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Comments on the pore radius distribution in near-planar stochastic fibre networks

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The pore radius distribution in near-planar stochastic fibre networks is known to be influenced by changes in the mean number of fibres per unit area and their distribution in the plane. Experimental data is presented that confirms the established result that the standard deviation of pore radii is proportional to the mean. The data shows also that this proportionality is the same for changes in the number of fibres per unit area and for changes in the uniformity of their in-plane distribution. Data from the literature suggests that processes that increase the mean pore radius, increase also the coefficient of variation of pore radii. Theoretical considerations and experimental data are presented that show that the coefficient of variation of pore radii is in fact constant for near-random and non-random stochastic fibre networks. © *2001 Kluwer Academic Publishers*

1. Introduction

The pore radius distribution in near-planar stochastic fibre networks such as paper, nonwoven fabrics, glass fibre filter mats, etc. is known to have a positive skew and to be well described by the lognormal or gamma distributions [1, 2]. Such networks typically have thickness many times less than a fibre length and the term 'near-planar' is applied here since a characteristic of their structure is that it is essentially layered with fibre axes oriented within only a few degrees of the network plane [3]. Measurements of the pore radius distribution, using displacement of fluid perpendicular to the plane of the network, have been presented by Bliesner [4] and Corte and Lloyd [1] for laboratory formed paper sheets. The mean areal density of a sheet is defined as the mean mass per unit area and for a given fibre type is determined by the mean number of fibres per unit area. Bliesner varied the mean areal density of sheets, and Corte and Lloyd varied the uniformity of the sheets at a constant mean areal density. This second property of fibre networks is important because commercially formed fibre networks exhibit a range of degrees of mass uniformity arising as a consequence of the interaction and agglomeration of fibres in the suspensions from which networks are formed.

The distribution of local averages of areal density, in *random* fibre networks, i.e. those with fibre centres distributed according to a two dimensional Poisson process and with uniformly distributed fibre axis orientations, were derived by Dodson [5]. It turns out that commercial fibre networks exhibit a broader distribution of local averages of areal density than that determined for random networks composed of the same constituent fibres [6].

The standard deviation of pore radii is plotted against the mean pore radius for the data of Corte and Lloyd [1] and those of Bliesner [4] in Fig. 1. The legends refer to the shape of the data markers and grey-shaded markers represent data for samples formed by the lamination of thin layers; such samples therefore have been formed by a discontinuous method and fall away from the overall trend. It is immediately apparent that the standard deviation of pore radii is proportional to the mean for changes in mean network areal density and its distribution. The coefficient of variation of pore radii is plotted against the mean in Fig. 2 for the same data; we note that processes that increase the mean pore radius, increase also the coefficient of variation of pore radii.

In a simulation study, Piekaar and Clarenburg [7] found the polygon area distribution in random *line* networks to be well approximated by a lognormal distribution; the standard deviation of pore areas was observed to be insensitive to the mean pore area as influenced by the number of lines per unit area. Expressions for the pore radius distribution in random fibre networks were derived by Corte and Lloyd [1]. Using the established results that for a random network of lines the mean number of sides per polygon is four and the distances between crossings are distributed according to the negative exponential distribution [8], they derived the probability density function for rectangular pore areas and hence that for the radii of circles having the same area. Their derivation showed, in agreement with experimental observation, the pore radius distribution to be lognormal in shape and the standard deviation of pore radii to be proportional to the mean such that

$$\bar{r} = \frac{\sqrt{\pi}}{4b}, \quad (1)$$

$$\sigma(r) = \frac{1}{b}\left(\frac{1}{\pi} - \frac{\pi}{16}\right)^{\frac{1}{2}}, \quad (2)$$

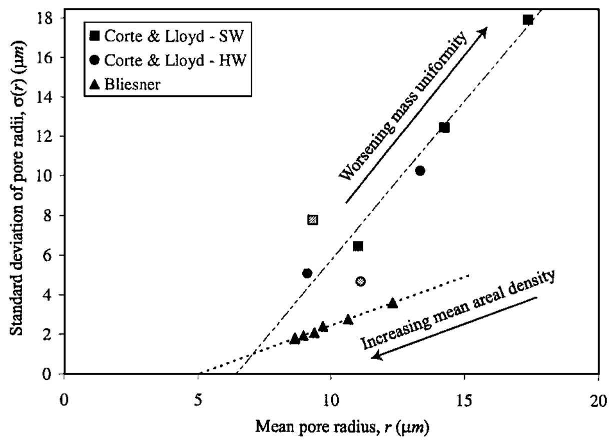

Figure 1 Standard deviation of pore radii plotted against mean pore radius. Data of Corte and Lloyd [1] for hardwood (HW) and softwood (SW) fibres and that of Bliesner [4]. Both data sets exhibit linearity and a negative intercept with the ordinate.

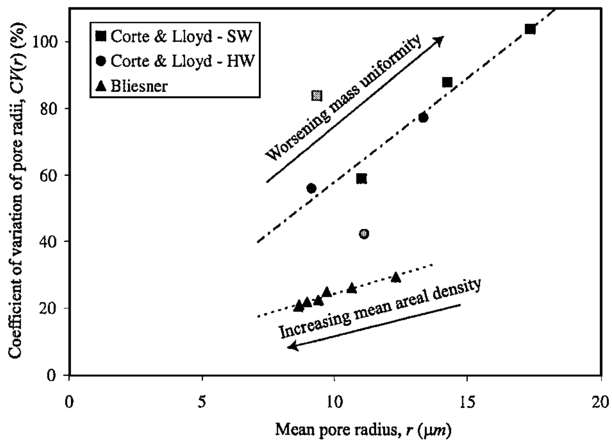

Figure 2 Coefficient of variation of pore radii plotted against mean pore radius. Data of Corte and Lloyd [1] for hardwood (HW) and softwood (SW) fibres and that of Bliesner [4]; increasing the mean pore radius increases also the coefficient of variation of pore radii.

$$= \frac{(16-\pi^2)^{\frac{1}{2}}}{\pi}\bar{r} \qquad (3)$$

where $\bar{r}$ is the mean pore radius (μm), $\sigma(r)$ is the standard deviation of pore radii (μm) and parameter b (μm^{-1}) characterises the negative exponential distribution with mean $1/b$ and variance $1/b^2$. It follows from Equation 3 that for *random* networks the coefficient of variation of pore radii is independent of the mean, in agreement with the observations of Piekaar and Clarenburg for pore areas.

Such good agreement between the theory of Corte and Lloyd and their experiments is somewhat surprising however as, by changing the structural uniformity of the networks they studied, thay had ensured that their networks were non-random. This was addressed by Dodson and Sampson [2] who rederived the theory of Corte and Lloyd using the gamma distribution to represent the distances between crossings in a fibre network. The gamma distribution has probability density function:

$$f(x) = \frac{b^k}{\Gamma(k)}\, x^{k-1} e^{-bx} \quad \text{for} \quad k > 0, \qquad (4)$$

where parameter k is a shape factor and parameter b is a scale factor such that the distribution has mean, $\bar{x} = k/b$ and variance, $\sigma^2(x) = k/b^2$; the negative exponential distribution is a special case of the gamma distribution when $k = 1$. On this basis, Dodson and Sampson give the probability density function for pore radii as,

$$g(r) = \frac{4\, b^{2k} \pi^k r^{2k-1} K_0(z)}{\Gamma(k)^2} \qquad (5)$$

where $z = 2br\sqrt{\pi}$ and $K_0(z)$ is the zeroth order modified Bessel function of the second kind. The mean and standard deviation of pore radii are given by,

$$\bar{r} = \frac{\Gamma\left(k+\frac{1}{2}\right)^2}{b\sqrt{\pi}\,\Gamma(k)^2} \qquad (6)$$

$$\sigma(r) = \bar{r}\left(\frac{k^2\Gamma(k)^4}{\Gamma\left(k+\frac{1}{2}\right)^4} - 1\right)^{\frac{1}{2}}. \qquad (7)$$

Thus, the mean and variance of pore radii, are characterised by the two parameters of the gamma distribution. We note that the probability density function given by Equation 5 is itself closely approximated by a gamma distribution with $k \mapsto \frac{1}{2}((16k^2+1)^{\frac{1}{2}} - 1)$ and $b \mapsto 2b\sqrt{\pi}$; also, in comparison with the distributions of Corte and Lloyd [1] and those of Bliesner [4], the pore radius distribution given by Equation 5 exhibited similar shape and skewness to a lognormal distribution with the same mean and variance. It follows directly from Equation 7 that the coefficient of variation of pore radii for non-random networks is dependent only on the parameter k; importantly, the pore radius theory of Dodson and Sampson includes the model of Corte and Lloyd for random networks as a special case when $k = 1$, such that Equation 7 recovers Equation 3.

The appropriateness of the gamma distribution to characterise pore radii in non-random fibre networks is reinforced by the recent work of Castro and Ostoja-Starzewski [9] who showed that the area-frequency of the radii of inscribed circles touching three sides of a polygon in a random fibre network are gamma distributed. Note also that the number frequency of inscribed circle radii in a random network was shown by Miles [8] to have a negative exponential distribution and that the gamma distribution has been shown recently to describe well the pore radius distribution in granular packings [10, 11].

Here existing theory is revisited and it is shown that the coefficient of variation of pore radii is, contrary to the accepted view, constant for changes in the number of fibres per unit area and the degree of spatial uniformity of their organisation. Experimental data to support this statement is presented.

2. Theory

Given an affine relationship between the standard deviations and mean values of a random variable, y in a system, the coefficient of variation of that variable is defined by the gradient and the standard deviation observed when the mean value is zero.

$$\sigma(y) = m\bar{y} + \sigma_0(y) \quad (8)$$

where $\sigma_0(y)$ is the standard deviation observed at $\bar{y} = 0$. The coefficient of variation is given by

$$CV(y) = m + \frac{\sigma_0(y)}{\bar{y}}. \quad (9)$$

Since the standard deviation of y is given by the square root of the variance, it must, by definition take real and positive values. Now, a real random variable with mean value zero can have a positive standard deviation if and only if it may take negative values. The variable of interest here is the pore radius r and, since $r > 0$ we expect that as the mean pore radius tends to zero, so does the standard deviation of pore radii.

As discussed previously, the pore radius distribution in near-planar fibre networks has a positive skew and is well described by the lognormal and the gamma distributions. For gamma distributed pore radii, we have

$$\bar{r} = \frac{k}{b}, \quad (10)$$

$$\sigma(r) = \frac{\sqrt{k}}{b}, \quad (11)$$

$$= \frac{\bar{r}}{\sqrt{k}}. \quad (12)$$

Since the gamma distribution holds for $k > 0$ we have,

$$\bar{r} \to 0 \quad \text{as} \quad b \to \infty$$

$$\sigma(r) \to 0 \quad \text{as} \quad \bar{r} \to 0$$

For lognormally distributed pore radii, we have

$$\bar{r} = e^{\frac{\sigma^2}{2}+\mu}, \quad (13)$$

$$\sigma(r) = \sqrt{e^{\sigma^2} - 1}\, e^{\mu+\frac{\sigma^2}{2}}, \quad (14)$$

$$= \bar{r}\sqrt{e^{\sigma^2} - 1}. \quad (15)$$

and therefore,

$$\bar{r} \to 0 \quad \text{as} \quad \mu \to -\infty$$

$$\sigma(r) \to 0 \quad \text{as} \quad \bar{r} \to 0$$

Thus, for the two distributions commonly used to characterise the pore radius distribution in stochastic porous materials, $\sigma_0(r)$ is zero.

Accepting that the relationship between the mean pore radius and the standard deviation of pore radii is linear for changes in mean network areal density and structural uniformity, the treatment given above suggests strongly that the coefficient of variation of pore radii is constant and equal to the gradient, m. For the gamma distribution we have $CV(r) = 1/\sqrt{k}$ and for the lognormal distribution we have $CV(r) = \sqrt{e^{\sigma^2} - 1}$. The increase in the coefficient of variation of pore radii observed with increasing mean pore radius by Corte and Lloyd and Bliesner and plotted in Fig. 2 is attributable to the negative values of $\sigma_0(r)$ obtained for their data.

TABLE I Properties of fibres used to prepare networks

	Mean width μm	Mean length mm	Linear density $gm^{-1} \times 10^4$
TMP	36.5	1.98	2.22
Chem.	38.7	2.41	1.16

3. Experimental

Samples of stochastic fibre networks were formed with mean areal densities of 20 gm^{-2}, 40 gm^{-2} and 60 gm^{-2} using natural cellulose fibres obtained from different woods treated by two different processes, thermomechanical (TMP) and chemical (Chem); samples were made also from a 50 : 50 blend of the two types. Samples were formed by filtration of a suspension over a standard woven wire fabric in a British Standard Handsheet Former; this equipment conforms to international standards for forming paper in the laboratory and is described in [12]. The fibres were chosen for their different morphologies and these are summarised in Table I. The linear density of a fibre is defined as its expected mass per unit length, so at a given mean areal density, networks formed from the Chemical fibres will have more constituent fibres per unit area than those formed from the TMP fibres.

The mass distribution in the networks was altered by forming at different mass concentrations in the suspension and by allowing time for the fibres in suspension partially to sediment before filtration. Both mechanisms allowed increased potential for fibre interaction in suspension and hence increased nonuniformity in the formed network. It should be noted that one set of networks for each fibre type and for the blend was formed using the mass concentrations and sedimentation times described in [12]; these conditions are known to produce networks with an approximately Gaussian distribution of mass density at the 1 mm scale close to that of a random fibre network formed from the same constituent fibres [6]. The degree of fibre interaction in suspension, induced through the range of experimental conditions, therefore produced manifestly non-random networks with a broader, approximately Gaussian, distribution of local areal densities than their corresponding random networks.

The pore radius distribution was measured using a capillary flow porometer, model CFP 1500 AEX manufactured by PMI Inc. The instrument automates the saturated head gas drive technique described by Corte [13] and conforms to ASTM standards [14]. The instrument was used to record the flow rate of dry nitrogen at a given pressure and the equations of Corte [13] were applied to the average pressure-flow response of three repeats to determine the pore radius distribution; a circular area of diameter 12 mm was used for each repeat. As expected, the thickness of the networks was influenced by the fibre type as well as the mean areal density, though were of order 50 μm, 100 μm and 150 μm for networks of mean areal density 20 gm^{-2}, 40 gm^{-2} and 60 gm^{-2} respectively; for recent studies of the influence of mass distribution on the distributions of thickness and density in stochastic fibre networks see Dodson *et al.* [15, 16].

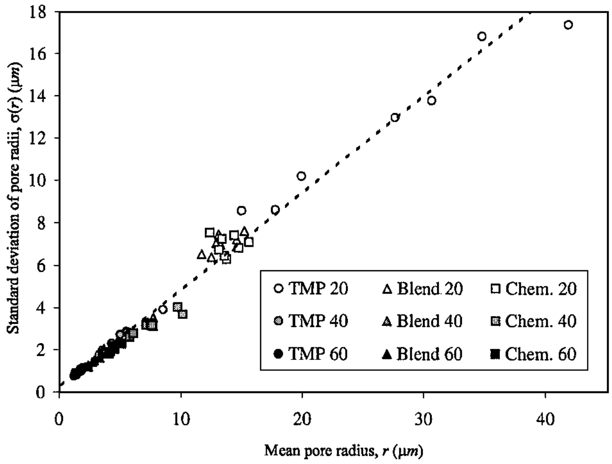

Figure 3 Standard deviation of pore radii plotted against mean pore radius. The relationship is highly linear and has an intercept close to the origin.

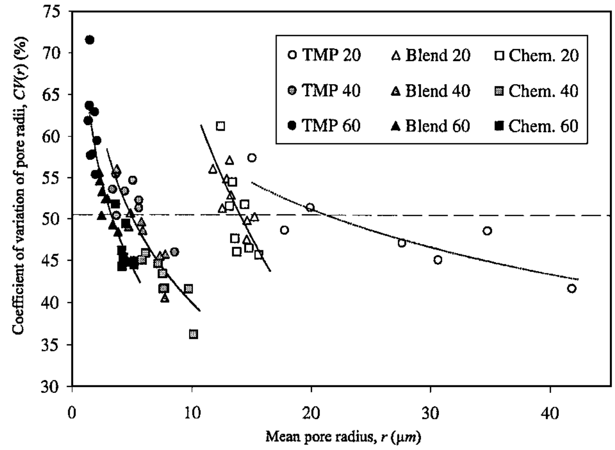

Figure 4 Coefficient of variation of pore radii plotted against mean pore radius. At a given mean areal density, increases in mean pore radii are associated with a decrease in coefficient of variation of pore radii. The decrease is however weak, and may be attributed to an artefact in the measuring system.

The in-plane distribution of mass was measured for each sample using β-radiography and image analysis following the technique described by Ng [17]; for this study, variability has been quantified as the coefficient of variation of local areal density, i.e. of mass per unit area, observed at the 1 mm scale measured within square zones of side 5 cm.

4. Results and discussion

The standard deviation of pore radii is plotted against the mean pore radius for all 71 samples analysed in Fig. 3. In agreement with the observations of Bliesner [4] for changes in areal density, and those of Corte and Lloyd for [1] for changes in mass distribution, the data show a clear proportionality between the standard deviation of pore radius and the mean pore radius, which in turn decreases with increasing mean areal density. Importantly however, the data show that changes in mean areal density and the distribution of areal density cause the mean and standard deviation of pore radius to move along the *same* line; also, for our fibres of similar width, but with different mean lengths and linear densities, the proportionality is insensitive to fibre morphology. A linear regression on the data presented in Fig. 3 gives

$$\sigma(r) = 0.462\bar{r} + 0.233 \qquad (16)$$

with a coefficient of determination of 0.978. So for our data we have the estimate of $\sigma_0(r) = 0.233$ compared with a value of -2.525 for the data of Bliesner and -10.498 for the data of Corte and Lloyd. Thus, for our data we have positive $\sigma_0(r)$ which implies therefore that processes that increase the mean pore radius will *decrease* the coefficient of variation of pore radii. This is illustrated in Fig. 4 where the dotted lines represent log-linear regressions on the data at 40 gm^{-2}, 60 gm^{-2} and the two groups of data at 20 gm^{-2} and are intended to be illustrative only; the broken horizontal line represents the mean coefficient of variation of pore radii observed across all data sets. Although the data shows the coefficient of variation of pore radii to decrease with increasing mean pore radii at a given mean areal density, the overall range is within $\pm 50\%$ of the mean and does not therefore represent a particularly large scatter. Also, the data for each fibre type within these groups exhibit a very narrow range of coefficients of variation of pore radii. The strongest trend in Fig. 4 is observed for the TMP fibres at a mean areal density of 20 gm^{-2} where there is a very broad range of mean pore radii. This may be attributable to the occurrence of pinholes or "through-pores" in the networks which could be easily observed in the samples and arise as a consequence of the high linear density of the fibres, which in turn reduces the number of fibres per unit area. Thus, to a first approximation, the coefficient of variation of pore radii appears insensitive to changes in the mean pore radius.

Naturally, from the discussion of the theory given above, we expect the intercept $\sigma_0(r) = 0$ and hence the coefficient of variation of pore radii to be constant. The non-zero intercept obtained for our samples is therefore presumably an artefact of the measuring system and indicates that the equipment slightly underestimates pore radii. Conversely, the systems used by Corte and Lloyd and Bliesner, whilst based on the same measuring principles, have seemingly overestimated pore radii. The fact that our data yields an intercept closer to the origin

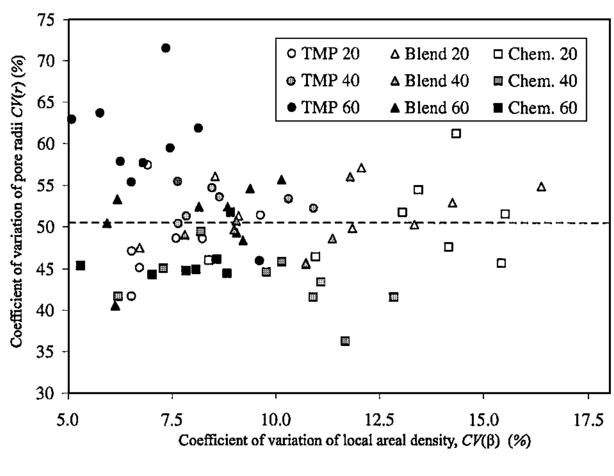

Figure 5 Coefficient of variation of pore radii plotted against coefficient of variation of local areal density. The horizontal line represents the mean coefficient of variation of pore radii for all samples.

is likely to be due to the greater experimental control and automation available through advances in technology. It is likely that the underestimate observed for our data arises from the implicit assumption in the theory associated with with the measurement technique, that pores are cylindrical.

The coefficient of variation of pore radii is plotted against that of the local areal density as measured by β-radiography at the 1 mm scale in Fig. 5. Here the insensitivity of the pore radius distribution to the mass distribution is readily apparent, there being no clear correlation for the whole data set or for classes of data grouped by fibre type or mean areal density.

5. Conclusions

Experimental data has been presented confirming the well established linear relationship between the standard deviation of pore radii and the mean pore radius in near-planar stochastic fibre networks. Unlike previous studies, a linear regression on the data has an intercept close to the origin suggesting that, to a first approximation, the coefficient of variation of pore radii in stochastic fibre networks is constant for changes in the mean number of fibres per unit area and in the uniformity of their distribution in the plane. Theoretical consideration of the lognormal and gamma distributions, which are known to describe the pore radius distribution well in a range of stochastic porous media, show that they allow for a constant coefficient of variation of pore radii.

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