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Spatially resolved, in situ elastic modulus of thermoset polymer amidst carbon fibers in a polymer matrix composite

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ABSTRACT

The mechanical properties of thermoset resins used in carbon fiber composites depend on their processing conditions. The inclusion of fibers into the resin locally affects the thermal balance, creates chemical inhomogeneities, and templates structural developments in the polymer near the fiber surface. In this study we use Raman and Brillouin light scattering to investigate the effect of carbon fibers on the mechanical properties of an epoxy matrix. Our results show that the longitudinal modulus of epoxy within a fiber tow is about 3.75% lower than the modulus of the epoxy outside of the tow. Furthermore, within a fiber tow, the modulus depends on the local packing density of the carbon fibers. Comparison between our Brillouin and Raman measurements suggest that the observed spatial inhomogeneity in elastic properties of the matrix is not a result of residual stresses within the matrix but more likely due to structural reorganization in the interfacial region.

1. Introduction

Polymer matrix composites are becoming materials of choice for constructing stiff, lightweight parts for a range of applications from aerospace and automotive components, to sporting goods. However, designing a composite part is significantly more challenging than for an equivalent part made of a single material. The mechanical properties of the composite are determined according to the properties of constituent materials and the processing conditions, such as mixing procedure, forming rates, temperature, and pressure used in manufacturing the composite. It is vital to understand how these processing conditions affect the final properties of the composite in order to optimize the performance of a manufactured part.

In the case of a thermoset matrix textile composite, a liquid polymer resin is forced into the interstitial spaces of the reinforcing textile and cured under controlled temperature and pressure conditions. In the bulk, a resin cures with limited constraints on shrinkage or diffusion. However when inclusions in the form of textile fibers are added to the polymer, they obstruct the free flow of the resin while it is still in liquid form. The surface of the reinforcing constituent has been demonstrated to alter the cure kinetics and final mechanical properties of the polymer network [1,2]. Volumetric constraints cause significant stress formation during the cure of thermoset resins [3]. Furthermore, fiber bundles within a composite can constrict the curing resin so that it causes microcracking of the resin matrix by the end of cure [4,5]. Finally, if the fibers have different heat conduction characteristics than the resin, thermal conditions for the curing of the resin will also be different from those observed in the bulk [6,7].

A good representative system for exemplifying this behavior is a carbon fiber textile composite with an epoxy matrix material. In this system the matrix is composed of two parts: an epoxy resin, and an amine hardener. These components are mixed and polymerize exothermically to produce a highly cross-linked network around the carbon fibers. In these systems, it has already been observed that the mechanical behavior of the composites is not well modeled using the bulk properties of the constituent epoxy and carbon fibers [8]. Finite element modeling of both metal and polymer matrix composites has shown that the shape and packing of fibers has an effect on the mechanical properties of a tow [9–11]. All of these studies demonstrate the need for further mechanical characterization of the matrix material within a fiber tow.

The small length scale at which the mechanical properties must be measured complicates characterization of the epoxy matrix within a composite. Common measurements of the elastic properties of polymer matrices rely on mechanically probing the sample surface. However, mechanical probes can be difficult to use in the confined spaces of a fiber tow. For example, nanoindentation close to the fiber–polymer interface is affected by the confinement of the

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matrix material near the interface, resulting in an artificially higher measured stiffness [12]. Brillouin light scattering measurements using microscope optics has been shown to resolve the mechanical behavior of materials at the micron scale [13,14]. Brillouin scattering probes the propagation and attenuation of thermal phonons that exist in all condensed matter at finite temperature. Therefore, no physical actuation is necessary to measure the elastic modulus. Additionally, the thermodynamic equilibrium of the sample is not disturbed because the momentum exchanged between the phonon and probing photon is small compared with the original phonon momentum. Deformations that would interfere with the mechanical constraints of the material near fibers are not required, and thus, confinement of matter in narrow spaces is not an issue for this technique. Furthermore, this technique can easily be combined with other optical analyses such as micro-Raman scattering, which is widely used as a tool for measuring structural deformations due to imposed or residual stress within a sample [15–17]. Because both methods are based on light scattering, their spatial resolution is primarily limited by the wavelength of light used. This enables measurements to be made in tightly confined regions and near interfaces.

In this investigation, we use Brillouin and Raman light scattering to measure the longitudinal modulus and residual stresses in the epoxy matrix of a carbon fiber reinforced composite. Our measurements reveal that the elastic response of the epoxy depends on its location relative to the fibers. Outside of fiber tows, the elastic modulus is close to that of bulk epoxy, cast without fibers, whereas within a fiber tow the modulus is linearly correlated with the local density of fibers surrounding the measurement spot. At the same time, our Raman measurements show that there is little connection between these changes and any existing residual stresses within the sample.

2. Methods and underlying formalisms

The composite system we chose for our study consists of eight layers of 45° braided carbon fibers embedded in a matrix of epoxy resin. The resin used is Epon 862, which was hardened with Epikure 9553, both manufactured by Hexion Specialty Chemicals. The average fiber diameter in our samples is 6 μm. Cubic samples were cut from the composite and mounted for polishing such that the axial tows lay parallel to the polishing plane. The sample was then polished using progressively finer compounds, ending with 0.25 μm SiC. The result of the polishing is a sample surface that appears smooth at 100× magnification on our microscope. For comparison, we also prepared bulk epoxy samples that were cut and polished in the same manner as the composite samples.

Our samples were imaged with an Olympus IX71 inverted microscope using a 100× objective lens. The field of view on the sample at this magnification measures 49 μm by 37 μm. Laser illumination for light scattering is provided by a 532 nm Coherent Verdi V2 laser through the objective lens. The laser spot size has a diameter of ~1.5 μm. Laser power at the sample is set to 0.5 mW. Scattered light is collected by the objective lens and exits through the back of the microscope. The scattered light is then directed to either the Brillouin spectrometer or the Raman spectrometer by repositioning a motorized mirror.

The Brillouin light scattering measurement consists of analyzing the light scattered from thermal phonons that naturally exist within matter at finite temperature, i.e., no external actuation is imposed on the specimen, which therefore remains in perfect thermodynamic equilibrium. A small fraction of these scattering events occur inelastically, emitting photons with a frequency shift proportional to the phonon propagation velocity. Moreover, considering that phonons constitute a density, and consequently a periodic and planar refractive index grating, light scattered from this grating must obey the Bragg diffraction condition

$$\boldsymbol{q} = \pm(\boldsymbol{k_s} - \boldsymbol{k_i}), \tag{1}$$

where $\boldsymbol{q}$ is the wavevector that describes the wavelength and propagation direction of the phonons probed, also called the scattering vector, and $\boldsymbol{k_s}$, and $\boldsymbol{k_i}$, are wavevectors of the scattered and incident light, respectively. Accordingly, the choice of scattering geometry allows one to single out phonons that propagate in a particular direction, and thereby ascertain the orientation of the underlying longitudinal and shear deformation. Because the velocity of sound is much smaller than the velocity of light, we can approximate:

$$|\boldsymbol{k_i}| = |\boldsymbol{k_s}| = \frac{n}{\lambda}. \tag{2}$$

Here, n is the index of refraction of the sample and λ is the wavelength of the incident light. From this approximation we calculate the magnitude of $\boldsymbol{q}$ as

$$|\boldsymbol{q}| = \frac{2n}{\lambda}\sin\left(\frac{\theta}{2}\right), \tag{3}$$

where θ is the angle between $\boldsymbol{k_s}$ and $\boldsymbol{k_i}$. Experimentally the scattering vector is determined by the laser wavelength and the angle between the illumination and collection optical paths. Because we use the same objective to illuminate the sample and to collect the scattered light, the scattering angle for our measurements is 180°. The phonon velocity of the medium can be calculated using the scattering vector, and the measured the frequency shift of the scattered light using

$$c_L = \frac{\omega_b}{|\boldsymbol{q}|} = \frac{\omega_b \lambda}{2n\sin\left(\frac{\theta}{2}\right)}, \tag{4}$$

where ω_b is the frequency shift of the scattered light. From this calculation we can then directly determine the longitudinal elastic modulus using the relation

$$\boldsymbol{M}' = \rho c_L^2 = \frac{E(1-\nu)}{(1+\nu)(1-2\nu)}. \tag{5}$$

Here E is the Young's modulus, ν is the Poisson's ratio, and ρ is the sample mass density. We collected all of our Brillouin spectra using a Sandercock six-pass tandem Fabry–Perot interferometer [18]. The spectrum of scattered light was analyzed by fitting the collected data with the appropriate expression of the dynamic structure factor using the open source peak fitting software package Fityk [19,20]. This yields peak position, i.e., the frequency shift, the peak intensity, and its full width at half maximum.

Whereas Brillouin scattering yields a measure of the stiffness of a sample, Raman scattering provides information about the deformation of the polymer network in a sample. Studies have demonstrated that the symmetrical stretching mode of phenylene around 1600 cm^{-1} is sensitive to the state of stress in a polymer [15–17]. As the tensile stress applied to the ring is increased, the peak shifts monotonically to a lower wavenumber. Furthermore, it has been found that the D and G bands in the Raman spectrum of carbon fiber shift to lower wavenumbers under the application of tensile stress [17,21]. The epoxy that we chose for our composite, Epon 862, contains two phenylene groups, which yield a cluster of three peaks between 1585 cm^{-1} and 1618 cm^{-1} (Fig. 1a). By analyzing the position of these peaks along with the locations of the D and G peaks of the carbon fiber spectrum (Fig. 1b), we can determine the state of stress of our sample relative to bulk epoxy and loose carbon fibers. We collected the Raman spectra using a Princeton Instruments TriVista triple monochromator with a 750 mm focal