TEMPERATURE-DEPENDENT DIELECTRIC MEASUREMENTS OF POLYACRYLONITRILE FIBERS DURING AIR OXIDATION

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ABSTRACT

Simple direct-current (DC) electrical conductivity measurements are widely used to measure the degree of carbon fiber processing during the latter stages of the carbonization, and during the graphitization, of polyacrylonitrile (PAN) fiber. Unfortunately, DC conductivity measurements are not possible for the oxidation stage and for the early stages of carbonization because the PAN conductivity is too low. Herein is described a simple microwave cavity technique for a continuous, non-contacting, in-situ, real-time measurement of the complex dielectric constant of PAN during the oxidation and early carbonization stages of carbon fiber manufacturing. The real and imaginary parts of the dielectric constant are good indicators of the degree of thermal processing in the PAN oxidation/stabilization process.

KEYWORDS: Carbon Fiber, Oxidative Stabilization of Polyacrylonitrile, Dielectric Properties

1. INTRODUCTION

Carbon fiber is a material with very high specific stiffness and strength and modest cost, hence is very attractive in weight-critical applications. It is employed extensively in structures that incur high cost penalties for excessive weight. Carbon fiber is also very attractive for use in heavy vehicle and light automotive platforms, where its use offers energy efficiency gains. However, investment returns for reducing weight on commercial heavy duty vehicles justify only small cost premiums for carbon fiber; furthermore, consumers and automotive manufacturers are unwilling to pay any cost premium on most automobiles. Various studies have indicated that carbon fiber needs to be priced around $4/lb. to become a pervasive material in heavy vehicle and automotive platforms. The present price for commercial grade carbon fiber ranges $6/lb. - $8/lb., depending on quality and form.

In conventional carbon fiber manufacturing, the polyacrylonitrile (PAN) precursor passes through a series of continuous and sequential processing steps (Figure 1), each of which causes

specific chemical, morphological and mechanical changes in the fiber. The carbon fiber is manufactured in a tow, which consists of from 3 to 60 thousand individual PAN or pitch filaments, with each precursor filament being only about 10 to 14 μm in diameter. The major processing steps include pre-treatments, oxidative stabilization (labeled "thermoset" in Figure 1), carbonization, graphitization, and post-treatments. A preliminary analysis of commercial grade carbon fiber cost (1) indicates that the principal cost elements are precursor (~43%), oxidative stabilization (~18%), carbonization (~13%), and graphitization (~15%), with various pre- and post-treatments, inspection, materials handling, etc. comprising the remaining costs. Cost reduction solutions have been under development for several years for all major cost elements. Oak Ridge National Laboratory is now investigating a new approach to oxidative stabilization that may significantly increase line speed and reduce cost. The proposed approach is based on the use of plasma processing technology, which ORNL has successfully applied to the carbonization and graphitization steps.
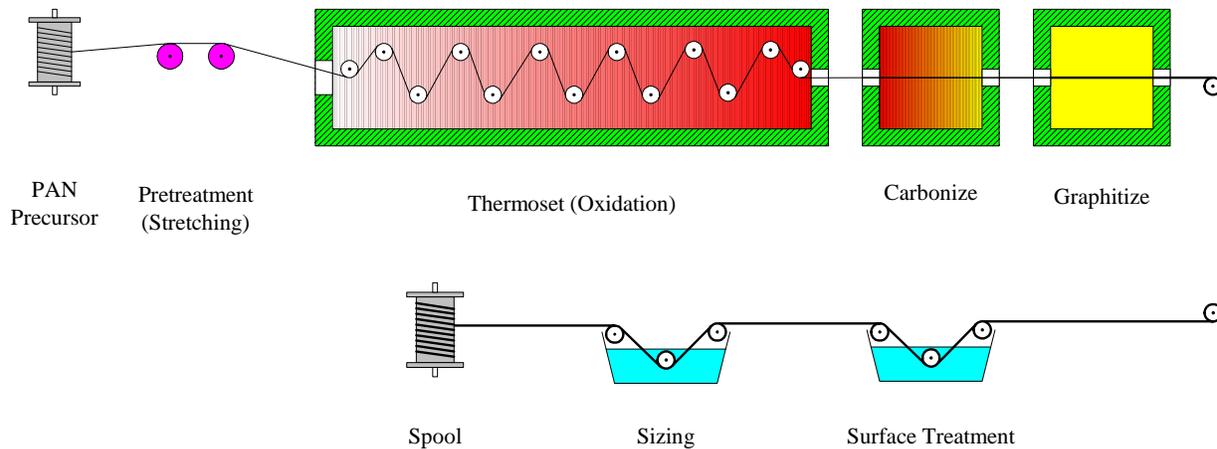
Figure 1. Typical processing sequence for PAN-based carbon fibers.

Oxidative stabilization cross-links and cyclizes the precursor. Cross-linking "stabilizes" the precursor, and the stabilization rate is primarily dependent on the availability of energy (usually heat) needed to drive the process. The cyclization reaction is a diffusion-controlled process that occurs optimally (but not necessarily) in an oxidizing medium. The cross-linking (stabilization) and cyclization (oxidation) reactions occur almost simultaneously; therefore the terms stabilization and oxidation are often used interchangeably. The term oxidative stabilization is sometimes employed to encompass both processes when conducted in an oxidizing medium. The precursor is converted from a thermoplastic to a thermoset material during oxidative stabilization; hence the term "thermosetting" is also used occasionally.

Oxidative stabilization is the most time-consuming and rate-limiting step in conventional carbon fiber manufacturing. Furthermore, it requires more space than all other steps combined. It normally involves the treatment of the fibers in an oxidizing atmosphere for two hours or longer at temperatures ranging from ambient to about 200°C to 270°C, while the fibers are maintained under tension in large furnaces. The thermoset fibers are subsequently carbonized at temperatures up to about 1,300°C to 1,600°C in an inert atmosphere (the carbonization step) and may be further heated up to as much as 3,000°C (the graphitization step).

Oxidative stabilization will greatly affect the final carbon fiber properties. During oxidative stabilization, the fibers experience dramatic morphological changes that transform them from thermoplastic material into thermoset, nonmeltable fibers, enabling them to endure further processing at higher temperatures without changing the fiber form. Incomplete oxidative stabilization can result in a "blow-out" of the of the fiber core during carbonization (2).

Several methods for PAN-precursor oxidation have been utilized. The most common method is oxidation in air, which usually requires hours to achieve full oxidation. The PAN-precursor can be heated in air up to (with the rate of heating being an important factor) in a batch process or by heating the precursor tow continuously as it is transported through furnaces or kilns containing several temperature zones.

Simple direct-current (DC) electrical conductivity measurements are widely used to measure the degree of carbon fiber processing during the latter stages of the carbonization, and during the graphitization, of PAN fiber. Unfortunately, DC conductivity measurements are not possible for the PAN oxidative stabilization stage and for the early stages of carbonization because the tow conductivity is too low to be easily measured. For example, oxidized PAN has a DC conductivity of $< 10^{-8}$ siemens/m (electrical resistivity $>10^{10}$ Ω-cm) (3). PAN is an even better DC insulator. Usually density measurements are the accepted methods (pycnometry and bulk) used to characterize the degree of PAN oxidative stabilization. Also, Wide-Angle X-Ray Diffraction and differential scanning calorimetry are two more sophisticated methods for these evaluations. However, they are slow, expensive and not quite suitable for R&D trials where a large number of measurements including a wide variety of processing technologies and conditions are investigated. Color has been the relied on to benchmark the degree of oxidative stabilization for PAN fibers. Color is somewhat subjective and process dependent however, and what was needed was an inexpensive, fast, and quantitative method to determine the degree of PAN processing during oxidative stabilization. Even though the DC conductivity of the PAN oxidation stabilization stage is very low, the high frequency electrical properties or "dielectric properties" are finite and easily measured. In this paper the real and imaginary parts of the dielectric constant, as measured by a resonant microwave cavity technique, are good indicators of the degree of thermal processing in the PAN oxidative stabilization process is demonstrated. Furthermore this microwave cavity technique is suitable for continuous, non-contacting, in-situ, real-time measurements of the PAN oxidative stabilization stage in an industrial processing line (4).

2. EXPERIMENTAL

2.1. Dielectric Background The measurement of the dielectric properties of materials is a very sensitive measurement technique for monitoring the morphology and composition of a wide variety of materials (5). The mechanism for microwave energy transfer into materials is complicated and consists of several contributions to the electric polarizability of molecules. Polarized molecules or atoms can rotate in response to an applied microwave electric field and can cause microwave energy to be transferred from the electric field into the material. The dielectric properties of materials are characterized by the complex permittivity (6), ε, given by,

$$\varepsilon = \varepsilon_o\left(\varepsilon' - j\varepsilon''\right), \qquad\qquad [1]$$

The permittivity of free space, ε_o, is 8.854×10^{-12} Farads/m, ε' is the real relative part of the complex permittivity, often referred to as the dielectric constant, and ε'' is the imaginary relative part of the complex permittivity, and $j = \sqrt{-1}$. The real part of the relative dielectric is a measure of the amount of energy stored in the dielectric due to an applied electric field and the imaginary part of the dielectric constant is a measure of the amount of energy dissipated in the dielectric due to an applied electric field. When a material is undergoing a complex series of chemical reactions, such as in the PAN oxidative stabilization process, the nature of the chemical bonds are constantly changing, and this change has a sensitive effect on the molecules' "electrical polarizability". It is well known that these changes are manifested in changes in the PAN dielectric properties. Another measure of dielectric loss is tanδ, or "loss tangent", which is defined as $\varepsilon''/\varepsilon'$. This term is not used in this study since it is a derived quantity from the more fundamental electrical parameters ε' and ε'', which are proportional to the amount of energy stored and dissipated, respectively, in a dielectric due to the presence of an applied electric field.

2.2 Experimental Hardware Configuration An experimental setup was constructed and is shown in Figure 2 below to measure the temperature-dependent dielectric properties of PAN fiber undergoing conventional oxidative stabilization.
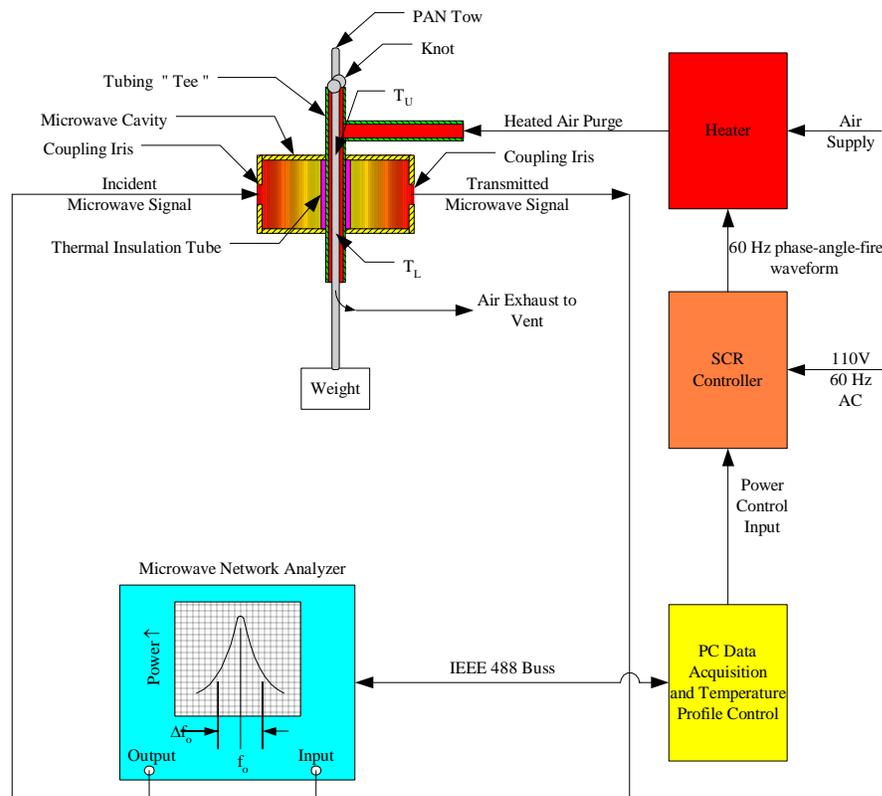
Figure 2. The experimental setup.

The rectangular microwave cavity is oscillating in the TE_{011} mode at 2.48 GHz and measures 7.21 cm wide by 3.40 cm high by 10.16 cm deep and is shown in Figure 3. The network analyzer sweeps the microwave frequency rapidly about the cavity resonance frequency at applied power levels less than 5 mW. No significant direct microwave heating of the PAN fiber occurs because the amount of thermal power (20 to 750 watts) to the process air is always much greater than the microwave power. The PAN tow is contained within a microwave-transparent tee that is centered in the microwave cavity near the peak of the cavity electric field. A microwave-transparent insulation tube that reduces the heat loss along the length of the main tube surrounds the tee. The tee extends far outside the cavity walls so that end-heating effects on the PAN tow do not occur inside the microwave cavity, thus securing the proper processing of the tow inside the cavity. Hot air enters the side arm of the tee and is partitioned between the top and the bottom of the tee so that the hot air can process both ends of the PAN tow in the tee inside of the cavity. The rest of the tee outside the cavity and the side arm are also insulated. The heated air was filtered for particulates and oil but not pre-dried to remove any residual water to mimic industrial conditions. The fibers were characterized for density to determine filament diameter and tow area prior to and after processing so that the tow volumes can be determined.
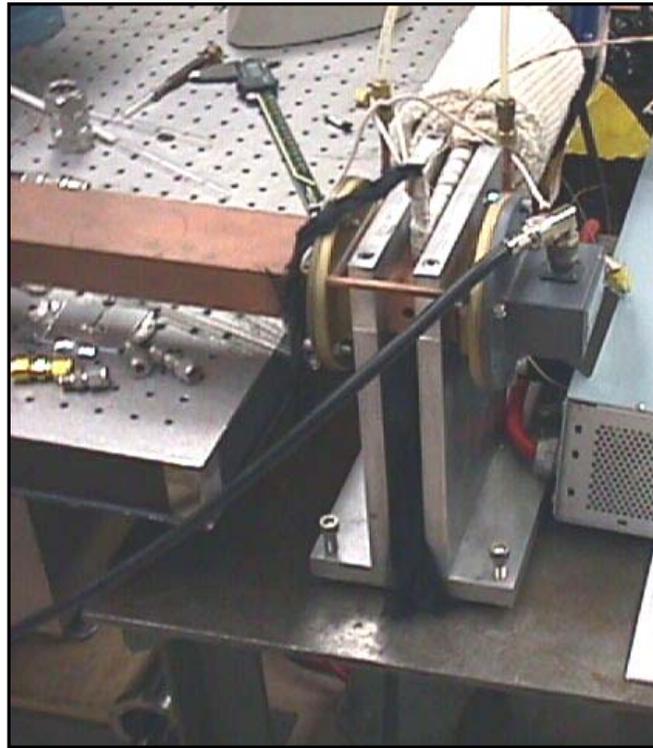
Figure 3. The microwave cavity.

2.3 Dielectric Measurements and Results A microwave cavity perturbation technique is used to measure the complex dielectric constant of the PAN fiber as the fiber is heated by air. A PC running Labview data acquisition and control software controls the air temperature and sends commands to a Hewlett Packard model 8753C microwave network analyzer to take frequency and bandwidth measurements of the cavity resonance. These frequency measurements can be

related to the real and imaginary relative permittivity by the following formulas derived from (7) as:

$$\varepsilon^{'} = 1 + \frac{V_c}{2V_t}\left(1 - \frac{f_t}{f_o}\right)$$ [2]

$$\varepsilon^{''} = \frac{f_t V_c}{4 f_o V_t}\left(\frac{\Delta f_t}{f_t} - \frac{\Delta f_o}{f_o}\right)$$ [3]

The empty cavity resonance frequency without the tow is f_o, f_t is the cavity resonance frequency with the tow inserted, Δf_o is the empty cavity bandwidth, Δf_t is the cavity bandwidth with the tow inserted, V_c is cavity volume (a constant during the measurements), and V_t is the tow volume (also assumed to be constant). The weight of the tow in the cavity and the tow density, as measured by pycnometry, determine the tow volume. The number of individual filaments in each tow is unimportant in comparing the dielectric properties of tows with different filament counts because only the tow density and weight enter into the calculation. In these types of measurements the cavity is set up empty and f_o, Δf_o, and V_c are measured. The PAN tow is then inserted and f_t, and Δf_t are measured as a function of temperature. Two type-K thermocouples measure the upper and lower processing temperatures, T_U and T_L respectively as shown in Figure 2. They are placed just outside the microwave cavity so as not to perturb the cavity electric field and are averaged to obtain the mean processing temperature. Typically the resonant frequency decreases ($f_t < f_o$) and the cavity bandwidth increases ($\Delta f_t > \Delta f_o$) when the tow is placed in the cavity. Therefore ε' and ε'' are positive real numbers. The temperature profile used to process the PAN tows was developed to mimic industrial oxidation stabilization profiles with heating rates of from 2° to 4°C/min and temperature ranges from 25° to 250°C. The frequencies and bandwidths were measured as a function of temperature every 4 s and the data was processed using equations [2] and [3] above to produce raw data that was later smoothed and then fitted to a 5th order polynomial to produce the analyzed data shown below. Figure 4 shows the real and imaginary parts of the relative dielectric permittivity as a function of processing temperature for two different PAN tows that were pre-dried in a vacuum oven for 24 hours at room temperature. This was done to remove water from the tow. The two runs demonstrate good run-to-run repeatability. The dielectric properties are shown to be almost constant or very slowly increasing up to about 100°C. Above 100°C the dielectric properties increase more rapidly, especially at the upper processing temperatures. The smooth, monotonic increase of the dielectric properties is remarkable since it is well known that dramatic changes occur in the PAN morphology and chemistry during the overall process (8,9). The original density of the PAN precursor was 1.2002 gm/cm³ and the final density of the fibers after processing was 1.3598 gm/cm³. The tow does lose some mass during the oxidative stabilization; however the data was not corrected for this loss. This was because there is a very small mass loss during industrial processing (10) and it was desired to mimic actual processing as much as possible. It is also possible to display the data as a volume independent quantity, $\varepsilon''/(\varepsilon'-1)$, since according to equations [2] and [3] the tow and cavity volumes cancel. This would eliminate the need to know the tow and cavity volumes for real-time, in-situ process measurements. However, this ratio

lacks the physics connection that the real and imaginary parts of the relative dielectric constant have.

A run was conducted without any pre-drying to compare to the pre-dried runs in Figure 4 to investigate the effect of absorbed water in the PAN precursor and is shown in Figure 5. Comparing the two cases, the differences in the died and non-dried PAN were minimal up to about 200°C indicating that water absorption plays no significant role in the dielectric properties of the PAN. Above 200°C both ε' and ε'' reach a maximum value and then decrease. However, this cannot be due to water since above 100°C all traces of water are evaporated and removed by the heated air purge. It is believed this effect is due to the initial process of carbonization where a significant loss of mass and a relative increase in the content of carbon compounds would be expected. Free, amorphous carbon is known to strongly absorb microwave energy (11), however this carbon in the bulk of the filaments in the precursor is strongly bound in other compounds and therefore does not strongly couple to the microwave energy.
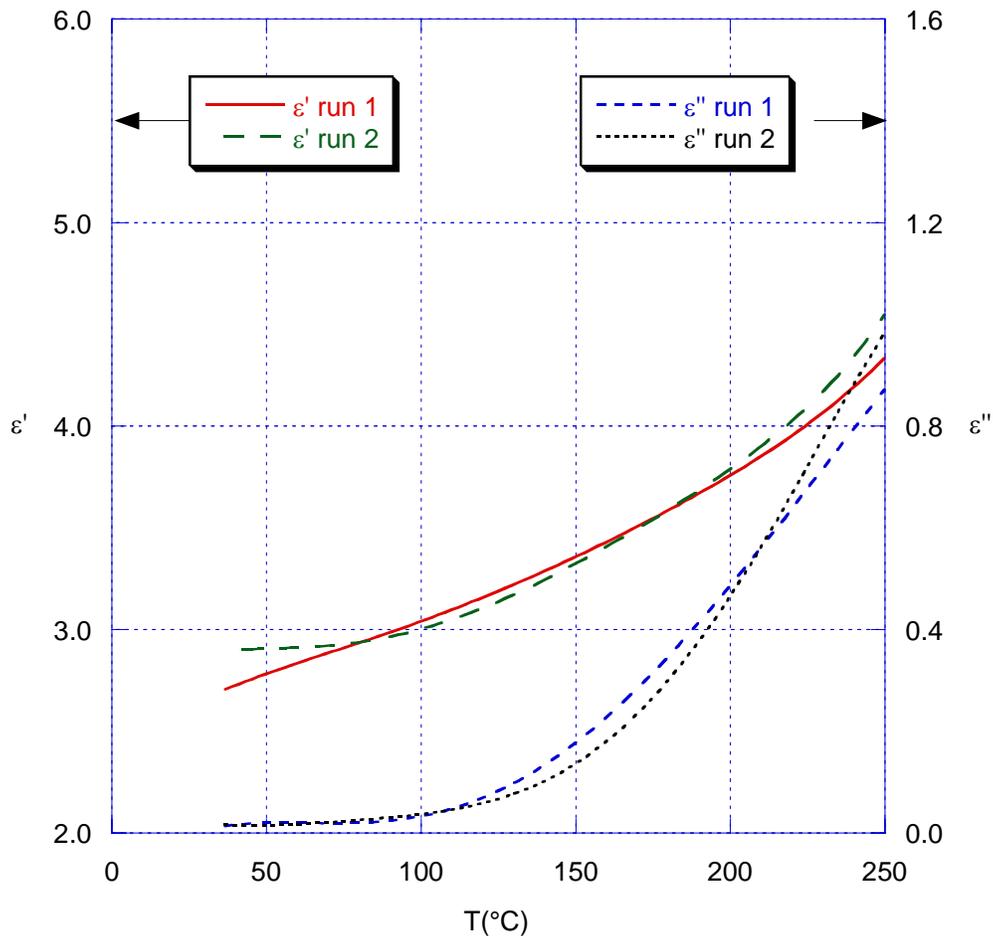
Figure 4. Dielectric properties for two different pre-dried PAN tows as a function of temperature.

The peak and subsequent drop off in both ε' and ε'' in Figure 5 occurs at temperature near 250°C. These phenomena also occurred in Figure 4 for both runs but at temperatures around 260°C. The data was limited to 250°C because this is generally the maximum temperature used in oxidation stabilization in industry. This peak shows up in Figure 5 because the measured temperatures were underestimating the real process temperature. Air currents were causing the thermocouple to shift to the wall of the quartz tube where the temperature is lower due to heat conduction losses may have caused this error.
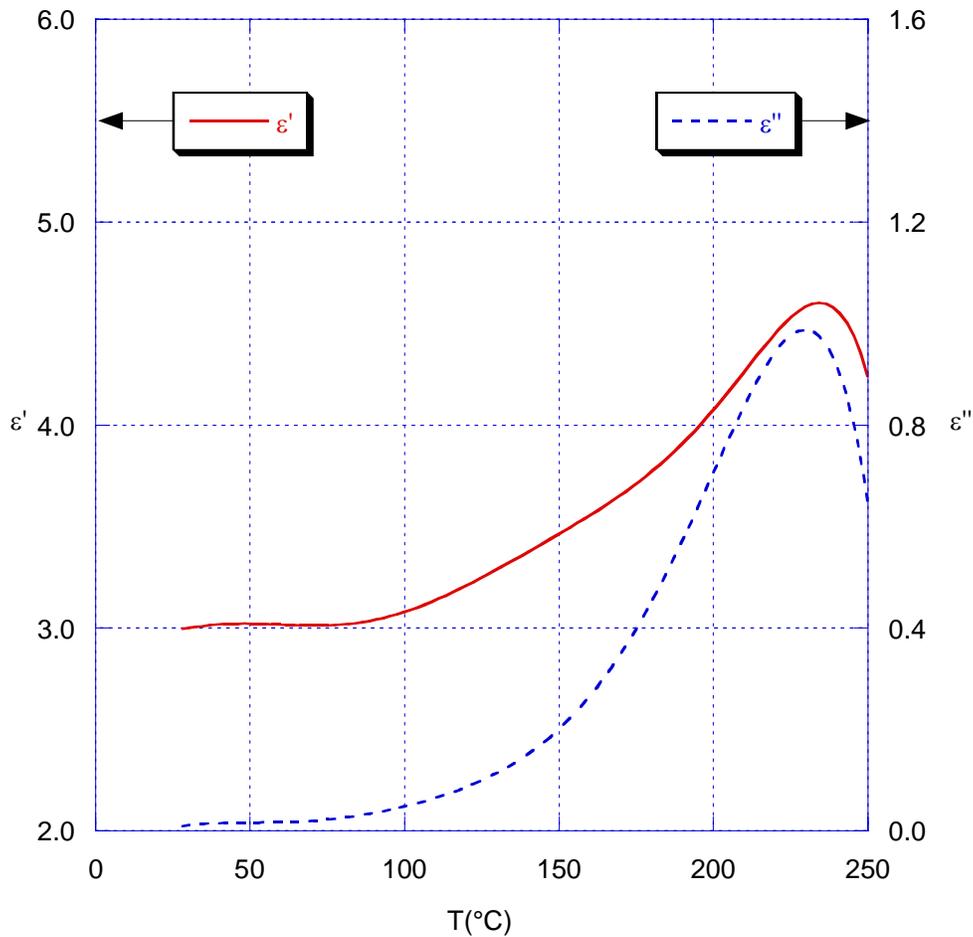
Figure 5. Dielectric properties of non-dried PAN.

Figure 6 shows the dielectric properties for fully oxidized PAN produced conventionally. This PAN has been previously oxidatively stabilized by industry up to 250°C. This fully oxidized PAN was re-heated using the same temperature profile, so that the values for ε' and ε'' at 250°C can be compared. It is seen that ε' and ε'' are 4.7 and 1.0, respectively, and compare favorably to the average of runs 1 and 2, for ε' and ε'' in Figure 4 at 250°C.

The slightly higher values in Figure 6 can be explained as follows. The industrial "fully oxidized" carbon fiber is in reality not 100% chemically fully oxidized. Because oxidative stabilization of PAN fiber requires a long processing time, the industrial approach is to reach

only an acceptable level of oxidation consistent with process economics. A central core consisting of non-oxidized material will characterize "fully oxidized" PAN filaments (12). A higher level of oxidation occurs when these filaments are subjected to another reheating/oxidation process. This explains the slightly larger values in ε' and ε'' over the entire temperature range due to reheating or reprocessing.
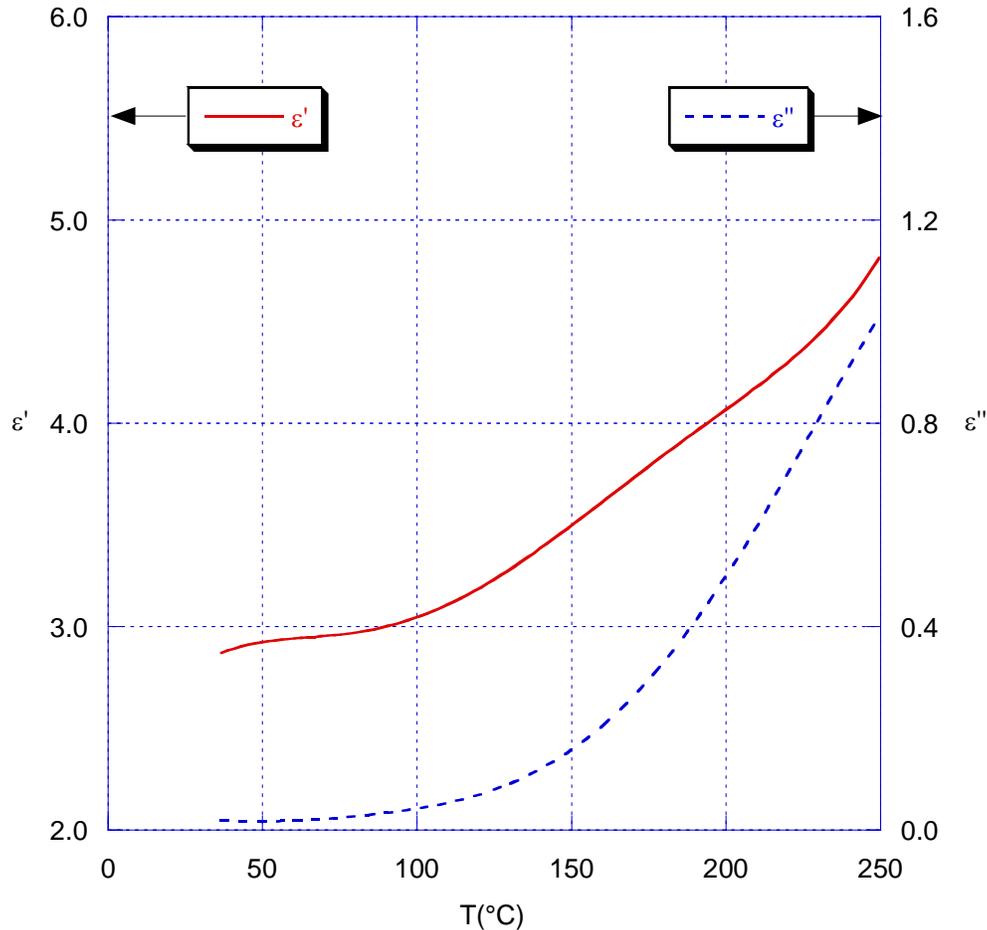
Figure 6. The dielectric properties for conventionally produced fully oxidized PAN as a function of temperature.

Figure 7 illustrates the dielectric properties of a 3000 filament, virgin, as-received, PAN precursor as a function of position along the PAN tow length, measured at room temperature. The PAN dielectric properties are fairly constant indicating a uniform linear density and geometry. A very small amount of impurities such as oils or resins will increase the values of ε' and ε' and ε'', especially if these impurities have higher intrinsic values of ε' and ε''. During this study, PAN precursor contaminated with oils was shown to have very high values for ε'' approaching 0.8 at room temperature, a factor of 40 higher than the values for ε'' shown in Figure 7 for clean, virgin PAN precursor. The 3000-filament tow was much smaller in cross section compared to other tows measured, which allowed the tow to be positioned off center in the cavity compared to the larger cross section tows. This positional error between the PAN tow

and the cavity center may explain some of the variability in ε'. The values for ε'' are consistent with those shown in Figures 3 and 4 at room temperature. Figure 7 shows that an on-line, real time, non-contacting process monitor is practical using the microwave resonance cavity method.
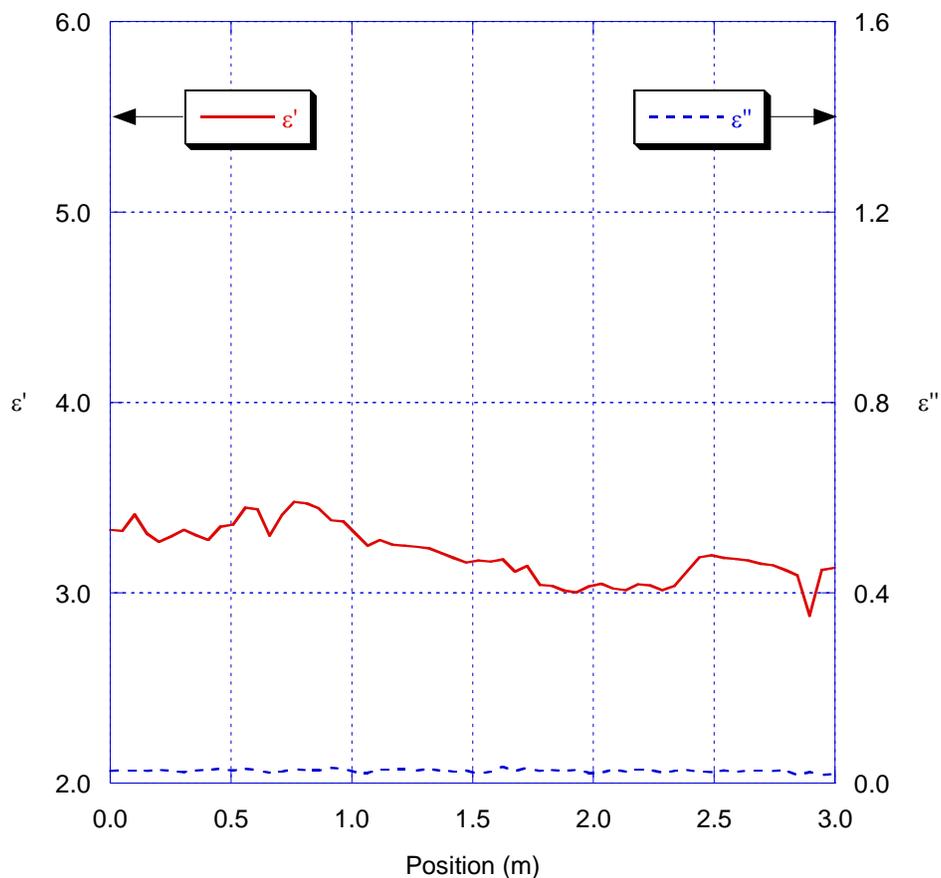
Figure 7. The dielectric properties of a 3000-filament tow at room temperature for virgin PAN precursor as a function of position along the PAN tow length.

3. COMMERCIALIZATION

This technique for monitoring the oxidative stabilization progress of PAN precursor has been patented by ORNL and is available for licensing.

4. CONCLUSIONS

When a material is undergoing a complex series of chemical reactions such as in the PAN oxidative stabilization process, the nature of the chemical bonds in the PAN is constantly changing, and this change has a sensitive effect on the molecules' electrical polarizability. This change is manifested in changes in the PAN dielectric properties. In spite of the complex chemistry (polymerization, cyclization, exotherms, dehydrogenation, etc.) involved in the oxidative stabilization of the PAN fiber, a relatively monotonically increasing dependence of the dielectric properties with process temperature (up to a certain temperature level) is seen. This

allows the microwave cavity technique to be used as a straightforward measure of the progress of PAN oxidative stabilization. Also, this technique is useful as a quality assurance check for the incoming PAN precursor, since small amounts of impurities and/or a change in the PAN chemistry can affect the dielectric properties. This work has demonstrated the successful application of a simple microwave cavity technique for a continuous, non-contacting, in-situ, real-time measurement of the complex dielectric constant of PAN during the oxidation and early carbonization stages of carbon fiber manufacturing. The real and imaginary parts of the dielectric constant are good indicators of the degree of thermal processing in the PAN oxidation/stabilization process.

5. ACKNOWLEDGEMENTS

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