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The effect of the production method on the mechanical strength of an alumina porous hollow fiber

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ABSTRACT

The mechanical strength of inorganic porous hollow fibers is an important property and is strongly affected by the production method. Three production methods for fibers are compared: non-solvent induced phase separation (NIPS), bio-ionic gelation with an internal multivalent ion source (BIG-I), and with an external ion source (BIG-E). The BIG-E fibers show insufficient mechanical integrity for strength analysis. Fibers prepared via BIG-I have a larger bending strength compared to fibers prepared using NIPS or BIG-E, combined with a larger scatter in their strength data. The large scatter likely originates from surface deformations present in the fiber wall, which can be reduced by further optimization of the production method. Statistical models are fitted to the measured strength data. The NIPS and BIG-I production methods yield fibers of which the strength distribution follows the Weibull model, presuming failure occurs at the weakest link.

1. Introduction

Ceramic porous hollow fibers receive increasing attention due to their high surface-area-to-volume ratio combined with unique features such as high chemical and thermal resistance, their porous structure or their catalytic and electrical properties [1]. Due to their properties, ceramic fibers are used for applications including membrane separation in challenging environments [2–5], as integrated electrode and/or catalyst [6–8], or as a micro reactor [9–11].

An important factor impeding the use of these fibers is their mechanical strength. The measured strength depends strongly on the measurement method and subsequent statistical analysis, as was recently demonstrated by our group [12]. The mechanical strength of porous ceramics often follows the Weibull model, which is based on a weakest-link hypothesis [13]. If a fiber fails, it is assumed to fail at its weakest link and by eliminating such a weaker link, one could improve the mechanical strength of the specimen [14,15]. Ceramic porous hollow fibers have many features that could be regarded as a weak link, for example pores, macrovoids, and surface scratches or deformations [15,16].

When the amount of defects increases, the probability of failure might start to deviate from the weakest link theory. This is the case, for example, when defects can interact and grow into larger defects, or when the amount of initial defects are large (such as pores). In this case a ceramic starts to follow a normal distribution [17]. Various production methods are used to fabricate inorganic porous hollow fibers and the most common method is based on non-solvent induced phase separation, which results in a characteristic morphology of the fiber wall. This morphology originates from the phase separation process, where polymer lean and polymer rich phases form. The polymer lean phase often results in the formation of large macrovoids, that can persist after thermal treatment. Recently, methods based on internal [18] or external [19] gelation of a sodium alginate were used to fabricate inorganic porous hollow fibers. The alginate-based method circumvents the formation of macrovoids completely, resulting in a different morphology of the fiber wall.

In this paper, we show that the three different production methods all lead to specific morphologies and microstructures, and show how these affect the mechanical strength of the fibers. We also include a detailed statistical analysis of the underlying failure model and analyze the implications of these models for system design.

2. Experimental

Alumina hollow fibers were prepared by non-solvent induced phase separation (NIPS) using a mixture of AKP30 α-Al_2O_3 powder (Al_2O_3, particle size of 0.3 μm, Sumitomo Chemicals Co. Ltd.

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Table 1
Spinning recipes and spinning conditions for the three different production methods.

Parameter	NIPS	BIG-I	BIG-E
PES	10.0 %	–	–
NMP	38.9 %	–	–
PVP K-95	1.0 %	–	–
AKP-30	49.1 %	12.4 %	12.6 %
Na-Alg	–	5.05 %	5.02 %
$CaCO_3$	–	0.15 %	–
Water	1.0 %	82.4 %	82.4 %
Bore liquid	H_2O	Lactic acid (pH = 1.41)	$CaCl_2$ (10 %)
Coagulation bath	H_2O	Lactic acid (pH = 1.41)	$CaCl_2$ (10 %)
Extrusion pressure	2 bar	2 bar	2 bar
Air gap	3 cm	1.5 cm	1.5 cm
Bore liquid flow rate	7 mL min^{-1}	14 mL min^{-1}	17 mL min^{-1}
Diameter spinneret	OD/ID = 2.0 mm/0.8 mm	OD/ID=2.0 mm/0.8 mm	OD/ID = 2.0 mm/0.8 mm
Drying after spinning	> 24 h	> 24 h	> 24 h

Japan), Polyethersulfone (PES, Ultrason, 6020P, BASF, Germany) and N-methylpyrrolidone (NMP, 99.5 wt%, Sigma–Aldrich, The Netherlands). Polyvinylpyrrolidone (M_W 1,300,000 kg mol^{-1}, Sigma–Aldrich, The Netherlands) was used as viscosity enhancer and de-ionized water (>18.2 MΩ cm^{-1}, Milli-Q Advantage A10, Millipore) was used as non-solvent. Prior to use, PES and AKP-30 were dried overnight at 120 °C; all other chemicals were used as received. The fibers were prepared using a standard method as described by Luiten-olieman et al. [20]. The recipe for fibers prepared using internal bio-ionic gelation (BIG-I) was based on earlier work [18]. A mixture of de-ionized water, AKP-30 α-Al_2O_3 powder, $CaCO_3$ (Sigma–Aldrich, The Netherlands) and sodium alginate (From brown algae, medium viscosity, Sigma–Aldrich, The Netherlands) was spun into a coagulation bath consisting of lactic acid (Sigma–Aldrich, The Netherlands). The pH was adjusted to be below 1.5. Fibers prepared via external bio-ionic gelation (BIG-E) were based on the work of Shukla et al. [19], in which a mixture of sodium alginate, AKP-30 α-Al_2O_3 powder and demineralized water was spun into a coagulation bath of $CaCl_2 \cdot 6\,H_2O$ (Sigma–Aldrich, The Netherlands). The full mixture composition and spinning conditions for all three recipes are given in Table 1.

2.1. Thermal treatment

After drying under ambient conditions, the fibers were thermally treated in air (100 mL min^{-1}) using a tubular furnace (STF16/610, Carbolite). The fibers prepared by NIPS were thermally treated at 300 °C for 1 h and at 1400 °C for 2 h. The fibers prepared by the two bio-ionic gelation methods were thermally treated at 110 °C for 1 h and at 1400 °C for 2 h. All heating and cooling rates were 5 °C min^{-1}. After thermal treatment, the fibers were cut to the desired length required for mechanical testing. For each production method, various sintering batches were prepared from one single spinning batch.

2.2. Mechanical testing

The 4-point bending strength of the fibers was measured at room temperature (20 ± 3 °C) and a relative humidity of 60 ± 20% using a 5564A mechanical testing bench (Instron) equipped with a 100 N load cell. All testing was carried out according to ASTM C1684-08 [21], which has been adapted as follows; (1) the rollers were not free to move laterally, (2) a hollow fiber was used instead of a rod, and (3) the material was porous instead of dense. The outer and inner span were 20 and 10 mm respectively. All fibers were tested as-fabricated and no surface treatment was carried out on the fibers. The load was measured at a constant compression rate of 0.5 mm min^{-1} and the maximum load at fracture was converted in the bending strength using:

$$\sigma_{f,j} = \frac{16 F_j K d_{out,j}}{\pi \left(d_{out,j}^4 - d_{in,j}^4 \right)} \quad (1)$$

here F_j is the force at fracture for specimen j, K being half the distance between the inner and outer roller (K = 0.5 ($L_{out} - L_{in}$)), and $d_{out,j}$ and $d_{in,j}$ the outer and inner diameter of specimen j.

This equation is modified for elliptical fibers when the ratio of the major to minor diameter is less than 0.95 [21]. In that case, either the minor or the major axis of the sample is aligned with the direction of the load. In the equation below, the subscript h and v refer to the horizontal and vertical axis.

$$\sigma_{f,j} = \frac{16 F_j K d_{out,h,j}}{\pi \left(d_{out,h,j}^2 d_{out,v,j}^2 - d_{in,h,j}^2 d_{in,v,j}^2 \right)} \quad (2)$$

The full details of the mechanical strength measurements and subsequent calculations is described in detail elsewhere [12,21,22].

2.3. Fiber characterization

The morphology of the fibers was investigated using a SM-6010 (JEOL) scanning electron microscope equipped with an EDS detector. Cross-sections of fibers were sputtered with a 5 nm chromium coating (Quorum Q150T ES). A Zeiss Axiovert 40 MAT optical microscope was used to analyze the roundness, inner and outer diameter of the fibers prepared using BIG-I. The pore size and porosity of the fibers were measured by mercury intrusion porosimetry with a Poremaster PM-33 (Quantachrome Instruments).

3. Data analysis

Three different probability distributions were used to describe the measured strength data. The data was fitted using a normal, lognormal and Weibull distribution, the rationale behind these specific distributions is based on other work [12,17,23,24]. In short; the Weibull distribution is often used for brittle ceramics and is based on the weakest link principle [13,25]. The normal and lognormal distributions are often proposed for, for example, porous ceramics where defect interactions can occur. In that case the weakest-link assumption is no longer long valid [15,16,26–28].

These three distributions all have 2 parameters that describe the shape and location of the distribution. These parameters were estimated using the `fitdist` function of Matlab, which fits the Weibull function using maximum likelihood methods, whereas for the normal and lognormal distributions the parameter is the square root of the estimate of the variance or the square root of the log of the

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