



Studying the Corrosion Protection Behavior of an Epoxy Composite Coating Reinforced with Functionalized Graphene Oxide by Second and Fourth Generations of Poly(amidoamine) Dendrimers (GO-PAMAM-2, 4)

M. Maadani¹, S. H. Jafari^{2*}, M. R. Saeb³, B. Ramezanzadeh⁴**, F. Najafi³, D. Puglia⁵

² School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box: 11155-4563, Tehran, Iran

³ Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran

⁴ Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran

⁵ Materials Science and Technology, Civil and Engineering Department, Università di Perugia, Loc. Pentima Bassa 21, 05100 Terni, Italy

ARTICLE INFO

Article history: Received: 24 Aug 2019 Final Revised: 31 Dec 2019 Accepted: 01 Jan 2020 Available online: 09 May 2020 Keywords: Epoxy nanocomposite poly(amidoamine) dendrimer graphene oxide corrosion resistance EIS.

ABSTRACT

n this research, graphene oxide (GO) nanoparticles were modified by second and fourth generations of poly(amidoamine) dendrimers in order to improve the particle dispersion quality in the epoxy matrix and therefore its barrier anti-corrosion performance. Confirmation on the GO surface modification by Polyamidoamine generation 2 (PAMAM2) and polyamidoamin generation 4 (PAMAM4) was carried out by Fourier transforms infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The corrosion protection properties of the epoxy composites against corrosive electrolyte (3.5 wt.% NaCl solution) was investigated by salt spray and electrochemical methods. The dispersion of unmodified and modified GO sheets in the epoxy matrix was studied by FE-SEM analysis. The FT-IR test results evidenced that the GO sheets were successfully modified with PAMAM 2 and 4 via the covalent binding mechanism. Salt spray and EIS test results revealed that the epoxy composites loaded with GO-PAMAM4 and PAMAM4 showed the highest improvement in the corrosion resistance. FE-SEM images from the fracture surface of the coatings revealed that the dispersion of GO sheets within the epoxy coating was improved after modification by PAMAM4. Prog. Color Colorants Coat. 13 (2020), 261-273© Institute for Color Science and Technology.

1. Introduction

Corrosion of the metallic substrates in exposure to outdoor conditions is an unavoidable and unpleasant fact in many industrial applications. A variety of protection methods has been applied to mitigate the corrosion of metals in different applications. Organic coatings are frequently used as one of the effective barrier anticorrosion systems on the metallic substrate. One of the most common resins which have been widely used for this purpose is epoxy. There are different types of epoxy resins that are used in different applications. They show good adhesion to the metal substrates, and because of the high cross-linking density, they can provide a good level of corrosion protection for metals. However, due to the

¹ School of Chemical Engineering, College of Engineering, University of Tehran, Kish International Campus, P.O. Box: 141763-3644, Tehran, Iran

presence of some micro-pores or defects in the coatings as well as coating deterioration in the outdoor condition, they cannot show long-term protection ability. In order to increase the lifetime of the organic coatings and postpone the coating deterioration in the corrosive environments, some fillers such as nanomaterials are added to the coating formulation [1, 2]. In this regard, Ganjaee et al. studied the impact of hybrid graphene oxide/Closite20A montmorillonite (MMT) nanoclay (NC) fillers on the anti-corrosion behavior of the epoxy film [3]. Ye et al. studied the super-hydrophobic polyhedral oligomeric silsesquioxane and functionalized graphene oxide via one-step condensation reaction [4]. Yang et al. studied the effect of polyaniline-modified graphene oxide on metal corrosion resistance improvement [5]. Yang et al. studied another novel modification of 3,4,9,10-perylene tetracarboxylic acidgraphene composite (PTCA-G) and reported the improvement of particles stability and dispersion in the epoxy coatings [6]. Chi et al. studied the correlation of the graphene sheets dispersion and barrier anti-corrosion properties [7].

Graphene oxide (GO) is an advanced material with unique properties like high Young's modulus (about 1100 GPa), tensile strength (130 GPa) and excellent impermeability properties against water, ions, and gases (like oxygen). GO has become an eminent nanoparticle for the improvement of final properties of epoxy resin. Specific 2D nano-scale GO sheets containing various oxygen functional groups, exhibit excellent electrical, optical, thermal, mechanical and chemical properties [8]. At low concentrations of GO nanoparticles, the modulus, tensile strength, and toughness can be significantly enhanced due to the formation of the highly cross-linked network. Consequently, the epoxy/GO nanocomposites have been frequently used in some electronic devices [9, 10], electromagnetic interference shielding [11] and aerospace [12]. The main challenge of using GO sheets in the polymer matrix is their poor interaction with the epoxy resin, leading to the poor dispersion of the particles. One common solution for this shortcoming is the chemical modification of GO sheets via different materials or polymers. For example, Pourhashem et al. applied an amino-silane on the graphene oxide to improve the anti-corrosion properties of the epoxy coating [13]. Sheng et al. analyzed the anti-corrosion behavior of the graphene oxide particles functionalized with aniline and reported significant improvement in the dispersion state of the particles and anti-corrosion behavior of the coating [14]. Zheng et al. modified the graphene oxide with urea-formaldehyde and reported remarkable improvement in the epoxy film barrier anticorrosion properties [1]. Yu et al. investigated the impact of covalent modification of the graphene oxide by metronidazole on the epoxy coating corrosion resistance improvement [15]. Different types of modifications have been performed on the graphene oxide. One attractive approach that has been rarely studied is the use of dendrimers. Nonahal et al. studied the cure kinetics of the epoxy coatings in the presence of graphene oxide nanosheets modified with the second generation of poly(amidoamine) dendrimer. However, the role of GO sheets modified via dendrimer on the anti-corrosion behavior of the organic coatings has not been studied yet [16]. Dendrimers were discovered in the 1980s by Donald Tomalia and his colleague [17]. They named these hyper-branched molecules as "dendrimers". Dendrimers can be prepared by divergent and convergent methods. In the divergent method, the dendrimer grows outside of a multifunctional core molecule. This procedure is efficient for producing a large number of dendrimers. In the convergent method, the dendrimer can be synthesized step by step, starting from the branches towards the core [18]. The structure of the dendrimer molecules consists of an atom or group of atoms named "core" and branches of other atoms named "dendron". The next generations are added at each synthetic cycle which has two steps [19].

In this study, for the first time, the GO sheets were modified by second and fourth generations of poly(amidoamine) dendrimers and applied to enhance the anti-corrosion properties of epoxy composite coating. The most significant aim of this research is to study the effect of PAMAM on the corrosion protection properties of the epoxy nanocomposite coating. For this purpose, salt spray and EIS tests were applied on both defected and undefected coatings. The modification of GO sheets by PAMAM2 and PAMAM4 was investigated by FT-IR and TGA methods.

2. Experimental

2.1. Materials

Epoxy resin (solid Resin) (EPON[™] 828) and hardener (EPIKURE F205) were provided from Huntsman Co., USA, and Hexion Inc. (Columbus, OH, USA), respectively. The extra pure Methanol, dimethylformamide (MDF), and Hydrochloric acid (HCl) were provided from Merck (Germany). Steel substrates (ST-12) were prepared from Mobarakeh steel Co. (Iran). Graphite was purchased from Kropfmuehl Graphite Co. (Germany) [20]. PAMAM 2 and PAMAM4 were prepared according to the method reported in [21].

2.2. GO sheets functionalization via second and fourth generations of PAMAM

GO sheets were synthesized according to the modified Hummer's method and the synthesis details are reported elsewhere [20]. The GO dispersion in methanol was obtained through a solvent exchange, centrifugation and sonication methods. In order to modify the surface of GO nanoparticles, 9.5 mL of GO dispersion in methanol was added to 11 mL of solutions of PAMAM second and fourth generations in methanol. Then, they were mixed under ultrasonication for 6 min in an ice bath. In the next step, the functionalized (GO-PAMAM2 GO and GO-PAMAM4) were filtered and washed with methanol three times to remove the excess PAMAM. The halfgenerations of PAMAM dendrimers (e.g., 0.5, 1.5, and

2.5) possess anionic surfaces due to the presence of carboxylate groups. The number of reactive sites of each generation is reported in Table 1. Therefore, PAMAM2 and PAMAM4 include 16 and 64 surface groups, respectively [22].

2.3. Metal substrates surface preparation and coating application procedures

0.15 wt.% unmodified and modified GO sheets were added to the epoxy resin and mixed via a mechanical mixer. Then, 0.15 wt.% PAMAM-2 and 4 were also added to the epoxy resin. After mixing according to equivalents, hardener was added to the epoxy resins without and with additives (with a molar ratio of 2:1 M/M of epoxy: hardener). Finally, the prepared composite coatings were applied on cleaned steel substrates (ST12) with thickness of 2 mm and dimension of 10×15 cm.

Before coating the surface by film applicator [23], the surface was polished by sandpapers (600, 800 and 1000 grades), rinsed with acetone, and finally washed with distilled water. The coated samples were cured in an oven at 80 °C for 2 h. The coating thickness after curing was $60\pm0.1 \mu m$. Table 2 presents the name and formulation of various coatings.

Generation	Molecular Mass (gr/mol)	Number of Surface groups
0	516	4
1	1428	8
2	3252	16
3	6900	32
4	14196	64
5	28788	128
6	57972	256
7	116340	512
8	233076	1024
9	466548	2048
10	933492	4096

Table 1: Some specifications of PAMAM dendrimers with ethylenediamine core [22].

Nanocomposite code	additive	Content (%)*	
Neat EP	-	-	
EP-GO	GO	0.15	
EP-GO- PAMAM2	GO-PAMAM2	1.65	
EP-GO- PAMAM4	GO-PAMAM4	1.65	
EP-PAMAM2	PAMAM2	1.5	
EP-PAMAM4	PAMAM4	1.5	
*Weight memory to a based on the solid mainly of main and hands on			

Table 2: Composition of the prepared nanocomposites.

Weight percentage based on the solid weight of resin and hardener.



Figure 1: Chemical structures and schematic view of PAMAM2 and PAMAM4 dendrimers.

2.4. Characterization

Chemical structure of PAMAM2, PAMAM4, GO, GO-PAMAM2, and GO-PAMAM4 was characterized by an FT-IR instrument (Spectrum one, PerkinElmer Inc., Boston, MA). For FT-IR analysis, a KBr pellet of each sample was prepared and tested in a transmission mode within the wavenumber range of 4000-450 cm⁻¹ with a resolution of 4 cm⁻¹. The number of PAMAM molecules attached to the surface of the GO particles can be determined using equation 1. The grafting ratio (Gr) was calculated by using equation 1. The determined values for GO-PAMAM2 and GO-PAMAM4 were 16.58 and 23.68 percent, respectively. These results proved the higher adsorption of PAMAM 4 on the GO sheets due to its higher functionality [24].

$$Gr = \frac{W_{(Modified-bare)}}{1 - W_{(Modified-bare)}}$$
(1)

Electrochemical impedance spectroscopy (EIS) was conducted on the coated samples to evaluate electrochemical behavior. For this purpose, 1 cm² of the metal substrates coated with the epoxy nanocomposite was selected for the test and the rest of the sample was sealed with a blend of beeswaxcolophony. An ACM-Gill instrument was employed for performing the EIS test within the defined frequency range of 100 kHz to 0.01 Hz at open circuit potential (OCP vs. Ag/AgCl) with ±10 mV peak-to-peak amplitude. For studying the repeatability of the electrochemical test data, the EIS measurement was carried out on three replications and the mean values were reported. For the non-scratched coatings, the test was performed after 9 and 34 days of immersion in 3.5 wt.% NaCl solution. The EIS measurements were also applied to the scratched coatings. For this purpose, a scratch of 0.5 cm in length was created on the coatings with a surgical knife. Then, the EIS measurements were conducted on these samples after 6 and 24 h immersion in 3.5 wt.% NaCl solution. In the EIS measurement, a three-electrode cell comprising of Ag/AgCl (reference electrode), platinum (counter electrode) and steel samples (working electrode) was

employed. The anti-corrosion performance of the nanocomposites was further analyzed by the salt spray test according to ASTM B117 (NaCl 5 wt.% solution). Before the test, scratches with 1 mm in width and 4 cm in length were created on the samples coated with epoxy coating. The microstructure of the fracture surfaces in different samples was investigated by FE-SEM (Supra 25, Zeiss, Germany).

3. Results and Discussion

3.1. FT-IR analysis results

The FT-IR spectra related to the GO, GO-PAMAM2, GO-PAMAM4, PAMAM2, and PAMAM4 samples are shown in Figure 2. It is clear from the figure that the spectra of PAMAM2 and PAMAM4 are approximately the same with slight displacements in the location of the peaks. PAMAM2 and PAMAM4 can be chemically bonded to the graphene oxide surface through the reaction between the amine groups of PAMAM and the epoxide groups of the GO. In addition, due to the presence of C=O groups in the PAMAM structure, the interactions between the GO and PAMAM maybe also in the form of hydrogen bonding and π - π interactions. The C-N bond stretching is seen at 1280.26 cm⁻¹ and 1275.05 cm⁻¹ for PAMAM2 and PAMAM4 samples, respectively. The bending vibration of N-H absorption band in PAMAM2 and PAMAM4 samples is visible at 1557.58 and 1557.42 cm⁻¹, respectively. The C=O absorption bands of PAMAM2 and PAMAM4 are observed at 1650.51 and 1651.65 cm⁻¹, respectively. Peaks at 2840.51 and 2934.51 cm⁻¹ in PAMAM2 and 2841.59 and 2936.40 cm⁻¹ in PAMAM4 are related to the C-H absorption bands. The stretching of the primary amines is visible in 3078.78 and 3077.56 cm⁻¹ in PAMAM2 and PAMAM4, respectively. For GO, the epoxy groups, acidic C=O bond, and O-H groups are clearly visible at 831.51, 1731.03 and 3429.64 cm⁻¹, respectively. According to graphs of GO-PAMAM4 and GO-PAMAM2, the location of OH groups moved to lower frequency because of merging two peaks. In fact, the FT-IR results further proved the reaction between NH₂ and graphene oxide groups.



Figure 2: FT-IR spectra of GO, GO-PAMAM2, GO-PAMAM4, PAMAM2, PAMAM4 samples.

Figure 3 shows the TGA results for GO, PAMAM2, PAMAM4, GO-PAMAM2, and GO-PAMAM4 samples. The first mass loss observed in the plots of all samples is below 100 °C, which is due to the removal of the water molecules adsorbed on the unmodified and modified GO sheets via physical hydrogen bonds (related to physically absorbed water). It is clear that the neat (unmodified) GO showed higher weight loss compared to other samples at this temperature range, demonstrating the decrement of the GO surface hydrophilicity properties after adsorption of PAMAM

266 Prog. Color Colorants Coat. 13 (2020), 261-273

molecules. The second mass loss was observed within the temperature range of 100-350 °C, which is related to the decomposition of labile oxygen-containing functional groups [24]. The lower mass loss of the modified GO than unmodified one indicates that the PAMAM could delay the GO functional groups' decomposition. However, the story is completely different at temperatures higher than 350 °C. The modified GO sheets showed lower thermal resistance than neat GO due to the PAMAM structure decomposition. According to the FT-IR and TGA test results, it has been proved that the GO surface was successfully modified by PAMAM molecules. Figure 4 shows the schematic view of GO modification by PAMAM2 and PAMAM4. The NH₂ groups of PAMAM2 and PAMAM4 could react with the epoxy and carboxylic groups of GO.

3.2. FE-SEM morphology analysis of fracture surface of the coatings

FE-SEM images (Figure 5) were taken from the crosssection of the coatings to study the fracture surface morphology and investigate the dispersion state of the nanoparticles in the epoxy matrix.



Figure 3: TGA thermograms of GO, PAMAM2, PAMAM4, GO, GOPAMAM2 and GOPAMAM4.



Figure 4: Schematic view of modification of GO with PAMAM2 and PAMAM4 dendrimers.



Figure 5: FE-SEM images of (a) EP, (b) EP-GO, (c) EP-GO-PAMAM2, (d) EP-GO-PAMAM4, and (e) EP-PAMAM2 coatings.

According to the FE-SEM images given in Figure 5, the neat epoxy (EP) and EP-PAMAM2 fracture surfaces are almost clean and smooth, indicating the brittle nature of the coatings. Nevertheless, adding graphene oxide and modified graphene oxide particles could change the coating behavior from brittle to ductile. By comparing the fracture morphologies of the samples including graphene oxide particles and modified graphene oxide, it can be seen than the behavior has changed from ductile with a sharp edge to ductile with a soft edge from graphene oxide to modified graphene oxide.

It is clearly visible from the FE-SEM images that the broken edges of the neat EP and EP-PAMAM2 samples are smooth which indicates the brittle fracture, while for the EP-GO, EP-GO-PAMAM2, and EP-GO- PAMAM4 samples, rough surface morphology was observed. The presence of less cracks and ruptures in the fracture surface of the coatings filled with the modified GO (especially GO-PAMAM4) than GO demonstrates that the modified GO could form stronger interactions with the epoxy matrix due to better dispersion properties. These observations are in accordance with the corrosion results where the modified GO, especially the one modified by PAMAM4, could result in higher corrosion resistance.

3.3. Corrosion studies of composite coatings

3.3.1. Salt spray test results

Visual images are provided from the surface of EP, EP-GO, EP-PAMAM2, EP-PAMAM4, EP-GO-PAMAM2,

and EP-GO-PAMAM4 samples exposed to salt spray test condition for 48 h and 28 days (Figure 6).

According to Figure 6, all samples except the blank epoxy show slight corrosion of the steel substrate adjacent to the scratch zone after 48 hours. However, after 24 days of exposure, results revealed severe coating blistering, reflecting the deterioration of the interfacial adhesion bonds and formation of corrosion products around and beneath the coatings without filler and the ones containing PAMAM2. According to the results, the PAMAM4 and EP-GO-PAMAM4 samples showed the best anti-corrosion performance. The neat epoxy coating showed the weakest anti-corrosion properties. These observations reveal that the PAMAM4 could better improve the coating barrier property (in the presence and/or absence of GO sheets) in comparison with the PAMAM2. The corrosion resistance in salt spray test for the scratched samples increases in the order of EP<EP-PAMAM2<EP-GO-PAMAM2<EP-GO<EP-PAMAM4, EP-GO-PAMAM4.

3.3.2. Electrochemical impedance spectroscopy (EIS) measurements

EIS test was performed on the non-defected coatings after 9 and 34 days of immersion in NaCl solution. The Bode plots of the samples are shown in Figure 7. According to the literature, the coating degradation extent can be studied through investigation of the lowfrequency impedance [25, 26], without modeling the impedance data by any equivalent circuit. So, the impedance values at 10 mHz were obtained from the Bode plots and reported in Figure 8 for various samples at two immersion times.



Figure 6: Visual images of the coatings after 48 hours (a to f) and 24 days (g to I) exposure to salt spray test; EP, (a, g) EP-GO, (b, h) EP-PAMAM2, (c, i) EP-PAMAM4, (d, j) EP-GO-PAMAM2 (e, k), and EP-GO-PAMAM4 (f, I).



Figure 7: Time-dependent Bode plots for the non-scratched pure epoxy and nanocomposite coatings after 9 (a) and 34 (b) days immersion in saline solution.



Figure 8: The impedance values at the lowest frequency (10 mHz) of the non-scratched samples after 9 and 34 days immersion in 3.5 wt.% NaCl solution.

As can be seen in Figure 8, the highest and the lowest impedance values after 9 days of immersion belong to the EP-PAMAM4 and EP-GO-PAMAM2 samples, respectively. The results after 34 days of immersion show that the highest impedance values of about 10^{8.4} ohm.cm² and 10^{8.2} ohm.cm² belong to the and EP-GO-PAMAM4 EP-PAMAM4 samples, respectively. The impedance values of the EP-PAMAM2 and EP-GO-PAMAM2 samples are lower than those of the EP-PAMAM4 and EP-GO-PAMAM4 samples. Results declared that all the samples showed higher impedance values than the neat epoxy. There is a significant impedance difference between neat epoxy and other nanocomposites after 34 days of immersion, Whereas in day 9, the impedance values of all samples were almost the same. The impedance value of the neat epoxy after 34 days is about 10^{5.2} ohm.cm², indicating 37.5% reduction in impedance compared to the initial immersion times. By comparing the impedance values after 9 and 34 days of immersion, a slight decrease from 10^{8.8} to 10^{8.5} ohm.cm² can be noticed which shows about 3.4% decrement in the logarithmic scale. In other words, PAMAM4 showed the best results among other samples in this research. The effect of PAMAM4 on the enhancement of the anti-corrosion properties of epoxy coating, either for direct application or as a modifier for GO, is obvious from the EIS results. Generally, results depicted that the PAMAM4 had a more significant role in the corrosion resistance improvement of the epoxy coating than PAMAM2. The presence of PAMAM4 on the GO nanoparticles improves the dispersion quality and as a result, the barrier action of the well-dispersed GO sheets in the epoxy matrix is the reason for the enhancement of the coating anti-corrosion properties after introducing the PAMAM4-GO particles. PAMAM4 could improve the corrosion resistance of the coating from two points of view. First, PAMAM4 has 64 surface groups that can more efficiently react with epoxy and the functional groups of GO particles than PAMAM2, which has only 16 surface groups. Second, PAMAM4 could have better barrier properties than PAMAM2 due to its dimensions and geometric aspects [18]. The breakpoint frequency $(f_{\rm b})$ values were obtained from the Bode plots where the phase angle becomes -45°. According to the literature, the f_b correlates to the amount of coating delamination [25]. Figure 7 illustrates that $f_{\rm b}$ values of all the samples are almost the same after 9 days of immersion. However, after 34 days of immersion, the $f_{\rm b}$ of the neat epoxy sample significantly increased (shifted to the higher frequencies), evidencing the progress of the coating delamination area. EP-GO-PAMAM4 samples showed no f_b changes even after 34 days of immersion, confirming that the coating could effectively restrict the diffusion of electrolyte into the coating/metal interface.

EIS test was also carried out on the coatings with an artificial defect after 6 and 24 h immersion in NaCl solution in order to study the electrolyte diffusion into

the coating/metal interface and its impact on the coating delamination. The Nyquist and Bode plots of these samples are shown in Figure 9. In addition, the impedance values at 10 mHz were provided from the Bode plots and are reported in Figure 10 for various samples. There is a direct correlation between the lowfrequency impedance value and the coating damage index. In the case of defected coating, the electrolyte can diffuse into the interface of the coating/metal, destructing the coating adhesion bonds due to the electrochemical reactions. Oxygen reduction reaction $(2H_2O+O_2+4e\rightarrow 4OH)$ leads to the increase of pH value beneath the coating on the cathodic regions, resulting in damaging the adhesion bonds and delamination of the coating. As a result of the coating delamination, the metal surface contact area with electrolyte can be increased, leading to the impedance value reduction. This means that the amount of impedance reduction correlates with the coating delamination in the case of the defected coating.

Figure 9 reveals that after 6 h of exposure, E-PAMAM4 and EP-GO-PAMAM4 samples showed the most impedance values. In addition, the E-GO sample showed the lowest impedance compared to the samples. The order of the impedance values after 24 h immersion for different samples is as follows: EP-PAMAM4 > EP-GO-PAMAM4 > EP-GO-PAMAM2 > EP-PAMAM2 > EP > EP-GO.

These observations revealed more coating delamination of the steel substrate in EP and EP-GO samples due to more corrosion reactions. The role of E-PAMAM4 and EP-GO-PAMAM4 particles in reducing the coating interfacial adhesion can be understood from the EIS results of the defected coatings.

The presence of PAMAM has a significant effect on the corrosion protection properties of the epoxy coatings. According to the experimental results, PAMAM4 is more effective than PAMAM2 mainly because PAMAM 4 has greater size and more surface groups in comparison with PAMAM2. It is well known that the geometry and dimensions of particles in epoxy have a significant effect on the barrier properties. PAMAM has a spherical shape and can protect the steel substrate against corrosion. PAMAM4 is greater than PAMAM2, so it contributes to better dispersion of GO and higher corrosion protection of the coating.



Figure 9: Time-dependent Bode (a and b) and Nyquist (c and d) plots for pure epoxy and nanocomposite coatings after immersion in 3.5 wt.% NaCl solution for 6 h (a and c) and 24 h (b and d) in scratched EIS test.



Figure 10: The impedance values (at 10 mHz) of the defected pure epoxy and different nanocomposites after 6 and 24 h immersion in 3.5 wt.% NaCl solution.

4. Conclusion

FT-IR analysis showed that graphene oxide sheets were successfully modified by PAMAM2 and PAMAM4 through covalent bonds. Besides, the grafting percentages of PAMAM on the graphene oxide particles were also calculated. Salt spray test results evidenced that the PAMAM4 and GO-PAMAM4 had the greatest impact on the improvement of the epoxy coating corrosion resistance. This is possible to view the more corrosion resistance of these samples not only after 48 hours but also after 28 days. Based on the EIS results, it was perceived that the presence of PAMAM4 in epoxy coatings has a significant impact on improving the impedance values in the day of 34 approximately 40% in comparison with pure epoxy resin. According to the FE-SEM results, the GO surface modification via PAMAM changed the brittle fracture of the epoxy coating to ductile one. Also, the presence of PAMAM4 and PAMAM2 caused the change of the ductile fracture with sharp edges to ductile fracture with soft edges. According to the improvement of corrosion resistance of the epoxy/PAMAM4 sample; the presence of PAMAM4 has a significant role in the quality of dispersion of GO particles in an epoxy matrix. This is the reason for the better anti-corrosion properties of epoxy coatings containing PAMAM4 and GO-PAMAM4.

5. References

- H. Zheng, Y. Shao, Y. Wang, G. Meng, B. Liu. Reinforcing the corrosion protection property of epoxy coating by using graphene oxide–poly (urea– formaldehyde) composites, *Corros. Sci.*, 123(2017), 267-277.
- B. Ramezanzadeh, Gh. Bahlakeh, M.H. Mohamadzadeh Moghadam, R. Miraftab, Impact of size-controlled p-phenylenediamine (PPDA)functionalized graphene oxide nanosheets on the GO-PPDA/Epoxy anti-corrosion, interfacial interactions and mechanical properties enhancement:

Experimental and quantum mechanics investigations, *Chem. Eng. J.* 335(2018),737-755.

- M. G. Sari, M. Shamshiri, B. Ramezanzadeh, Fabricating an epoxy composite coating with enhanced corrosion resistance through impregnation of functionalized graphene oxide-co-montmorillonite Nanoplatelet, *Corros. Sci.*, 129(2017), 38-53.
- Y. Ye, D. Zhang, J. Li, T. Liu, J. Pu, H. Zhao, L. Wang, One-step synthesis of superhydrophobic polyhedral oligomeric silsesquioxane-graphene oxide and its application in anti-corrosion and anti-wear fields, *Corros. Sci.*, 147(2019), 9-21.

- N. Yang, T. Yang, W. Wang, H. Chen, W. Li, Polydopamine modified polyaniline-graphene oxide composite for enhancement of corrosion resistance, *J. Hazard. Mater.*, 377(2019), 142-151.
- 6. T. Yang, Y. Cui, Z. Li, H. Zeng, Sh. Luo, W. Li, Enhancement of the corrosion resistance of epoxy coating by highly stable 3, 4, 9, 10-perylene tetracarboxylic acid functionalized graphene, *J. Hazard. Mater.*, 357(2018), 475-482.
- M. Cui, S. Ren, J. Pu, Y. Wang, H. Zhao, L. Wang, Poly (o-phenylenediamine) modified graphene toward the reinforcement in corrosion protection of epoxy coatings, *Corros. Sci.*, 159(2019), 108-131.
- D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, *Chem. Rev.*, 112(2012), 6027-6053.
- D. Chen, H. Feng, Ji. Li, Electrically conductive rubbery epoxy/diamine-functionalized graphene nanocomposites with improved mechanical properties, *Compos. Part B Eng.*, 67(2014), 564-570.
- P. Mancinelli, T. F. Heid, D. Fabiani, A. Saccani, M. Toselli, M.F. Fréchette, S. Savoie, E. David, Electrical conductivity of graphene-based epoxy nanodielectrics, *Annual Report Conference on IEEE.*, 2013, 772-775.
- J. Liang, Y. Wang, Y. Huang, Y. Ma, Z. Liu, J. Cai, Ch. Zhang, H. Gao, Y. Chen, Electromagnetic interference shielding of graphene/epoxy composites, *Carbon*, 47(2009), 922-925.
- 12. Y. Li, R. Umer, A. Isakovic, Y. Abdul Samad, L. Zheng, K. Liao, Synergistic toughening of epoxy with carbon nanotubes and graphene oxide for improved long-term performance, *Rsc. Adv.*, 3(2013), 8849-8856.
- 13. S. Pourhashem, M. R. Vaezi, A. Rashidi, M. R. Bagherzadeh, Distinctive roles of silane coupling agents on the corrosion inhibition performance of graphene oxide in epoxy coatings, *Prog. Org. Coat.*, 111(2017), 47-56.
- 14. X. Sheng, W. Cai, L. Zhong, D. Xie, X. Zhang, Synthesis of Functionalized Graphene/Polyaniline Nanocomposites with Effective Synergistic Reinforcement on Anticorrosion, *Ind. Eng. Chem. Res.*, 55(2016), 8576-8585.
- 15. Z. Yu, L. Lv, Y. Ma, H. Di, Y. He, Covalent modification of graphene oxide by metronidazole for reinforced anti-corrosion properties of epoxy coatings, *Rsc Adv.*, 6(2016), 18217-18226.
- M. Nonahal, H. Rastin, M. R. Saeb, M. Ganjaee Sari, M. Hamedian Moghadam, P. Zarrintaj, B.

How to cite this article:

Ramezanzadeh, Epoxy/PAMAM dendrimer-modified graphene oxide nanocomposite coatings: Nonisothermal cure kinetics study, *Prog. Org. Coat.*, 114(2018), 233-243.

- 17. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, A new class of polymers: starburst-dendritic macromolecules, *Polym. J.*, 17(1985),117.
- 18. G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol, *J. Org. Chem.*, 50(1985), 2003-2004.
- E. Abbasi, S. Fekri Aval, A. Akbarzadeh, M. Milani, H.Tayefi Nasrabadi, S. Woo Joo, Y. Hanifehpour, K. Nejati-Koshki, R. Pashaei-Asl, Dendrimers: synthesis, applications, and properties, *Nanoscale Res. lett.*, 9(2014), 247.
- 20. M. Ramezanzadeh, M. Asghari, B. Ramezanzadeh, Gh. Bahlakeh, Fabrication of an efficient system for Zn ions removal from industrial wastewater based on graphene oxide nanosheets decorated with highly crystalline polyaniline nanofibers (GO-PANI): Experimental and ab initio quantum mechanics approaches, *Chem. Eng. J.*, 337(2018), 385-397.
- R. Esfand, D. Tomalia, Laboratory synthesis of poly (amidoamine)(PAMAM) dendrimers, *Dendrimer Dendritic Polym.*, 45(2001), 587-604.
- 22. B. Klajnert, M. Bryszewska, Dendrimers: properties and applications, 2001.
- 23. Gh. Bahlakeh, B. Ramezanzadeh, M. Ramezanzadeh, Corrosion protective and adhesion properties of a melamine-cured polyester coating applied on steel substrate treated by a nanostructure cerium– lanthanum film, *J. Taiwan Inst. Chem. Eng.*, 81(2017), 419-434.
- 24. M.Jouyandeh, O. Moini Jazani, A.H. Navarchian, M. Shabanian, H. Vahabi, M.R. Saeb, Surface engineering of nanoparticles with macromolecules for epoxy curing: development of super-reactive nitrogen-rich nanosilica through surface chemistry manipulation, *Appl. Surf. Sci.*, 447(2018), 152-164.
- F. Mansfeld, C. Tsai, Determination of coating deterioration with EIS: I. Basic relationships, *Corrosion*, 47(1991), 958-963.
- 26. D. Xia, S. Song, J. Wang, H. Bi, Z. Han, Fast evaluation of degradation degree of organic coatings by analyzing electrochemical impedance spectroscopy data, *Trans. Tianjin Univer.*, 18(2012), 15-20.

M. Maadani, S. H. Jafari, M. R. Saeb, B. Ramezanzadeh, F. Najafi, D. Puglia, Studying the Corrosion Protection Behavior of an Epoxy Composite Coating Reinforced with Functionalized Graphene Oxide by Second and Fourth Generations of Poly(amidoamine) Dendrimers (GO-PAMAM-2, 4), Prog. Color Colorants Coat., 13 (2020), 261-273.

