Progress in Organic Coatings 76 (2013) 1814–1818

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Effect of cross linking degree and adhesion force on the anti-corrosion performance of epoxy coatings under simulated deep sea environment

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ARTICLE INFO

Article history:
Available online 17 June 2013

Keywords:
Crosslink density
Adhesion force
Anti-corrosion performance
Epoxy coatings
Deep sea environment

ABSTRACT

Deep sea exploitation represents the future direction for its abundant resources, while organic coatings can play a very important role in ocean engineering for corrosion protection. In this paper, under simulated deep sea environment in the laboratory, the effect of the crosslink density and the adhesion force of the coatings on the anti-corrosion performance of two different types of epoxy coatings was studied by using electrochemical impedance spectroscopy (EIS) and adhesion test. The results showed that the deterioration of coatings' property of corrosion protection under simulated deep sea environment was much faster than that of under normal pressured seawater. However, the diffusion velocity of water molecule through epoxy coatings decreased with increasing of the crosslink density and the adhesion force of the coatings. Therefore, the capability of corrosion protection could be improved by increasing the density of crosslink of the coatings within some extent and by increasing the adhesion force of the coatings.

1. Introduction

Oil and gas exploitation in deep ocean environment implies challenging harsh corrosive environments for structural materials since the hydrostatic pressure and the different dissolved oxygen (DO). Thus, the corrosion problem of materials in deep ocean condition must be considered due to the hydrostatic pressure influencing the diffusion of the water and dissolved oxygen through the coating.

Therefore, the present work aimed at the effect of hydrostatic pressure on the corrosion protection of the coatings which had different crosslink density. The anti-corrosion behavior of two epoxy coating with different crosslink density was investigated through a series of under simulated deep sea environment in the laboratory test in artificial seawater solution during which only the hydrostatic pressure was changed, all other parameters (DO, temperature, etc.) remaining constant.

2. Experimental

2.1. Experimental setup

Experiments were conducted at simulated deep sea equipment (Fig. 1) which can control the solution pressure by a compressor pump. A typical three-electrode cell was used with a saturated calomel electrode (SCE) (GD-I, BRICEM, China) as the reference electrode, a large piece of platinum plate with a surface area of over 4 cm^2 as the counter electrode, and a coated carbon steel specimen as the working electrode.

2.2. Coating preparation

The substrates material was carbon steel, which has a composition of 0.20% C, 0.32% Si, 0.56% Mn, 0.033% P, 0.032% S and Fe as the balance.

The specimens with a 20 mm diameter were machined from a carbon steel rod and embedded in the epoxy resin. The electrode surface was polished to 600 grade wet silicon carbide paper, degreased with acetone, cleansed with distilled water and dried in a compressed hot air flow.

E44 coating was prepared using epoxy resin with 213–244 epoxy equivalents as binder (obtained from Blue Star Resin Company (China)), polyamide 651 (obtained from Blue Star Resin Company (China)) as curing agent. The E44 coating was cured at room temperature for 12 h, followed by curing at 60 °C for 12 h. The thickness of the dry coatings was 190 ± 5 μm, as determined using a Positector 6000 Coating Thickness Gages (DeFelsko Corporation, USA). The crosslink density of E44 coating was 86%.

E12 coating was prepared using epoxy resin with 714–1110 epoxy equivalents as binder (obtained from Blue Star Resin Company (China)), dicyandiamide (obtained from Jinchen Chemical

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http://dx.doi.org/10.1016/j.porgcoat.2013.05.022

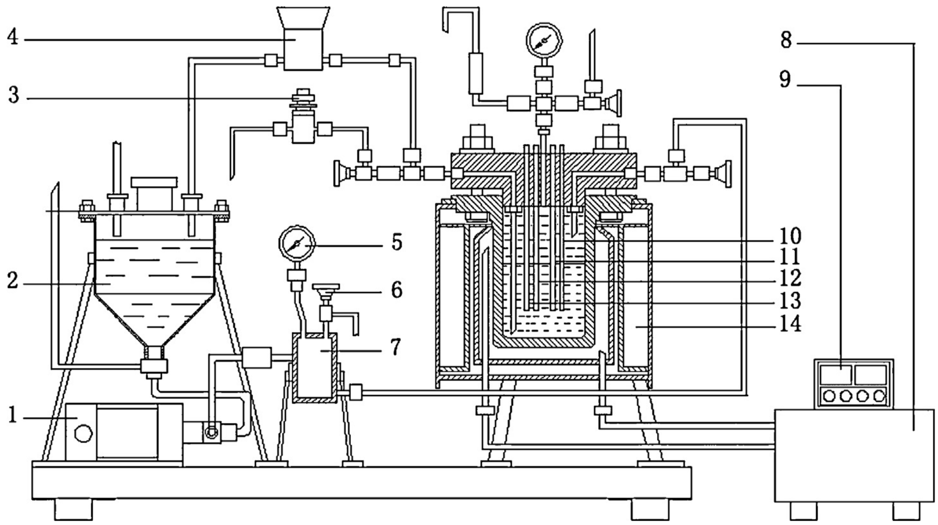

Fig. 1. Schematic diagram of the experimental setup for deep ocean corrosion study. (1) Booster pump, (2) artificial seawater pot, (3) discharge port, (4) inching valve, (5) pressure gauge, (6) valve, (7) buffer pot, (8) thermostatic bath, (9) temperature monitor, (10) thermocouple, (11) reference electrode, (12) counter electrode, (13) working electrode, and (14) pressure kettle.

Table 1
The composition of the artificial seawater.

Compound	Concentration (g/L)	Compound	Concentration (g/L)
NaCl	24.53	$NaHCO_3$	0.201
$MgCl_2$	5.20	KBr	0.101
Na_2SO_4	4.09	H_3BO_3	0.027
$CaCl_2$	1.16	$SrCl_2$	0.025
KCl	0.695	NaF	0.003

Company (China)) as curing agent. E12 coating was cured at 220 °C for 10 min. The thickness of the dry coatings was 100 ± 5 μm. The crosslink density of E12 coating was 98%.

2.3. Crosslink density measurements

The crosslink density of the coating was measured with solution extraction. The coating was cut out to some little pieces about 200 mg weight. These pieces were weighted by means of a digital balance (Sartorius CP225D) with a precision of 0.00001 g for the original weight (W_0). These pieces were put into the Soxhlet extractor and were extracted at the boiling point with acetone for 48 h. After extracted for 48 h in acetone solution, these pieces were weighed again in order to obtain the final weight (W_1). The crosslink density of the coating was calculated via Eq. (1).

$$\text{Crosslink density} = \frac{W_0 - W_1}{W_1} \times 100\% \qquad (1)$$

2.4. EIS measurements

EIS measurements were performed on Autolab PGSTAT302 potentiostat (made in Netherlands). A three-electrode cell was used employing the coated carbon steel as working electrode with an exposed area of 9.8 cm^2, a Pt plate as counter electrode and a saturated Ag/AgCl (saturated KCl) electrode as reference electrode, respectively. The tests were performed at room temperature in artificial seawater. The composition of artificial seawater was listed in Table 1. The concentration of the dissolved oxygen concentration is 7.5 mg/L. The impedance data were collected at the open circuit potential with a 20 mV sinusoidal AC perturbation over a frequency range of 100 kHz–10 mHz. The data were acquired in four cycles at each frequency for providing good precision at all frequencies.

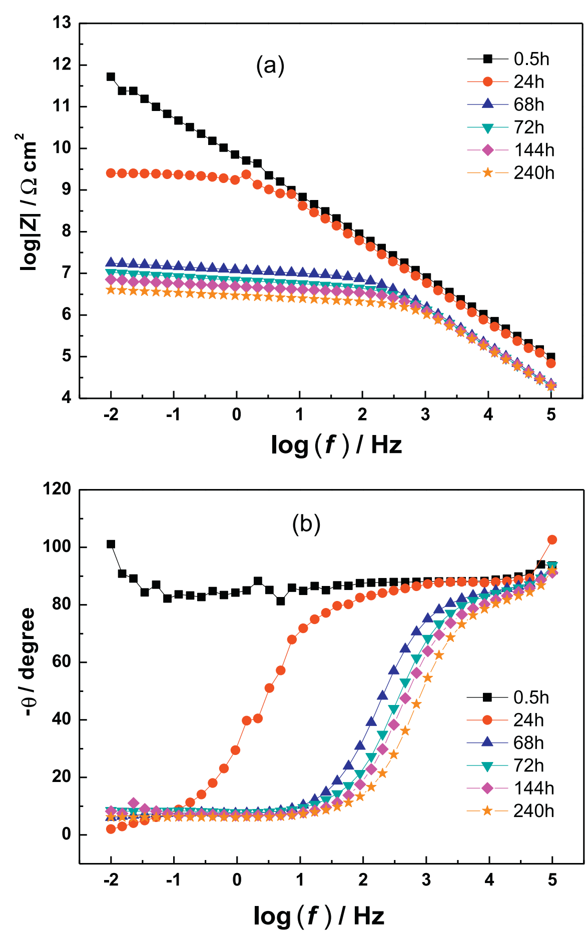

Fig. 2. EIS results for E44 coating at normal hydrostatic pressure (a) Nyquist plot; and (b) Bode plot.

More than three specimens from each series were measured for good reproducibility.

3. Results and discussion

In order to characterize the corrosion protection of the coatings of different crosslink density, EIS measurement was carried out.