Reliability on Coating Pull-Off Adhesion Strength Test

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Abstract

The pull-off adhesion strength measured by the ASTM D4541 standard for marine coating system depends on several factors such as coating thickness, dolly size, curing time of the coating and adhesive, skills of the test operator. The effect of these factors on the adhesion strength is not well understood. In this work, the following three factors – coating curing time, drying time followed by water immersion test and the coating thickness and their impact on adhesion strength of the heavy-duty marine amine-cured epoxy coating system were investigated. We found that (1) the longer curing time, the higher pull-off strength, it may be due to higher crosslinking density of the coating; (2) the longer drying time after water immersion, the higher pull-off strength, it may be due to the evaporation of water molecule at the coating-substrate interface; (3) pull-off strength increases as coating thickness increases due to the diminishment of bending effect.

Keywords : pull-off strength, curing time, thickness of the panel, adhesion test
Introduction

One of the key properties for any protective coating system is its adhesion to steel substrates or other painting system. If it doesn’t have sufficient adhesion, a coating will fail. It is of vital importance, therefore, to evaluate adhesive strength accurately.

Recently, the adhesion test in a coating evaluation project is usually done in accordance with ASTM D4541. This method assesses the adhesion of a single coating or a multi-coat system of paint by measuring the minimum tensile stress necessary to detach or to rupture the coating in a direction perpendicular to the substrate.

Factors that typically affect the tensile pull-off adhesion test results are (1) thickness of the test substrate, (2) dolly size, (3) degree of cure, (4) degree of drying after water immersion, (5) type of test instrument, (6) skills of the test operator, (7) consistency and rate of load, and (8) morphology of the surface\(^1\). In this paper, we only try to evaluate the following three parameters; curing time, drying time after water immersion and coating thickness.

EXPERIMENTAL METHOD

All steel substrates (thickness, 3 mm) were blasted to Sa2.5 cleanliness with around 70 \(\mu m\) anchor profile. All blasted steel surfaces were cleaned using acetone to remove grease or oil contamination of the surfaces before application of each coating system. The substrates were coated with a commercial polyamine epoxy coating, via an airless spray gun. The selected coating materials were commercial epoxy coatings currently used widely in ship building industries for water ballast tanks and other water immersion services.

The pull-off strength test was performed according to ASTM D4541, by PATTI (Pneumatic Adhesion Tensile Test Instrument) which uses compressed air from a canister and a dolly diameter of 0.5 inches. All dollies used in the experiment were cleaned with acetone in order to remove any contamination.

Effect of the curing time

Pull-off strength measurements for the coating system with dry film thickness, 300 \(\mu m\) were carried out as a function of curing time 7, 14, 28, 56 days (23 °C) after immediately spraying paint onto the steel surface. The two component epoxy adhesive with adhesion strength over 15 MPa was applied for joined of dolly with the coatings. The curing time for the adhesive was 24 hours. To investigate the relationship between curing time and degree of cure for a heavy-duty coating system, the differential scanning calorimeter (DSC) was used in order to investigated the correlation about glass transition temperature (Tg) and pull-off strength.
Effect of the drying time after water immersion

The coated steel panels were cured at 22~24 °C for 2 weeks and postcured at 50 °C for 2 weeks. The coating samples (DFT, 300 μm) were immersed in the tap water tank at 50 °C for 14 days. After the immersion, pull-off strength test was carried out as a function of drying time at 23 °C.

Effect of the coating thickness and scoring around dolly

The coated substrates were cured at 22~24 °C for 7 days. Pull-off measurements were carried out as a function of average dry film thickness (D.F.T.). The average dry film thickness on the 3 mm steel substrate were 150, 300, and 1000 μm. The adhesion specimens were prepared according to the same method as that for the curing time effect test of the coating. Scoring around the dolly before the pull-off strength test was applied for some coating samples.

Results and Discussion

Effect of the curing time

Figure 1 and 2 indicate that Tg of the coating increases with the curing time and the pull-off strength also increases. Increase in Tg is a reflection of the conversion of the film from a viscous liquid to a viscoelastic solid. These viscoelastic changes accompany the morphological progression of molecular compaction. The first step is setting up a large amount of low molecular weight pre-polymer (unreacted epoxy resin and terminal group of polyamine). This is followed by the establishment of a substantially rigid network between partially cross linked epoxy resin and unreacted epoxy resin, which markedly restricts further molecular motion to occur. However, for reasons of insufficient 7 days curing times, pull-off adhesion strength is relatively low (12.6 MPa). Additional cross linking which may take place within the newly established network will not markedly affect any further molecular motion and Tg will converge on the specific point. Accordingly, for curing time of 56 days, pull-off strength reaches to the maximum 14.5 MPa same as value as pull-off strength of the fully cured epoxy which was obtained by the curing condition of 25°C-2 weeks followed by 50°C-2 weeks oven curing. Tg of the cured epoxy leveled off for 66 °C as shown in Figure 1, although molecular weight within the established network may continue to increase. It is obvious that the pull-off strength is a function of the degree of cure for the coating material.

Effect of the drying time after water immersion test

A model for wet adhesion loss and blister formation was proposed by Leidheiser and Funke. Their model requires three conditions: a through-film pathway for water transport, a disbonding site for water accumulation, and a driving force to facilitate transport of water. Adhesion loss initiates as water
accesses the disbonding and propagates as the water accumulates in multiple layers at the interface\textsuperscript{4,5}. Eventually, this multilayered accumulation of water splits. Then, it undergoes a peeling propagation into film areas surrounding the original site of disbondment as further volumes of water accumulate and the leafing edge of the forming blister is mechanically stressed. The model is summarized in Figure 3.

The resistance to the coating pull-off force will depend on the drying time for the loss of the water molecule. The relationship between adhesion strength and the drying time was investigated, and the results are shown in Figure 4. The pull-off strength increases with drying time after the water immersion because of water evaporation and the recovery of adhesion. The coating adhesion was almost fully recovered after 1200 hours drying as compared with the original pull-off strength, 14.5 MPa.

Figure 5 indicates the morphology of the test sample surfaces after the pull-off adhesion test after different drying time. Higher percentage of coating can be seen after longer drying time. It is a clear evidence to recover the adhesion after water evaporation from the coating/steel interface.

For the property test of coating after immersion, undercutting from scribe\textsuperscript{6} is one of important test method because it is easily accessible wet adhesion test. Results from undercutting indicate that water evaporation increases rapidly until 24 hours same behavior as the pull-off adhesion strength as shown in Figure 6. It is required to evaluate adhesion strength of the coating no later than 24 hours after picking up the specimens out of the immersion bath when wet adhesion test is performed.

**Effect of the coating thickness and scoring around dolly**

Figure 7 shows that the relationship between pull-off strength and coating DFT. It is readily seen that the pull-off adhesion increases with the DFT. All materials yield to a degree when subjected to pull or compression stresses, even if only a few nanometers\textsuperscript{7}. Therefore, in association with the film thickness, the thick film may restrict bending of the substrate as the pull-off force applied to the coating.

In ASM D4541, it is mentioned that the scoring around the dolly is prohibited, whereas it is an essential requirement in ISO 4624 standard. The intention with this part was therefore to test the influence of these 2 parameters on the pull value. The obtained mean results are also shown in Figure 7. The higher pull-off strength was measured when the circumference around the dolly was not cut, than when it was, as the same coating thickness, but the difference decreases as the thicker coating. It is noted that the relatively thinner coating have relation to adjacent films of the dolly edge and the higher difference is achieved.
Conclusions

Following conclusions can be made through the study of the effect of three factors on pull-off adhesion strength for the epoxy coatings.

1) The pull-off strength of the coating highly depends on the degree of curing of the coating.

2) For the wet adhesion evaluation after water immersion, the pull-off test should be performed within 24 hours after it is out of water because the coating adhesion will be gradually recovered.

3) For pull-off adhesion strength measurement of the coatings with various thicknesses, it should be cautioned that the bending factor is minimized for thicker coatings resulting in higher pull-off adhesion strength.

REFERENCES

[6] ASTM D7087, Standard test method for an imaging technique to measure rust creepage at scribe on coated test panels subjected to corrosive environments
Figure 1. Glass transition temperature variation as a function of curing time

Figure 2. Pull-off strength variation as a function of curing time
Figure 3. Schematics of wet adhesion loss and blister formation at the coating substrate interface.
Figure 4. Effect of pull-off strength as a function of the drying time of films after water immersion test
Figure 5. Optical microscopic surface morphology of the coating detached steel surface as a function of the drying time after the water immersion test
   a) 1 hour,   b) 120 hours, c) 240 hours, d) 1200 hours
Drying time of films after water immersion [hours]

**Figure 6.** Effect of undercutting from scribe and pull-off strength as a function of the drying time of films after water immersion test.

**Figure 7.** Pull-off strength for a diverse coating thickness with and without scoring around dolly.