

## **Dicyclopentadiene Polyester Resin Risk Assessment**

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Dicyclopentadiene is a reactive monomer used in substantial volume as a key raw material by the unsaturated polyester resin industry. Although the chemistry was well understood from a technical perspective, the process safety considerations were not well documented. Following some initial work internally, an opportunity was seized to initiate a collaborative study of the risks posed by this reaction chemistry under the umbrella of the Composites Fabricators Association Process Safety Committee. Committee members supply DCPD resins to the composites industry. Benefits of this effort have included access to incident and near miss experiences; shared costs for carrying out stability testing using adiabatic runaway calorimetry and continuous addition studies; and access to best practices for improving DCPD process safety. Limitations, such as the need to protect proprietary formulation data, have not seriously impacted work on the common half-ester reaction step, but have required some follow-up studies by individual companies. This successful effort to enhance reactive chemical safety may provide a useful model for other companies working to improve their safety performance and PSM compliance.

### **Background**

As part of our efforts to comply with the ACC Responsible Care® Process Safety Code, OSHA's Process Safety Management Standard, and EPA's RMP regulation Reichhold's Corporate Engineering/EHS groups initiated internal reviews of our chemistries based on risk. Developing documentation to confirm the adequacy of the existing relief systems was a key objective of these studies.

Reichhold is a supplier of specialty resins to many industries. All of our production occurs in batch reactor systems, with various configurations in use. Most plants use process computer control systems of varying degrees of sophistication. Early on in our program we developed a risk prioritized ranking of processes based on their known hazards and our operating experience. Exothermic systems where one or more feeds were staged or fed continuously because of heat removal limitations were recognized as

potentially “higher risk”. The Dicyclopentadiene (DCPD) polyester resin process came out at the top of the list, and follow-up evaluations started in 1998.

During this phase, we were expanding production into several new locations and the need for relief sizing data became critical. At about the same time, we started to participate in an industry sponsored ad hoc group focused on Process Safety Management. This group, the Composite Fabricators Association Process Safety sub-Committee (CFA – PSC) was composed of key manufactures that supply resin to the Composites Industry. The CFA has headquarters in Washington DC and has members throughout the U.S. In total, about 800,000,000 pounds of DCPD based resin is used annually in the U.S., with consumption growing at ~3% a year. These resins find application in the marine industry, and offer certain performance advantages and costs savings over conventional resins.

As this group met, and began to share the events and near misses they had experienced over the previous 7 years, it became very obvious that all of us had experienced near-catastrophic problems in DCPD resin production, particularly with the first stage half-ester (DCPD/Maleic Anhydride / H<sub>2</sub>O) reaction. We all needed better data on the runaway reaction and decomposition potential of the system following loss of cooling, operator error, or mischarge of reactants. It was at this point that we decided to cost share adiabatic calorimetric testing to learn more.

We elected to use the umbrella of the CFA to contract with a third party consultant and selected General Physics Corp. because of their expertise in this area. General Physics coordinated the testing and carried out DIERS calculation for a 5,000 gallon reference (“benchmark”) reactor system to allow comparison of the various cases examined. Each company was free to take the data and utilize it to evaluate their own reactors. Each member company has gone on to look at their safety critical control systems, operating procedures, and other safety systems to appropriately manage the risks identified.

There was no effort to develop an “industry standard”. Other than the final benchmarking reports from the testing, there was no published data. Six of the seven members are using the data as they see fit. (Dow Chemical did not participate because they do not make DCPD resins. Dow has fully participated in other Committee activities and has been a valuable contributor to other projects.)

**CFA Resin Managers Committee:**  
Process Safety sub-Committee (PSC):

- Ashland Chemical
- Interplastics, Corp.
- Alpha-Owens Corning
- McWhorter (Eastman)
- Cook Composites
- Reichhold, Inc.
- Dow Chemical

The information in this paper highlights this very successful approach to sharing data, non-proprietary process information, and process safety approaches within an industry.

### **CFA Member Concerns and Sponsored Test Program**

The DCPD incident history of the CFA - PSC members led them to identify certain key concerns, which were addressed in a cost-shared calorimetry program administered through the CFA and run by General Physics Corporation. These concerns are summarized below:

1. Stability of Intermediate and Final Products
2. Esterification (Second Stage Reaction) Runaway Potential
3. Effect of Half Ester Order-of-Addition (Staging)
4. Half Ester Maleic Anhydride Shot Size Impact
5. Half Ester Heat of Reaction and Accumulation Potential with Continuous MA Addition

In addition to these concerns, the severity of several of the industrial events led to considerable interest in enhancing reactor system engineering and administrative controls. Since some credible scenarios were found to be so severe that realistic relief systems could not mitigate them, there is a real need to reduce their severity and likelihood. There is also a very real need to enhance the effectiveness of plant personnel in detecting and responding to reactive events in the DCPD-MA-H<sub>2</sub>O system. These aspects are addressed later in this paper.

PSC members appreciated the vigorous nature of the half-ester reaction. However, the stability of the half-ester and blended styrene / full-ester products was not as well understood. Screening low phi-factor tests were run on Hazard Evaluation Laboratory's PHI-TEC II calorimeter. The results were gratifying in showing minimal decomposition potential for the half-ester up to 215°C, with a modest decomposition reaction initiating at this temperature. The styrene/resin product tested reacted vigorously, but gelled with negligible pressure generation. Both results were consistent with commercial scale field experience.

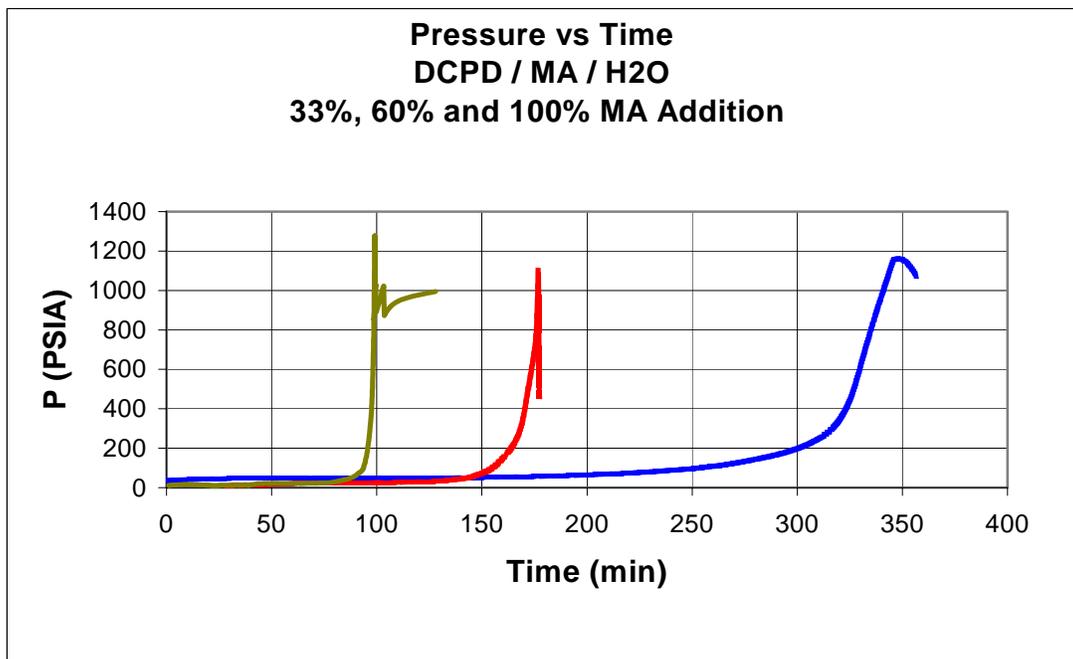
Industrial experience with the completion (esterification) reaction had generally shown it to be wholly endothermic. However, there were isolated reports of small exotherms occurring at the end of this step. A single low phi-factor test on this reaction failed to exhibit any detectable exotherm but did produce small amounts of non-condensable gases upon extended heating at commercial conditions. While this does not appear to pose a major threat, PSC members are now aware of the potential for pressure build-up at the end of the completion reaction, and can modify their procedures and control programs accordingly.

The half-ester reaction has been practiced at various times with Maleic Anhydride (MA), DCPD, or H<sub>2</sub>O as the limiting component. Low phi-factor testing using 1/3 stoichiometric addition of the limiting component revealed sharp differences in behavior for these cases. Pre-charging MA and H<sub>2</sub>O (DCPD shot addition) led to the formation of high-melting maleic acid, causing plugging of instrumentation and generating a sharp, gassy runaway reaction, with a maximum heating rate of 94°C/minute. Addition of H<sub>2</sub>O to precharged DCPD / MA resulted in an extremely sharp, gassy reaction with a maximum self-heating rate of 240°C/minute. In both of these cases, it was difficult for the pressure compensation system to keep up with the extreme rate of pressure rise, and the test cells were damaged. In contrast, the runaway behavior of 1/3 stoichiometric MA addition to precharged DCPD / H<sub>2</sub>O was comparatively mild, with a self heating rate of 3°C and tempered (vapor pressure dominated) behavior at modest pressures, although decomposition eventually did occur. The presence of free water appears to be extremely valuable in slowing the onset of decomposition, and helps ensure that relieving pressures are reached at modest temperatures and reaction rates.

Maleic Anhydride staging was clearly the preferred addition method for the half ester reaction. Low phi-factor tests were run using shot sizes of 33%, 60% and 100% of stoichiometric MA (Figure 1). The repeat test at 33% gave very similar results to the test run above. The 60% shot size run was much more serious. A maximum self-heating rate of 97°C/minute was measured. The 100% run was extremely severe, with a maximum self-heating rate of 211°C/minute.

The calculated rupture disc size for the 100% MA shot size decomposition approached the diameter of the 5,000-gallon reactor evaluated as a benchmark for these cases.

**Figure 1**



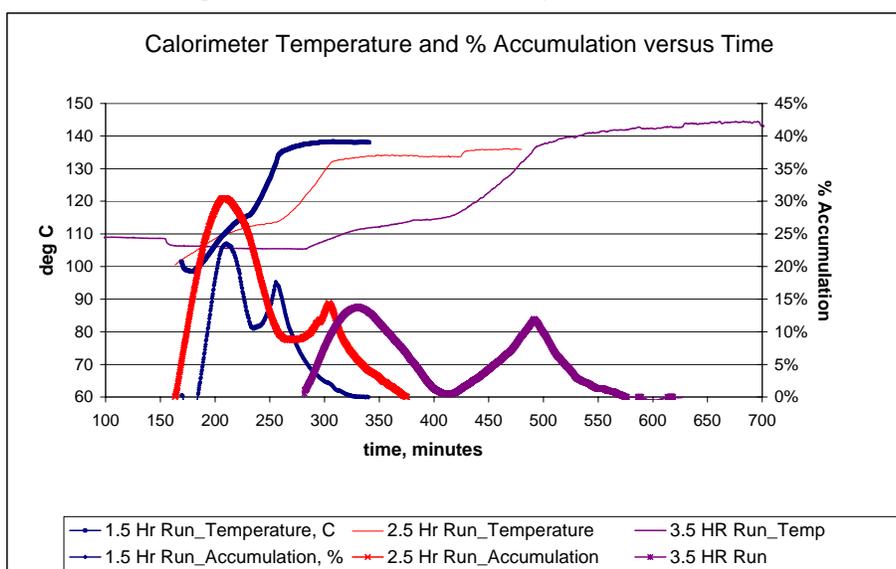
**Pressure Versus Time Behavior for Three Adiabatic Runs**

One adiabatic run was made in an attempt to simulate a commercial mis-charge incident that resulted in excess MA being added to a completed half-ester material. This resulted in a gassy runaway with a maximum self-heating rate of over 6°C/minute. The contrast with the 1°C maximum self-heating rate for the neat half-ester decomposition was presumably due to decarboxylation of the MA, although no gas samples were collected for analysis from these runs. The behavior in this test was generally consistent with that observed during the full-scale incident.

A series of reflux calorimetry runs were made at the one liter scale to measure the heat of reaction under simulated commercial conditions. The data generated by these tests allows a rough estimate to be made of the heat release potential (accumulation) that might result from loss of cooling during continuous maleic anhydride addition to a half ester reactor. Continuous MA addition is a possibly lower risk approach to carrying out the half ester step, and could also lead to reduced cycle time, which is economically attractive.

Figure 2 illustrates the approximate “loss of cooling” energy release potential as a function of time, with rate of MA addition as a parameter. The accumulation % is inferred as the difference between the fractional MA feed and the measured fractional heat release. While useful, variation in reaction initiation time following the start of MA feed to the reactor vessel led to significant variation in the calculated accumulation values, raising significant safety issues for this approach to running the half ester reaction.

**Figure 2 Reflux Calorimetry Test Results**



One very fast addition rate run (not shown) was aborted when the cooling capacity of the overhead condenser was exceeded and the reactor temperature began to increase rapidly.

The calorimeters used in these tests were custom modified versions of HEL's "Simular" reaction calorimeters.

The calorimetry testing carried out as part of the CFA PSC program was successful in identifying and roughly quantifying a number of significant safety concerns with the DCPD-MA-H<sub>2</sub>O system, and helped to shed light on the behavior exhibited in a number of commercial scale incidents reported by CFA members. The very serious consequences of loss of cooling when either DCPD or H<sub>2</sub>O is utilized as the staged material, or when a full MA shot (all-in scenario) was utilized had not been well understood prior to this study. Clearly, the order of addition utilized, and the maximum credible shot size that can be added in the half ester step need to be reviewed by all manufacturers of these resins, with MA staging and shot sizes of 33% or less strongly preferred. The potential for foaming demonstrated in several commercial scale incidents, the possibility of delayed initiation of reaction, and a demonstrated sensitivity to overheating and mis-feed of MA all highlight important safety issues.

Based on the shared experience of the members and the results of the test program, an integrated approach to DCPD resin process safety is clearly called for.

### **Controls, Upgrades and Training**

Being armed with good process safety information is the first critical step in identifying needed safety improvements for any manufacturing facility. The Process Safety Committee has shared the following possible approaches.

➤ Possible Safety Critical Control Systems:

- Redundant flow measurements for each feed stream – mass flow meters or a combination of mass meters and weigh tanks;
- Positive shut-off capability to prevent raw materials from entering the reactor inadvertently.
- Real time heat balance surveillance control systems that calculate the actual heat removed by the cooling system and compare it with the expected heat generation from the feeds. This takes a process computer to accomplish reliably.
- Agitator interlocks with feed streams to shut off or prevent feeds if the agitator shaft is not turning.
- Temperature profile interlocks that compare the actual rate of temperature rise with the expected temperature based on the time into the batch;
- Pressure profile interlocks to compare the actual pressure in the reactor with the expected pressure. This would indicate loss of overhead cooling or pluggage of the vapor system.

➤ Possible Process Upgrades:

- Evaluate existing rupture disc sizes and upgrade “relief valve only” systems. Shared experience clearly shows the tendency of this system to foam and for the foam matrix to decompose into a lava-like material that can plug off the overhead relief system. Relief valves cannot be relied on to work reliably in this service, as they have opened, closed, and then failed to re-open. Use RDs only
- Consider independent emergency cooling systems (city water or firewater) and power supplies on a plant-by-plant basis. Final selection of the most cost-effective system will depend on local conditions and the desired degree of redundancy.
- Consider emergency glycol cooling (quench) that can be used to cool the batch and possibly prevent temperature drifts to the decomposition regime.
- Consider moving to continuous feed of MA to better and more reliably control the exotherm. Multiple shots can be used but are subject to higher risk of error.
- Carefully consider need for / design of catch tank and reactor dump systems (this is an open issue)

➤ Enhanced Operator Training for DCPD Emergencies:

- PSM training elements are essential so operators clearly understand the risks posed by this process and the value of the redundant safety programs mandated by a good Process Safety Management program.
- Process Overview that clearly documents the “process safety” risks posed by the exothermic reaction chemistry.
- Process Safety Information that is consistent between plants in the same company so that everyone who ‘touches’ the process is working from the same base (manufacturing, technical, maintenance, EHS, etc .)
- DCPD Hazard Communication Training - review of MSDS for MA and DCPD – with particular emphases on exposure risks.
- Process Chemistry – half ester and second stage – this must be presented in layman’s terms that operators can understand. Using complex chemical formulas may be good for the technical chemist but is baffling to operators.
- Process Safety Awareness – safety critical alarms, interlocks, trips – once everyone understands that safety critical interlocks are needed to protect vessel and plant integrity, the meaning of functional testing, emergency shutdown procedures, MANAGEMENT OF CHANGE, Pre Startup Safety Review, and Process Hazard Analysis take on new and more relevant meaning.

### **Ongoing Activities - Path Forward:**

The collaborative focus of the Process Safety Committee on basic DCPD chemistry is over for now. Our focus in the near future is targeted at developing a useful, basic, operator training manual for unsaturated resin manufacturing that we can all use. Taking the best elements from each company and joining forces to identify the “best-of-the-best” will provide rich dividends in safer operation of our plants.

Of great value is the continued sharing of process safety events and near misses to add to the base of “credible scenarios”. A single location may not experience a problem for many years and become too casual about the kind of events really can happen. Even global operations can benefit. A recent event at a DCPD plant in South Africa owned by a parent company of a CFA member was recently discussed. This major release was caused by loss of cooling. Sharing approaches to emergency backup systems has also proven beneficial as experienced is gained in their design and installation.

### **Conclusion:**

In conclusion we wish to thank the CFA and the member companies of the Process Safety Committee for their support both financially and structurally for enabling this activity. Without their guidance and support, our efforts to share experiences, costs, and solutions would not be possible.

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