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Using of organosilane in the formulation of epoxy coatings containing cerium nitrate: assessment of dispersion and corrosion resistance

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Abstract

Structure and corrosion resistance behavior of epoxy coatings containing cerium nitrate and different amount of organosilane was investigated. Corrosion resistance behavior of coating systems was characterized by using electrochemical impedance spectroscopy (EIS) and polarization techniques. Also Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to evaluate dispersion of cerium nitrate pigments in the presence of organosilane. Furthermore, flexibility of coatings was studied by using of cupping test. Increment of 10 wt% of organosilane into the coating formulation led to the superior dispersion of cerium nitrate and also highest corrosion protection performance.

Keywords: organosilae, agglomeration, cerium nitrate, dispersion, steel corrosion

1 Introduction

For many years, chromate conversion coatings have been widely used for corrosion protection of structural metals. The advantages of chromate conversion coatings are their passivation

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ability, self-healing nature, ease of application and electrical conductivity. However, the carcinogenic effects of chromates have generated serious safety problems. Currently, an urgent task for the innovative coating is to search for effective, low cost and environmentally compliant coatings [1-3].

Using of corrosion inhibitors and silane pretreatment are popular in recent years. Among the most effective anti-corrosion species, rare-earth salts present good corrosion inhibition properties in addition to environmental friendliness [4]. Also pre-treatments based on functional silane coatings present prime technological interest because these coatings provide divergent chemical functionalities on a wide range of substrates either metallic or non-metallic [4-6].

Among the rare earth salts, cerium compounds widely were used as corrosion inhibitors. The corrosion inhibition properties of cerium nitrate have been widely discussed in literature [7-12]. However, very little is known on the mechanisms involved in such process [7].

Using of silane in organic coating containing corrosion inhibitor pigments has been studied in recent years. It has been claimed that the presence of silane coupling agents leads to a significant improvement of filler and pigment dispersion in resin (figure 1). This improvement results from displacement or modification of the moisture layer, giving reduced clumping of particles and improved wet ability by polymer. Improved dispersion often results in less air occlusion, giving fewer voids and reduced slurry viscosity [13].

In this paper, the effect of γ-glycidoxypropyltrimethoxysilane (γ-GPS) on dispersion and corrosion protection of cerium nitrate pigment in epoxy resin was investigated. Also the optimum value of organosilane, for achieving the highest corrosion resistance, in the coating formulation was determined by electrochemical methods. Also the structures of coatings and dispersion of pigments were studied by Scanning Electron Microscopy (SEM), Atomic Force

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Microscopy (AFM). Furthermore cupping test was used to show effect of γ-GPS on flexibility of prepared film.

2 Experimental

Cold rolled carbon steel panels (6.5 cm × 6.5 cm × 0.3 cm) were used as metallic substrate. The panels were subjected to a sequence of a chemical cleaning and a mechanical surface polishing with emery papers from #400 to #1000 to remove any trace of dirt any surface oxides. Prior to the coating application, the panels were ultrasonically cleaned by acetone and an alkaline solution (0.3 mol/L of NaOH solution) at 60 ˚C for 10 min, respectively.

For the preparation of silane solution, 50 parts of γ-glycidoxypropyltrimethoxysilane (γ – GPS) (Sigma Aldrich Co (Germany)) were diluted with about 950 parts methanol. The pH was adjusted to 4.5 (using acetic acid) and the resultant solution allowed to hydrolysis prior to use.

The liquid epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBPA) (Epon 828) from Shell Chemicals. Four formulations with 0, 5, 10 and 15wt. % γ –GPS and 2wt. % cerium (III) nitrate hexahydrate (Alfa Aesar (Germany)) were prepared.

After introduction of the γ –GPS and cerium nitrate into the formulations, the coating solutions mixed by using a propeller stirrer at 1600rpm for 30 min at room temperature. After stirring, the solutions were sonicated for 20 min at 40 ˚C. The temperature of vessels was fixed by an external cooling bath. The ultrasonication process was performed at a frequency of 20 kHz with an inlet ultrasound power of around 1W/mL (UIP 1000 ultrasonic processor, Hielscher ultrasound technology). After mixing and sonication, the steel substrate panels were coated by using draw bar to make 90µm wet-film thickness (resulting in a (DFT) of about). Coatings were allowed to cure for 1 h at 115 ˚C. the dry film thickness (DFT) of coating films were about 60 µm.

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To investigate the electrochemical properties, Potentiosat/Galvanostat (Autolab PGSTAT 302N (Italy)) was used for polarization tests with scan rate of 0.55mV and Electrochemical Impedance Spectroscopy (EIS) from 5mHz to 100kHz with amplitude of 10mA.

The used tool for Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques were Philips XL 30 (Netherland) and (Nanosurf easyScan 2 AFM, (Switzerland)) respectively. To study the flexibility of coatings, the cupping test was performed according to BS 3900-part E-4 on a TCB Cupping tester manufactured by TQC. The degree of deformation is digitally recorded at a resolution of 0.01 mm.

3 Results and discussions:

3.1 Electrochemical tests:

Tafel diagrams of four scratched samples containing 0, 5, 10 and 15.wt% of γ-GPS, are shown in figure 2. These tests were performed after 24 hours immersion of coated plates in 3.5.wt% NaCl solution. As depicted in figure 2, sample with 10.wt% of γ-GPS has the lowest I_{corr} and E_{corr} and so the best corrosion resistance.

In figure 2, the reduction of I_{corr} indicates a geometric blocking effect of active metal reaction sites. It seems that the penetration of electrolyte into the silane film (containing cerium inhibitor), local anodic and cathodic reactions start to occur at the metal surface. The areas where the cathodic reactions occur (at high pH) should trigger the release of cerium as cathodic inhibitors [14]. According to table 1, the sample with 10.wt% organosilane have the better corrosion inhibition efficiency. This means optimum value for γ –GPS was 10 wt. %.

Figure 3 shows the Electrochemical Impedance Spectroscopy (EIS) spectra of coating samples containing 0,5,10 and 15 wt. % of γ –GPS after 1, 15 and 30days immersion in 3.5.wt% NaCl solution. One simple method to evaluate barrier property of prepared film is comparing the Nyquest radius of EIS spectra. As depicted in figure 3, in different immersion times, the sample

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with 10wt. % of γ-GPS has larger radius. The reason for lower corrosion resistance of the sample with 5wt. % γ-GPS, compared with the sample containing 10wt% of γ –GPS, is the lack of enough silane to cover the cerium nitrate pigments and poor dispersion of pigments. On the other hand, the protection of sample containing 15 wt% of γ –GPS is lower than that of sample containinhg 10 wt % of γ –GPS. This observation may be due to agglomeration and also condensation of organosilane, therefore cerium pigments could not disperse in 15 wt% sample as well as 10.wt% sample and decrease in barrier property of resultant film.

Figure 4 represents the EIS data which were fitted by equivalent electrical circuits (EECs). Due to the deviation between capacitance related to coating and "pure capacitance", capacitance element (C) in equivalent electrical circuit is replaced by constant phase element (Q). Furthermore Q_{dl} and R_{ct} represent double layer capacitance and the charge transfer resistance (R_{ct}). EIS parameters were reported as tables 2-4.

After one day after immersion, the EIS spectra for the coatings show two time constants (fig 4) due to the existence of pinholes and corrosive electrolyte immediately reached. The coating doped with 10wt. % γ-GPS shows the highest resistance and the highest capacitances after 30days of immersion, suggesting that these samples have the best anticorrosion property. High resistances and low capacitances reveal a more protective coating. Furthermore, the capacitances of the coating containing 15 wt. % γ-GPS are more than that of 10wt. % γ-GPS samples, and also their resistances are lower in all time intervals. The evolution of the coating resistance and coating capacitance suggests that there is an optimum concentration of silane for doping of the cerium nitrate solutions.

With attention to table 2, the coating delamination growth could be responsible for decrease of R_f and increase of Q values. The sample with 10wt. % γ-GPS results lower dropping in film resistance, this is due to good protection ability of cerium nitrate in this mixture, means that γ-

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GPS has the best effect on dispersion and leaching of cerium nitrate to cover defects . The coating samples containing 5 and 15 wt. % γ-GPS have a significant change in their resistance and capacitance values. It seems that diffusion and penetration of water and ions into the coatings cause the increment of capacitances.

3.2 Surface morphology (SEM and AFM microscopy)

To study of the effect of γ-GPS values on film structure, SEM and AFM techniques were carried. As shown in figure 5, the roughness of sample containing 15wt. % of γ-GPS is more than that of the sample containing 10 wt. % of γ-GPS. Figure 5 shows the columnar γ-GPS structure which have larger value and lower magnify in sample containing 15.wt% of γ-GPS respect to the sample containing 10.wt% of γ-GPS. This roughness difference shows the ability of cerium nitrate to distribute in epoxy matrix with various values of γ-GPS. The amounts of γ-GPS over than 10 wt. % causes inverse effect on cerium nitrate distribution and also its leaching and film forming on defect area.

Figure 6 shows the AFM images of different coating samples. As shown in figure 6(c), homogenous, better arranged nano-structure and compact film is obtained for the coating sample containing 10.wt% of γ-GPS. These SEM results are compatible with AFM results.

From AFM images of figure 6, the root-mean-squared roughness (RMS) of the coating sample containing 10.wt% γ-GPS film was about 29.5 nm while the RMS for coating sample containing 15 wt% of γ-GPS was 89.7 nm. The AFM images clearly show that the coating sample containing 10wt% of γ-GPS is less heterogeneous than the other samples. These results suggest that the films formed in the presence of 10.wt% γ-GPS are less porous and more organized. These features help to improve the corrosion protection properties of these films.

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3.3 Deformation results (mechanical properties):

Figure 7 shows the deflection resistance values of different coating films using cupping test.

As shown in figure 7, the sample containing 10 wt% of γ-GPS has the highest resistance against cracking. Increment of γ-GPS more than 10wt% of γ-GPS led to inverse effect on flexibility of prepared films. On the other hand, figure 7 shows that the dispersion of cerium nitrate pigments in the coating sample containing 5% of γ-GPS is not sufficient. Also, flexibility of the coating sample containing 15wt% of γ-GPS was affected by agglomeration. The poor dispersion affected the flexibility of resultant coatings.

For achieving the highest coating film flexibility, regardless of filer size and shape, intimate contact between the matrix and mineral particles (pigments) is essential, since air gaps represent points of zero strength. Thus, coating flexibility is improved by good wetting of the minerals by the resin and further enhanced when the matrix is adhered to the mineral surface via chemical bonding [15].The results of cupping test show that γ-GPS has an effective role in wetting and dispersion of cerium nitrate in epoxy binder.

Finally, good dispersion of cerium nitrate pigments in epoxy resin using optimum amount of organosilane led to the superior corrosion resistance of resultant films. Usage of γ-GPS as cross linker between pigments and epoxy binder enhances dispersion and leaching ability of cerium nitrate to release in defects and make a protective layer.

4. Conclusions

- Cerium nitrate pigment as a rare-earth material alongside with organosilane can be used as good alternative for toxic chromate coatings.
- γ-GPS as an organosilane can act as surfactant and dispersing aid for cerium nitrate pigment in epoxy resin media .

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- The amount of usage of organosilane in the coating formulation is critical, low amount of organosilane causes insufficient dispersion of rare earth pigment and higher amounts of organosilane leads to the agglomeration. It seems that the optimum amount of organosilane is about 10 wt% in the coatings formulation.

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Table Captions

Table 1: Potentiodynamic polarization results in the presence of different amounts of γ-GPS.

Table 2: EIS parameters of coating samples containing different amounts of % γ-GPS after different times of immersion

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Figure Captions

Figure1: schematic for the improvement of dispersion of pigments using silane coupling agents [13]

Figure 2: Polarization curves of coating samples containing different amounts of γ-GPS

Figure 3: Nyquist plots of samples with different values of organosilane in various after different immersion times. a: one day ,b:15 days and c:30

Figure 4: equivalent electrical circuits for modeling the EIS data

Figure 5: SEM of sample containing: a) 15.wt% γ-GPS and b) 10.wt% γ-GPS

Figure 6: AFM scan (5µm × 5µm) of coating films containing: a) 0 wt% ,b) 5 wt% , c)10 wt% and d) 15.wt% of γ-GPS.

Figure 7: Deformation results of cupping tests for the coatings containing different amounts of γ-GPS.

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Table 1: Potentiodynamic polarization results in the presence of different amounts of γ-GPS.

Sample no	Wt % of γ-GPS	E_{corr} (V vs. (Ag/AgCl))	I_{corr} (A/cm^2)	$ß_c$ (mV/dec)	$ß_a$ (mV/dec)	η%
1	0(blank)	-0.7469	9.205e-6	0.24	0.136	-
2	5	-0.741	1.172 E-6	0.09	0.203	87.3
3	10	-0.702	1.05 E-6	0.078	0.194	88.5
4	15	-0.703	1.67E-6	0.146	0.217	81.9

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Table 2: EIS parameters of coating samples containing different amounts of % γ-GPS after different times of immersion

Sample	$R_s(\Omega)$	$Q_{dl}(\Omega.S^{-n})$	$R_{ct}(\Omega)$	$Q_f(\Omega.S^{-n})$	$R_f(\Omega)$	Time of immersion (day)
No γ-GPS	48	0.0007	168	0.00008	985	1
5wt.% γ-GPS	49	0.0005	239	0.0003	3719	1
10 wt.% γ-GPS	52	0.0008	304	0.0012	4521	1
15wt.% γ-GPS	52.2	0.0005	338	0.0011	4021	1
No γ-GPS	40	0.0005	411	0.0003	1632	15
5wt.% γ-GPS	52.5	0.0027	453	0.0013	5621	15
10 wt.% γ-GPS	52	0.0015	762	0.0005	12064	15
15wt.% γ-GPS	52.6	0.004	365	0.0013	6037	15
No γ-GPS	43	0.0007	122	0.0002	1783	30
5wt.% γ-GPS	49	0.0004	122	0.005	2194	30
10 wt.% γ-GPS	52	0.0011	842	0.0008	7125	30
15wt.% γ-GPS	52	0.0034	341	0.0011	5191	30

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Figure 1

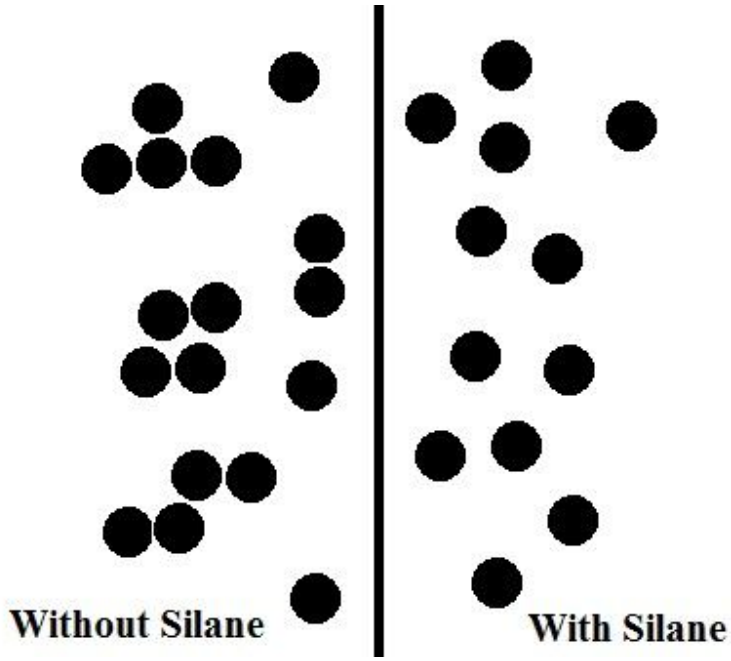

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Figure 2

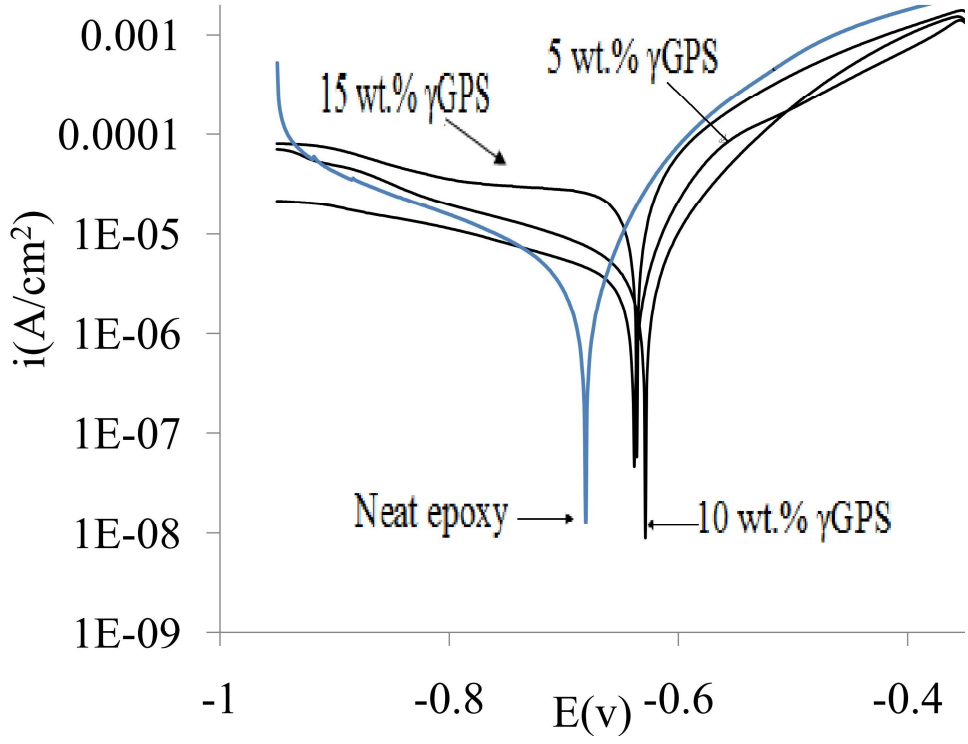

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Figure 3.a

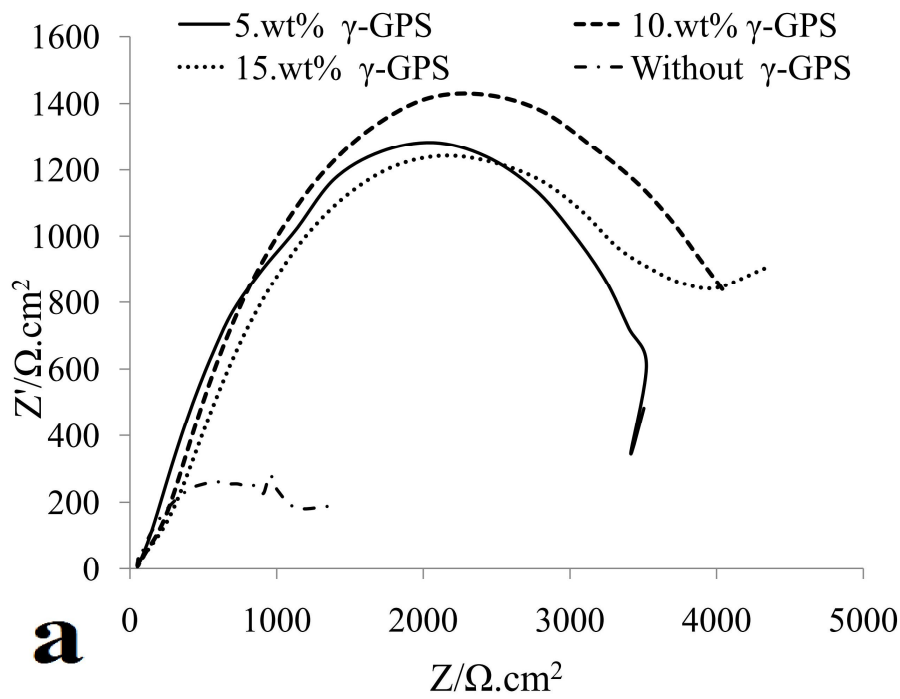

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Figure 3.b

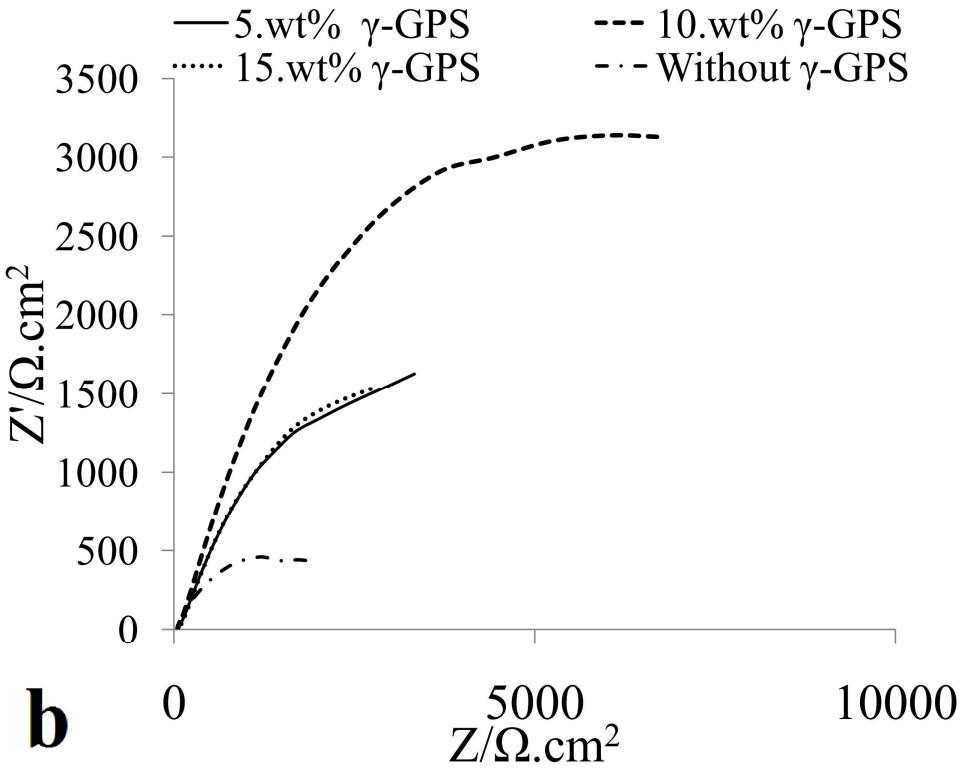

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Figure 3.c

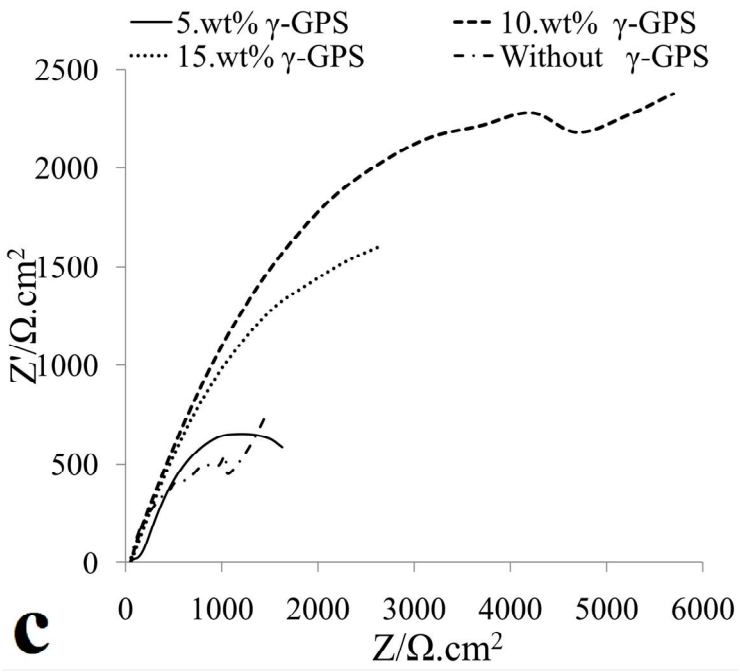

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Figure 4

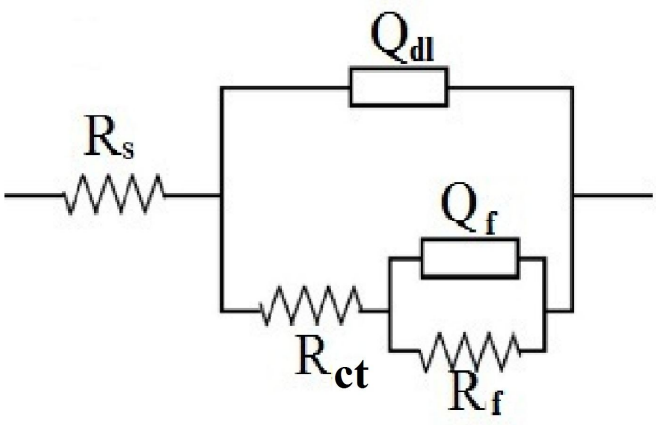

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Figure 5

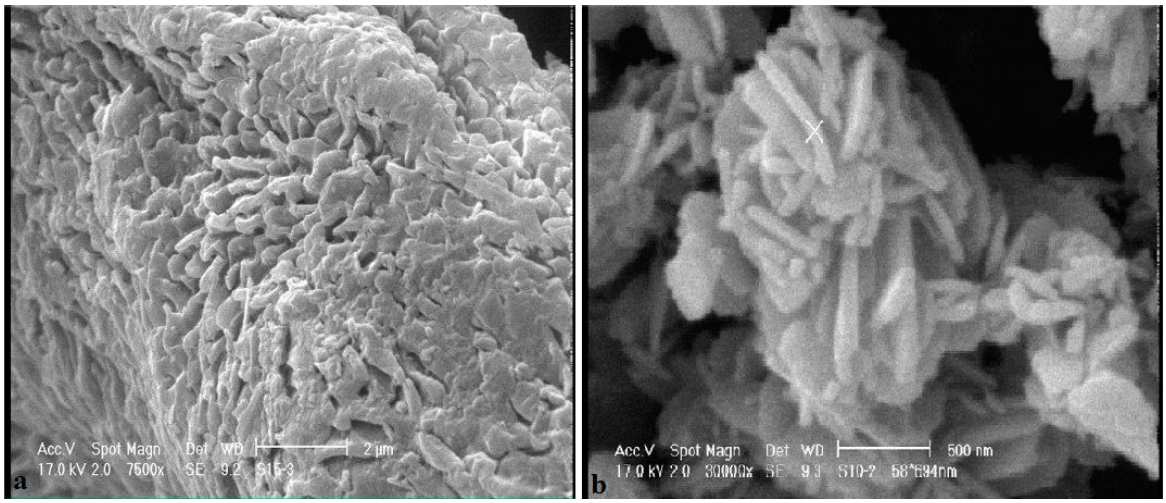

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Figure 6

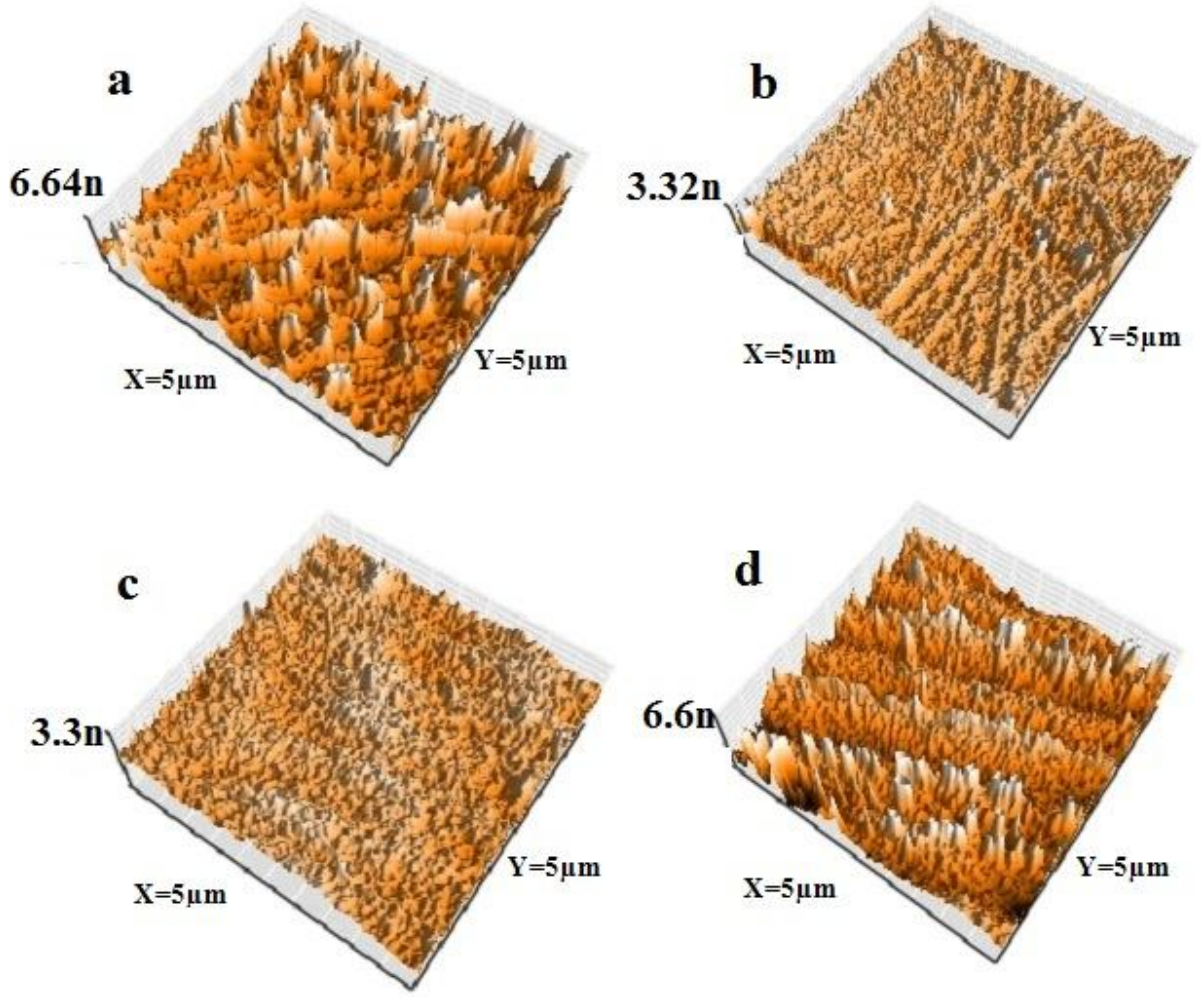

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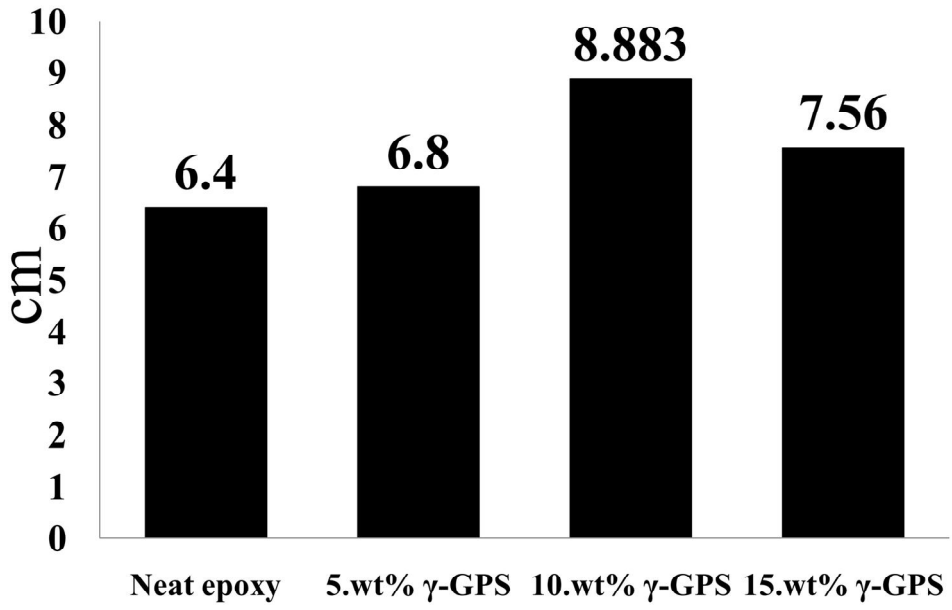
Figure 7



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