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COMPARISON OF CAPILLARY FLOW POROMETRY AND MERCURY INTRUSION POROSIMETRY IN DETERMINATION PORE SIZE DISTRIBUTION OF PAPERS

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ABSTRACT

Capillary flow porometry and mercury intrusion porosimetry achieved a good agreement in determining the pore size distribution in papers for the top layers of corrugated board. Differences in the papers composition as well as structure can be easily detected by changes in the measured parameters, thus allowing a better understanding their behaviour at processing and use. Water absorption is mainly dependent on the diameter of the large pore and to a lesser extent from the diameter of medium pore, surface free energy of paper and the swelling ability of recycled and bleached pulp fibres.

KEYWORDS: Capillary flow porometry, mercury intrusion porosimetry, paper, porous structure, water absorption.

INTRODUCTION

The paper porosity is an important structural parameter, which is extensively used in much research, especially in pollutant migration analysis, ink absorption analysis, glue setting and penetration, final glue bond strength, paper properties evaluation and so on (Huang and Duan 2010, Ninnes et al. 2011). The paper possess a two- or three-dimensional pore structure depending on fibre properties, basis weight, formation and other manufacturing processes, like wet pressing or calendaring, which can affect the voids between the fibres. The pulping method and treatments of the fibres affect their flexibility, collapsibility, external fibrillation and fines production, which in turn affect the compactness of the paper and thereby the pore structure. Due to the highly irregular structure of fibres and the fibre web, no unambiguous definition exists for thickness, density or porosity of paper (Niskanen 1998). Although all of these properties can be

measured, the results strongly depend on the measurement method and its resolution. Applying the general definition of porosity to paper, pore volume consists of all the space outside the solid materials included in the paper. Three kinds of pores (through, blind and closed) are normally found in paper (Fig. 1). Pore structure, which affects the permeability, is naturally closely related to the structure of the fibre network. Permeability is a meaningful quantity only if fluid is allowed to flow through the fibre network. Thus, a connected interfibre pore volume must exist through the system; i. e. the pore system must percolate.

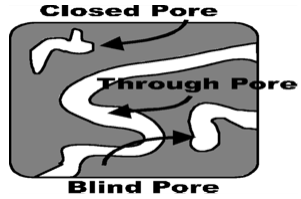

Fig. 1: Closed, blind and through pores in paper.

Macroscopic and microscopic techniques are used for pore structure characterization of the paper. Microscopic techniques include methods like high-resolution light and electron microscopy and also x-ray scattering examination of tiny areas, which are time consuming and expensive. Macroscopic techniques based on liquid extrusion, liquid intrusion and gas adsorption are inexpensive and can be run quickly. However, no one technique enables to measure all the properties. Also, the same property is often measured differently by various techniques. Liquid extrusion porosimetry is the only technique that can measure the volume of through pores. Mercury intrusion porosimetry and gas adsorption techniques measure the volume of through and blind pores. Capillary flow porometry enables to measure constricted diameter of the through pores and flow distribution, but does not allow to measure pore volume distribution.

Capillary flow porometry

Capillary flow porometry is a liquid extrusion technique in which the differential gas pressure and flow rates through wet and dry samples are measured. Pore diameters, the largest pore diameter, the mean flow pore diameter, pore distribution, envelope surface area and gas permeability are computed. Liquid permeability can be also measured by this technique. Principle of capillary flow porometry is shown in Fig. 2.

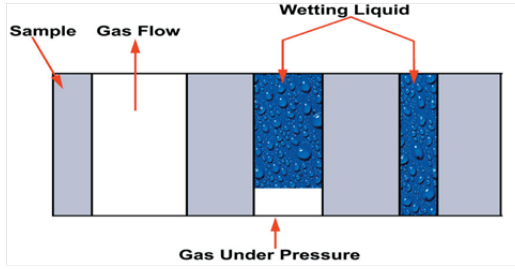

Fig. 2: Principle of capillary flow porometry (Jena and Gupta 2002).

In this technique, a wetting liquid is used to fill the pores of the sample. The liquid whose surface free energy with a solid ($\sigma_{solid/liquid}$) is less than the surface free energy of the solid with gas ($\sigma_{solid/gas}$) would wet the solid. A wetting liquid fills the pores spontaneously, but removal of

the liquid from pores is not spontaneous. A non-reacting gas can be used to displace a liquid from pores. Provided work done by the gas is equal to the increase in surface free energy required for the replacement of the low free energy of sample-liquid surface by the high free energy of sample-gas surface as is shown in Fig. 3 and described by Eq.1

$$\Delta p\, dV = (\sigma_{solid/gas} - \sigma_{solid/liquid})\, dS \quad (1)$$

where: Δp - differential pressure,
dV - increase in volume of gas in the pore,
dS - increase in solid/gas interfacial area and the corresponding decrease in solid/liquid interfacial area.

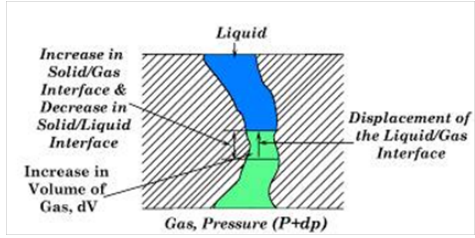

Fig. 3: Displacement of wetting liquid in a pore by a gas (Denbigh 1968)

Consideration of equilibrium between surface energy leads to Eq.2

$$(\sigma_{solid/gas} - \sigma_{solid/liquid}) = \sigma \cos \theta \quad (2)$$

where σ and θ are surface energy and contact angle of the wetting liquid. From Eq.1 and Eq. 2 resulting Eq. 3

$$\Delta p = \sigma \cos \theta \, (dS/dV) \quad (3)$$

In the case of circular pore geometry in cross-section, a modified Young-Laplace equation is used, which is most of the time referred to as the Washburn Eq. 4

$$\Delta p = 4 \sigma \cos \theta / D \quad (4)$$

In case of other pore geometry in cross-section (slit, elliptical and rectangular) is necessary to use shape factors 0.71, 0.72 and 0.75, this means that the actual pore size is smaller than measured. This correction results from the fact that essentially all instruments assume circular pore geometry.

Mercury intrusion porosimetry

Mercury intrusion porosimetry is a well known technique that has been widely used for pore structure measurement. This technique provides a wide range of information, e.g. the pore size distribution, density and surface area. It was used for characterization of specific papers and pigment coatings (Vähä-Nissi et al. 1998, Johnson et al. 1999, Alince et al. 2002; Donigian et al. 1997). The suitability of mercury intrusion technique was used to determine the pore structure of different kinds of woods, pulp handsheets and commercial paper sheets (Moura et al. 2005).

The principle of this technique (Webb and Orr 1997) is based on the fact that mercury does not wet most substances and, therefore, will not penetrate pores by capillary action, unless it is forced to do so. Liquid mercury has a high surface energy 485 $mJ \cdot m^{-2}$ and also exhibits a high contact angle 137° against most solids. Entry into pore spaces requires applying pressure in inverse proportion to the pore diameter (Eq. 4). In mercury porosimetry, the sample is first evacuated, then surrounded with mercury and, finally, pressure is applied to force mercury into the void spaces whilst monitoring the amount of mercury intruded. Data of intruded volume of mercury versus applied pressure are obtained and the pressures are converted to pore sizes, using Eq. 4. For the calculation of the paper pore diameter, shape factor 0.75 was applied (Lieshout 2006, Kettle et al. 1997).

The aim of this study was to compare the determination the pore size distribution of papers for the top layers of corrugated board by the method of capillary flow porometry and mercury intrusion porosimetry.

MATERIAL AND METHODS

Material

Paper A - liner from unbleached pulp fibres, basic weight 100 $g \cdot m^{-2}$ (Stora Enso).

Paper B - testliner from recycled fibres, basic weight 126 $g \cdot m^{-2}$ (Smurfit Kappa).

Paper C - testliner, top side from bleached pulp fibres and back side from recycled fibres, basic weight 127 $g \cdot m^{-2}$ (Rondo Ganahl).

Paper D - testliner, top side from bleached pulp fibres and back side from recycled fibres, basic weight 140 $g \cdot m^{-2}$ (Rondo Ganahl).

Paper E - testliner from recycled fibres, basic weight 127 $g \cdot m^{-2}$ (Rondo Ganahl).

Methods

Capillary flow porometry was used for measurement of pore size distribution using the analyzer ADP 3 (Pulp and Paper Research Institute, Slovak Republic) with pressure from 3.5 to 125 kPa. As testing liquid, silicone oil Lukosiol M 200 with surface energy of 22.8 $mJ \cdot m^{-2}$ and viscosity of 200 mPa.s was used. The permeability of pores in paper was determined on the basis of measurement of air flow at a various pressure difference Δp measured on dry sample (Q_S) and on sample saturated with testing liquid (Q_N).

The pore diameter was determined from Eq. 4 based on the pressure difference Δp. The pore size distribution was evaluated from the air flow values. Relative permeability (X) is related to total paper permeability and is expressed as a percentage. It was calculated from the flow Q_S and Q_N at each pressure differences according to Eq.5:

$$X = (Q_N / Q_S) \times 100 \quad (\%) \tag{5}$$

Pore size is a diameter of circle inscribed into pore intersection regardless of its shape. From the distribution curve, two parameters were determined: the the large pore diameter b5 and the medium pore diameter b50 in μm. The large pore b5 corresponds with air permeability of the first 5% from the total amount of air passed through the paper. The medium pore b50 characterizes pore size at which one half of the total air flow was passed through paper. Distribution curve was obtained from ten parallel measurements.

Mercury intrusion porosimetry was used as comparison technique for determination of pores size distribution. The porosimeter P2000 (Carlo Erba, CE Instruments, Italy) with range of pressure 0.15-200 MPa was used. The principle of determination of the size and distribution of pores by mercury intrusion porosimetry comprises sequential injection of mercury into the pores of the paper. Mercury has a very high surface energy and therefore does not wet the surface of the paper. In the experiment, paper sample was placed in a pycnometer, which was evacuated for 0.5 hours at pressure of 13.3 kPa, to remove all adsorbed impurities from the sample surface. Subsequently, the pycnometer was filled with mercury, the pressure was gradually increased, and the volume of mercury pressed in the pores was recorded at each pressure value. The pore diameter was determined from the pressure difference Δp according to Eq.4 and the total volume of pressed mercury corresponds to the total pores volume with a diameter larger than D. The integral distribution curve expresses the dependence of the relative pore volume on their diameter. From the distribution curve of relative volume pore, the diameter of the large pore D5 and the medium pore D50 in μm was determined. Distribution curve was obtained from ten parallel measurements.

Water absorption was determined by two methods, by passing the paper through the water column in the laboratory size press Werner Mathis AG (Switzerland) and by method $Cobb_{300}$ according to STN EN ISO 535. The passing of paper through size press was at a constant speed of 5 $m \cdot min^{-1}$ and a pressure between the rubber rolls of 20 $kN \cdot m^{-1}$. The water absorption on both sides of the paper in the size press is often expressed by weight of water per area of 1 m^2. For papers of different basis weight, the water absorption is expressed as a percentage. The time of contact between the paper and water in the size press was 5 seconds. According to the $Cobb_{300}$ method, the paper contact with water is one-sided and the contact time is more than 50 times longer than in the size press.

RESULTS AND DISCUSSION

Two different techniques were used to characterize the pore structure in papers for the top layer of corrugated board. Capillary flow porometry measures constricted diameter of the through pores and flow distribution, while mercury intrusion porosimetry measures the volume of through and blind pores.

Fig. 4 shows permeability distribution of constricted through pores depending on their diameters in papers A, B, C, D and E determined by capillary flow porometry. Papers B and E have significantly higher permeability as well as the diameter of the large and medium pores compared to papers A, C and D.

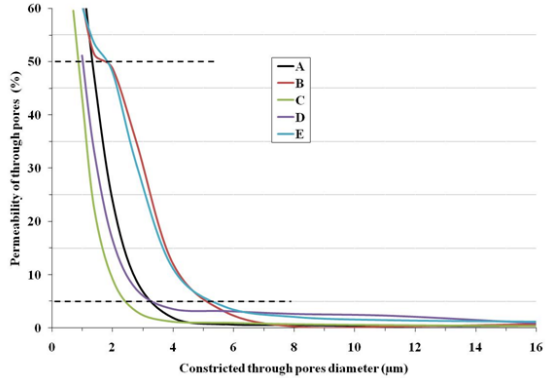

Fig: 4 Permeability distribution of constricted through pores depending on their diameters in papers A,B,C,D and E determined by capillary flow porometry.

Fig. 5 depicts volume distribution of through and blind pores depending on their diameters in papers A, B, C, D and E, determined by mercury intrusion porosimetry. The results for the analyzed papers were similar to those obtained by capillary flow porometry (Fig. 4). Papers B and E have significantly higher volume and diameter of pores compared to papers A, C and D, but the differences were found for papers A and D. From the two distribution curves (Fig. 4 and Fig. 5), the large pore diameter b5 was determined at 5% of the total permeability of constricted through pores (capillary flow porometry), respectively D5 at 5% of the total volume of through and blind pores (mercury intrusion porosimetry). Medium pore diameter b50 was determined at 50% of the total permeability of constricted through pore, respectively D50 at 50% of the total volume of through and blind pores.

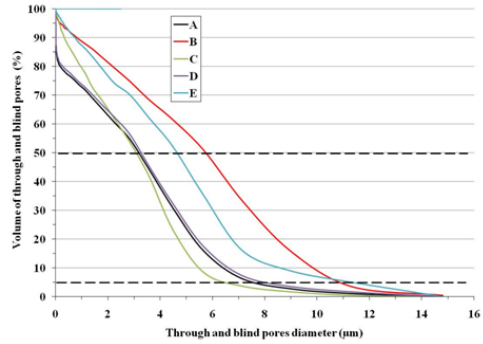

Fig. 5: Volume distribution of through and blind pores depending on their diameters in papers A,B,C,D and E determined by mercury intrusion porosimetry.

Tab. 1 shows the large and medium pore diameters in the papers A, B, C, D and E for the top layer of corrugated board, which were determined by capillary flow porometry and mercury intrusion porosimetry (Fig. 4 and Fig. 5). Differences in pore diameters of individual papers determined by these methods are related to the fact that by capillary flow porometry, constricted through pore diameter D1 (Fig.6) were measured, while by mercury intrusion porosimetry, through and blind pore were measured.

Tab. 1: Pore diameters in papers for the top layer of corrugated board.

Technique	Capillary flow porometry *	Mercury intrusion porosimetry**
Large pore diameter (μm)		
Paper A	3.3	7.5
Paper B	5.1	10.9
Paper C	2.4	6.5
Paper D	3.5	7.9
Paper E	5.3	11.2
Medium pore diameter (μm)		
Paper A	1.4	3.2
Paper B	1.9	5.9
Paper C	0.9	3.1
Paper D	1.0	3.3
Paper E	1.8	4.8

* Constricted through pore; ** Through and blind pores.

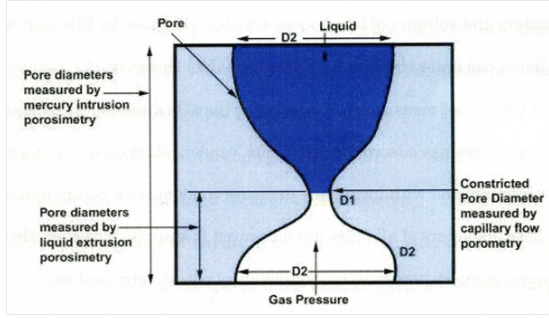

Fig. 6: Pore diameters measured by various techniques (Jena and Gupta 2002).

The relationship between the large and medium pore diameter in papers A, B, C, D and E measured by capillary flow porometry and mercury intrusion porosimetry is shown in Fig. 7. The x-axis represents pore diameters determined by the capillary flow porometry. The through and blind pore diameters, determined by the mercury intrusion porosimetry are indicated on the y-axis. The through and blind pore diameters were 2-3.4 times greater than the restricted through pore diameters. This ratio increased with decreasing of pore diameters. The correlation between constricted through pore diameters determined by capillary flow porometry and through/blind pore diameters determined by mercury intrusion porosimetry was very good. The correlation coefficient was R 0.988.

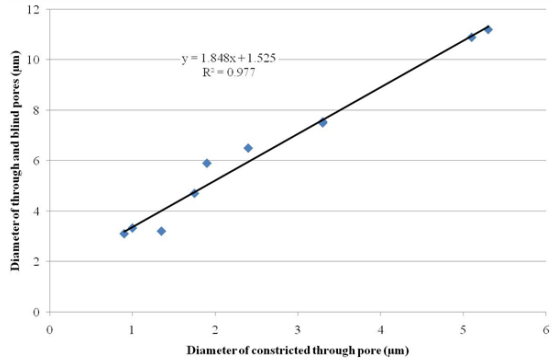

Fig. 7: Comparison of the pore diameters in papers A, B, C, D and E determined by capillary flow porometry and mercury intrusion porosimetry.

The pore diameters affect the ability of the paper to absorb liquids. The relationships between water absorption evaluated by the short-term (5 s) transition of the paper in the size press and by $Cobb_{300}$ method are shown in Fig. 8 and Fig. 9. The pore diameters determined by capillary flow porometry are marked with blue diamonds and by mercury intrusion porosimetry with red squares. Relationships between water absorption and large pore diameter achieved correlation coefficients from 0.889 to 0.946. The influence of medium pore diameter on water absorption was significantly lower and the correlation coefficients were from 0.661 to 0.863 (data unshown). Water absorption determined by $Cobb_{300}$ method was 8-10 times higher than determined by passing of paper through size press due to a 55-fold increase of the contact time of the paper with water.

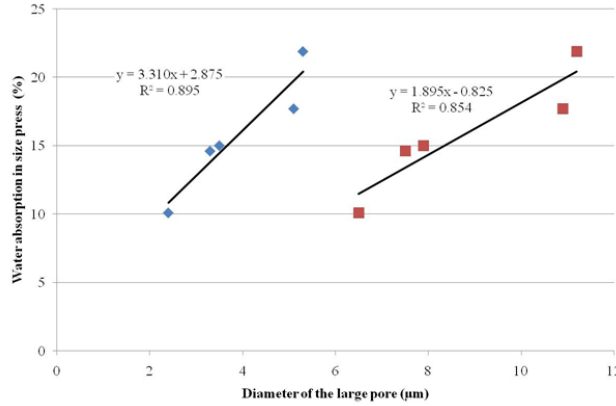

Fig. 8: Dependence of water absorption in size press on large pore diameter of papers A, B, C, D and E (Capillary flow porometry – blue diamonds; Mercury intrusion porosimetry – red squares).

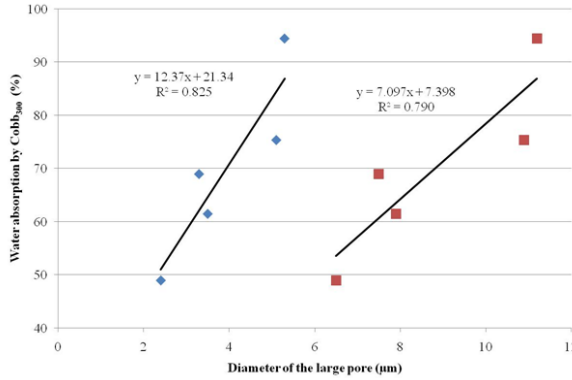

Fig. 9: Dependence of water absorption determined by $Cobb_{300}$ on large pore diameter of papers A, B, C, D and E (Capillary flow porometry – blue diamonds; Mercury intrusion porosimetry – red squares).

CONCLUSIONS

Two techniques, capillary flow porometry and mercury intrusion porosimetry were used to evaluate the papers used as the top layers of corrugated board. Constricted through pore diameter, flow distribution and air permeability were measured by capillary flow porometry. Through and blind pore volume; volume distribution and pore diameters were measured by mercury intrusion porosimetry.

Analysis of the obtained data using the two techniques gave more interesting information on pore diameter, permeability distribution of constricted through pores and volume distribution of through and blind pores. Through and blind pore diameters in papers were 2-3.4 times larger than constricted through pore diameters and a good correlation between them was found.

Large pore diameter of paper has crucial effect on water absorption. Relationships between water absorption and large pore diameters achieved correlation coefficients from 0.889 to 0.946. The influence of medium pore diameter on water absorption was significantly lower. Water absorption determined by $Cobb_{300}$ method was 8-10 times higher than determined in size press.

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