Electrical Sensing of Shelf-Cure Properties of Polymeric Prepreg Materials

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ABSTRACT: Most polymeric thermoset materials change (cure) slowly as they lie in storage; a prime example of this is composite prepreg materials. These changes are generally vitrification, and are not readily observable using some of the standard cure-monitoring methods, such as DSC and FTIR, which sense mainly the gelation process. Evidence of this observation is presented, along with the successful results of an effort to monitor this shelf-cure process using a simplified resistivity meter. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 337–342, 1997

Key words: shelf cure; gelation; vitrification; prepregs

INTRODUCTION

Polymeric materials are being used in an ever-increasing number of applications, from decorative packaging to engineered structural components. The variety of polymers being used today is also growing. The field of high-performance composite materials has been dominated by the use of thermoset polymers, which are often used in their B-stage. A B-stage thermoset composite material is one wherein the fibers have been immersed in fresh thermoset resin (often epoxy) and then flattened and partially cured. This B-staged material is made in large volumes, often in large rolls, and is purchased and stored in this form by the company which will then turn it into a finished product. B-staged materials continue to cure slowly, dependent mainly on the temperature to which they are exposed. The B-staged composite material is often known as prepreg, since it is fiber which has been preimpregnated with thermoset resin.

To avoid premature curing of these prepreg materials, they are often stored at reduced temperatures (0°F). The manufacturer of the composite end product must take the responsibility to determine the cure level or usability of the prepreg material at the time of its consolidation into a finished product. This is presently done most often by one of two methods: (1) careful monitoring of the temperature history of the prepreg material and adhering closely to the specifications of the prepreg manufacturer; and (2) testing the tack and/or flexibility (drape) of the prepreg material prior to layup. Both of these methods have their problems, and owing to the need for conservatism in assessing the usability of the prepreg, much good material is discarded before its time, increasing waste and costs. This article discusses a possible solution to this problem, due to the recent development of an electronic device capable of monitoring the shelf cure of these prepreg materials.

Thermoset composite materials are typically cured under very carefully controlled and monitored conditions of temperature and pressure, usually in an oven or an autoclave. The final quality of the finished part is heavily dependent on the cure cycle conditions, so this elevated temper-

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ature cure process is where essentially all research has focused. No single method has proven ideal in monitoring this process, so numerous methods have been developed. Some of the methods include Fourier transform infrared (FTIR) spectroscopy,[1–3] Raman spectroscopy (similar to FTIR),[4] differential scanning calorimetry (DSC),[3] thermocouples,[5] pressure transducers,[6] acoustic wave emission monitoring,[7] fluorescence optrode cure sensors,[6] dynamic mechanical analysis (DMA),[3] microwave dielectric analysis,[8] dielectric sensing,[9–11] and fluorescence spectroscopy.[12]

Before this work was begun, each of the preceding methods was studied to find the best potential method for monitoring shelf cure. It was known in advance that some challenges would exist, for the chemical and rheological changes that occur during shelf cure are different from those that occur during the cure process. In addressing the shelf cure, or aging, of a prepreg, Ahn et al. stated that "the aging process may be somewhat different from the curing process taking place at elevated temperatures since aging may be retarded by vitrification before gelation."[13] Gelation is defined by Pascault and Williams as "the incipient formation of a network with infinite weight-average molecular weight"[14]; vitrification is defined in the same reference as "involv[ing] a transformation from a liquid or rubbery state to a glassy state." These two processes are further differentiated by Enns and Gillham in their description of the phase diagrams of thermosets with a high T_g.[15] They show that significant gelation cannot occur without an elevated cure temperature, while vitrification can occur simply with the passage of time. Therefore, a major difference between the solidification of a thermoset resin under shelf cure, as compared to an elevated-temperature cure, is that very little gelation occurs, and the hardening is primarily due to vitrification.

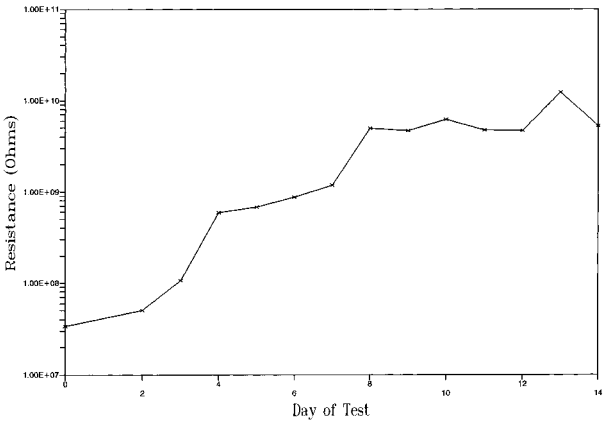

Figure 1 Sensor resistance as a function of shelf-cure time for EPON DPL-862 resin.

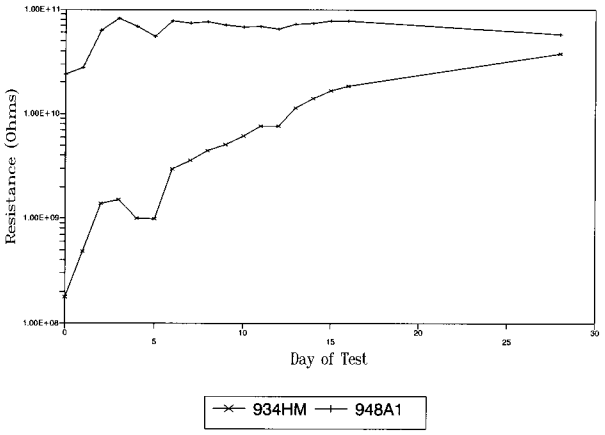

Figure 2 Sensor resistance as a function of shelf-cure time for 948A1 and 934HM resins.

BACKGROUND

One of the outgrowths of the shelf-cure process as described above is that some of the present methods for determining extent of cure, most notably DSC and FTIR, would be essentially of no use in monitoring shelf cure, since these methods are sensitive primarily to the changes that occur at elevated temperatures as a result of the gelation process. Because the focus of this study was to find an effective means for determining the degree of shelf cure, it was not thought that these methods would be successful. To verify this hypothesis, three units of epoxy resin (type 934HM from ICI Fiberite) were removed from cold storage (0°F) and subjected to room-temperature aging (shelf cure). As each day of shelf cure passed, three tests were performed on the samples: FTIR, DSC, and manual observation of viscosity/hardness. This hypothesis was proven to be true, as will be shown in the next section.

Earlier work done by R. Scott Merrell[16] on thermoset shelf cure found that of several methods evaluated for shelf cure monitoring (including those mentioned in the preceding section), the dielectric sensors showed the greatest promise for a real-time, simple test method. Subsequent work

by Barry M. Lunt showed that: (1) the electronics necessary for dielectric monitoring of shelf cure could be greatly simplified over the use of a microdielectrometer; (2) the sensor could be built using commonly available technology; and (3) these simplified components could detect a great deal of variation in the dielectric response of a thermoset resin as it underwent shelf cure. The simplified shelf cure monitoring apparatus was later named Cross-Check and was patented (U.S. Patent #5,432,435). It uses low-frequency (<5 Hz) and low-amplitude AC signals (<2 V_{p-p}) and an interdigitated comb electrode to measure the AC resistivity of the material under test.

EXPERIMENTAL

The experimental part of this work was conducted in four stages. In stage 1, Cross-Check was used to test the resistivity of Epon DPL-862 (Shell) epoxy resin as it underwent shelf cure (see Fig. 1). The DPL-862 resin was removed from cold storage (0°F), allowed to warm to room temperature, then mixed with the stoichiometric amount of Epon Curing Agent W. The viscosity was noted by observation, and the resin was applied to the Cross-Check sensor and a resistivity measurement was taken. For each of the subsequent 14 days, the resin on the sensor was observed for viscosity (or hardness, as the shelf cure progressed) and was measured for resistivity.

In stage 2 this same procedure was repeated for two other resins: ICI Fiberite 948A1 and 934HM. These resins require cold storage, and are autocatalyzing. The resins were removed from cold storage, allowed to warm to room temperature, then a sample of each was placed on the Cross-Check sensor. Daily measurements and observations were made for the next 15 days; a final measurement and observation was made at 28 days (see Fig. 2).

In stage 3, DSC and FTIR were used to measure the shelf cure of the 934HM resin (Fig. 3). Accordingly, a 25-day test was completed using FTIR, and a 30-day test was completed using DSC. As in stage 2, the resin was removed from cold storage and daily measurements were taken.

Stage 4 involved the use of tack and drape tests. In some companies, such as ICI Fiberite, the degree of shelf cure for prepreg materials is evaluated using a tack and drape test.[17] This 2-part pass/fail test provides a qualitative measure of the state of a prepreg material. For the tack test, a 1″ × 4″ sample of prepreg material is pressed against the surface of a 10″ × 10″ polished stainless steel plate (see Fig. 5), and the plate is then place at a 45° angle with the prepreg mate-

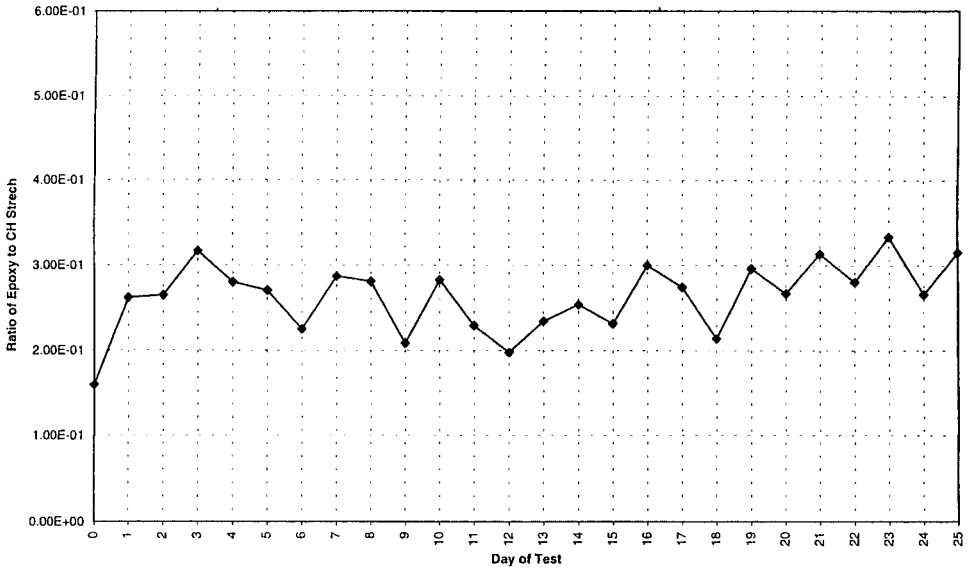

Figure 3 FTIR ratio of epoxy peak to CH stretch for 934HM resin as a function of out-time. CH stretch at 1763–1682 wave numbers; epoxy ring at 922–822 wave numbers.

rial facing down. After 10 min, the prepreg sample is examined to see if any portion has peeled back from the plate, or has separated from the surface of the plate. Prepreg that is still usable for layup will have sufficient tack to remain pressed against the plate.

For the drape test, a 1″ × 4″ sample of the prepreg is wrapped tightly around a .025″ diameter polished stainless steel mandrel (see Fig. 6). The prepreg sample is then examined to determine if any fibers were kinked as they were wrapped around the mandrel. Prepreg that is still usable for layup will show no signs of kinking.

In industry, tack and drape tests of this kind are a pass/fail type of test. For our purposes, it was desired to develop some kind of scale whereby the relative degree of tack and drape could be assessed, so that these data could then be correlated to the resistivity measurements. Accordingly, M. R. Cox developed a set of tack and drape conformance descriptors, which permitted a somewhat subjective but quantitative assessment of the viscoelastic condition of the prepreg sample. The outcome of these tack and drape tests was a number between 0 and 5 for each test type; 0 represented fresh prepreg, fully conforming to the test, while 5 represented aged prepreg, no longer passing the tack or drape test.

A sample of fresh carbon-fiber prepreg, along with a sample of the diluted 934HM resin batch from which it was made, was obtained from ICI Fiberite. These samples were shipped together in the same package, so that they both experienced the same environmental conditions. Upon arrival, a sample of the resin was placed on a Cross-Check sensor, and a test strip was cut from the roll of prepreg and subjected to the specified tack and drape tests. The resin and prepreg samples were then stored together, and the tests were repeated daily for the next 15 days.

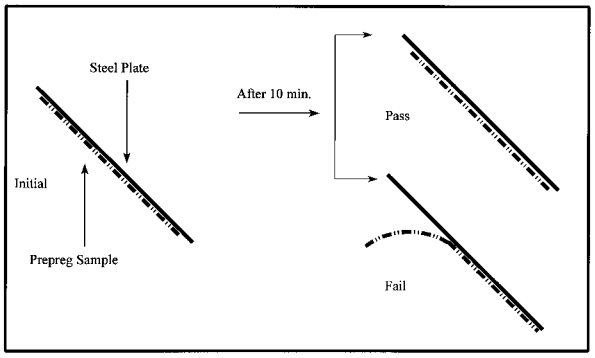

Figure 5 Tack test depiction.

RESULTS AND DISCUSSION

Stage 1

The manufacturer (Shell) specified an out-time of 7 days for the EPON DPL-862 resin; this out-time corresponded well with the measured resistivity of the resin (Fig. 1), and the observed viscosity/hardness of the resin.

Stage 2

The 948A1 resin had an out-time specification of 180 days; the out-time specification for the 934HM resin was 10 days. Based on these specified out-times, it was expected that over the

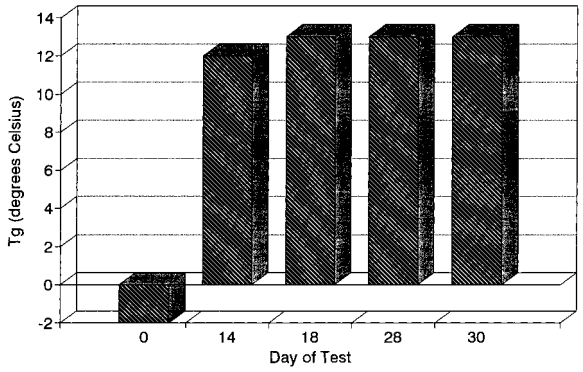

Figure 4 Glass transition temperature of 934HM resin as a function of out-time.

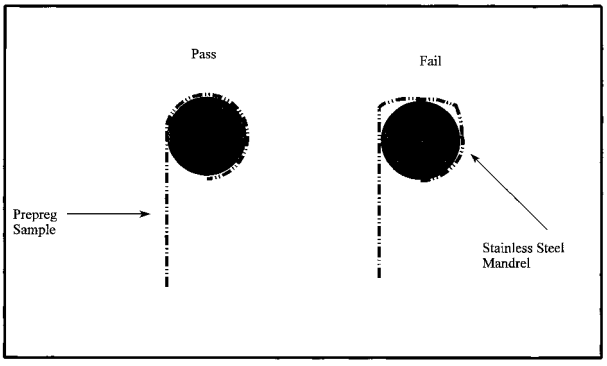

Figure 6 Drape test depiction.

course of a 28-day test, the 948A1 resin would not change significantly in its resistivity, while that of the 934HM resin would change significantly. The measured results confirmed this expectation, as shown in Figure 2.

In the search for a method of monitoring shelf cure, these results were very promising. However, they were not yet correlated to an industry-standard method of monitoring cure.

Stage 3

FTIR and DSC are well-accepted in industry for monitoring the cure process. The results of these tests are shown in Figures 3 and 4, respectively.

As seen in Figure 3, the resin showed essentially no change over the 25-day test using FTIR, even though the resin had completely hardened (vitrified). While it is arguable that there may be some slope to the trend shown in Figure 3, it is at best very slight, and is basically lost in the day-to-day variation. From this, one would conclude that either the resin had not undergone a change or that FTIR did not prove to be sensitive to the shelf-cure process. Since it was physically obvious that the resin *had* undergone a change, one must accept the latter.

The DSC results were more positive, but only slightly more so. As seen in Figure 4, the T_g changed by only 15°C over the period of the 30-day test. When we consider that there was a ±2°C repeatability error in the DSC measurements, we are left to conclude that while DSC can be used to verify the shelf-cure trend, it is too insensitive to shelf-cure processes to prove highly useful. However, while it may not be useful for monitoring shelf cure, it does confirm that something happens to the 934HM resin during shelf cure, mostly during the first 14 days.

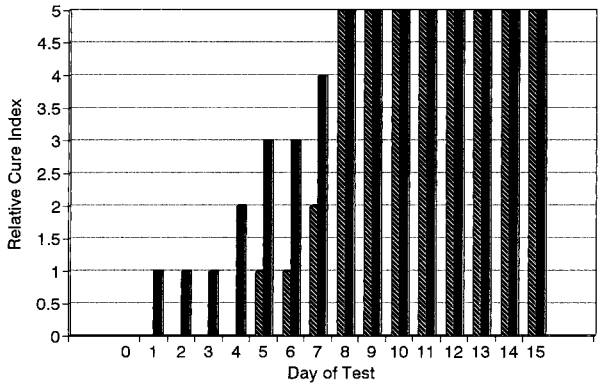

Figure 7 Cure index for the tack and drape test.

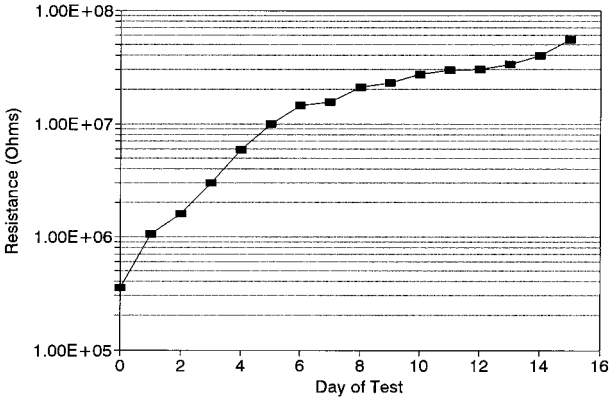

Figure 8 Resin resistivity as a function of out-time.

Stage 4

The results of the tack and drape test, correlated to resistivity, are shown in Figures 7 and 8. It can be seen from these graphs that the resistivity of the resin correlates well with the observed tack and drape properties of the prepreg material.

CONCLUSION

The process of shelf cure in thermoset resins is not readily observable nor quantifiable using FTIR, and is difficult to obtain adequate resolution using DSC. Tack and drape test methods can be used for periodic sampling of the shelf-cure condition of the resin, but are not readily adaptable to continuous monitoring. The simplified resistivity-measuring device used in this work has shown great promise in both measuring and continuously monitoring thermoset resin shelf cure.

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