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A novel multifunctional coating prepared by internal and external inhomogeneous modification of porous fillers

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ABSTRACT

Novel lypohydrophilic porous fillers that can function as micro-reservoirs to store lubricating oil as a low-friction and anticorrosive agent in a composite coating were developed. The novel oily particles were added to an epoxy resin (EP)-based coating to study the effect of lubricating oil on the anti-corrosion and the low-friction performance of the coating. The electrochemical impedance spectroscopy and the sliding wear tests demonstrated that the oily particles can significantly improve the barrier property and the wear-resisting performance of the EP coating. Furthermore, the friction coefficient of epoxy resin-25% lubricating celatom coating (0.4) was lower than that of the epoxy resin-25% PVDF coating (0.55), and the wear rate was lower by a factor of eight. The enhanced wear resistance can be mainly attributed to the lubrication performance of the lubricating oil stored in the porous particles. In addition, the hydroxyl group on the porous particles enhanced the crosslinking with the epoxy resin.

1. Introduction

The deterioration of metal-based infrastructure used in industrial and domestic installations has become a serious problem; the maintenance costs related to corrosion of engineering metals is estimated to constitute a significant part of the gross national product of every country [1,2]. In recent years, organic coatings, such as paints, have been widely applied for the protection of metals owing to the ease of application. However, the amount of volatile organic compounds used in paints need to be reduced in order to protect the environment and prevent the wastage of resources [3–5]. In this regard, waterborne coatings, powder coatings, and high solids coatings have attracted increasing attention [6,7].

It is well-known that coatings act as passive barriers impeding the passage of oxygen, water, and ions, and also resist the movement of ions at the metal/electrolyte interface [8]. The main factors that reduce the service life of a coating are abrasion and aging. Replacement of the protective coating significantly affects the operation of equipment, which has a negative impact on the profit. Therefore, improving the wear resistance and the barrier properties of coatings is the best possible solution. The sheet, hard and abrasion resistant fillings, such as montmorillonite, corundum, and glass fibres have been widely used in practical applications owing to their low costs [9]. However, these conventional fillers have several disadvantages such as, high water-absorbing quality, poor compatibility with polymers, and poor acid-resistance properties.

In recent years, researchers have discovered that the use of graphene sheets [10], hexagonal boron nitride [11], etc. as fillers and microencapsulation technologies [12] can markedly improve the anti-corrosion properties of certain polymer coatings. These materials and methods are very effective and render good dispersibility, sheet barrier property, and functionalisation to the coating. However, cost-effective production of these advanced materials is necessary in order to progress from academic research to industrial application and production. Therefore, it is important to develop a simple method to realise improved sheet barrier performance along with anti-corrosion, low-friction, and anti-wear properties by self-lubrication.

In this context, we studied the effect of lubricating oil on the corrosion and friction performance of epoxy resin (EP) coatings. Traditionally, lubricating oil is applied to reduce friction between surfaces. However, this method cannot be applied to the inner walls of pipelines. Even though researchers have examined addition of lubricating oil directly into coatings, this method was found to be impractical [13]. Therefore, a functional carrier to incorporate the lubricating oil uniformly in the coating without affecting the mechanical properties of the coating needs to be developed. Celatom is a kind of

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macro/microporous natural mineral with abundant raw material sources [14]. In addition, as an inorganic mineral, celatom exhibits high resistance to acids and alkalis and has good mechanical properties. The presence of a hydroxyl group on the surface of the celatom makes it easily modifiable. Although celatom has been widely used to prepare decorative coatings, large-scale applications of these particles are considerably limited because of its porosity and hygroscopic nature.

Taking into account the above-mentioned issues, we developed a novel method to synthesise an oil carrier with hydrophilic porous particles by internal and external inhomogeneous modification of the celatom. A hydroxyl group was formed on the external surface of the celatom, and the internal surface was modified with an oleophilic group to attract lubricating oil. In addition, the presence of the long chain group and the hydroxy group on the surface will make the particle spread in both water and organic solvents. The composite coating consisting of the oily, porous fillers showed excellent barrier and low-friction properties. It is expected that this research will pave the way for the fabrication of novel low-friction, wear-resistant, and anti-corrosion coatings for industrial applications.

2. Materials and methods

2.1. Materials

PVDF powders (FR904) were purchased from Shanghai 3F Co., Ltd (China). Organosilicon epoxy resin was purchased by Hubei Xinsihai Chemical Company, China. The ethyl acetate was bought from Huadong Reagent Factory, Shenyang, China. Celatom were supplied by Ningbo haishu ding chong chemical Co., Ltd (China). NaOH were purchased from Tianjin Fuchen chemical reagent factory. All reagents were used as received. Hydrogen peroxide (H_2O_2, AR), formic acid (HCOOH, AR), phosphoric acid (H_3PO_4, AR) and sodium chloride (NaCl, AR) were obtained from Aladdin Reagent Co., Ltd (China). Lubricating oil is in grade of 10w-30 and it was purchased from Sinopec lubricant Co., Ltd (China). Deionized water was used for all experimental process.

2.2. Preparation of the oily functional fillers

A certain amount of celatom (10 g) and NaOH (2 g) were put in 50 ml beaker containing 40 ml 10% H_2O_2 water solution. The above solution was reacting through stirring for 4 h. After filtration and drying, the hydroxylated celatom was obtained.

10 g hydroxylated celatom and 1 g oleic acid were put into 40 ml hydrothermal reactor containing 30 ml ethyl alcohol and keep the reactor in the 120 °C oven for 120 h. After filtration and drying, the oleic acid modified celatom was obtained.

10 g oleic acid modified celatom and 0.6 g phosphoric acid were put in 50 ml three-necked flask containing 1.6 g formic acid. Then 9 g H_2O_2 was added drop-wise at a rate in 5 min at 45 °C. After 0.5 h, raised the temperature to 60 °C for about 1.5 h, and the resulting mixture was filtration and drying. Then the powders and 40 g formic acid were placed into the flask and the mixture was kept at 60 with stirring for 2 h. After filtration and drying, the internal and external inhomogeneity modified celatom was obtained.

Then 10 g modified celatom was put in 50 ml beaker containing 5 g lubricating oil and 8 ml ethyl acetate. After stirring for 10 min, the mixture was put into vacuum drying oven at 10 kpa and 60 °C for 4 h. Then the oily functional filler was obtained.

2.3. Preparation of coatings

The steel plate (1100 grade, 80 mm × 80 mm × 3 mm) was treated by sand blasting (ISO8501-1:1988), and then ultrasonically washed in absolute alcohol for 10 min.

Epoxy resin coating (EP coating): 10 g epoxy resin were ultrasonically dispersed in 10 ml ethyl acetate solvent for 30 min to obtain the uniform coating precursors.

Epoxy resin-25% lubricating celatom coating (EPLC coating): 10 g epoxy resin and 2.5 g oily functional filler were ultrasonically dispersed in 10 ml ethyl acetate solvent for 30 min to obtain the uniform coating precursors.

Epoxy resin-25% pvdf coating (EPP coating): 10 g epoxy resin and 2.5 g PVDF powders were ultrasonically dispersed in 10 ml ethyl acetate solvent for 30 min to obtain the uniform coating precursors.

Epoxy resin-10% lubricant coating (EPL coating): 10 g epoxy resin and 1 g lubricant oil were ultrasonically dispersed in 10 ml ethyl acetate solvent for 30 min to obtain the uniform coating precursors.

After that, the coatings were prepared by spraying the above solution on the as-treated steel plates. Finally, the sprayed coating was calcined at 180 °C for 90 min to get the solidified coatings. All the prepared coatings are at the average thickness of 250 ± 20 μm.

2.4. Characterization

The reaction mechanisms of the prepared samples were characterized by Tensor27 infrared spectrometer (FT-IR).

Scanning electron microscopy (SEM) was used to observe the surface morphologies of the samples. The element contents of the samples were measured by Energy Dispersive Spectrometer (EDS).

The coatings were exposed to 3.5% w/w NaCl solution for 7, 15 and 60 days. Then, the electrochemical impedance spectroscopy (EIS) was utilized in order to investigate the corrosion protection properties of the epoxy coating on the steel substrates with the differentmulti-functional TiO_2(w) carrier additive coatings. The experiment was done by an AUTOLAB 86183 at amplitude and frequency range of ± 10 mV and 100 kHz–0.01 Hz, respectively. The corrosion potention (E_{corr}) of the steel substrate was obtained from the open circuit potential at the equilibrium state of the system.

The friction and wear tests of pure EP, EPL, EPC and EPLC coatings were conducted with a MPX-2000 wear tester (Xuanhua Testing Manufactory, China) by a pin-on disk configuration under dry conditions, as seen in Fig. 4. In this study, the applied loads was 2 MPa, and the sliding velocities was 0.76 m s^{-1}. A standard test duration was 3 h. The specimens in all the experiments were cuboid with dimensions of 8 cm × 8 cm × 3 mm. The pin is a stainless steel cylinder with dimensions of 3 cm (high) × 3 mm (diameter). Before each test, the surfaces of stainless steel pin was ground to a smooth finish with 1000 grit paper and then wiped clean with anhydrous ethanol. Three repeated tests of each specimen were conducted in each wearing condition and the average value of the three testing results was adopted. After the wear test, SEM was used to study the microstructures of the worn surfaces.

The specific wear rate [Wear rate (cm^3/N m)] was calculated as:

$$\text{Wear rate} = \frac{W}{L \cdot \rho \cdot F_N} \quad (1)$$

where W is the mass loss (g), L is the sliding distance (m), ρ is the density of the sample (g/cm^3), and F_N is the normal load (N).

The thickness of the prepared coatings was measured by Coating Thickness Gauge (SaluTron ComBi-D3, Germany). To ensure the authenticity of the data, the thickness for each sample was obtained from the average measurement of five different areas. The measured data of the thickness of the prepared coatings are shown in Table S1.

3. Results and discussion

3.1. Surface characterization of different samples

The process for the internal and external inhomogeneous modification of the celatom is illustrated in Fig. 1. The scanning electron microscopic (SEM) images (Fig. S1) show that the celatom preserves the porous structures. First, the celatom was pre-processed using a solution