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Investigating corrosion protection properties of epoxy thermal insulators through cyclic corrosion test

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ABSTRACT

For preparing epoxy based thermal insulations three types of hollow glass microspheres with different particle sizes 70, 115, and 170 μm were used. Thermal conductivity of coatings in the absence and presence of hollow spheres were evaluated. Thermal conductivity of microsphere containing insulations was found to be much less than epoxy coatings. Hollow spheres with 170 μm diameter showed better insulating properties. Epoxy thermal insulations were exposed to accelerated cyclic corrosion test conditions, and then corrosion resistance reduction of coatings was evaluated by electrochemical impedance spectroscopy. Results showed that microspheres can not only improve insulating properties but also raising corrosion protection features of epoxy coating during 37 days of exposure to cyclic corrosion conditions. Impedance modulus at low frequency (0.01 Hz) of 170 μm hollow sphere containing epoxy coatings were 1.10 and 530 ohm cm2 after 37 days, respectively.

1. Introduction

One of the most common ways to reduce waste of energy is using thermal insulation. Based on today's problems of common thermal insulations such as glass wool and stone wool led to using new type of insulation classified as modern insulations. Nowadays, this technology is used in buildings, pipes and storage tanks, oil, gas, and petrochemical industries to reduce thermal conductivity through coatings. In this study, Hollow Glass Microspheres (hereafter HGM) were used as thermal insulator additive which have been added to an organic coating; these thermal insulation coatings could also cover some other requirements of industries such as protection against corrosion which for the first time this aspect has been reported in this paper. Due to existence of corrosive species in oil, gas, and petrochemical industries, one of the most essential features of these type of coatings' is their protection against corrosion, and in fact, direct and indirect energy loss can be prevented.

Generally, organic coatings can decrease electrolyte penetration rate of the coating/metal interface by making a physical barrier in the way of corrosive agents. However, barrier properties of coating are negatively influenced during coating exposure to corrosive electrolyte [1,2], so it is necessary to enhance stability of the coating during exposure to harsh environmental conditions.

Epoxy based coatings have been widely used due to their distinguished mechanical, thermal, electrical, and corrosion properties [3]. However their properties completely depend on their formulation. Many researches have been conducted on HGM containing epoxy coatings, most of them studied mechanical electrical and thermal conductivity properties [4–9]. Park and Yung illustrated that adding HGM into epoxy reduced the thermal expansion of coating while significantly improved glass transition temperature and mechanical properties of composite [10,11]. According to the researches, a great deal of attention has been attracted on thermal insulating properties of HGM since hollow cores enable tremendous thermal shielding ability, and this makes them promising candidates for application in thermal insulating composite materials [12,13]. There have been attempts to investigate the durability of these kinds of coatings; for this purpose, various methods have been presented for quality assurance, among them Prohesion™ is a standard test method (ASTM G85), containing both wet and dry conditions (solution spray for 1 h at 25 °C followed by 1 h exposure at air in 35 °C). The Prohesion™ test was designed with cyclic dry and wet conditions that would accelerate the coating failure [14].

The aim of this study was to investigate the effect of HGM on insulating and corrosion protection properties of HGM-epoxy coating. Cyclic dry and wet conditions and electrochemical impedance spectroscopy were employed for evaluating of HGM-Epoxy coatings.

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Table 1
Properties of epoxy resin (EPIRAN-01 X-75).

property	value
Epoxide Equivalent Weight (EEW)	434–555 g/eq
Epoxy Group Content	0.180–0.230 mol/100g
Viscosity @25 °C	6000–12000 Mpas

2. Experimental

2.1. Materials

Epoxy resin (EPIRAN-01 X-75) was purchased from Khouzestan Petrochemical Company (Iran), and its curing agent was a polyamidoamine (Aradur 115, Huntsman Co., USA) (Table 1).

HGMs were obtained from our laboratory, ICST, Iran [15] (Table 2). Byk 051 defoamer was purchased from Byk-chemi Company in Germany.

2.2. Sample preparation

15 wt.% of HGM with mean particle size of 70, 115, and 170 μm were dispersed in epoxy resin by a mechanical stirrer in 1200 rpm stirring rate for 30 min. And after that anti-foaming agent was added into the mixture, before application of mixture on plain carbon steel plates, the mixture was placed in a vacuum oven for 10 min. Vacuum oven pressure and temperature was set on 0.6 atmosphere and 40 °C. Mixture ratio of epoxy resin/hardener was 2.75. The mixture was applied by a film applicator on the chemically degreased and mechanically abraded steel panels with 400 and 600 emery papers. After applying the coating on the plain carbon steel plates, curing process was initiated: Two hours in environment for vaporization of high portion of its solvent and then twenty hours in vacuum oven with 40 °C following with one hour in 60 °C, the samples were kept for five days out of oven for completion of cure process. All the prepared coatings were cured in a vacuum oven for removing air and solvent entrapments; after curing, the dry film thickness was 250 ± 20 μm.

2.3. Temperature reduction efficiency (TRE)

For evaluating the thermal insulating properties of coating, four temperature sensors from TQC Company (the Netherlands) were used.

Two coated panels, a reference (coating without hollow sphere) and coating containing 15 wt.% of HGMs, were placed on a heater. Temperature changes on the coatings' surfaces were traced utilizing the sensors. Temperature reductions efficiency (TRE) in the presence of HGMs was calculated according to the following equation:

$$\text{TRE} = \Delta T/T_1 \times 100 \quad (1)$$

T_1 is the temperature of the coating surface in the absence of hollow spheres, and ΔT is the temperature difference between the coatings with and without micro hallow spheres.

2.4. Cyclic corrosion test (CCT)

Cyclic corrosion test was carried out according to ASTM G85 with Equilam instrument (G1, Brazil). The chamber conditions were evaluated by CorroSW software, version 2.16. The panels were exposed to wet/dry cycles: 1-h $(NH_4)_2SO_4$/NaCl-based electrolyte spray at room temperature and dried for 1-h at 35 °C for 1400 h. The corrosion protection property of exposed samples was evaluated by EIS at different time intervals.

2.5. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a common method for investigating corrosion protection behavior of coatings [16–19]. In this study, impedance measurements were carried out in a three-electrode system made by ACM Instruments Gill AC (UK). Samples were evaluated using Ex-situ method which means the samples were taken out from CCT chamber and then were fixed on a rubber stopper using a clamp with O-Ring to place the cell on the sample. Ag/AgCl electrode and graphite rod were used as reference electrode and auxiliary electrode, respectively. About 15.89 cm^2 of the coated metals were exposed to diluted Harrison solution electrolyte (3.5% ammonium sulphate, 0.5% NaCl) and the rest was sealed using a 75/25 beeswax–colophony mixture. The applied frequency range was 10 kHz to 10 MHz, and the perturbation was 10 mV. The Sequencer software was used for data analysis and determining the equivalent circuit.

2.6. Scanning electron microscopy (SEM)

This technique was used to analyze the surface and bulk morphology of the samples to evaluate the state of dispersion of HGM in the epoxy matrix. Scanning electron micrographs were taken with LEO 1455VP (England).

3. Results and discussion

3.1. Temperature reduction efficiency (TRE) of HGM-epoxy coatings

TRE of 15 wt.% of HGM containing coatings with three different mean particle size were measured and calculated according to Eq. (1). Fig. 1 shows the TRE versus HGM particle size; the higher particle size, the better insulating property and TRE. So, it represents better thermal barrier properties of the coating containing larger HGM (170 μm). It may be due to higher amount of vacuum in larger particles resulting in reduction of the effective thermal conductivity of the coating [20]. The vacuum inside the Hollow glass microspheres causes the heat insulating properties since the thermal conductance of vacuum is very low, so by increasing the glass particles the insulating properties would be improved.Heat insulation property of larger hollow micro-sphere filled systems is better than smaller sphere filled systems. This is because, when the thickness/diameter of hollow micro-sphere is constant, the larger the sphere diameter, the more the gas in the sphere (density decrease), leading to reduction of the effective thermal conductivity of the filled systems [21].

In first instance, improving thermal insulating property of epoxy coating was considered by adding HGM additive in epoxy composite. As 170 μm HGM showed best thermal insulating results it has been selected to be evaluated for its corrosion protection property as well.

3.2. Corrosion protection properties of epoxy insulator coatings

Corrosion protection property in this type of coatings is inevitable. So, HGM should not have undesirable effects on corrosion protection of these coatings. For this purpose, the coating containing 15 wt.% of

Table 2
Properties of HGM.

Hardness (Mohs)	Oil absorption (%)	Density (g/cm3)	Thermal conductivity (W/mk)	Dielectric constant	pH-Value	color	Chemical Composition(wt.%)
3.5–4	20–40	0.3–0.6	0.03–0.2	2–3	7–8.5	grey	SiO2:58–65, Al2O3:28–33, Fe2O3 < 4