Dielectric Measurements of PAN Precursor and Stabilized Fibers

J.Hofele[1a], G. Link[1] and J. Jelonnek[1,2]

IHM[1], IHE[2], Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

[a]hofele@kit.edu

***Abstract* — Given that the carbon fiber production is an energy intensive process, new approaches are investigated. One option might be dielectric heating, but in order to design an efficient applicator, the knowledge of the temperature dependent dielectric properties is a requirement. In this paper the focus is on the dielectric measurements of the Polyacrylonitrile (PAN) precursor fibers and stabilized fibers. A measurement system was developed that is capable to monitor in-situ changes of the dielectric properties during the stabilization process of the PAN fiber. First results show that the losses of the PAN fiber are strongly varying with the temperature. Additionally, the change in the dielectric properties due to the chemical transformation during the stabilization process can be tracked. The strong temperature dependency is decreasing with a higher degree of stabilization.**

***Keywords* — dielectric measurement, in-situ monitoring, PAN fiber, stabilization, carbon fiber production**

I. Introduction

Carbon fiber composites are already used in a large number of lightweight applications such as the aerospace and automotive industry because of its high strength to weight ratio [1]. But in order to increase the utilization, the material costs have to be reduced compared to steel or aluminum. Sunter et al. specify the practical minimum energy needed for the carbon fiber production to be 330 MJ/kg [2] whereas Fruehan et al. state 8.2 MJ/kg for liquid steel [3]. The carbon fiber production process comprises multiple steps. First fibers are spun from a polymer precursor solution, then it passes two major stages: the initial stabilization and the final carbonization stage. During the stabilization stage, different chemical reactions take place such as oxidation, cyclization and dehydration. Depending on the chemical composition, the reactions take place at temperatures between 180 °C and 300 °C. The chemical transformation during the stabilization stage leads to an exothermic reaction. The heat release has to be considered in the control of the input power, the heating rates and holding times. The most significant energy saving is expected at the stabilization stage [4]. Hence, new energy efficient production processes for the stabilization stage are necessary. Microwave heating might be one of the solutions. In [5] Zhang et al. compare microwave and conventional heating of PAN fibers. They state that microwave heating has a shortening influence on the reaction time and improves the fiber surface. In [5] the fibers are attached to a ceramic rod but no dielectric properties are provided neither for the ceramic rod nor for the PAN fibers. It can be assumed that the microwave was predominantly heating the ceramic rod at the beginning of the heating up phase, which heated the fiber via thermal conduction. Only later a direct microwave heating might take place, but as no dielectric properties are provided it is not possible to definitely draw this conclusion. In [6] dielectric properties of PAN fibers are presented, but only to a limited range in temperature and also without any information about the final stabilization degree, as the cooling down was not recorded and a holding time was not provided.

For the successful design of an appropriate direct heating system, the knowledge of the temperature-dependent dielectric properties of the raw material together with the chemical process during the production is mandatory. In the following, a measurement system to measure the temperature dependent dielectric properties during the complete stabilization stage and its results are described.

II. Theory

For the dielectric measurements, the perturbation method is used. The perturbation of the electromagnetic field in the resonant cavity results from the introduction of the dielectric material. The dielectric properties of the fibers are calculated from the changes in the resonant frequency and quality factor [7]:

$$\varepsilon_\mathrm{r}' = \frac{1}{A}\frac{f_\mathrm{ref} - f_\mathrm{s}}{f_\mathrm{ref}}\frac{V_\mathrm{c}}{V_\mathrm{s}} + 1$$

$$\varepsilon_\mathrm{r}'' = \tan\delta \cdot \varepsilon_\mathrm{r}' = \frac{1}{B}\frac{Q_\mathrm{ref} - Q_\mathrm{s}}{Q_\mathrm{ref} Q_\mathrm{s}}\frac{V_\mathrm{c}}{V_\mathrm{s}} \cdot \varepsilon_r'$$

where ε_r' is the relative dielectric constant, tan δ is the dielectric loss tangent and ε_r'' is the relative dielectric loss factor, f_{ref} and f_s are the resonance frequencies of the unperturbed and perturbed cavity, respectively. Q_{ref} and Q_s are the corresponding quality factors. V_c and V_s are the volumes of the cavity and the sample. The calibration factors A and B depend on the sample and cavity geometries, the sample permittivity as well as on the final cavity wave pattern. The calibration of A and B is done with the help of CST Microwave Studio within the range of the expected dielectric properties.

III. Experimental Setup

A. Setup

The complete measurement system is shown in Fig. 1. The measurement is performed in a cylindrical TM_{010}-mode cavity using the perturbation method around 2.5 GHz with a quality factor of the empty cavity of about 10000. The height and radius

of the cavity are 45 mm. An N-Type port with a pin antenna is used as input and an SMA port also with a pin antenna as output. A 12 k PAN fiber, representing a bundle of 12000 filaments, is located in a quartz tube that is placed along the maximum electric field of the TM_{010}-mode. The quartz tube position is fixed with the help of Teflon insulation ring. A HP 8720D Network Analyzer measures the resonance frequency and quality factor of the system. For the temperature dependent measurements a heater, type MK-45R from Zinser GmbH, Germany is used. It was modified in order to use an analog control for the heater power to control the hot air temperature. Pressurized air of one bar is used as input air flow.

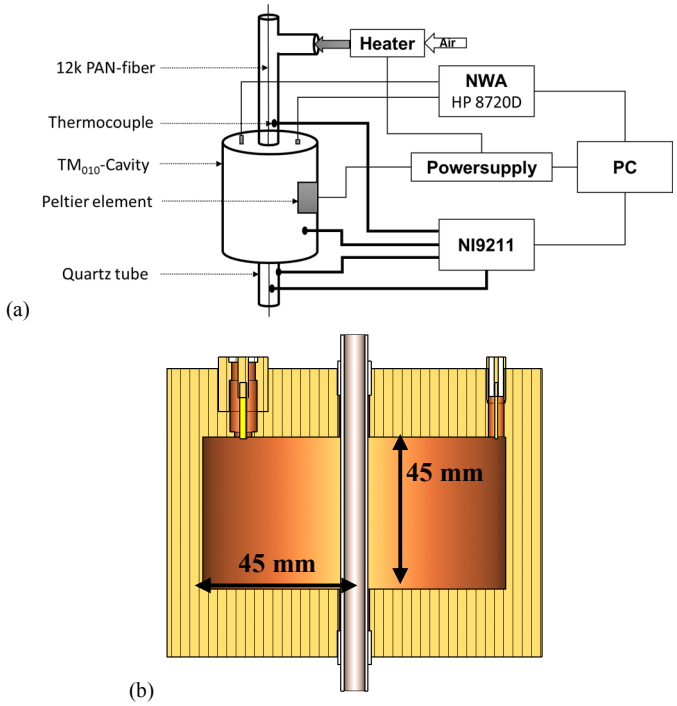


Fig. 1. (a) Schematic of the measurement setup (b) TM_{010}-Cavity cross section

The air is heated up as it passes the heating cartridge and is channeled into the quartz tube where it heats the PAN fiber. A NI-9211 thermocouple input module is used to measure the temperature by use of type K thermocouples with an accuracy of +/- 2.2 °C and a measurement sensitivity of 0.07 °C. Two thermocouples are placed in the quartz tube at the entry and the exit point of the cavity to measure the air flow temperature. A third one is used to measure the quartz tube temperature and a forth for the cavity temperature. Using a 180 W Peltier element the cavity temperature can be stabilized to a preset value of typically 20 °C with an accuracy of +/- 0.3 °C.

B. Measurement Error

The accuracy of the measured dielectric properties is influenced by the following main parameters: temperature of the cavity and quartz tube, positioning of the quartz tube, simulation accuracy, NWA measurement, estimation of the sample volume.

Since the cavity perturbation with the PAN fiber is rather small at the room temperature, the precise measurement of the dielectric constant depends strongly on the accuracy of the measured resonance frequency of the empty cavity. This can be significantly improved by stabilizing the cavity temperature to 20 °C +/- 0.3 °C. For the allowed temperature span of +/- 0.3 °C the frequency shift due to the thermal expansion of the cavity is +/- 11.6 kHz. This leads to a shift of the dielectric loss factor which is smaller than 1%. A change in the quartz temperature leads to a frequency shift. Thus to distinguish the effect of the PAN fibers from the effect of the quartz tube, the temperature dependent frequency shift of the empty quartz tube is measured separately for each set of process parameters and used as reference. The impact of the quartz tube position is minimized by using the junction of the quartz tube as a stopping mechanism when inserted into the cavity and the Teflon insulation ring to keep it in the field maximum. The simulation error can be neglected compared to the error from the sample volume and the NWA measurement.

In order to evaluate the dielectric properties, the knowledge of the sample volume is key. The fiber consist of multiple filaments, but with a filament diameter of about 10 µm, they are not suitable to use in the CST calibration. A simplification has to be made and the sample volume approximated. This was done in the form of a cylinder with an effective fiber diameter, see Fig. 2.

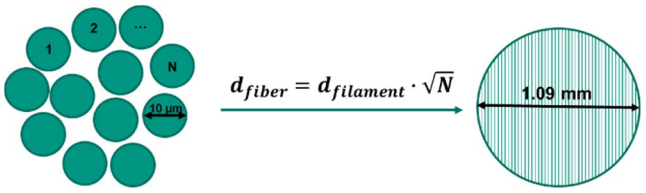


Fig. 2 Effective fiber diameter

The fiber diameter can be calculated from the filament diameter or with the help of density and mass measurements, which lead to new error sources. This is also considered in the overall error evaluation. Over all known errors the loss factor ε_r" is measured with an absolute accuracy of +/- 0.0017 for the virgin PAN fiber. During the stabilization process, the losses rise with increasing temperatures and decrease with the ongoing chemical reaction. The maximum error in the expected range of the loss factor ε_r" is calculated to be +/- 0.23. The stabilized fiber is measured with an accuracy of +/- 0.003. The temperature, resonance frequency and quality factor are measured every 4.6 seconds. Also the full S_{21} resonance curve is measured and logged in order to fit a Lorentzian resonance function to the results after the measurement. This allows improving the measurement accuracy, in particular for measurements in a range with low signal to noise ratio.

IV. Measurement Results

Mimicking the conventional process as close as possible, a heating rate of 30 °C/min was chosen for all measurements. In conventional heating ovens, the fiber passes different temperature stages between 200-300 °C. For this reason process temperatures in that range were chosen for the measurements. As a first test, the temperature of the air flow along the length of the cavity was measured in order to verify that a constant

temperature was inside the cavity. In Fig. 3, the results of four runs show a temperature drop along the length due to heat losses to the Teflon insulation ring, the cavity wall, the quartz tube and the surroundings. For all runs the input temperature was set to 260°C. Run 1 and 2 were done consecutively, as well as run 3 and 4. The thermocouple, although fixed to at one end was able to move in the air flow, so that the positioning was not completely reproducible, which explains the small differences in the measured temperatures.

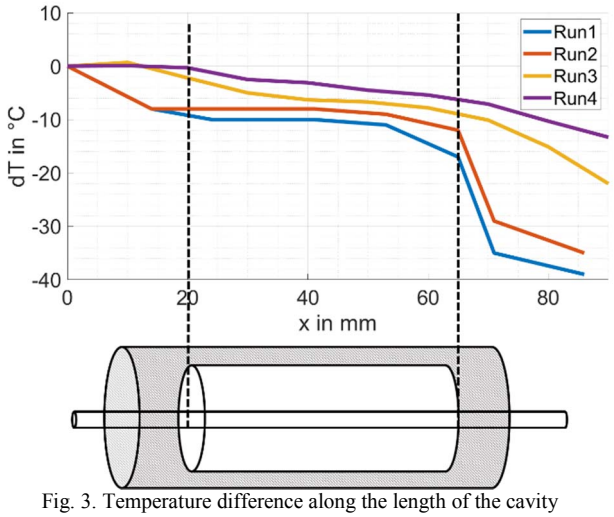
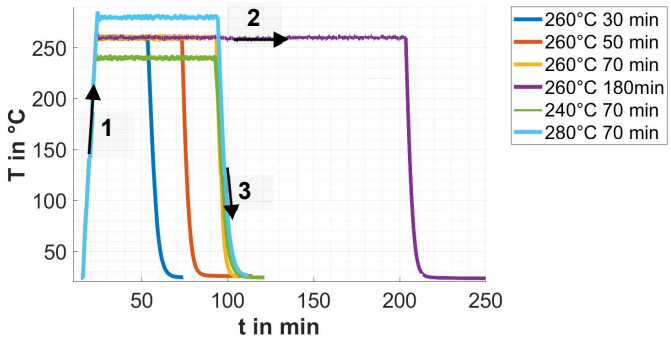


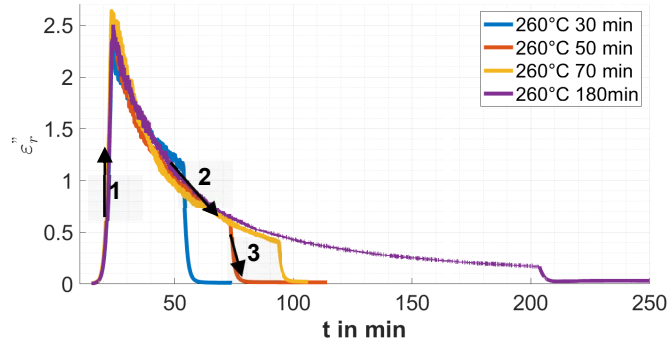
Fig. 3. Temperature difference along the length of the cavity

The temperature inside the cavity is about 10 °C smaller than at the input just outside the cavity. As the temperature drop inside the cavity also stays under 10 °C the process temperature is assumed to be constant. During the dielectric measurement, the thermocouples cannot be placed too close to the inside of the cavity, as the metal tip is perturbing the electric field. The temperature measured at the input is used as reference value.

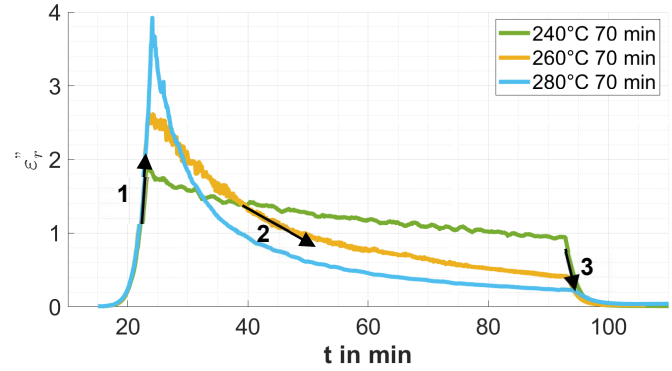
As heating rate, final temperature and holding time have a great influence on the chemical reaction, they also affect the dielectric properties. In Fig. 4 the measurement results can be seen for different process parameters for heating the PAN fibers. The process phases are marked by (1) heating up phase, (2) holding at the final temperature and (3) cooling down phase. A strong temperature dependency of the dielectric loss factor is visible for the heating up phase. Considering all process parameter sets, it can be said that for a virgin PAN fiber the loss factor rises two orders of magnitude with increasing temperature. It decreases again with the ongoing chemical reaction that unfolds during the holding time, see phase 2. The dielectric loss factor after the stabilization back at room temperature vary for different final temperatures and holding times due to different stabilization degrees. The varying stabilization degrees are also evident from the densities measured after the processing. This can be seen for different holding times in Fig. 5. For shorter holding times a stronger increase in density and loss factor is visible, as most chemical changes are taking place. The chemical reactions slow down with longer holding times, as most of the molecules have reacted.



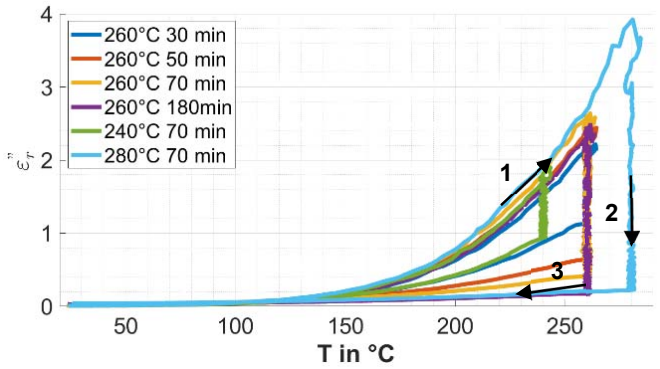
(a) Applied heating profile



(b) Comparison of the dielectric loss change for a finale temperature of 260 °C and different holding times plotted versus time



(c) Comparison of the dielectric loss change for different finale temperatures and a constant holding time of 70 min versus time



(d) Comparison of the dielectric loss change for different process parameter sets versus Temperature

Fig. 4. Results of the temperature dependent dielectric loss measurements for PAN fibers

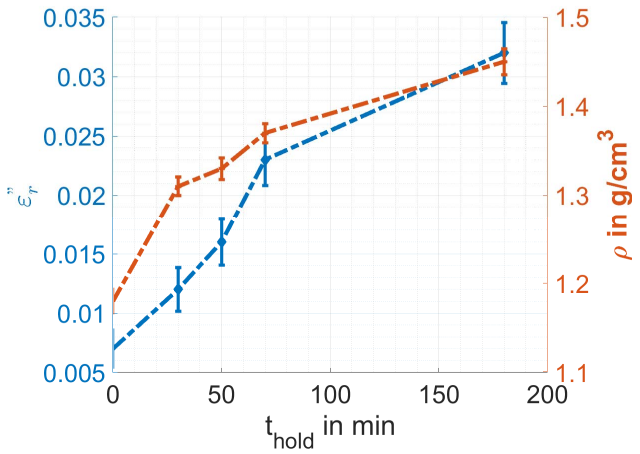


Fig. 5. Loss Factor and density at room temperature after processing at 260 °C for different holding times

Literature values for stabilized PAN fibers of different chemical compositions are in the range from 1.34 g/cm^3 to 1.39 g/cm^3 [9] (SGL Carbon). Similar density results are achieved for holding times of 50 and 70 min. For the dielectric properties the only publication found was by Paulaskas et al. [6], however the chemical composition is unknown, hence, a direct comparison is not advisable.

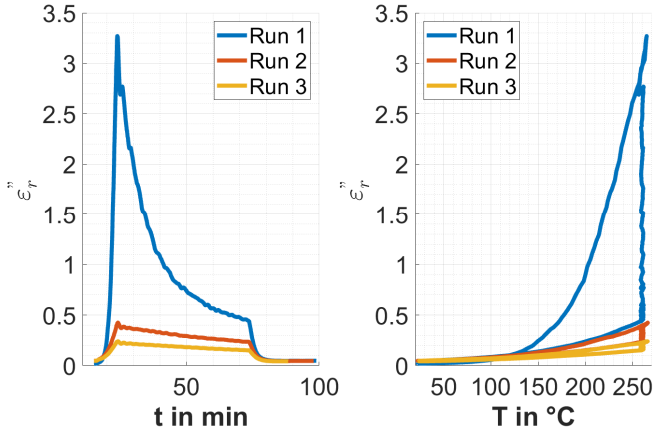


Fig. 6. Comparison of the temperature and time dependency of the loss factor of PAN precursor and stabilized fibers

In order to increase the knowledge on the PAN precursor and stabilized fiber, a comparison between the PAN precursor and stabilized fibers was executed. A PAN fiber was heated three times with the same process parameters, with a holding time of 50 min at 260 °C. The temperature dependency decreases for every run, as can be seen in Fig. 6. Between run 1 and 2 the greatest difference is visible concerning the temperature dependency. The chemical change seems still to lessen for run 2 and 3 over the holding time which might lead also to a higher degree of stabilization. But a Fourier- Transform Infrared (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC) measurement or density measurement should be conducted for a final conclusion.

V. Conclusion

A measurement system is presented, that allows to track the change of the dielectric properties of PAN fiber during the stabilization stage. The measurements during the stabilization stage show a significant temperature dependency of the dielectric properties. More importantly, the measurement system allows to follow the chemical process which changes a precursor fiber into a stabilized fiber. The chemical change is visible from the decrease of the loss factor during the process even though the final temperature is reached and kept constant. The tracking in the change of the loss factor will allow to recognize e.g. hot spots in the process and to determine the end of the stabilization stage. The system was also used to show a decrease in the temperature dependency of the loss factor of stabilized fibers depending on the stabilization degree. As different process parameter sets lead to varying dielectric properties and stabilization degrees, the next step will be to determine the degree of the stabilization precisely with the help of other measurement techniques. The knowledge of the stabilization degree is also helpful when looking more intensive at the reaction kinetics. Clearly, the knowledge of the temperature dependent dielectric properties provides a much better view on the transients in the chemical process during microwave heating of PAN fibers during the stabilization phase.

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