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Influence of surface modified ilmenite/melamine formaldehyde composite on the anti-corrosion and mechanical properties of conventional polyamine cured epoxy for internal coating of gas and oil transmission pipelines

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ABSTRACT

To support the corrosion protection behavior and mechanical performance properties of conventional epoxy utilized for internal coating of gas and oil transmission pipelines, the present approach was performed to prepare different high build epoxy coating formulations modified using various amounts of processed ilmenite/melamine formaldehyde composite (IMFC) cured by poly amine hardener. X-ray diffraction (XRD) analysis was implemented to assure the phase identification of the crystalline ilmenite particles. Dynamic light scattering measurements were accomplished to measure the particle size distribution of micro-sized ilmenite particles. The lamellar shape of the prepared ilmenite pigment particles ($FeTiO_3$) was illustrated by transmission electron microscope (TEM) investigation. Flaky-like nature and the arrangement in overlapping plates of ilmenite particles were confirmed by scanning electron microscope (SEM) technique. Energy dispersive analysis of X-rays (EDX) was performed to ensure the elemental composition of ilmenite pigment particles. FTIR characteristic spectra for melamine formaldehyde resin, ilmenite/melamine formaldehyde composite (IMFC), conventional polyamine cured epoxy and polyamine cured ilmenite/melamine formaldehyde epoxy composite were done. The anti-corrosion performance properties of the considered IMFC epoxy coating formulations against unmodified blank conventional epoxy were studied by accelerated corrosion experiment (salt spray chamber) after 500 h exposure in 5% NaCl solution. The obtained results revealed a significant improvement in the rust grade, blistering size, color tolerance and adhesion strength of IMFC modified epoxy coated steel films with increasing the loading level (%) by weight of the nanocomposite modifier in the coating film. To confirm the previous concept, mass loss method was performed. The mechanical performance properties of these films were investigated by adhesion pull-off, bend, impact and abrasion coating tests to confirm their application efficiency. From the recorded results, the adhesion properties, elongation character, resistance to rapid deformation and film stiffness of these coatings increased significantly with increasing the amount of IMFC modifier.

1. Introduction

Epoxy coatings have been widely utilized to protect various steel petroleum structures from environmental attack because of its excellent chemical resistance, outstanding processability, high electrical insulating properties and strong adhesion affinity to heterogeneous materials [1,2]. The elevated corrosion resistance of thermoset epoxy coatings refers to high cross-linking density, appropriate adhesion strength and that contain many hydroxyl groups [3,4]. Corrosion of metallic surfaces in oil fields has generated much concern with regard to material loss, especially in tanks, casings, tubing, pipelines, and other equipment. In some areas, saline environments are the primary agents that lead to corrosion [5]. It has been illustrated that there is a decrease in the corrosion protection of organic coatings after short immersion time. This can be mainly attributed to the hydrolytic degradation of the coating exposed to the corrosive electrolyte. Coating degradation leads to increase in some pores and crevices. The corrosive electrolyte can permeate underneath coating through the pores and crevices. This can result in corrosion products creation and therefore decrease in adhesion of the coating to metal at the coating/metal interface. Attempts were carried out to improve the anti-corrosion behavior of the organic paints containing some inorganic pigments such as lamellar micaceous iron oxide (MIO) which is essentially a type of hematite, lamellar aluminum and Zn-dust [6–10].

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Most of the pigments, prime (high hiding power) and extender (low hiding power) are carefully processed to physically and chemically modifications to satisfy specific requirements such as color, opacity, gloss, abrasion resistance, ease of dispersion, chalk resistance and reducing cost. Ilmenite is a non-toxic pigment contains titanium-iron oxide mineral with the idealized formula ($FeTiO_3$). It is a weak magnetic black or steel-gray solid. From the commercial perspective, ilmenite is the most important ore of titanium dioxide pigment. Egyptian ilmenite ore was utilized after grinding to micro-sized scale as an anticorrosive pigment and mechanical property promoter for internal epoxy coating of gas transmission pipelines [11].

Melamine resin or melamine formaldehyde (also shortened to melamine) is a hard, thermosetting plastic material made from melamine and formaldehyde by polymerization. It is used to cross-link with alkyd, epoxy, acrylic, and polyester resins, used in surface coatings. Melamine-formaldehyde resin formed via the condensation of formaldehyde with melamine to give, under idealized conditions, the hexa-hydroxymethyl derivative [12]. Melamine-based resins used in several applications, (for example, in the production of protective coatings for steel structures and floor covering), since melamine allowed forming polymers with relatively high thermal stability and excellent dielectric properties [13–15].

The main aim of this work includes two objects. The first object is to modify the conventional epoxy coating used for internal coating of gas and oil transmission pipelines (blank) with different amounts of the processed ilmenite/melamine paste to prepare some novel ilmenite/melamine composite epoxy coating formulations. The second object is to investigate the anti-corrosion and mechanical performance properties of these composite coating formulations on the carbon steel surface to confirm its field application efficiency.

2. Materials and experimental methods

2.1. Materials

2.1.1. Chemicals

The epoxy resin (D. E. R 671-X75), epoxide percentage (75%), density at 25 °C (1.09 g/ml), flash point (28 °C), nonvolatile content (78 wt/g), shelf life (24 months), was conducted by Dow Chemical Company. Polyamine curing agent (ipox ER2072), Color: faintly yellow, molecular formula: $C_{10}H_{22}N_2$, molecular weight (g): 170.25, melting point (°C): 10, flash point (°C): 27, was submitted by ipox Chemicals Company. Benton was obtained from Chemical Partners Company. Melamine resin (Itamin M 172) was obtained from Galstaff Multiresine S.p.A Company. Blankfixe was obtained from Impexinvest LLC. Red iron oxide pigment was obtained from HANGZHOU AIBAI CHEMICAL CO., LTD, China. Talc was obtained from Green Egypt Company. Xylene and ethylene glycol were used in technical grades and obtained from El-Mohandes Chemicals Company, Egypt.

2.1.2. Ilmenite ore ($FeTiO_3$, iron titanium oxide pigment)

A large deposit of Egypt occurs in Wadi Abu Ghalaga in the South Eastern Desert. Ilmenite was analyzed by Thermo ARL ADVANT XP-385 XRF model and its physicochemical properties are listed in Tables 1 and 2.

2.1.3. Preparation of the carbon steel samples and its composition

The carbon steel samples utilized as a part of the present work were divided into working specimens with dimensions 5 cm x 10 cm x 2 mm for salt spray test and mass loss method. The samples used for pull-off adhesion, impact and bend coating tests were with dimensions 15 cm x 10 cm x 0.8 mm and those used for abrasion test were with 100 mm square rounded corners and with ¼ inch (6.3 mm) hole centrally located on each specimen. The specimens were mechanically polished with emery paper, washed with acetone and distilled water before coating application, and its chemical composition is presented in Table 3.

2.2. Preparation of micro-sized ilmenite particles [$FeTiO_3$]

Micro-sized ilmenite particles were prepared by solid-phase milling method. The Lab Testing 911 Metallurgist ball mill was used to grind ilmenite aggregates obtained from ilmenite mine for 3 h in a grinding chamber to get the highest degree of ilmenite fineness range at sub-micro-sized and micro-sized scales.

2.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns of ilmenite particles were measured by using a Panlytical X'pent PRO (Netherlands) with monochromated Cukα radiation with scattering reflections recorded for 2θ angle between 4 and 79 corresponding to d-spacing between 0.134 and 0.373 nm. To confirm the resolution of the diffraction peaks with standard reproducibility in 2-theta (± 0.005), the sample measurements were recorded by using monochromator and detector which were used to generate focusing beam geometry and parallel primary beam. The standard diffraction data were identified according to the International Center for Diffraction Data (ICDD) software with PDF-4 release 2011 database.

2.4. Dynamic light scattering (DLS) measurements

Zeta potential and dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS (Malvern, UK) with a He-Ne laser (633 nm) using a non-invasive backscatter method (detection at 173° scattering angle). Correlation data were fitted, using the method of cumulants, to the logarithm of the correlation function, yielding the diffusion coefficient, D. The hydrodynamic diameters (DH) of the PCVs were calculated using D and the Stokes− Einstein equation ($DH = kBT/3\pi\ \eta D$, where kB is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity (η = 0.8872 cP for water). The polydispersity index (PDI) of vesicles (represented as 2c/b2, where *b* and *c* are first- and second-order coefficients, respectively, in a polynomial of a semi-log correlation function) was calculated by the cumulative analysis. Size distribution of the vesicles was obtained by the non-negative least-squares (NNLS) analysis.

2.5. Preparation of ilmenite/melamine composite paste (IMFC)

The prepared micro-sized ilmenite pigment was added to melamine formaldehyde resin in parts as 80:20 by ratios. Then, isobutanol solvent was added with strong stirring until complete dispersion of ilmenite pigment particles through the melamine resin was made to form a homogeneous suspension. Ethylene glycol was added to the formed suspension as a leveling agent with the percentage of 1.4%, and dioctyl phthalate (DOP) was added up to 0.6% percentage, and intense stirring for 20 min was performed until the ilmenite/melamine composite paste (IMFC) would be formed.

Table 1
Physical properties of ilmenite pigment.

Character	Color	Bulk density (g/cm^3)	Specific gravity	Mohs Scale of hardness	Luster	Oil absorption gm/100 gm	Refractive Index
Result	Black	2.20	4.45	6 – 6.50	Metallic	8.00	2.94