Test Method

Thermal and volumetric property analysis of polymer networks and composites using elevated temperature digital image correlation

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A B S T R A C T

Digital Image Correlation (DIC), which exploits non-contact advantages and full-field analysis, provides more data in-situ that are not possible with traditional techniques. In this work, elevated temperature digital image correlation techniques were applied to a glassy polymer network via thermal expansion and contraction experiments to study volumetric behavior during the curing process. A glassy epoxy network was tested in both cured and under-cured states and heated to the ultimate cure temperature. Matrix volume changes due to both thermal expansion and cure shrinkage were quantified. Concurrently, the thermal expansion of aerospace-grade composite laminates was also observed in matrix and fiber-dominant directions. Additionally, the strain-free temperature of a non-symmetric composite laminate was identified through thermal compensation of process-induced curvatures. Finally, laminate dimension changes were related to the strain-free temperature as means to probe process-induced strains within composite laminates. Thermal properties of the neat matrix and composite laminates were compared to traditional techniques, validating the benefit of elevated temperature digital image correlation for composite matrix qualification.

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1. Introduction

The rising exploitation of polymer composites for use in primary and secondary structures of aerospace, automotive and marine applications is significant and requires further exploration into manufacturing and design parameters. For the proliferation of composite materials, property simulation of new chemistries has become vital to the aerospace community. In this, understanding property development of composites during the manufacturing stage is essential for simulation. The development of thermal, mechanical and rheological properties of thermoset matrices through the multiple stages of manufacturing is complex, and a holistic understanding of key properties is critical for model development and accuracy. While significant effort has been put into the testing, modeling and prediction of property development, there is a continuous demand for test improvement for enhanced material performance analysis. As simulation of composite materials continues to multiply across all size scales, it becomes critical to understand, at a fundamental level, the developing properties and physical changes that take place within the matrix during cure.

Molecular-level strains are introduced within the matrix due to volume changes during the manufacturing of continuous fiber composite laminates, and lead to a number of failure modes including geometry deformation, matrix micro-cracking and ply delamination, among others [1–3]. The sources of these strains are complex, ranging from material properties to processing factors such as tooling material or autoclave thermal gradients; however, a clear consensus exists that dominant contributing factors include a differential in the coefficients of thermal expansion (CTE) between the matrix and reinforcement and, to a lesser extent, matrix chemical shrinkage. Understanding the magnitude of these contributing factors, as well as any potential areas for control, is critical for material and process qualification.

The basics of strain creation with a composite material involve constraint placed on volume changes of the matrix by the fiber environment. The community agrees that a strain cannot build until the matrix has developed an appreciable mechanical strength; a number of authors have shown that, in the processing of thermoset networks, strain creation begins on gelation [1,4]. In this rubbery state, however, strain relaxation is significant, and molecular segments are able to rearrange to dissipate energy [5]. As molecular weight continues to build throughout cure, the polymer

network's ability to realize these cooperative motions decreases until the point of vitrification, at which point continued reaction slows drastically and a number of network properties significantly change. For example, vitrification marks measurable increases in Young's, shear and bulk moduli, and increases in moduli correspond with increases in relaxation times [6]. For this reason, it is assumed that strain relaxation ceases upon vitrification and this corresponding temperature is often denoted as the strain-free temperature [7–9]. Due to high values of moduli upon vitrification, additional reaction and bond formation imparts strain as the matrix continues to cure, and may also increase the strain-free temperature [4]. From this glassy state, the material still must undergo cooling from the cure temperature to room temperature. This corresponds with a significant change in matrix volume inducing sizeable thermal residual strains, which are considered to be the largest contributors to process-induced strain within composite materials [10].

Due to the multifaceted mechanisms of strain creation, the measurement of residual strains is complex. While tools such as classical laminate theory allow for the calculation of residual strains based on constituent material properties, techniques which directly measure the strains are not common. Unlike more established polymer analysis techniques, there is a lack of consensus within the community to a preferred method to measure or represent the magnitude of strains. Strain measurement devices such as Fiber Bragg grating sensors and strain electric gauges raise question as to at which point the measurement becomes valid during the cure due to the developing interface between the part and the sensor [10]. Conversely, techniques which measure laminate dimension changes or developing mechanical strength of uncured, impregnated fibers, such as dynamic mechanical or thermomechanical analysis, do not represent the environment present in the manufacturing of high performance composite laminates [4,11]. Because of the implications of in-situ techniques such as these, deformation of laminates from initial, pre-cured to final cured states continues to be a common method for researchers. In this, process-induced strains are examined through either curvature reduction of an angled part or by the introduction of curvature upon curing a flat laminate of a non-symmetric laminate sequence. In each scenario, it is understood that the magnitude of residual strain relates to the deviation of mold geometry. In the case of an angled tool, a decrease in interior angle, also called "spring-in," corresponds to an increase in residual strain within the laminate. Conversely, the creation of curvature upon the curing of a flat, non-symmetric laminate is also related to the magnitude of residual strain, wherein increased curvature corresponds to increased residual strain. These techniques are based on measurements made before and after laminate curing. This limits the knowledge of process-induced strain development to an initial (prior to curing) and final (after curing) conditions. We believe heating cured laminates to elevated temperatures provides additional insight into the residual strain state, and offers an additional response to laminate deformation. Further, we show that a single experimental setup can be used for accurate measurement of critical matrix properties which serve as the contributing factors to process-induced strains within continuous fiber composite laminates.

2. Experimental

2.1. Materials

CYCOM 977-3 prepolymer matrix and prepreg was supplied by Cytec Aerospace Materials and used as received.

2.2. Glassy polymer network preparation

The prepolymer matrix was heated and degassed at 125 °C (10^{-3} Torr) and cast into silicone molds (internal cavity $130 \times 12 \times 6$ mm). It was then cured by the manufacturer's recommended cure cycle (MRCC) (temperature ramp at 1.8 °C/min to 177 °C, 6 h isothermal hold). For chemical shrinkage studies, samples were removed from the oven after a 30 min isothermal hold at 177 °C and quickly cooled to room temperature. Samples approximately $15 \times 12 \times 6$ mm were manually prepared from the cast $130 \times 12 \times 6$ mm bars.

2.3. Composite laminate preparation

Prepreg materials were stored in vacuum-sealed containers at sub-ambient temperatures, and equilibrated at room temperature prior to use. Flat composite panels (30.48×30.48 cm) were fabricated into unidirectional (UD) $[0_8]$, off-axis (OA) $[0_4/45_4]$, and non-symmetric (NS) $[0_8/90_8]$ laminates on flat Invar tools with steel caul plates. Panels were cured by the manufacturer's recommended cure cycle (1.8 °C/min to 177 °C, 6 h hold) in an American Autoclave under vacuum bag and pressure ($\sim 10^{-3}$ Torr and 0.689 MPa, respectively) to fully compact plies and assure void-free laminates. Panels were machined into 2.54×7.62 cm coupons using a diamond saw fitted with cutting fluid. Due to non-traditional lay-up sequences, some coupons developed cracks during machining and were not used. Non-symmetric $[0_8/90_8]$ and off-axis $[0_4/45_4]$ laminates exhibited significant concave curvature with respect to the 90 ° and 45 ° faces, respectively.

2.4. Thermal characterization

Parallel plate rheological experiments were conducted to determine the gelation point of the prepolymer matrix through the MRCC on a Thermal Analysis (TA) ARES-G2 rotational rheometer using 8 mm aluminum plates with a 0.3 mm gap and frequency of 1 Hz. The development of the shear storage (G') and loss (G'') moduli were observed, with the $G' = G''$ crossover used for the identification of gelation, which occurred at 30 min into the isotherm at 177 °C.

The volumetric properties of the epoxy networks were also determined from thermomechanical analysis (TMA) in comparison to results from elevated temperature DIC. Cured matrix cubes approximately $10 \times 10 \times 10$ mm were manually cut and polished. The experiments were conducted using a Thermal Analysis (TA) Q400® instrument fitted with a quartz stage and macro expansion probe. Specimens were heated at 1 °C/min from 25 °C to 177 °C using a 0.05 N force. Linear coefficients of thermal expansion were determined by the slope of a linear fit to sample length vs. temperature curves from 25 to 50 °C. Laminate measurements were taken parallel and perpendicular to the fiber direction (0 ° and 90 °, respectively) using 1×1 cm UD $[0_8]$ specimens.

2.5. Elevated temperature digital image correlation

Digital image correlation (DIC) measures specimen deformation by tracking random surface patterns in gray-scale image sets from the un-deformed to deformed states, allowing for non-contact full-field analysis of surface strain. [12–14]. DIC strain analysis was conducted using a GOM Optical Measuring Techniques ARAMIS 3D Deformation Analysis System (Trilion Quality Systems). Specimens were speckle coated to create a non-uniform surface pattern using high-temperature white and black aerosol paints with a black solid basecoat and white speckles in the appropriate size range of 2–5 pixels. [15]. In the case of composite laminates, a basecoat was not