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Influence of surface modified nanoilmenite/amorphous silica composite particles on the thermal stability of cold galvanizing coating

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ABSTRACT

The present approach investigates the use of novel nanoilmenite/amorphous silica composite (NI/AS) particles fabricated from ilmenite nanoparticles ($FeTiO_3$ NPs) and synthesized amorphous silica grains to improve thermal stability of the cold galvanizing coating. Transmission electron microscopic (TEM) images demonstrated that both nanoilmenite and nanocomposite particles were of flaky-like nature and the average diameter of the particles is 20 nm. The lamellar shape of the nanocomposite and spherical nature of Zn-dust particles were illustrated by scanning electron microscopy (SEM) micrographs. Different alkyd-based cold galvanizing coating formulations were modified using uniformly dispersing various amounts of the processed nanocomposite particles as a modifier to form some engineering nanocomposite coatings. Thermal stability of the nanocomposite and Zn-dust particles was determined by thermo-gravimetric analysis (TGA). From the obtained results it could be observed that the weight loss (%) as a feature of the thermal stability in case of the nanocomposite particles was 2.9 compared to 85.9 for Zn-dust powder grains. Derivative thermo-gravimetric (DTG) measurements were done under nitrogen atmosphere for the cured cold galvanizing coating samples heated from room temperature to 1000 °C. The obtained results revealed that the maximum decomposition temperature point in the third degradation step for 6% nanocomposite surface modified cured sample (CG-F) was detected at 693 °C and was less value for unmodified conventional cold galvanizing coating (CG-A) at 612 °C. The increase in thermal stability with increasing the concentration of nanocomposite particles could be mainly attributed to the interface surface interaction between the nanocomposite particles and alkyd resin matrix in which enhancing the inorganic-organic network stiffness by causing a reduction in the total free spaces and enhancement in the cross-linking density of the cured film then, requires high energy to cleave it.

1. Introduction

Cold galvanizing coating is an organic single-component coating of a minimum 92% by weight zinc in dry film thickness (DFT). It gives the same cathodic protection as hot-dip galvanizing, but it is applied as paint. This type of coatings requires no mixing with other chemicals to make it cure. Cold galvanizing coating acts as an active coupling to the steel parent metal to form an electrolytic bond. It is called a duplex system in which offers a cathodic protection and a passive layer (as paint). Cold galvanization is considered eco-friendly system when cured (hardened) and can be used even for water storage tanks.

The incorporation of nanoparticles/fillers as additives has been observed to improve the thermal stability of polymeric coatings [1,2]. Nanocomposites are produced using two or a greater amount of the solid phase, at least in one dimensional nano-level size (1–100 nm). The solid phase can be amorphous, semi-crystalline, grain, or a blend. The solid phase can likewise be organic, inorganic, or a combination. The application of the nanoparticles (NPs) for the preparation of polymer nanocomposites (NCs) compared to micro-additives offered high surface to volume ratios and an increase in the interfacial reactivity of NPs with the polymer matrix in order to achieve significant improvement for polymer properties with simultaneous decrease in the final product price [3–5]. It has been investigated that application of zinc oxide (ZnO) as nano-sized pigment improves mechanical and thermal properties of alkyd-based coatings [6].

An enhancement in the thermal stability of polymethyl methacrylate (PMMA) by adding silica nanoparticles had been

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investigated [7]. The thermal stability by adding silica/zirconia or silica/titania nanoparticles to PMMA was investigated, which led to the formation of organic-inorganic network [8]. Evaluation of the thermally stimulated dielectric properties of zinc oxide (ZnO) nanoparticle-modified poly (vinylidene fluoride) system had been done [9]. The improvement in thermal stability and fire retardancy of PMMA due to the presence of TiO_2 and Fe_2O_3 nanoparticles had been studied [10].

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. Ilmenite is the most important ore of titanium dioxide pigment. Egyptian ilmenite ore was utilized after grinding to micro-sized scale as anticorrosive pigment in preparation of novel anticorrosion epoxy coating formulations for steel structures in petroleum fields [11]. The effect of surface modified TiO_2 nanoparticles on thermal properties of long oil alkyd resin-based coatings were studied [12]. Thermogravimetric analysis (TGA) measurements in argon atmosphere were performed. From TGA curves of TiO_2-cetyl gallate and TiO_2 nanoparticles (NPs) modified with imine based on 3,4-dihydroxybenzaldehyde and oleylamine (TiO_2-DHBAOA) it could be observed that, the thermal stability of TiO_2-DHBAOA NPs is higher than thermal stability of TiO_2-cetyl gallate NPs.

This investigation aimed to prepare novel fabricated nanoilmenite/amorphous silica composite particles as a modifier and evaluate its influence on the thermal stability behavior of cold galvanizing coating through thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) measurements to be suitable for application on hot surfaces such as steel flares.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Soya short oil alkyd resin and Benton were conducted from Chemical Partners Company. Zinc dust was conducted from WL Company for Paints and Chemicals. White sand, potassium and sodium feldspars, calcium carbonate, boron, zinc, aluminum and zirconium oxides were obtained from ARKAN for Industry and Mining. BYK-066 N (polysiloxanes with ingredients as 2,6-dimethyl 4-heptanone and 2-butoxyethanol dissolved in diisobutyl ketone) was obtained from BYK-Chemie USA Inc. Xylene, ethylene glycol, n-butyl glycol and DOP (dioctyl phithalate) were obtained from El-Mohandes Company for Chemicals and Trading and used in technical grades.

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

A large deposit of Egypt occurs in Wadi Abu Ghalaga in the South Eastern Desert. The area comprises the eastern portion of Hamata Sheet, 30 km of Red Sea and 100 km South Marsa Alam. Ilmenite was analyzed by Thermo ARL ADVANT XP-385 XRF model and its physicochemical properties are shown in Tables 1 and 2.

2.2. Methods and techniques

2.2.1. Preparation of ilmenite nanoparticles [$FeTiO_3$(NPs)]

Ilmenite nanoparticles as a pigment were prepared by a solid-phase milling method. The planetary ball mill PM 200-RETSCH-short grinding times was used to grind 20 μm size ilmenite powder for 12 h in an automatic grinding chamber with two grinding stations to obtain the highest degree of ilmenite fineness reachs nano-sized scale.

2.2.2. Synthesis of amorphous silica composite (AS) particles

Amorphous silica particles were prepared by mixing 70.5% by weight of Egyptian white sand (source of SiO_2), 3% potassium feldspar (source of K_2O), 1.14% sodium feldspar (source of Na_2O), 6.9% calcium carbonate (source of CaO), 0.5% boron oxide (B_2O_3), 0.3% zinc oxide (ZnO), 17.1% aluminum oxide (Al_2O_3) and 0.5% zirconium oxide (ZrO_2) after grinding process to reach 0–75 μm size powder range for 20 min in a collection column. Heat treatment (fusion) for the powder mixture at 1350 °C in ITALO oven was carried out until a molten liquid was obtained then, water quenching operation at temperature 30 °C was made [13] and grinding the final product to 20 μm size powder. The final product specific gravity was measured at 2.78 g/cm^2 and Mohs scale of hardness equal 7.9. XRF analysis of amorphous silica composite was described in Table 3.

2.2.3. Preparation of nanoilmenite/amorphous silica composite (NI/AS) particles

Nanocomposite (NI/AS) particles were prepared by mixing 20 g of nanoilmenite and 80 g of synthesized amorphous silica composite particles as 20:80% by weight for 20 min. The mixture formed was added gradually to 40 g ethylene glycol and 10 g BYK-066 N (polysiloxanes with ingredients as 2,6-dimethyl 4-heptanone and 2-butoxyethanol dissolved in diisobutyl ketone) and stirring by using Ultrasonic Devices for 45 min till a suspension with homogeneous appearance be formed to obtain the nanoilmenite/amorphous silica composite paste. Then, the suspension was dried at 70 °C for 24 h. After milling, the product is made up of fined black powder [14].

Table 1
Characterization of Egyptian ilmenite ore.

Character	Color	Bulk density (g/cm^3)	Specific gravity	Mohs scale of hardness	Oil absorption gm/100 gm	Refractive index
Result	Black	2.2	4.45	6–6.5	8	2.94

Table 2
XRF analysis of Egyptian ilmenite ore.

Element	Fe_2O_3	TiO_2	SiO_2	MgO	Al_2O_3	CaO	ZnO	MnO	V_2O_5	Cr_2O_3	ZrO_2
Result%	49.78	33.76	6.94	4.79	2.96	0.79	0.29	0.25	0.24	0.11	0.09

Table 3
XRF of the synthesized amorphous silica.

Component	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	ZnO	ZrO_2	B_2O_3
Percent (%)	70	0.01	17.3	0.05	6	1.14	1.2	3	0.3	0.5	0.5

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