Cure evaluation of Intelimer® latent curing agents for thermoset resin applications

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Abstract:

Latent catalysts provide tremendous process flexibility and manufacturing versatility in thermoset applications. One method of creating latency in a formulated resin system is to encapsulate the active ingredient with an impermeable barrier, thereby blocking its reactivity until an externally controlled stimulus triggers its release (e.g., thermal activation). A novel encapsulation technology featuring Intelimer® polymers will be presented. Intelimer polymers are crystalline materials with sharp, well-defined melting points that can be used for the protection and controlled delivery of active catalysts into formulated resin systems. Areas to be explored include unsaturated polyester (UPE) and epoxy formulations, where Intelimer polymer encapsulated catalysts have demonstrated significant improvements in ambient stability without compromising reaction kinetics at thermal onset. In UPE applications, for instance, the pot-life of a formulated mixture has been extended from minutes to days at ambient temperature. Similarly, one-component epoxy formulations containing Intelimer latent catalysts have demonstrated year-long shelf-stability while maintaining rapid reaction at cure temperature. Next generation curing agents that take advantage of these unique properties are being formulated and will be discussed.

Introduction:

One-component formulations have gained increased attention in thermoset applications over recent years.[1-5] These formulations show prolonged stability over standard two-component formulations due to the presence of latent catalysts / accelerators. Latent accelerators are designed to extend the working life of a formulated mixture by passivating the activity of the catalyst until triggered by an external stimulus. As such, they effectively decouple the pot-life of the mixture from its cure speed.[1-5] By comparison, two-component formulations start reacting as soon as they are mixed together, have a limited processing life, and must be freshly prepared at their point of use.[6]
The impetus for using latent catalysts is to gain the ability to create fully formulated resin systems with long storage life that can be applied directly by the end-user. This, in turn, helps guarantee consistency and improve process efficiency. It also leads to financial savings in terms of labor, cost-in-use, transportation and shipping.

One method for generating latent catalysts is encapsulation, such as core-shell and matrix encapsulation (Figure 1).[2,4,6] In each of these techniques, the activity of the catalyst is physically blocked by a barrier until release. Core-shell encapsulation describes the use of a thermoplastic wall (shell) that is hermetically sealed around a catalyst (core). This technique provides excellent protection for the catalyst, but is often limited by diffusion through the thermoset resin after release (i.e., catalyst is released from the core, but cannot spread through the resin without agitation or mixing).

Matrix encapsulation describes the entrapment of catalyst in a polymeric network. This technique provides a benefit over core-shell encapsulation because the matrix can be milled into a fine powder and dispersed through the reaction mixture, thereby eliminating the diffusion problem described above. Unlike the core-shell technique, matrix encapsulation is often limited by sluggish release kinetics (i.e., broad glass transition temperature of most typical polymers) and by premature catalyst leaching from amorphous segments of the polymer.

**Figure 1.** Core shell vs. matrix encapsulation.
The focus of the present work is on the development and applicability of a special class of matrix encapsulated catalysts utilizing Intelimer® polymers as the encapsulant. Intelimer polymers are crystalline materials with a sharp, well-defined melting point (Figure 2). The melting point and crystalline nature of the polymer are controlled by the presence of aliphatic side-chain crystallizing (SCC) groups. Unlike most typical polymers, the sharp phase transition from crystalline solid to amorphous liquid enables fast catalyst release.[7, 8] And, the crystalline structure provides strong catalyst protection at temperatures below the switch (Figure 2).[7, 8] Thus, the Intelimer technology provides an excellent platform for protecting and delivering active ingredients in thermoset mixtures.

**Figure 2.** (a) Intelimer® polymer is a crystalline polymer with a sharp, well-defined phase transition. (b) The phase transition is referred to as a “switch” temperature due to the marked change in property from impermeable solid to permeable, amorphous liquid. (c) The switch temperature can be systematically tuned across a broad range.
The concept for latent catalyst development using Intelimer polymers involves passivation of the catalyst within the crystalline network of the polymer (Figure 3). The catalyst may be incorporated into the crystalline network by physical blending (i.e., traditional matrix encapsulation approach) or through deliberate covalent attachment (i.e., covalently modified polymer). The differences of these two methods will be explored herein and an in-depth discussion of two covalently modified polymers will be presented. One modified polymer is an imidazole-based catalyst for epoxy applications (Intelimer® 7004 Polymer). The other is a cobalt-based catalyst for unsaturated polyester applications (Intelimer® 6050 Polymer). Both examples will be used to illustrate the performance benefits and developmental capabilities of this unique latency technology.

![Inteimer crystalline structure](image)

**Figure 3.** Latent catalysts can be developed by intercalating active ingredients into the crystalline structure of an Intelimer polymer.

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**Experimental:**

**Epoxy applications:**
Tertiary amines encapsulated within an Intelimer polymer (e.g., Intelimer 7004 polymer, 16 wt% imidazole, 12 phr, mean particle size 5-15 \( \mu \)m) were vigorously mixed into liquid epoxy resin (LER), gently heated to 40 °C for 15 h to promote material integration, and stored at ambient prior to analysis. Pot-life was measured according to the time required for the formulated mixture to double in viscosity. Cure profiles were monitored using a differential scanning calorimeter (DSC) from 25 – 200 °C at 10 °C / min. Cure rates were determined according to the time required for the reaction mixture to achieve peak exotherm under isothermal conditions at 80, 100, 120, and 150 °C.

**Unsaturated polyester applications:**
Cobalt naphthenate (6 wt% elemental cobalt) and an Intelimer cobalt complex (2 wt% elemental cobalt) were incorporated into unsaturated polyester resin at equivalent cobalt concentrations. These mixtures along with a sample of blank unsaturated polyester resin (control) were combined with methylethylketone peroxide (MEKP) and property build was monitored using a rheometrics dynamic analyzer (RDA) by measuring elastic modulus while heating from 30 to 120 °C at 20 °C / min.
Results and Discussion:

Epoxy applications:

Long ambient stability coupled with fast activation at thermal onset has long been pursued in the epoxy industry with limited success, but the Intelimer technology appears poised to meet this challenge. Latent catalysts are particularly appealing for adhesive and composite epoxy applications because of the process flexibility and ability to rework materials that they afford to both the formulator and to the end-user.

The present investigation focuses on the use of encapsulated tertiary amine catalysts for the acceleration of epoxy resin homopolymerization (Figure 4). Tertiary amines do not possess active hydrogen atoms and, so, they initiate polymerization without cross-linking into the evolving network like primary and secondary amines.$^{[6, 9]}$ As a result of this homopolymerization, tertiary amines accelerate cure even at low active loading levels (e.g., 2-5 phr with a tertiary amine vs. 25-50 phr with a primary or secondary amine).$^{[6, 9]}$ This aspect of tertiary amines is particularly important for encapsulated catalysts – where the ratio of wall material to active ingredient may be high – and is further important for one-component formulations – where the addition of too much solid product may compromise the physical, rheological or mechanical properties of the formulated material.

![Figure 4. Tertiary amines initiate and propagate epoxy resin homopolymerization.](image-url)
One common tertiary amine used in a wide range of epoxy applications is imidazole.\textsuperscript{[10-12]} The cure profile, viscosity stability, and thermal properties of imidazole and imidazole-based derivatives have been intensively studied and reported elsewhere.\textsuperscript{[10, 12]} As such, an imidazole derivative, 2-ethyl-4-methyl-imidazole (EMI-24, e.g., Imicure® EMI-24 curing agent\textsuperscript{†}) will be used as a model system for probing the influence of encapsulation with Intelimer polymer on the latency and cure performance of the catalyst.

The pot-life of the free amine EMI-24 is 9 hours at ambient (i.e., approximately 1 standard working day).\textsuperscript{[13]} This level of stability is not adequate for most one-component applications, but can be substantially improved by encapsulation with an Intelimer polymer. As shown in Table 1, Intelimer polymer encapsulation extends the pot-life from hours (free amine) to weeks (matrix encapsulation, Intelimer® 7024 polymer) or even years (covalently modified, Intelimer® 7004 polymer). This heightened degree of ambient stability is extremely advantageous for one-component formulations, particularly that of the covalently modified polymer.

\textbf{Table 1}

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Structure</th>
<th>Encapsulation Method</th>
<th>Pot-life (25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imicure® EMI-24</td>
<td></td>
<td>None.</td>
<td>9 hours</td>
</tr>
<tr>
<td>Intelimer® 7024 Polymer</td>
<td></td>
<td>Matrix encapsulation.</td>
<td>1 week</td>
</tr>
<tr>
<td>Intelimer® 7004 Polymer</td>
<td></td>
<td>Covalently modified polymer.</td>
<td>&gt; 1 year</td>
</tr>
</tbody>
</table>

\textsuperscript{†}2 phr active catalyst, LER, ambient. All catalysts were obtained from Air Products and Chemicals Inc. and used as received.
Accordingly, cure properties of the covalently bound imidazole catalyst were analyzed by DSC using a formulation that contained 2 phr active in LER (Figure 5). The cure profile is shown in the inset of Figure 5. Thermal onset ($T_o$) for the homopolymerization reaction is 130 °C.

Cure speed was measured by monitoring the time required to achieve maximum exotherm using isothermal DSC scans at 80, 100, 120, and 150 °C. The results of this investigation are plotted in Figure 5. As expected, cure speed increases with increasing temperature and is fastest at temperatures near the catalyst activation temperature. The reaction proceeds in less than 5 minutes at the thermal onset point, suggesting that encapsulation does not restrict catalytic activity and that imidazole is rapidly exposed from the crystalline matrix.\(^\text{A}\) The combination of superior protection at ambient and fast reaction at thermal onset has tremendous potential in one-component formulations and may have strong implications across broad areas of epoxy research.

\(^\text{A}\) Unlike typical matrix encapsulation in which the catalyst is released from the polymer, the catalyst is exposed but not released from Intelimer 7004 and other covalently modified polymers.

**Figure 5.** Thermal cure performance of Intelimer 7004 polymer in isothermal DSC scans. Cure speed is very rapid at temperatures near thermal onset (130 °C) for catalyst. Cure profile of Intelimer at 2 phr active ingredient in LER is shown in the inset.
Achieving chemical control using Intelimer technology:

It is possible to control the performance of Intelimer latent catalysts using two independent variables: polymer and amine. The polymer controls both the storage capacity (i.e., percent crystallinity) and thermal stability (i.e., melting point) of the product. Figure 6, for example, shows that the melting point of the polymer can be varied from 0 to 80 °C by simply adjusting the length of the SCC groups.

**Synthetic control: Polymer**

![Figure 6. The melting point of the polymer / release point of the active ingredient can be tuned by changing the chain length of the SCC groups.](image)

In a similar fashion, the amine can be used to adjust cure and reaction properties (i.e., onset temp, cure speed, etc.) of the resulting product. Using a series of encapsulated experimental amines\(^B\) the thermal onset temperature has been tuned from 80 to 200 °C (Figure 7). The sharp profile of each of these amines suggests that the Intelimer wall does not negatively impact catalyst release (or exposure) and that snap cure can still be achieved.

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\(^B\) Provided by the Amine Center of Excellence in the Materials Research Center at Air Products and Chemicals Inc., Allentown, PA 18195
The ability to control switch temperature and reaction onset with fast cure suggests that polymer-catalyst combinations can be strategically designed to accommodate specific cure schedules. This concept is supported by Figure 8, where the isothermal cure speed of a matrix encapsulated experimental amine (To = 80 °C) is shown to be comparable to the performance of the Intelimer 7004 polymer (To = 130 °C) at thermal onset (i.e., both materials cure in ~ 5 min at their respective onset temperatures). A challenge – particularly with low activation temperature amines – is in achieving comparable latency for the matrix encapsulated amines to their covalently modified analogs; research efforts in this area are ongoing.

**Figure 7.** The thermal onset temperature of the reaction mixture can be adjusted through deliberate chemical modifications to the encapsulated active ingredient. Onset temperatures in the range 80-200 °C have been achieved.

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**Figure 8.** Isothermal cure profile for Intelimer 7004 polymer (To = 130 °C) and an encapsulated experimental amine (To = 80 °C). Both products exhibit cure speeds of ~ 5 min at thermal onset.
Unsaturated polyester (UPE) applications

The usefulness of an encapsulated catalyst in unsaturated polyester (UPE) applications is similar to that in epoxy applications. In UPE applications, the reactivity of the accelerator (e.g., cobalt catalyst) is blocked from its surrounding environment (e.g., UPE resin and methylethylketone peroxide, MEKP) in order to prolong the working life of a formulated mixture. Accordingly, the ability to tailor the chemistry and properties of Intelimer catalysts (discussed above) will also benefit UPE as well as a wide variety of other thermoset applications.

One application being considered is pipe restoration in a process known as “cured-in-place pipe” (CIPP).\textsuperscript{[14-16]} CIPP involves the insertion of a felt liner impregnated with UPE resin, MEKP and accelerator into an existing pipe infrastructure (Figure 9); followed by heat curing.\textsuperscript{[14-16]} The cured liner forms a smooth, uniform surface along the internal diameter of the pipe, which replaces damaged areas and improves material flow through the pipe. The CIPP technique also eliminates the need to remove or uncover existing pipes from the ground, thereby improving safety, allowing laborers to use their time more effectively, reducing service delays and road closures, and lowering costs.

Latent catalysts are beneficial for CIPP applications because they extend the amount of time available for transportation and installation of impregnated liners into the pipes. The catalysts are activated by passing warm water ($T > T_o$) through the pipes.\textsuperscript{[14-16]} As such, the discussion will now turn to understanding the latency and cure speed of an encapsulated UPE catalyst.

\textbf{Figure 9.} Cured-in-place-pipe being fed into existing pipe infrastructure. The felt liner (shown in blue) is impregnated with UPE resin, MEKP, and accelerator. As the resin cures, a new, smooth, uniform surface is created along the internal diameter of the pipe.
The performance of an Intelimer cobalt complex (Intelimer 6050 polymer, 2 wt% elemental cobalt) was compared against a standard cobalt naphthenate (6 wt% elemental cobalt)[17] and cobalt-free control sample in a UPE resin / MEKP mixture. As can be seen in Figure 10, the cobalt naphthenate complex accelerates the reaction such that there is less than 20 minutes latency from inception to gel time. This is not ideal for CIPP applications, especially not when large volumes or long distances of pipe necessitate repair. The encapsulated cobalt complex, on the other hand, is stable for more than 40 hours and allows ample time for the liner to be impregnated with the resin/accelerator/peroxide mixture, transferred to the worksite, and installed prior to reaction onset (Figure 10).

Figure 10. Gel time comparison of cobalt naphthenate, encapsulated cobalt, and a cobalt-free control.

The cure rate and elastic modulus of these materials were monitored by RDA. Figure 11 shows the outcome of this analysis. All three samples achieved nearly equivalent final modulus, and, as expected, the two cobalt containing formulations reacted faster than the cobalt-free control. It does not appear that the Intelimer polymer has a negative influence on cure speed or performance in UPE applications, whereas it does offer greater than two orders of magnitude improvement in gel time over its unencapsulated analog.
Conclusion

Intelimer technology provides a utilitarian means of establishing latency in thermoset catalysts for diverse applications. The crystalline nature and sharp melting point of the polymer allows for thorough protection and efficient release of the encapsulated catalyst. The epoxy and UPE applications explored herein demonstrate that the reactivity of the released catalyst is not impaired by encapsulation, and that cure speed and final cure properties meet the required specifications for many practical applications. Perhaps the greatest benefit to Intelimer polymer encapsulation is that structure-property relationships can be used to design latent catalysts to fulfill specific performance needs; such a technology has the potential to revolutionize work processes and research philosophies across the thermoset industry.

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References


