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MODELING OF FIBER SPINNING FLOWS OF PRE-CERAMIC POLYMER MELTS

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Procedura de obținere a materialelor ceramice plecând de la polimeri (PDCs) este un proces chimic în care polimeri pre-ceramici sunt descompuşi termic, în atmosferă controlată, în materiale ceramice ce nu conțin legături de oxigen. Fibrele ceramice se obțin în urma trefilării topiturii de PDCs, urmate de coversie termică prin piroliză. În vederea analizei proprietăților viscoelastice a polimerilor pre-ceramici în timpul trefilării, s-a construit un sistem special microscopic pentru vizualizarea fibrelor astfel obținute. Pe baza măsurării variației diametrului fibrelor la ieşirea din duză se poate calcula viscozitatea extensională a topiturii analizate. Scopul final al acestui studiu este de a stabili corelațiile dintre proprietățile reologice ale PDCs în mişcările de forfecare şi cele extensionale, în vederea optimizării procesului de trefilare.

The polymer-derived ceramics (PDCs) route is a chemical process in which pre-ceramic polymers are thermally decomposed in a controlled atmosphere into non-oxide covalently bonded ceramics. Ceramic fibers are prepared in a melt-spinning process followed by the thermal conversion of green fibers. In order to investigate the viscoelastic properties of pre-ceramic polymer during spinning, a special microscopic set-up was built up in the close chamber to visualize the emerging filament. Based on the measurement of the fiber diameter at the exit from the die, one can compute the corresponding extensional viscosity of PDCs. The final goal of this study is to establish correlations between the rheological properties in shear and extension for PDCs, in order to determine the proper working condition for obtaining high quality fibers.

Keywords: fiber spinning, pre-ceramic polymer, viscoelasticity

1. Introduction

Non-oxide ceramic fibers are considered to be the best lightweight thermo-structural material due to their good properties in thermal shock resistance, creep resistance and relatively high tensile strength and modulus values. In preparation of fine-diameter fibers, the polymer-derived ceramics (PDCs) route in which pre-ceramic polymers are thermally decomposed, in a controlled atmosphere, into non-oxide covalently bonded ceramics showed great advantages. It offers good

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control of compositions and structures, and the ability to process particular shapes that are difficult or even impossible by conventional routes, [1].

Ever since first synthesis of a SiC ceramic material from polycarbosilanes precursors was done by Yajima et al. [2], significant progress were made in the development of novel synthesis routes to pre-ceramic polymers. The silicon-based polymers have proven to be promising tractable compounds for production of technologically important ceramic components such as fibers, microfibers, protective coatings, porous materials or complex-shaped bulk parts. Many examples of ultra high temperature stable polymer-derived ceramic have been published. Among them, the quaternary Si-B-C-N materials have attracted high interest due to their exceptional high temperature and oxidation stability, [3 – 4].

In consideration of processing polymer-derived ceramic fibers, one of the demanding problems is to develop polymers with appropriate rheology and melt-stability to allow for continuous melt-spinning. The melt-spinning process involves an extrusion process of the polymer from molten state and an on-line fiber drawing that stabilizes the fiber line, reduces the fiber diameter and alignment of the polymeric chains along the fiber-axis, see Fig. 1. The preparation of polymer-derived ceramic fibers with reliable, improved or new properties requires the control of the spinning and pyrolysis processes, with the understanding of the basic phenomena that take place during such processes.

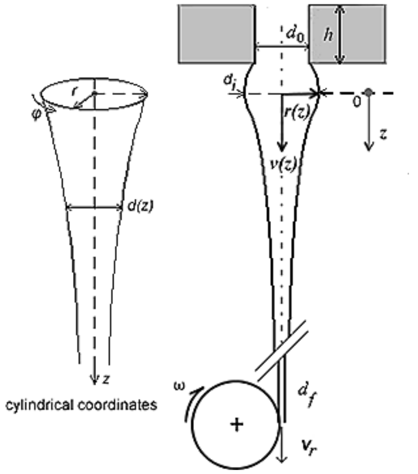

Fig. 1. Schematic representation of the fiber-spinning process.

In present paper, a one-dimensional (1D) model of an axial-symmetric fiber spinning process is utilized into the analysis, for details see [5]. The 1D analysis starts from some assumptions:

1. The melted polymer is considered to be incompressible fluid and to flow is steady.

2. Exit “elastic phenomenon” such as die swell is ignored. The position of $z = 0$ is taken at the point of maximum die swell (see Fig.1.)
3. For $z \geq 0$ the filament is assumed axisymmetric and that is does not rotate. The diameter of the fiber $d(z) = 2R(z)$ is a monotonous decreasing function and the motion within the filament is considered pure-extensional. Velocity and normal stresses distributions are assumed to be uniform across the flow area.
4. For steady and isochoric motions of thin fibers ($d < 1$ mm), inertia, gravity, surface tension and air friction can be neglected.

Under those assumptions, the mass, momentum and energy balances applied to the fiber are given by:

$$Q = A(z)\cdot v(z) = A_0 \cdot v_0 = ct \tag{1}$$

$$0 = \frac{d}{dz}\left[A(z)(\sigma_{zz} - \sigma_{rr})\right] \tag{2}$$

$$\rho C_p v(z)\frac{dT}{dz} = -\frac{2h}{R(z)}(T(z) - T_0) + (\sigma_{zz} - \sigma_{rr})\frac{dv}{dz} \tag{3}$$

where in equation (1) Q is the flow rate, v(z) and A(z) = $\pi R^2(z)$ are the velocity and the cross area of the fiber; in (2) $\sigma_{zz} - \sigma_{rr}$ is the tensile stress within the fiber (σ_{zz} and σ_{rr} are the normal stresses on the z-direction and r-direction of the fiber, respectively) and in (3) ρ is the mass density; C_p is the heat capacity, h is the heat transfer coefficient at the surface of the filament, T(z) is the polymer temperature along the spin line, T_0 is the temperature of the environment. One defines $\dot{\varepsilon} = \frac{dv}{dz}$ as the characteristic extensional strain rate of the spinning motion.

It is essential to recognize that fiber spinning process involve extensional deformation and the extensional viscosity is the unique material function to describe its rheology. It is expressed as:

$$\eta_e = (\sigma_{zz} - \sigma_{rr})/\dot{\varepsilon} \tag{4}$$

while taking into account of the effect of temperature, according to Arrhenius law:

$$\eta_e(\dot{\varepsilon}, T) = \eta_e(\dot{\varepsilon}, T)\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{5}$$

where E is the activation energy for this material, R is ideal gas constant.

In the present procedure, the function $R(z)$ is experimentally measured for a given flow rate and the viscosity, $\eta_e(\dot{\varepsilon}, T) = \eta(z)$ and temperature, $T(z)$, along the fiber line are computed from (2) and (3).

A special microscopic optical set-up was built up in the melt-spinning chamber to visualize the emerging filament at the exit of the die, see Fig. 2. The diameter of the fiber along the spinline (in steady spinning) is measured based on the microscopic pictures and approximated with an exponential or polynomial function, which in a non-dimensional form is used to determine the melt extensional viscosity from (2) and (3).

With the aim to design and calibrate a procedure to achieve an online measurements of fiber diameter and quality control of the fiber along the spinline, the study starts with polycarbomethylsilane sample (PCS), and then apply it to a novel SiBCN polymer, [6]. In this paper only the results for PCS are shown.

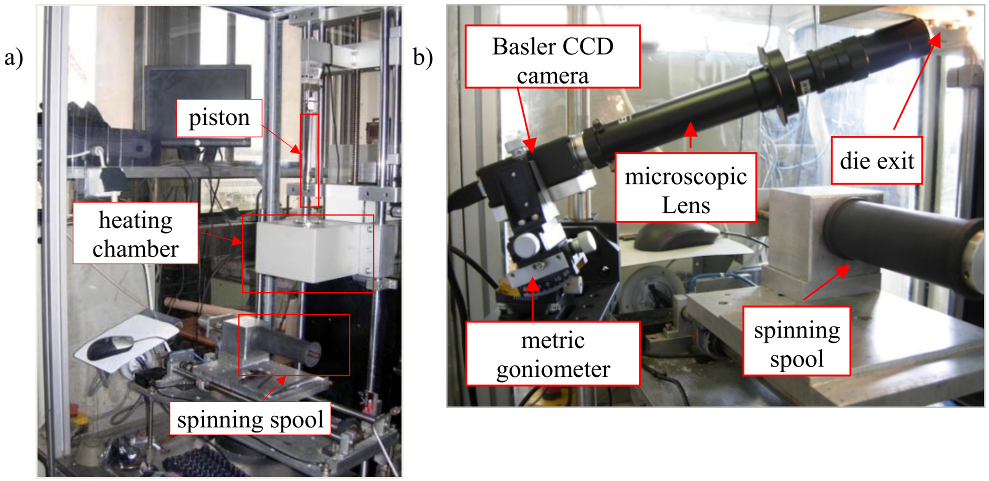

Fig.2. Fiber spinning apparatus (a) and visualization setup (b).

2. Experimental

Rheological properties of PCS, chemical formula is $(C_2H_6Si)_n$ purchased from Aldrich Co., are measured using a Physica MCR 301 rheometer equipped with the heat and temperature controlled cell for polymer investigations. Oscillatory strain and stress controlled test have been performed with the plate and plate geometry of 25 mm diameter and nominal gap of 0.3 mm. For each sample, several isothermal frequency sweep tests were conducted in the linear viscoelastic regime (controlled strain amplitude: $\gamma = 0.01\,[-]$), at four different temperatures from spinning experiments, in order to establish the temperature influence on materials rheology and the reproducibility of the measurements. The results are presented in Fig. 3.

Polymer fibers were prepared using a lab-scale melt spinning apparatus. Polymer melt were heated up in a heating chamber until an appropriate viscosity was obtained and under the movement from the piston the polymer were extruded out through heated elements, containing a filter and spinneret of a single capillary with diameter $d_0 = 0.2$ mm. By the stretching from rotating spool in downstream, continuous fibers were drawn through the die. The fiber geometry was recorded at the exit of the die using a visualization setup that is composed of BASLER CCD camera linked to a computer, microscopic lens VZM™ 1000i, light source with semi-rigid gooseneck light guide, and supporting platform with metric goniometer that can do precise angular adjustment, see Fig. 2 for the visualization setup. To analyze the acquired picture, under the same visualization conditons, pictures of a diameter-known fiber are first taken as a reference. Calibration is done accoding to the reference and measurement of diameter along the spinline is obtained by image anaysis software.

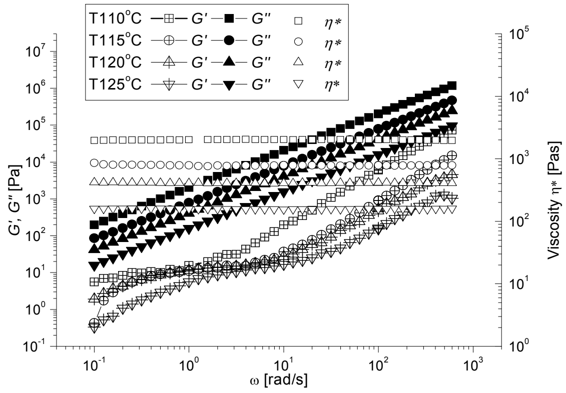

Fig. 3. Dynamic moduli and complex viscosity at reference temperatures for PCS samples.

3. Results and Discussions

From the rheological test results, it is observed that in molten state, the low molecular weight PCS displays constant viscosity in the frequency domain. Furthermore, as showed in Fig.3, loss modulus G'' is always of one order larger than storage modulus G', indicating that the rheological behavior of the polymer melt is dominated by viscous part over elasticity. As temperature increases, it shows a trend that G', G'' are going towards parallel at high frequency, which indicates a gel-like structure characteristic (at gel point, the ratio between two modulus does not depend on the sweeping frequency [7]). The viscosity dependence on temperature is represented in Fig. 4. The analysis of the dynamical shear viscosity data from Fig. 3 disclose that spinning can be obtained in good conditions, at all tested temperatures, at rates corresponding to □ > 10 s-1 , since

G" > G' and G' > 103 Pa, [5]. In fiber spinning process of PCS, two groups of samples were spun under different spinning conditions, see Tab. 1.

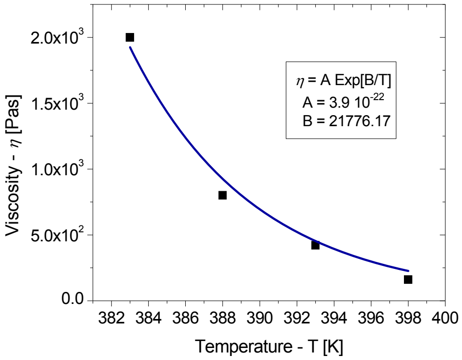

Fig.4. Zero shear viscosity as function of temperature for PCS; the experimental values are fitted with the Arrhenius law.

Table 1

Fiber spinning conditions of PCS.

PCS samples	Piston velocity V_p (mm/min)	Flow rate Q (mm^3/min)	Spinning Temperature Ts (°C)	Take up velocity V_r (m/min)
S1-A	1	64.44	117	117.34
S1-B	1	64.44	120	117.34
S1-C	1	64.44	125	117.34
S2-A	1	64.44	125	41.46
S2-B	1	64.44	125	73.98
S2-C	1	64.44	125	117.34

The samples in group 1 were spun at different spinning temperature changing from 117°C to 125°C while keeping the same flow rate and take-up velocity. Fig.5 shows the pictures of PCS in group 1 and corresponded dimensionless fiber diameter $D(z) = d(z)/d_0$ *vs* non-dimensional spinline z. It can be seen that at 117°C, the curve of the fiber diamter evolution has a steeper slop than the ones in higher temperatures. It is due to significant higher viscosity as evidenced in rheology test (Fig.3). Under the same take-up velocity, the one with higher viscosity has higher resistance to the applied extensional force, it means the bulk part of fluid would tends to mantain its shape. While under the stretch forces, it shows greater changes in evolution of fiber diamter along the spinline. For the spinnig at higher temperatures 120°C and 125°C respectively, no significant changes in shapes were observed from each other probably due to their relatively close viscosity values. In group 2, samples undergo varied take-up velocities by varying the rotating speed of the spool. Under these conditions, at same spinning temperature and flow rate, increasing the take-up velocity leads to much decreased diameter of fiber along the spinline, for details see [6].

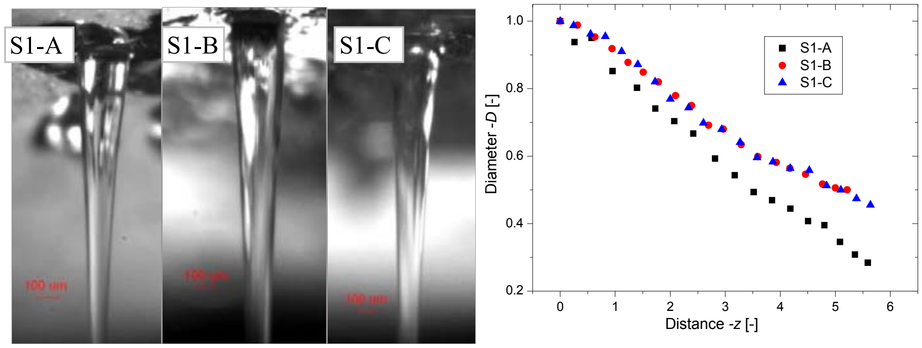

Fig.5. Pictures of PCS in fiber spinning process (probes S1, see Tab. 1) and their measured dimensionless fiber diameter *D*(z) along spinline z.

The obtained *D*(z) profile and the measured shear viscosity value are used as input data for the proposed 1D model. Using *Mathematica* code, the extensional viscosity during spinning is computed from equations (2) and (3).

It is evident that the most important input data is the *D*(z) function, which is depend on the quality of the pictures. Therefore, the graphical procedure to measure the evolution of the fiber geometry along the z-direction is the main task of the work, see also Fig. 6.

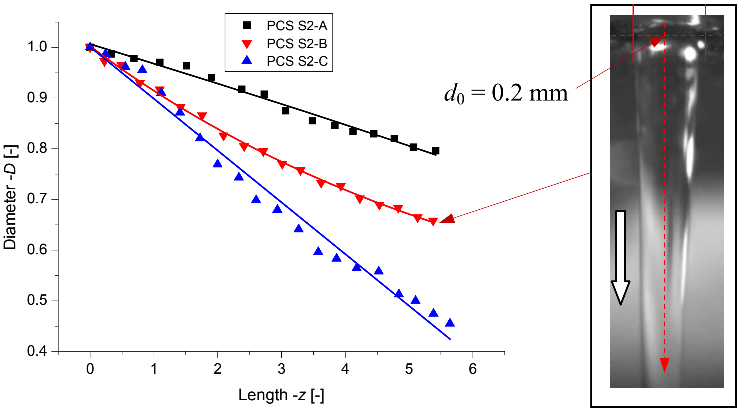

Fig. 6. Non-dimensional function *D(z)* for some PCS samples (measurements are limited at a length of $5d_0$ from the exit of the die).

4. Conclusions

Modeling of PCS pre-ceramic polymer in fiber spinning process was performed in this work, based on the measurements of fiber diameter along spinline during the process. The results from the shear tests performed by oscillatory rheometry are accomplished with the numerical computation of the corresponding extensional viscosity, see Fig. 7, for a complete rheological characterization of the samples. One conclude that good spinnability of the tested samples is determined not only by particular shear properties, see §3, but also by the extensional thinning viscosity during spinning. The main goal of our further studies is to correlate the shear rheology with the extensional rheology, in order to obtain a general criteria to appreciate quantitatively the fiber spinnability of PDCs.

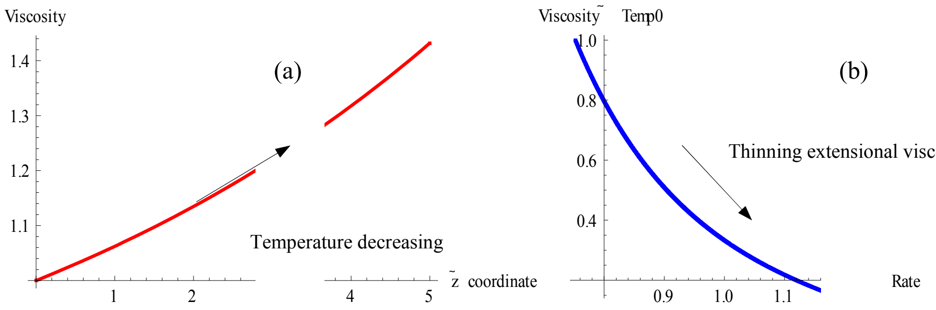

Fig. 7. Extensional viscosity for PCS sample S2-B, see Tab. 1; a) viscosity variation along the spinnline, b) viscosity dependence on strain rate, at constant temperature.

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