Research Letter

Raman Spectroscopy for the Nondestructive Testing of Carbon Fiber

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The goal of this research is to evaluate the potential of Raman spectroscopy as a method of condition assessment for carbon fiber composite materials used in high performance situations such as composite overwrapped pressure vessels (COPVs). There are currently limited nondestructive evaluation (NDE) technologies to evaluate these composite materials in situ. Variations in elastic strain in the composite material can manifest from degradation or damage, and as such could provide a tool for condition assessment. The characterization of active Raman bands and the strain sensitivity of these bands for commercially available carbon fibers are reported.

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1. INTRODUCTION

Carbon fiber-epoxy composites are commonly used as the wrapping materials for composite overwrapped pressure vessels (COPVs). The fiber/matrix composite overwraps a metal or plastic liner and carries the majority of the tensile load when the vessels are pressurized. COPVs of this design are common for carrying natural gas in alternative fuel vehicles, and the use will likely increase as the hydrogen economy expands as a clean and cheaper solution for fuel. Tanks of this design are also common in aerospace applications due to the high strength to weight ratio of the carbon materials. The composite material may be exposed to impact damage, prolonged periods of stress, and environmental degradation. These stresses and damage are typically not visible, and effective methods for the nondestructive evaluation (NDE) of vessels during their service lives are needed to ensure safe operation. The results reported here are part of a study to explore if Raman spectroscopy has the potential to contribute to the condition assessment and NDE of the carbon composite COPVs. Initial measurements to determine if critical Raman peaks can be observed in common, commercially available materials, are reported. Exploration of the strain sensitivity of certain peaks is also discussed.

Carbon fibers are made of graphite-like material, with variations in their structure depending on their method and source of production. Raman spectroscopy is a laser method using inelastically scattered light to investigate vibrational, rotational, and other low-frequency modes of interaction between molecules. Raman bands are sharp peaks in the spectra that can be associated with vibration modes at a molecular level. Early studies on graphite materials revealed that a Raman band at $\sim 1585\text{ cm}^{-1}$ can be related to C-C vibrations in graphite and is present in all carbon fibers. Another band in polycrystalline graphite was found at ~ 1330 and can be related to the boundaries of the graphite crystals. Thus it can be related to particle size and structural disorder effects [1]. It is also found that the ~ 1330 band is associated with poorly graphitized fibers and the band will disappear at higher graphitization temperatures. This Raman band is commonly known as the “disorder” induced line and is more prevalent in low modulus/low heat treatment fibers [2].

From literature, there are several more Raman bands found in carbon fiber depending on the level of graphitization, laser power and wavelength, and source of material. For convenience, a letter notation is used to refer to the bands. The ~ 1330 and $\sim 1585\text{ cm}^{-1}$ are assigned as D- and G-lines, respectively. The strong G-line is present due to

the hexagonal ring structure with E_{2G} symmetry of graphite crystal. The weak D-line is of A_{1G} symmetry and is present in disordered forms of carbon. At low firing temperatures, the D band will exhibit broad lines [3, 4]. For nongraphitized fibers, a D'-line is present at $\sim 1620\text{ cm}^{-1}$. At higher firing temperatures, it can be detected as a shoulder of the G-line. An overtone of the D-line is present at ~ 2720 as the G'-line. Although it is present as an overtone of the D-line, it is more closely linked to Raman characteristics such as intensity and FWHM to the G-line [2]. Another band present is the G''-line at $\sim 2950\text{ cm}^{-1}$, often referred to as a combination band; at a frequency roughly the sum of the D- and G-lines is likely a combination of the two [5]. As previously stated, different fibers and composites may contain additional bands due to their material characteristics.

It has been found from previous research that Raman bands present in the spectra of carbon fiber are strain sensitive. With an increase in applied tensile strain, Raman bands shift to lower frequencies and tend to broaden in peak width [6]. Conversely, with applied compressive strain the Raman bands will shift to higher frequencies [7]. The principal reason for these frequency shifts is due to bond anharmonicity, producing a decrease in bond modulus and vibrational frequencies with an increasing stress [8]. For carbon fibers, the shift is dependent upon the fiber modulus, with stiffer fibers exhibiting a greater frequency shift. The slope of this linear relationship is referred to as the Raman frequency gauge factor (RFGF). The RFGF has been found to increase as the frequency of the Raman band investigated increases. So for the same fiber, the RFGF value should increase from the D-line to the G-line to the second-order Raman bands [7]. For the G-line at 1585 cm^{-1} , frequency shifts (RFGF) have been found on the order of $10\text{ cm}^{-1}/\%$ applied strain for PAN-based fibers and $12\text{ cm}^{-1}/\%$ applied strain for pitch-based fibers [6, 9].

The RFGF has the potential to contribute to the condition assessment of the carbon-wrapped COPVs by providing engineering knowledge of the state of stress in the surface of COPVs as a means of detecting damage or degradation of the COPV. Initial measurements reported here provide foundational data on the Raman response of commercially available fibers in their as-marketed conditions.

2. EXPERIMENTAL

The carbon fibers and strands were obtained from various sources. Table 1 lists each of the fibers tested and their critical properties. The Nippon Graphite Fiber Corporation supplied our high-modulus pitch-based carbon fibers. The Toray Carbon Fiber samples are PAN (Polyacrylonitrile)-based fibers. The T700S fiber is a high strength, standard modulus fiber typically used in commercially COPVs. The T1000 fiber is ultrahigh strength and used in critical applications such as aerospace COPVs.

All testing to date has been conducted using a Renishaw Raman spectrometer with a 20x microscope for zooming in on individual fibers. An incident laser wavelength of 752 nm has been used with varying laser power. Samples were either cut into small pieces and laid on a platform or cut into

FIGURE 1: Raw spectra with D, G, D', and G' Raman bands identified of pitch-based Nippon Graphite Fibers using a 752 nm excitation laser.

FIGURE 2: Raw spectra with D and G Raman bands identified of PAN-based fibers using a 752 nm excitation laser.

6" (15.24 cm) pieces and put in an in-house machined steel load frame for applying strain. The load frame is rectangular with grips on the ends and a cylindrical rod in the center that can be raised to apply tension. Strain can be calculated using Pythagorean's theorem.

3. RESULTS

Reproducible spectra were obtained for all types of carbon fibers listed, with distinct, active Raman bands from literature identified using a 752 nm incident laser. For the pitch-based fibers, four bands, D, G, D', and G', have been identified as shown in Figure 1. The PAN-based fibers have just the D and G bands present, as shown in Figure 2. Both types of fibers exhibit a large hump in the spectra present from $1700\text{--}2500\text{ cm}^{-1}$ with an off-center peak around 1950 cm^{-1} , which is thought to be an experimental artifact.

Our results have shown that there is a frequency shift for the peaks of the D and G bands of the PAN-based fibers. The raw spectra prove to be difficult to work with due to the variance in data points near the peaks, so peak shift measurements are conducted using smoothed forms of the spectra.

To analyze the spectra produced from the carbon fiber, commercial software PeakFit was used. The software enables the user to shape functions to the peaks produced by the spectra and remove or filter errant data from the spectra. For the spectra, deconvolution with a quadratic base line and a 96% filter is fit to a Lorentzian amplitude. The processed

TABLE 1: Physical properties of carbon fibers tested.

Fiber type	Tensile modulus		Tensile strength		Elongation	Density
	GPa	Msi	MPa	Ksi		
Nippon (pitch)						
YS-95A	900	131	3530	510	0.3	2.19
CN-90	860	125	3430	500	0.4	2.19
CN-80	780	114	3430	500	0.5	2.17
CN-60	620	90	3430	500	0.6	2.12
Toray (PAN)						
T700	230	33.4	4900	711	2.1	1.80
T1000	294	42.7	6370	924	2.2	1.80

FIGURE 3: Zoom-in of a raw and processed spectra of T1000 carbon fiber showing D and G band shifts with 0% and 1.83% applied strain.

peaks can be analyzed in many ways. The peak frequency location can be examined for each spectrum. Figure 3 shows the peak shift for the D and G bands of a PAN-based fiber, including both the raw and processed data, for a strain of 1.83%. It is found that peak locations for a given Raman band change linearly as a function of applied strain.

4. CONCLUSIONS

Reproducible Raman spectra for both types of carbon fiber samples have been found using a 752 nm incident laser, with Raman bands D, G, D', and G' identified. Strain dependence of the D and G bands is demonstrated for the PAN-based fiber. Both the D and G bands have been found to decrease in resonance frequency as applied tensile strain increases. This observation is also supported in the literature by previous research in this field. From our initial results, it appeared that the peak frequency decreased approximately 10 wave-numbers/percent applied strain. These results indicate that Raman spectroscopy has some ability to make strain measurements in commercially available carbon fibers. Such measurements have the potential to be used as a tool for NDE in inspections and reliability assessment of carbon fiber composite materials.

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