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Preparation, characterization, and analysis of anti-corrosion subsea coatings

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Abstract Within this work, a two-component anti-corrosive epoxy primer formulation, Sigma-cover[TM] 280, and its resulting films were prepared and evaluated. The optimum coating time following formulation was extended by adding an appropriate amount of solvent as a controlled thinner. The draw down coating method was identified to be a reproducible and a robust paint film deposition process. Gravimetric analysis, Differential scanning calorimetry (DSC), and through-dry testing were used in the characterization of the curing and drying behavior of each applied primer film. The shortest time for achieving a through-dry state occurred with thinner films cured at the higher temperature, as seen in the film curing/drying. The minimum covercoating time and full cure time of the paint films, cured under the different conditions, were evaluated by means of its dryness, hardness, and curing state studies/characterization.

Keywords Epoxy, Subsea coatings, Paint, Curing, Anti-corrosion

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Introduction

The demand for offshore oil and gas products, designed for use in the subsea oil and gas recovery industries, is increasing at an unprecedented growth rate and is expected to exceed that for onshore production.[1] Technological progress has resulted in the possibility of exploring oil and gas fields at water depths of up to 3000 meters, using subsea products that can withstand a temperature range of −40 to 340°C and withstand a pressure of up to 30,000 psi.[2,3] Worldwide, installed offshore oil and gas recovery processes and equipment have been used in several different subsea environments, giving an uninterrupted service life of up to 25 years.[3]

Anti-corrosion, subsea coatings create products that meet the requirements for long-term exposure to subsea surface applications, encountered at extreme working conditions, including temperature, pressure, and the subsea-related structure-surface contamination.[4,5] Multi-layer coating systems, with the sequence of primer, undercoat(s) and finishing coat, are commonly applied as the anti-corrosion subsea coatings with a minimum overall dry film thickness (DFT) of 350 microns (DNV RP B401:2005–Category III). Each "layer" in any protective multi-layer coating has a specific function, with its recommended DFT.[6]

Current, commercially available, two-part epoxy coating formulations are known to be fit for the purpose for subsea surface applications.[7–9] These complex formulations and their deposition, as governed by available paint technical guidance, have been designed with this quality as the major requirement. There is a drive within industry for the provision of equal quality protective coatings, whose performance is realized using a significantly shorter curing/stabilization time. This need must be addressed if the scope of application of these types of coating is to be broadened, thus shortening the subsea fabrication turn-

around time. With a view of providing a greater understanding of the importance of composition factors, the objective of this work was to collate relevant scientific factors and data, to assist in the coating application in terms of the efficiency of existing commercial coating production processes, thus optimizing production processes, while providing some technological advancement.

Experimental

The Sigmacover 280 coating formulations (PPG) were prepared by mixing the epoxy coating-red brown base (PPG) and the epoxy coating hardener (PPG) in a volume ratio setting of 80:20, at 15°C. All of the sample films were prepared within a recommended DFT range, to replicate industrial practice for epoxy anti-corrosive primer coatings, as used in the offshore oil and gas product industry.[10] The "thinning" formulations, prepared additionally for viscosity evaluation (Brookfield DV-I Prime, Spindle No. 6, 60 rpm), contained Thinner 91–92 (consisting of 2-methyl-1-propanol, 1,3-dimethyl-benzene, ethylbenzene, o-xylene and toluene as detected by a Shimadzu GCMS QP2010) in the volume ratios 100:5 and 100:10.

After the tinplate panels were stabilized on the impression bed (RK print coat instrument), the freshly prepared primer formulations were applied to the degreased tinplate panel (Pro Test Panels Ltd.) by the draw down coating method using a casting knife film applicator (Elcometer®), resulting in two sample series with a DFT of 70 ± 2 μm and one sample series with a DFT of 150 ± 2 μm. Upon completion of the paint film sample preparation, one sample was (DFT: 70 ± 2 μm) left to cure at 15°C and 45% relative humidity (RH). The other two samples were immediately transferred to the Gallenkamp hot box oven, which was set at a temperature of 30 ± 2°C, RH of 44%, for further analysis.

The analysis of cross-sectioned, cured film sample was carried out using a JEOL JSM-6610 LV Scanning Electron Microscope (SEM). The DFT was established using a DFT coating thickness gauge (PosiTest®, that conforms to ISO 2178/2360/2808), with an accuracy found to be ± 8% against the SEM cross section analysis results. Film drying analysis was carried out gravimetrically (Oertling). To determine the weight loss rate of residual solvents from the films at later stages of film curing, approximately 10 mg sample were obtained from the coating film and placed onto a TGA (TA Instruments Q50 TGA unit) platinum pan before being heated in the temperature range from 25 to 200°C, at a constant heating rate of 10°C/min, followed by isothermal heating at 200°C for 30 min in a streaming nitrogen atmosphere. The sample through-dry state was analyzed using a through-dry tester (Erichsen®, ISO 9117-1:2009). Film curing was characterized using a TA Instruments Q20 DSC unit. Prior to each DSC run, a

small amount of sample obtained from the sample paint film (approximately 10 mg) was sealed in a DSC Aluminum pan. After the sample pan was settled, the DSC cell was subsequently heated at a constant rate of 10°C/min under a constant flow of nitrogen (50 mL/min) over a temperature range of 0–500°C.

Results

As an important factor that will influence the coating film thickness and the quality of the finished coating, the flow characteristics of the epoxy coating formulations were investigated. The results are depicted in Fig. 1.

As shown in Fig. 1, following mixing, the viscosity of all sample formulations increases with time due to solvent evaporation and the cross-linking process. The viscosity did not reach a stable value before the stated pot life. The formulations with more "thinning" showed a slower viscosity increase than those with less "thinning." The experimental results indicate that the optimum time for draw down coating at 15°C should be within approximately 5, 6, or 7 h after formulation for 0, 5, or 10% (v/v) "thinned" formulations.

To evaluate the paint film sample construction process (draw down coating) reproducibility, a series of primer films was prepared over a period of 3 days. Coatings were undertaken three times over 3 days at the same applicator setting (400 μm), by means of the draw down coating method. The resulting film DFT is shown in Table 1.

SD is the standard deviation. The relative standard deviation (RSD) can be used to analyze the precision and the reproducibility of the film construction process.[11] It is defined as the ratio between the SD and the mean. Table 1 shows the film DFT reproducibility
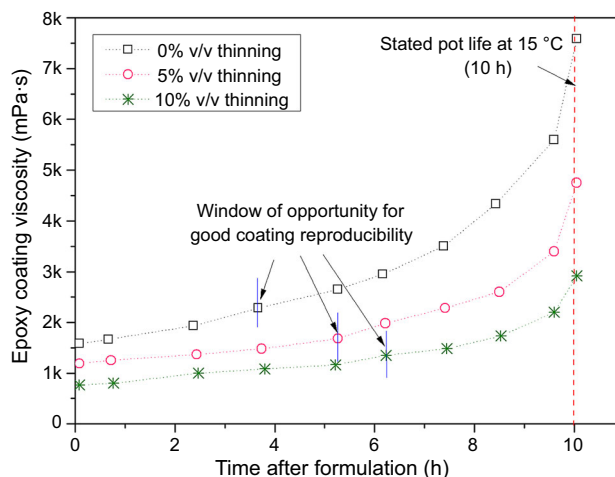

Fig. 1: Viscosity of epoxy coating formulation vs time. The red dashed line indicates the stated pot life (ISO 9514:2005) of formulations at 15°C. The solid blue short lines indicate the time when poor coating reproducibility could be expected to occur (Color figure online)

Table 1: Reproducibility of dry film thickness (DFT) measurements for the film construction process

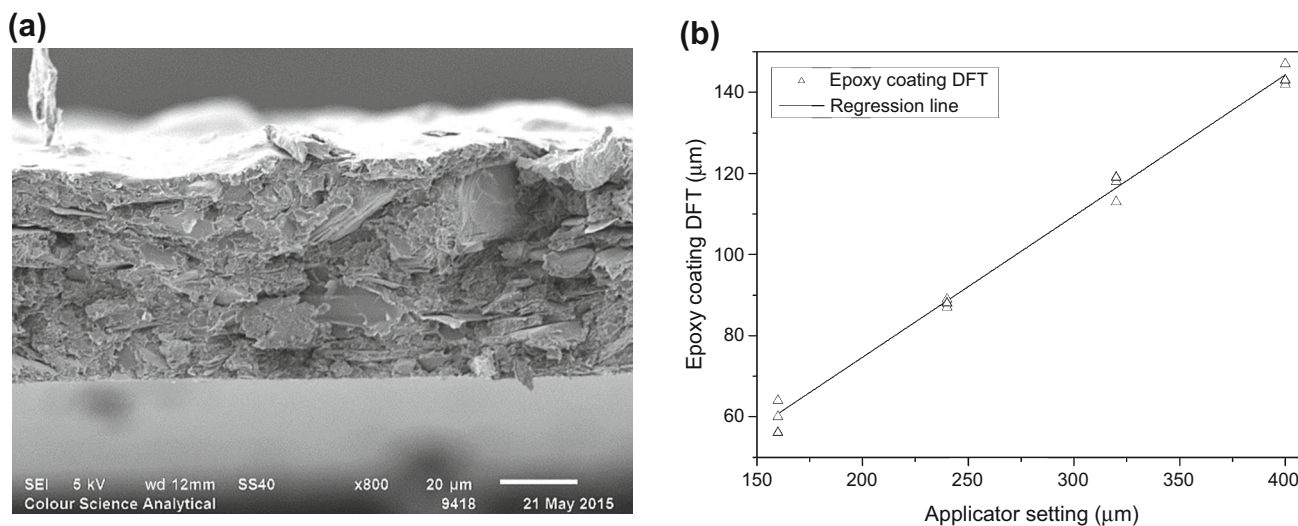| Day	DFT values					
	First time (μm)	Second time (μm)	Third time (μm)	Mean (μm)	SD (μm)	RSD (%)
1	142	147	143	144	2	1.4
2	140	147	146	144	3	2.1
3	143	146	145	145	1	0.7

(a)

(b)

Fig. 2: SEM electron-micrograph of epoxy coating cross-sectioned film with a DFT of 60 ± 2 μm (left, ×800) and the applicator setting plots of the DFT (right). The right-hand graph gives a slope that is a useful parameter for predicting the behavior of the epoxy coating film DFT, based on the applicator setting (160 $\leq S_{coat}^{\circ} \leq$ 400 μm) at 15°C

measurements for the film construction process, giving the RSD (%) of the DFT.

As shown in Table 1, the highest mean value was 2.1% (Day 2) and the lowest value was 0.7% (Day 3). The RSD values were relatively low. These results indicate that the draw down coating method gives a reproducible DFT of the paint film sample on a tinplate panel.

An example of an SEM electron-micrograph of a paint film cross section (left) and the DFT characterizations (right) are illustrated in Fig. 2.

The SEM electron-micrograph indicates that a homogeneous solid structure had been formed. In the DFT characterization trace, an approximately proportional relationship: DFT = $\beta + \alpha \cdot S_{coat}$ (R^2 = 0.99, 160 $\leq S_{coat}^{\circ} \leq$ 400 μm) was found. The regression line from results (right-hand graph in Fig. 2) determines the constants of proportionality (coating constants) that were α = 0.35 and β = 3.88.

It was found that, within the recommended DFT range, the proportionality relationship was valid when other two-component epoxy coatings (Sigmaguard 720, Sigmacover 456, Phenguard 935, Phenguard 930, Sigmaline 780 from PPG) are prepared at different tem-

peratures (15, 20, and 25°C). Differences concern the coating constants (β and α). Although the quantitative analysis of parameters to determine the coating constant has not yet carried out, it was clear that the speed of application, applicator setting, surface critical tension of the tinplate panel, and the viscosity of the product are key parameters in influencing the coating constants. The fact that the coating constants are comparable for different paint types indicates that the total thickness deposited by draw down coating is consistent with repeat to changes in the applicator setting.

Figure 3 relates the curing (J/g) and drying (wt%) behavior of samples with their different DFT, cured at different temperatures.

Gravimetric analysis was carried out to evaluate the film physical drying process in terms of film drying extent (wt%). The sample film curing status was characterized in terms of exothermic energy (J/g) by measuring the latent heat of reaction of the curing via determination of the post-curing peak energy on DSC thermograms.[12–14] That is, the greater the exothermic energy, the more curing extent.

Upon completion of the paint film sample preparation, the crosslinking process occurs in conjunction
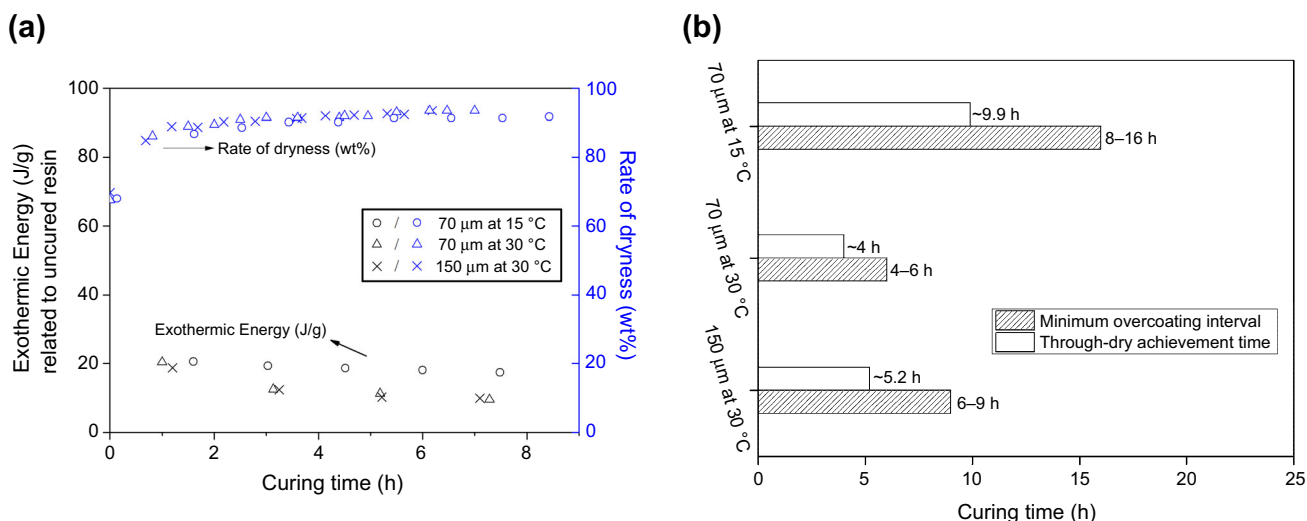
(a)

(b)

Fig. 3: Sample curing/drying behavior evaluation (left) and the comparison of through-dry achievement time against the stated minimum overcoating interval (right)

with the solvent evaporation process.[15] As expected, a higher rate of solvent evaporation and curing occurs at 30°C. Shorter times were also investigated to achieve a through-dry state using samples cured at 30°C. Compared to thinner films (70 μm), thicker films (150 μm) needed a longer period of drying and curing as indicated in the longer time taken to achieve a through-dry state. In contrast, the epoxy coating with a DFT of 70 μm, curing at 30°C exhibited a significantly shorter time to achieve the through-dry state. This was also the trend with the minimum overcoating interval and full cure required time. It is clear that the necessary state of film dryness and hardness is vital if one needs to apply further coats of paint (minimum overcoating interval).

Discussion

The viscosity evaluation of the epoxy coating formulation suggests that the presence of thinner solution slows down the rate of viscosity increase. Flow property evaluation has been shown to offer a promising test method for establishing the practical "pot life" of a two-component epoxy coating formulation.

The results obtained from the SEM evaluation and DFT gauge reproducibility measurements suggest that the total thickness that is deposited by draw down coating is robust with respect to the applicator setting. The coating method utilized shows good reproducibility with respect to film thickness. Therefore, this method should also be useful for the preparation of other coating types.

Although published work has reported the use of thermal analysis to evaluate the curing of epoxy resin, there is a lack of information with respect to the quantitative analysis of the curing of commercial epoxy coating systems. Data obtained from thermal analysis and gravimetric analysis suggest that both the DFT and the curing temperature have an effect on the epoxy coating film curing and the drying behavior, and therefore affect the through-dry time, the overcoating interval time and the time of full cure. However, due to the relatively low ratio of epoxy resin precursor to other components present in the epoxy paint formulations, the exothermic energy related to the residual heat of reaction was somewhat lower than that obtained for the single-component epoxy systems that other workers have studied.[12–14] The values for the exothermic energy prove to be more consistent at the later drying stages, after the bulk of any residual solvent has been removed.

Conclusions

The epoxy coating formulation and its resulting films were successfully prepared and evaluated. The formulations with more "thinning" showed greater delay of the curing. The reproducibility of the draw down coating method used for epoxy paint applications was established, which allowed differential DFT values of the paint film to be obtained in a reproducible manner. A less film drying and curing extent occurred in the thicker film cured under lower temperature. This trend was supported by the through-dry test results.

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