Insight — Application Note 3.02

Applications of Dielectric Cure Monitoring

Understanding composite and thermoset cure

When working on a new composite or a new formulation of a thermoset, the cure process is essentially unknown. What happens when the material is heated? When is the best time to apply pressure to squeeze out voids? How fast does the material react at different temperatures? Dielectric cure monitoring, also known as *dielectric analysis* (DEA), complements more conventional thermal analysis techniques of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) to bridge the gap between laboratory and manufacturing environments.

Characteristics of thermoset cure

Dielectric cure monitoring measures a polymer's resistivity (ρ) and permittivity (ε'), which are dielectric properties. In general resistivity provides the most useful information about cure state. More specifically, before gelation the change in *frequency independent resistivity* (ρ_{DC}), due to the flow of mobile ions, is often proportional to the change in mechanical viscosity. To emphasize this relationship, the term *ion viscosity* (*IV*) was coined as a synonym for frequency independent resistivity.

A thermoset cures when monomers react to form polymer chains then a crosslinked network. The reaction is usually exothermic—generating heat—and may additionally be driven by the heat of a press or oven. A plot of log(ion viscosity) is a simple way to characterize the progress of cure and Figure 2-1 shows the behavior of a typical thermoset with one ramp and hold step in temperature.

At first as temperature increases, the material softens or melts and mechanical viscosity decreases. Mobile ions also experience less resistance to movement and ion viscosity decreases. At this point the reaction is still slow.

As the material becomes hotter, the cure rate increases. At some time the accelerating reaction begins to dominate; mechanical viscosity reaches a minimum then the material becomes more viscous. Electrically, the increase in ion viscosity due to polymerization overcomes the decrease in ion viscosity due to higher temperature. Ion viscosity also reaches a minimum then increases due to

chain extension, which presents a greater and greater impediment to the flow of ions.

The gel point is the beginning of infinite network formation or crosslinking. At gelation mechanical viscosity rapidly increases until it becomes infinite. Although viscosity becomes immeasurable at the gel point, the change in ion viscosity continues to provide useful information and after gelation is often proportional to the change in modulus. As a result, DEA can follow material state throughout cure.

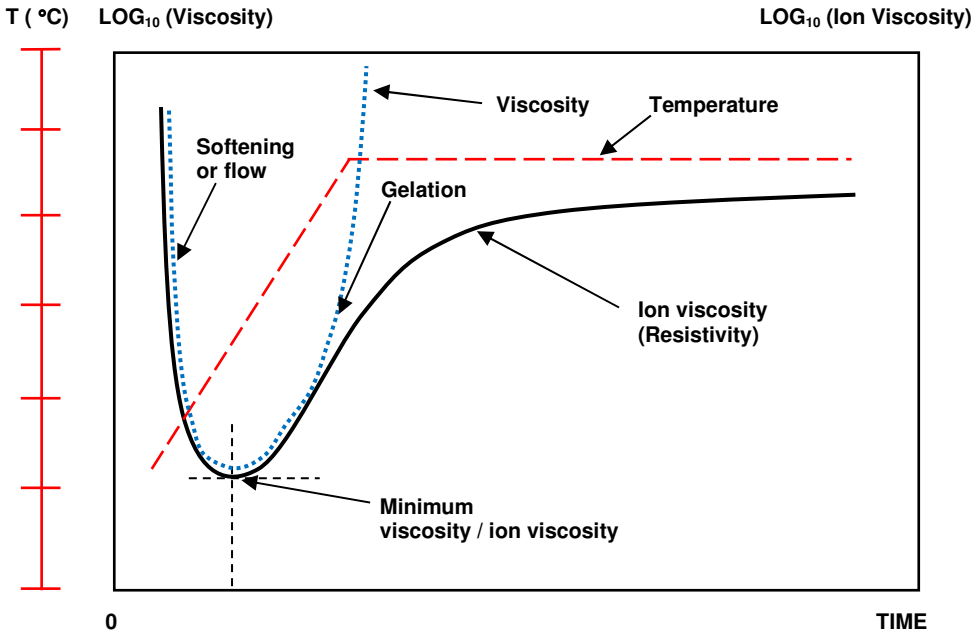


Figure 2-1
Typical ion viscosity behavior of thermoset cure during thermal ramp and hold

As cure progresses, ion viscosity increases continuously until the concentration of unreacted monomers diminishes and the reaction rate decreases. Consequently, the slope of ion viscosity also decreases and eventually reaches a value of zero when cure has stopped completely.

Differential scanning calorimetry

Differential scanning calorimetry, one method for studying polymers, measures glass transition temperature T_g, which changes with cure state. For a particular epoxy, Figure 2-2 shows T_g measured with DSC and compared with results from dielectric cure monitoring.

Each DSC data point requires curing the material to a chosen time, quenching the sample to stop cure and then performing the DSC analysis. This test must be repeated at multiple points during processing to obtain enough data to see the cure curve—a very tedious and repetitive task. In contrast, the cure curve from dielectric cure monitoring was obtained from a *single* test.

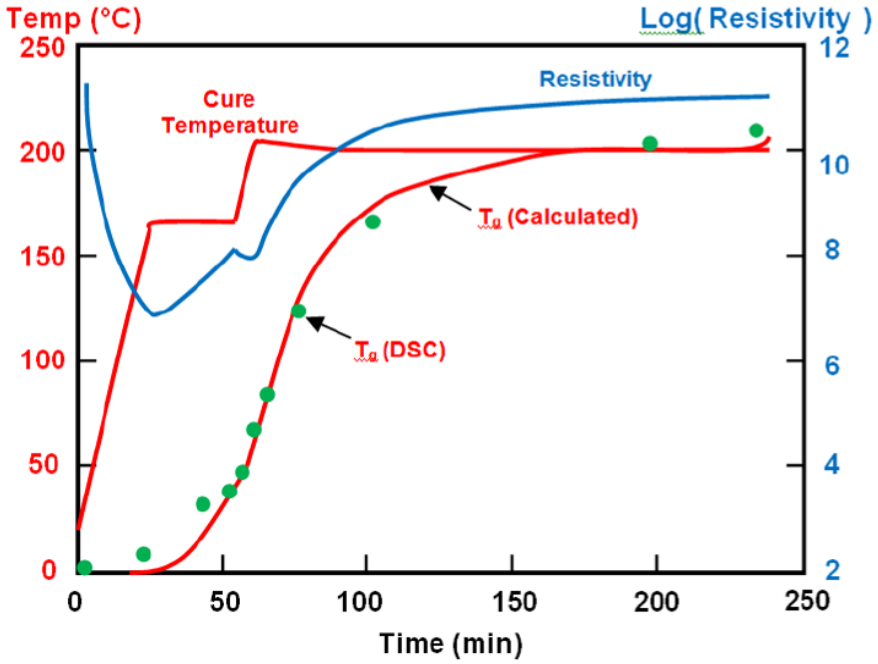


Figure 2-2
Data comparing DEA and DSC tests[1]

Glass transition temperatures from dielectric measurements come from a calculation that yields *Cure Index*, and in this case happen to overlay DSC data very well. Furthermore, the frequency independent resistivity—ion viscosity—provides information about viscosity and modulus, which DSC cannot do. Ion viscosity shows the time of minimum viscosity, the time of maximum reaction rate and the end of cure. All this information is available quickly and in real time, in contrast to the delay between process and test for DSC.

Even if DEA and DSC data do not superimpose as neatly as in Figure 2-2, a direct correspondence still exists between DEA and DSC measurements. One can use dielectric cure monitoring to very quickly evaluate the progress of cure under given conditions, change those conditions, observe the result and change conditions again as often as necessary. Sample preparation for DEA is very simple—apply material to a sensor and heat it. After using DEA for rapid iterations to reach a final formulation or process, *then* DSC can verify thermal-physical properties, saving time, effort and expense.

Dynamic mechanical analysis

Dynamic Mechanical Analysis is a second common technique for studying thermoset cure. Depending on the operating mode, DMA can measure certain moduli for either the early part of cure or the later part of cure. DMA is a direct measure of mechanical properties such as viscosity or modulus, but a single mode usually does not work for the entire cure. Furthermore, some DMA methods require careful sample preparation for consistent results.

Dielectric cure monitoring can supplement DMA because ion viscosity is often directly proportional to the change in viscosity before gelation and to the change in modulus after gelation. Note that DMA can detect gelation but DEA cannot. Gelation is a mechanical phenomenon due to the onset of crosslinking. Although a rapid increase in ion viscosity coincides with the increase in viscosity that accompanies crosslinking, no distinct electrical event occurs at this time.

With proper frequency selection, DEA can measure electrical properties that directly relate to mechanical properties during the entire cure. In fact, the overlap between DEA and DMA data is generally recognized, and at least two major manufacturers of thermal analysis instruments offer combined DMA-DEA test cells. Simultaneous DMA-DEA tests extend the portion of cure during which mechanical properties can be measured or inferred.

Again, dielectric cure monitoring may be used to easily evaluate preliminary formulations or processes, allowing rapid iterations to achieve a desired result. At the end of development, DMA can then verify mechanical properties.

DEA in the process development cycle

DEA, DSC and DMA each measures different material properties. DEA does not replace either DSC or DMA, but instead compliments them. In R&D or process development, DEA has the advantage of very simple sample preparation and the ability to make measurements during the entire cure in real time. Dielectric cure monitoring can accelerate R&D by deferring the need to make laborious DSC or DMA tests until near end of development.

Dielectric analysis or cure monitoring requires a sensor that is in good contact with the material under test. If the sensor is reusable, it is typically embedded in a platen or mold, which has the advantage of reducing long-term costs over many thousands of tests. If the sensor is disposable, the material is placed on the sensor and after the test everything is either stored for purposes of documentation or thrown away. After connecting the sensor to dielectric

measurement instrumentation, software controls the measurement process—acquiring, storing and processing the data. If necessary, the material is compressed for good contact with the sensor and then heated to initiate cure.

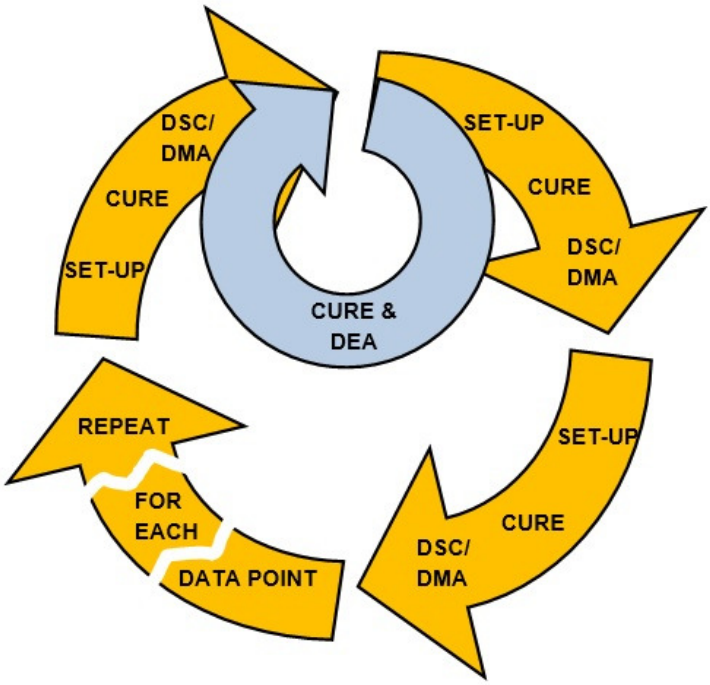


Figure 2-3
Dielectric Analysis (DEA) enables rapid feedback in the process development cycle

DEA has the advantage of allowing material tests in a wide variety of conditions, both in the laboratory, the QA/QC bench or the manufacturing floor. No other method has this versatility. Dielectric cure monitoring may be performed in an oven, on a hot plate, in a press or mold, in an autoclave or in an actual part being developed or manufactured. When embedded in a part or a large mass of material, the dielectric sensor can directly measure the effect of an exotherm on the rate of cure.

In contrast, DMA is confined to a laboratory. If the sample is liquid, it must be tested in a special cell or impregnated in a matrix of some kind. If the sample is solid, it must be prepared with a specific geometric configuration. DSC is similarly limited to a laboratory, and the sample confined to a tiny DSC pan.

DEA in manufacturing

During the manufacture of composites, parts are typically cured using a fixed recipe for temperature and time. This process can be compared to baking a cake at 175 °C for 30 minutes—at the end of that time the cake might or might not be done. The baker must stick a toothpick into the cake to test it. If the cake is not done then it must stay in the oven and be tested again later. If testing the cake is not possible, the only choice is to bake it longer, maybe for 60 minutes—but then it might burn.

DEA is currently is most often used to confirm that parts are made consistently. For example, the nominal cure of an automobile body panel made of sheet molding compound (SMC) might look like Figure 2-4. By comparing characteristic features of the curve, known as *Critical Points*, the cure of every panel can be judged against this nominal curve. Results for each panel can be recorded for statistical quality control (SQC). Deviations beyond defined limits indicate that something in the curing process has drifted and information from the cure is available to correct the problem. Thus, part quality is assured.

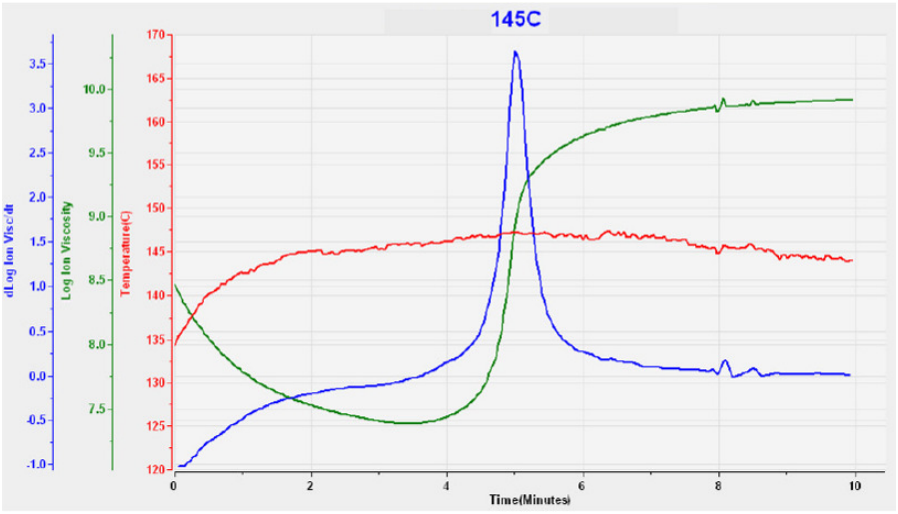


Figure 2-4
Typical sheet molding compound (SMC) cure

For highly critical parts such as composite aircraft or spacecraft components, every step in manufacturing is documented, both to record that the part is made according to specification and for analysis in the event of failure. Many manufacturers measure temperature of the part as a very indirect and inaccurate way to infer the progress of cure. DEA, however, measures ion viscosity, which is a sensitive probe of cure state. So dielectric cure monitoring is valuable for documentation because no other technique can observe cure state in manufacturing and in real-time.

Closed loop process control

Related to productivity is the possibility of closed loop process control. The cure profile of a thermoset or composite varies with temperature and the time to end of cure decreases with increasing temperature—expected behavior for a thermally driven reaction.

One study of closed loop process control used the hardware of Figure 2-5 at a company that manufactures commercial SMC products.

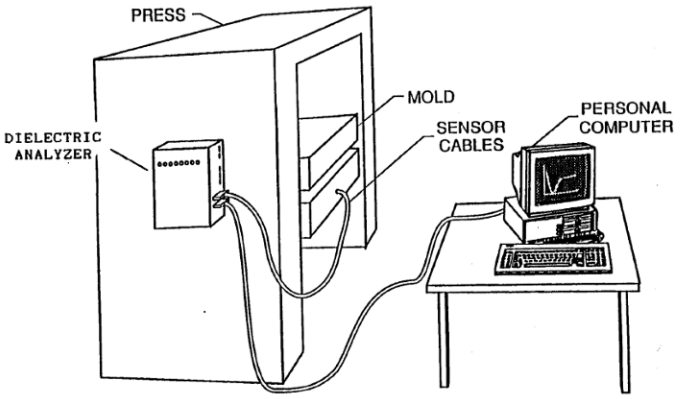


Figure 2-5
Closed-loop process control with dielectric cure monitoring[2]

Manufacturers of molded thermosets use timers to determine when products are cured and may be removed from a press. This standard practice must allow for normal variation in process temperature and other factors that affect cure. To be conservative, demold time is chosen to guarantee that all parts are good, with the result that some parts may be cured longer than necessary. Over many thousands of parts, the use of timers wastes considerable time, effort and productivity.

In this study a reusable dielectric sensor was embedded in the lower mold of a 2000-ton press. The sensor was coated with mold release before each charge of SMC was loaded. Then the press was closed. Upon detecting end of cure, the dielectric cure monitor automatically issued a signal to open the press.

Figure 2-6 shows the distribution of cure time during production of about 1000 parts. A fixed timer setting would have been 60 seconds to ensure 100% good parts. In comparison, closed loop control with dielectric cure monitoring reduced average press cycle time to 50 seconds.[2] This 10 second reduction would have saved $70,000/year/press in labor costs alone.

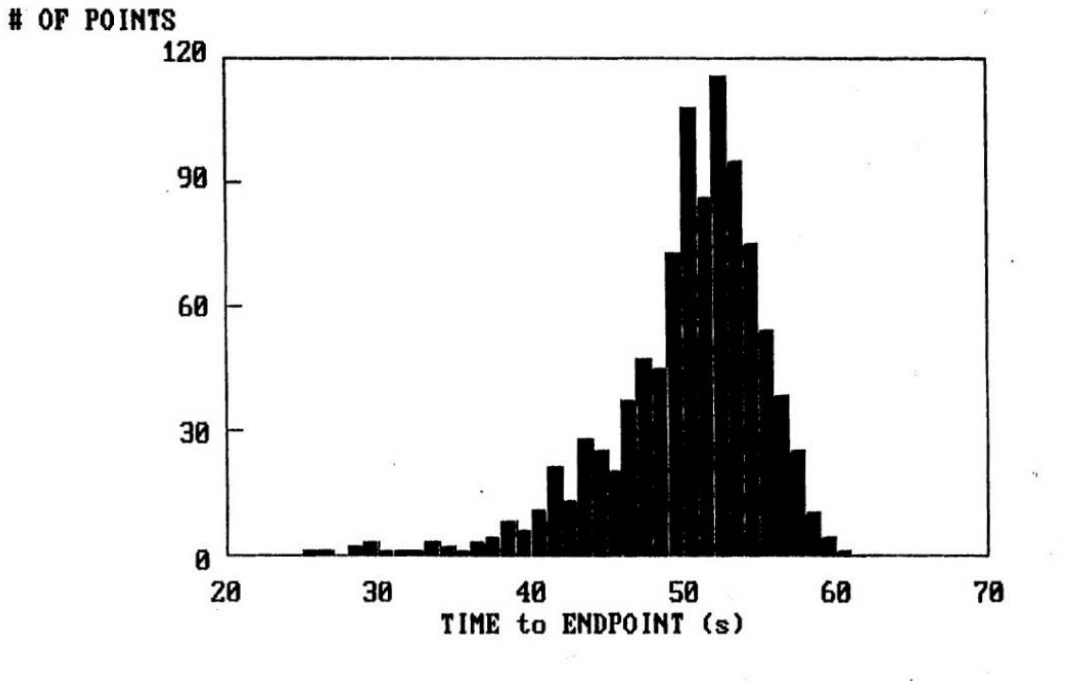
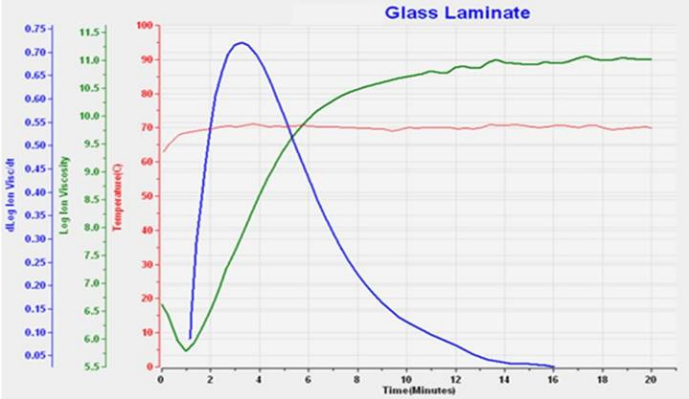


Figure 2-6
Distribution of SMC cure time for 1000 parts[2]

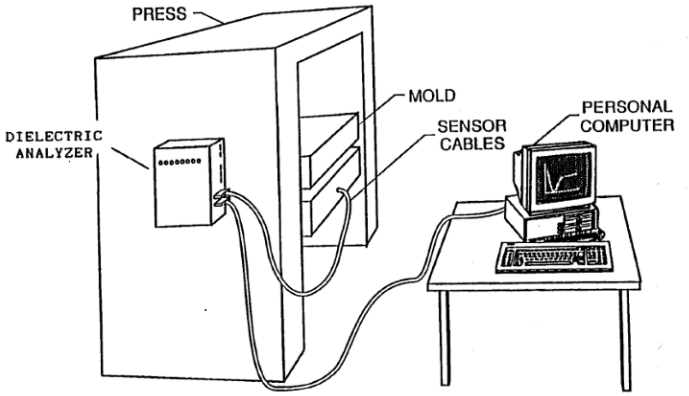
A convergence of cure monitoring technologies

For large composite structures, such as a wind turbine blade, bridge beam or an aircraft fuselage, DEA-based closed-loop control is on the verge of becoming a reality. Two critical technologies of a large scale, closed-loop control heating system have existed for decades: dielectric cure monitoring, commercialized in the 1980s, and the demonstration of closed-loop molding control with dielectric cure monitoring in 1992.[2]

Most recently, Spirit AeroSystems of Wichita, Kansas developed the third critical technology: an intelligent, multi-zone heated tool that replaces an autoclave.[3] This tool allows complete control of the curing process with real-time monitoring and feedback, adjusting cure time for individual segments of a part—depending on its geometry and thermal requirements—and reducing cycle times, cutting production costs and decreasing energy use. Although the Spirit AeroSystems tool uses temperature for control information, it is only a small step to incorporate dielectric measurements for feedback about material state.



a. Dielectric cure monitoring (ca. 1980)



b. DEA closed loop feedback control (1992)[2]

c. Intelligent control of multi-zone heating (2018)[3]

Figure 2-7
Technologies for closed-loop control in the production of large structures

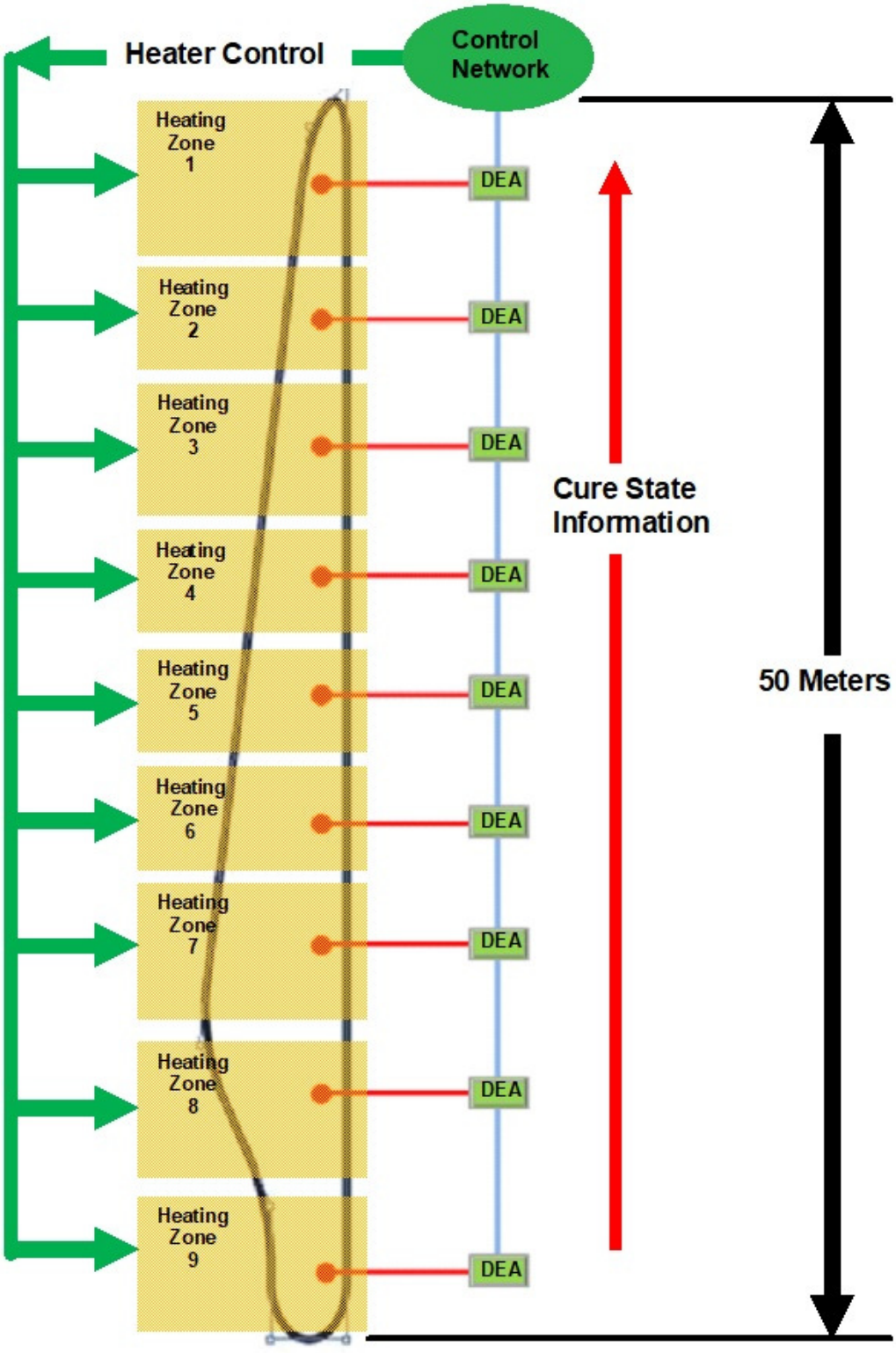


Figure 2-8

Distributed DEA for closed loop process control
(Wind turbine blade manufacture)

The convergence of these technologies comes at a time when the development of larger and larger wind turbine blades is crucial to the rapidly growing renewable energy sector. These blades, often more than 50 meters long, are fabricated in a mold. The thickness of the blade, the exotherm and the thermal environment vary along its length. Consequently, widely spaced locations cure at different rates. Manufacturers must use trial and error to determine the optimum demold time. Removing a blade too soon can damage it because of insufficient stiffness, and removing a blade later than necessary reduces throughput.

Dielectric sensors installed in the mold at strategic locations—every five meters along its length, for example—can determine when cure along the entire part has reached a desired point. Only at that time would the wind turbine blade be removed from its mold.

With the use of independent heaters and distributed DEA instruments, as in Figure 2-8, like the Spirit AeroSystems tool, dielectric measurements would allow a closed-loop control system to adjust heating so the entire structure cures at a uniform rate for optimum throughput. As a benefit, if a factory ships even as little as one more blade a week, or reduces scrap by one blade a week, profitability increases.

Dielectric cure monitoring is a simple electrical measurement that requires minimal sample preparation or skill to perform. In addition, the same sensors and measurement techniques may be used in research, quality control and manufacturing applications. Dielectric analysis correlates with measurements from more conventional laboratory tests, such as differential scanning calorimetry or dynamic mechanical analysis. As a result, DEA can act as the "go between" that brings information from the research lab to the manufacturing floor, and from the manufacturing floor to the manager responsible for product quality.

References

1. Day, D.R., *Dielectric Properties of Polymeric Materials*, Micromet Instruments, (1988). (Figure has been redrawn for clarity)

2. Day, D.R. and Lee, H.L., "Analysis and Control of SMC Part to Part Variations," Session 13-C of *Proceedings of the 17th Annual Conference, Composites Institute, the Society of the Plastics Industry, Inc., Feb 3-6, 1992*.

3. Spirit AeroSystems, "Spirit AeroSystems Develops New Composites Manufacturing Technology," Press release, Dec 14, 2017. https://www.spiritaero.com/release/136953/spirit-aerosystems-develops-new-composites-manufacturing-technology

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