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DETERMINATION OF AN OPTIMUM RESIN TRANSFER MOLDING PROCEDURE USING FDEMS SENSING TECHNIQUES *

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ABSTRACT

Resin transfer molding (RTM) of three-dimensionally stitched fabrics promises to be a cost effective process for obtaining composite parts of exceptional strength. The technique eliminates many problems involving prepreg preparation, storage and layup. It replaces, on the other hand, the single step cure process with a two stage impregnation and cure process. Of particular importance therefore is selecting and controlling the viscosity during impregnation and cure. In this paper, we report on the use of in situ frequency dependent electromagnetic sensors (FDEMS) for selecting and controlling the viscosity of the RTM resin during impregnation and cure.

INTRODUCTION

Resin transfer molding (RTM) of advanced fiber architecture materials promises to be a cost effective process for obtaining composite parts with exceptional strength. The technique permits the use of three-dimensionally stitched fabrics, textile riveted plys, which significantly enhance the compression after impact strength. The technique also eliminates many problems involving prepreg preparation, storage and layup. On the other hand, it replaces the single step cure process with a two stage impregnation and cure process. As a result, of particular importance is control of the viscosity both during impregnation and cure. In situ sensors which can observe these processing properties both prior to infiltration and within the RTM tool during the fabrication process are essential.

The objective of this exploratory study was to use frequency dependent electromagnetic sensing (FDEMS) to select and control the viscosity during resin transfer molding, both in impregnation and cure. In studies of epoxies, polyimides, phenolics and unsaturated polyesters, FDEMS has been shown

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to be a convenient automated instrumental technique for in situ monitoring of the processing properties of these thermoset resins continuously throughout the cure process. FDEMS is able to monitor the progress of cure including reaction onset, point of and magnitude of maximum flow, fluidity, solvent evolution, buildup in modulus, approach to T_g, reaction completion and degradation [1–5]. These determinations are often approximate, involving multiple complex measurement techniques. Further they are often inaccurate because they are not made in situ and continuously in the process environment. FDEMS measurements are particularly useful as they can be conveniently made both in a laboratory and in situ in the tool during processing in the fabrication environment. Measurements are made continuously throughout the entire fabrication cycle. Further, FDEMS provides a convenient computerized method for recording, storing and comparing resin processing properties throughout cure. As such FDEMS can be used to evaluate and control resin properties prior to use, to provide a signature verifying the cure process during fabrication and to provide in situ sensor feedback for intelligent closed loop control of fabrication.

EXPERIMENTAL

The Dek Dyne FDEMS sensor * permits measurements of both the permittivity ϵ' and the dielectric loss factor ϵ'' in the Hz–kHz region, where ionic effects are generally observed, and in the kHz–MHz region, where dipolar effects are seen. The ability to monitor this entire frequency range and to simultaneously observe both the ionic and dipolar molecular probes is extremely valuable for in situ monitoring of the cure process.

Frequency dependent electromagnetic measurements (FDEMS) were made with Dek Dyne sensors software, and equipment available through Polymer Laboratories, Inc., Amherst, MA. Simultaneous measurements were made on several samples. Measurements at frequencies from 50 Hz to 1×10^6 Hz were taken at regular intervals throughout the cure cycle using the FDEMS sensor and were converted to the complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$.

Dynamic mechanical measurements were made using a Rheometrics RDA-700 rheometer at 1.6 Hz and used to compute the magnitude of the complex viscosity.

Measurements were made on a Shell Epon diglycidylether bisphenol A (DGEBA) resin transfer molding resin RSL 1282 with the aromatic amine curing agent 9470.

* Enquiries regarding the FDEMS sensor and instrumentation should be directed to D. Kranbuehl.

THEORY

Measurements were made of the capacitance, C, and conductance, G, using the Dek Dyne sensor. The complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was calculated from:

$$\epsilon' = \frac{C_{\text{material}}}{C_0} \tag{1}$$

and

$$\epsilon'' = \frac{G_{\text{material}}}{C_0 2\pi f} \tag{2}$$

at each of 10 frequencies between 50 Hz and 1 MHz. This calculation is possible when using the Dek Dyne sensor whose geometry independent capacitance, C_0, is invariant over all measurement conditions.

Both the real and the imaginary parts of ϵ^* can have an ionic and a dipolar component [1,6]. The dipolar component arises from restricted diffusion of bound charge of molecular dipole moments. The dipolar term is generally the major component of the dielectric signal at high frequencies and in highly viscous media. The ionic component often dominates ϵ^* at low frequencies, low viscosities and/or higher temperatures.

Analysis of the frequency dependence of ϵ' and ϵ'' or C and G in the Hz–MHz range is, in general, optimum for determining both the ionic mobility conductivity, σ, and a mean dipolar relaxation time, τ. These two parameters are directly related on a molecular level to the rate of ionic translational diffusion and dipolar rotational mobility and thereby to changes in the molecular structure of the resin which reflect the reaction rate, changes in viscosity-modulus and the degree of cure.

DISCUSSION

Figure 1 is a diagram of the resin transfer molding process. Resin is placed in the bottom of the mold. The glass, Kevlar or graphite cloth is placed on top of the resin. The pressure plate is laid on top and the entire assembly bagged for cure in an autoclave or press. The problem addressed in this study was that this DGEBA resin transfer molding resin is so fluid that excess amounts of resin bleed out during the cure process. This creates resin depleted areas in the cured laminate. To alleviate this problem, FDEMS sensors were used to monitor and tailor the advancement of the resin's viscosity such that full impregnation occurred but excess bleed did not.

To accomplish this task the ionic and the dipolar mobility as measured by the FDEMS sensor was correlated with the buildup in viscosity and modulus of the resin. Figure 2 shows the FDEMS sensor output during a 6 h/121°C

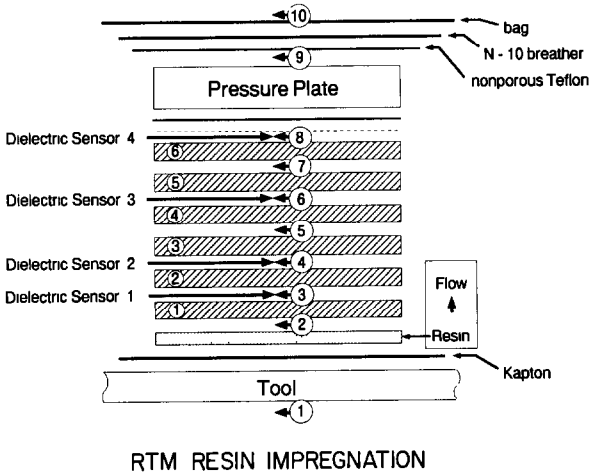

Fig. 1. Diagram of vacuum bag, resin, cloth and sensor layup.

isothermal cure. Figure 2 plots the variation in $\epsilon''(\omega)$ multiplied by the angular frequency, ($\omega = 2\pi f$). By scaling ϵ'' in this way, all of the experimental values of ϵ'' are conveniently displayed on a single plot. More importantly, plots of $\epsilon''\omega$ make it relatively easy to visually determine when the low frequency magnitude of ϵ'' is dominated by the mobility of ions. A detailed description of the frequency dependence of $\epsilon^*(\omega)$ due to ionic, dipolar and charge polarization effects has been previously described [1,2].

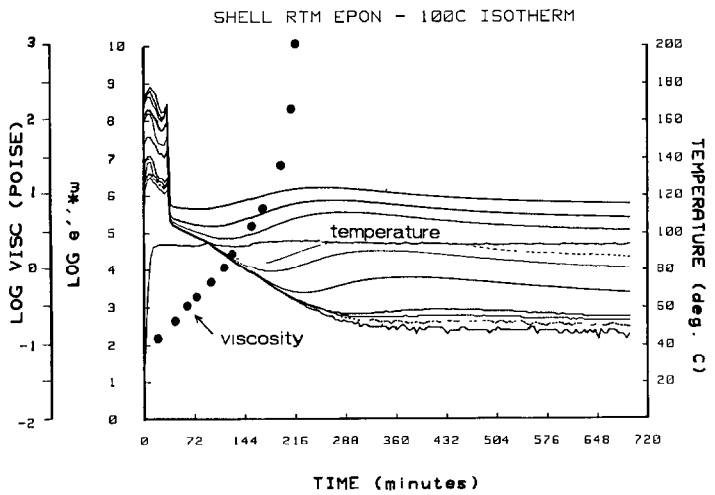

Fig. 2. Plot of $\epsilon''\omega$ (lines) measured at 50 Hz, 125 Hz, 250 Hz, 500 Hz, 5 kHz, 25 kHz, 50 kHz, 250 kHz, 500 kHz and 1 MHz (bottom to top). Also plotted is viscosity (●) and temperature.

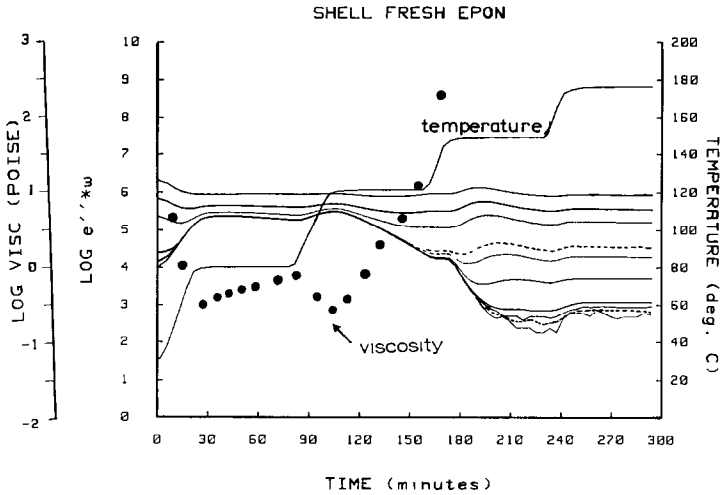

Fig. 3. Plot of $\epsilon''\omega$ (lines), viscosity (●) and temperature measured at the frequencies in Fig. 2 during the cure cycle with holds of 80 °C, 121 °C, 150 °C, and 177 °C.

In summary, if we neglect charge polarization effects, which are usually small at frequencies above 10 Hz, the magnitude of the low frequency overlapping values of $\omega\epsilon''(\omega)$, can be used to measure the variation in magnitude of the ionic mobility. When ionic mobility is the dominant molecular contribution to ϵ'', $\omega\epsilon''(\omega) = (8.85 \times 10^{-14})\sigma$ where σ $(\Omega^{-1}$ $cm^{-1})$ is the conductivity.

Also shown in Fig. 2 is the viscosity versus time for the curing resin. As seen in Fig. 2, the overlapping $\epsilon''\omega$ lines monitor the drop in ionic mobility which in turn reflects the increase in viscosity during cure. In fact, during the initial 40 min both the viscosity and the ionic mobility undergo a similar change, indicating the ionic mobility is linearly tracking viscosity.

Dipolar relaxation peaks occur between 40 min and 200 min as the glass transition temperature of the hardening resin increases with the corresponding increase in degree of cure. These dipolar peaks can be correlated with degree of cure and/or hardness. Thus the time of occurrence of a particular peak in ϵ'' for a given frequency can be used to monitor the time of occurrence for a particular degree of advancement or hardness of the curing resin.

Figure 3 shows a similar plot of the FDEMS sensor values of $\epsilon''\omega$ (50 Hz to 1 Mhz) throughout the first two stages of the recommended cure cycle consisting of holds at 80 °C and 121 °C. Again, the overlapping low frequency ϵ'' values (ionic mobility) and the ϵ'' peaks (dipolar mobility) track the advancement of viscosity, modulus and T_g of the resin during the cure process.

Finally, the FDEMS sensor was cured to monitor and control the advancement of the resin to a less fluid state prior to impregnation and cure.

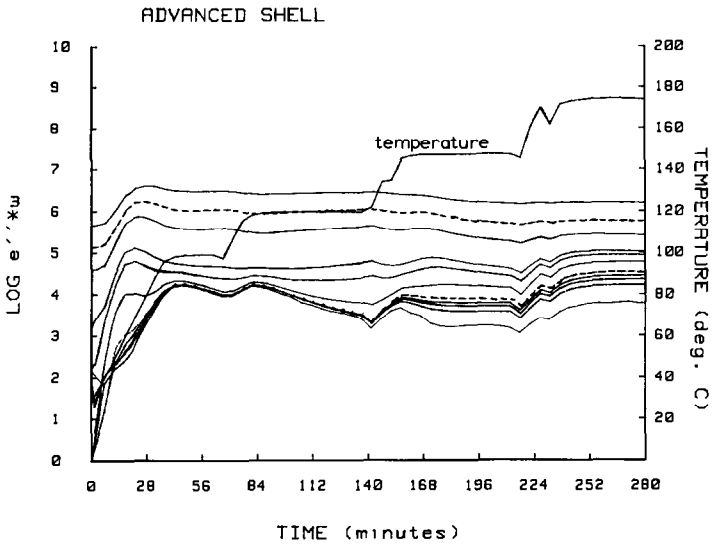

Fig. 4. Plot of $\epsilon''\omega$ (lines) and temperature for previously advanced resin measured at the frequencies in Fig. 2 during the cure cycle.

This was accomplished by allowing the resin to react at 100 °C until the FDEMS measured ionic mobility dropped to a predetermined point which was comparable to that of another resin which did not exhibit excessive bleed. The advanced resin was then cured using the complete cure cycle. Figure 4 is a plot of $\epsilon''\omega$ for the advanced resin which can be compared with the original fresh resin. The low frequency values of $\epsilon''\omega$ in the advanced resin (Fig. 4) are a factor of 10 lower than in the fresh resin (Fig. 3). Thus the FDEMS sensor advanced resin displays a uniform reduction in fluidity over the entire cure cycle as measured by the ionic mobility, i.e. low frequency values of ϵ^*. Use of the resin whose advancement was monitored and controlled by the FDEMS sensor output eliminated all of the excess bleed and resin depletion problems associated with the fresh RTM resin.

CONCLUSION

Frequency dependent electromagnetic measurements have been shown to be a sensitive and convenient in situ technique for in situ monitoring and controlling the resin's processing properties during cure in the mold. The FDEMS sensor was used to advance and adjust the RTM's fluidity thereby eliminating excess bleed and resin depleted areas without changing the cure cycle.

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