

Determination of surface area and pore volume of holocellulose and chemically modified wood flour using the nitrogen adsorption technique

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Abstract Very low surface area (ca. $0.5 \text{ m}^2/\text{g}$) and a low pore volume (ca. $0.002 \text{ cm}^3/\text{g}$) have been obtained for oven dried wood, using the nitrogen adsorption technique. The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was used as a final solvent. However, the resulted surface area (ca. $6 \text{ m}^2/\text{g}$) and a pore volume values (ca. $0.015 \text{ cm}^3/\text{g}$) indicated that such a structure is in no way representative of a fully swollen cell wall. By using solvent exchange drying (SED), it is possible to preserve the swollen pore structure of holocellulose samples. However, with samples which contain significant amounts of lignin, such as native wood, it is not possible to prevent re-collapse of the pores. This problem arises because as micropore swelling occurs, the surrounding lignin network of the cell wall is stretched. When the molecules occupying the micropores are removed, the lignin returns to its original configuration, re-collapsing the micropores in the process. Chemical modification resulted in significant reduction in surface area and pore volume, possibly a result of pore blocking by the large acyl group.

Bestimmen der inneren Oberfläche und des Porenvolumens von Holocellulose und chemisch modifiziertem Holzmehl mit Hilfe der Stickstoffadsorptions-Methode

Zusammenfassung Sehr geringe Oberflächenanteile (ca. $0,5 \text{ m}^2/\text{g}$) und Porenvolumina (ca. $0,002 \text{ cm}^3/\text{g}$) wurden in ofengetrocknetem Holz mit Hilfe der Stickstoffadsorptions-Methode gefunden. Die Mikroporenstruktur in Holzmehl blieb nach Trocknen durch Lösemittelaustausch (SED) teilweise erhalten, insbesondere, wenn Toluol als letztes Lösemittel verwendet wurde. Allerdings zeigen die ge-

messenen Oberflächen (ca. $6 \text{ m}^2/\text{g}$) und Volumina (ca. $0,015 \text{ cm}^3/\text{g}$), daß solche Strukturen keineswegs den Verhältnissen in der gequollenen Holzzellwand entsprechen. Bei Holocellulosen kann die Porenstruktur des gequollenen Zustands nach Lösemittelaustausch erhalten werden. In Proben, die beträchtliche Mengen an Lignin enthalten, wie ursprüngliches Holz, ist es jedoch nicht möglich, den Kollaps der Poren zu verhindern. Das Problem ergibt sich dadurch, daß aufgrund des Quellens der Mikroporen das umgebende Lignin-Netzwerk der Zellwand gestreckt wird. Wenn die Lösemittel-Moleküle in den Mikroporen durch Trocknen entfernt werden, kehrt das Lignin in die ursprüngliche Konfiguration zurück und verschließt so die Mikroporen wieder. Chemische Modifizierung hatte eine beträchtliche Verringerung der Flächen und Volumina zur Folge, womöglich durch Blockieren der Poren durch die großen Acetylgruppen.

1 Introduction

The cell wall of wood exhibits porosity of molecular scale dimensions, due to the partial filling of space between the cellulose microfibrils by lignin, hemicelluloses and extractives. These spaces are generally referred to as microvoids. Understanding the geometry of the microvoids is of great importance in order to understand processes such as a chemical pulping and bleaching, wood decay, wood-water relationships and the chemical modification of wood. A variety of physical techniques are available for determining the geometry of the micropores of the cell wall and these include, gas sorption isotherms, mercury intrusion porosimetry, solute exclusion, thermoporosimetry, nuclear magnetic resonance and microscopic techniques. These methods and the factors which must be considered when analysing results were reviewed recently (Hill and Papadopoulos 2001, Papadopoulos and Hill 2003). The purpose of this communication is to make an approach to investigate the cell wall porosity of unmodified wood, and for the first time in the literature of chemically modified wood, using the nitrogen adsorption technique.

2 Experimental

2.1 Wood modification reactions

Wood modification reactions were performed as described previously (Hill and Papadopoulos 2001). Sapwood

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samples of dimension 20 mm×20 mm×5 mm (radial × tangential × longitudinal) were cut from freshly-felled kiln dried Corsican pine and Scots pine. Samples were carefully smoothed with sandpaper to remove loosely adhering fibres, then placed in a Soxhlet extractor for solvent extraction using toluene/methanol/acetone (4:1:1 by volume) for eight hours. Samples were dried in an oven for 8 h at 105°C. Samples were removed from the oven, transferred to a vacuum desiccator and allowed to cool to ambient temperature over silica gel. Prior to reaction, each sample was weighed on a four figure balance. Samples (five replicates) were then vacuum impregnated with dry pyridine (over KOH) for one hour, then transferred to a flask containing pyridine set in an oil bath at 100°C. Samples were allowed to equilibrate in the hot pyridine for one hour. After heating for one hour, the sample batch was transferred to a round bottom flask containing a one molar solution of hexanoic anhydride in pyridine set in an oil bath at 100°C. At the end of the reaction period, the flask was removed from the oil bath, the hot reagent decanted off and ice cold acetone added to quench the reaction. Samples were kept in the acetone for 1 h, before being transferred to the Soxhlet apparatus for solvent extraction, as previously detailed. Samples were then oven dried at 105°C for 8 h and weight gain due to reaction recorded.

2.2

Preparation of wood flour

Corsican or Scots pine unmodified and modified sapwood were ground using a hammer mill and sieved to a size of 40 mesh. Before grinding, each piece of wood was dipped into liquid nitrogen for approximately 20 seconds to avoid excess heat generation.

2.3

Determination of holocellulose content

Holocellulose was determined according to the method described by Browning (1902).

2.4

Preparation of aerogels

Extractive free wood flour (or holocellulose) (Corsican or Scots pine) was left in a fume hood for several days to allow the organic vapours to evaporate off. The wood flour (or holocellulose) was then vacuum impregnated with deionised water and allowed to soak for 48 h with two water changes. Soaking time was not found to be an important parameter in surface area determination (Merchant 1957). Subsequent to this the wood flour (or holocellulose) was put into extraction thimbles, transferred to Soxhlet apparatus and solvent exchanged with wet methanol (for 1 day), absolute (dry) methanol (for 1 day) and finally with dry toluene (or pentane) (for 1 day). During the exchange with absolute methanol, linde molecular sieves (4 Å) were put in the flask in order to adsorb all water diffusing from the wood flour (or holocellulose). Apart from soaking in water and in wet methanol, all other procedures were carried out under a blanket of dry nitrogen in sealed (parafilm) vessels. Toluene (or pentane) saturated wood flour (or holocellulose) were then trans-

ferred directly to a drying apparatus set in an oil bath at 50°C, and dried for 5 h under a stream of dry nitrogen. Prepurified nitrogen was dried by passage through a tube of magnesium perchlorate during the period of drying. Samples were kept under nitrogen for 1 h to cool down, before being transferred to a glove box. Subsequent to this, approximately 0.3 g of solvent exchange dry wood flour (or holocellulose) was weighed out, under nitrogen, on a four figure balance, set inside the glove box, and transferred to the sample tube ready for the determination of surface area, in a Micromeritics Gemini 2375 surface analyser. The machine first frees the samples of moisture and atmospheric gases. Then the sample temperature is reduced to that of liquid nitrogen for the gas to be adsorbed. The adsorbing gas (N₂) is admitted in incremental doses to various pre-set partial pressures (Webb and Orr 1997). The accumulated gas quantity adsorbed *versus* gas pressure data at one temperature are then graphed to generate the adsorption isotherm. The data are then treated in accordance with gas adsorption theories (BET) to arrive at a specific surface area value for the sample in units of square metres per gram (m²/g).

3

Results and discussion

3.1

Surface area and pore volume determination of unmodified wood flour and holocellulose

The results from the determination of surface area and pore volume of oven dried and solvent exchange dried unmodified Corsican and Scots pine wood flour and holocellulose are presented in Table 1. From this, it can be seen that a very low surface area (ca. 0.5 m²/g) and a low pore volume (ca. 0.002 cm³/g) have been obtained for oven dried wood and this is in agreement with the results reported in the literature (Stone et al. 1966; Stone and Scallan 1968a). This is a result of the micropore network in the cell wall collapsing when the wood is dried. During the oven-drying of water saturated wood, powerful capillary condensation forces operate to bring

Table 1. Surface area (m²/g) and pore volume (cm³/g) of oven dried (OD) and solvent exchange dried (SED) unmodified wood flour and holocellulose

Table 1. Anteil der Oberfläche (m²/g) und des Porenvolumens (cm³/g) in ofengetrockneten (OD) und durch Lösemittel-austausch getrockneten nicht modifizierten Holzmehlen und Holocellulosen

Species	History	Final Solvent	Surface area	Pore volume
Wood flour				
Corsican pine	O.D	–	0.58	0.0024
Corsican pine	SED	Pentane	1.12	0.006
Corsican pine	SED	Toluene	6.63	0.015
Scots pine	O.D	–	0.51	0.0021
Scots pine	SED	Pentane	1.21	0.009
Scots pine	SED	Toluene	5.93	0.013
Holocellulose				
Corsican pine	SED	Pentane	77.7	0.061
Corsican pine	SED	Toluene	23.2	0.044

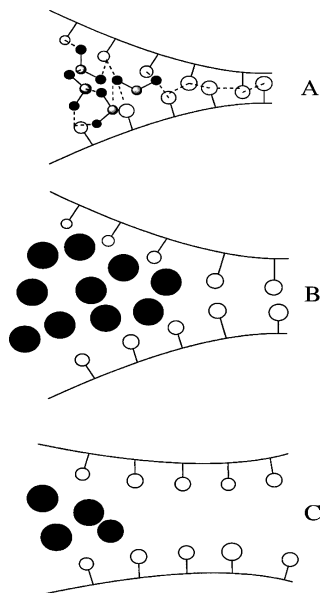


Fig. 1. Schematic illustrating various models for cell wall pore collapse due to (A) drying from a water saturated state, (B) drying of wood via solvent exchange and (C) drying of wood pulp via solvent exchange

Abb. 1. Schematische Darstellung verschiedener Modelle des Kollaps von Zellwandporen aufgrund von (A) Trocknen aus einem wassergesättigten Zustand, (B) Trocknen von Holz durch Lösemittelaustausch und (C) Trocknen von Zellstoff durch Lösemittelaustausch

the walls of the micropores together (Fig. 1A), resulting in the formation of extensive hydrogen bonding networks between the sides of the micropores. To quote Tarkow et al. (1966) a 100 Angstrom void, on losing its water, experiences a collapsing force of about 150 atmospheres.

The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was the final solvent. However, the resulted surface area (ca. $6 \text{ m}^2/\text{g}$) and pore volume values (ca. $0.015 \text{ cm}^3/\text{g}$) indicated that such a structure is in no way representative of a fully swollen cell wall and were in agreement with published results (Stone and Scallan 1965; 1968b; Stone et al. 1969, 1971). The effect of final solvent on surface area is discussed later.

During the solvent exchange process, a swelling solvent (dry methanol) is gradually replaced by a non-swelling solvent (toluene or pentane), the molecules of which occupy the cell wall microvoids, thereby preventing collapse of the structure. However, if these occluding molecules are removed, then collapse of the structure occurs, although in this case there may not be such extensive H-bonding networks formed (Fig. 1B). The collapse of the porous structures is controlled by surface tension forces at the liquid vapour interface; thus if supercritical drying is employed then such collapse is prevented (at least as far as wood holocellulose or pulp is concerned, see later). An additional factor in this latter case is the elasticity of the cell wall, which is largely controlled by the lignin. When a bleached wood pulp is solvent exchange dried from a

never dried state, surface areas in the region of $100\text{--}200 \text{ m}^2/\text{g}$ and pore volumes of $0.2\text{--}0.4 \text{ cm}^3/\text{g}$ are reported (Stone and Scallan 1965). In this study, a surface area of $77.7 \text{ m}^2/\text{g}$ was obtained for SED of holocellulose using pentane as a final solvent (see Table 1). This larger measured surface area is undoubtedly partly a result of the removal of the lignin leading to the increase in the void content of the cell wall, but there is also a contribution from the reduced elasticity of the cell wall (Stone 1964). In this latter case, collapse of the micropores is incomplete when solvent exchange drying is employed (Fig. 1C). It should be noted that the conditions under which the final solvent are removed from the substrate affect the pore structure considerably. Tarkow et al. (1966), citing Stamm and Hansen (1937), noted that shrinkage of the substrate occurs when the final replacement liquid is evaporated from the material below the critical temperature of the liquid.

Weatherwax and Caulfield (1971), found that the specific surface area of solvent exchange dried wood pulp was dependent upon the method of removal of the final solvent. Thus when hexane was removed in a stream of nitrogen, a lower specific surface ($43 \text{ m}^2/\text{g}$) was recorded compared with a method where the final solvent was carbon dioxide (WAC aerogel), which was carefully removed above the critical temperature (specific surface $144 \text{ m}^2/\text{g}$). This difference arises due to liquid/air surface tension forces acting upon the capillary walls and partially collapsing the pores, when drying is attempted below the critical temperature of the final solvent. Note however, that a very large difference is found in the surface area between solvent exchange dried wood and wood pulp, indicating the importance of lignin in both occluding and collapsing the pores.

3.2

The effect of final solvent on surface area

The effect of final solvent on surface area is presented in Table 1. From this, it can be seen that with holocellulose samples, a larger surface area was obtained using pentane as a final solvent. However, the opposite was true with wood flour, where larger surface area was obtained using toluene as a final solvent. Merchant (1957), reported increased surface area values of water-swollen and SED cellulose fibres with increased molecular size of the final solvent, and concluded that this behaviour was the result of differences in properties of the different solvents; however, further details were not given. Such properties may include polarity, surface tension and viscosity of the final solvent.

The same behaviour was observed in this study on SED wood flour samples. However, the opposite was true on holocellulose samples. This behaviour may be due to other than molecular size and shape factors, since the opposite would have been observed if molecular size and shape had an effect on surface area. In that case, the presence of lignin would have prevented the larger and more rigid molecule of toluene to gradually replace the non-swelling agent (methanol) during the solvent exchange process, and as a result lower surface area would have been obtained.

Table 2. Surface area (m^2/g) and pore volume (cm^3/g) of solvent exchange dried (SED) modified and unmodified samples using toluene as a final solvent

Tabelle 2. Anteil der Oberfläche (m^2/g) und des Porenvolumens (cm^3/g) von durch Lösemittelaustausch getrockneten modifizierten nicht modifizierten Proben mit Toluol als letztem Lösemittel

Species	Surface area	Pore volume
Corsican Unmodified	6.63	0.018
Corsican modified with hexanoic anhydride (29.6 WPG)	1.65	0.015
Scots Unmodified	5.93	0.013
Scots modified with hexanoic anhydride (32 WPG)	1.78	0.01

3.3

Surface area and pore volume of modified wood

Although the SED process did not fully preserve the swollen pore structure of the wood cell wall, as discussed above, it was still thought that comparison between the surface area and pore volume of unmodified and modified wood flour samples would be of interest. For this reason, Corsican and Scots pine sapwood, heavily modified with hexanoic anhydride, was selected and solvent exchange dried with toluene as a final solvent. The choice of heavily modified wood with hexanoic anhydride was based in the observation made by Hill and Jones (1999) and by Papadopoulos (2001), that the apparent void volumes created within the cell wall increase as the molecular size of the substituent increases.

The results from the determination of surface area and pore volume of modified Corsican and Scots pine wood with hexanoic anhydride are presented in Table 2, along with the results of unmodified wood. It can be seen that chemical modification resulted in significant reduction in surface area and pore volume. This may be a result of blocking pores due to chemical modification. It may be that such void volume that is created is inaccessible to the gas (ink-bottle bottles) (Walker 1993).

Overall it appears, that in order to fully preserve the swollen pore structure of the wood cell wall, it is imperative to partially degrade the lignin to various extents without extraction of the lignin fragments. By breaking up the cross-linking network of the lignin macromolecule, it may be that this will limit the ability of this molecule to shut the cell wall pores after drying. Several approaches are possible including exposure to UV radiation and exposure to white rot fungi attack.

4

Conclusions

Very low surface area (ca. $0.5 \text{ m}^2/\text{g}$) and a low pore volume (ca. $0.002 \text{ cm}^3/\text{g}$) have been obtained for oven dried wood, using the nitrogen adsorption technique. The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was used as a final solvent. However, the resulted surface area (ca. $6 \text{ m}^2/\text{g}$) and a pore

volume values (ca. $0.015 \text{ cm}^3/\text{g}$) indicated that such a structure is in no way representative of a fully swollen cell wall. By using solvent exchange drying (SED), it is possible to preserve the swollen pore structure of holocellulose samples. However, with samples which contain significant amounts of lignin, such as native wood, it is not possible to prevent re-collapse of the pores. This problem arises because as micropore swelling occurs, the surrounding lignin network of the cell wall is stretched. When the molecules occupying the micropores are removed, the lignin returns to its original configuration, re-collapsing the micropores in the process. Chemical modification resulted in significant reduction in surface area and pore volume, possibly a result of pore blocking by the large acyl group.

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