The pore radius distribution in paper. Part II: The effect of laboratory beating

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Abstract

An experimental investigation into the effects of different beating processes on the pore radius distribution in paper is presented. Standard handsheets were formed from fibres beaten in four laboratory beaters with different actions. The relationship between the mean pore radius and the standard deviation of pore radii was found to be linear and to pass close to the origin such that the coefficient of variation of pore radii was insensitive to beating type or duration. Changing the formation of sheets formed from one beating condition did not affect the relationship between the mean pore radius and the standard deviation of pore radii. The relationship between mean pore radius and density was found to be dependent on beater type and very sensitive to the presence of fines. The dependence of air permeability and light scattering coefficient on mean pore radius exhibited some dependence on beater type reinforcing the importance of coupling pore radius distributions with porosity when considering the influence of void structure on the physical properties of paper.

Introduction

In the first part of this series of articles [1], the linear relationship between the standard deviation of pore radii and the mean pore radius was shown to be the same for changes in grammage and formation; the effect of grammage being greater than that of formation. The void structure of sheets formed from a given fibre type is influenced primarily however by stock preparation processes such as beating and refining and by wet-pressing; secondary effects include drying processes and calendering.

The effect of wet-pressing on the pore size distribution was investigated by Corte and Lloyd [2] who pressed sheets of nominal grammage 190 $g\,m^{-2}$ formed from hardwood and softwood fibres and found the mean pore radius to decrease with increasing density and to be proportional to the standard deviation with an intercept close to the origin.

Corte and Kallmes [3] investigated the effect of mean grammage, $\bar{\beta}$ ($g\,m^{-2}$) and beating on the maximum pore radius, r_{max} (μm) as measured by a liquid displacement method. Their results confirmed the theoretical expectation that, for a given furnish, the maximum pore radius was inversely proportional to grammage such that

$$\bar{\beta}\, r_{max} = K$$

where K ($g\,m^{-1}$) is a constant that was found to decrease only slightly with beating.

There are few studies in the literature that consider the effect of beating and refining on the pore size distribution. Yamauchi and Kibblewhite [4, 5] and more recently Görres *et al.* [6] used

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mercury porosimetry to investigate the contribution of different fibre fractions to the void structure of handsheets. Yamauchi and Kibblewhite found that the contribution of short fibres and fines to the consolidation of the sheet was greatest at high press pressures [4] though the effect was less for TMP fibres [5]. Görres *et al.* [6] found the coefficient of variation of specific pore volume to be approximately constant with a value of 50 % for all furnishes considered.

Here we present the results of a laboratory investigation into the influence of beating on the pore radius distribution in paper. A range of beating processes have been investigated, each with a different action; the influence of fines generated during beating has been investigated also. The measured pore radii are compared with measurements of sheet density, air permeability and optical properties.

Experimental

Four laboratory beaters were used to beat a Bleached Kraft Pine pulp; the beaters chosen were the PFI mill, the Valley beater, the Medway beater and the Lampen mill with a 5 *kg* ball. In the Valley and Medway beaters, the working action is that of two barred surfaces; in the PFI mill the action is that of a barred surface against a smooth surface and in the Lampen mill the action is that of two smooth surfaces. As such we expect a significant range of fibre length reduction, internal and external fibrillation, swelling and fines generation to be covered by the four processes. The beating conditions are summarised as,

Lampen: 30, 60, 90 *min*,

PFI: 3000, 6000, 9000 *rev*,

Valley: 10, 20, 40, 60, 80 *min*,

Medway: 2, 4, 6 *min*.

As a rule of thumb, and to guide the interpretation of data, we expect fibre shortening and fines generation to be greater for Valley and Medway beaters, and fibre swelling to be greatest for the Lampen mill; the PFI mill having an intermediate effect.

A standard disintegration was performed in addition to the beating conditions given above. Standard handsheets were made for each condition and from a 1:1 $w:w$ blend of pulps beaten for 3000 and 6000 *rev* in the PFI mill.

As the pulp used was not the same as that used in Part I of this study [1], two additional sets of non-standard handsheets were formed from the pulp beaten for 40 *min* in the Valley beater. These samples were formed with poorer formation than standard by increasing the time between stirring and draining the suspension to 60 and 120 *s* allowing increased flocculation in the suspension and therefore in the handsheets. These additional conditions therefore allowed investigation of how the changes in pore structure caused by beating compare to those observed for changes in formation; these being similar to those caused by changing grammage [1].

Fines were generated by carrying out an additional Medway beating for 20 *min*. The beaten stock was passed through a Sommerville Fractionator fitted with a 200 mesh and and the material passing through the mesh was collected on a clean muslin cloth. Fines-free samples of the pulps beaten for 30 *min* in the Lampen mill and for 6000 *rev* in the PFI mill were prepared by fractionating the stock for 30 *min* in a Sommerville Fractionator fitted with an 80 mesh and collecting the material retained on the mesh. Handsheets were made from blends of these fines-free fractions and the fines generated in the Medway beater. A series of handsheets with target grammage of 60 $g\,m^{-2}$ were formed from known masses of fines-free pulp blended with different quantities of fines such that the grammages of the sheets allowed an estimate of the fines fraction *in* the sheet to be made.

Conditioned handsheets were tested according to standard for grammage, thickness, air permeability and the reflectances R_0 and R_∞. The pore radius distribution was measured using a capillary flow porometer, according to the method described in Part I of this series of articles [1]. The Schopper-Riegler wetness of all whole-pulps was measured but no correlation was observed between this and measurements of the pore radius distribution; accordingly this measure is not discussed in the following sections.

Results and Discussion

For each beating condition, the mean pore radius and standard deviation of pore radii decreased with increasing beating, as expected. The standard deviation of pore radii is plotted against the mean pore radius in Figure 1; data associated with fines-free samples are labelled, 'FF' in this and all subsequent plots. It is immediately apparent that beating has had a significant effect on the pore radius distribution, and that, independent of beating type and duration, the standard deviation of pore radii is proportional to the mean as was observed for changes in grammage and formation [1]. The smallest pore radii are observed for the furnishes with controlled addition of fines and for the 4 *min* and 6 *min* Medway beaten samples; note that the grammages for the sheets containing fines were around 5 $g\,m^{-2}$ above those of the other samples and therefore there is a weak grammage effect in the observation of smaller pore radii for these samples. Interestingly, the sample formed from a blend of the pulps beaten in the PFI mill for 3000 *rev* and 6000 *rev* lies closer to the point obtained for the 3000 *rev* treatment than that for the 6000 *rev* treatment, suggesting that the more lightly beaten fibre dominates the pore structure for this blend.

For the sample beaten for 40 *min* in the Valley beater, the effect of worsening formation was to increase the mean pore radius and the standard deviation, as observed in Part I for other fibres [1]. Importantly, these changes in formation caused the data to fall on the same line as that given for changes in beating. Since the effects of formation and grammage give a single relationship between the standard deviation of pore radii and the mean pore radius, then the result implies that for a given fibre type, one relationship should hold for changes in formation, grammage and beating.

Denoting the mean pore radius, $\bar{r}$ (μm) and the standard deviation of pore radii, $\sigma(r)$ (μm), regression on the data presented in Figure 1 yields,

$$\sigma(r) = 0.519\,\bar{r} + 0.064 \tag{1}$$

with coefficient of determination 0.975. Naturally, this regression is weighted considerably by the points on the far right of the axes where data is sparse. Regression on only those data with $\bar{r} < 1.0\ \mu m$ yields,

$$\sigma(r) = 0.653\,\bar{r} + 0.012 \tag{2}$$

and this has coefficient of determination 0.942; note however that this expression has an intercept significantly closer to the origin than that given by Equation (1).

The coefficient of variation of pore radii is plotted against the mean pore radius in Figure 2. The broken line represents the mean coefficient of variation of pore radii for the full data set and this was 66.9 %; the mean coefficient of variation of pore radii for samples with mean pore radius less than 1 μm was 68.6 % and both these values are close to the coefficient of $\bar{r}$ in Equation (2). There is a weak decrease in the coefficient of variation of pore radii with increasing mean pore radius. In the first part of this paper [1], we proposed that the coefficient of variation of pore radii may be considered approximately constant for changes in formation and grammage; this may be considered to apply also, and indeed more strongly, for the beating conditions investigated here.

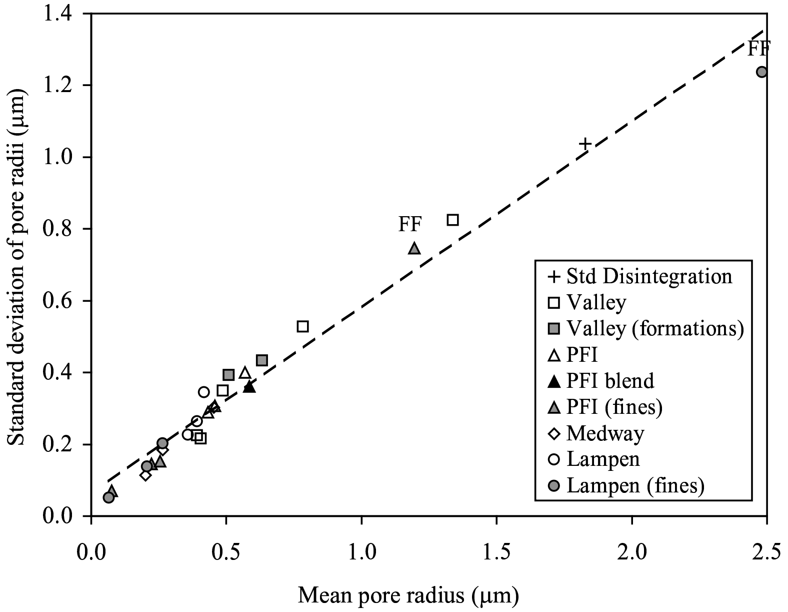

Figure 1: Standard deviation of pore radii plotted against mean pore radius. Legends indicate beating type and forming variables; broken line represents linear regression on the data; points labelled 'FF' represent fines-free fractions. The relationship is independent of beating type, formation and fines fraction and regression on the data passes close to the origin.

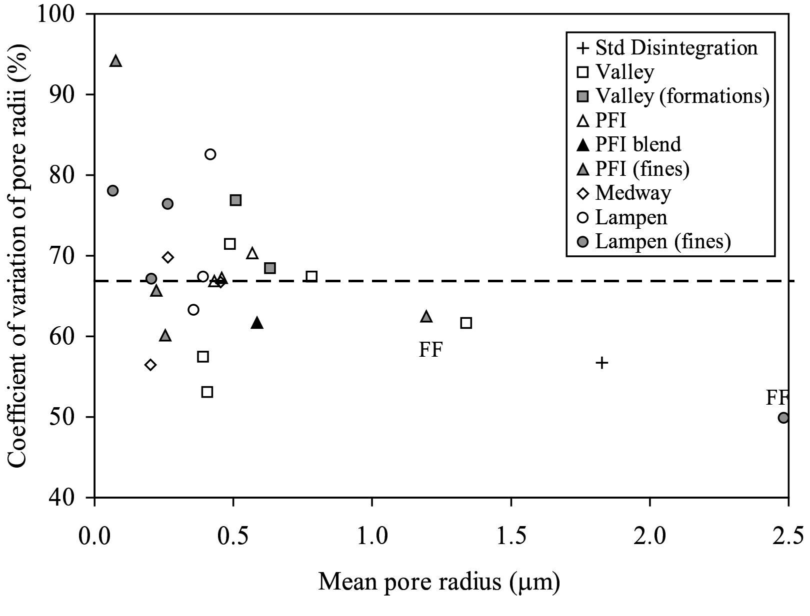

Figure 2: Coefficient of variation of pore radii plotted against mean pore radius. The coefficient of variation of pore radii decreases with increasing mean pore radius though the effect is very weak and the coefficient of variation of pore radii may be considered approximately constant.

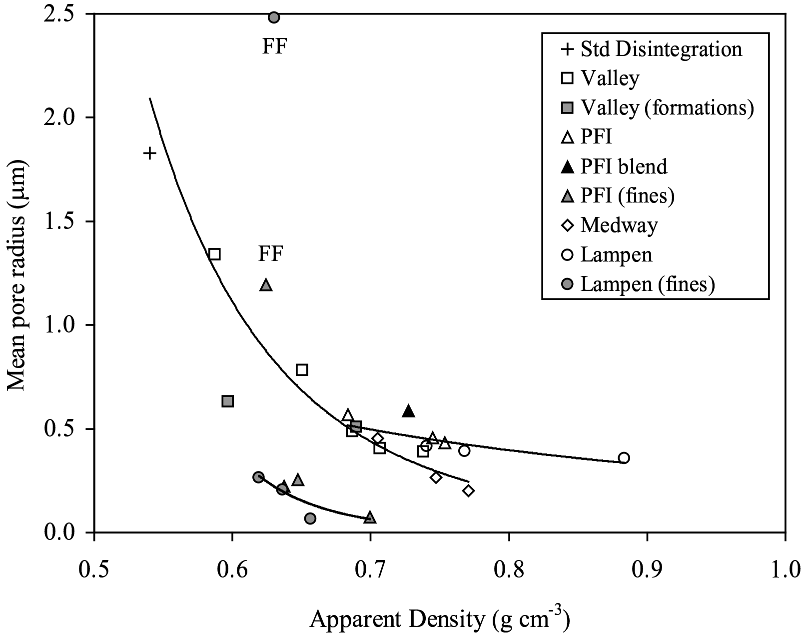

Figure 3: Mean pore radius plotted against apparent density. The expected decrease in mean pore radius with increasing density is observed, though the nature and fraction of fines in the furnish allow small pores to be observed at low densities.

The relationship between mean pore radius and apparent density is shown in Figure 3. As expected, the mean pore size decreases with increasing density, *i.e.* decreasing porosity. For more detailed analysis of these data it is illustrative to divide them into three groups as indicated by the lines in Figure 3; these represent simple power law fits and should be considered illustrative only. The data for the standard disintegrated fibre and that beaten in the Valley and Medway beaters show a steep decrease in mean pore radius with increasing density. The sheets formed from fibre beaten in the Lampen and PFI mills exhibit higher densities, though the mean pore radii are larger than those observed for the Medway beaten pulps at similar densities. Interestingly, the sheets formed with controlled addition of fines from the PFI and Lampen beaten fibres exhibit lower densities and lower mean pore radii; this suggests that the long fibre fraction dominates the total pore volume, whilst the fines fraction dominates its structure. This result suggests that in an industrial context, careful choice of refiner type should allow reduction of pore radii without compromising density.

The air permeability is plotted against the mean pore radius in Figure 4; for clarity, the data are plotted on logarithmic scales. Generally, the data fall in one group and there is little dependence of the overall relationship on beater type. Interestingly, the sheets formed from the pulp beaten in the Lampen mill show a steep dependence of air permeability on mean pore radius; indeed Figure 3 shows that the 60 and 90 *min* Lampen beatings generated the more dense of our samples and yet these were not the least permeable. Also sheets formed from the blended PFI beaten pulp exhibited similar mean pore radii to those of sheets formed from the fibre beaten for 3000 *rev*, but are less permeable. The precise nature of these dependencies is not clear; coupled with the data presented in Figure 3 they suggest that there is potential for altering the pore radius distribution whilst holding sheet density and air permeability constant.

The results reinforce the importance of the pore size distribution in considering the flow resistance of paper. The measurement of the pore radius distribution arises from the flow behaviour of the sheet; since the mean pore radius, and hence the distribution of pore radii, may differ at a given density, it follows that flow models characterising the pore space by the global average porosity, such as the Kozeny-Carman equation, are insufficient to characterise global average flow

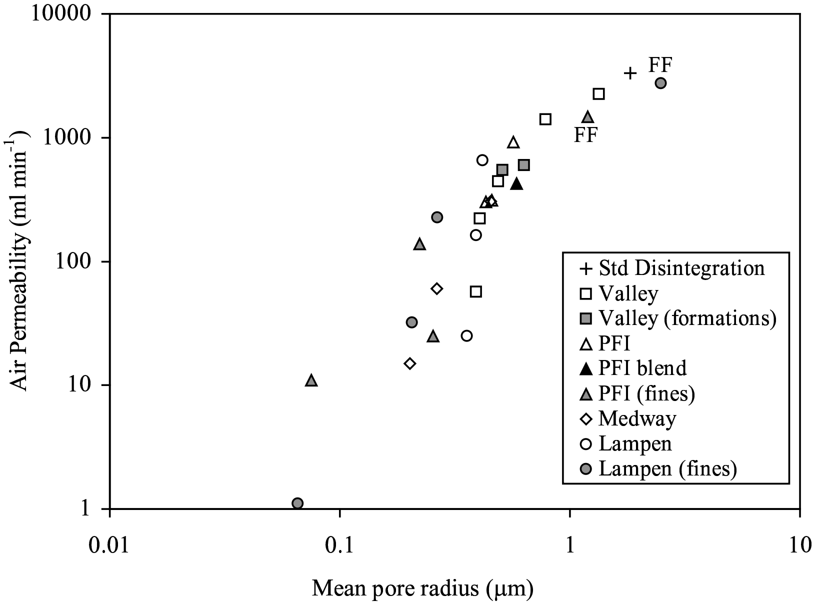

Figure 4: Air permeability plotted against mean pore radius. Generally, the data fall in one group with little dependence on beater type. The most dense samples however were not necessarily the least permeable.

behaviours. Of course, our analysis tells us only the *relative* frequency of pores with given radii; accordingly flow models considering the void structure should combine the porosity and the pore radius distribution.

Having targeted the contribution of the long fibre fraction to the grammages of the sheets containing additional fines and knowing the grammages of the formed sheets, we are able to estimate the fines content of these samples. The mean pore radius is plotted against fines content in Figure 5. The fines-free fraction of the Lampen beaten pulp studied has a significantly greater mean pore radius than the fines-free fraction of the PFI beaten pulp studied. At a retained fines content of 20 % and above however, the mean pore radii of the pulps are similar.

The specific light scattering coefficient was calculated from the measurements of R_0 and R_∞ and grammage using the Kubelka-Munk theory [7]. This is plotted against the mean pore radius in Figure 6. Since both mean pore radius and the specific light scattering coefficient are expected to decrease with increasing sheet density, the general trend to the data presented in Figure 6 is broadly as expected. The relationship between the pore radius distribution and light scattering in coated and filled papers is well established, see for example [8, 9], and has been shown for general classes of porous media by Gate [10]. For our unfilled samples, the data show again the importance of coupling pore radius distribution and density. In particular the steep dependence of scattering coefficient of mean pore radius shown for the samples beaten in the Lampen mill is likely to be a consequence of the greater density of these samples, as shown in Figure 3. Naturally, light scattering is independent of the inter-fibre void structure at scales above the maximum wavelength of light; accordingly the data at scales above 0.7 μm are included in Figure 6 for completeness only.

Conclusions

The results of an experimental investigation into the effects of laboratory beating on the pore radius distribution in paper have been presented. We have seen that the standard deviation of pore radii is proportional to the mean with one relationship holding for all beaters and beating times considered. A consequence of this result is that the coefficient of variation of pore radii is

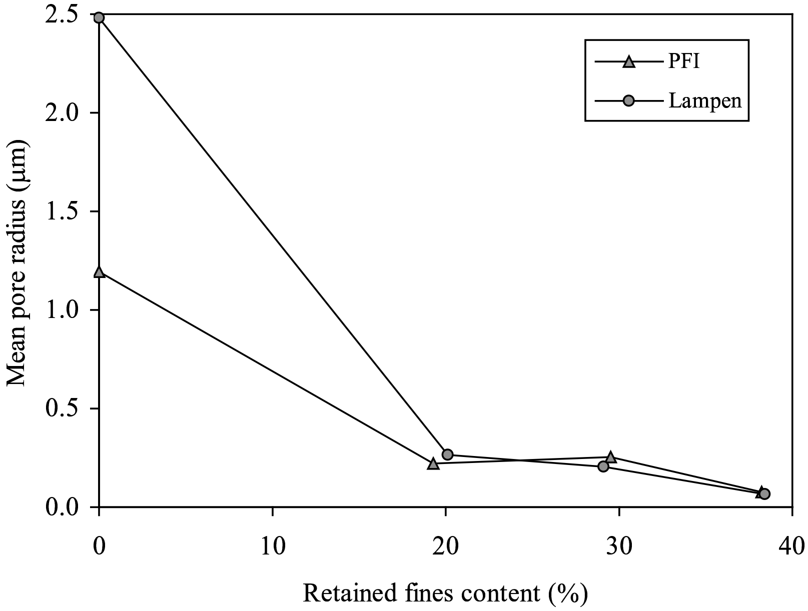

Figure 5: Mean pore radius plotted against retained fines content. At fines fractions of 20 % and above, the fines determine the structure of the void space; though for these pulps the density is determined by the long-fibre fraction.

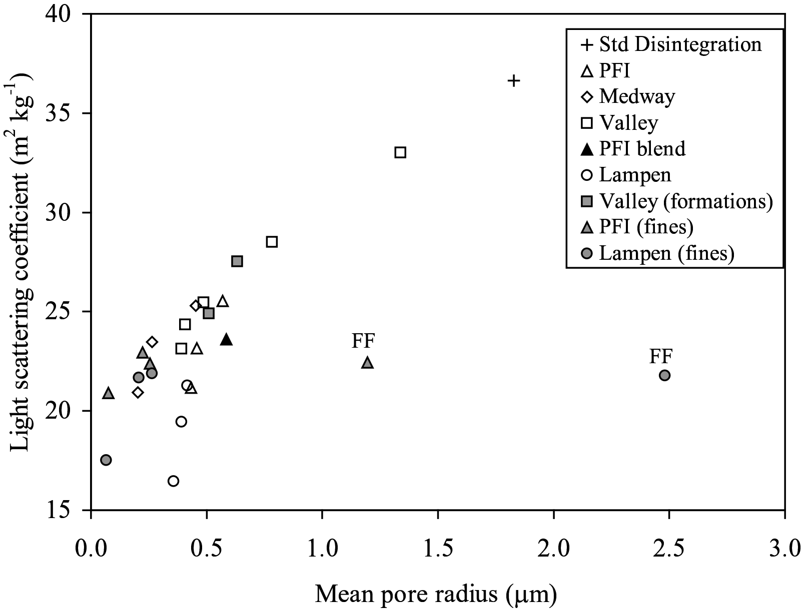

Figure 6: Light scattering coefficient plotted against mean pore radius. The light scattering increases with increasing pore radius but shows some sensitivity to beater type as a consequence of the different sample densities.

approximately constant. Altering the formation of sheets formed from one beating condition did not affect the relationship between the standard deviation of pore radii and the mean pore radius. The relationship between the mean pore radius and the apparent density of the sheets has been shown to be dependent on beater type and very sensitive to the presence of fines. A consequence of this is that the air permeability and light scattering coefficient are dependent on both mean pore radius and apparent density. The presence of fines has a strong influence on the pore radius distribution of the sheet whilst the long-fibre fraction has a stronger influence on sheet density.

Acknowledgments

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