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In-situ cure monitoring of an out-of-autoclave prepreg: Effects of out-time on viscosity, gelation and vitrification

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ABSTRACT

The cutting, lay-up and bagging of out-of-autoclave (OOA) prepregs for composite part fabrication can take from several days to weeks, depending on the desired part size. This period of ambient temperature "out-time" induces resin polymerization/cross-linking, and affects critical physicochemical phenomena such as minimum viscosity, gelation, and vitrification. Therefore, the capability to monitor out-time at ambient conditions and to understand its influence on key resin properties is valuable to minimize waste and increase efficiency. In this study, the dielectric properties of out-of-autoclave (OOA) carbon/epoxy prepreg aged from 0 to 7 weeks are investigated. The measured dielectric data is used to develop an in-situ out-time monitoring method at ambient condition. Furthermore, the effects of out-time and out-life on critical physicochemical parameters are identified.

1. Introduction

Recent studies have shown out-of-autoclave (OOA) prepreg processing via vacuum-bag-only (VBO) consolidation to be a viable and potentially cost-effective alternative to autoclave cure [1–3]. OOA prepregs are cured under a much lower maximum compaction pressure of 101,325 Pa (1 atm), and voids are suppressed by evacuating entrapped air and volatiles through a microstructure that is initially only partially impregnated (by design), and that is infiltrated by surrounding resin during cure [1]. The physicochemical properties of the resin thus govern the rate at which this microstructure evolves, and must be understood and appropriately controlled to ensure successful part manufacture. Therefore, the adverse effects that derive from prolonged out-time, or room temperature exposure time before cure are arguably even more critical in OOA processes than in autoclave processing.

1.1. Background

Out-time causes polymerization/cross-linking of the resin at ambient temperature, adversely affecting tack and drape and potentially leading to unacceptable porosity levels in cured parts due to inhibited flow [3–6]. For OOA prepregs, out-time was shown to cause pervasive porosity once the out-life was exceeded [4]. Therefore, accurate methods to monitor out-time and to predict the effects of out-time on the key resin properties are necessary. Investigators have measured out-time of prepregs using differential scanning calorimetry (DSC) [3] and analyzed the resin's physicochemical parameters (minimum viscosity, gelation, and vitrification) using DSC [7], rheometry [8,9] and dynamic mechanical analysis (DMA) [10]. Among these, DSC and rheometry techniques have been particularly useful. However, DSC measurements are mass-specific, and the exact amount of resin within a prepreg sample is difficult to quantify. Similarly, rheometry requires neat resin film for viscosity data. In addition, both tests are conducted ex-situ, on small samples, in idealized conditions.

Dielectric analysis is both non-invasive and highly sensitive to degree of polymerization, and is thus appealing [9,11–13]. Recent studies have shown that dielectric analysis can be used to identify physicochemical transformations in prepregs during cure, highlighting the possibility of distinguishing both micro- and macroscopic information using appropriate signal processing. The minimum viscosity and gelation state of the resin were identified as a maximum and an inflection in ionic conductivity, respectively, during isothermal cure. Furthermore, vitrification can be detected by tracking α-relaxation time from the dipolar contribution of the dielectric loss at a frequency of 0.1 Hz. These correlations can be used to understand specific changes in the physicochemical parameters and process-critical moments associated with out-time. However, such systematic studies have not yet been reported.

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In a recent study, we investigated the effects of out-time on the rate of cure and viscosity evolution of an OOA prepreg and developed accurate predictive models from DSC and rheometer data [14]. Furthermore, we proposed accurate correlations between dielectric behavior and resin cure kinetics and viscosity, thus demonstrating the potential for an in-situ process diagnostic to dynamically monitor cure. In the present study, we analyze a large thermochemical, thermomechanical and dielectric dataset to specifically determine the effects of out-time on several resin properties of interest to composites processing. The two key objectives of the study are: (1) to establish correlations between dielectric properties and the key processing transitions of minimum viscosity, gelation and vitrification; and (2) to investigate the effects of out-time and out-life on these moments.

2. Experimental procedure

This experimental procedure was previously described in [14], but the current study considers a second, previously undiscussed set of data.

2.1. Materials

We selected an OOA prepreg consisting of eight-harness satin (8HS) carbon fiber fabric and a toughened epoxy resin (CYCOM® 5320-1, Cytec Engineered Materials Inc.). The resin content of the 5320-1/8HS is 36% by weight, and the fabric areal weight is 375 g/m^2. Prepreg was used for dielectric analysis, while neat resin film was used for modulated DSC (MDSC) and rheometry. The specified out-life at ambient temperature was 30 days [16], and samples were stored below −12 °C before use. The samples were then conditioned at 21 ± 2 °C and 51 ± 5% relative humidity for 7 weeks.

2.2. Modulated Dynamic Scanning Calorimetry (MDSC)

MDSC was conducted under a nitrogen purge (TA Instruments Q2000). Applying sinusoidal temperature modulation on top of the linear temperature ramp allows signal separation of the total heat flow into reversing and non-reversing components. The reversing component of heat flow depends on heat capacity and heating rate, while the non-reversing kinetic component directly indicates the cure exotherm [3,7]. For each dynamic measurement, a constant temperature ramp from −60 °C to 280 °C at a rate of 1.7 °C/min with a temperature modulation of ±0.5 °C/min was applied. For isothermal measurements, dwells were performed at 93 °C, 107 °C and 121 °C, and a temperature modulation of ±0.5 °C/min was applied over the dwell period.

2.3. Rheometry

Rheological measurements were performed (TA Instruments AR2000) using 25 mm aluminum parallel plates at a gap setting of 0.5 mm. All tests were conducted under constant oscillatory shear at frequency of 1 Hz and at strain of 0.25%, within the Newtonian plateau regime. Isothermal dwells were performed by heating at 10 °C/min to 93 °C, 107 °C and 121 °C and holding until 90% of the machine-specified maximum torque (200 mN·m) was required for shear displacement.

2.4. Dielectric analysis

Dielectric measurements were conducted with a dielectric monitoring system (DETA SCOPE™, ADVISE E.E., Greece). Coplanar electrodes were used as the sensor, which generated fringing electric field lines (~100 μm) penetrating into the dielectric material (the epoxy resin in the prepreg), thus enabling non-invasive measurements. To insulate the sensor from the conductive carbon fiber bed, thin (10 μm) glass fiber layers were first placed over the sensor. Laminated prepreg samples 3 mm thick were placed within a thin picture-frame spacer containing a thermocouple. Finally, top and bottom plates with embedded heating cartridges were used to uniformly heat the sample. A sinusoidal voltage of 10 V and a frequency scan over the range from 1 Hz to 1 MHz were used for each measurement. The comparison of the input and the return signals was automatically carried out in real-time within the system software. The isothermal dwell heating profile was the same as that used for rheometry measurements, with heating at 10 °C/min to 93 °C, 107 °C and 121 °C.

3. Principles of dielectric analysis

The electrical response of a thermoset resin during cure is better understood in terms of the two major immittance functions: complex impedance (Z^*) and complex permittivity (ε^*). The complex impedance, Z^*, relates directly to electric circuitry, and correlates well with cure kinetics and viscosity evolution during cure [14,15]. Permittivity, ε^*, on the other hand, permits detailed analysis of the physicochemical changes during cure through complex analysis [9,11,12]:

$$\varepsilon^* = \varepsilon' + \varepsilon'' \tag{1}$$

where ε' is a real part and ε'' is an imaginary part of ε^*. ε'' can be further divided into two parts for the thermoset resins as [9,11,12]:

$$\varepsilon'' = \varepsilon_i'' + \varepsilon_d'' \tag{2}$$

where ε_i'' is the ionic conductivity contribution and ε_d'' is the dipolar contribution. The former term, ε_i'', dominates at low frequencies through a linear drop. Subtraction of ε_i'' from ε'' yields ε_d'', and allows analysis of the dipolar relaxation of the thermoset resin.

Ionic conductivity (σ) is also related to ε_i'' by [9,11,12]:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon_i'' \tag{3}$$

where ε_0 is the free space permittivity of 9.85 pF/m [13]. The motion of ionic species reflects macroscopic viscosity.

4. Determination of physicochemical parameters

4.1. Out-time monitoring

Ex-situ methods for monitoring out-time were investigated by tracking changes to the B-stage glass transition temperature ($T_{g,0}$) and the total heat of reaction (ΔH_{rxn}), as measured by MDSC. Glass transition manifests as an inflection point in the change in specific heat within the reversing heat flow, while the heat of reaction is directly obtained by integrating the non-reversing heat flow [3].

The method developed in this study for monitoring out-time *in-situ* involves measurements of the conductivity σ at ambient temperature (chosen here as 30 °C for stability) via dielectric analysis. The thermoset resin contains significant amounts of ionic impurities introduced during resin preparation. Thus, the resin transformation from liquid-like states toward solid-like states during out-time will cause a decrease in measurable σ, even at ambient temperature. In contrast to rheological measurements, dielectric analysis involves measurement of ionic species motion, thus avoiding the limitations associated with material viscosity/stiffness near gelation.