

FINAL REPORT

Shelf-Stable Adhesive for Reduction of Composite Repair Hazardous Waste

SERDP Project WP-1579

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List of Acronyms Used

Acronym

DCDA

DSC

EMI

HAP

IST

MI

Monuron

SSERA

SWRI

VOC

Definition

dicyandiamide

differential scanning calorimetry

2-ethyl-4-methylimidazol

hazardous air pollutant

Infoscitex Corporation

1-methylimidazole

3-(4-chlorophenyl)-1,1-dimethylurea

shelf-stable epoxy resin adhesive

Southwest Research Institute

volatile organic content

ABSTRACT

The U.S. Air Force and U. S. Navy, along with their suppliers, have a significant need to reduce the amount of waste generated during composite aircraft manufacture and repair. Large aircraft repair facilities spend millions of dollars each year to replace and discard expired epoxy film adhesives. One-part epoxy adhesives that can be stored at ambient temperature for up to one year would enable critical improvements in the environmental impact, performance, and total costs of composite repair process.

The objective of this three-year program was to develop a non-hazardous one-part epoxy film adhesive that is stable at ambient temperatures for up to one year and can be mechanically and/or thermally activated immediately prior to use. The new adhesive will significantly reduce waste without releasing volatile organic compounds (VOCs) or hazardous air pollutants (HAPs). Our approach leverages novel microencapsulant formulations that do not interfere with the epoxy curing process and produce an adhesive that is compatible with existing film formulations and processes. The reactivity of the adhesive is preserved at higher temperatures and for longer periods of time by microencapsulating the curing accelerant and allowing it to be released under controlled conditions. Key components of the proposed technology are (1) the use of accelerants with low toxicity and environmental impact, and (2) their encapsulation with materials that have very low permeability and will not interfere with the epoxy curing process.

1. OBJECTIVE

The objective of this work was to prove the feasibility of developing a non-hazardous one-part epoxy film adhesive that is stable at ambient temperatures for up to one year and can be mechanically and/or thermally activated immediately prior to use. The new adhesive would significantly reduce waste without releasing volatile organic compounds (VOCs) or hazardous air pollutants (HAPs). Our approach leveraged novel microencapsulant formulations that do not interfere with the epoxy curing process and produce an adhesive that is compatible with existing film formulations and processes. Once our shelf-stable epoxy resin adhesive (SSERA) is activated, it would be rapidly, safely, and reliably used to repair military and commercial composite structures found in aircraft, ships, amphibious, and tactical vehicles.

The key objectives of this program were to demonstrate that:

1. Our microencapsulation approach is compatible with commonly used epoxy resins and catalyst accelerants
2. The microcapsules can be incorporated into existing film adhesive formulations without affecting the chemical or mechanical performance of the adhesive
3. Curing of the SSERA can be activated by mechanical and/or thermal methods
4. SSERA has superior residual chemical reactivity than comparable un-encapsulated adhesive formulations.

Infocitex Corporation (IST) worked closely with its main manufacturing partners, Thies Technology, Henkel North America, and Northrop Grumman, to ensure that its work was informed by industry practice and each of these goals was met. Thies Technologies assisted IST in developing manufacturing processes for IST's encapsulated materials, while Henkel North America assisted IST in developing and evaluating a film adhesive formulation that can be directly compared to Henkel's Hysol EA 9628. Northrop Grumman and Henkel North America provided advice and technical guidance regarding the performance evaluation of the novel adhesive. IST has also worked closely with representatives from the U. S. Navy and the U. S. Air Force to ensure that the methods and performance of the new technology meet customer needs and adds value to DoD operations.

2. BACKGROUND

2.1 SERDP Relevance

Conventional repair of composites used in military applications results in the release of significant amounts of VOCs and HAPs. Significant amounts of solid waste are also generated as a result of repair processes. Improvement of composite repair technologies is clearly needed to reduce environmental burdens and abatement costs. To address this need, IST, in collaboration with Northrop Grumman, Henkel North America, the U.S. Air Force, and U.S. Navy, proposes to develop an innovative no-VOC, no-HAP composite repair adhesive technology that will dramatically reduce the amount of waste generated during composite repair operations. These technologies promise to revolutionize repair processes with respect to performance, waste minimization, cost savings, and protection of the environment.

2.2 Composite Repair Adhesives

Composite repair adhesives come in many forms, including paste, film, and liquid shims. These materials are frequently used with uncured or partially cured pre-impregnated epoxy composites to repair composite structures. Repair adhesives are available as either one-part or two-part systems. Two-part systems consist of a resin and an activator-accelerant that are combined just prior to use. Isolation of the activator-accelerant from the resin enables a good shelf-life but has significant inherent deficiencies, such as:

- System components must be accurately combined. Errors in the relative proportions of each component will result in a resin with less than optimum properties.
- Air entrainment during the mixing process must be avoided and if generated must be removed prior to use. If the introduced air is not removed the resulting repair will not provide the desired and expected performance.
- Excess material is usually prepared to avoid batch to batch variations, resulting in greater waste than one-part adhesive systems.

One-part adhesive systems are now recognized by the aerospace industry as a superior choice due to their ability to provide:

- Control over bond line thickness
- Improved mechanical properties
- Reduced risk of entrapped air in the bond line
- Improved quality control by eliminating component mixing

The main disadvantage of one-part systems is that curing agents and accelerants must be pre-mixed with the adhesive resin and therefore, stored at low temperature to prevent initiation of curing reactions. Even at reduced temperatures, the curing reactions occur slowly, thereby decreasing the shelf-life of the adhesives. The shelf-life of a typical aerospace structural film adhesive used for composite repair is about 6 months when stored at 4 °C and may be extended to approximately one year if stored at -18 °C. Every time a large roll of valuable film adhesive is

removed from the storage freezer to have sections cut off for immediate use, the unused portion becomes exposed to warmer environments and undergoes some degree of curing with measurable loss of adhesive qualities. This accumulation of thermal history resumes every time the roll is taken out for use and returned to the freezer. The material replacement costs and regulatory compliant disposal costs generated by expired film adhesives is significant, easily exceeding millions of dollars per year for large aircraft repair facilities [1,2]. In fact, United Airlines justified the fabrication of a dedicated facility to test and re-qualify shelf expired film adhesives based solely on the cost savings from reducing material purchases and minimizing waste [3].

The DoD and commercial sectors have a strong need and preference for one part epoxy resin-based film adhesives to efficiently, reliably and cost effectively facilitate composite repairs. It would also be desirable if these repair materials could cure at temperatures below 100 °C. Most composite repair materials are engineered to cure at temperatures above 121 °C. When repair temperatures exceed 100 °C, composite parts subjected to repair can delaminate as the absorbed water turns to vapor. These damaged parts, in turn, add to the overall waste disposal burden. To meet this demand, a new composite repair film adhesive technology is needed that does not contain, release or use VOCs and HAPs, can be stored at room temperature for extended periods of time without loss of properties, and can cure at temperatures below 100 °C.

The aerospace-grade film adhesive that is currently used by the DoD for a majority of their repairs is an epoxy film adhesive that cures at 121 °C. Two examples of approved products in this market are EA 9628 film adhesive from Henkel Loctite (formerly Dexter-Hysol) and FM 73 film adhesive from Cytec. Our goal in this program was to develop a cost savings, shelf-stable, reduced waste generation and environmentally friendly composite repair material technology that will reduce waste and eliminate the need for refrigeration.

2.3 Manufacture of Film Repair Adhesives

Henkel Loctite provided us with guidance regarding film adhesive manufacture and our use of component materials. Henkel has developed a hot melt process for manufacture of epoxy film adhesive that is used extensively for repair of composite structures. In this hot melt process, a solid, high molecular weight epoxy resin is melted, blended with curing agent and accelerator components and then deposited onto the nip between large rollers containing top and bottom release films and an inner layer of nonwoven polyester fiber scrim for bond line thickness control. The epoxy resin becomes forced into the nonwoven scrim and exits the series of post forming rollers as finished film adhesive, sandwiched between release plies. This film adhesive is wound up on rolls and stored immediately in a freezer until ready for shipment.

Here, we worked with key components of Henkel's film adhesive product line as a hand-mixed resin system. In future development efforts, the current accelerant will be replaced by a microencapsulated accelerant that will become uniformly blended into a film adhesive produced at Henkel's prototype line.

2.4 Microencapsulation Process

Microencapsulation is used in a wide variety of applications to isolate materials from their surroundings. There are hundreds of different techniques that have been developed to encapsulate solids, liquids, and gases. The work discussed here considered two approaches: spinning disk and complex coacervation.

The spinning disk process is a physical method for microencapsulating particles or droplets developed by Professor Richard E. Sparks of Washington University (St. Louis, MO). During this process, the core material and the coating material are forced toward a spinning disk, producing a mixture of coated particles and small particles of pure coating material (**Figure 1**) [4]. The resulting material can be separated by size using simple methods such as sieving, which also allows the pure coating particles to be reused. Potential advantages of this method include:

- The solid particles can be as small as 5 μm
- Equipment cost is low
- It is not necessary for the shell material to wet out the core material. The process would force the core into the coating material, which solidifies before it can flow away from the core.
- Can economically produce multiple pounds of material

Complex coacervation is a widely used chemical method for microencapsulating particles or droplets first developed during the 1940's and patented into a practical commercial process by scientists at the National Cash Register in the 1960's [5]. The classic example of this process involves a water-immiscible core material suspended in aqueous solution, followed by the addition of—and reaction between—gelatin and gum Arabic at a low pH and above 35 °C (**Figure 2**). The gelatin and gum arabic will react into a polymer that will coat the core material and can be crosslinked into a durable shell; careful control of composition, temperature, and pH allow for the formation and collection of usable microcapsules. These parameters are highly interrelated, with the phase separation process affecting the composition of the encapsulant, which in turn affects the ability of the encapsulant to wet the core phase, the barrier properties of the encapsulant, and the release characteristics of the microcapsule. Thus, it has been very difficult to quantify the influence of the process parameters on the coacervation process despite extensive research.

Microcapsules containing monuron, a commonly used catalyst accelerant for epoxy resins, have been previously fabricated using a complex coacervation process. Earlier efforts by our team to develop a shelf-stable epoxy film adhesive used crosslinked gelatin as a monuron encapsulant. It was later found that the method is similar to that described in a Canadian patent [6]. In this approach, monuron is first dispersed into an aqueous solution of gelatin using mechanical agitation. Since monuron is insoluble in water, the mixture forms an emulsion. A coacervating agent, such as sodium metahexaphosphate, is then added to this emulsion. After mixing, dilute acetic acid is added to adjust the pH. Addition of the acetic acid results in the phase separation of the emulsion into two incompatible liquid phases. One phase, the coacervate, has relatively high concentrations of both the accelerant and encapsulant (monuron and gelatin); the second

phase, the supernatant, has low concentrations. The compositions of these two phases, and the pH at which phase separation occurs, are governed by factors such as the ionic strength of the initial solutions, temperature, and the molecular weight of the core and shell materials. The coacervate preferentially adsorbs onto the surface of the dispersed monuron, forming a coating that fully encapsulates the particles. The mixture is cooled and formaldehyde or glutaraldehyde is then added to crosslink the gelatin coating. A second cross-linking step can be performed using tannic acid to produce a relatively hard, smooth surface and prevent particle agglomeration.

Our previous experience with developing a shelf-stable epoxy film adhesive [7,8] has led us to conclude that the microcapsule shell must be capable of withstanding brief high temperature excursions (up to 120 °C) for almost one minute in order to be processed into a hot-melt product on Henkel's prototype film adhesive manufacturing line. Furthermore, the microcapsule shell must have outstanding barrier properties and must completely cover the surface of the active material. If as little as one percent of the accelerant escapes from the microcapsule, unacceptable curing reactions will occur. Thus, a highly cross-linked polymer or glassy microcapsule shell is best for this application. It should be noted that these materials will not be amenable to release using a simple thermal trigger, such as the curing heat cycle itself. The microcapsule must be small enough to reside within an adhesive film during the repair process and the encapsulation properties of the finished composite. In a previous Air Force-funded effort to develop a shelf-stable film adhesive [7,8], we found that particles with sizes of 20-50 μm, loaded into test specimens at a loading of 6 wt. % did not adversely impact the tensile lap shear and floating roller peel strength properties of the film adhesive. Since these particles are very small, they could be opened using a brief and temporary thermal spike to rupture the capsules and release the accelerant before the curing reaction begins.

Additional efforts to encapsulate monuron to improve the shelf-stability of one-part epoxy film adhesive have been carried out at the Southwest Research Institute (SWRI) [9]. SWRI used paraffinic wax as an encapsulant, an approach that suffered from two critical shortcomings:

- Diffusion of epoxy resin through the shell limited the shelf-life. As storage temperature increased, the rate of reaction increased and thus the shelf-life of the adhesive decreased further.
- Monuron was released from the microcapsule by melting the wax encapsulant. The wax became a contaminant in the adhesive and tended to migrate to the adhesive/substrate bondline. As a result, adhesion strength was adversely affected.

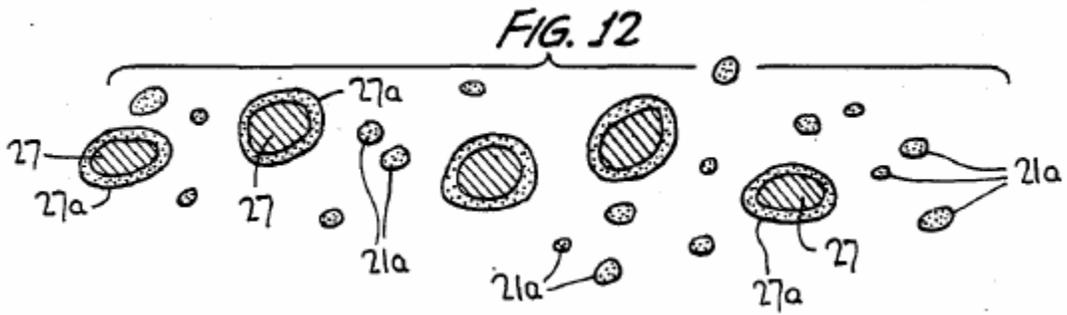
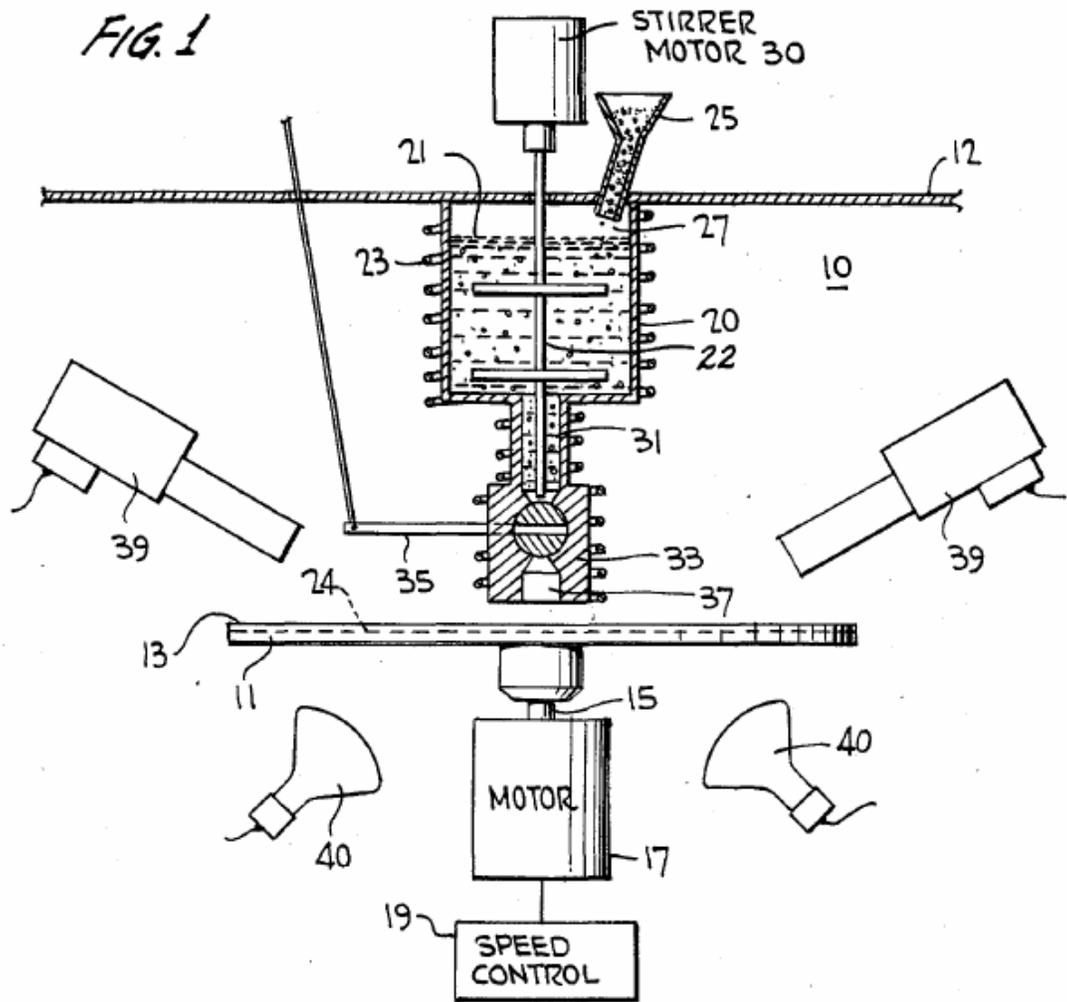


Figure 1: Schematic of the spinning disk microencapsulation process developed by Prof. Robert E. Sparks at Washington University in St. Louis [4]. The top drawing ("Fig. 1") illustrates a sample apparatus, where (12) denotes the top boundary of an enclosed spray chamber (other walls not illustrated), (11/13) denotes the spinning disk driven by a motor (17). The core material is fed by a funnel (25), while the coating material is held in reservoir (20). The bottom drawing ("Fig. 12") illustrates the mixed product from this process: small particles made solely of coating material and larger coated particles.

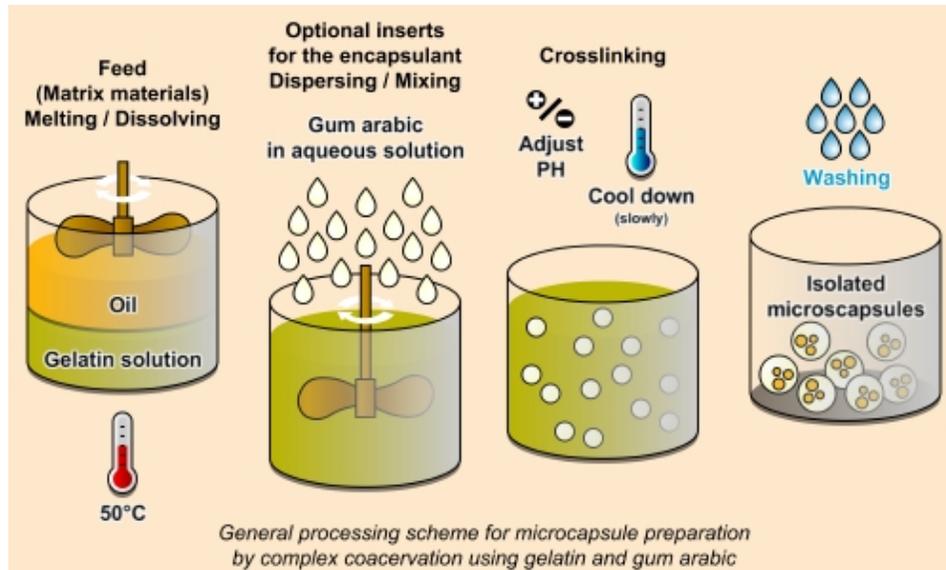


Figure 2: Schematic of a typical microencapsulation process using the complex coacervation method [10].

2.5 Shelf Life of Film Adhesives

The conventional method for determining shelf-life stability of a thermally-cured epoxy adhesive resin system is to store individual specimens of fully-formulated adhesive in separate convection air ovens over a period of several months at temperatures ranging between ambient and 177 °C. Samples of each temperature are then removed periodically for evaluation of their chemical reactivity. Although some laboratories use viscosity measurements to assess residual reactivity, we prefer the efficiency and resolution of differential scanning calorimetry (DSC). However, unsupported paste adhesives like the prototypes produced during this work undergo settling and phase separation of the accelerant and curing agent during the long times required for conventional aging. Such separation does not imply a loss of reactivity due to chemical aging, but would lead to inconsistent DSC test results. Thus, an accelerated shelf-stability test was conducted within the DSC (*Section 3.3*).

3. MATERIALS AND METHODS

3.1 Materials

Film adhesives – The baseline adhesive formulation that was used in this project was similar in composition to the Hysol EA9628 film adhesive system and was created based upon suggestions offered by Dr. Anastasios Melisaris of Henkel Loctite. The system consisted of an epoxy resin blend (92 wt. %), dicyandiamide (DCDA) latent catalyst (5 wt. %), and a catalyst accelerator (3 wt. %). The epoxy resins used were either a blend of 95 wt. % DER 331 (Dow Chemical, Midland MI) with 5 wt. % DER 661 (Dow Chemical), or a blend of 95 wt. % EPON 898 (Miller-Stephenson, Danbury CT) with 5 wt. % DER 661. The blend based on EPON 898 was used in cases where a large amount of material was needed, as the DER 331 was only available in one-liter batches.

Catalyst accelerant – Three catalyst accelerants were investigated during this effort. The default catalyst accelerant was monuron (3-(4-chlorophenyl)-1,1-dimethylurea), but samples containing 1-methylimidazole (MI) and 2-ethyl-4-methylimidazole (EMI) were also evaluated for their ability to decrease the cure temperature of the adhesive system (**Table 1**).

Table 1: Curing catalysts investigated during this effort.

Chemical Name	Solubility	Melting Point (°C)	Boiling Point (°C)
monuron (3-(4-chlorophenyl)-1,1-dimethylurea) [11]	solid	173-174	NA
1-methylimidazole [12]	miscible	-6	198
2-ethyl-4-methylimidazole [13]	soluble	47-54	292-295

Encapsulants – Materials investigated as possible encapsulants included gelatin and various types of carrageenans. Carrageenans are polysaccharides extracted from algae that can form gels at room temperature and were chosen to provide a more thermally stable barrier to diffusion of accelerant and/or epoxy resin through the capsule's walls [14].

3.2 Microencapsulation

Microcapsules containing the catalyst accelerant were produced by the spinning disk and complex coacervation processes. We sought advice regarding the spinning disk method from Prof. Robert E. Sparks, inventor of the spinning disk method and former Professor at Washington University. Prof. Sparks advised us that coating monuron solid particles and water-insoluble imidazole liquids with thermally-reversible gels, such as carrageenans and gelatin, was readily achievable on a spinning disk apparatus. However, this method produces a large quantity of gel microparticles that do not contain core material, leading our team to select the complex coacervation method for experimental trials.

Microcapsules produced using the complex coacervation method were obtained from two sources: Microtek Laboratories (Dayton, OH) and Thies Technology (Henderson, NV). Dr. Curt Thies is a long-time expert in the field of microencapsulation, a former professor at Washington University, and a previous collaborator on our earlier attempts at developing a shelf-stable adhesive. Microtek provided samples of monuron microcapsulated in gelatin, while Thies Technology provided samples of monuron microcapsulated in gelatin, carrageenans, and gelatin-s. Our best results in this project were achieved using microcapsules fabricated via Dr. Thies' process techniques. Through Dr. Thies' understanding of the effects and interactions of the coacervation process parameters, we were able to reduce the batch-to-batch variability of the cross-linked gelatin microencapsulation process. **Figure 3** illustrates steps involved in microencapsulation via the complex coacervation process used in this project.

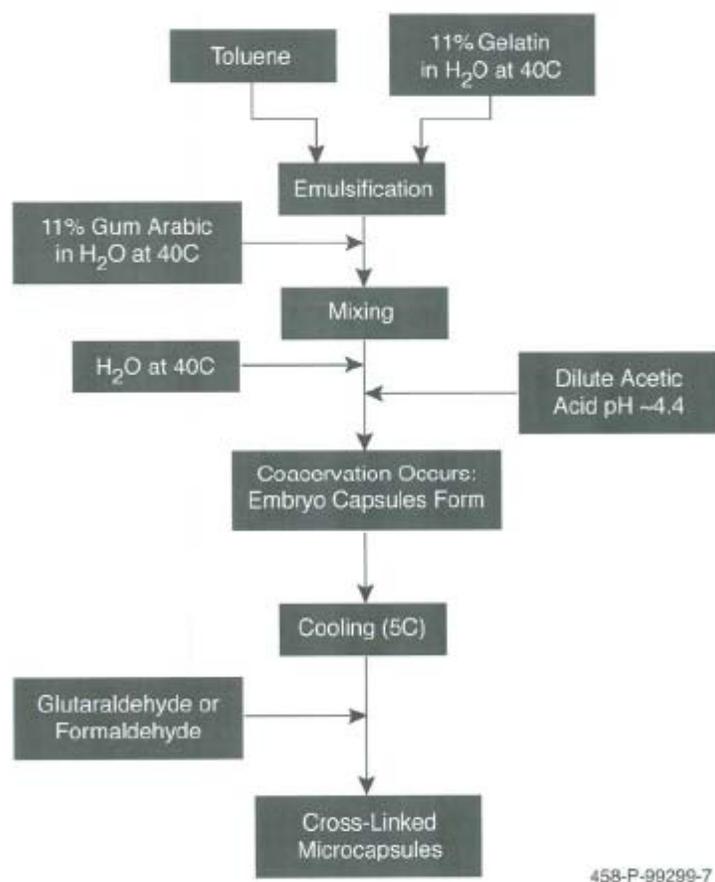


Figure 3: Schematic of the complex coacervation process developed by Dr. Curt Thies to microencapsulate the catalyst accelerant in IST's shelf SSERA [15].

3.3 Thermal Characterization and Shelf Stability

The adhesive systems and their components were characterized using a Perkin-Elmer Series 7 DSC. DSC was used to determine glass transition temperatures, measure melting points, estimate mixture compositions, and monitor the curing process. The compositions of the microencapsulated catalyst accelerants produced by Microtek and Thies Technology were

calculated by comparing the melting endotherms of the encapsulated accelerants to that of the pure accelerants.

The shelf-life stability of encapsulated and non-encapsulated adhesives was calculated by an accelerated in-situ DSC method. The formulations of the evaluated adhesives are listed in **Table 2**. As explained in *Section 2.5*, conventional shelf-stability tests require aging for a period of months, which results in phase separation of unsupported film adhesives such as the ones produced here. Instead, we elected to perform a series of DSC experiments where the adhesive samples were preheated in-situ prior to testing. The high heat transfer rate of DSC allowed such an experiment to be completed in less than two hours. First, specimens were heated at 10 °C/min to a series of increasing temperatures (40, 65, 85, and 110 °C) for one hour and then rapidly cooled to room temperature. Then, samples were crushed with mortar and pestle to enable release of the catalyst accelerant, as described in *Section 3.4*. Crushed samples were reheated from 25 to 225 °C at 10 °C/min to assess their chemical reactivity from their curing exotherm. A residual reactivity was calculated as a percentage of the curing exotherm of a fresh adhesive sample of the same composition.

Table 2: Composition of the adhesives used in the accelerated shelf-stability tests.

Component	Reference Adhesive System (wt. %)	Encapsulated Adhesive System (wt. %)
Epoxy resin	93	92.5
DCDA	5	4.9
Catalyst accelerant	2	1.9
Encapsulant	0	0.7

3.4 Release of Catalyst Accelerant

Two mechanisms were envisioned for releasing the microencapsulated accelerant: crushing of the capsule walls and melting of the encapsulated monuron. In the crushing release mechanism, the epoxy resin is activated immediately prior to use by passage of the film adhesive between rollers of an applicator device (**Figure 4**). During passage between the rollers, high nip pressure would crush microcapsule components of the resin, releasing the curing accelerator and mixing it into the adhesive resin via shear. This process was evaluated by grinding samples with a mortar and pestle to crush the capsules and blend them into the catalyzed resin.

In the thermal release mechanism, the epoxy resin is activated immediately prior to use by passage of the film adhesive between the heated rollers of an applicator device. Low roller pressure may be necessary to distribute the resin. This release mechanism was evaluated using DSC.

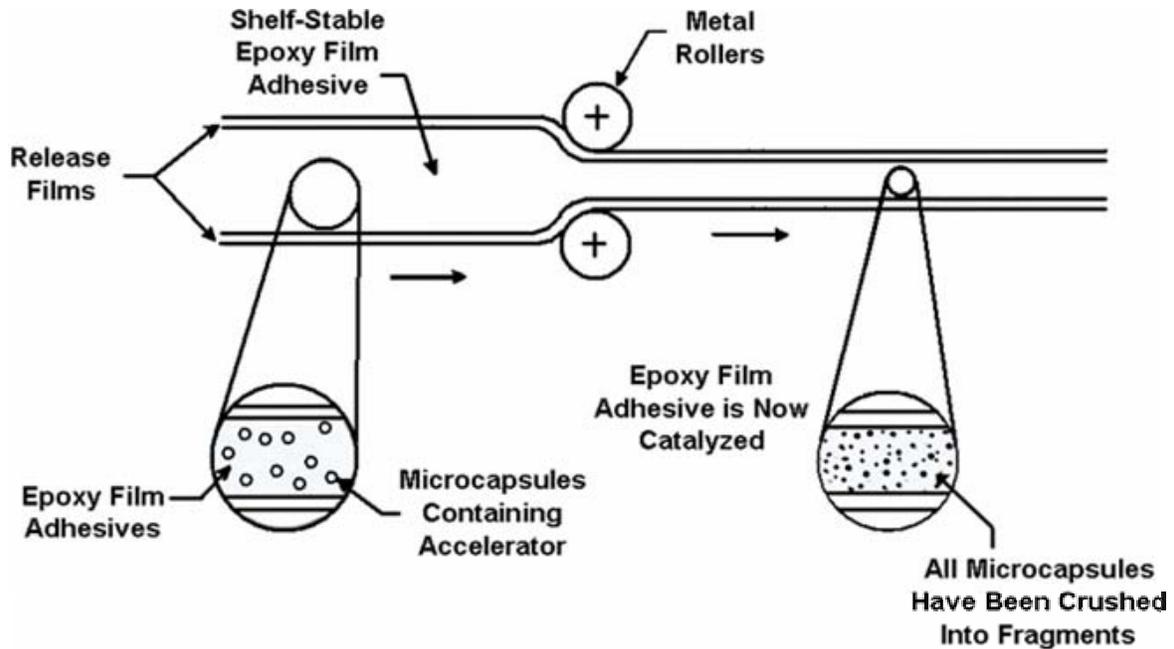


Figure 4: IST's process for releasing microencapsulated catalyst accelerator upon demand within an epoxy film adhesive.

3.5 Mechanical Characterization

The adhesive strength of one of the formulations containing carrageenan-blend microcapsules was compared to an un-encapsulated adhesive via lap shear tests. Specimens were prepared by bonding aluminum as specified in ASTM D1002 [16], with the exception that only one half inch overlap was used rather than one full inch. The reduced overlap was chosen after initial trials showed fracture in the aluminum adherents due to exceptionally high adhesive strengths rather than in the bond line.

4. RESULTS AND DISCUSSION

4.1 Curing Temperatures

The curing temperatures of three candidate catalyst accelerants were evaluated by DSC. **Figure 5** shows the exothermic transition for our baseline adhesive system containing 3 wt. % monuron. This monuron-based adhesive showed a cure onset of 147 °C and a peak at 164 °C. A MI containing adhesive showed a lower cure onset at 111 °C and a peak at 128 °C, as shown in **Figure 6**. A slightly lower range of curing temperatures was shown by an EMI adhesive, which showed an onset of 119 °C and a peak at 125 °C, as shown in **Figure 7**.

The development of a low temperature cure initiation epoxy adhesive resin offers many potential benefits over elevated temperature cure adhesive formulations. MI showed promise as reactive catalyst accelerator that initiated epoxy cure below 100 °C, however, it was found to be toxic and could not be evaluated in microencapsulated form. Alternate, non-toxic, reactive imidazole catalysts such as isopropyl imidazole were identified for encapsulation and may be evaluated in future encapsulation efforts.

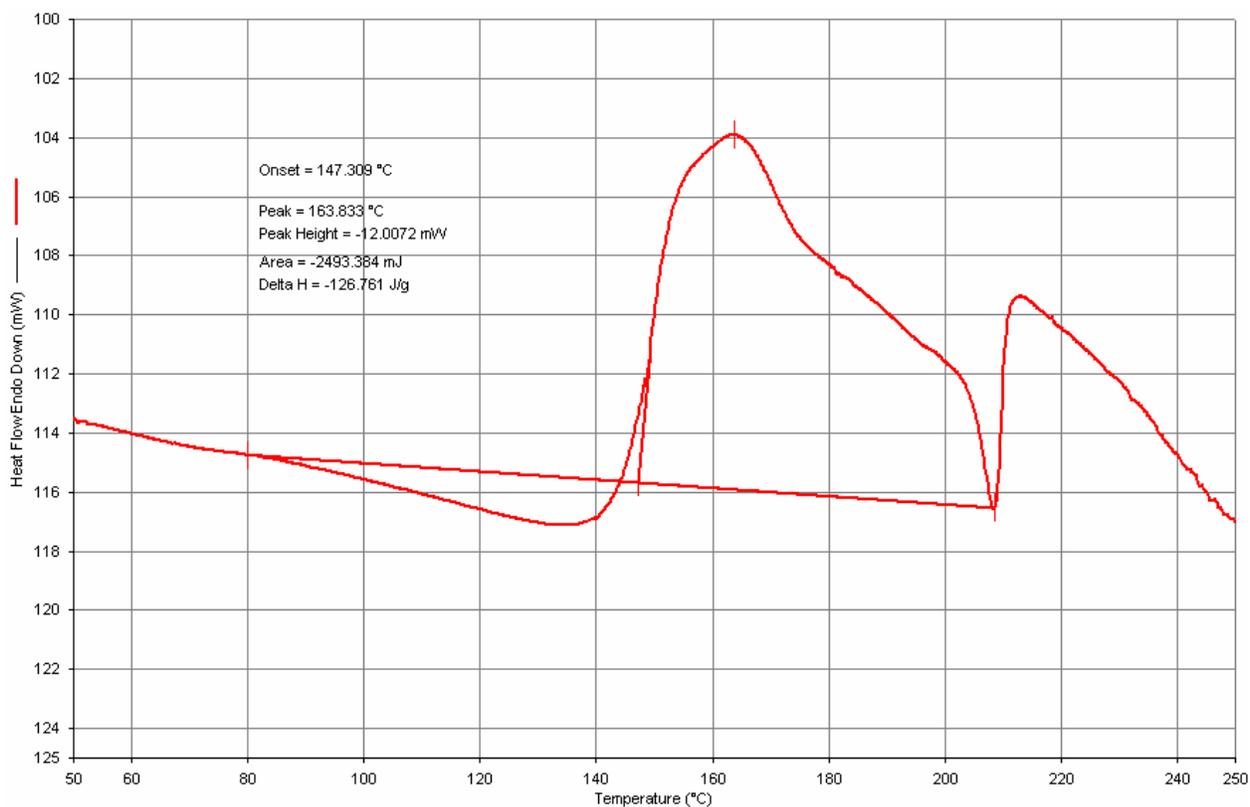


Figure 5: DSC trace of the base adhesive formulation with 3 wt. % monuron as the catalyst accelerant.

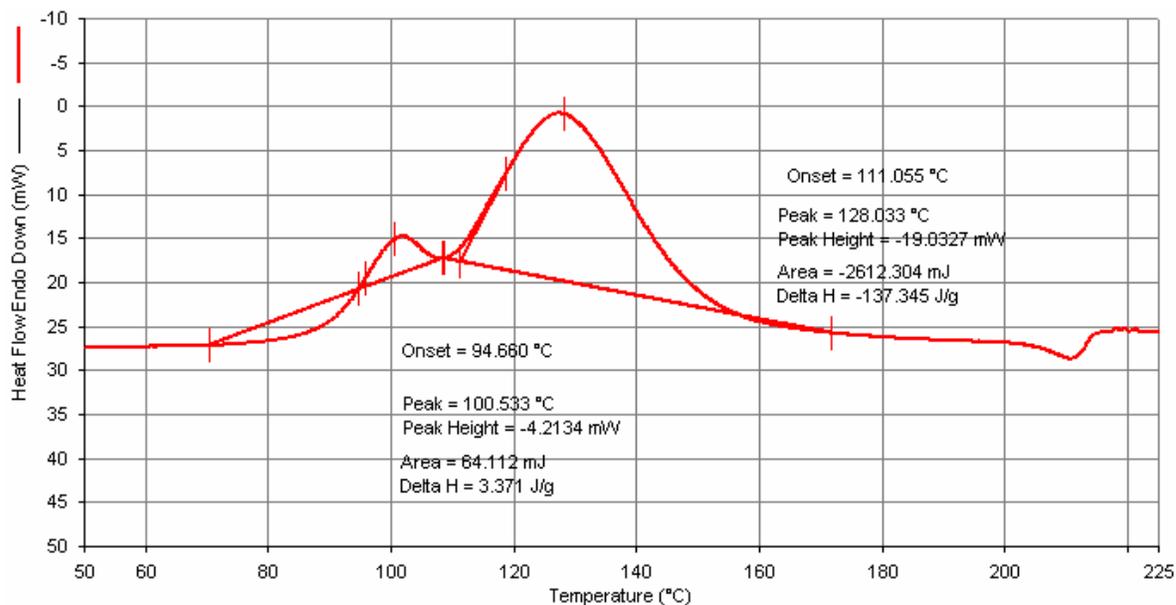


Figure 6: DSC trace of the base adhesive formulation with 3 wt. % MI as the catalyst accelerant.

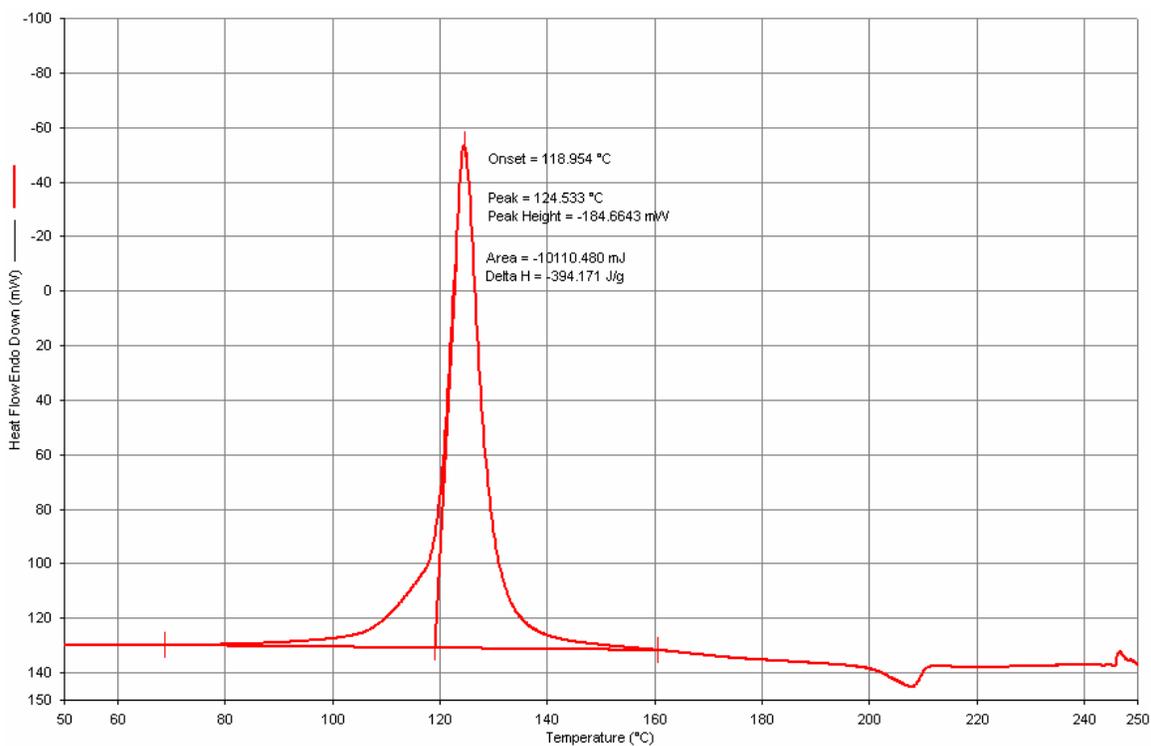


Figure 7: DSC trace of the base adhesive formulation with 3 wt. % EMI as the catalyst accelerant.

4.2 Microencapsulation

Gelatin-encapsulated monuron was custom-produced for Infoscitex by Microtek and Thies Technology via complex coacervation methods. The typical size of the Microtek capsules was approximately 50-75 μm (via optical microscopy), and the monuron content was calculated at 87 wt. %. The Thies Technology capsules had a monuron content of 75 wt. %. We also evaluated three types of carrageenan microcapsules provided by Thies, which had a typical size of about 40 μm , with some capsules as small as 10-25 μm in diameter. The monuron content of the Thies microcapsules varied between 45 and 68 wt. %, depending on the specific encapsulant formulation (**Table 3**).

Figure 8 and **Figure 9** show the DSC melting endotherms of un-encapsulated and a microencapsulated monuron (Thies carrageenan blend) at 178 °C. The microencapsulated sample shown in **Figure 9** has a monuron content of 54 %. DSC analyses of the various microcapsule types showed that some of the Microtek microcapsules seemed to contain exposed monuron, either on the exterior of the capsules or via incomplete encapsulation. Thus, further testing was performed only on the carrageenan blend capsules produced by Thies.

Table 3: Monuron loading on sample microcapsules, as calculated via DSC melting endotherms.

Product	ΔH (J/g)	Loading (%)
Un-encapsulated Monuron	124.6	100
Microtek gelating capsules	108.5	87
Thies capsules type A	56.7	45
Thies capsules type B	78.3	68

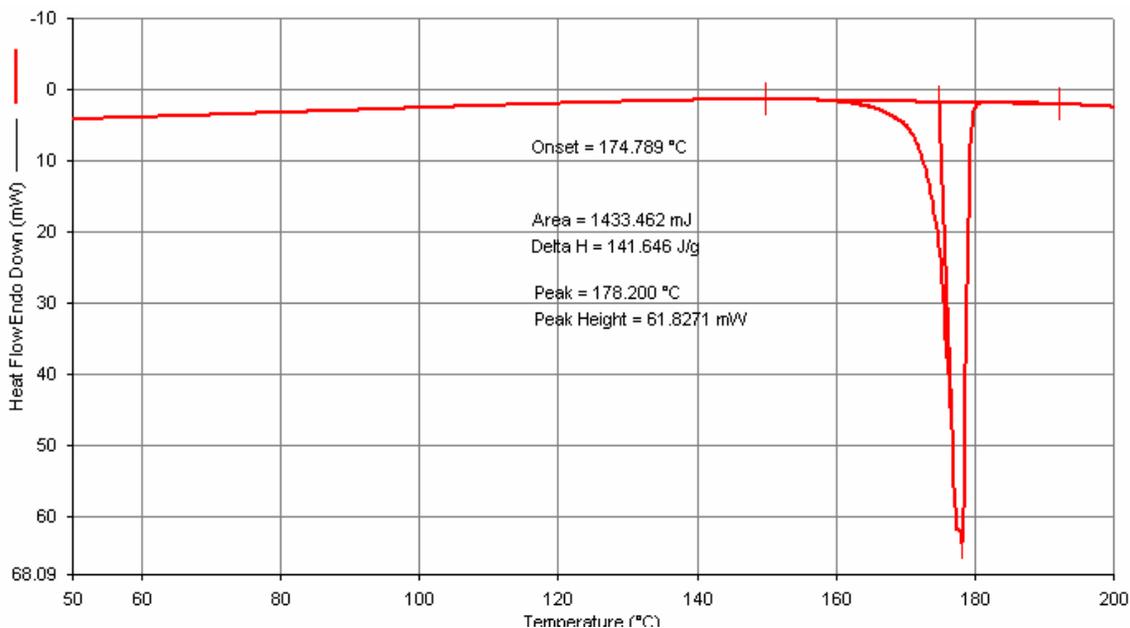


Figure 8: DSC trace of neat monuron showing its melting endotherm at 178 °C.

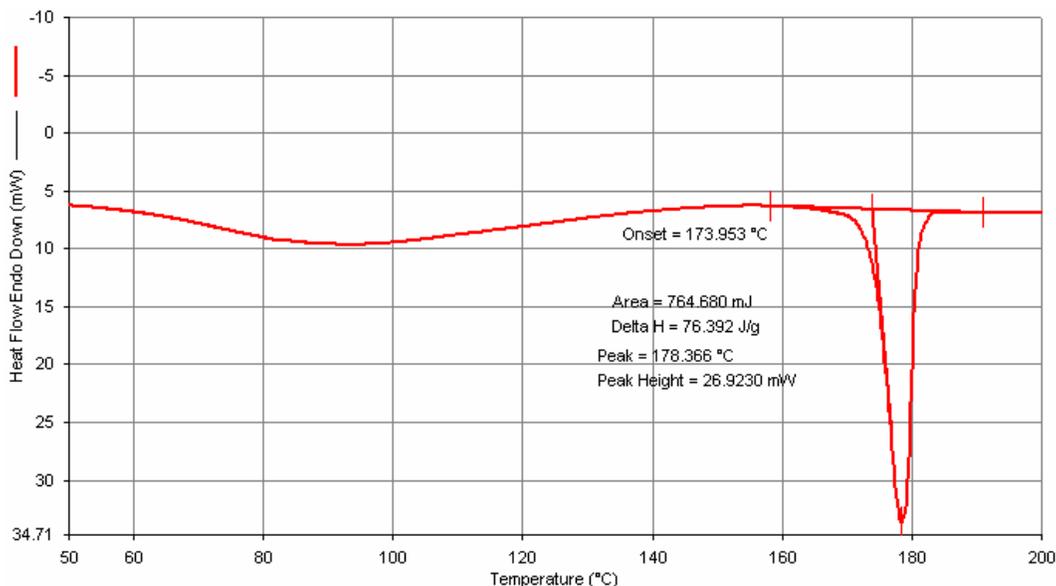


Figure 9: DSC trace of monuron microencapsulated with a carrageenan blend, showing its melting endotherm at 178 °C. The calculated monuron content for this sample is 54 wt. %.

4.3 Catalyst Release

Two release mechanisms were investigated during this project: mechanical and thermal. In the mechanical approach, the microcapsules would be crushed open to expose the monuron core. In the thermal approach, the microcapsules would be burst open by briefly exposing the adhesive to a temperature above the melting point of monuron.

DSC traces of the adhesive containing crushed microcapsules exhibited a cure exotherm very similar to the control adhesive (**Figure 10**). Samples with crushed microcapsules exhibited an exotherm with an onset of 156 °C and a peak at 166 °C (**Figure 10**), versus an onset of 147 °C and a peak at 164 °C for control samples. It was observed that crushing microcapsules smaller than 25 µm within epoxy resin was difficult and inefficient, and that future experiments should evaluate using larger microcapsules (> 25-50 µm).

In a laboratory demonstration of the thermal release mechanism, adhesives containing microencapsulated monuron exhibited a delayed cure exotherm peaking at 210 °C (**Figure 11**). We believe that the overlap between the melting of the monuron and the curing of the resin is a result of release of the monuron from the capsules after reaching its melting point 175 °C. However, the increase in curing temperature is undesirable because it is above the boiling point of water, as previously discussed in *Section 2*.

We now believe that the best mechanism for release of the catalyst accelerant is one that primarily relies on mechanical crush of the microcapsules, where heat may be applied to promote resin flow and the diffusion of capsule fragments. The epoxy adhesive would be passed between heated nip rollers of a film dispensing device immediately prior to use. Within the nip, fractured microcapsules and free monuron catalyst will be mixed into the resin by shear. Following passage through the nip, the adhesive will be rapidly cooled back to room temperature in contact with a

third cooling roll. Film adhesive thus dispensed will be ready for immediate use without generation of waste.

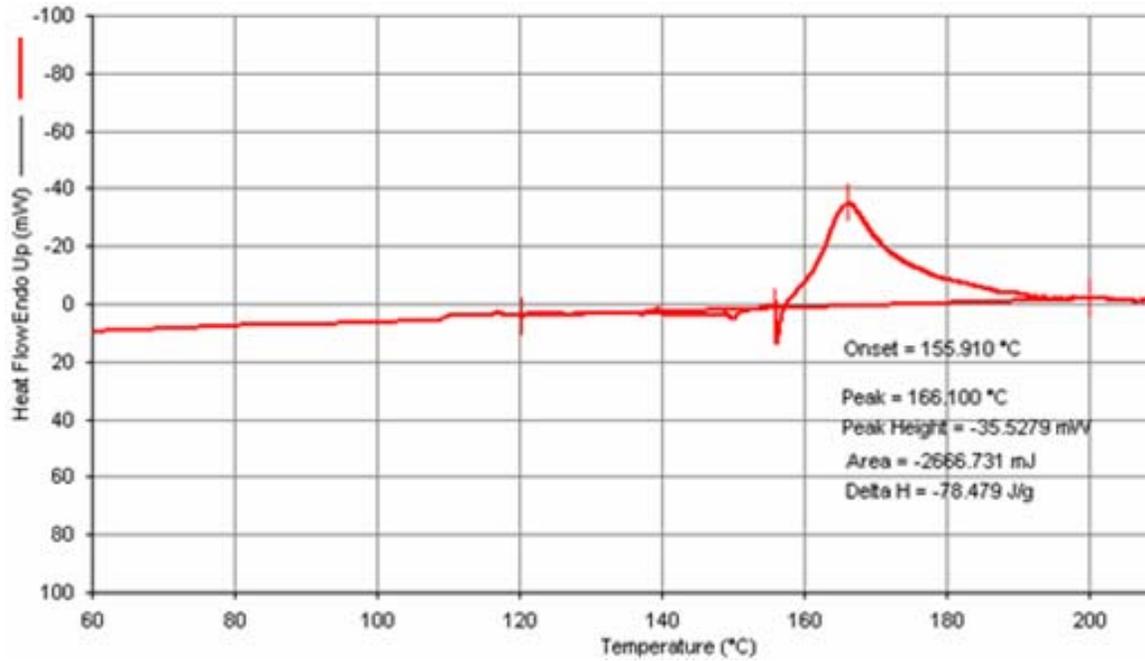


Figure 10: DSC trace of adhesive containing microencapsulated monuron, after crushing the mixture with mortar and pestle. Monuron was successfully released by crushing the capsule walls, as shown by the exothermic transition peaking at 166 °C.

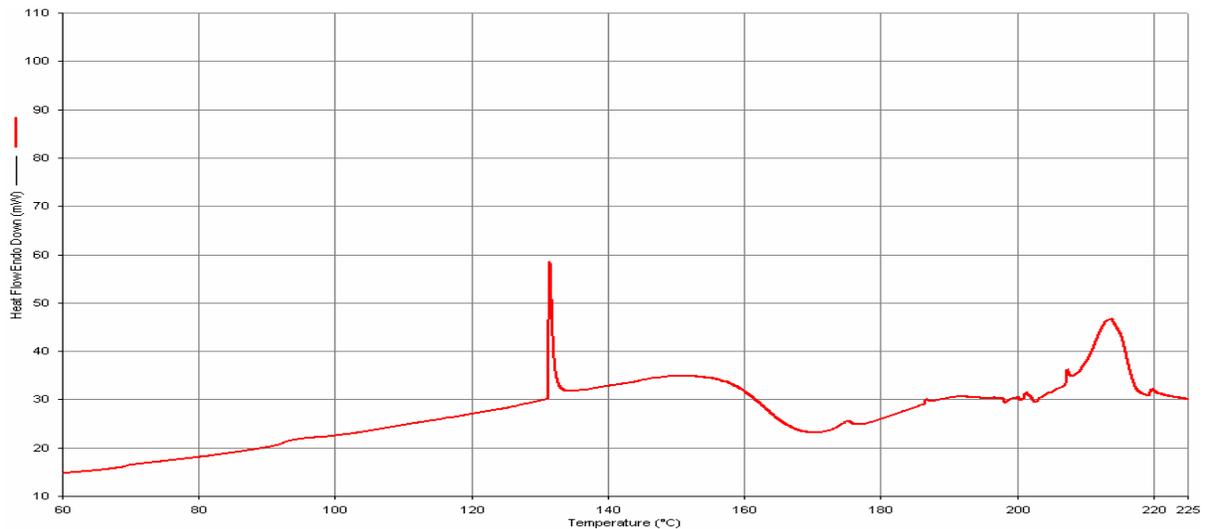


Figure 11: DSC trace of adhesive sample containing encapsulated monuron, after being exposed to a heat spike of about 180 °C.

4.4 Shelf-Stability

Figure 12 shows the residual chemical reactivity of thermally aged adhesives containing un-encapsulated and microencapsulated monuron. The residual reactivity was calculated from the normalized curing exotherms of the aged samples, as previously described in *Section 3.3*. The DSC traces of the aged and reference samples are shown in *Appendix A*. Adhesives containing microencapsulated monuron showed a distinct improvement in residual reactivity as compared to the un-encapsulated reference formulation. It should be noted that these tests offer only a direct comparison between materials and cannot be correlated directly to conventional shelf stability tests (*Section 3.3*).

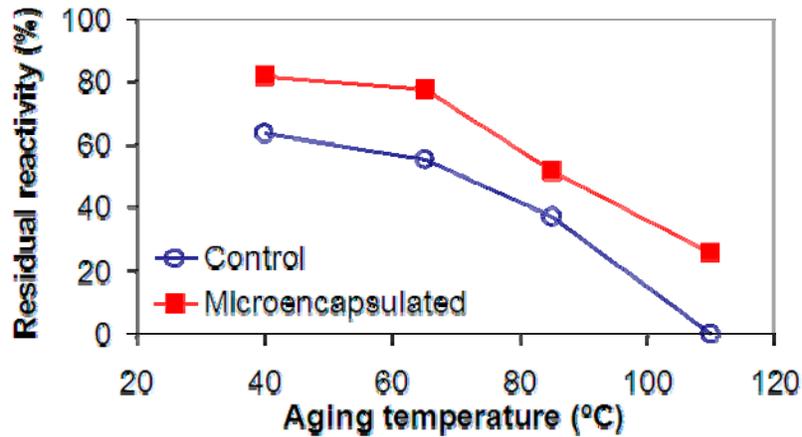


Figure 12: Percent activity of control and microencapsulated adhesive samples as a function of temperature exposure.

4.5 Mechanical Characterization

Table 4 shows the lap shear strength of equivalent encapsulated and un-encapsulated adhesive formulations. The samples containing microencapsulated monuron were comparable in lap shear strength to the controls (14.1 ± 1.5 vs. 15.3 ± 3.6 MPa), showing that the encapsulation and release process had worked successfully during these preliminary tests. The results shown here are for samples that failed via cohesive failure of the adhesive rather than adhesive failure of the bond line, as specified by ASTM D1002.

Table 4: Mechanical behavior of lap shear specimens using IST’s novel adhesive system, SSERA. Our microencapsulated-monuron adhesive system shows the same mechanical strength as the control adhesive system.

	Lap shear strength			
	Control		SSERA	
	MPa	psi	MPa	psi
Average	15.3	2221	14.1	2038
Std Dev	3.6	520	1.5	214

4.6 Summary of Phase I Results and Accomplishments

Table 5 summarizes the specific results of this project.

Table 5: Phase I objectives versus accomplishments.

Phase I Objective	Accomplishment
Evaluate different encapsulation methods and select the most promising.	Complex coacervate and spinning disk microencapsulation methods were investigated. Complex coacervate method demonstrated most reliable results
Evaluate low temperature epoxy resin catalyst accelerator systems to enable void-free adhesive cure initiation below 100 °C.	MI reduced onset of cure from 144 °C to 94 °C, However, it was determined to be toxic, and should not be pursued further. EMI reduced onset of cure temperature from 144 °C to 100 °C. Non-toxic isopropyl imidazole was identified for future evaluation.
Prepare microencapsulated catalyst accelerator samples for evaluation in epoxy resin adhesive.	Five types of microcapsules were prepared and a carrageenan blend was selected for further mechanical and stability tests.
Demonstrate release of monuron accelerator into shelf-stable epoxy adhesive upon demand	Crushing of microcapsules within resin to expose the monuron core was successfully demonstrated using a mortar and pestle. Thermal release mechanism was successfully demonstrated by heating adhesive rapidly to cure temperature followed by rapid cooling.
Demonstrate comparable epoxy adhesive strength for microencapsulated and control adhesive system.	Lap shear strength for the microencapsulated and control adhesive specimens were equivalent (14.1 ± 1.5 vs. 15.3 ± 3.6 MPa).

5. CONCLUSIONS AND RECOMMENDATIONS

We have successfully demonstrated the feasibility of developing a shelf-stable adhesive system via microencapsulation of the catalyst accelerant. Thermal analysis of microcapsules made from carrageenan blends showed that they formed an effective barrier between commonly used, bisphenol-based epoxy resins and monuron, a typical catalyst accelerant. The encapsulated monuron was made available for curing by means of mechanical and thermal activation methods. The mechanical method was found to be most compatible with the overall requirements for this application. SSERA samples activated in this manner showed equivalent performance to un-encapsulated control samples during lap shear tests and superior shelf-stability after accelerated thermal aging.

Future development of a non-hazardous, shelf-stable, one-part epoxy film adhesive will require the microencapsulation of catalyst accelerants with lower toxicity and environmental impact. Our collaborators at Henkel Loctite have proposed the use of fenuron as a substitute for monuron. We believe that our microencapsulant formulation will be compatible with fenuron, or a number of other accelerants, because of its superior ability to prevent migration of the epoxy resin into the capsules. Further work would also involve the fabrication of film adhesive prototypes at Henkel's development facilities in northern California, conventional shelf-stability tests, and a fuller set of mechanical tests under the advice of Northrop Grumman.

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APPENDIX A: Accelerated Shelf-Stability Tests

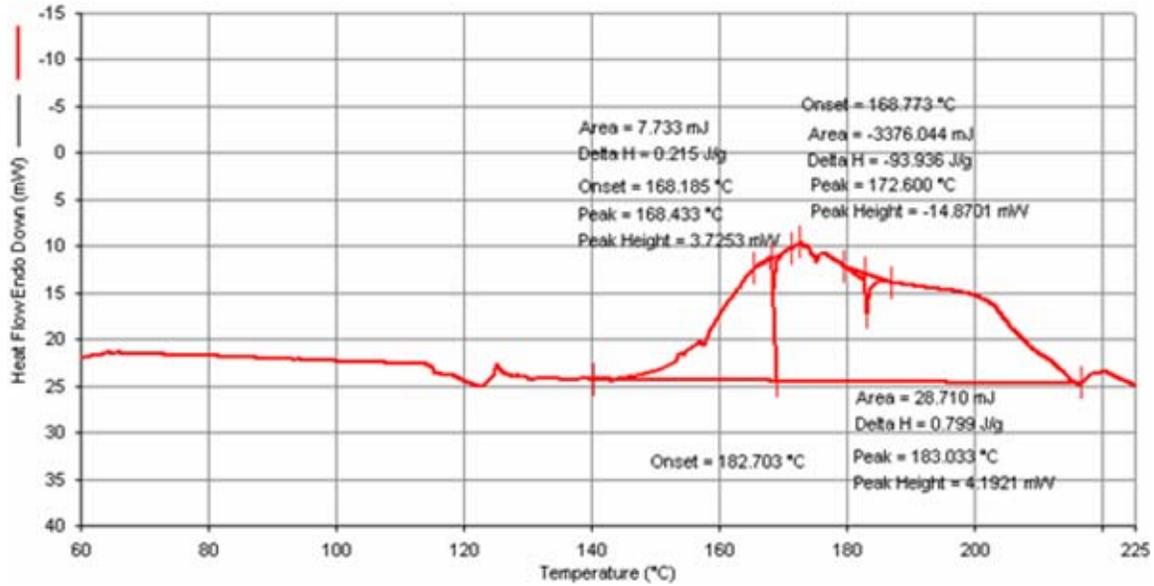


Figure 13: DSC trace of reference adhesive formulation used during shelf-stability tests. This sample contains monuron as the catalyst accelerant and was not aged. $\Delta H = 94 \text{ J/g}$.

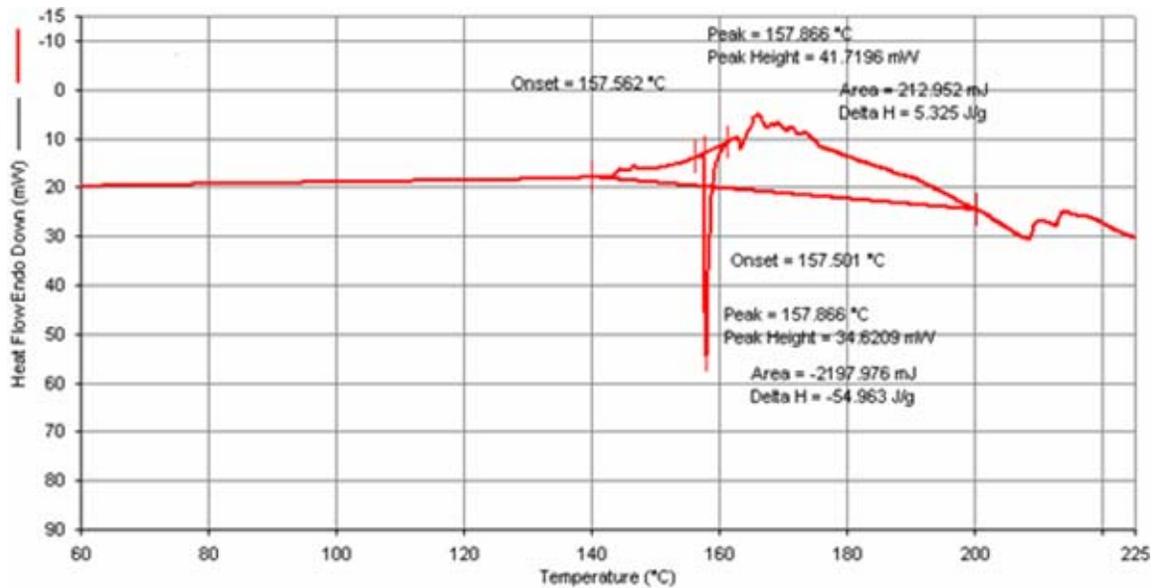


Figure 14: DSC trace of reference adhesive formulation used during shelf-stability tests. This sample contains monuron as the catalyst accelerant and was aged at 40 °C for 1 hour. $\Delta H = 60 \text{ J/g}$, or 64 %.

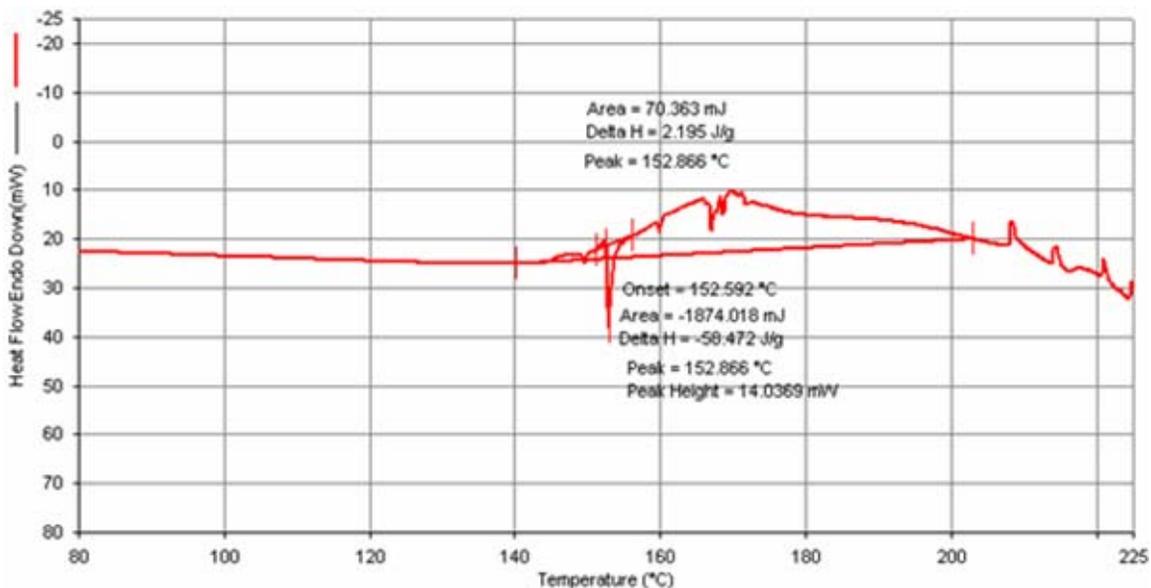


Figure 15: DSC trace of reference adhesive formulation used during shelf-stability tests. This sample contains monuron as the catalyst accelerant and was aged at 65 °C for 1 hour. $\Delta H = 53 \text{ J/g}$, or 56 %.

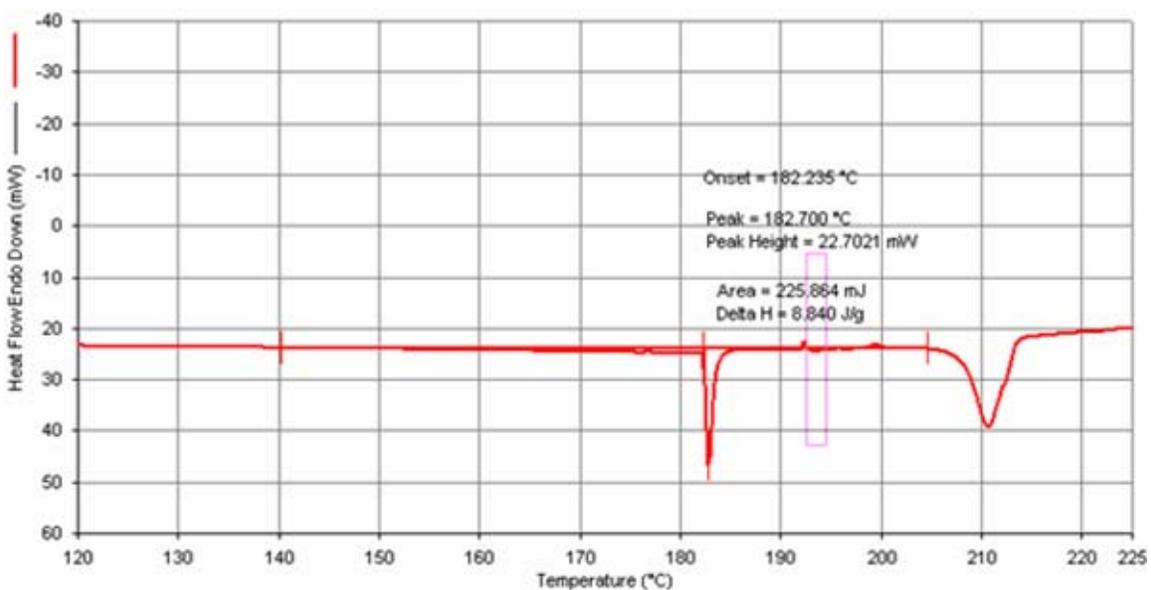


Figure 16: DSC trace of reference adhesive formulation used during shelf-stability tests. This sample contains monuron as the catalyst accelerant and was aged at 110 °C for 1 hour. No exotherm was observed in the curing temperature range of 140 to 205 °C, indicating that the sample was no longer reactive.

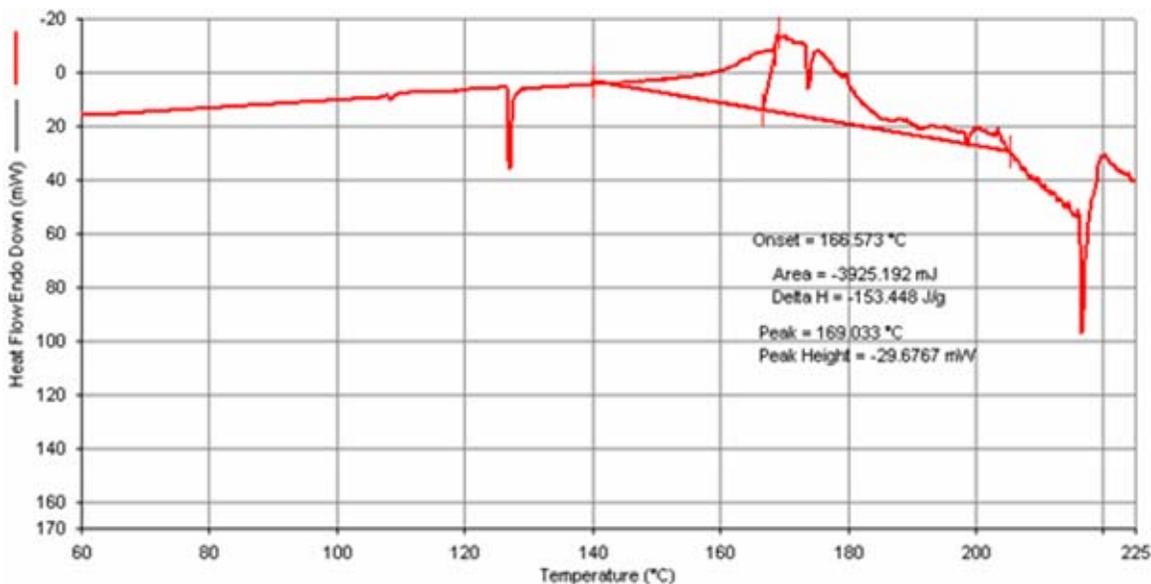


Figure 17: DSC trace of capsule-containing adhesive formulation used during shelf-stability tests. This sample contains monuron and was aged at 40 °C for 1 hour. $\Delta H = 155 \text{ J/g}$, or 82 % of the un-aged encapsulated catalyst accelerant.

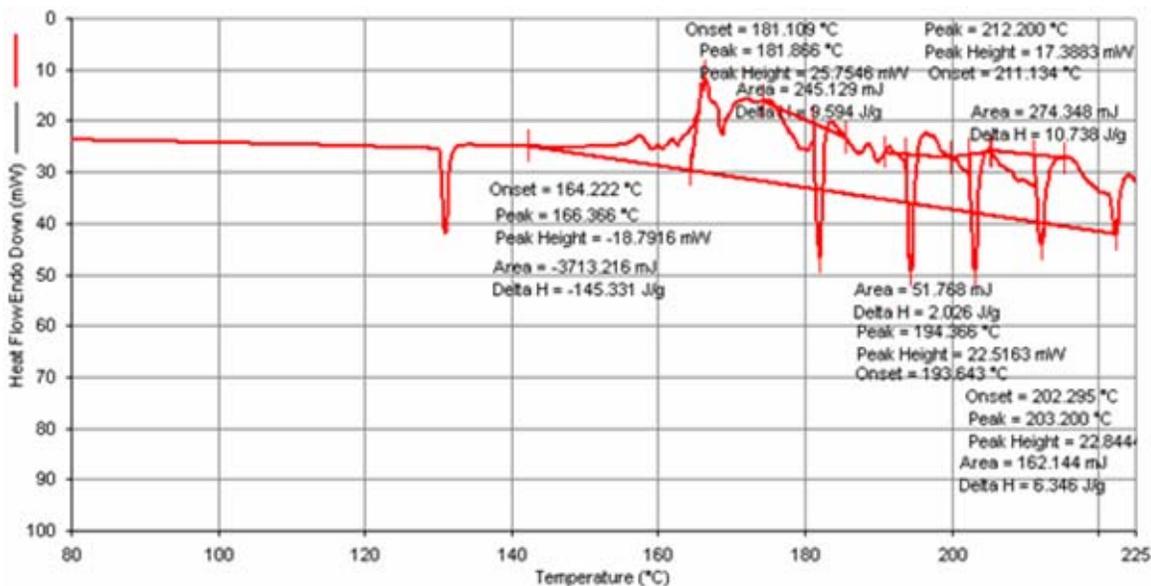


Figure 18: DSC trace of capsule-containing adhesive formulation used during shelf-stability tests. This sample contains monuron and was aged at 65 °C for 1 hour. $\Delta H = 148 \text{ J/g}$, or 78 % of the un-aged encapsulated catalyst accelerant.

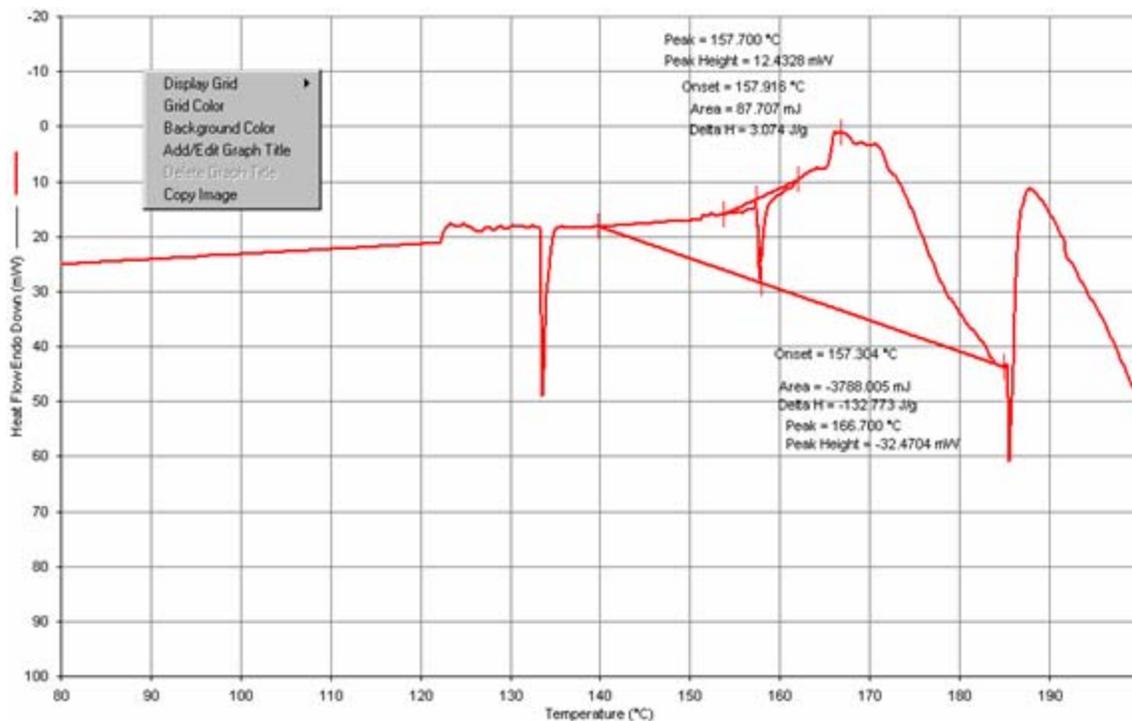


Figure 19: DSC trace of capsule-containing adhesive formulation used during shelf-stability tests. This sample contains monuron and was aged at 85 °C for 1 hour. $\Delta H = 133 \text{ J/g}$, or 70 % of the un-aged encapsulated catalyst accelerant.

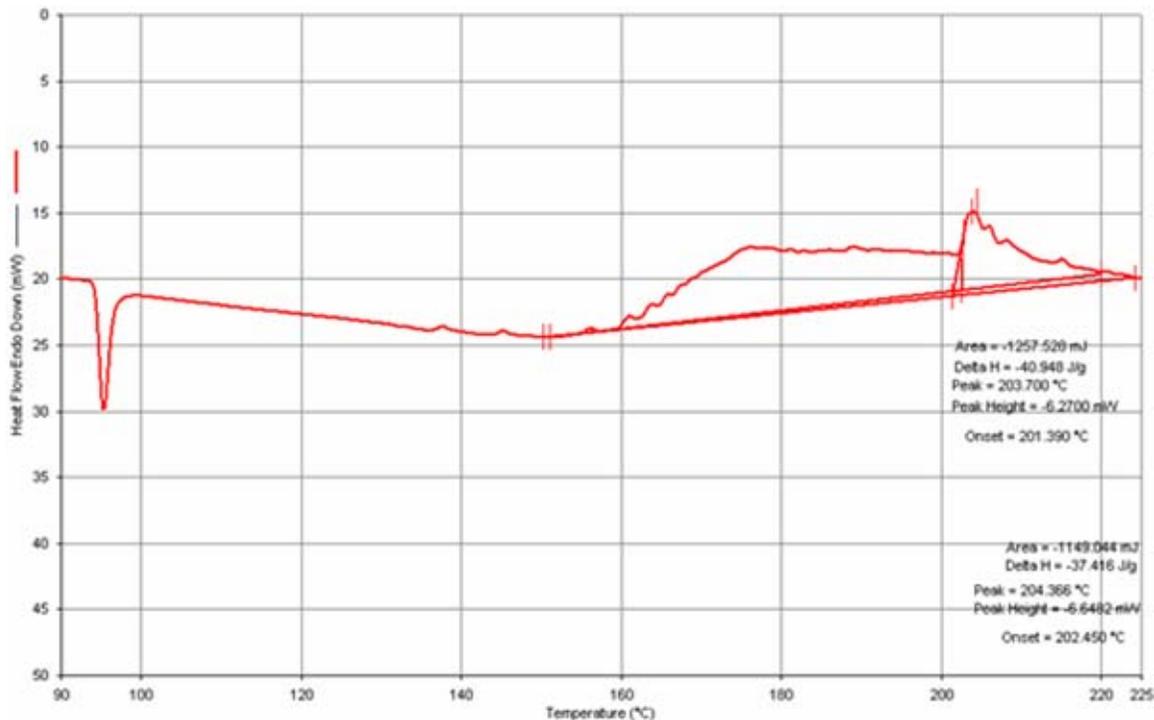


Figure 20: DSC trace of capsule-containing adhesive formulation used during shelf-stability tests. This sample contains monuron and was aged at 110 °C for 1 hour. $\Delta H = 41 \text{ J/g}$, or 22 % of the un-aged encapsulated catalyst accelerant.