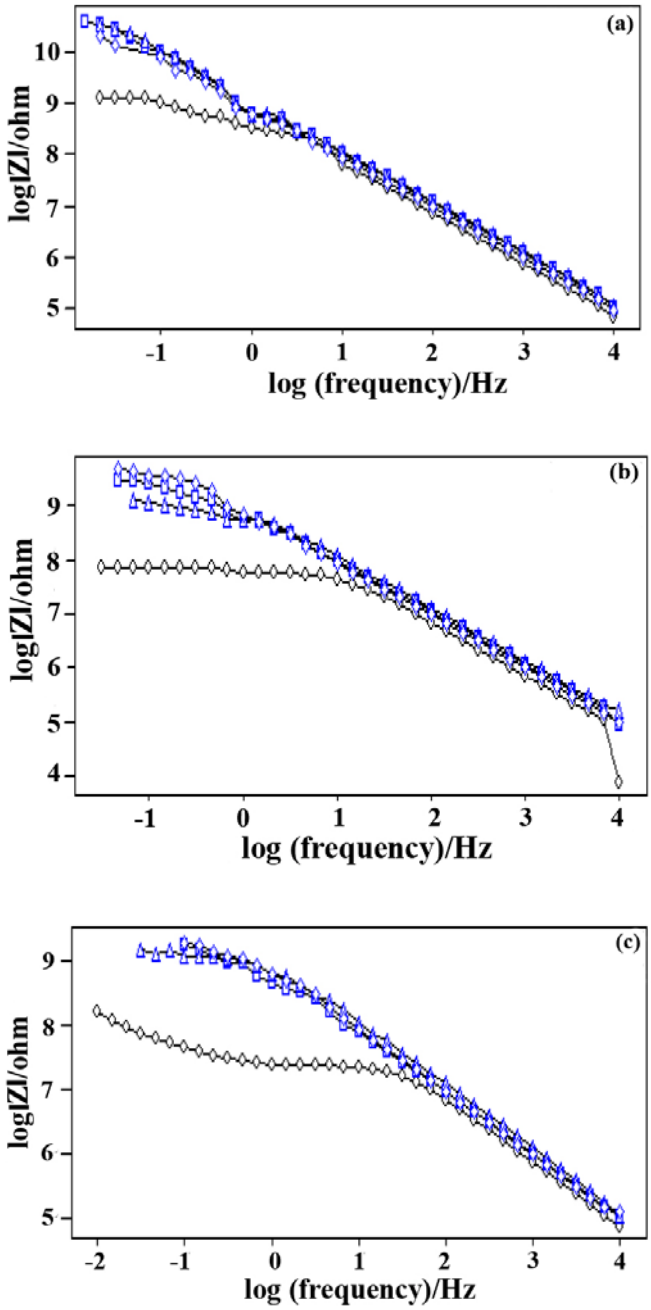

Figure 3: Bode plots of epoxy/silica nanocomposites during different immersion times: (O) blank, (Δ) 2.5, (□) 5, (◊) 7.5, (a) 1day (b) 30 days and (c) 60 days immersion in hydrophobic silica; (a′) 1day (b′) 30 days and (c′) 60 days immersion in hydrophilic silica.

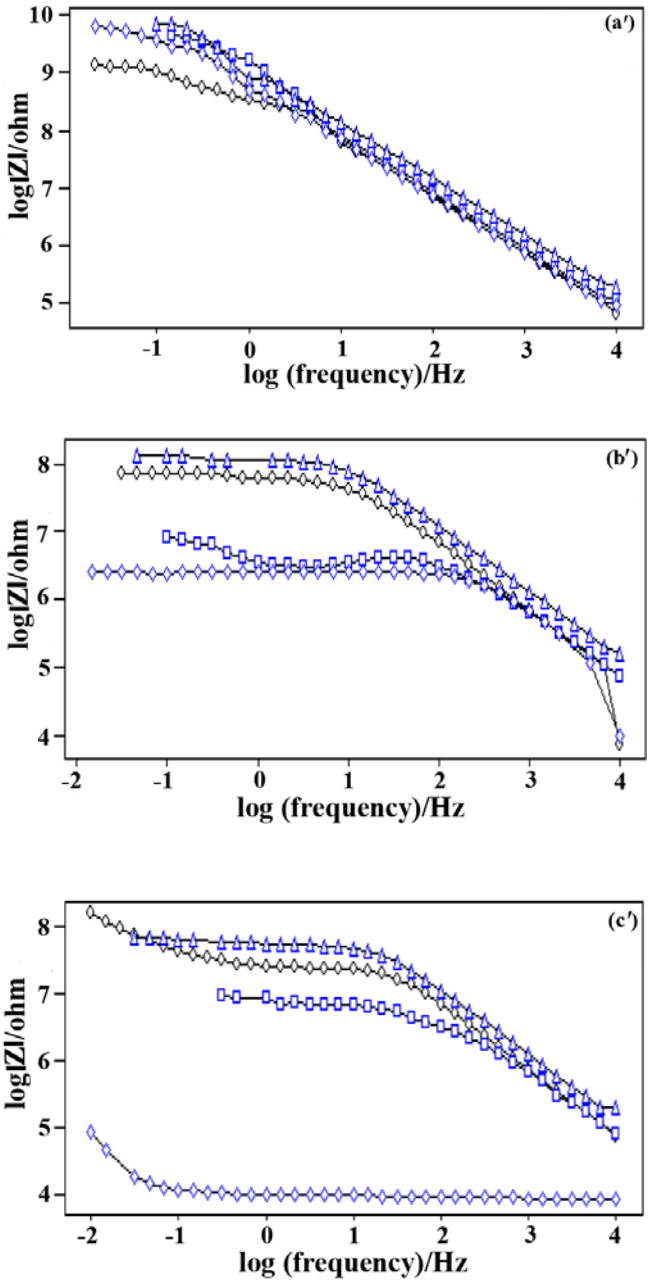

Figure 3: Continued.

Table 6: Absolute phase values at high frequencies.

Immersion day	Hydrophilic silica			Hydrophobic silica			Blank
	2.5%	5%	7.5%	2.5%	5%	7.5%	
1	90	90	90	89	90	89	90
30	89	90	89	84	82	80	90
60	90	89	90	84	81	-	89

It can be seen that by adding the hydrophilic nano silica to the epoxy coatings, the corrosion resistance of the coatings (i.e. R values) increases. On the other hand, the presence of hydrophobic nano particle causes the decrement of corrosion resistance of nano composite coatings.

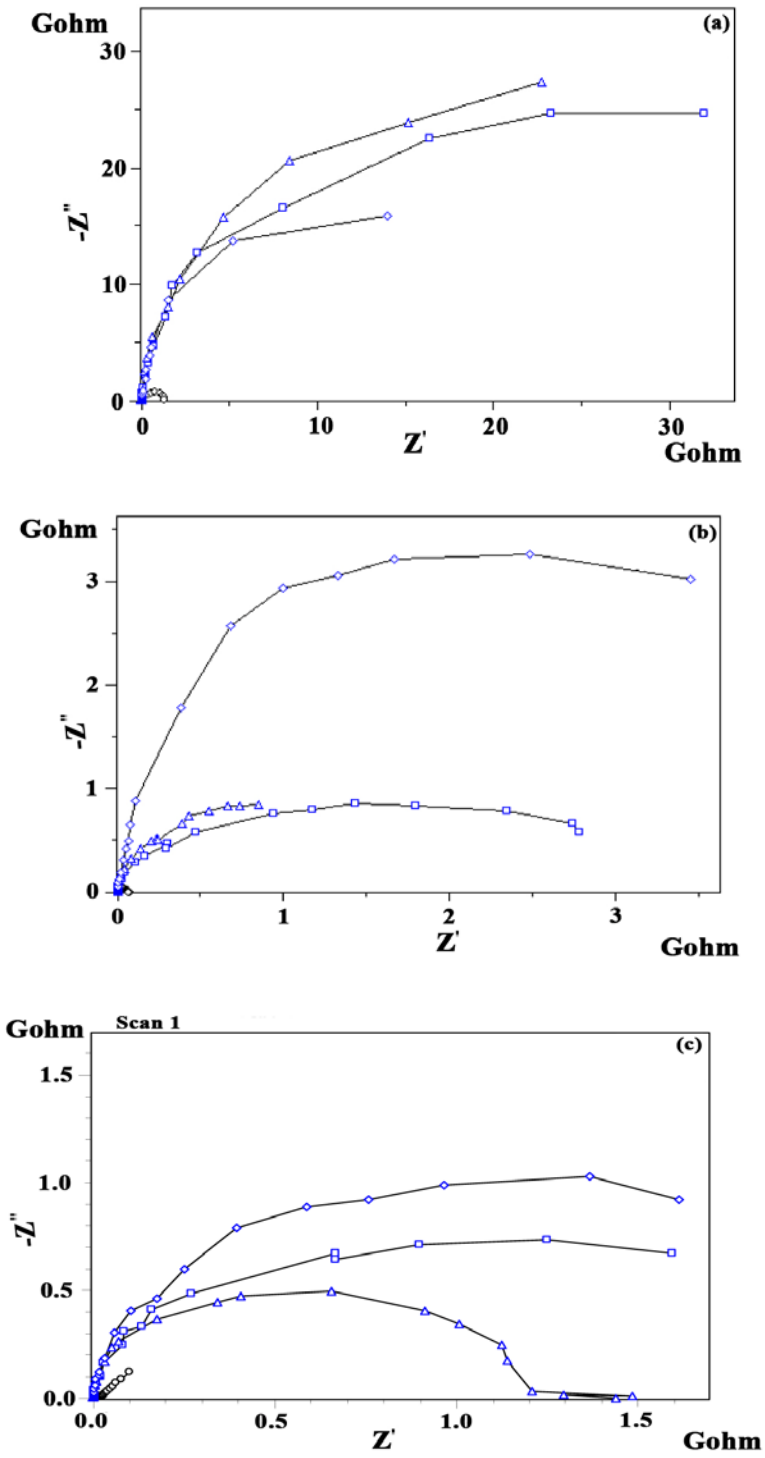

Figure 4: Nyquist plots of epoxy/silica nanocomposites during different immersion times (O) blank, (Δ) 2.5, (□) 5, (◊) 7.5, (a) 1day (b) 30 days and (c) 60 days immersion in hydrophilic silica; (a′) 1day (b′) 30 days and (c′) 60 days immersion in hydrophobic silica.

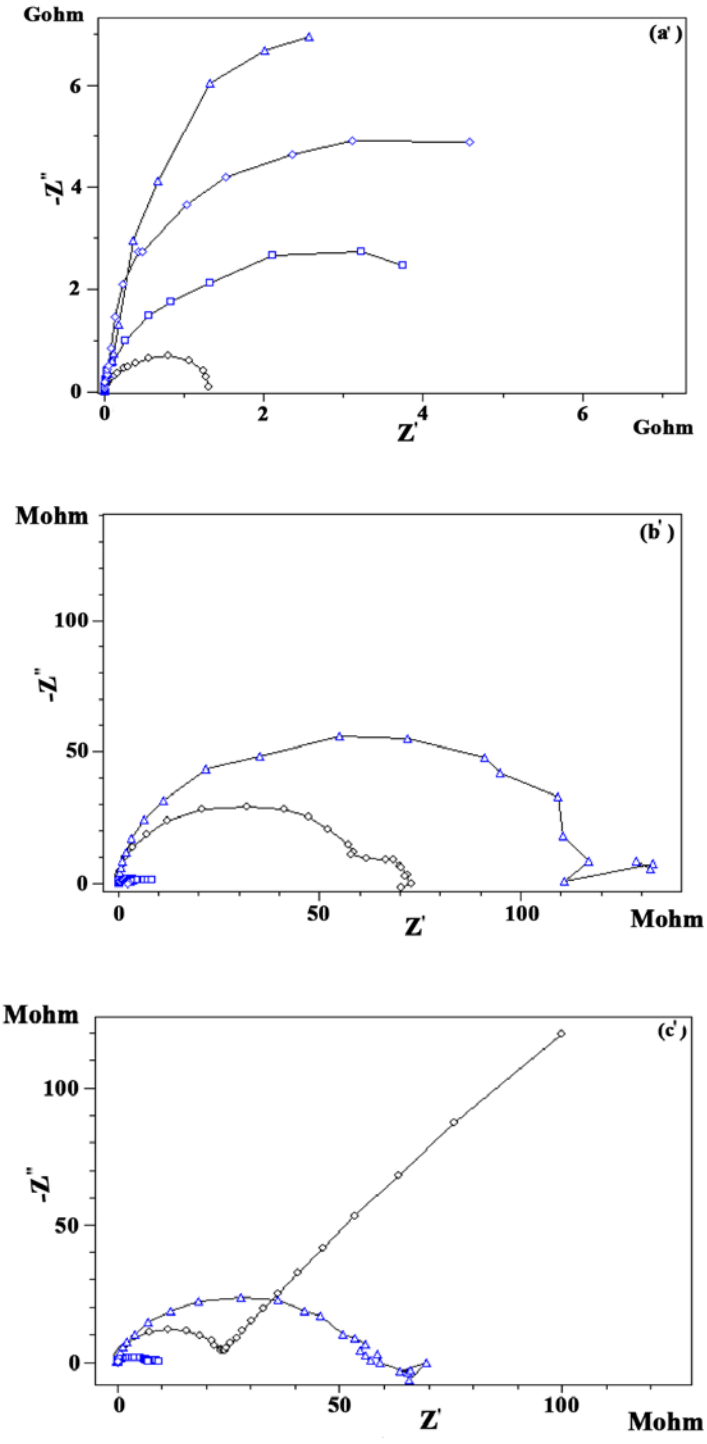

Figure 4: Continued.

Bode plots show that during different immersion times, the decrement of log IZI values at low frequencies that show the total resistance of coating system in hydrophilic nanocomposites is less than that of the epoxy and hydrophobic nanocomposite coatings. It can be concluded that the hydrophilic nano particles can make tortuous path for penetration of corrosive ions of electrolyte, causing a delay in corrosion process.

From Tables 3-6 it can be seen that the changes in C values are negligible during the immersion time, so the nanocomposites show resistive behavior.

4. Conclusions

According to the obtained results it can be seen that the presence of hydrophilic nano silica can improve the corrosion protection of epoxy nanocomposite in comparison to epoxy coatings and epoxy/hydrophobic silica nanocomposites. The hydrophilic nano silica does not have any considerable effect on the Tg and consequently on the crosslinking density of the coatings. Hydrophobic nano silica reduces the Tg and crosslinking density of nanocomposites. The less the crosslinking density of coatings, the easier the penetration of corrosive ions through the film and less corrosion resistance of the coatings. Besides, the agglomerates in the epoxy/ hydrophobic silica nano composite coatings (SEM images) are defects that can reduce the corrosion resistance and corrosion protection property of the nanocomposites by simplifying the ions transmission through the coating.

Acknowledgement

The authors sincerely thank the Center of Excellence for Color Science and Technology for making this investigation possible. We would also like to thank Miss Golnaz Yousefi for her help throughout the project.

5. References

1. R. Selvaraj, M. Selvaraj, S. V. K. Iyer, R. Selvaraj, M. Selvaraj, S. V. K. Iyer, Studies on the evaluation of the performance of organic coatings used for the prevention of corrosion of steel rebars in concrete structures, *Prog. Org. Coat.*, 64(2009), 454-459.
2. A. Kalendová, D. Veselý, J. Stejskal, Organic coatings containing polyaniline and inorganic pigments as corrosion inhibitors, *Prog. Org. Coat.*, 62(2008), 105-116.
3. G. Grundmeier, W. Schmidt, M. Stratmann, Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation, *Electrochim. Acta*, 45(2000), 2515-2533.
4. L. Jianguo, G. Gaoping, Y. Chuanwei, EIS study of corrosion behavior of organic coating/ Dacromet composite systems, *Electrochim. Acta*, 50(2005), 3320-3332.
5. J. Ou, J. Wang, J. Zhou, Sh. Liu, Y. Yu, X. Pang, Sh. Yang, Construction and study on corrosion protective property of polydopamine-based 3-layer organic coatings on aluminum substrate, *Prog. Org. Coat.*, 68(2010), 244-247.
6. Z. Ranjbar, S. Montazeri, M. Jalili, Optimization of a Waterborne Epoxy Coatings Formulation via Experimental Design, *Prog. Color Colorants Coat.*, 2(2009), 23-33.
7. B. Nikravesh, B. Ramezanzadeh, A. A. Sarabi, S. M. Kasiriha, Evaluation of the corrosion resistance of an epoxy-polyamide coating containing different ratios of micaceous iron oxide/Al pigments, *Corros. Sci.*, 53 (2011), 1592-1603.
8. S. González, I. C. Mirza Rosca, R. M. Souto, Investigation of the corrosion resistance characteristics of pigments in alkyd coatings on steel, *Prog. Org. Coat.*, 43(2001), 282-285.
9. Sh. K. Dhoke, A. S. Khanna, Effect of nano-Fe_2O_3 particles on the corrosion behavior of alkyd based waterborne coatings, *Corros. Sci.*, 51(2009), 6-20.
10. M. Rashvand, Z. Ranjbar, S. Rastegar, Nano zinc oxide as a UV-stabilizer for aromatic polyurethane coatings, *Prog. Org. Coat.*, 71(2011), 362-368.
11. M. Rashvand, Z. Ranjbar, S. Rastegar, Preserving anti-corrosion properties of epoxy based coatings simultaneously exposed to humidity and UV-radiation using nano zinc oxide, *J. Electrochem. Soc.*, 159(2012), C129-C132.
12. Sh. Ashhari, A. A. Sarabi, S. M. Kasiriha, D. Zaarei, Aliphatic polyurethane-montmorillonite nanocomposite coatings: preparation, characterization,

and anticorrosive properties, *J. Appl. Polym. Sci.*, 119(2011), 523-529.

13. X. Zhang, F. Wang, Y. Du, Effect of nano-sized titanium powder addition on corrosion performance of epoxy coatings, *Surf. Coat. Technol.*, 201(2007), 7241-7245.
14. R. Zandi-Zand, A. Ershad-Langroudi, A. Rahimi, Silica based organic–inorganic hybrid nanocomposite coatings for corrosion protection, *Prog. Org. Coat.*, 53(2005), 286-291.
15. H. B. Lu, Y. Hu, M. H. Gu, S. C. Tang, H. M. Lu, X. K. Meng, Synthesis and characterization of silica–acrylic–epoxy hybrid coatings on 430 stainless steel, *Surf. Coat. Technol.*, 204(2009), 91-98.