NANO REACTIVE POLYMER BASED ON POLYANILINE AS ASPHALT MODIFIER FOR ANTICORROSION APPLICATION

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Abstract

Recently, the application of nanotechnology in the corrosion protection of metals has gained momentum. On the other hand, polymers are used as corrosion inhibitor coatings that are physically, chemically or electrochemically deposited on the metal substrate. Although asphalt has low cost, high cohesive nature, rheological properties and high thermal resistance but it is not practically used on a large scale in anticorrosion applications. So, the aim of this research is to use the nanotechnology science in preparing modified asphaltic materials to produce new and more qualified anti-corrosive coatings. To achieve this aim, nanoparticles of polyaniline (PANI-H_2SO_4) using template free polymerization method are prepared and characterized by FTIR, XRD and SEM. Another nonreactive polymer of type low density poly ethylene (LDPE) has been used for comparison purpose. The two types of modifiers have mixed with asphalt of type 85/25 in different percentages as 2, 4, 6, 8& 10٪by the weight of the virgin bitumen. The modified asphalt samples have physically tested and the morphology by SEM has conducted. The ability of modified bitumen samples to serve as corrosion protective coatings for carbon steel has examined by open circuit potential-time (E_{ocp}-time), and potentiodynamic polarization in 0.5 M HCl solution. The results revealed that all the prepared samples show a good behavior as anticorrosive materials and bitumen modified by PANI-H_2SO_4 is the most qualified material as it had protection efficiency of 99.996 % with respect to uncoated CS while the protection efficiency of PMA/LDPE is 99.98 %.

Keywords : Nanopolymer, polyaniline, polymer modified asphalt, anticorrosive coating.

Introduction

Bitumen, which remains after crude oil processing and catalytic cracking [1], is a sticky, black and highly <u>viscous</u> liquid or semi-solid material that is a complex mixture of four main components– saturates, aromatics, resins and asphaltenes (SARAs). Because of the complexity of this material, the complete internal structure of asphalt is not yet known with sufficient certainty. The composition of asphalt varies with the source of the crude oil and the method of manufacturing. The first three groups are usually lumped together under the name maltenes. The complexity, aromaticity, heteroatom content, and molecular weight increase in the order S < A < R < As [2,3].

Asphaltenes represent the heaviest part of asphalt, with the hydrogen-to-carbon ratio as low as 1.15 (per mole) [4]. Thus, bitumen composition and temperature strongly influence the mechanical properties and microstructure of bitumen [5]. Regarding its end-use, asphalt behaves as   a viscoelastic material at usual in-service

temperatures, showing mechanical/rheological properties suitable for its traditional applications [6,7] that range from the construction of road pavements to more specialized purposes, such as waterproof membranes for the roofing industry [8&9].

Traditionally, the performance of bitumen has been improved through the utilization of additives such as virgin polymers waste polymers. The addition of different types of polymers to bitumen has been shown to improve its performance in a broad range of in-service temperatures [10].

Blending of asphalt with polymers forms multiphase systems, and the properties of asphalt–polymer blends depend on the concentration and the type of the used polymer. The effect of a polymer usually starts to be significant at concentrations of about 4–6%. Polymers that have been commonly used to modify bitumen include styrene–butadiene–styrene copolymer (SBS), styrene–butadiene rubber (SBR), styrene–isoprene–styrene copolymers, ethylene vinyl acetate (EVA), polyethylene (PE), ethylene–butyl acrylate and others [11–14].

Polymers are physically dispersed into bitumen, giving rise to a modified binder consisting of scattered domains of swollen polymer all over a bituminous continuous phase, with improved mechanical properties as a result of weak physical interactions between the polymer domains and the bitumen compounds. However, the above listed polymers usually present a very low compatibility with bitumen, and phase separation may eventually occur in the event of the blend being stored at high temperature in absence of stirring [15].

Recently, reactive polymers are being considered as novel bitumen modifiers, aimed to improve bitumen-polymer compatibility, and reducing the quantity of additives required. Reactive polymers are capable of forming chemical bonds with some bitumen molecules, improving the mechanical behavior, storage stability and temperature susceptibility of the resulting binder [16, 17–21].

The modification capability of MDI–PEG prepolymer as a reactive polymer comparing with (SBS), recycled thermoplastic polymers (EVA/LDPE blends), and crumb tire rubber as a non-reactive polymers was previously studied [17]. All the non-reactive polymer modified bitumen samples studied are largely unstable during storage at high temperature, while MDI–PEG modified bitumen remains homogeneous as a result of chemical reactions between -NCO groups of the reactive polymer with polar groups of bitumen compounds.

In general blends of bitumen with polymers may thus have a number of applications and one of these applications is used as protective coatings. Protective coatings are employed to protect steel structures from corrosion due to exposure in corrosive media, such as salt spray, high humidity, ultraviolet radiation and other weather conditions. These coatings function by providing a barrier between the surface and corrosion inducing elements. Key attributes in the performance of protective coatings are, therefore, good adhesion to substrate, a low permeability to ions, water, gases and other corrosive species of the service environment. The aim of this research is to use the nanotechnology science in preparing modified asphaltic material to produce new and more qualified anti-corrosion materials.

2. Materials

- Blown asphalt of type 85/25 was obtained from Suez For Petroleum Co. and having characteristics as illustrated in Table 1.

Table 1: Characteristics of the bitumen studied

Test	ASTM standard	Value
Penetration@25°C,100g,5s (0.1mm)	D5	25
R&B softening point (°C)	D36	85
Ductility at 25°C (cm)	D113	14
Asphaltenes content (wt. %)	D3279	38

- Two different types of polymers have been used as modifying agents:
Polymer (1): non reactive polymer of type LDPE
Melt flow index (MFI) = 1.2 g/10 min, density = 0.921 kg/m^3,   Tm = 110 °C.
Polymer (2): laboratory synthesized nano reactive polymer of polyaniline-H_2SO_4 (PANI-H_2SO_4). Aniline (ANI) monomer is purchased from Merck Co. and is distilled under reduced pressure prior to use. Ammonium peroxidisulfate of AR grade is purchased from Merck Co. All other chemicals are analytical grade and are used as received.

3. Experimental work

The experimental work included the following steps:

3.1. Laboratory synthesis of polyaniline

Polyaniline was prepared by template free method [22–25] by mixing the aqueous solution of (1.23 mm) ammonium peroxidisulfate, an oxidant, and (2.5 mm) aniline dissolved in 50 ml of 1M sulfuric acid. A weighed amount of aniline was dissolved in diluted sulfuric acid while agitated continuously. Once perfectly dissolved, ammonium peroxidisulfate dissolved in water was added at 0-5 °C. The individual stages of this process were accompanied by the color changes. Polyaniline was created in the form of both a precipitate and as a film that covered the walls of the reaction container. The precipitated mixture was left until the next day. Then the mixture was filtered through on a paper filter. The product was rinsed with distilled water, diluted sulfuric acid, and acetone. The so prepared PANI sulfate (hereinafter referred to as 'PANI- H_2SO_4') was dried in air and then at 60 °C in an oven.

3.2. Characterization of synthesized polyaniline

The (FT-IR) absorption spectra of the PANI samples was recorded using a "Pruker Spectrometer"; Model "Vector 22"; in Micro Analytical Center – Cairo University. Particle size and morphology of prepared PANI were evaluated by scanning electron microscopy using SEM model quanta FEG attached with EDX Unit, with accelerating voltage 30 K.V., magnification 250x up to 1000000x and resolution for Gun.1m. Samples were coated with gold. The crystallinity of the prepared PANI was determined by conventional powder X-ray diffraction (XRD) using a Philips differactrometer (type PW 3710). The patterns were run with Ni-

filtered copper radiation (CuKα = 1.5404 °A at 30 kV and 10 mA) with a scanning speed of 2 θ = 2.5 ° min $^{-1}$.

3.3. Modified bitumen preparation

The asphalt was heated in an iron container. When the asphalt temperature reached 120&170°C for reactive and non reactive polymers respectively, a low-shear mixer was dipped into the can and set to 1200 rpm. The polymers were added gradually (about 0.5 g/min) while keeping the temperature within the range of ±5 °C during the polymer addition. Polymer modifiers were added in portions of 2, 4, 6, 8 and 10%, and the processing times were (0.5, 2 hr) for reactive and non reactive polymers, respectively. Finally, the obtained polymer modified asphalt (PMA) samples were further characterized.

3.4. Characterization of modified bitumen

PMA samples were tested for conventional test methods and scanning electron microscopy analysis as in the following:

3.4.1. Conventional bitumen tests

The base and PMA samples were subjected to the following conventional bitumen tests; needle penetration at 25 °C, softening point and ductility.

3.4.2. Scanning electron microscopy

Scanning electron microscopy has been used to investigate the microstructure of the PMA by determining the state of dispersion of the polymer within the base bitumen as well as characterize the nature of the continuous and discontinuous phase. By far, scanning electron microscopy is the most valuable method for studying the phase morphology of polymer modified asphalt [26], as it allows the observation of the homogeneity and the structure in the raw state [27]. The bitumen rich phase appears dark or black, whereas the polymer rich phase appears light. Samples of each PMA are prepared (for imaging purposes) by placing a drop of heated bitumen sample between microscope slides. PMA are then examined at room temperature under SEM model quanta FEG that used for characterize the prepared PANI.

3.4.3. Testing of corrosion resistance properties

The anticorrosive properties of the proper modified bitumen samples are examined by open circuit potential-time (E_{ocp}-time) and potentiodynamic polarization, measurements, in 0.5 M HCl solution as electrolyte. All measurements are performed on VoltaLab 80 (PGZ402 & VoltaMaster 4) Universal Electrochemical Laboratory. Carbon steel plates (20 mm × 20 mm × 2 mm) coated with the PMA samples are used as working electrodes while Pt and SCE were the counter and reference electrodes respectively. The area of 1 cm² was used for testing. The Tafel plots measurements are carried out at sweep rate of 20 mV/s and within the potential range from –900 to –400, –700 to –300, –700 to –300, and from –1000 to –300 mV for [carbon steel (CS), Asphalt, Asphalt/LDPE, and Asphalt/PANI- H_2SO_4] respectively. Tafel lines extrapolation method was used for detecting Icorr, Rp (polarization resistance), corrosion rate values and protection efficiency (P_{EF}%) for

the studied systems. The Corrosion rate calculated as a number of mm of iron thickness corroded per year (the Atomic mass, Valence, Density and Working electrode area are used to calculate the corrosion rate).

4- Results and discussion

4-1: Characterization of PANI particles

4.1.1. FT-IR spectra:

Figures 1 shows the FT-IR spectra of PANI- H_2SO_4. In these figures vibration bands at 1112, 1291, 1459 and 1572 cm^{-1} in the figure are the characteristic bands for polyaniline. In this spectrum the peaks at 1459 and 1572 cm^{-1} are assigned to C=C stretching of the benzenoid and quinoid rings respectively and the peak at 1242 cm^{-1} which is characteristic of PANI-ES form is also seen [28].. The peak at 3388 cm^{-1} is assigned to N-H stretching of Benzenoid ring [29]. The peak at 1291 cm^{-1} is assigned to C-N stretching of the secondary amine of PANI backbone. The peaks at 1112 cm^{-1} can be assigned to an in plane bending vibration of C-H (mode of N=Q=N, Q=N$^+$H–B and B–N$^+$H–B) which formed during protonation [30]. Therefore, the FT-IR technique confirms the PANI-HCl preparation.
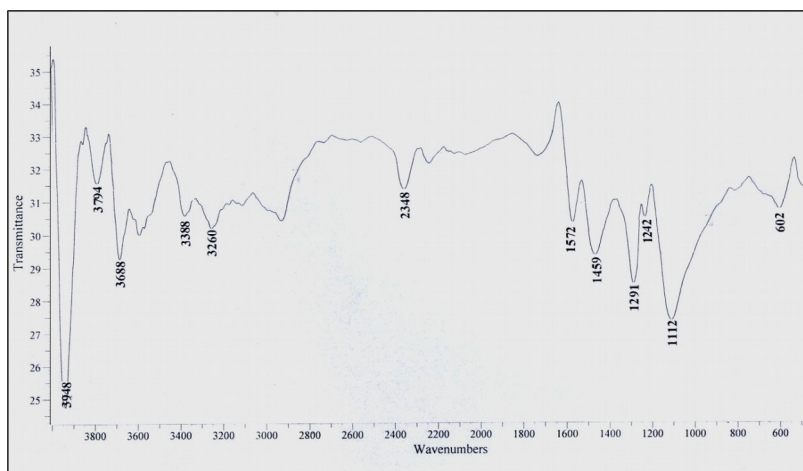

Fig 1: FT-IR Spectra for PANI- H_2SO_4

4.1.2. Scan Electron Microscopy:

The aniline polymerization in acidic medium results in the formation of a protonated, partially oxidized form of PANI. This process under the test conditions leads to nano particle PANI- H_2SO_4 [31, 32]. Figure 2 shows SEM micrographs of the PANI- H_2SO_4 nanoparticles in which particles possess different distribution size.
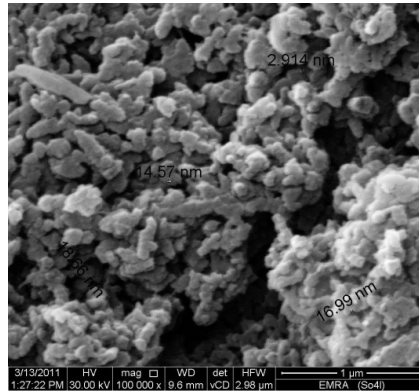
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Fig 2: SEM photograph of PANI- H₂SO₄

4.1.2.X-Ray Diffraction:

X-ray diffraction is a versatile and non-destructive technique used for identification of the crystalline phases present in solid materials and for analyzing structural properties of the phases. Therefore, X-ray diffraction patterns are recorded for PANI-H₂SO₄ nanopolymer (Fig. 3). The characteristic peaks are observed at 2θ = 6.445°, 20.25°, 20.70°and 26.38°. Presence of these peaks in the XRD pattern confirms the formation of PANI-H₂SO₄ nanopolymer. The intensity of the XRD pattern peaks can be influenced by crystallinity or by polyaniline chains order in polymer structure. According to Fig. 3, the alignment and the intensity of the peaks suggest that the prepared PANI-H₂SO₄ has relatively crystalline structure.
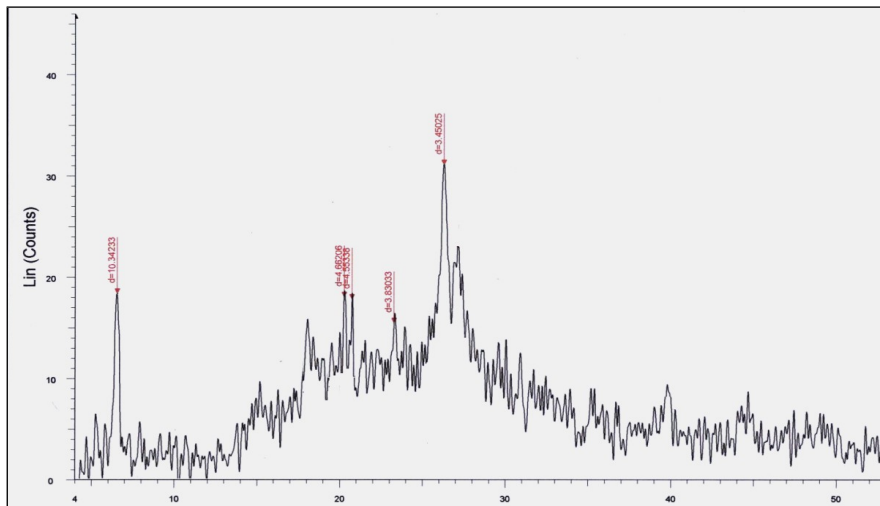

Fig. 3: X-ray diffraction patterns of PANI- H2SO4

4-2: Characterization of modified bitumen

4.2.1. *Conventional tests:*

The effect of LDPE and nano PANI-H$_2$SO$_4$ modification on the properties of the base bitumen can be seen in Table 2. There is a decrease in penetration and ductility values and an increase in softening point temperatures with increasing polymer contents. This trend is relatively uniform for the PANI-H$_2$SO$_4$ based samples. However, there is a significant large decrease in the penetration values and a considerable increase in the softening point temperatures of LDPE based samples comparing to PMA using nonreactive polymer. The increase in softening point temperature, which is an indicator of the stiffening of PMA [33], is favorable since bitumen with higher softening point may be less susceptible to permanent deformation [34].

Polymer modification reduces temperature susceptibility (as determined by the penetration index—PI) of the bitumen. Lower values of PI indicate higher temperature susceptibility [26]. Asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation at high temperature [35]. As seen in Table 2, all PMA samples exhibit less temperature susceptibility compared to base bitumen with increasing polymer content. LDPE based PMA yield higher PI values compared to PANI based PMA, especially at lower polymer contents.

Table 2: Conventional properties of PMA

% Content						Property	Type
10	8	6	4	2	0		
5	6	7	8	10	25	Penetration (mm)	LDPE
150	143	138	133	123	85	Softening point(°C)	
4	6	8	9	11	14	Ductility (cm)	
5.9	5.8	5.7	5.6	5.2	3.3	Penetration index PI	
10	13	16	19	23	25	Penetration (mm)	PANI-H$_2$SO$_4$
127	118	110	105	94	85	Softening Point(°C)	
9	10	11	12	13	14	Ductility (cm)	
5.4	5.3	5.0	4.88	4.17	3.3	Penetration index PI	

SP: Softening Point.
PI = (1952−500×LogP$_{25\,°C}$−20×SP)/(50×LogP$_{25\,°C}$−SP−120)

4.2.2. *Microstructure*:

The microstructure of PMA samples has been investigated by using a scan electron microscope by characterizing the nature of the continuous phase, fineness of the dispersion of the discontinuous phase as well as the description of the phases and shapes. A distinction can be made between the PMA samples whose continuous phase of a bitumen matrix with homogenous dispersed polymer particles. Scan electron microscopy images of PMA/LDPE with different ratio were showed with base bitumen in Fig. 4. In the images, the dispersed polymer phase appears light while the bitumen phase appears dark. A clear distinction regarding the homogeneity of the phases is observed between the different modified samples as seen in Fig. 4. PMA with the polymer content (4%), reveal the finest homogenous dispersion of

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polymers and as indicated in Fig. 4, the homogeneity of the LDPE based PMA lowers as the polymer content increases.

a) Base bitumen

b) 2% LDPE

c) 4% LDPE

d) 6% LDPE
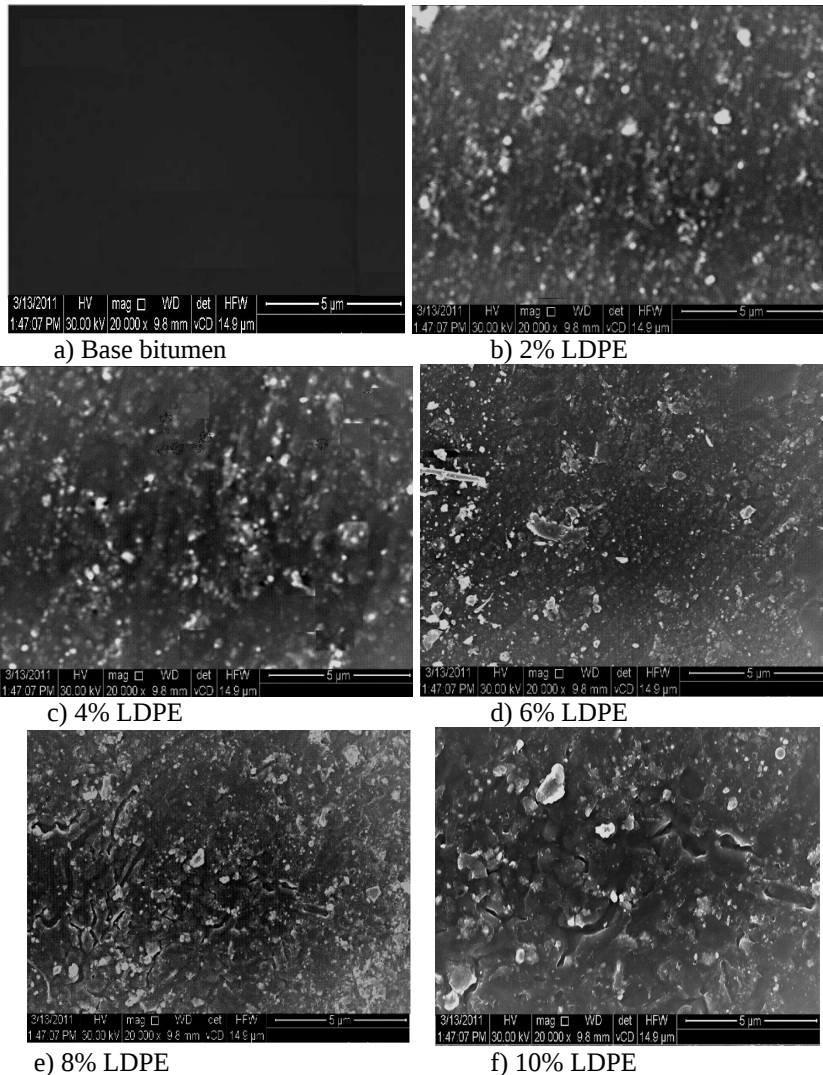

e) 8% LDPE

f) 10% LDPE

Fig. 4: SEM of PMA with LDPE

Fig.5 shows the scan electron microscopy images of PMA/PANI- H_2SO_4 with different ratio. In the images, the dispersed polymer phase appears light while the bitumen phase appears dark. PMA with the same polymer content (4%) seems to be the continuous homogenous dispersion phase for the polymer in the asphaltic matrix and the homogeneity of the PANI-H_2SO_4 based PMA lowers as the polymer content increases. It should be mentioned that the appearance of continuous polymer matrix in the case of PMA with PANI-H_2SO_4 seems to be more compatible with the

asphaltic matrix since this type of polymer is included in the reacted system and as a consequence of chemical reactions between -NH groups of the reactive polymer with polar groups (-OH) of bitumen compounds..
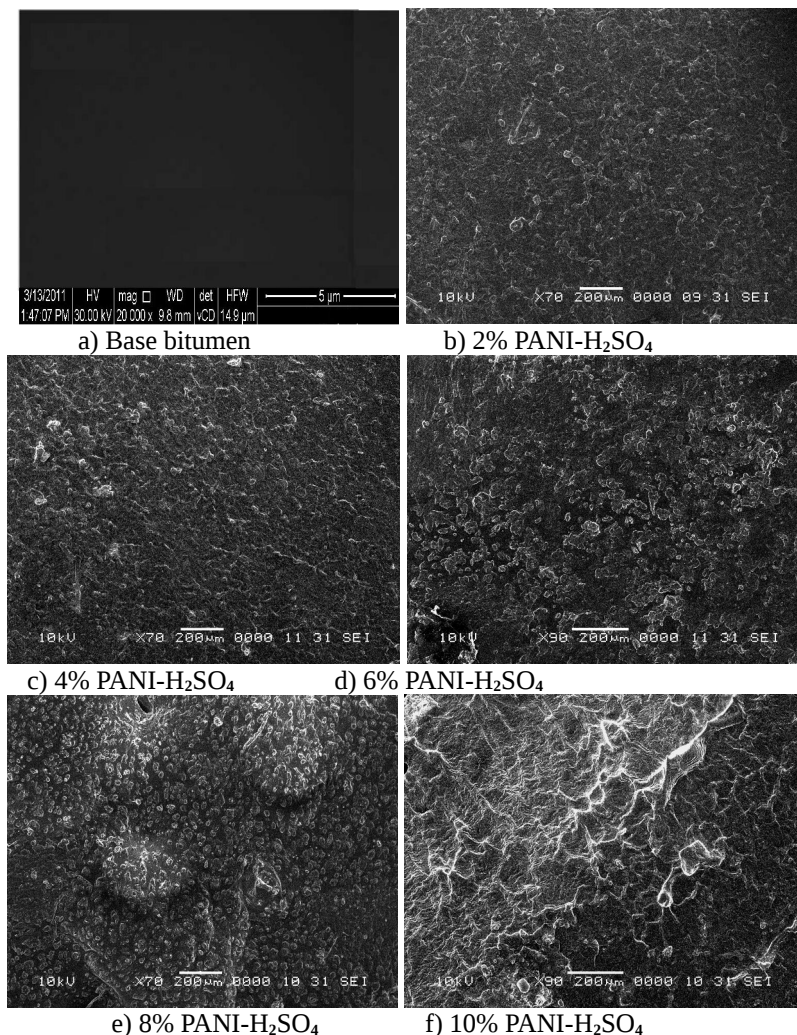

a) Base bitumen

b) 2% PANI-H_2SO_4

c) 4% PANI-H_2SO_4

d) 6% PANI-H_2SO_4

e) 8% PANI-H_2SO_4

f) 10% PANI-H_2SO_4

Fig. 5: SEM of PMA with PANI-H2SO4

4-3: Corrosion protection performance

According to the previously mentioned results of the physical and morphological tests, the percent of 4% is the proper percent for addition of both nano reactive and nonreactive polymer modifiers. So, the modified asphaltic materials with this percent were selected to be tested to serve as corrosion protective coatings for carbon steel.

4.3.1: Open circuit potential measurements

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   Potential - time curves measurements are carried out to investigate corrosion behavior of carbon steel (CS) in 0.5 M HCl in the presence and absence of the modified asphaltic materials. Fig. 6 shows E_{ocp} -time curves obtained in corrosive medium. It is clear from Fig. 6 that the initial E_{ocp} value of uncoated electrode of carbon steel (CS) is - 706 mV (vs. SCE) and remains almost constant after 30 min of immersion time. The initial E_{ocp} of CS/Asphalt is found to be on the cathodic side of PMA samples but more positive (−530 mV) than that of CS (−706 mV), but after 30 min of exposure time to corrosive environment, the E_{ocp} shifts to more cathodic region (−640 mV). On the other hand, the coatings containing PMA have a healing effect i.e. although there is a decrease in the E_{ocp}; it shifts to more anodic side, where the E_{ocp} value of CS/ PMA-LDPE is initially (−470 mV) and finally (−550 mV) and that of CS/PMA-PNI-H_2SO_4 is initially (-430 mV) and finally (−510 mV). This tendency to shift the E_{ocp} to potentials more noble than the uncoated electrode of carbon steel is the greatest in case of PMA/PANI-H_2SO_4.
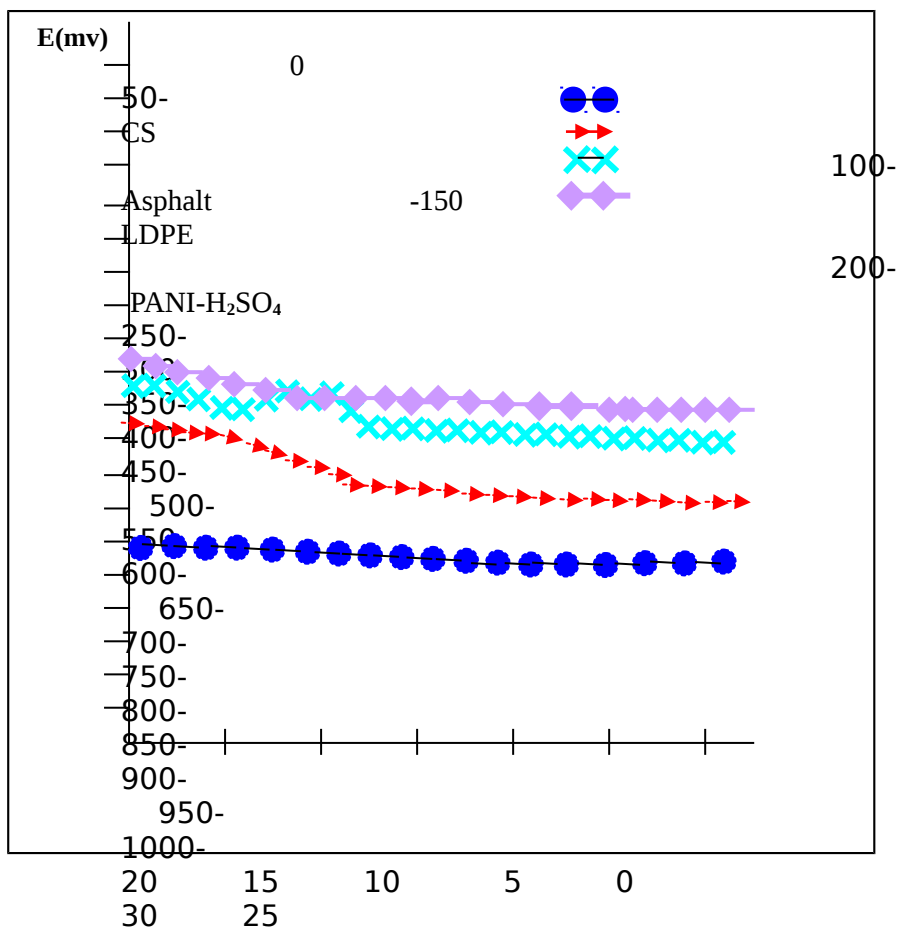
Time (min)

Fig. 6: Eocp-time curves of uncoated CS, CS/Asphalt, CS/PMA-LDPE   and CS/ PMA-PANI-H₂SO₄ in 0.5M HCl

4.3.2: Potentiodynamic polarization measurements

The polarization curves for base asphalt, PMA/LDPE and PMA/PANI-H$_2$SO$_4$ coatings on carbon steel (CS) electrodes immersed in   a 0.5 M HCl are illustrated in fig.7. Potentiodynamic polarization is useful for compression of relative performances of various types of coatings being tested under the same conditions [36]. The examination of Fig. 7 shows that presence of coatings on CS considerable reduces currents.

In fact for PMA, the E_{ocp} remains on the anodic side of the other values even after exposure to corrosive media. The positive shift in the value of E_{ocp} compared to that of CS as well as base asphalt coated steel clearly indicates the high corrosion resistance provided by these coatings.
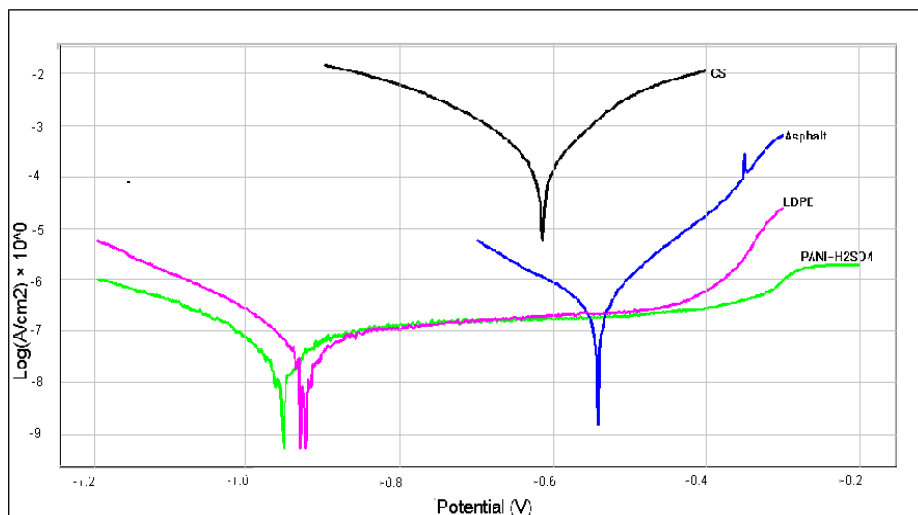

Fig. 7: Potentiodynamic polarization curves of coated and uncoated carbon steel electrodes immersed in 0.5 M HCl solution. The different types are indicated near the curves.

The corrosion parameters calculated from Tafel plots for CS, base asphalt, PMA/LDPE and PMA/PANI-H$_2$SO$_4$ measured are summarized in Table 2. The corrosion current, Icorr, for all the three coated-electrodes are less than that observed in the uncoated CS. The lowest value of Icorr indicated that the PMA/PANI-H$_2$SO$_4$ coated CS electrode have the highest corrosion inhibition. However, base asphalt, PMA/LDPE coated electrodes still exhibited effectively corrosion protection than the uncoated CS as identified by the corrosion currant shown in Table 2.

On the other hand, the polarization resistance, Rp, can be evaluated from the Tafel plots, according to the Stearn–Geary equation [37]:

$$R_p= b_ab_c/2.303(b_a+b_c)Icorr$$

Here, Icorr is the corrosion current determined by an intersection of the linear portions of the anodic and cathodic curves, and ba and bc are the anodic and cathodic Tafel slopes ($\Delta E/\Delta \log I$), respectively. The protection efficiency (P_{EF}%) values are estimated using the following equation [38]:

$$P_{EF}\% = 100\times[CR \text{ (uncoated)} − CR \text{ (coated)}] / CR \text{ (uncoated)}$$

As expected, the incorporation of polymers into asphalt led to an increase of Rp value. Moreover, Rp value of PMA/PANI-H_2SO_4 is the highest value. It also indicated that the PMA/PANI-H_2SO_4 coating exhibited excellent anticorrosion effect even better than the PMA/LDPE coating.

The order of the protection efficiency can be as follows:

CS< CS/asphalt<CS/asphalt PMA/LDPE <CS/asphalt PMA-PANI-H_2SO_4. This may led to the conclusion that modified bitumen with reactive polymers could greatly inhibit the steel corrosion compared with nonreactive polymers and unmodified bituminous coating. Consequently, the advantage of protection by conducting polymer coating is that the coatings get more tolerance to pin holes due to their passivation ability.

The conducting polymer coating polyaniline stabilizes the potential of the metal in the passive region and maintains a protective oxide layer on the metal. It has been stated that the doped conducting polymer will generate an electric field which will restrict the flow of electrons from the metal to an outside oxidizing species thus preventing the corrosion [39]. Moreover, it is assumed that, the PANI coating protect the iron from corrosion by controlling both the anodic and cathodic reactions. The adsorption on anodic sites occurs through pi-electrons available on the conjugated aromatic ring and lone pair of electrons of nitrogen atoms, decreases anodic dissolution of iron by interacting with empty orbital of the metal. In acidic solution, the PANI acts as protonated species. These protonated species adsorb on the cathodic sites of the iron and reduce the evolution of hydrogen [40].

Table 3: corrosion parameters calculated from Tafel plots

Electrode type	I corr.	R_p	Corrosion Rate	P_{EF}%
CS	0.6447 mA/cm²	102.03 ohm.cm²	7.540 mm/Y	_
CS/asphalt	0.3111 µA/cm²	56.38 kohm.cm²	3.638 µm/Y	99.95
CS/PMA-LDPE	0.0938 µA/cm²	537.56 kohm.cm²	1.097 µm/Y	99.98
CS/PMA-PANI-H_2SO_4	21.5643 nA/cm²	842.90 kohm.cm²	252.2 nm/Y	99.996

5- Conclusions

The chemical synthesis of reactive PANI-H_2SO_4 nano -fibers are achieved by template free polymerization and characterized with FT-IR, XRD and SEM. The

prepared PANI and LDPE are used for modifying asphalt of penetration grade 85/25. From the resulted data, it can concluded that a nano reactive (PANI-H_2SO_4) and non reactive (LDPE) polymers are able to improve and enhancement the mechanical properties of asphalt. Asphalt modification with LDPE yields the largest values of softening point and the lowest values of penetration, which may be attributed to the oxidation of the maltene fraction during processing. On the other hand, PANI-H_2SO_4 modified asphalt samples are processed at lower temperature (120 °C) and during shorter processing time (30 min) than non-reactive polymer-modified asphalt, and this relatively low processing temperature avoids significant asphalt hardening. The improvement of asphalt properties by PANI-H_2SO_4 with low processing temperature is a consequence of chemical reactions between -NH groups of the reactive polymer with polar groups (-OH) of bitumen compounds. The anticorrosive properties of PMA are examined by electrochemical measurements, including Eocp-time, potentiodynamic polarization which made on coated CS in 0.5 M HCl. It is found that PMA coatings are able to provide much better protection than base asphalt coatings, but PANI-H_2SO_4 based coating seems to be the best one, that it gives protection efficiency equal to 99.996 % of uncoated CS with corrosion rate equal to 252.2 nm/Y. On the other hand the protection efficiency of LDPE based coating is 99.98 % with corrosion rate equal to1.097 µm/Y. The highest inhibition properties of PMA/PANI-H_2SO_4 are related to passivation and barrier effect, while, corrosion performances of base asphalt and PMA/LDPE are related with their barrier effect only.

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