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Simultaneous dynamic mechanical analysis and dielectric analysis of polymers[1]

David D. Shepard[a,*], Benjamin Twombly[b]

[a] Micromet Instruments Inc., 7 Wells Avenue, Newton Centre, MA 02159, USA
[b] The Perkin-Elmer Corporation, 50 Danbury Road, Wilton, CT 06879, USA

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Abstract

Dynamic mechanical analysis (DMA) and dielectric analysis (DEA) measurements were made simultaneously in a Perkin-Elmer DMA 7e connected to a Micromet Instruments Eumetric System III Microdielectrometer. Simultaneous DMA-DEA experiments were performed during the non-isothermal cure of an epoxy-glass prepreg. The results showed the techniques to be complementary. DMA provided gel point and vitrification information while DEA provided relative viscosity change, rate of reaction, and was highly sensitive to the end of reaction. The gel and vitrification points identified by DMA were correlated to the DEA data.

Keywords: DMA; Dielectric analysis; Epoxy-glass prepreg

1. Introduction

Dynamic mechanical analysis (DMA) and dielectric analysis (DEA) are two thermal analysis techniques commonly used to study the processing behavior of polymers. The use of both DMA and DEA in monitoring the curing process of thermosetting resins is well documented [1–4]. DEA is of a particular advantage in the monitoring of thermoset cure because the measurements can be made in processing environments such as ovens, presses, and autoclaves. This allows DEA to be used as a production monitoring and control tool as well as for laboratory studies. The versatility of DEA has led to previous studies on correlating the physical properties of thermosetting resins with the DEA re-

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* Corresponding author.

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sponse [5]. Correlations with other techniques determined through simultaneous measurements are preferred because they eliminate outside variables and can be made more efficiently. Simultaneous DEA measurements with other techniques have been made in a rheometer to correlate the DEA response with actual polymer viscosity [6] and in a DSC cell to correlate with degree of cure [7]. Simultaneous dynamic mechanical analysis and dielectric analysis (DMA-DEA) allows mechanical properties measured through DMA to be correlated with the dielectric properties measured through DEA.

DMA and DEA are complementary techniques in that they measure similar properties, but in different ways so that each can provide information that the other cannot. For example, in curing systems, gelation is not easily identified through DEA but DMA is a good indicator of gelation. Conversely, DMA is not very sensitive to the end of reaction while DEA is extremely sensitive in this area. The ability of the two techniques to provide complementary information about polymer behavior is a result of the fundamental nature of each technique. In DEA, an electrical field is applied to one electrode and the resultant current amplitude and phase lag at the other electrode are measured. The electrical excitation is a sinusoidaly varying voltage of a chosen frequency. The amplitude and phase lag of the current passing through the sample are used to calculate the permittivity and loss factor of the sample. The ion viscosity (DEA viscosity or electrical resistivity) is extracted from the loss factor data and is related to the mobility of ions in the polymer. Important information that can be obtained include relative viscosity change, cure rate, cure state, and end of cure.

In DMA, an oscillating mechanical stress is applied to the sample and the resultant amplitude and phase lag are measured. The applied mechanical stress is a sinusoidaly varying force of chosen amplitude and frequency. The resultant displacement and phase lag are used to calculate storage modulus, loss modulus, tangent delta, and viscosity. Important material properties that can be identified include flow, absolute viscosity, gel time and vitrification.

Simultaneous DMA-DEA measurements can be made because of the similarities in measuring systems between the two techniques. Dielectric measurements are classically made by placing the sample to be measured between two electrically conductive parallel plates. DMA measurements are also commonly made using a similar geometry so that simultaneous DMA-DEA measurements can be made without altering the fundamental measurement geometries of either technique. Either the parallel plate or cup and plate measuring systems can be used in the DMA to make the simultaneous measurements. It is also possible to insert a remote dielectric sensor into the DMA and perform simultaneous DMA-DEA. This paper discusses the configuration of a simultaneous DMA-DEA system and its use in studying the non-isothermal cure of a epoxy-glass prepreg.

2. System configuration

The simultaneous DMA-DEA measurements were made using a Perkin-Elmer DMA 7e Dynamic Mechanical Analyzer and a Micromet Instruments, Inc. Eumetric System III Microdielectrometer equipped with mid conductivity interface (Fig. 1). The experiments were performed in the DMA 7e using the parallel plate measuring system. A Perkin El-

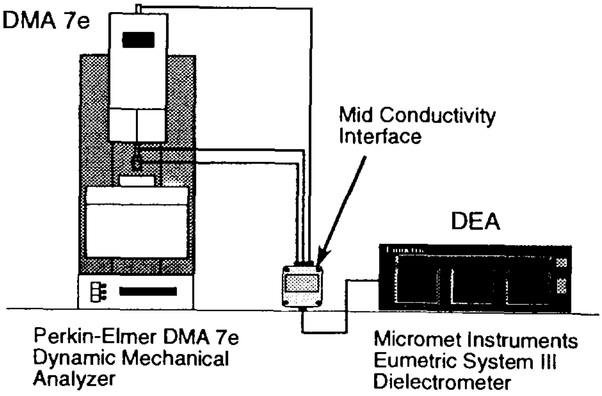

Fig. 1. Simultaneous DMA-DEA.

mer DEA Interface kit was used to modify the DMA 7e and provide the proper electrical connections to the microdielectrometer. The modifications to the DMA 7e are shown in Fig. 2 and consisted of:

(1) electrically isolating the sample tube and connecting it with the shield on the mid conductivity interface;
(2) electrically isolating the bottom plate (or cup) of the measuring system and connecting it with the excitation on the mid conductivity interface;
(3) extending the core rod and connecting it to the ground on the mid-conductivity interface.

The DMA 7e was programmed in its normal manner through the DMA 7e controlling computer using the Perkin-Elmer 7 Series/UNIX Thermal Analysis Software. The Microdielectrometer was programmed through a separate controlling computer using the

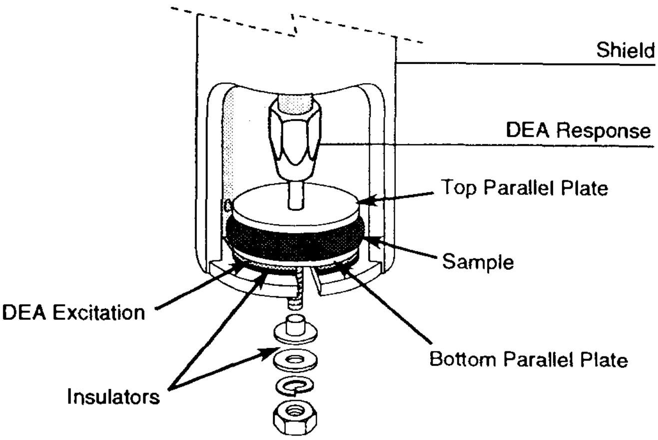

Fig. 2. DMA-DEA parallel plate geometry.

Micromet Standard Dielectrometry Package. The only interaction between the DMA 7e and the microdielectrometer was through the electrical connections to the mid-conductivity interface. This configuration allows both instruments to be operated independently when not performing simultaneous experiments. For data analysis the DMA and DEA data must be plotted separately using their respective software packages. Alternatively, the data files can be converted into an ASCII format and plotted on other software packages.

3. Experimental

A 1.1 mm thick sample of Epon 828 epoxy-glass prepreg (DGEBA-DDS) was placed in the DMA between 10 mm diameter parallel plates. A static force of 550 mN and a dynamic force of 500 mN at a frequency of 1 Hz was applied by the DMA. The DMA furnace was programmed to ramp from 23°C to 200°C at a rate of 3°C min^{-1} and hold at 200°C for 60 min. The microdielectrometer was programmed to measure the dielectric properties at frequencies of 1, 10, 100, 1000, and 10 000 Hz.

4. Results

In Fig. 3, the combined DMA storage modulus and ion viscosity data are plotted versus time during the non-isothermal cure of the Epon 828 epoxy-glass prepreg. From the start of the run to 7 min, the DMA Storage Modulus exhibited a decrease and a shoulder due to flowing of the prepreg between the parallel plates. From 7 to 41 min a continual decrease in the DMA storage modulus and ion viscosity were observed due to the decreasing viscosity of the prepreg as it was heated. Near 41 min both the DMA storage

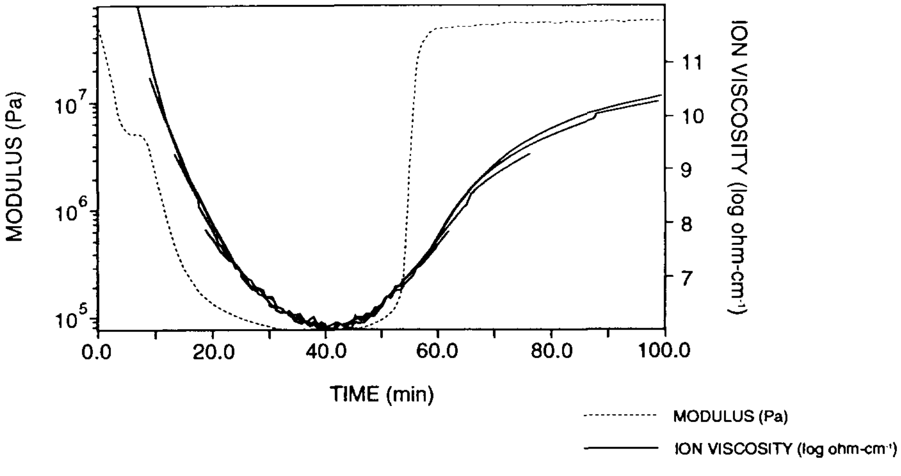

Fig. 3. Simultaneous DMA-DEA of an Epon 828 prepreg.

modulus and ion viscosity reached a minimum showing that the minimum viscosity of the resin had been reached. The DMA storage modulus curve was much flatter than the ion viscosity in the viscosity minimum region. This was caused by the DMA reaching a lower measurement limit and thus became less sensitive to the viscosity change than was the ion viscosity. Noise in the ion viscosity data in the minimum viscosity region can be attributed to the large amplitude of the parallel plate displacement significantly changing the sample thickness. This effect was not observed on thicker samples and experiments with smaller amplitudes.

At 55 min the DMA storage modulus increased sharply which is commonly defined as the gel time. The ion viscosity continually increased through this period showing the increase in viscosity and cure state of the resin. The gel point as identified by DMA occurred after the minimum in ion viscosity but before its maximum rate of increase. At 60 min the DMA storage modulus leveled indicating vitrification of the resin. This correlated well with the maximum rate of increase in the ion viscosity. After leveling, the storage modulus was insensitive to further cure of the resin. The ion viscosity continued to increase rapidly showing it was highly sensitive to the reaction that occurs after vitrification.

5. Conclusions

Simultaneous DMA-DEA measurements were made by connecting a Perkin-Elmer DMA 7e with a Micromet Eumetric System III Microdielectrometer. The measurements were made in the DMA using the parallel plate measuring system. The simultaneous DMA-DEA measurements provided a fast, efficient method to completely characterize the curing of an epoxy-glass prepreg in a single experiment. The DMA data identified gelation and vitrification of the resin which are important events during the processing of thermosetting resins. These events were then correlated to the DEA data which provided continuous relative viscosity change information. The DEA data was much more sensitive to the reaction that occurred after vitrification. Since DEA measurements can also be made in processing environments, the information that simultaneous DMA-DEA provides in laboratory experiments can also be directly used in process development and production applications.

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