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Investigation of the corrosion protection behavior of natural montmorillonite clay/bitumen nanocomposite coatings

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ABSTRACT

The influence of clay particles on the corrosion properties of bituminous coating was studied. Different percentages of natural montmorillonite clay (Cloisite Na^+) were added to emulsified bitumen in water to make 2 wt.%, 3 wt.% and 4 wt.% of clay/bitumen nanocomposite coatings. The coatings were applied on steel 37. Optical microscopy and transmission electron microscopy (TEM) were employed to study the structure of nanocomposite. To investigate the anti-corrosion properties of the coated panels, electrochemical impedance spectroscopy (EIS) was used. The findings indicated that the addition of clay nanolayers improved corrosion resistance of the coatings. Moreover, increasing clay loading up to 4 wt.%, increased the corrosion resistance.

1. Introduction

Bitumen, obtained from petroleum refinery bottoms, is a thermoplastic containing bituminous materials. Because of its low cost, inherent cohesive nature, rheological properties and good thermal resistance, this material has been widely used as sealants, binders, waterproof coatings and paving materials [1].

Bitumen is a natural polymer that has low molecular weight with viscoelastic property [2]. Over the years, polymeric coatings have been developed due to their useful barrier properties. However, pristine polymeric coatings are still permeable to corrosive agents such as water, oxygen and destructive ions like Cl^-, H^+, SO_4^{2-}. In order to enhance the barrier properties of these polymeric coatings, various kinds of additives such as extenders and inorganic pigments have been used by a great number of researchers [3–6]. The addition of polymers to bitumen is known to enhance service properties such as improved thermo mechanical resistance, elasticity, and adhesive properties [7]. However, bitumens which are modified with polymers are expensive, difficult to operation and incompatible [8]. Therefore, further efforts have been made to find new modifiers.

Recently, the layered silicates have been widely used to modify polymers [9]. Layered silicate, which consists of layers of tetrahedral silicate sheets and octahedral hydroxide sheets, is a type of mineral materials with low cost and abundance [10]. Polymer chains can be intercalated into the interlayer of clay, in order to disperse the clay into the polymer matrix at nanometer scale. These lead to the significant improvements in the thermal, mechanical and barrier properties of polymers [11–15].

Montmorillonite (MMT) was used to improve both the physical and rheological property of bitumen [16,17]. Nevertheless, previous researches do not report any information regarding the effect of MMT on the anticorrosion properties of bitumen. Hence, the aim of this study is to investigate the corrosion protection behavior of natural montmorillonite clay/bitumen nanocomposite coatings on steel.

2. Experimental

2.1. Materials

Panels of steel 37 (6.5 cm × 6.5 cm × 0.3 cm) were used as metallic substrates. The panels were sandblasted to Sa2 ½ (according to ASTM D609) and kept in desiccator. Prior to coating, the panels had been degreased with toluene and acetone. TW315 is a kind of bitumen emulsified in water which is complied with BS3416 type I standard as waterproof coating. Max volatile compounds of TW315 is 60 wt.% and max organic compounds is 1 wt.% and its viscosity with Ford cup number 2 at 23 °C is 30–60 s. TW315 was provided from Tiva Co. The natural montmorillonite clay (Cloisite Na^+ or Na^+-MMT) as an additive was prepared from Southern Clay Product Co. Some properties of the latter are shown in Table 1.

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Table 1
Natural montmorillonite nanoclay (Cloisite Na^+) pigment properties.

Particle size	Color	Density	Moisture content	X-ray results (d_{001})
<25 μm	Off-white	2.86 g/cc	4–9%	1.17 nm

2.2. Preparation of nanocomposites

Three set of nanocomposite samples containing 2, 3 and 4 wt.% of Cloisite Na^+ were prepared as described below through solvent intercalation technique. At first, the stoichiometric amounts of Cloisite Na^+ were added to 10 ml of distilled water to make 2, 3 and 4 wt.% mixtures. Then, by a propeller, the mixtures were mechanically stirred at 1000 rpm for 120 min at room temperature. Afterward, they were sonicated for 90 min in an ice bath. The ultrasonic lab device UP200H (200 W, 24 kHz) with an amplitude of 100 and cycle gage of 1 was used for sonication purpose. Secondly, the stoichiometric amounts of TW315 which were added to the mixtures to make 2, 3 and 4 wt.% of nanocomposite coatings were being blended mechanically for 45 min. The coatings were labeled as PNC2, PNC3 and PNC4 of which PNC standard for polymer nanocomposite and the number indicated the weight percent of clay used in the mixtures. The coatings were applied on the panels using 100 micrometer baker film applicator Elcometer according to ASTM D823-95(2012). The thickness of the dry film was measured by Elcometer 415 and was found 60 ± 5 μm.

2.3. Nanocomposites structural characterization

The optical homogeneity of the water/clay dispersion and the effect of sonication process on de-agglomeration of clay aggregates were examined using a BX-50 Olympus optical microscope.

To evaluate the intercalation/exfoliation of nanoclay in the bitumen matrix, TEM experiment was performed using Philips CM30. TEM expands the qualitative understanding of the internal structure and can directly provide information on morphology and defect structures in real space [18,19].

2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) is a non-destructive and useful technique for studying, measuring, and estimating coating durability [20]. The EIS measurements were performed using Auto lab PGSTAT 302N coupled with frequency response analyzer (FRA) 1260, over a frequency range of 100 kHz to 1 mHz with 10 mV amplitude of sinusoidal voltage at open circuit potential. Neat bitumen was applied as a reference coating to evaluate nanoclay/bitumen mixture. Fitting of the experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home written least square software based on Marquardt method for optimization of the functions and Macdonald weighting for the real and imaginary parts of the impedance [21,22]. Three conventional electrode cells were used for electrochemical measurements. 3.5 wt.% NaCl solution was employed as electrolyte. Coated panels acted as working electrode with an exposed area of 2.009 cm^2. Platinum and a saturated Ag/AgCl electrode were employed as a counter and reference electrode, respectively. The setup of the cell was placed in a Faraday cage.

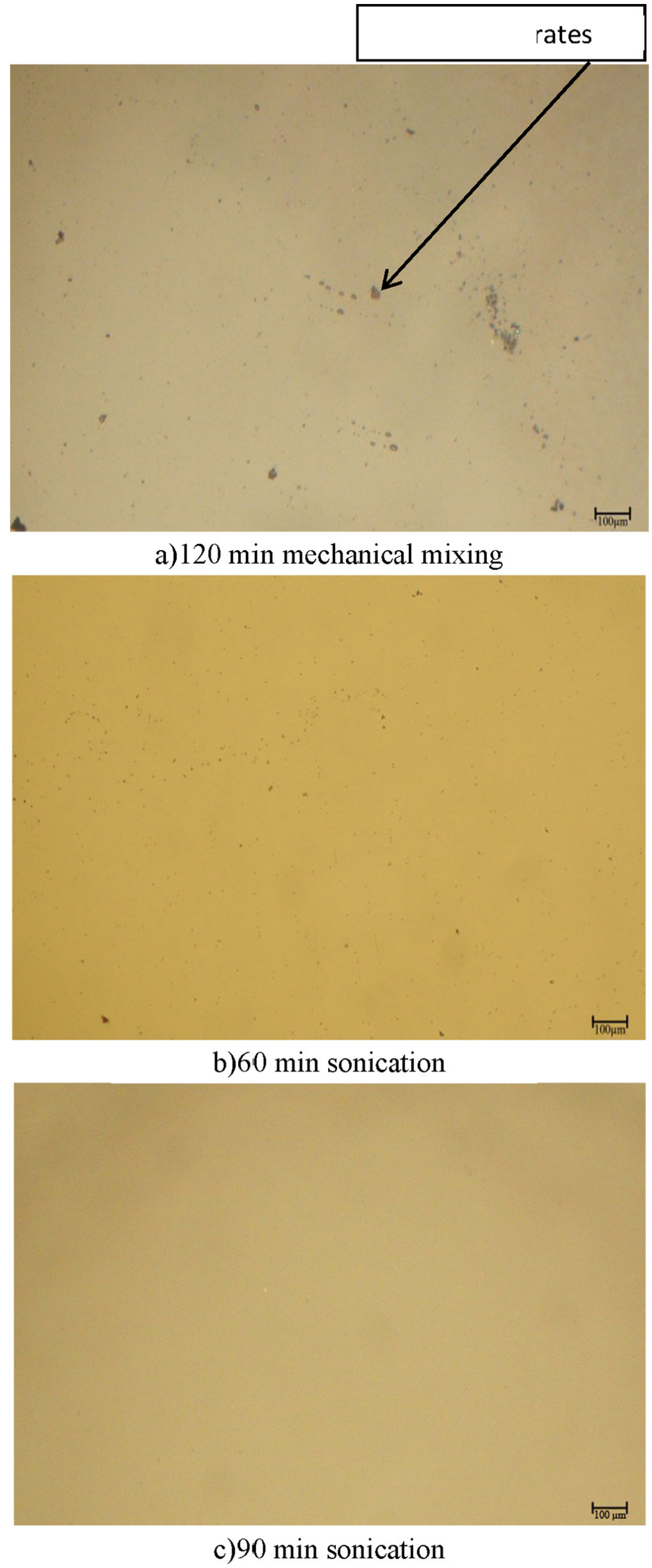

Fig. 1. Optical micrographs of 4 wt.% clay/water suspensions after 120 min mechanical agitation (a), after 60 min sonication (b) and after 90 min sonication (c).

3. Results and discussion

3.1. Optical microscopy

Optical microscopy was used to ensure the dispersion of nanoclay in water before adding them to the bitumen (TW315). Dispersion was made in water containing 4 wt.% clay. Fig. 1 presents the optical micrographs of 4 wt.% clay/water suspensions after 120 min of mechanical agitation and 60 min and 90 min of sonication process respectively in sections a, b and c. Agglomerates were formed due to cohesive forces between clay stacks during