A Simplified Approach to Formulating for High-Temperature and High-Pressure Applications

Many protective coatings markets have recently seen high demand for better performing coatings or linings. For example, with enhanced oil recovery, many more assets are now used throughout these processes from the oil/water separation tanks to the acid injectors. The temperatures are higher and corrosive environments are more severe. Formulation chemists are working hard, trying to push the extent of the performance of typical resin systems, but it seems that most of the development has been done and the extent of the performance available has been maximized. However, before throwing in the towel and going to expensive alloys ... maybe something was overlooked.

This article will look at how to formulate for high-performance properties, in particular, high-temperature immersion applications with epoxy thermoset coatings, and the impact of formulation additives on achieving this performance. The data presented will show how minor adjustments in formulation can have a significant impact on coating performance. More specifically, it will show that with proper dispersant selection, the viscosity of the coating system can be reduced, leading to increased filler loadings and ultimately higher performance. Furthermore, data will show how going through a step-by-step formulating process, from resin selection to choosing the right defoamer, can provide for higher-performing coatings than typically seen with the selected chemistries.

Purpose

The requirements for protective coatings are ever-changing, mainly driven by regulations calling for VOC reduction. If the coating isn’t directly targeted by regulation, the market containing the asset it protects may be. Currently, one of the most dynamic protective coatings markets is the energy market of oil and gas which has exploded with asset creation that needs protection from a very diverse range of environments. In the enhanced oil-recovery process pipes, tanks and other separation vessels must be protected from acidic, high-salt and high-temperature environments. As reserves are depleted, new ways of extracting thicker, sand-laden oil have been developed. One such method is by injecting steam into the ground and extracting the oil and water mix into separating tanks. Steam is pumped deep into the ground at around 600 F to lower the viscosity of thick oil and essentially push it towards extraction well bores. The material being extracted contains hydrogen sulfide, salt, water and solvent at high pressure and temperatures as high as 400 to 500 F. The mixture comes out of the ground at 200 to 250 F and is pumped into separation tanks. All of the steel work, inside and out, must be coated with the highest-performing coating chemistry available. If there is a weakness in the coating chemistry it will definitely be exposed here.

Before jumping into formulating for such coating applications, the methodology for evaluation of coatings for these
considering the corrosive nature of the extracted oil. So other, more expensive options such alloys, begin to find applications. Formulating for such environments is very difficult, but not impossible. Adhering to formulations of the past and assumptions that haven’t been evaluated will only limit the possibilities of realizing the full potential of the chemistries available. The new formulation should contain only those materials that add value to the properties and application. There are some general guidelines that can be adhered to that provide the basis for heat and pressure resistance and take much of the initial screening out of the process.

Resin Selection
A first step in formulating for high-temperature applications, either dry or wet, is to select the proper base resin. In making this selection, the main properties of concern are functionality and glass transition temperature (Tg). The molecular weight (MW) of the resin backbone between crosslinks can be determined for a linear polymer by taking the MW divided by the functionality minus 1. This applies to a linear polymer only, but shows the general principle of functionality increasing the crosslink density of the polymer. The MW between crosslinks or crosslink density (Mc) will indicate what the relative Tg of the final crosslinked film will be at high conversion, given a similar phenolic backbone content. A high Tg (or crosslink density) results in a lower permeation rate, given that there is lower free volume or space in the polymer for molecules like water vapor to permeate through. Lower Tgs are generally more flexible which means that there is more spacing within crosslinks allowing molecules to pass through the polymer and therefore, a flexible coating is generally less corrosion resistant. Achieving a high Tg through the reaction of the functional sites will provide a higher chemical resistance. The simple comparison is a novolac resin versus a bisphenol-A resin with the novolac having much higher corrosion resistance.

The other property that a high Tg will impact is the coefficient of thermal expansion (CTE). There are two rates of dimensional change of a polymer (measured by thermal mechanical analysis or TMA). The rate below the Tg will be much lower than the rate above the Tg. This is critical when heating a coating above its Tg. The stress of expansion along with the softening of the coating will cause the coating to buckle and lose adhesion to the steel
substrate which has a much lower CTE.

A simple room-temperature (RT)-cured bisphenol-A epoxy without fillers will soften above its Tg and lose adhesion seen with the translucent blister caused by expansion even on small panels (Fig. 1). There are other ways to manipulate the CTE besides Tg that will be discussed with incorporation of various fillers.

It is generally accepted that a higher Tg will result in lower permeation and higher heat resistance. This is true, but without a post-cure, the coating will only react so far, typically yielding similar Tgs to RT cure. The percent of conversion of the reactive sites needs to be considered when choosing a resin for a coating formula. A higher Tg with a higher functional resin may only be marginally realized due to the coating vitrifying well before the desired conversion was obtained (Table 1).

Resins will typically have a specific cure schedule with various curing agents to allow for high conversion, but it’s generally not feasible to adhere to such a cure schedule for these coating applications. The ability to post-cure a steel structure isn’t normally possible due to size and location. Another consideration is the amount of stress that a polymer coating experiences with high functionality and increased conversion. For example, a standard resin used for high performance is a novolac phenolic resin with multiple reactive sites per molecule. The increased branching and connection of the network creates tremendous stress due to shrinkage and lack of mobility. The free volume of the coating is decreased, lowering the permeability which is a great benefit, but for high-temperature applications, the coating is exposed to temperatures that will push the conversion of the coating to greater than 90 percent, which could cause shrinkage as high as 10 percent. The stress accumulation typically culminates with cracking either at temperature or more commonly when the coating is allowed to cool (Fig. 2). Therefore, the selection of the resin for high-temperature applications isn’t as simple as going to a novolac, higher-functional resin. Actually, it is likely that the addition of a reactive diluent will be necessary to decrease viscosity to aid application which will then decrease the crosslink density anyway. Add to that, many formulations will include a mono-glycidyl ether diluent which detracts from MW and ultimately, from performance. And that’s just the epoxy portion.

There are many more types of resin that will react with epoxide groups to create a polymer coating. Amines, amides, amidoamines and thiols are most widely used. The amine group is probably the most common available in a variety of different MWs and structures. With so many choices, what is the logic behind the selection for high-temperature coating applications? The most important characteristics to assess in an amine curing agent are how volatile the curing agent is and whether or not it contains material that will volatilize at the service temperature. Many of the curing agents will contain a catalyst such as bisphenol-A, nonyl phenol or benzyl alcohol. Without the catalyst, cure times of many of the amines with a standard bisphenol-A epoxy would be fairly slow which could cause application issues. With the formulations going towards higher solids or ultimately 100%-solids systems, the use of the catalyst isn’t as necessary due to the

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<th>Table 1: DSC Data</th>
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<tr>
<td>RT Cure for 7 days</td>
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<tr>
<td>Epoxy bis-A / Polyamide blend</td>
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<td>Epoxy bis-A / Cycloaliphatic amine</td>
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<td>Epoxy bis-A / 1, 3 BAC</td>
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<td>Post cure at 110 °C for 7 days</td>
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<td>Epoxy bis-A / Polyamide blend</td>
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<td>Epoxy bis-A / Cycloaliphatic amine</td>
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Fig. 1: Epoxy coating exposed for short duration at 350 to 400 °F.

Fig. 2: Novolac epoxy coating exposed for short duration at 350 to 400 °F.
lack of solvent to retard the reaction. Many of the standard cycloaliphatic amine curing agents will contain anywhere from 30-to-50 percent weight benzyl alcohol. Benzyl alcohol, which has a boiling point of 402 F, will volatilize out of the coating. As it leaves the coating, stress is applied across the coating with the adhesion to the substrate and cohesion of the polymer resulting in the coating cracking or delaminating from the substrate or both (Fig. 3). The use of these catalysts should be taken into consideration with regard to the temperature of service for the coating. In addition to temperature performance, it’s quite possible that regulatory bodies will eliminate them from formulations regardless, so formulating without them is inevitable. As a side note, the volatility of all formulation components needs to be in line with the end use temperature. For high-temperature performance, the MW of the coating needs to be as high as possible to overcome the stress. With this in mind, primary pendant amine functional curing agents are preferred to maximize the network by reduction in steric hindrance.

Extender Selection
The next step in the formulation is choosing the filler or extenders that are typically added to lower the cost of the formulation. Higher-performing fillers are micas, micaceous iron oxide and glass flake. These fillers provide a less permeable film due to orientation of the plates in a laminar order, creating a more tortuous path for water vapor. Decrease in permeation with increased filler content is limited by the viscosity increase. Another group of “fillers” are fibers or high aspect ratio particulates that reinforce the resin to provide tensile strength and increase resistance to thermal deformation with shrinkage or expansion. Glass fibers such as chopped mat or woven roving work very well at bringing the CTE down to that of steel or concrete substrates. However, the glass fibers do little to benefit the permeation rate. Ideally, a filler or combination of fillers would perform both tasks; lowering permeation and decreasing the CTE, which is one of the most critical properties for high-temperature performance.

Particulate fillers have been well-documented at associating with resin molecules and decreasing the mobility of the polymer chains to reduce the stress in the polymer by reducing the CTE — with incremental increases in the volume of filler, the CTE will decrease. It has been well-established that adding filler to a resin will make the resin more thermally stable and lower the permeability by reduction in polymer-free volume.

Formulation Additives
Once a resin system is selected and an efficient filler determined, a functional coating exists, but the formulation may not be suitable for spray or trowel application because the neat resin and high filler loading required for the necessary performance criteria resulted in high viscosity.

The first option typically employed by a contractor or applicator is to thin the material with a solvent. However, the smallest amounts of solvent can inhibit corrosion-protection performance by being retained in the polymer matrix, and increasing the free volume of the coating which increases permeation. Another typical option is to heat the material to lower the viscosity with a heated plural component airless system which is quite expensive and difficult to control in certain environments.

Therefore, the formulator must select the correct dispersant for the particular filler particle that will dissociate the filler particle from the resin allowing for lower viscosities, particularly at low shear. This will allow for a few formulating benefits. The first is having the ability to add more filler which will likely lower the cost of the formulation substantially. Many of the filler materials are less than $0.50 per pound and resins can be as high as $3.00 per pound. This concept not only increases the profit margin, but may also allow for the use of very expensive resins and monomers with better properties. The ability to add more filler can also benefit the performance of the coating with regard to corrosion and heat resistance. The added filler, regardless of aspect ratio or dimensions, will lower permeation of a coating due to decreasing the free volume of the polymer. The data in Table 2 (p. 46) show the magnitude of water vapor permeation reduction with the...
addition of round ceramic microspheres, to a bisphenol-A epoxy resin coating. Even without platy fillers the permeation rate can be lowered closer to that of a flake-filled resin. However, the amount of filler needed is significantly higher than the amount of glass flake that would typically be needed to create the same tortuous path as a plate-like particle. Achieving a higher loading of filler by using the proper dispersant also impacts the CTE without significantly influencing Tg. The additional filler content provided with the proper dispersant could provide an edge in permeation and heat resistance with a single filler type.

Along with the obvious cost benefit and polymer property enhancement, the right dispersant can be the best approach to releasing entrained air that occurs during the manufacturing or application process. The entrained air leads to early failure by yielding higher permeation rates with voids and possible pinholes in the coating. Most of the solutions to the air-entrapment problem are based on silicone chemistry and incompatibility giving a de-aerating effect. This may provide some benefit, but introduces something very incompatible into the coating that may cause other problems.

A more complete solution is found in the synergy between a dispersant, defoamer and wetting agent — use of the dispersant to wet out the fillers in production displacing the air on the surface of the particle, a compatible polymer defoamer to facilitate coalescence of the air to increase buoyant force, and a wetting agent to provide a slight increase in the movement of the air out of the film. It’s even possible, with some optimization, to allow for a lag in the recovery of viscosity after shear is applied, which will allow for just enough time during application for the air to move out of the film.

Summary

It is very difficult to formulate a long-lasting high-performance coating that resists the heat and pressure criteria of certain markets such as oil and gas production. As a formulating chemist, it may seem that all the resin combinations have been attempted and with today’s regulations, other options aren’t permitted. Then when something does show promise, the applicator doesn’t want to invest in the special equipment necessary to apply it correctly. Many of these coatings make it 95 percent of the way to commercialization and just can’t cross the finish line. This is where formulation additives can provide more of a benefit in the formulating process than once thought. They can ultimately provide the ability of fine tuning with small additions that can provide great advances in performance in a performance driven market.

About the Author

Andrew Recker is a technical service specialist for the formulation additives business in BASF’s dispersions & pigments division and focuses on industrial coatings applications. He holds a Bachelor of Science from the University of Toledo and a MBA from Cleveland State University. Recker has also completed the NACE CIP Level 2.

He has worked in research and development for several companies over the past 14 years in various markets. Recker’s experience ranges from pressure-sensitive adhesive development for a tier one automotive supplier to protective coatings for high-value steel structures. He has spent much time researching the corrosion process and methods of protection from barrier type to passivation. Through his development work, Recker has produced novel ideas for patent applications still pending. His immediate interests are value creation and development of possible cross-over technologies as applied to the industrial coatings markets.

References

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