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HIGHLIGHTING A UNIVERSAL BEHAVIOR IN THE PERMEABILITY OF FIBROUS CARBONS

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Introduction

Fluid flow through porous media is of great interest for engineering sciences. As far as fibrous carbons are concerned, phenomena encountered in filters, adsorbents, catalyst supports, fuel cells, membranes and composites manufacturing process depend critically on permeability.[1]
Although many works have been devoted to this topic, studies related to carbon materials are scarce, despite their major impact in many applications. The obvious increase of permeability with the open porosity was successfully accounted for by either Kozeny-Carman or Tomadakis-Sotirchos (T-S) equations. The latter, supposedly free of adjustable parameters, is particularly suitable for describing the permeability of random fiber beds.[2]
But most studies lack a critical discussion of the corresponding parameters, whose values were predicted for a few ideal cases, which cannot be correctly used especially for non-woven fibrous carbon materials, for which the fabric architecture controls the physical properties. As a result, very different permeabilities can be measured at similar porosities, and vice-versa.
In the present work, the static air permeability of not less than 18 different fibrous carbons was measured and fitted with the T-S equation, with the aim of finding some potentially universal behavior for the tortuosity. A universal curve linking the bulk tortuosity to the so-called Archie's exponent is presented, which encompasses many fibrous materials, carbonaceous or not.

Materials and Methods

Ex-PAN (polyacrylonitrile) or ex-Rayon (regenerated cellulose) commercial fibrous carbons ranging from needle-punched soft felts to chemically bonded rigid boards through rigidized soft felts were thoroughly investigated in terms of general structure (SEM), total porosity, average fiber diameter, and through-thickness (out-of-plane) air permeability.
The latter was measured by applying two international standards (ISO 9053:1991 and ASTM C522-03(2016)) and by using Darcy's law, given that viscous interaction between the fluid and the porous solid is the main source of pressure drop.

Results and Discussion

The various commercial origins of the fibrous carbons and the differences in fiber type and/or assembly process resulted in different morphologies. One of the most remarkable characteristics of carbon nonwovens is their high porosity (varying from 87.50 to 95.70%), regardless of fiber diameter, rigidity, or felt formation technique, increasing in the order: rigid boards $\leq$ rigidized soft felt $<$ soft felts (Fig. 1). SEM observations evidenced that all carbon non-wovens were anisotropic and made of randomly laid/dispersed fiber layers, united by needle-punching and/or chemical bonding, and presenting large pore sizes between carbon fibers. The latter have precursor-dependent microstructure as well as different cross-section shapes and diameters.

Studying the fluid transport behavior in carbon non-wovens is important before selecting one or the other fibrous material for its final use.[3] The reduced permeability, k/r^2, where k is the permeability and r the fiber radius, as a function of porosity, ε, presents the general porosity-dependent behavior shown in Fig. 1 within each defined family of carbon non-wovens, but still no unifying trend can be seen. Consequently, failed attempts to model such behavior (Eq. [1] and Fig.1) motivated us to try to find a universal relationship embracing all measured values.

$$\frac{k}{r^2} = \frac{\varepsilon}{8\,(\ln\varepsilon)^2}\left(\frac{\varepsilon-\varepsilon_p}{1-\varepsilon_p}\right)^{\alpha}\left(\frac{\varepsilon-\varepsilon_p}{(1+\alpha)\varepsilon-\varepsilon_p}\right)^2 \qquad [1]$$

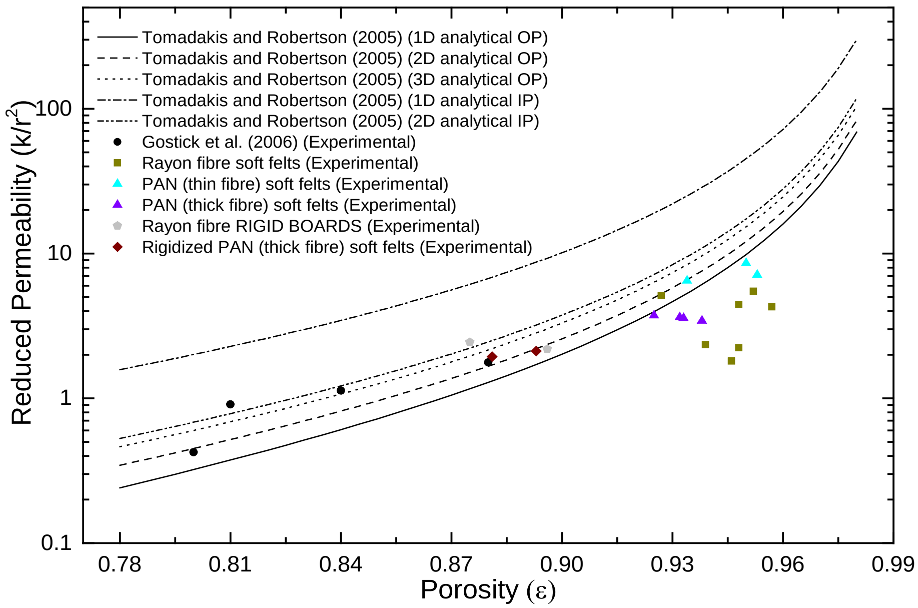

Figure 1 . Out-of-plane reduced permeability k/r^2 of tested fibrous carbon materials and few other ones from the literature, as a function of overall porosity ε. The curves correspond to the application of Tomadakis – Sotirchos (T-S) model (Eq. [1]).[2]

The Archie's coefficient α and the viscous tortuosity η_v (through the Kozeny constant $K_c = 2\eta_v$) were further calculated (Eq. [2]) from measured porosity, fiber diameter and permeability, thus neglecting the non-zero percolation threshold ε_p, as simulated for high materials' porosities.

$$\frac{(1+\alpha)^2}{\varepsilon^{\alpha}} = \frac{K_c}{2} = \frac{\varepsilon\, r^2}{8k\,(\ln\varepsilon)^2} \qquad [2]$$

A clear correlation between these two parameters was evidenced, so all data were perfectly aligned on one single *master curve* (Fig. 2). Additional mathematical analysis revealed that the obtained solution is always unique within [0; +∞[. This finding strongly suggests that α is not a free parameter, estimated from idealized fiber structures (Fig. 2), but may be seen as an intrinsic property of the complex and tortuous fibrous carbons, thereby leading to permeability values lower than those estimated by the model. Further, a clear correlation between Archie's coefficient and tortuosity is proved to hold when broadening our material's ranges with additional 106 fibrous materials, having porosities within the range 34.6 up to 99.5% and complying with the fit.

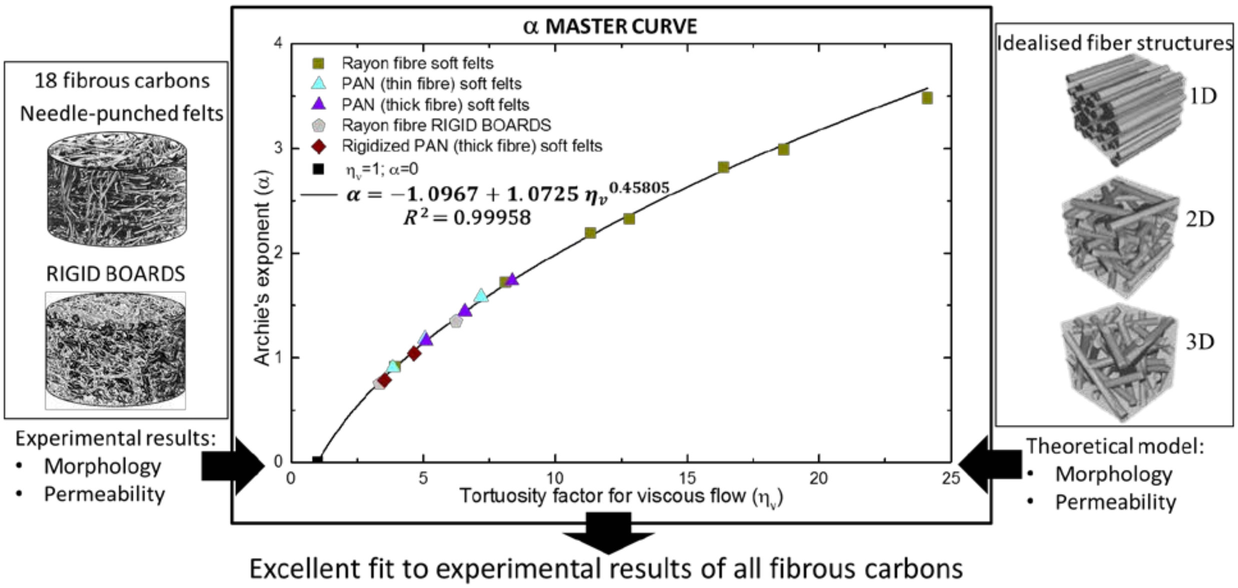

Figure 2 Archie's coefficient, α, vs. viscous tortuosity factor, η_v, for all fibrous carbon materials investigated here, calculated from Eq. [2], i.e., assuming a ε_p of zero. Overview of tested (left) and idealized fibrous 1D, 2D or 3D-type structures (right).

Conclusion

A full set of 18 carbon materials with different porous structures and hence different permeabilities, was investigated. Grouped samples revealed consistent behaviors within limited ranges of structures or porosities, but no general trend or analytical model could be fitted to the whole set of samples. Calculated Archie's coefficient appears as an intrinsic property, purely defined by the studied material geometry, not dependent on the idealized 1D, 2D or 3D-type of flow. In contrast, the parameters of the T-S model are fixed, and are therefore irrelevant to a broader range of fibrous structures. So, the proposed *α master curve* encompasses fibrous materials within broad ranges of porosities and structures. Based on this new equation (Fig. 2), all fibrous materials are classified according to their Archie's coefficient, thus leading to an outstanding predicting character.

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