

**Study of 100% Solids Liquid Epoxy Pipeline Coatings in Low Temperature Application:
Curing Reaction Versus Performance Characteristics**

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ABSTRACT

The curing responses versus performance characteristics of four commercial 100% solids epoxy pipeline coating products were experimentally and analytically investigated for the potential use in field pipeline maintenance at low application and cure temperature of 0 °C.

In this study, an advanced cure monitoring program was employed for the investigation, involving percentage of cure and glass transition temperature (T_g) by Differential Scanning Calorimetry (DSC), pull-off adhesion, and Shore D hardness techniques. A better understanding of the coatings' low temperature behaviors was gained through the integration of the cure status with the evolution of mechanical and bonding strength as a function of the cure time. With an effort to identify the minimum cure duration for return to service but ensuring a satisfactory degree of curing to yield reasonable properties, additional experimental trials were also carried out to examine the change in impact resistance over cure time and the development of the blistering resistance in hot water immersion. Lastly, the suitable epoxy coatings chosen from the cure monitoring program were further examined in the qualification program, including Cathodic Disbondment and hot water soak tests, to confirm and build confidence on their reliability in the long-term performance.

Key words: 100% solids liquid epoxy coating, low temperature, DSC, percentage of cure, T_g, pull-off adhesion, Shore D hardness, impact, blistering resistance, cathodic disbondment, hot water immersion

INTRODUCTION

Liquid epoxy coatings have been used extensively in buried and immersed pipelines as field joint coatings and maintenance coatings due to their attractive properties, such as high chemical and corrosion resistance, good physical-mechanical properties, and strong adhesion to various substrates (compatibility with different mainline parent pipeline coatings)¹. With the continuous evolvement in epoxy/curing agent technologies, liquid epoxies have been formulated in 100 % solids to comply with the VOCs emission regulatory requirements. In light of practical and economic drives, some 100% solids

epoxy coatings are also formulated with fast cure and low temperature cure properties, so their application can be extended to winter season and be able to accommodate shorten maintenance scheduling. It is normally claimed that 100 % solids epoxy products can cure down to temperatures in the 35 °F (2 °C) range, and typically take approximately 48 hours to “fully cure” at these temperatures.²

In the past^{3, 4}, the performances of several selected low temperature cure liquid-applied coatings (vinyl esters, polyurethanes and liquid epoxies) were compared and discussed to explore their fitness for purpose for pipeline maintenance. The studies revealed that the examined vinyl esters and polyurethane coating samples generally cured quicker than the liquid epoxy sample at the low temperature of 0 °C, nevertheless the liquid epoxy coating sample demonstrated the best Cathodic Disbondment (CD) testing performance. Another superiority noted for the test epoxy coating was that the coating may also be suitable as coating repairs to fusion bonded epoxy coated pipelines with higher operating temperatures of up to 65 °C, while the performance data has limited the use of the other tested liquid-applied coatings to the service temperatures of 40 °C or below.⁴

The present work focuses on the study of 100% solids liquid epoxy coatings. The low temperature curing responses of four commercial epoxy coating products from four different suppliers were comparatively examined and analyzed to screen out unsuitable coatings and to gain a better knowledge of the cure status, the corresponding mechanical and bond properties versus cure time. Therefore, an advanced cure monitoring program was employed to achieve the purpose. The associated performance characteristics with cure time including the development of the blistering resistance in hot water immersion and impact resistance were also examined. The effort was to identify the minimum cure duration for returning to service but ensuring a satisfactory degree of curing to yield reasonable properties. At the end, the suitable epoxy coatings chosen from the cure monitoring examinations were enrolled into the qualification program, including CD and hot water soak tests, to confirm and build confidence on their reliability in the long-term performance.

The spray application of most 100% solids liquid epoxy coatings requires plural component spray equipment, but for small and medium sizes of field repairs, cartridge spray and brush applications apparently are more practical and economical. In this regard, all samples used for the study were prepared with spray cartridges and/or by brush. Additionally, the variation in the cure behavior and the yielding mechanical properties of the same coating prepared by the two application approaches were discussed in this paper.

CURE MONITORING TECHNIQUES

The cure monitoring program consists of the percentage of cure and T_g by Differential Scanning Calorimetry (DSC), pull-off adhesion, and Shore D hardness. The program incorporates the change in cure status of the epoxy coatings with the evolution of mechanical and bonding strength. The rationales behind the consideration of each technique are elucidated below.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a popular thermal analysis tool for direct determination of the enthalpy associated with the process of interest. Since the crosslink occurs in the curing process of thermosetting systems are exothermic in nature, DSC technique is widely used to characterize the curing reactions of epoxy resins. The basic theory is that the heat evolution recorded by DSC is proportional to the extent of consumption of reactive groups. The resulting exothermic peak can be integrated to obtain the enthalpy of reaction (ΔH), and then the corresponding percentage of conversion or the degree of cure (α) at each cure time t can be calculated.^{1, 5} The formula is described as follows:

$$\alpha = \frac{\Delta H(0) - \Delta H(t)}{\Delta H(0)} \quad (1)$$

where: $\Delta H(0)$ is total heat of reaction measured from the first scan of the freshly prepared liquid epoxy mixtures and $\Delta H(t)$ is the amount of residue heat measured from the DSC dynamic scan that performed on the cold-applied epoxy coating systems after cured at the temperature for different periods.

Additional benefit provided by DSC is that the glass transition temperature (T_g) can also be determined in the same thermal scan.⁶ The T_g is normally defined as the temperature boundary where a thermosetting polymer transits from a rigid “glassy” state to a pliable “rubbery” state, so it is a direct measurement of molecular mobility. Beyond the temperature range, the mobility of the molecular segments increases significantly, while below the temperature range, whole molecules lock in place and cannot move away from each other.⁷ The knowledge of T_g evolution during the curing progress can help in analyzing and predicting the change in chemical and physical-mechanical states of the materials under study. The importance of the T_g concept is well-recognized and no need to further emphasize. The T_g of a thermosetting system strongly depends on its degree of cure and is influenced by composition of the resin molecule, curing temperature, and curing time, etc.⁷ The relationship between T_g and conversion degree in the curing reaction is often deemed as a central concept in analyzing cure phenomena.⁸ Several authors have investigated the use of T_g as an appropriate parameter for monitoring the cure process. Wisanrakkit and Gillham found that T_g increases nonlinearly with conversion in crosslinking systems makes it even more sensitive in the later stages of reaction and proposed to use T_g as the prime parameter for monitoring the complete cure process.⁹ The literature review and the past experiences showed that the percentage of conversion by DSC is extensively accepted by the coating industry and coating laboratories to monitor the curing progress of thermoset coatings, but somehow T_g is rarely used for the purpose.^{3-5, 10}

Based on the above, both conversion degree and T_g parameters were adopted by the current cure monitoring program to trace the cure states of the examined 100% solids liquid epoxy coatings.

Pull-off Adhesion Strength

Pull-off adhesion testing is widely used to give a direct indication and provide quantitative measurements for the bonding strength of a coating to a substrate or the cohesion strength of the coating in a tension normal to the surface.¹¹ The basic procedure of the technique is to secure loading fixtures perpendicularly to the surface of coatings being tested, and then a tensile force is increasingly applied to the surface by the use of a portable pull-off adhesion tester until the loading fixture is detached due to a failure occurs within the test system. Cohesive strength of a coating is a measure of the force of attraction between the molecules, or the force required to tear the coating apart. This property is dependent on the coating's constituents (e.g. the base resins, fillers, etc.), and affected by the cure status. G. Smith¹² explored the use of tensile test to assess cure behaviors of both low and high solids epoxy-based paint systems using the coating free film samples. The study was intended to relate T_g with mechanical property so as to establish a new/better method. It was observed that both T_g and tensile techniques appear to show similar trends with cure.

Inspired by G. Smith's idea, pull-off adhesion technique was incorporated into the program to monitor the development of the cohesion strength of the coatings as a function of cure time. The concept is built upon when a coating is under-cured, the cohesive strength of the coating film is low and makes it the weakest link within the system. In this case, the determined pull-off adhesion strength will be the force required to tear the coating film apart, reflecting the cohesion strength of the coating at the cure stage. For the standard pull-off test, an adhesive is required to secure the pull-off fixture to the solid coating surface. However, this approach will be not applicable for the current work due to the cure issue of the adhesive

at low temperatures. Since the liquid coating mixtures themselves can act as adhesives, all pull-off fixtures were directly attached to the wet films immediately after each coating application.

Shore D Hardness

Among a few well-accepted practices by the industry to assess the degree of cure, Shore D hardness is probably one of the most frequently used methods, especially in the field. The technique provides a simple, convenient and fast indication of the degree of cure and the time for inspection and backfilling. When a two-part liquid applied coating is under cure or the mixing ratio of the two components is off, the obtained hardness values would remain lower than the value listed in the coating technical data sheet. For most pipeline coating products, the benchmark shore D hardness values are normally determined by the coating manufacturers at ordinary ambient temperature of $(20 \pm 3) ^\circ\text{C}$ according to ASTM D2240¹³.

As mentioned earlier, T_g affects physical-mechanical state of a material, so the hardness property of a coating has strong correlation with its T_g . When the environment temperatures change to above T_g , the coating will correspondingly change from a hard and glassy state to a soft and rubbery state, and then the obtained Shore D hardness will be lower than it was determined at a temperature below T_g . Conversely, partially cured coatings may seem sufficiently hardened at cold temperatures and give relatively higher hardness values than they will show at the ordinary ambient temperature. Therefore, it is meaningful to monitor and correlate the progress of the Shore D hardness of a coating with its cure status at the low temperature of $0 ^\circ\text{C}$. With such efforts, the Shore D hardness may then be a valid indicator for the coating at this temperature.

EXPERIMENTAL PROCEDURE

Test Samples Preparation

Four 100% solids liquid-applied epoxy coating products were used for this investigation and identified as coating 1 to coating 4. All coatings are designed for buried pipe corrosion protection and rehabilitation. The coatings are also featured with fast dry to allow quick QC and backfill/return to service and can be applied in cold weather and cured in low temperatures. Table 1 shows the samples and test matrix for the four coatings. Although both spray cartridge and brush grades are available for coatings 1 to 3, coating 1 was found to be rather difficult to apply by brush at $0 ^\circ\text{C}$ even with the assistance of a plastic scraper, due to the corresponding viscosity of the coating mixture at cold surface was high and very limited number of panels could be finished within the pot life. In this case, the coating was only examined for the spray cartridge prepared samples. Coating 4 does not supply with spray cartridge, so only the brush grade was checked in the cure monitoring program for comparison.

Table 1. The Samples and Test Matrix of The Four Coatings

Product	Application	Cure Monitoring	Blistering Resistance	Impact	Qualification Program
Coating 1	Spray	Tested	Tested	Tested	Tested
Coating 2	Spray	Tested	Tested	Tested	Tested
	Brush	Tested	Tested	/	/
Coating 3	Spray	Tested	Tested	/	/
	Brush	Tested	Tested	/	/
Coating 4	Brush	Tested	Tested	/	/

For the DSC tests to determine the total exothermic heat of reaction ($\Delta H(0)$), the fresh liquid coating samples were either manually mixed from brush kits or immediately taken from just sprayed wet coating films. For the specimens used to monitor the cure progress and performance evaluation, the coatings were spray cartridge and/or brush applied to the blasted carbon steel coupons. In terms of the surface preparation, all carbon steel coupons were first solvent cleaned to SSPC-SP1 using acetone and then blasted to SSPC-SP10/NACE 2 with anchor profiles of 3.2 - 4 mils achieved. The dimensions of the coupons were 50 x 140 x 6.35 mm (2 x 5.5 x 0.25 in.) for the cure monitoring examinations and 100 x 100 x 6.35 mm (4 x 4 x 0.25 in.) for all other tests. All applications were carried out following the coating manufacturer's qualified application procedures (MQAP). For the spray application, each spray cartridge was pre-heated to the required temperature before the use. The blasted coupons for the cure study were first conditioned overnight in a temperature-controlled chamber at 0 °C with desiccants added to control the moisture and the application was then completed in the chamber at the temperature. After each application, the pre-cleaned pull-off dollies were immediately attached to the coupons prepared for the cure monitoring. The application for the qualification tests were carried out in a temperature-controlled refrigerated trailer at 0 °C. All applied coupons were then cured at 0 °C environment with proper ventilation.

Test Methods

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a TA Instruments Discovery 25 Modulated DSC with RCS40 cooling system. The test procedure followed ASTM D3418¹⁴. The purge gas flow rate to the cell was 50 mL/min with nitrogen and heating rate was 20°C/min. Samples were encapsulated in DSC aluminum pans and scanned in the DSC unit from -40 °C to 250 °C. In this work, T_g was taken as the half height of the transition interval. The percentage conversion was calculated as per the formula 1 described previously.

Pull-off Adhesion

Pull-off adhesion was performed using a PATTI Quantum pull-off adhesion tester at 0 °C. The test procedure followed ASTM D4541¹¹. Prior to each measurement, the panel was taken out from the temperature chamber and the coating was scored around the loading fixture through the coating to substrate. The panel was then promptly returned to the low temperature chamber. After the temperature of the panel returned and stabilized at the curing temperature of 0 °C, the panel was taken out again from the chamber and the pull was immediately completed on the panel.

Shore D Hardness

Shore D Hardness was performed using a PTC Shore D durometer. The test procedure followed ASTM D2240¹³. All measurements were completed at 0 °C.

Impact Test

The impact test was carried out according to CSA Z245.20¹⁵ clause 12.12 at 0 °C. 100 x 100 x 6.35 mm (4 x 4 x 0.25 in.) coupons were used for the investigation to eliminate the test coatings potentially chipping out from the narrow edges that normally observed on 25 x 200 x 6.35 mm (1 x 8 x 0.25 in.) coupons in the previous work⁴. The impact energy of 1.5 Joules was applied periodically to check any improvement in impact resistance over time. This additional test was included in the experimental trials designed to understand the change in coatings mechanical behavior in response to the improved cure status.