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Effect of Moisture Sorption on Microstructure and Properties of Paper

Amitkumar. C. Jain & Richard A. Cairncross
Department of Chemical Engineering, Drexel University
31st & Market Street, Philadelphia, PA, USA.

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Abstract

Dry paper is composed of ribbon-shaped paper fibers randomly oriented in the plane of the sheet. Paper fiber cross-sections transform from elliptical in the pulp slurry to ribbon-like on drying due to capillary pressure of water contained in the lumen of the paper fiber. On contacting a dry paper with water or simply exposing the paper to high humidity, paper fibers tend to regain their initial elliptical cross-sectional shape due to breakage of hydrogen bonds and relaxation of drying stresses. Fiber expansion is the resultant of swelling of the fiber wall and opening of the collapsed lumen. A single-fiber model is presented to predict the fiber cross-sectional shapes at various stages during drying and/or moisturization. Swelling of paper fibers affects the physical and transport properties of paper. Predicted cross-sectional shapes of paper fibers are mapped onto an idealized unit cell model of paper structure to predict the effective diffusion coefficient and permeability of paper as function of fiber swelling. The model predicts that the effective diffusion coefficient drops as relative humidity decreases and that there is a sudden drop in effective diffusion coefficient as the fibers collapse from elliptical to ribbon-like cross-sections.

Single Fiber Deformation Model

On contacting dry paper with water or simply exposing paper to high humidity, fibers within the paper expand (Forseth 1998). Fiber expansion is the resultant of the swelling of the fiber wall and opening of the collapsed lumen (Figure 1). Contact with water breaks hydrogen bonds and releases drying and calendaring stresses (Forseth and Helle 1997).

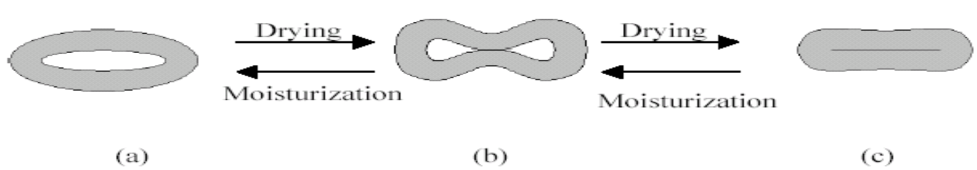

Figure 1: Schematic of paper fiber cross-sectional shape at various stages of drying and/or moisturization. The cross-sectional shape of paper fiber changes from (a) elliptical in the pulp slurry to (b) bi-lobed when partially dried to (c) ribbon-like shape in completely dry paper.

The shape of the cross-section of the paper fiber after pressing and before entering the drying section is assumed to be elliptical. The change in cross-sectional shape of paper fibers during drying, calendaring and re-moisturization is modeled as deformation of a thick walled tube under imposed trans-mural pressure using a commercial finite element solid mechanics package (ABAQUS). To simulate the fiber collapse during drying, it is assumed that the pressure in the interior of the tube is less than the pressure on the exterior of the tube, i.e. water in the tube is under tension via capillary pressure. For a given geometry, deformation of a paper fiber is a function of only ratio of trans-mural pressure (P_c) to the elastic modulus (E) of the fiber wall. As a *base case* for predicting fiber deformation, the shape of the fiber is taken to be elliptical with the inner major and minor axis length 7.5 μm and 5.0 μm, respectively (Figure 2). The fiber wall thickness is 5.0 μm. The fiber wall is assumed to be nearly incompressible (Poisson ratio 0.49). Figure 2 displays the predicted change in cross-sectional area (total and lumen) with absolute P_c/E. There are three zones of deformation, (I) nearly elliptical compression of fiber, (II) buckling of paper fiber leading to bi-lobed shape of the paper fiber cross-section and (III) collapse of fiber lumen to ribbon shape. For a hypothetical paper in which water in present only in the lumen (i.e. not between the fibers or within the fiber wall) this curve and Kelvin's equation are sufficient to predict the adsorption isotherm of paper (Jain & Cairncross 2003)

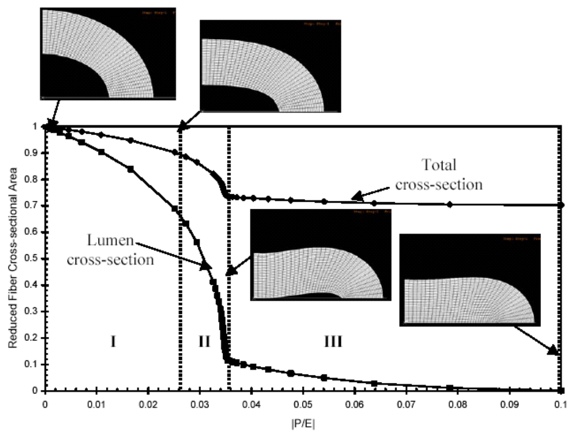

Figure 2: Predicted collapse of paper fiber versus trans-mural pressure (P_c/E). The change in cross-sectional area of the lumen and the total fiber (lumen + wall) are both plotted as a fraction of their un-deformed area. Inset plots show the computational mesh at various stages of deformation.

Unit Cell Model of Paper Structure

Paper is a thin flexible, fibrous web composed of cellulosic fibers deposited upon each other, randomly oriented in the plane of the paper. For predicting physical and transport properties of paper, the paper structure is approximated by an idealized unit cell (Figure 3). The solid region in the unit cell corresponds to

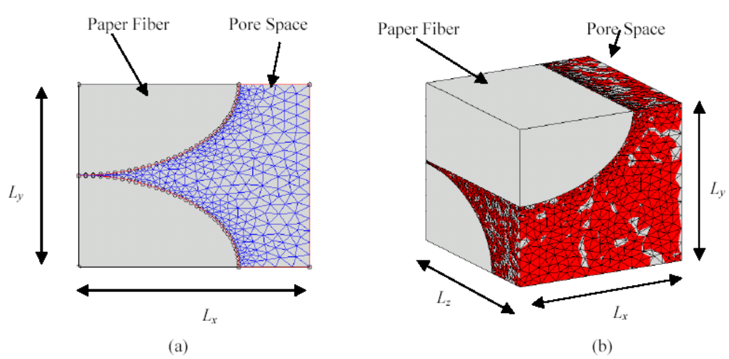

Figure 3: Idealized unit cell model of paper fiber structure used to predict physical and transport properties of paper. (a) 2D unit cell model of paper, fibers are arranged in a two dimensional array and parallel to each other. (b) 3D unit cell model of paper, fibers are parallel in each layer and perpendicular in adjacent layer

fiber space and meshed region correspond to macro-pore space. From the unit cell model structure and the predictions from the single fiber deformation model, changes in porosity and moisture content during drying and moisturization have been predicted.

The moisture transport in the pore space between the fibers in the idealized unit cell models is described by steady state diffusion through stagnant air in the macro-pore space between the fibers.

$$D_o \nabla^2 C_p = 0 \qquad (1)$$

C_p is the concentration of water vapor in air and D_o is diffusion coefficient of water vapor in air. Concentration boundary conditions are applied at the inflow and outflow plane.

$$C_p = C_{in} \qquad @\ y=0 \qquad (2)$$

$$C_p = C_{out} \qquad @\ y=L_y \qquad (3)$$

C_{in} and C_{out} are the water vapor concentrations at the inflow and the outflow plane. No-flux conditions are applied at the fiber surfaces. Symmetry conditions are used at the four transverse sides of the unit cell. This model predicts steady-state diffusion in the macro-pore space between the upper and lower surfaces of the unit cell. From the predicted flux through the unit cell and the imposed concentration difference, an effective diffusion coefficient is estimated:

$$\frac{D_{eff}}{D_o} = \frac{L_y}{C_{in} - C_{out}} \frac{1}{L_x L_z} \int_{Inflow\ Plane} \underline{n} \bullet \nabla C \, ds \qquad (4)$$

D_{eff} is effective diffusion coefficient of water vapor in paper. The shape of a fiber predicted from the single fiber deformation model is mapped onto the unit cells using MATLAB to create finite element meshes. The mesh is imported into finite element package FEMLAB for diffusion predictions.

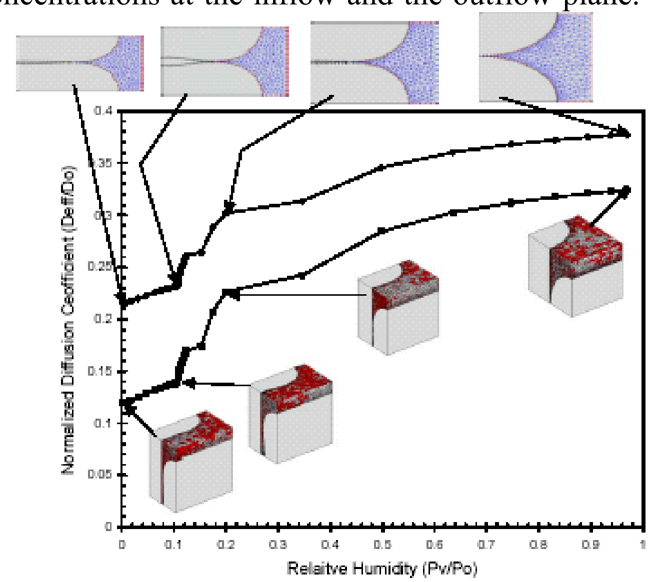

Figure 4: Predicted effective diffusion coefficients versus equilibrium relative humidity for paper with dry porosity of 0.27 and paper fiber of Young's modulus E = 8.8 GPa.

Figure 4 shows the prediction of effective diffusion coefficient versus relative humidity for unit cells shown in Figure 3(a) and Figure 3(b). Qualitatively the effective diffusion coefficient curves for 2D and 3D unit cell are similar. The effective diffusion coefficient curves show a sharp increase in effective diffusion coefficient in the range of 12-20 % relative humidity. The idealized 3D unit cell model predicts lower diffusion coefficients than idealized 2D unit cell model due higher tortuosity in the 3D geometry. The effective diffusion coefficient is directly proportional to cross-sectional area for diffusion (A_{inflow}) and inversely proportional to L_y & tortuosity. There are three regions of the effective diffusion coefficient curve: collapsed fiber (0-12 % relative humidity), transition region (12-20 % relative humidity) and open fiber (20-100 % relative humidity).

Figure 5 shows the comparison between predicted and experimental values of the effective diffusion coefficient of dry paper for a range of paper porosity (RH = 0%). The predicted diffusion coefficients from the 3D unit cell are closer to experimental measurements (Goel, Ramaswamy et al., 2002 and Nilsson & Stenstrom, 1995). However, the experimentally measured effective diffusion coefficients are significantly lower than the predicted values; this discrepancy is likely due to uncertainties in the dimension and stage of deformation of paper fiber (equilibrium relative humidity) of the paper used for the experiments. The 3D unit cell model of paper also does not account for three-dimensional deformation of paper fibers near the fiber-fiber contact points, which could significantly alter the predictioned effective diffusion coefficient.

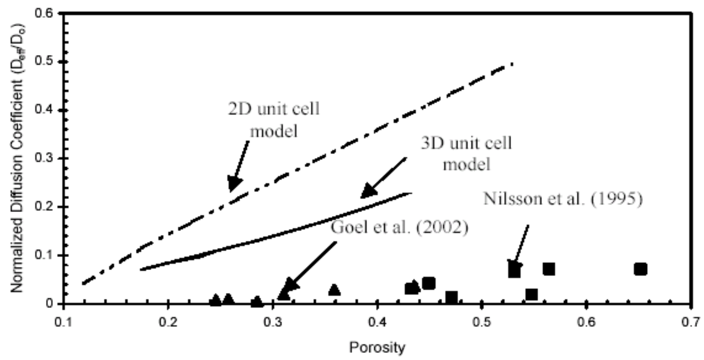

Figure 5:Comparison of model prediction with experimental data from Goel, Ramaswamy et al. (2002) and Nilsson & Stenstrom (1995). Paper is assumed to be dry and made of fiber with ribbon shape cross-section

Conclusions

A model for predicting deformation of a single fiber during drying and/or re-moisturization is presented. The model predicts the cross-sectional shape of paper fiber at various drying and re-moisturizing stages neglecting swelling of the fiber wall. For a given paper fiber, fiber deformation is a function of ratio of trans-mural pressure (P_c) to Young's modulus (E). Mass transport equations are solved in the macro-pore space of the unit cell to predict effective diffusion coefficients of paper. A 3D idealized unit cell model of paper structure predicts lower effective diffusion coefficient than 2D due to the increase in tortuosity. Effective diffusion coefficient of paper is function of dry porosity and equilibrium relative humidity. Predictions of idealized 3D unit cell model of paper are closer to the published experimental measurements of effective diffusion coefficient of paper (Nilsson and Stenstrom, 1995; Goel, Ramaswamy et al., 2002).

References

1. Forseth, T. and T. Helle (1997). Effect of moistening on cross-sectional details of calendared paper containing mechanical pulp. Journal of Pulp and Paper Science, 23(3), J95-J100.
2. Forseth, T. and T. Helle (1998). Moisture-induced roughening during "Water Coating" in precalendared wood-containing paper. Journal of Pulp and Paper Science, 24(10), 301-307.
3. Goel, A., S. Ramaswamy, et al. (2002). Brownian motion random walk simulations in 3D structures of paper and board. International Paper Physics Conference, Skeneattles, NY.
4. Jain, A. and R. Cairncross (2003). Predicting macroscopic properties of paper from its microscopic structure. Chemical Engineering Science, Submitted.
5. Nilsson, L. and S. Stenstrom (1995). "Gas diffusion through sheets of fibrous porous media." Chemical Engineering Science **50**(3): 361-371