Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Anti-corrosion and wear resistance properties of polymer composite coatings: Effect of oily functional fillers

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ARTICLE INFO

Article history:
Received 14 November 2017
Revised 19 January 2018
Accepted 23 January 2018
Available online xxx

Keywords:
Organic coating
Celatom
Low friction
Corrosion resistance
Functional filler

ABSTRACT

We herein report the development of carbon-modified porous fillers that function as micro-reservoirs to store lubricating oil as a low-friction and anticorrosive agent in a composite coating. These novel oily particles were added to an epoxy resin (EP)-based coating to study the effect of a lubricating oil on the anti-corrosion and friction performances of the coating. Analysis by electrochemical impedance spectroscopy and sliding wear tests demonstrated that the presence of particles containing the lubricating oil significantly improved the barrier properties and the wear resistance of the EP coating. It was therefore apparent that the carbon surface modification of the Celatom filler improved the compatibility of both the filler towards the resin. Thus, the addition of fillers containing lubricating oil further improved the wear resistance and anti-corrosion properties of the coatings.

1. Introduction

Due to their outstanding strength and ductility, metals are commonly employed in the engineering and construction of industrial materials and structures [1]. In this context, carbon steel is widely used as a construction material in industry due to its comprehensive performance, low cost, and good plasticity [2–3]. However, in humid and harsh conditions, the corrosion of steel inevitably takes place, thereby significantly impacting the economics of such systems [4]. Thus, to slow down the corrosion process, the treatment of metal surfaces to introduce barriers is common method to ultimately protect the metal from corrosion under harsh environments. Although various methods have been developed to inhibit metal corrosion, using organic coatings is one of the most promising methods [5]. It is generally known that epoxy (EP) resins are widely used in coatings due to their favorable mechanical properties, excellent corrosion resistance, and stable chemical properties. However, to prevent such systems contributing to the ongoing worldwide pollution issues, the use of volatile organic compounds should be restricted [6]. In such a big background, EP powder coatings without emission of VOC pollutants have received increasing attention. However, most EP resins tend to be brittle and their poor wear resistance is difficult to guarantee long term protection performance as good protective coatings.

Thus, to overcome the shortcomings of traditional organic coatings, the addition of nano/micro-fillers into the EP resin have been reported [7], where the primary coatings are modified by conventional fillers such as corundum, glass fibre, kaoline, and montmorillonite. As a result, the hardness, wear resistance and corrosion resistance of the primary coatings can be improved. However, due to the inhomogeneous nature of conventional filler particle size, upon the addition of such fillers to the coating, the uneven distribution between the fillers becomes obvious, which resulting in a reduction of the barrier properties of coatings. However, a number of novel materials for the modification of these coatings have recently been developed, including graphene sheets [8,9] and hexagonal boron nitride [10,11]. Indeed, the addition of such materials to certain polymer coatings has been found to markedly improve the anti-corrosion properties of the coatings, mainly due to their sheet barrier properties [12], good dispersibility and their effective functionalization [13].

However, up to now the application of such novel materials in powder coatings has been limited by two key issues. Firstly, two-dimensional materials, such as graphene and hexagonal boron nitride are very difficult to distribute evenly in the powders. Secondly, a cost-effective production method for these advanced

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https://doi.org/10.1016/j.jtice.2018.01.031
1876-1070/

materials is necessary to progress from academic research to industrial applications and production. The development of a simple method to improve the sheet barrier performances, anti-corrosion, low friction and wear resistance of powder coatings is therefore of particular importance.

Indeed, lubricating oil is a key material in industry, as it is extensively applied to reduce friction between two interfaces. Herein we just thinking that the preparation of a self-lubricating and long-life coating where the lubricating oil is evenly distributed throughout the powder coating would be desirable. However, the direct addition of lubricating oils into powders is generally not possible, as it results in uneven dispersion in the coating matrix [14]. Furthermore, to permit deposition of the lubricating oil in the micro/nano-container, the container should exhibit good crush resistance properties to prevent deformation during preparation of the coating. In recent years, some shells and microcapsules [15,16] are newly developed materials that can store lubricating oil in the coatings. The lubricating oil stored in the shell and microcapsules is stable and easy to disperse in coatings. However, the lubricating oil will be released thoroughly when the shell and microcapsules are destroyed.

Considering the above-mentioned issues, we herein report the development of a novel method for the synthesis of an inorganic oil carrier by surface carbonizing porous particles of Celatom filler. Following the formation of hydroxyl groups on the external surface of the Celatom, modification using an alkyl phosphate carbon source will be carried out. After calcination, we expect that the resulting composite coating consisting of oily, porous fillers will exhibit excellent barrier and low friction properties. In addition, the influence of the conductive carbon on the barrier properties of the coating will be discussed to examine the influence such materials on the coating properties. It is expected that this research will pave a way to fabricate a novel low friction, wear resistance and anti-corrosion coatings for industrial applications.

2. Materials and methods

2.1. Materials

18 alkyl phosphate ($C_{18}H_{39}O_4P$, referred as $C_{18}P$) were purchased from Shanghai Zhixin chemical Co., Ltd (China). Commercial EP powder (E-42) was supplied by Qingdao Meiheng Co. Ltd (China). Celatom were supplied by Ningbo Haishu Ding Chong chemical Co., Ltd (China). All reagents were used as received. Lubricating oil is in grade of 10 w-30 and it was purchased from Sinopec lubricant Co., Ltd (China). NaOH were purchased from Tianjin Fuchen chemical reagent factory. 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 5 g $C_{18}P$ were put into 100 ml hydrothermal reactor containing 50 ml ethyl alcohol and keep the reactor in the 70 °C water bath for 0.5 h. After filtration and drying, the $C_{18}P$ modified Celatom was obtained. The obtained powder was calcined at 500 °C for 8 h under N_2 atmosphere by degradation of the alkyl groups. Then the carbon modified filler was obtained.

Then 10 g carbon 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 oil contained surface functionalized filler was obtained.

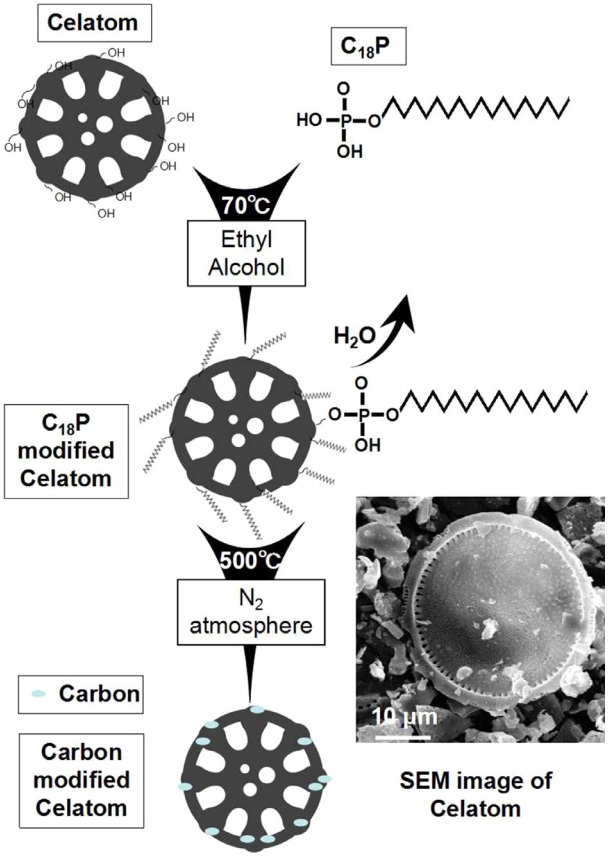

Fig. 1. Schematic representation of the modification of a Celatom particle.

2.3. Preparation of different coatings

The steel plate (1100 grade, 80 mm × 80 mm × 1 mm) was treated by sand blasting (ISO8501-1:1988), and then ultrasonically washed in absolute alcohol for 10 min. Pure EP coating (EPC): 2.0 g EP powder was sprayed with an electrostatic system onto the treated steel plate. Celatom EP coating (CEPC): 2.0 g EP and 0.4 g Celatom powders were mixed in massing machine at 600 r/min. Carbon modified Celatom EP coating (MCEPC): 2.0 g EP and 0.4 g carbon modified Celatom powder were mixed in massing machine at 600 r/min. Oily celatom EP coating (OCEPC): 2.0 g EP and 0.4 g oily Celatom powders were mixed in massing machine at 600 r/min.

Finally, all the EP coatings were obtained after calcinated at 180 °C for 2 h.

All the prepared coatings are at the average thickness of 250 ± 10 μm. Samples for the EIS test are at the average thickness of 100 ± 5 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 Coating Thickness Gauge (SaluTronComBi-D3) was applied to measure the thickness of the samples, which was obtained from the average value of five different areas. The coatings were exposed to 3.5% w/w NaCl solution for 30 d Tafel plots were obtained by scanning the potential from −250 to 250 mV above E_{corr} at a scan rate of 20 mV/min. Then, the electrochemical impedance spectroscopy

Please cite this article as: C. Wang et al., Anti-corrosion and wear resistance properties of polymer composite coatings: Effect of oily functional fillers, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.031