Automated Method for Characterizing Temperature Dependent Dielectric Materials

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Abstract

Among the various methods to accelerate curing thermoset polymers, such as epoxy, involves the use of radio frequency (RF) fields. In this, the polymer precursor materials are placed in a microwave reactor, high power RF fields are introduced, and the electrical (or for that matter, magnetic) loss mechanisms convert the RF power to heat and therefore inducing curing. One of the most challenging aspects of such curing methods lies in the fact that the materials being cured undergo chemical change during the process. This results in a time-dependent change in the electrical properties of the materials. It is therefore important to have accurate data on the material's electrical properties as a function of both temperature and extent of cure. This paper describes an apparatus designed to facilitate such measurements.

Keywords: Measurement Systems, Material Measurements, RF Polymers, Thermoset Polymers.

1. Introduction

Polymers are typically categorized in a variety of ways. One of the simplest is: thermoplastic vs. thermoset polymers. A thermoplastic polymer is one that has it polymer chains already formed and can be re-melted any number of times. Examples of common thermoplastic materials are polycarbonate – used in eyeglasses – and high density polyethylene – used in many beverage containers. Thermoset polymers on the other hand form their polymer chains during processing and cannot be re-melted once formed. Perhaps the most common example of a thermoset material is epoxy.

Curing thermoset materials can be accomplished in many ways. For example, a curing agent can be mixed with the polymer precursor. For example, epoxy adhesive that can be purchased in hardware stores use this approach as does common fiberglass epoxies. The role of the curing agent is to initiate the curing process, in effect, act as a catalyst. During processing, heat is often produced and the material undergoes a chemical change. A measure of this composition change is termed the extent of cure (X) expressed as a percentage. Zero percent indicates that no curing has occurred while 100% means that the polymer has completed its curing.

As these materials cure, they undergo a compositional change that results in a change in permittivity (for this paper, only non-magnetic materials are considered). It is important to characterize these materials as a function of both the temperature and extent of cure to properly design a curing process. It has been shown that the curing process has an impact on the various properties of such polymers. A review of such issues is given in [1]. Achievement of a reproducible and high quality cure often requires accurate knowledge of the dielectric properties of the material during the process.

In this paper, a method for measuring the complex permittivity of such materials is presented. In particular, the apparatus designed and built at Michigan State University allows for more rapid and accurate measurements in addition to simplifying the procedure. First, a description of the dielectric properties of a common thermoset system is described.

2. Permittivity of DEGBA/DDS

An industrially significant epoxy system is DGEBA (diglycidyl ether of bisphenol A, DER332 from DOW)/ DDS (diaminodiphenyl sulfone, TCI America). The chemical representation of DGEBA is shown in Figure 1.

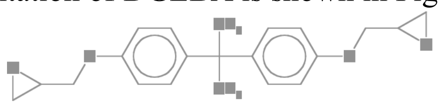

Figure 1. Chemical structure of DGEBA.

while the structure for DDS is shown in Figure 2.

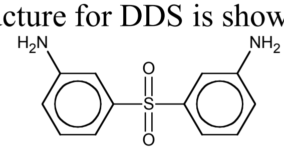

Figure 2. Chemical structure of DDS.

This system is also one that is fairly well-understood – e.g. the thermal, mechanical, and chemical properties -- and hence makes a good system for study. It is instructive to consider the processing techniques involved in using RF fields for cure-enhancement. It is important to characterize the permittivity of this system during cure. Below is a description of the process.

In preparing neat epoxy resins, stoichiometric DGEBA and DDS (2.79:1 by weight) were mixed in a glass beaker. The mixtures were well stirred by hand in a 130°C oil bath until the DDS was completely dissolved (in approximately five minutes). Finally, the resins were degassed at 0.02 bar at 100°C for five minutes.

A single frequency field applicator was used along with cavity perturbation theory to heat epoxy resins and assess their dielectric properties. The cavity is shown in Figure 3.

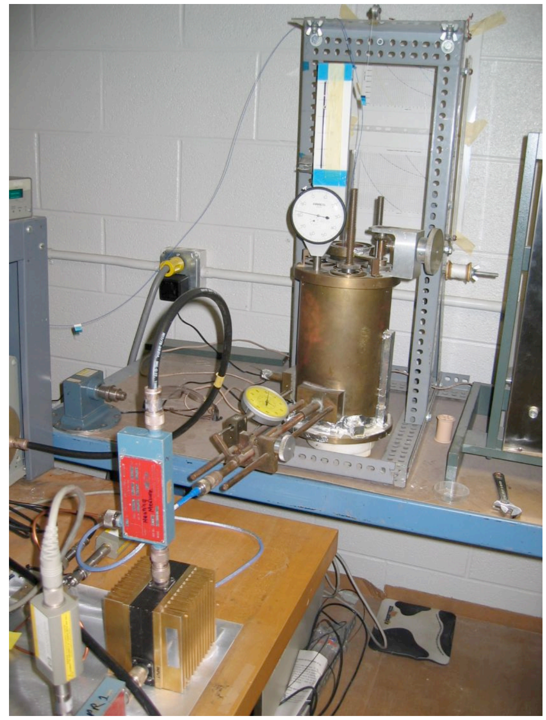

Figure 3. Illustration of the single-mode cavity. The switch system is in the lower-left corner of the figure.

Note that it is adjustable so that it can be tuned to be resonant as the load changes its dielectric properties. In this, the loss present in the material being processed is used to convert microwave power to heat. As can be seen in Figure 5, this loss term can be significant. The high-power excitation is shunted away from the processing cavity and a sweep generator/oscilloscope is connected to utilize the cavity perturbation method for evaluating the dielectric properties of the sample. After a quick measurement, the high-power port is re-connected and the sample is heated further to measure the material's properties at a higher frequency. Details of experimental equipment can be found in [2]. Next, the specific procedure for the samples presented herein is given.

The degassed epoxy resins were poured into a Teflon holder. The Teflon holder with a fluoroptic probe was located at the position of the highest electric field for the TM_{012} cavity mode at 2.45 GHz. The fresh samples were heated to react at 145°C for specified reaction time periods, e.g. 1, 5, 20, and 100 minutes, with the exception of those for the 0% cured epoxy resin, which were heated to 100°C. Thereafter, the single frequency microwave curing system was switched to become a low-power swept frequency diagnostic system. Measurements of temperature and dielectric properties using the swept frequency method [3-6] were made during free convective cooling of the samples. The cooled samples were analyzed with a Differential Scanning Calorimeter to determine the residual heat of reaction per gram and the extents of cure for the samples.

An example of the measured properties for the DGEBA/DDS system is given in Figures 3 and 4 (presented previously in [7]). The data in Figures 3 and 4 represent average values over a number of data gatherings to minimize random errors. Collection of such data is manual. Indeed, it involved physically swapping the high-power port with the low-power oscilloscope port. This is a time-consuming process resulting in relatively few data points. In a recent paper, the collection of this data was used to identify the relaxation mechanisms for this polymer system [7] as well as a model for the permittivity as a function of the temperature and extent of cure. Such a model can be used to improve the processing techniques being developed at MSU.

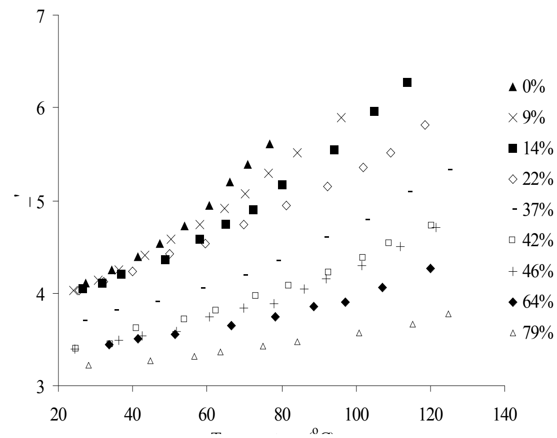

Figure 4. Dielectric constant vs. temperature and extent of cure for DGEBA/DDS at 2.45 GHz.

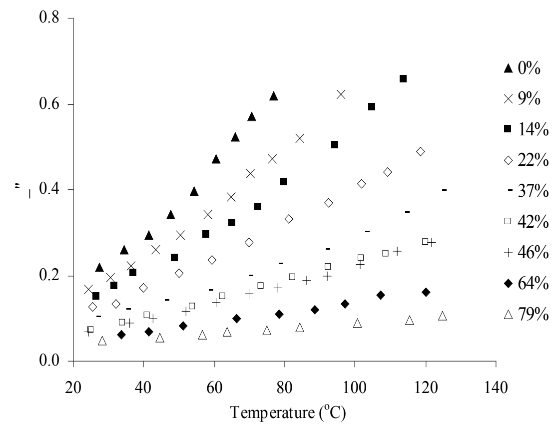

Figure 5. Dielectric loss term vs. temperature and extent of cure for DEGBA/DDS at 2.45 GHz.

3. Automated Apparatus

To reduce the tediousness, and to improve accuracy, a microwave switch system was developed at Michigan State to automatically switch between the high power source and the sweep generator/oscilloscope. This switch system is composed of two small RF switches, including a PIN diode switch, and a mechanical coaxial transfer switch. When the high-power source is shunted away from the single-mode cavity, the power from the source is dumped into a coaxial matched load through the coaxial transfer switch. The low power sweep generator is then fed into the cavity through the coaxial transfer switch. Using the PIN diode switch, the reflected power from the cavity is then fed into a diode detector connected to the Y axis of an oscilloscope. The scope is then used in conjunction with the sweep generator to display resonant frequency. The dielectric properties of the material are then determined using this information displayed on the oscilloscope. An illustration of the switch system is shown in Figure 6.

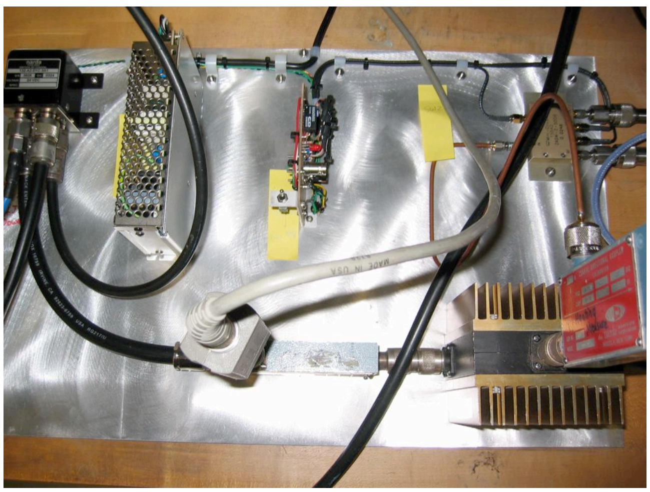

Figure 6. Illustration of the microwave switch system.

Near the center of Figure 6, toggle switch is used to control the device. Alternatively, the switch system has been designed for interface with a computer running LabView.

To demonstrate that the switch system is functioning properly, a DEGBA sample was tested both using the switch system and via the traditional manual operation. Figures 7 and 8 illustrate the comparison between manual measurement and measurement using the switch system. Note that in these, the manual measurements were made a number of times and averaged to remove random experimental bias. At the time of this submission, only a single experiment using the switch system was possible, and so there is some difference due to not averaging the results. Nevertheless, the trends are clearly present and indicate that the switch system is functioning properly.

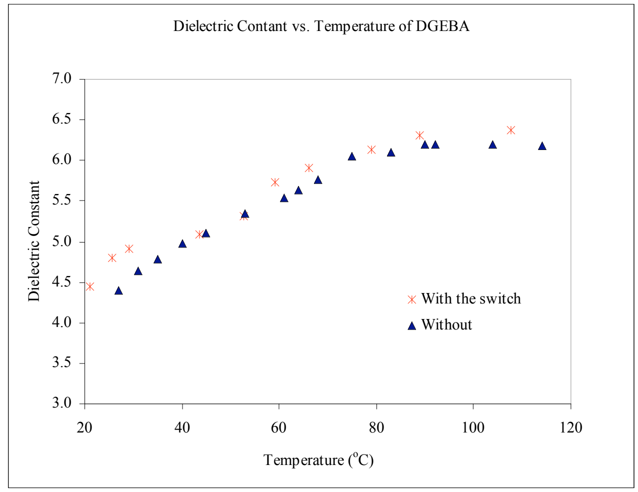

Figure 7. Dielectric constant for DGEBA as measured manually and with the microwave switch system.

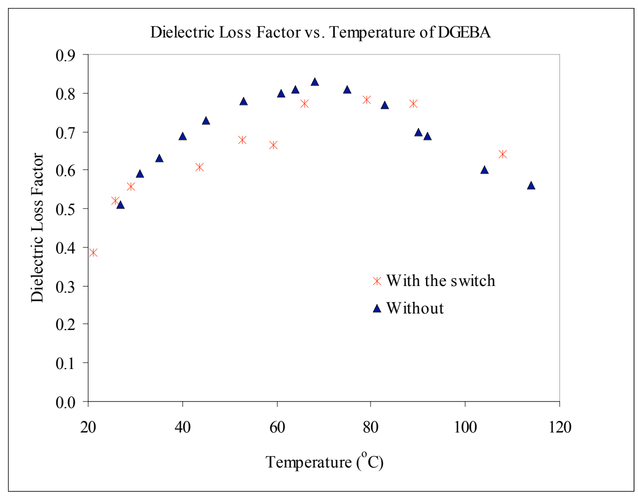

Figure 8. Dielectric loss term for DEGBA as measured manually and with the microwave switch system.

4. Conclusions

In this paper, a description of one method for characterizing the dielectric properties of a thermoset polymer during cure is presented. In this, a high-power microwave source is used to excite a single-mode cavity applicator. The loss mechanism associated with the thermoset precursors is used to convert the RF power to heat. This heat then causes a compositional change, thereby modifying the dielectric properties of the material being cured. These dielectric properties are measured using a sweep generator and an oscilloscope using time honored cavity perturbation methods.

This paper introduces a microwave switch system that takes the place of manual switching. The effect is a more simple and reliable measurement as well as greater efficiency. A more detailed description of the switch system will be given at the meeting.

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References

1. L. Zong, S. Zhou, N. Sgriccia, M.C. Hawley, L.C. Kempel, "A Review of Microwave-Assisted Polymer Chemistry (MAPC)", *J. Microwave Power and Electromagnetic Energ.,* **38** (1), p.49 (2003).
2. J. Jow, Ph.D. Thesis, Michigan State, East Lansing, MI, 1988.
3. J. Slater, *Rev. Mod. Phys*., 18, p. 441ff, 1946.
4. R.F. Harrington, Time Harmonic Electromagnetic Fields, IEEE Press, 2001.
5. A. Parkash, J.K. Vaid, and A. Mansingh, "Measurement of Dielectric Parameters at Microwave Frequencies by Cavity Perturbation Technique", *IEEE Trans. Microwave Theory and Techniques*, 27, p. 791ff, 1979.
6. O. Klein, S. Donovan, M. Dressel, G. Gruner, "Microwave Cavity Perturbation Technique: Principles/Applications", *Intl. J. of Infrared and Millimeter Waves*, 14, pp. 2423-2517, 1993.
7. L. Zong, S. Zhou, R. Sun, L.C. Kempel, and M. Hawley, “Dielectric analysis of a crosslinking epoxy resin at a high microwave frequency,” J. Polymer Science Part B: Polymer Physics, 42, pp. 2871-2877, 2004.