

Polyurethane/*f*-Oil Fly Ash-ZnO Atmospheric Corrosion Protective Coating

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ABSTRACT

Acid-functionalized oil fly ash (*f*-OFA-COOH) was reacted with zinc oxide (ZnO) for the in-situ growth of an inhibitor (ZnO) on functionalized oil fly ash, forming *f*-OFA-ZnO. *f*-OFA-ZnO was used to synthesize waterborne polyurethane (WBPU) dispersions with defined *f*-OFA-ZnO contents. The dispersions were used as a protective coating on mild steel. The protective properties varied with *f*-OFA-ZnO contents. The maximum adhesive strength, highest water contact angle and minimum water swelling were recorded using 2.00 wt% *f*-OFA-ZnO. All coatings were exposed near a seaside to evaluate their atmospheric corrosion protective properties. Most of the coatings corroded slightly. A significant improvement in corrosion protection was observed for only the coatings with higher *f*-OFA-ZnO contents, which were prepared by the in-situ polymerization method

Key words: Polyurethane, ZnO, coating

INTRODUCTION

Corrosion occurring in atmospheric conditions is called atmospheric corrosion. The factors that can tune this type of corrosion are atmospheric criteria such as rain, dust, UV light, humidity and marine aerosols [1, 2].

Protective coatings are usually applied on metal surfaces to protect the metal and their structure from atmospheric corrosion. The trickiest part is choosing a proper coating because the protective properties of coatings also deteriorate with environmental variations. Thus, a protective coating that is very good in one area might not work in another area. A protective coating should be selected by considering local environmental factors [3, 4].

Many protective coatings are available commercially. Among them, polyurethane (PU) is a protective coating used very widely to protect metal surfaces from atmospheric corrosion. Unfortunately, its protection ability deteriorates under harsh atmospheric conditions, such as high-intensity UV light, high temperatures and marine aerosols. To avoid this deterioration in protective properties, different methods have been adopted in the last decade. Different additives and inhibitors are mixed with PU coatings to improve their protective properties. Many different fillers are also mixed with PU to improve

its protective properties. However, mixing additives, inhibitors and fillers in coating solutions can destroy the shelf-life of coating dispersions. The adhesive and mechanical properties of the final coating also deteriorate by the excess loading of additives, inhibitors and fillers. Currently, academic and industry people are looking for a single filler/inhibitor/pigment to fulfill all protection purposes [5-7].

Industrial waste material is a heavy burden worldwide. Oil fly ash (OFA) is a well-known industrial waste material. The use of OFA in construction started in the last century. However, a large amount of OFA is unused and simply use for land filling in many countries [8].

Zinc oxide (ZnO) is well known for its antibacterial effect, UV-shielding ability and corrosion resistance and applied to PU coatings [7]. To achieve these protective properties, ZnO is added either by in situ polymerization or after polymer preparation in a blending process. The maximum protective properties are achieved at certain ZnO content. This optimum content is quite confusing, as researchers have used different contents in their prepared PU/ZnO dispersions and coatings.

In this study, ZnO was in situ grown on OFA by a functionalization reaction. The ZnO functionalized OFA (*f*-OFA-Zn) was used to prepare a WBPU/*f*-OFA-Zn dispersion. Both in situ polymerization and blending processes were applied to prepare the dispersions, namely, WBPU/*f*-OFA-Zn-P and WBPU/*f*-OFA-Zn-B, respectively. With fixed monomer contents, the *f*-OFA-Zn contents were also varied during dispersion preparation (see Table 1). All the prepared dispersions were coated onto a mild steel surface. All the coatings were evaluated to determine their protective properties under lab and harsh weather conditions near a seaside where marine aerosols are very common. In addition, high-intensity UV light is also present there.

Table 1: Composition of the coatings

Coating	Composition (Mole)					<i>f</i> -OFA-ZnO (wt%)
	Polyol	Hydrophilic agent	Neutralizer	Chain extender	Isocyanate	
WBPU	0.725	0.925	0.925	0.350	2.000	..
WBPU/ <i>f</i> -OFA-Zn-P-5	0.725	0.925	0.925	0.350	2.000	0.50
WBPU/ <i>f</i> -OFA-Zn-B-5	0.725	0.925	0.925	0.350	2.000	0.50
WBPU/ <i>f</i> -OFA-Zn-P-10	0.725	0.925	0.925	0.350	2.000	1.00
WBPU/ <i>f</i> -OFA-Zn-B-10	0.725	0.925	0.925	0.350	2.000	1.00
WBPU/ <i>f</i> -OFA-Zn-P-15	0.725	0.925	0.925	0.350	2.000	1.50
WBPU/ <i>f</i> -OFA-Zn-B-15	0.725	0.925	0.925	0.350	2.000	1.50
WBPU/ <i>f</i> -OFA-Zn-P-20	0.725	0.925	0.925	0.350	2.000	2.00
WBPU/ <i>f</i> -OFA-Zn-B-20	0.725	0.925	0.925	0.350	2.000	2.00
WBPU/ <i>f</i> -OFA-Zn-P-20	0.725	0.925	0.925	0.350	2.000	2.50
WBPU/ <i>f</i> -OFA-Zn-B-20	0.725	0.925	0.925	0.350	2.000	2.50

Polyol= Poly (tetramethyleneoxide glycol, number-average molecular weight = 2000 g/mol)

Hydrophilic agent = 2, 2- dimethylol butyric acid (DMBA)

Neutralizer = Triethylamine (TEA), Chain extender = Eethylene diamine (EDA)

Diisocyanate = Isophorone diisocyanate (IPDI), OFA = Oil fly ash

EXPERIMENTAL PROCEDURE

Functionalization of OFA

OFA was functionalized by the in-situ growth of a corrosion inhibiting/UV-shielding /radical scavenging/marine aerosol protecting material based on our previous report [8]. ZnO was chosen to act as this multifunctional material. The OFA was first treated with an acid mixture ($H_2SO_4:HNO_3= 3:1$) at

175 °C for 12 h to make COOH-functionalized OFA, which was further reacted with ZnO in the presence of cetyltrimethylammonium bromide at 105 °C for 11 h.

WBPU dispersion preparation by in situ polymerization

The pristine WBPU dispersion was prepared based on our previous reports [7, 8].

WBPU/*f*-OFA-Zn-P dispersion preparation by in situ polymerization

The WBPU/*f*-OFA-Zn-P dispersions were prepared through in situ polymerization based on our previous report [8]. All the basic monomers, PTMG, DMPA and IPDI (90 wt%), were charged for 2 h to prepare NCO-terminated prepolymers. The premixed (by ultrasonication) IPDI (10 wt%) and *f*-OFA-Zn solution was added to the prepolymer and stirring was continued for 1 h. Next, TEA, H₂O and EDA/H₂O were added to complete the neutralization, dispersion and chain extension steps. An organic solvent, methyl-ethyl-ketone (5.0 wt%), was also mixed before the neutralization step to control the highly viscous prepolymer.

WBPU/*f*-OFA-Zn-B dispersion preparation by blending

f-OFA-Zn was not added during the in-situ polymerization method. The pristine WBPU dispersion was used during the preparation of the WBPU/*f*-OFA-Zn-B dispersion. *f*-OFA-Zn was added directly to the WBPU dispersion and stirred for 1 h.

Preparation of the film

A proper amount of the dispersion (10 g) was poured onto a round disc (diameter of 7 cm) and dried for 48 hours at room temperature. Films with thicknesses of approximately 0.5 mm were withdrawn from the disc. To remove the solvent completely, the film was further dried at 60°C for 6 hours and vacuum dried at 80°C for 6 hours.

Mounting coatings onto a mild steel sheet

The dispersion was mounted onto a steel sheet with an applicator. The coatings were dried completely before being used for certain tests.

Characterization

FTIR spectroscopy was used to identify the coating structure. The coating hydrophobicity was evaluated by water contact angle and water swelling (%) tests. The adhesive strength of the coating was evaluated by pull-off tests. The initial screening of the UV-shielding ability of the coatings was conducted by UV-vis spectroscopy analysis. The corrosion protection analysis was conducted by EIS analysis. The real field exposure test was performed at Jubail and KFUPM Beach for a defined length of time. All the mentioned tests were performed based on our previous reports [7, 8].

RESULTS

OFA was functionalized by acid treatments to make COOH-functionalized OFA particles, denoted as *f*-OFA-COOH. The acid group reacted with ZnO to make ZnO-functionalized OFA (*f*-OFA-ZnO). Five different defined contents (0.50, 1.00, 1.50, 2.00 and 2.50) were used to prepare the dispersions. All the dispersions were stable after preparation, and no precipitation or phase separation layer was observed. At the early stage of the dispersion shelf life, the stability was not affected by the two different preparation processes. However, as time progressed, the dispersions were unstable. In all cases, the shelf life was higher for the in situ polymerized dispersions. All the films and coatings were also smooth, and none of them were brittle. The distribution of *f*-OFA-ZnO in the coating was determined by SEM analysis. At low contents, the *f*-OFA-ZnO particles were not affected by the process. The *f*-OFA-ZnO particles were distributed homogeneously for contents up to 1.50 wt%. Agglomeration was noticed for *f*-