Insight — Technical Overview 2.00
Applications of Dielectric Cure Monitoring

Introduction

When working on a new thermoset, 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 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.

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 1 shows T_g measured with DSC and compared with results from dielectric cure monitoring.

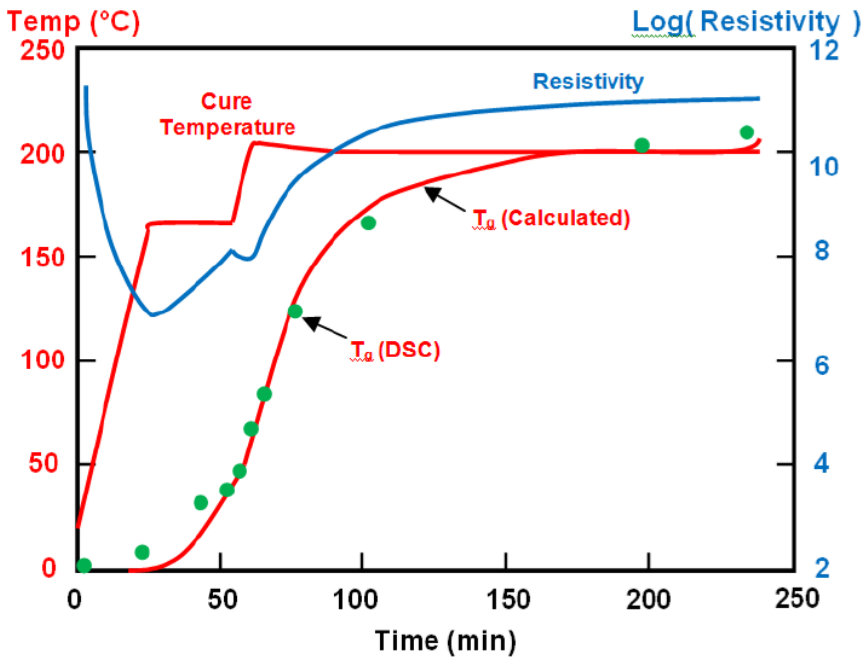

Figure 1
Data comparing DEA and DSC tests[1]

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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.

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 1, 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

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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.

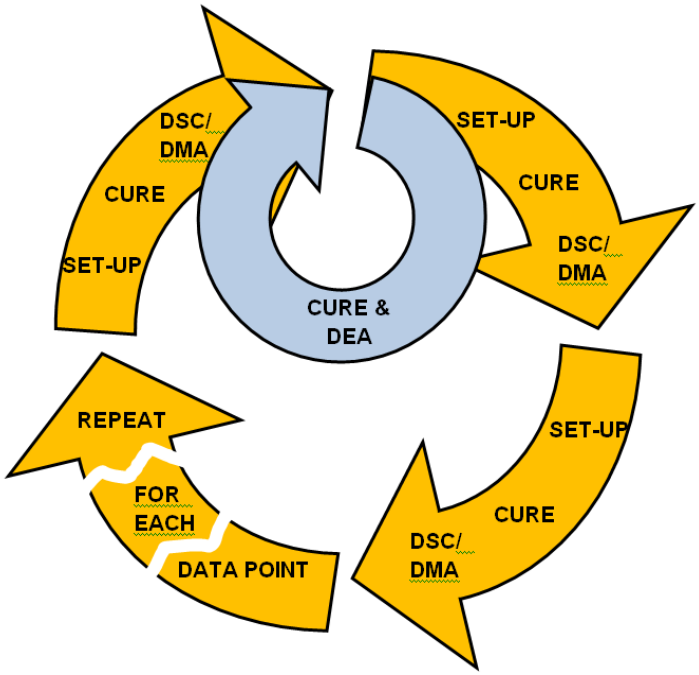

Figure 2
Dielectric Analysis (DEA) enables rapid feedback in the process development cycle

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

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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.

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.

Ion Viscosity Behavior During Cure

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

Although viscosity becomes immeasurable at gelation, ion viscosity continues to provide useful information, and is often proportional to the change in modulus after gelation. As a result, DEA is useful for following material state through the entire cure.

A thermoset cures when monomers react to form polymer chains then a network. The reaction is usually exothermic—generating heat—or is driven by the heat of a press or oven. Mechanical viscosity and ion viscosity typically follow curves like those of Figures 3 and 4. Initially, mechanical viscosity decreases as temperature increases and the material softens or melts. Ion viscosity also decreases as mobile ions experience less resistance to movement. At this point the reaction is still slow.

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Mechanical viscosity reaches a minimum—a point of zero slope—when the accelerating reaction dominates and the material becomes more viscous. Ion viscosity reaches a minimum at about the same time then increases due to chain extension, which presents a greater and greater impediment to the flow of ions.

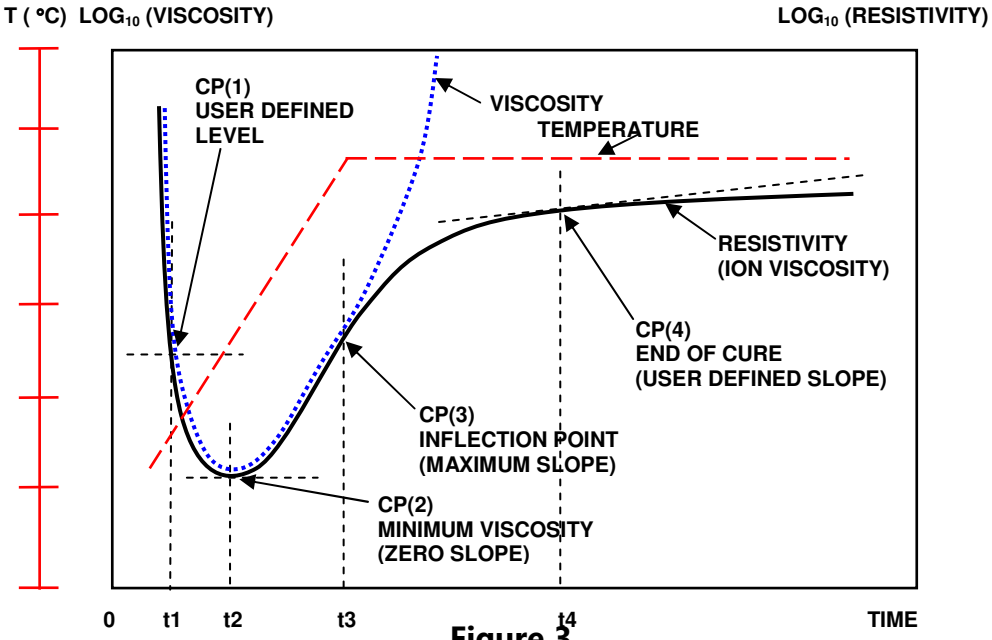

Figure 3
Mechanical viscosity and ion viscosity in a curing thermoset

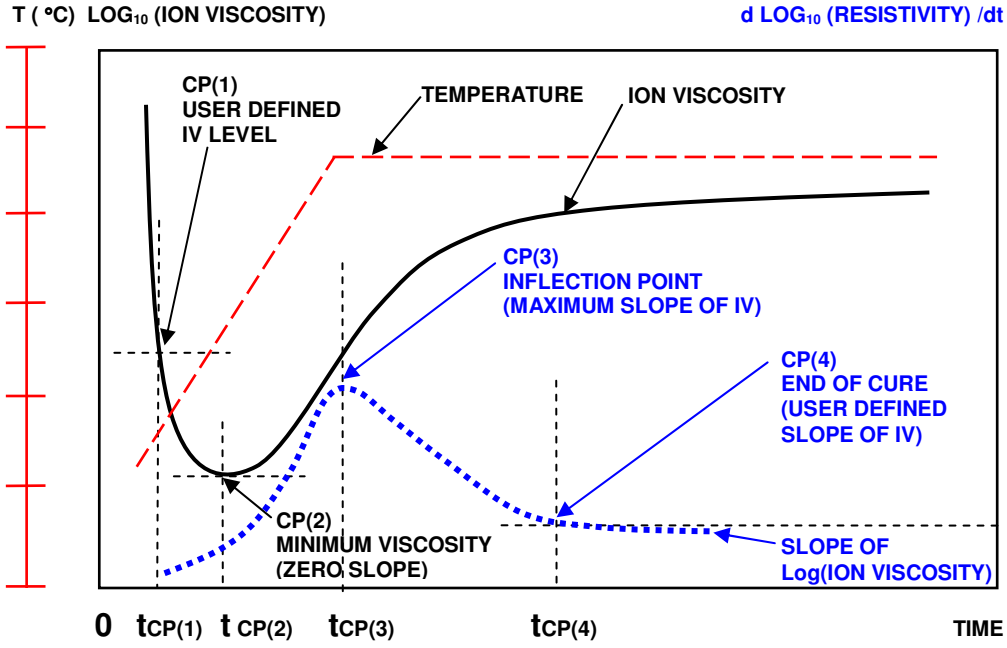

Figure 4
Ion viscosity, slope and Critical Points in a curing material

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Eventually the reaction slows and mechanical viscosity becomes immeasurable at the gel point. Around this time ion viscosity is no longer proportional to mechanical viscosity. Ion viscosity continues to change, but more and more slowly, approaching a limit at the end of cure.

Four Critical Points, which identify particular events, characterize the cure of a thermoset:

- **Critical Point 1—CP(1)—Onset of flow**
  - Ion viscosity passes a user defined level
  - Indicates material has reached the sensor
- **Critical Point 2—CP(2)—Minimum viscosity**
  - Ion viscosity reaches minimum
  - Hardening from cure overcomes softening from temperature increase
  - Approximately same time as minimum mechanical viscosity
- **Critical Point 3—CP(3)—Maximum slope**
  - Slope of ion viscosity reaches maximum
  - Ion viscosity inflection point
  - Point of maximum reaction rate
  - Associated with gelation but not indicating gelation
- **Critical Point 4—CP(4)—Critical slope**
  - Slope of ion viscosity reaches user defined value
  - Chosen slope represents degree of cure that depends on application
  - Can identify end of cure

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 5. By extracting and comparing Critical Points, the cure of every panel can be judged against this

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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.

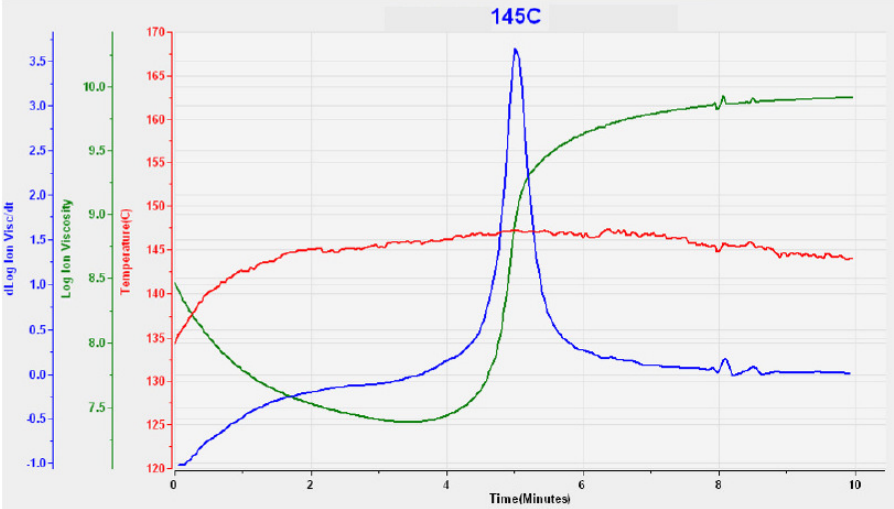

Figure 5
Typical sheet molding compound (SMC) cure

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.

Productivity in manufacturing can benefit most immediately from dielectric cure monitoring, especially for high value components like wind turbine blades. These blades, often more than 50 meters long, are fabricated in a mold. The thickness of the blade, which affects the exotherm, and the rate of cure both vary along its length. Manufacturers use experience and guesswork to determine cure time before removing the blade from its mold. But removing a blade too soon can cause cracks because it is not stiff enough, and removing a blade later than necessary reduces throughput.

Dielectric sensors could be installed in the mold at strategic locations, or perhaps every five meters along its length, for example. Dielectric cure

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monitoring can determine when cure along the entire part has reached a desired point, and only at that time would the wind turbine blade be demolded. As a result, if a factory ships even as little as one or two more blades a week, profitability increases.

Closed loop process control

Related to productivity is the possibility of closed loop process control. Figure 6 shows how Critical Points vary with temperature for the sheet molding compound of Figure 5. As expected, the time to end of cure, CP(4), decreases with increasing temperature.

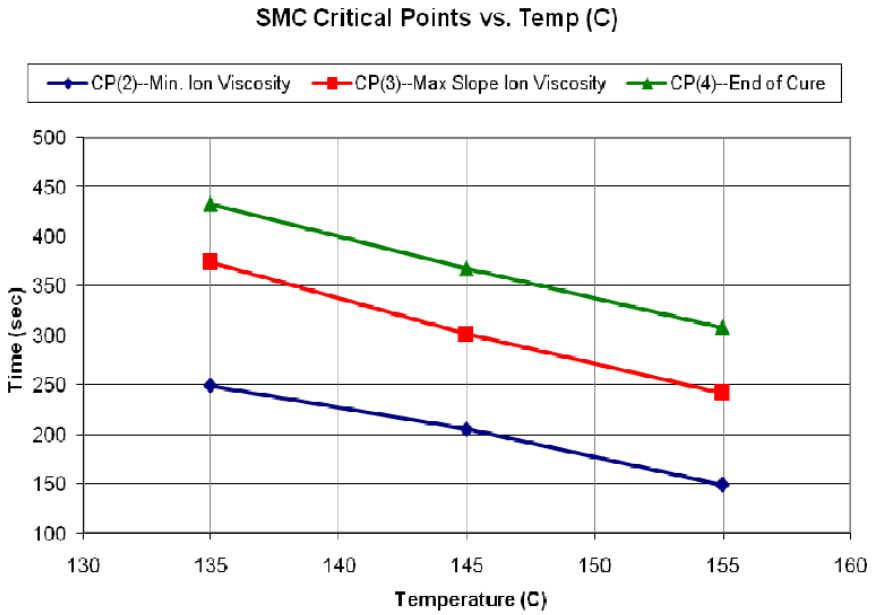

Figure 6
Variation of Critical Points with temperature

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.

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One study of closed loop process control used the hardware of Figure 7 at a company that manufactures commercial SMC products. A reusable dielectric sensor was embedded in the lower mold. The sensor was coated with mold release before each charge of SMC was loaded. Then the 2000-ton press was closed. Upon detecting end of cure, the dielectric cure monitor automatically issued a signal to open the press.

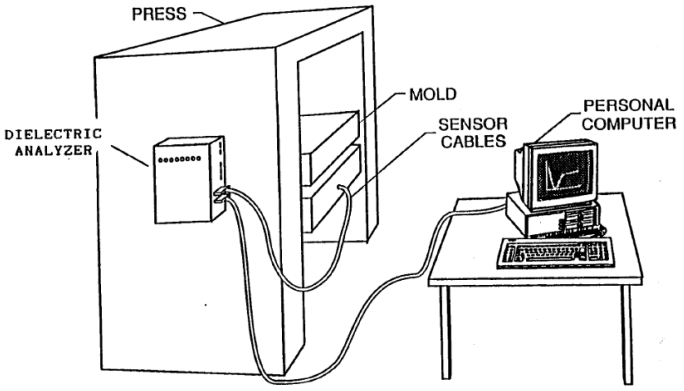

Figure 7
Closed-loop process control with dielectric cure monitoring[2]

Figure 8 shows the distribution of cure time during the 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.

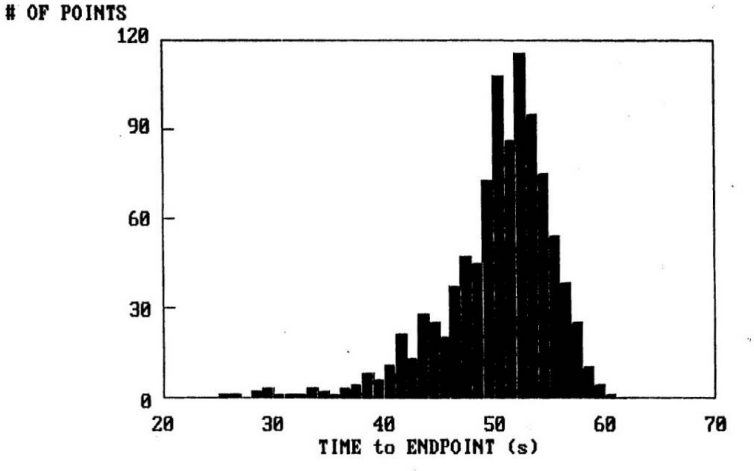

Figure 8
Distribution of SMC cure time for 1000 parts[2]

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In large composite structures, such as a wind turbine blade, bridge beam or an aircraft fuselage, different locations cure at various rates because of differences in thickness and thermal environment. If sections of a large part have independent heaters, then dielectric measurements can provide feedback for a control system. This system can adjust temperatures so all sections cure at a uniform rate for optimum throughput.

Conclusion

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*.

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