Scavenge moisture and cut pinholes in a trice

Oxazolidine latent hardeners in polyurethane systems

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The popularity of polyurethane chemistry in construction sealants is growing. However, moisture ingress and pinholing can be a problem. Oxazolidine latent hardeners can overcome these drawbacks.

Whilst there have been a number of technical advances in the resins used in construction sealants, polyurethane (PU) chemistry continues to offer the best balance between cost and performance. The chemistry is highly versatile, with aromatic and aliphatic prepolymer systems offering the formulator a range of properties to meet differing performance requirements. The addition of oxazolidine latent hardeners reduces the negative effects of moisture and speeds up reaction. The main advantages PU offers over other technologies are better mechanical strength the absence of toxic by products of the cure mechanism (in contrast to the production of methanol in silane-cured systems), better substrate adhesion and ease of subsequent coating. The traditional method of curing PU sealants is to use the reaction of the terminal isocyanate groups of the polyurethane binder with moisture. This process requires a high level of isocyanate to give effective cure, which in turn leads to toxicity issues concerning residual isocyanate monomer. Another problem is the production of carbon dioxide during the reaction. This results in pinholing, a phenomenon which can then compromise the integrity and aesthetics of the finished coating.

An effective way to eliminate such gassing and improve the cure performance of the sealant is to introduce an oxazolidine latent hardener. Such a product allows the formulator to combine the benefits of this type of hardener with a prepolymer at a much lower isocyanate level. Typically, this can be reduced by as much as 10-15%. The benefits of introducing oxazolidine latent hardeners into aromatic PU sealants are:
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Results at a glance

» Elimination of gassing
» Excellent through cure in thick film applications (compared to moisture cure/aldimine systems)
» Retention of good workability of the sealant (skinning control)
» Excellent early hardness development, as measured by Shore, through hardener crosslinking
» No significant negative impact on mechanical strength or shrinkage through crosslinking at recommended levels of addition of the hardener
» No detrimental effect on UV resistance

Gassing eliminated

Traditionally, PU sealants are cured by the reaction of terminal isocyanate groups with moisture. A side product of this reaction is the generation of carbon dioxide. This remains trapped in the cured sealant system. Figures 1 and 2 illustrate cured aromatic PU prepolymers (MDI & TDI) mixed with two oxazolidine latent hardeners, hardener A (“Incozol LV”) and hardener B (“Incozol EH”), typically at a level of 2 % w/w, compared to the same prepolymers cured only with moisture.

The addition of an oxazolidine latent hardener not only eliminates sealant defects created by gassing, but also promotes faster through-cure (see Figure 3). This reflects the ability of oxazolidine latent hardeners to hydrolyse quickly and crosslink the PU prepolymer compared to the water-isocyanate reaction.

The addition of an oxazolidine latent hardener does not have a significant impact on PU-prepolymer viscosity and, consequently, does not affect the workability of the sealant. The initial viscosities of the oxazolidine/prepolymer blends shown in Figure 4, indicate the influence of the latent hardeners on the systems. Hardener A either reduces or retains the viscosity whilst hardener B increases it slightly. These differences offer options for formulators to retain the desired workability of the system.

As regards storage stability, as expected, TDI-based mixes are more stable than MDI systems due to the increased reactivity of MDI prepolymers. For TDI systems, mixing with a latent hardener shows an initial viscosity rise when moisture ingress during mixing and handling occurs. However, stability is excellent, with little rise in viscosity, as long as the containers are sealed from the atmosphere.

In the case of MDI mixes, the stability is lower than with TDI. The data in Figure 5 reflects the inclusion of 2 % oxazolidine in MDI prepolymer mixes. Dilution of the binder

Figure 1: MDI prepolymer cured without oxazolidine (left), cured with 2 % hardener A (centre) and cured with 2 % hardener B (right)

Figure 2: TDI prepolymer cured without oxazolidine (left) and cured with 2 % hardener A (right)
and curing agent in fully formulated systems with dry, inert fillers affords improved stability. The addition of latent hardeners does not significantly alter physical properties such as hardness and tensile strength in the cured PU system. Crosslinking at low levels does not detrimentally alter sealant performance. In general, hardener B slightly increases the hardness and tensile strength of PU polymer, while hardener A somewhat reduces the hardness and tensile strength. This is due to the nature of their respective backbones.

**Formulation hurdles**

Today, formulators using polyurethane also face a number of hurdles when trying to achieve the desired film properties and appearance. Whether the target is a high-gloss finish for a volatile organic component-compliant coating, a fast curing adhesive or a strong, flexible defect-free sealant, the issues facing formulators when attempting to develop new technologies with PU include:

- Retaining and improving performance cure and physical properties of PU systems
- Meeting legislation demands such as volatile organic component reduction
- Reducing toxicity by decreasing isocyanate concentration

One of the biggest issues is the ongoing battle to deal with the presence of moisture often attracted through hydroscopic polyols and solvents or present in pigments, fillers and plasticisers. The reaction of moisture with isocyanate can seriously compromise performance (for example, properties such as film strength). Furthermore, appearance properties can be affected by the generation of carbon dioxide. The oxazolidine technology offers an alternative low-toxicity solution to formulators of both one and two-component polyurethane systems in overcoming moisture-related formulation issues. All oxazolidine products are triggered by the reaction with moisture and it is their preferential reaction that helps the formulator limit the moisture-isocyanate reaction problem. Oxazolidine products can be used in aliphatic and TDI-based prepolymers. A number of grades are suitable for use in MDI systems. However, oxazolidine products offer benefits over and above just inhibiting the reaction with moisture. Some of these are described below in more detail.

Formulators of sealants, adhesives and high-build elastomeric coatings are always striving to improve performance properties. Traditionally, polyurethane systems incorporate a high level of isocyanate to speed up the cure rate to an effective level. This often requires the incorporation of toxic catalysts such as lead, mercury and, more recently, variants using tin. Oxazolidine technology however, offers a number of routes forward. For example, high-solid, one-component systems can incorporate oxazolidines in a number of ways. The presence of an oxazolidine not only reduces the problems associated with CO₂ generation and subsequent gassing, but also enables PU manufacturers to reduce the level of isocyanate present in the formulation. This is achieved by activating the oxazolidine, initially latent in the formulation, by mixing it with the formulation components to yield in-can stability. On application, and subsequent exposure to moisture, the oxazolidine-moisture reaction yields amino-alcohol functionality which can affect a through cure at much lower isocyanate concentrations, by a so-called...
‘moisture-triggering’ route. This approach allows formulators to reduce prepolymer total-isocyanate contents from typically 10-15 % to much lower toxicity levels of 2-5 %. Therefore oxazolidine products can help formulators achieve this aim with their selection based on property requirements. Furthermore, the oxazolidine latent-curing agent imparts an increased level of crosslinking through its four-functionality structure (two secondary-amine and two primary-hydroxyl groups). This helps formulators improve cure rate and impart additional tensile strength to the coating, adhesive or sealant.

Other routes are also available to formulators through the use of oxazolidines. The reaction of a hydroxyl-functional oxazolidine enables PU formulators partially to end-cap the isocyanate groups in the prepolymer further to reduce isocyanate content. This approach also imparts other benefits such as early tensile-strength development through latent in-situ crosslinking on exposure to moisture.

Continued legislative pressure is forcing polyurethane formulators to find ways of significantly reducing the amount of solvent used in products to make them more environment friendly. Low-viscosity, oxazolidine-reactive diluents such as hardener A, allow the design of two-component, PU, high-solid systems, with the added benefit of eliminating gassing. Hardener A is a four-functional, bis-oxazolidine curing agent that significantly reduces hydrogen bonding through its carbonato-link and has a low viscosity of 50cps. This allows formulators effectively to reduce the viscosity of the product mixture. Therefore, formulators can continue to use the same application tools. Thus eliminating the need to retrain operators or dispose of the contaminated waste associated with using alternative water-based products.

**Better film appearance**

The addition of an oxazolidine to a product can also improve coating appearance. The elimination of carbon dioxide pinholes from coatings, which occur as a result of the moisture-isocyanate reaction, by the preferential reaction of a moisture scavenger, provides further significant benefits for the formulator. Pinhole defects lead to problems such as downglossing or more significantly can compromise film integrity leading to weaknesses such as loss of film strength or ease of attack by a chemical reagent.

Oxazolidine technology has been adopted in a wide array of polyurethane coating, sealant and adhesive applications. The polyurethane-coatings sector has chosen this technology for use in two-component, high-solid systems for applications in the automotive, marine, wind-turbine and aerospace sectors. The use in one-component polyurethane coatings is restricted to the industrial-maintenance sector.

Oxazolidines are widely used in one-component aliphatic and aromatic polyurethane cartridge sealants. These high-performance, elastomeric, polyurethane sealants require no mixing and typically no priming to promote adhesion to many substrates, including concrete and masonry.

There is a growing interest in the use of oxazolidines in the production of one-component, reactive, hot-melt adhesives, where they accelerate the cure rate and improve both green strength and crosslink density.