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Non-Cracked Epoxy Nanogel Composite as Anticorrosive Coatings for Aggressive Marine Environment

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Cured epoxy coating crack is one of the drawbacks that can be solved by using self-healing preembedded nanomaterials to be an advanced prospective approach. In this work sodium montmorillonite modified with crosslinked nanogels based on smart sensitive N-isopropyl acrylamide (NIPAm) copolymers with nonionic monomer as N-vinyl pyrrolidone (VP) and ionic monomer of 2-acrylamido-2-methyl propane sulfonate sodium salt (AMPS-Na). The particle size, morphology, zeta potential, thermal stability and surface activity of Na-MMT nanogel in distilled and sea water were determined. The blending of Na-MMT nanogels with epoxy during the curing and their effects on exfoliation of Na-MMT and morphology were investigated. The corrosion inhibition efficiency of the cured epoxy embedded with Na-MMT nanogel as organic coats for steel was studied using salt spray resistance up to 1000 h.

Keywords: Embedded epoxy, Coatings, Salt spray, corrosion inhibition, steel.

1. INTRODUCTION

Epoxy resin is one of the most widely organic coatings used to protect the steel used in different industrial applications of petroleum and petrochemicals from corrosion [1-3]. The main advantages of coatings are the barrier, adhesion and inhibiting features that improved lifetime of coatings were affected by micro-cracks, pine hole and different coating defects and deformation due to mechanical damages [4-6]. These defects decrease the anticorrosive performance coating/metal system, change the adhesion between coats and metal and reduce the barrier and inhibiting properties that can lead to rust, blistering, reduction in stability of the adhesion bond and degradation of coating and substrate[7-9]. The filler based on organic and inorganic pigments such as zin, clay, silica were widely used in formulation of anticorrosion coats and a variety of severe environments because of their unique property of protecting the metal even after instances of slight mechanical damage [10-14]. The nanomaterials based on silicate, exfoliated clay, nanoparticles including carbon nanotube achieved excellent results to enhance the protective properties of coatings, adhesion, mechanical properties and to improve its initial barrier properties [15-17]. The present work aims to use nanogel composites based on exfoliated clay to act as self-healing materials to repair the mechanical defects and cracks obtained during the curing of epoxy matrix without affecting the coating performance.

The organic polymeric nanomaterial composites based on linear, hyperbranched and crosslinked nanogel have been used to modify the mechanical, viscoelastic characteristics, thermal and barrier properties etc. of organic coatings [18-24]. The enhancement is usually referred to the interfacial interactions with the polymer segments and extremely high surface area of nanocomposites [25–27]. The challenges for the application of the nanocomposites in organic coatings were attributed to the dispersion of the nanoparticles inside the organic coating networks and elimination the possible interactions between the particles to avoid the presence of aggregations and agglomerations [28–30]. These disadvantages can be prevented by using amphiphilic or surface active nanogel composites that usually modified by different methods to approach the nature of the nanocomposite and organic coating matrix phases together [31-33]. In this respect, our research group intended to use low cost nano-layered silicate, that known as Montmorillonite (MMT) or Nanoclay, to prepare amphiphilic nanogel composite with superior surface active properties [34-36]. The modification mechanisms are based on exfoliation or increasing the interlayer distance of the lamellae of silicate layers to enlarge the space between silicate galleries. Moreover, the coating of this layer with surface active nanogels increased the surface properties of nanoclay.

In this work, the effect of polymer chemical structure on the surface activity of sodium-MMT(Na-MMT) and its exfoliation was investigated to explore the using of modified Na-MMT nanogel composites as anticorrosive and self-healing materials for mechanical defected epoxy organic coatings. The surface morphology of the Na-MMT was examined by using transmission and scanning electron microscopy (TEM and SEM).

2. EXPERIMENTAL

2.1. Materials

All chemical were purchased from Aldrish Sigma company. Hydrophilic sodium montmorillonite (Nanomer ® PGV; Na-MMT) used as clay mineral, N-isopropyl acrylamide (NIPAm) monomer, nonionic monomer N-vinyl pyrrolidone (VP), ionic monomer of 2-acrylamido-2-methyl propane sulfonate sodium salt (AMPS-Na, chermical crosslinker *N*,*N*-methylenebisacrylamide (MBA), radical polymerization initiator ammonium persulfate (APS), radical polymerization activator *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) and poly(vinyl pyrrolidone) stabilizer (PVP with molecular weight 40,000 g/mol) were used without purification. The commercial epoxy resin SigmaGuard ^{TM} CSF 650 produced by Sigma Coatings, SigmaKalon Group at volume ratio between epoxy resin and hardener by volume is 4:1was used as epoxy matrix to act as coat for steel.

The Na-MMT/NIPAm-AMPS nanogel was prepared in our previous work [37]. The crosslinking copolymerization of NIPAm with VP with 50/50 mol ratio in presence of 10 mol% of MBA was carried out after dispersion of Na-MMT (1g) in 100 mL of ethanol/water (60/40 Vol %) and PVP (1 g) with the same reported procedure [37].

2.2. Preparation of epoxy/Na-MMT nanocomposites coats

Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na copolymer nanogel composites were blended with different weigh ratios ranged from 0.1 to 3 wt.% in epoxy resins and sonicated with ultra-sonication rod to complete nanogel powder dispersion. The Na-MMT copolymer nanogel epoxy composite was mixed with polyamine hardener with mixing volume ratio 4:1 Vol. %. The epoxy hardener mixture was sprayed on the blasted and cleaned steel panels at dry film thickness (DFT) of 100 µm. The system was cured at room temperature and tested after 7 days. The same procedure was repeated without addition of nanogel to prepare blank cured epoxy coat.

2.3. Characterization

The thermal stability were determined using thermogravimetric analysis (TGA; TGA-50 SHIMADZU at flow rate 50 ml/min and heating rate of 20 ◦C/min), the morphology of Na-MMT copolymer nanogels was investigated using high resolution transmission and scanning electron microscope (HR-TEM, SEM using a JEOL JEM-2100 electron microscope at an acceleration voltage of 200 kV), and the dispersion stability particle diameter, polydispersity index (PDI) with surface charges (zeta potential; mV) using dynamic light scattering (Laser Zeta meter Malvern Instruments; Model Zetasizer 2000) were evaluated.

The surface tension and receding contact angle of Na-MMT were determined using drope shape analyzer (DSA-100). Na-MMT nanogels were compressed as thin films to measure the contact angle between them and water droplet.

2.4. Adhesion and salt spray resistance of epoxy nanocomposites coats:

The blasting of steel panels and the adhesion strength values of the coatings were evaluated according to ASTM D4541 using a PosiTest digital Pull-Off adhesion tester (DeFelsko) with 20 mm dollies. The corrosion inhibition efficiency test of cured epoxy nanocomposites on steel panels was evaluated using salt spray resistance of test ASTM- B117.

3. RESULTS AND DISCUSSION

The present work aims to modify the Na-MMT with two different types of NIPAm crosslinked copolymer nanogel to convert it to be amphiphilic nanogel particles that have great tendency to response for corrosive environments. For this purpose, VP and AMPS-Na as nonionic and strong ionic monomers are used to copolymerize with NIPAm using radical solution polymerization method in the presence of MBA, APS and TEMED as crosslinker, initiator and activator, respectively. The scheme for synthesis of Na-MMT/NIPAm-AMPS-Na and Na-MMT/NIPAm-VP amphiphilic nanogels is illustrated and described in previous work [37]. The cosolvent based on ethanol/water (60/40) and PVP were found to be a suitable solvent and stabilizer to disperse Na-MMT in aqueous solution to increase their intercalation with NIPAm, VP and AMPS-Na monomers to diffuse among silicate galleries of Na-MMT. The ratios of NIPAm either with VP or AMPS-Na will affect the intercalation or exfoliation degree of Na-MMT at temperature above their lower critical solution transition temperatures (LCST). In this respect, the reactivity ratios of NIPAm/AMPS-Na and NIPAm/VP copolymers are 0.46 / 0.52 and 1.13/0.025, respectively [38, 39]. It was found that alternate copolymers of NIPAm/VP can be formed with low contents of PNIPAm or PVP homoplymers. The NIPAm/AMPS-Na forms block copolymer contains large quantity of NIPAm and PAMPS-Na homopolymer. It is expected that the exfoliation of Na-MMT greatly increases in the presence of NIPAm/VP more than NIPAm/AMPS-Na nanogel.

3.1. Characterization of Na-MMT copolymeric nanogel composites

Table 1. TGA data of amphiphilic Na-MMT nanogels and percentages of crosslinking polymerization.

Na-MMT Nanogels modifier	Degradation steps		Actual amounts relate to Na-MMT (Wt%)	Crosslinking copolymerization %
	Temperature range ^{o}C	Weight loss (%)		
NIPAm/Na-AMPS	50-300	8	31	90.32
	300-650	64		
	residue at 650 ^{o}C	28		
NIPAm/VP	50-350	8	59	98.3
	350-650	34		
	residue at 650 ^{o}C	58		

The crosslinking copolymerization of NIPAm with VP or AMPS-Na percentages (Wt. %) using MBA as crosslinker and Na-MMT as inorganic nanomaterials and their thermal stability at elevated temperature were determined using TGA as plotted in Figure 1 and tabulated in **Table 1**. The data confirm that the Na-MMT/NIPAm-VP contains lower nanogel content (34 Wt %) than Na-MMT/NIPAm-AMPS-Na (64 %) nanogel composite. Moreover, the crosslinking percentage (Wt. %) of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composite are 98.3 and 90.32 %, respectively. This means that the crosslinking of alternate copolymer based on NIPAm-VP has great ability to crosslink with MBA than block NIPAm-AMPS-Na copolymer. Moreover, the presence of high nanogel polymer content based on NIPAm-AMPS-Na increases the probability to intercalate or to exfoliate the Na-MMT galleries as described in previous work [**37**].

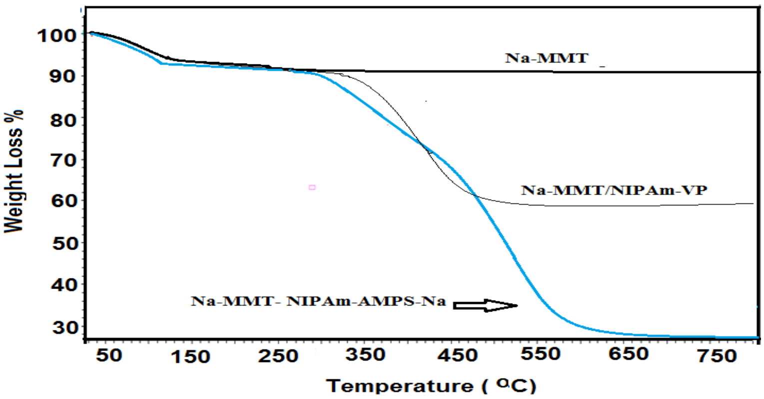


Figure 1. TGA thermograms of Na-MMT and its nanogel composites.

The surface morphologies of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composites can be evaluated from HR-TEM micrographs as represented in **Figure 2 a and b**. It was noticed that Na-MMT/NIPAm-VP (**Figure 2 a**) has uniform spherical morphology contains intercalated and exfoliated silicate galleries of Na-MMT. The Na-MMT/NIPAm-AMPS-Na nanogel composite (Figure 2b) contains stretched non-uniform spherical morphology with exfoliated Na-MMT sheets as discussed in previous work [**37**].

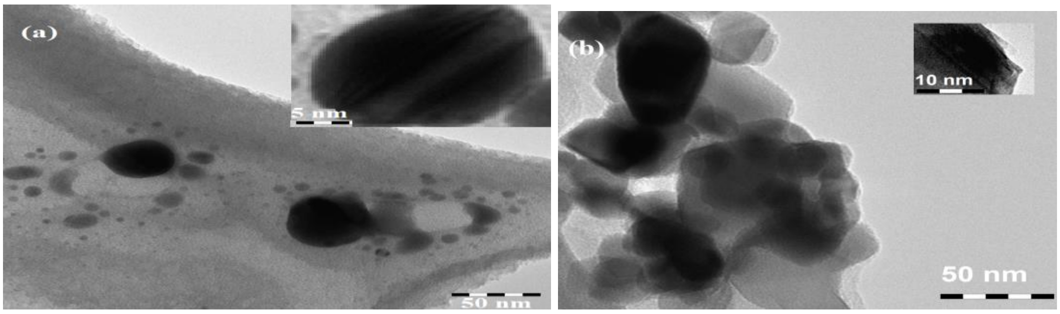


Figure 2. TEM micrographs of a)-MMT/NIPAm-VP and b) Na-MMT/NIPAm-AMPS-Na nanogel composites.

The particle size, PDI and zeta potential of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composites are determined in distilled and filtered sea water and represented in Figures 3a- d and listed in Table 2. Careful inspection of data listed in Table 2 to explore that the particle size (nm) and PDI of Na-MMT/NIPAm-AMPS-Na nanogel increased in sea water more than distilled water. This data confirms that the prepared Na-MMT/NIPAm-AMPS-Na nanogel has great sensitivity to absorb water due to its sensitivity as strong polyelectrolyte to salt. The particle size (nm) and PDI of Na-MMT/NIPAm-VP nanogel reduced in sea water more than distilled water due to collapse of networks.

Table 2. The DLS and Zeta Potential measurements of the Na-MMT nanogels.

Na-MMT nanogels	solvent	DLS		*Zeta Potential (mV)		
		Particle size(nm)	PDI	pH 4	pH 7	pH 9
Na-MMT	water	30 ± 12	1.23	-18.10	-20.44	-30.50
NIPAm/AMPS-Na	water	65 ± 10	0.356	- 22.27	-29.60	-32.33
	Sea water	1215 ± 45	0.531			
NIPAm-VP	water	140± 8	0.478	-15.81	-26.5	-17.37
	Sea water	75± 15	o.238			

*The all measurements were carried out in 10^{-3} M KCl

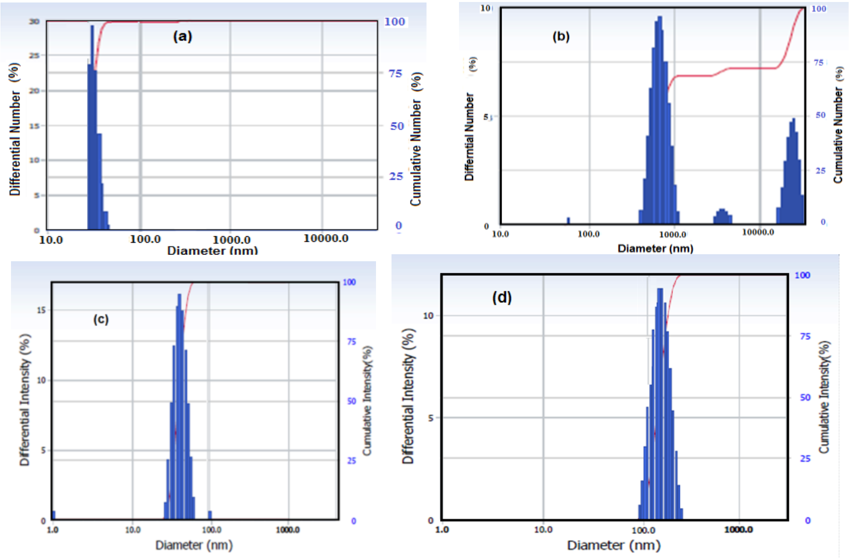


Figure 3. DLS data of Na-MMT/NIPAm-AMPS-Na in a) distilled water, b) sea water and Na-MMT/NIPAm-VP using c)distilled water and d) sea water.

These data agree in harmony with the surface activity data as discussed in previous section. The stability of nanocomposites dispersions in water is confirmed from zeta potential data (Table 2) that they have more negative value than Na-MMT and -25 (mV) as confirmed from previous works [37, 40].

3.2. Effect of salt on surface activity of Na-MMT composites

The surface activity of the prepared Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composites can be determined from their adsorption isotherms, that based on the relation between their surface tension in distilled water or filleted sea water and their concentrations (ln (c) mol/L), as represented in Figure 4. The adsorption parameters such as their concentration at air/ water interface or surface excess (Γ_{max}, mol/ cm^2) and their minimum surface area of molecule at interface (A_{min}, nm^2/molecule) are calculated in either fresh or sea water and represented in Table 3 as described in previous work [37].Moreover, the aggregation of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composites in aqueous solution is determined from the critical aggregation concentration (cac; mol/L) as confirmed from Figure 4. Careful inspection of data indicates that the cac values were reduced for Na-MMT/NIPAm-VP nanogel in sea water more than fresh distilled water. Moreover, Na-MMT/NIPAm-AMPS-Na nanogel does not aggregated in bulk sea water solution and behaves as strong electrolyte and cannot act as amphiphilic nanoparticles in sea water [41]. This means that Na-MMT/NIPAm-AMPS-Na will absorb water and their particle size increased due to strong hydrophilicity of SO_3Na groups. This observation can be referred to the formation of strong repulsive forces between dissociated polymeric chains resulting in a higher osmotic pressure. [41]. On the other hand, the increment of Γ_{max} and lowering of A_{min} for Na-MMT/NIPAm-VP nanogel in sea water more than fresh distilled water indicates that this nanogel composite possesses high surface activity in sea water. However, Na-MMT/NIPAm-VP nanogel shows lower surface activity in water than Na-MMT/NIPAm-AMPS-Na as determined from Table 3. These observations are referred to the strong ability of Na-MMT/NIPAm-VP nanogel to collapse in sea water more than Na-MMT/NIPAm-AMPS-Na nanogel composite [42-45]. The formation of alternate nonionic NIPAm-VP copolymer controlled the gelling of Na-MMT/NIPAm-VP in sea water more than fresh distilled water [42].

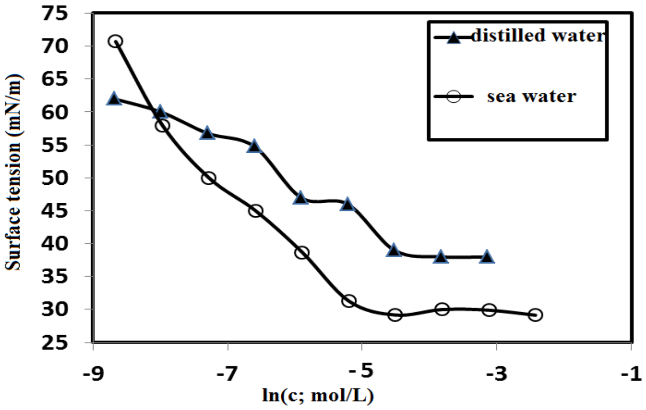


Figure 4. Adsorption isotherm of Na-MMT/NIPAm-VP nanogel at 25 °C in aqueus solution.

The contact angle data of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na nanogel composites discs with either sea or distilled water are determined and listed in Table 3. The data confirmed that the Na-MMT/NIPAm-VP forms hydrophobic layer more than Na-MMT/NIPAm-AMPS-Na nanogel composite as determined from higher contact angle data (Table 2). The lower of contact angle data of Na-MMT/NIPAm-AMPS-Na in sea water than Na-MMT/NIPAm-VP confirms that the wettability and diffusion of salt in nanogel based on NIPAm-AMPS-Na in sea water are much higher than NIPAm-VP.

Table 3. Surface activity parameters of amphiphilic Na-MMT nanogels in water at 25 °C.

Na-MMT Nanogels modifier	water	cac mol/L x 10^3	γ_{cac} mN/m	$\Delta\gamma = \gamma_o - \gamma_{\pi cac}$ mN/m	$(-\partial\gamma / \partial \ln c)$	Γ_{max} x 10^{10} mol/cm^2	A_{min} molecule	Contact angle (degree)
NIPAm/AMPS-Na	distilled	2.7	32.2	40.0	8.774	0.370	0.450	35.7
	Sea	-	48.3	23.5	-	-	-	23.4
NIPAm/VP	distilled	7.4	38.7	33.5	5.185	0.218	0.765	44.8
	Sea	5.4	30.9	40.9	10.13	0.615	0.268	53.2

3.3. Salt Spray resistance of cured epoxy coatings in the presence of Na-MMT copolymer nanogel composites:

It is well known that the cured epoxy polyamides or polyamines coatings are widely used anticorrosive organic coatings as primer or top coats for steel used in onshore or offshore petroleum equipment [46]. The micro cracks produced from heat evolved during the curing of epoxy resin affect the anticorrosive performances of epoxy system as one of the preferred coating systems that used to protect steel. Self-healing materials contain smart micro or nanocapsules or flexible nanogel networks showed great efficacy to fill the cracks and to self-repair the defected coats [47]. In the present work, the epoxy resin was blended with salt responsive nanogel composite based on Na-MMT, and cured with polyamine hardener as illustrated in the experimental sections. Different weight percentages of Na-MMT/NIPAm-VP and Na-MMT/NIPAm-AMPS-Na ranged from 0.1 to 3 Wt. % were used to select the suitable nanogel composites to repair the mechanical defects of cured epoxy system. It was previously reported that the clay minerals can be used as self-healing ceramic composite protective coating due to their ability to swell in water and expand when water diffused in cracks and consequent blocking of the defects [48]. This characteristic can be controlled when clay minerals used as anticorrosive blend coatings for steel. In this respect, Na-MMT mineral was exfoliated or intercalated with NIPAm copolymers to increase its dispersions in epoxy matrix to fill the cracks and to self-repair the defected coats. The cracks of epoxy matrix without using Na-MMT nanogel composites (blank) and dispersions of these composites in epoxy matrix can be investigated using SEM for cryogenic fractured epoxy coats as illustrated in Figure 5 a-f. Inspection of the blank morphology (Figure 5 a and b) it is found that the cracks and voids are formed. The incorporation of Na-MMT nanogel (Figure 5 c, d) will fill the cracks and void with NIPAm nanogel and Na-MMT layers. It was also observed that the best 1 Wt % of Na-MMT/NIPAm-VP is sufficient to form exfoliate Na-MMT (Figure 5e). Moreover, increment of Na-MMT/NIPAm-AMPS-Na up to 3.0 Wt. % leads to form aggregates and agglomerates (Figure 5f). It was also found that the dispersion of Na-MMT nanogels were not dispersed as individual platelets and they were exfoliated as epoxy–intercalated tactoid Na-MMT platelets [49].

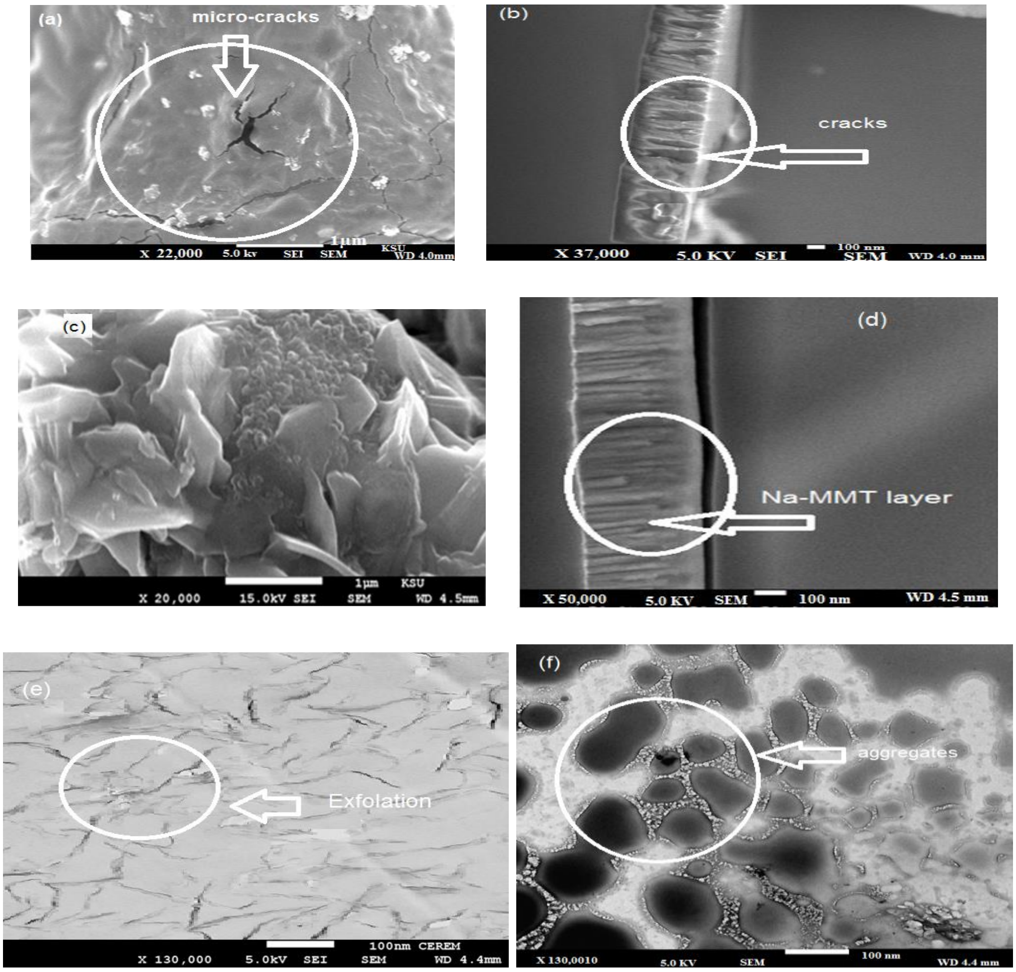


Figure 5. SEM of cured epoxy matrix a) blank, b) cryogel fractured blank, c) cured epoxy NaMMT/NIPam-AMPS-Na (1.0 Wt %), d) fractured epoxy NaMMT/NIPam-AMPS-Na (1.0 Wt %), e) Surface of cured epoxy embedded NaMMT/NIPam-VP (1.0 Wt %) and f) cured epoxy embedded NaMMT/NIPam- AMPS-Na (3.0 Wt %).

Adhesion test or pull-off resistance is the important property of organic coatings that used to investigate the bond strength between epoxy matrix or modified epoxy matrix and steel substrate [50].The adhesion strengths of coatings are determined and listed in Table 4. It was observed that the adhesion strength of the blank epoxy coating was 5 MPa which was attributed to the bond formed between hydroxyl groups, formed from curing of bisphenol epoxy with polyamine hardener, and steel substrate [51]. The cured modified epoxy resins with Na-MMT/NIPAm-VP nanogels show greater of the adhesion properties more than epoxy modified with Na-MMT/NIPAm-VP nanogels, which increased with increment of their contents from 0.1 to 3.0 Wt. % (Table 4). This observation can be referred to the presence of more OH groups of silicate layers due to exfoliation of Na-MMT/NIPAm-VP up on embedded with cured epoxy matrix [52]. Moreover, the filling of cracks with nanogel (Figure 5c) increases the adhesion between epoxy matrix and the native oxide layer (formed on the metallic substrate in short contact with the atmosphere before application of the organic coating) [53].

Table 4. Pull-off and Salt Spray Resistance of epoxy embedded with Na-MMT nanogel composites at 30 °C.

Cured epoxy-Na-MMT copolymer	Pull- off resistance (MPa)	Nanogel ratio	Exposure time (hours)	Disbonded area %	Rating Number (ASTM D1654)
blank	5	0	300	9	6
NIPAm-VP	12	0.1%	1000	3	8
	16	1%	1000	1	9
	14	3%	1000	10	6
NIPAm-AMPS-Na	9	0.1%	750	20	5
	13	1%	750	5	7
	10	3%	750	30	4

The corrosion resistance of carbon steel coated with cured epoxy matrix or modified epoxy matrix can be evaluated by accelerated corrosion salt spray tests on scratched samples. The salt spry test results were represented for selected photographs after time exposure to salt spray test in Figure 6 and Table 4. The maximum exposure times for epoxy blank, cured epoxy with Na-MMT/NIPAm-AMPS-Na and Na-MMT/NIPAm-VP are 300, 650 and 1000 h, respectively. It was evaluated from the rusting formation, adhesion failure and delamination degrees of coatings (Table 4). Careful inspection of photographs (Figure 6) indicates that the accumulation of corrosion products produced for a pure epoxy coatings cured epoxy with Na-MMT/NIPAm-AMPS-Na (3 Wt. %) is observed at the scratches. Moreover, for epoxy coatings containing Na-MMT nanogel, it was found that the corrosion products produced at agglomerates of Na-MMT nanogels that increased in Na-MMT/NIPAm-AMPS-Na more than Na-MMT/NIPAm-VP although the corrosion degree was lower compared to a blank of unmodified epoxy coating. It was also noticed that the rust creep age from scribe of the pure epoxy coating was higher than that of epoxy coatings containing Na-MMT nanogels as observed in Figure 6 and Table 4. The salt spray test results confirm that the presence of Na-MMT/NIPAm-VP embedded with epoxy matrix improves the corrosion resistance of the epoxy coating and repair the defected coats. Moreover, these results confirm the inhibitory action of Na-MMT nanogel composites or nanoparticles as confirmed from our previous data to use different corrosion tests such as electrochemical impedance measurements [34-36].

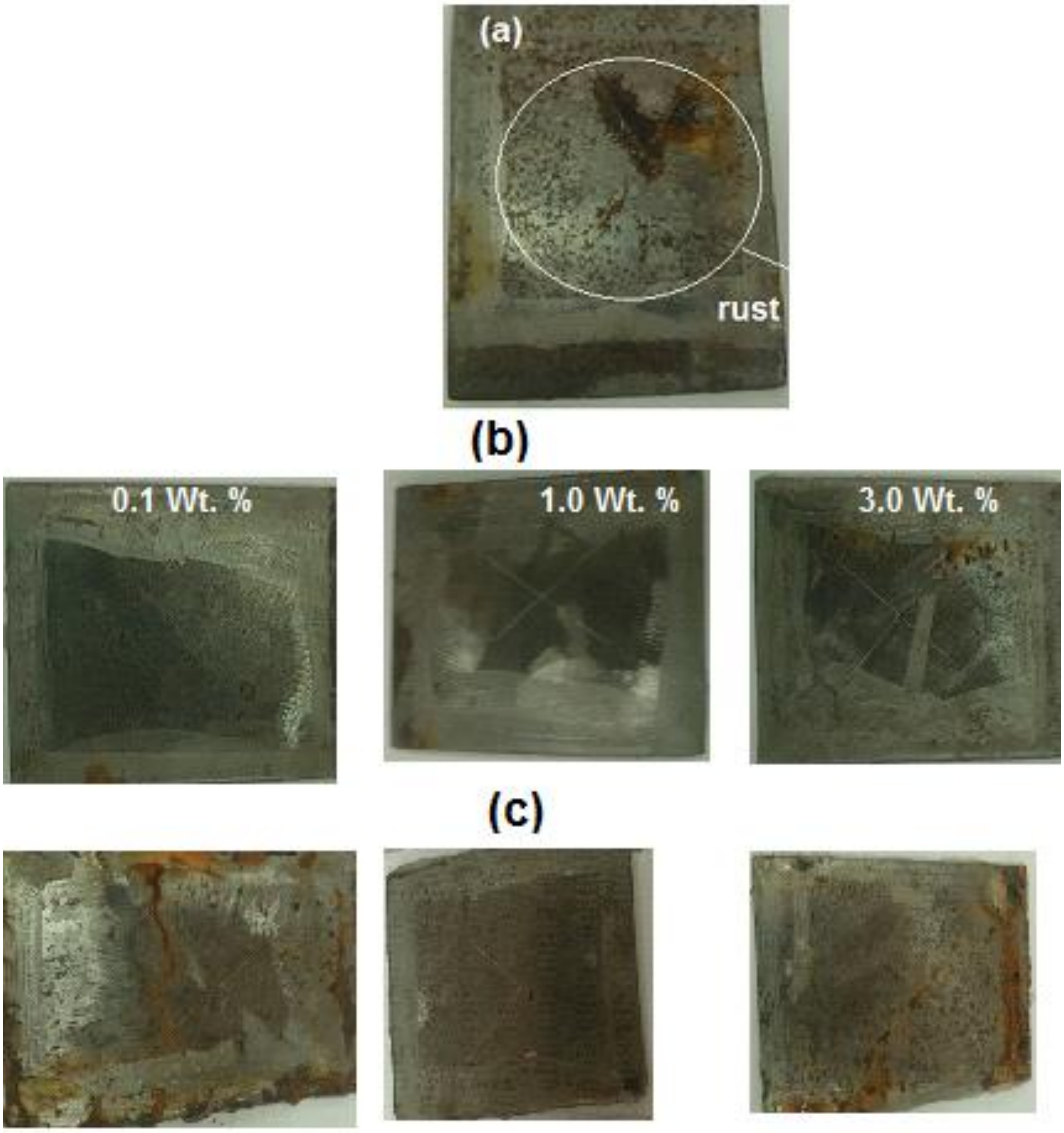
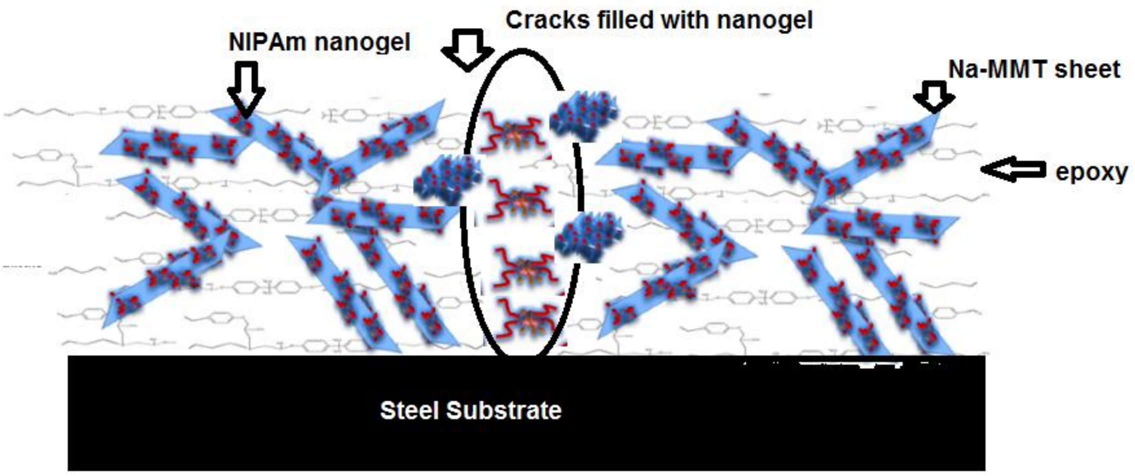


Figure 6. Salt spray photos of tested panels a) blank after exposure 300 h, b) cured epoxy embedded with different ratios of Na-MMT/ NIPAm-VP after exposure 1000 h and c) cured epoxy embedded with different ratios of Na-MMT/ NIPAm-AMPS-Na after exposure 1000 h.

The anticorrosion mechanism for application modified epoxy with of Na-MMT/NIPAm-AMPS-Na and Na-MMT/NIPAm-VP as a protective coat for steel is illustrated in Scheme 1. The filling of epoxy matrix with exfoliate Na-MMT and nanogel prevent the penetration of both salt or water into organic coatings through cracks with increment the adhesion strength between epoxy and steel surfaces. The inhibition effect of Na-MMT/NIPAm-VP is higher than Na-MMT/NIPAm-AMPS-Na which can be explained by the low swelling characteristics of Na-MMT/NIPAm-VP in water electrolyte. The Na-MMT/NIPAm-VP can be probably leached to cracks or scratches with higher amount to limit the corrosion extent.



Scheme 1. Mechanism of repair of epoxy matrix embedded with Na-MMT nanogel composites.

4. CONCLUSIONS

The NIPAm-VP andNIPAm-AMPS-Na nanogel show great ability to exfoliate the Na-MMT sheets. The particle size data confirm that the particle size (nm) and PDI of Na-MMT/NIPAm-AMPS-Na nanogel increased in sea water more than distilled water. Moreover, the prepared Na-MMT/NIPAm-AMPS-Na nanogel has great sensitivity to absorb water due to its sensitivity as strong polyelectrolyte to salt. Na-MMT/NIPAm-VP nanogel shows lower surface activity in water than Na-MMT/NIPAm-AMPS-Na. These data were referred to the strong ability of Na-MMT/NIPAm-VP nanogel to collapse in sea water more than Na-MMT/NIPAm-AMPS-Na nanogel composite**.** The formation of alternate nonionic NIPAm-VP copolymer controlled the gelling of Na-MMT/NIPAm-VP in sea water more than fresh distilled water.The filling of epoxy matrix with exfoliate Na-MMT and nanogel prevent the penetration of both salt or water into organic coatings through cracks with increment the adhesion strength between epoxy and steel surfaces. The inhibition effect of Na-MMT/NIPAm-VP is higher than Na-MMT/NIPAm-AMPS-Na which can be explained by the low swelling characteristics of Na-MMT/NIPAm-VP in water electrolyte. The Na-MMT/NIPAm-VP can be probably leached to cracks or scratches with higher amount to limit the corrosion extent.

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