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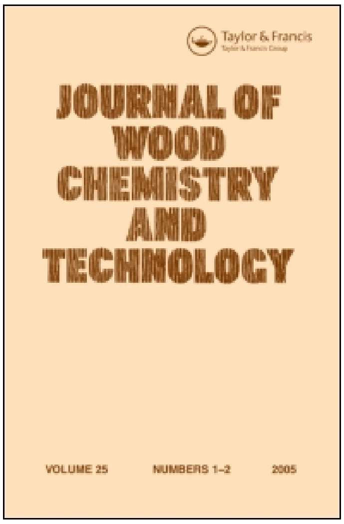

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Elsa M. L. Ehrnrooth[a]
[a] Paper Technology Department, Swedish Forest Products Research Laboratory, STOCKHOLM, Sweden

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CHANGE IN PULP FIBRE DENSITY WITH ACID-CHLORITE DELIGNIFICATION

Elsa M. L. Ehrnrooth
Swedish Forest Products Research Laboratory
Paper Technology Department
Box 5604, S-114 86, STOCKHOLM, Sweden

ABSTRACT

The densities of acid-chlorite delignified Asplund spruce fibres with degrees of delignification between 0 and 62.4 % were determined. The density measurements were carried out at 23°C in mixtures of carbon tetrachloride and toluene, using a density gradient column. The density of the dry fibres increased linearly with decreasing lignin content and the density of lignin and holocellulose in situ were found to be 1397 and 1541 kg/m^3 respectively. Assuming a density of 1559 kg/m^3 for α-cellulose, the density of hemicellulose in situ was calculated to be 1520 kg/m^3. The physical implications of the measured values are discussed. It is concluded that there is no change in the density of holocellulose or lignin between 20 and 62.4 % delignification. It is suggested that the densification of the fibre during the initial stage of delignification is due to increased order in the hemicelluloses.

INTRODUCTION

The density or its reciprocal, the specific volume, is one of the most important polymer properties from both a practical and theoretical point of view. The density can be used for the characterization of polymers. Within a given family of polymers for instance, the density is closely related to the degree of crystallinity[1], and in composite polymers and copolymers the

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density is directly related to the weight fraction of homopolymers. Density determinations are commonplace in the characterization of man-made polymers and regenerated cellulose, but they have been applied less in the study of the structure and composition of native cellulose and wood fibres. A likely reason for this is that the intricate porous structure of native fibres also complicates the evaluation of the results obtained.

The present study describes the measurement of the density of Asplund-type spruce fibres of different final lignin contents. Special emphasis has been placed on the drying of the fibres prior to the measurements. The dryness of the fibres, the accessibility of the fibre to the solvents and the interaction between the solvents and the wood polymers are discussed. From the relationship between the chemically determined lignin content and the measured specific volume, numerical values for the density of lignin and holocellulose are deduced. Finally the influence of delignification on the physical state of the wood polymers is discussed.

BACKGROUND

Early investigations of the density of cellulose and wood fibres have been reviewed by Hermans[2] and Stamm[3]. The densities of wood and cellulose fibres have been determined using water and non-swelling liquids as displacement media. Measurements of the density of cellulose in water and at different moisture contents have given information about the interaction between cellulose and water and the crystallinity of native and regenerated cellulose[4]. Dry-volume densities are determined in non-swelling liquids[2]. When the dry-volume density of a cellulose fibre is determined, there are three general conditions which should be met: the specimen should be absolutely free from water, the dry solid substance should not interact with the liquid medium into which it is immersed during measurement and the specimen should be completely accessible to the liquid medium. The last condition means that the liquid should be able to fill all the void volume of the specimen which is not occupied by the solid substance.

All fibre walls contain pores, the size and distribution of which vary depending on the history of the fibres. If densities are to be measured by the method of solvent displacement a distinction must be made between macropores and micropores. According to Hermans[2], whose concepts have been adopted in this work, micropores are inherent elements of the solid homogeneous fibre composite material, while pits, capillaries, cracks, voids, defects etc. constitute the macropores.

The fibres are considered to be completely accessible to a liquid medium if the liquid fills the macroporous space of the fibre. The solvents are considered not to interact with the solid homogeneous substance if they do not penetrate the micropores. Native fibres have a broad distribution of pore sizes and shapes. Thus the distinction between micropores and macropores is arbitrary and may be considered as a means of describing the ability of the solvent to swell the solid substance. For solvents which do not swell the solid substance the contribution of the micropores to the total volume occupied by the solvent is very small. The contribution of the micropores should be eliminated by choosing a liquid with no ability to swell the cell wall substances. It also follows, that it is only relevant to talk about the density determined in a given solvent.

The densities of wood fibres have been determined using different methods and different non-swelling liquids. Earlier work was carried out using pycnometric[5-7] and suspension[7-10] methods. In more recent work, density gradient columns have been used[11-14]. Toluene[5-7] and mixtures of carbon tetrachloride and toluene[7,9,10,12], chloroform[13,14], xylene[11] or benzene[8], have been used as displacement media.

Density measurements have provided a valuable tool in the study of the structural features of wood fibres. Howsmon and

Marchessault[15] showed a linear relationship between the density and the equilibrium moisture content of ball milled cellulose pulps and established a numerical value for the specific volume of amorphous cellulose. Orr and coworkers[11] found that the degree of substitution of a chemically modified cotton was linearly related to the density. Studies relating the beating rate of pulp[12] and the mechanical properties of wood[5,6] to the measured dry density have also been reported. The density and its inverse, the specific volume, are generally additive physical characteristics[16]. Therefore the specific volume, v_f, of the wood fibre can be calculated from the specific volumes and weight fractions of its constituent polymers, using the general formula:

$$v_f = \Sigma w_i \cdot v_i \qquad (1)$$

where w_i and v_i are the weight fractions and the specific volumes of the wood polymers.

The additivity of the specific volumes of cell wall components has been utilized and confirmed in many studies. Beall[8] measured the density of isolated hemicelluloses of hardwoods and softwoods and found that the density of wood calculated from the relative amounts and densities of the isolated wood constituents agreed with the experimental values. Stamm and Sanders[3,9] showed that the specific volume of wood is equal to the sum of the weight fraction contributions of the specific volumes of holocellulose and lignin. Stamm[10] also studied the relationship between structural variations of lignin and their specific gravities by calculations based on the additivity of molar volumes. Kellogg and coworkers[17] evaluated the accuracy of determining the cell wall density of hardwoods and softwoods using the densities of the isolated wood polymers. The correlation between the measured and calculated values was so poor that Kellogg concluded that the densities of some of the wood polymers must be different in situ than in the isolated state. Paulson[13] demonstrated that the lignin content distribution in pulp fibres can be calculated from measured densities, utilizing theoretical values for the density of lignin and holocellulose. Tichy and Procter[14] investigated the lignin content distribution of several pulps. The relationship between the average lignin content and the average fibre density confirmed the additivity of the specific volumes. From the measured fibre densities numerical values for lignin and holocellulose were derived.

RESULTS AND DISCUSSION

Cell Wall Density

To measure the density using mixtures of carbon tetrachloride and toluene as a displacement medium the fibres should be absolutely dry and the cellulose and lignin should not interact with, but be as completely accessible as possible to, toluene and carbon tetrachloride.

The interaction between cellulose and carbon tetrachloride has been studied by Lauer and Davidson. Lauer[18] showed that carbon tetrachloride and toluene are absorbed by native cellulose fibres but have no influence on the fibre volume. Davidson[19] showed that measurements of the density of cotton in benzene, toluene, chloroform, carbon tetrachloride, and nitrobenzene, after preparation of samples at room temperature, yielded practically the same value.

Schuerch[20] showed that native and low molecular weight lignins were insoluble in carbon tetrachloride. Theoretically the interaction between polymers and solvents can be estimated in terms of the Hildebrand parameter[21] or by comparing dielectric constants according to Ekman and Lindberg[22]. The ability of solvents to swell or dissolve lignin increases as their Hildebrand parameter approaches a value of 11. The Hildebrand parameter for carbon tetrachloride is 8.6[20]. Solvent mixtures with dielectric constants between 12.5 and 17.5 are good solvents for lignin[22]. The dielectric constants of carbon tetrachloride and toluene are 2.2 and 2.4 respectively[23]. It thus seems justifiable to state that the lignin and holocellulose do not interact with toluene or carbon tetrachloride.

The results of the density measurements on wood fibres having degrees of delignification from 0 to 62.4 %, dried according to three different methods, are shown in Table 1.

The solvent-exchange-dried and super-dried fibres have the same densities at corresponding degrees of delignification. The densities of vacuum-dried fibres are about 10 to 20 kg/m^3 lower than those of the solvent-dried fibres, over the whole range of delignification. During the initial delignification step between 0 and 20 % delignification, the density of both vacuum-dried and solvent-dried fibres increases roughly as much as during the further delignification between 20 and 60 %.

Both the vacuum-dried and the super-dried fibres have been air dried initially after the delignification (Fig. 3). As there can be no fundamental structural difference between two identical air-dried samples, the difference in density of the vacuum-dried and super-dried samples must reflect non-structural differences between the fibres. It can generally be anticipated that the higher the measured density values are, the closer they are to the real density of the fibre. We therefore assume that the density of the super-dried fibre represents the density of the solid substance and that the low density of the vacuum-dried fibre is caused by the presence of water or air. If we assume that the low density of the vacuum-dried fibre is caused by water only, the water content corresponding to the density decrease can be calculated from the data in Table 1. If it is assumed that the super-dried fibres are completely dry, that the specific volumes

TABLE 1

Mean Densities of Wood Pulp Fibres in Carbon Tetrachloride-Toluene at 23°C.

Degree of Delignification	Total Lignin Content	Density		
		vacuum-dried	solvent-exchange-dried	super-dried
%	%	kg/m^3	kg/m^3	kg/m^3
0	26.3	1462.9	1485.0	-
0.4	26.2	1468.8	1488.7[1]	-
4.6	25.1	1477.8	1496.0[1]	-
4.9	25.0	1477.7	1490.1	-
6.1	24.7	1475.4[1]	1496.5	-
8.4	24.1	1482.7	1499.1[1]	1499.8
11.4	23.3	1481.2	1502.2[1]	-
14.4	22.5	1491.6[1]	1504.7[1]	-
20.9	20.8	1500.4	1515.8[1]	-
22.1	20.5	1495.7	-	-
25.5	19.6	-	1508.4	-
25.9	19.5	-	1507.2	-
27.0	19.2	1498.4	-	1515.3
35.7	16.9	1494.5	1516.2	1513.6
42.2	15.2	-	1512.1	-
46.8	14.0	1504.2	1521.9	-
51.0	12.9	-	1522.6	1518.6
52.1	12.6	-	1522.6	-
56.7	11.4	-	1529.0	1521.6
62.4	9.9	1509.4	1530.2	-

[1] Value from single experiment.

of fibre and water are additive, and that the specific volume of the bound water[4] is $0.865 \cdot 10^{-3}$ m^3/kg, the mean water content of the vacuum dried fibres would be about 4 %. This value is high and it is therefore believed that the reason for the low density values is partly the presence of entrapped air.

The solvent-exchange-dried and super-dried fibres have the same delignification history but their drying background is different. The solvent-exchange-dried fibres originate from never-dried fibres in which the voids created by delignification are still open. The super-dried fibres on the other hand originate from air-dried fibres, in which some of the macropores have closed during drying. Westman and Lindström[4] found that the crystallinity of cellulose hydrogels is independent of the water content. It is here assumed that the holocellulose crystallinity of air-dried and solvent-exchange-dried fibres is the same at a given lignin content. Thus the solvent-exchange-dried and the super-dried fibres should differ only in macroporosity. The densities of super-dried and solvent-exchange-dried fibres are, however, the same at a given lignin content. Thus, the measured density must be independent of the macroporosity of the fibres. Consequently, the super-dried and solvent-exchange-dried fibres are totally accessible to the displacement liquids. This suggests that these density measurements on super-dried and solvent-exchange-dried fibres meet the criteria for the determination of density.

Density of Wood Polymers

The specific volumes of the delignified fibres have been calculated from the densities of solvent-dried fibres between 0 and 62.4 % delignification. The results are shown in Table 2. From a chemical point of view the delignified fibres can be classified into two categories[24]. Between 0 and 20 % delignification there is an increasing chemical modification of the lignin. Between 20 and 62.4 % delignification the fibres differ only in relative contents of protolignin and holocellulose. The different behaviour above and below 20 % delignification can also be seen in Fig. 1. Two different regression lines for the specific volume have been computed, based on the data in Table 2. The results are shown in Fig. 2, where the two straight lines represent the specific volume versus lignin content for solvent-dried fibres above and below 20 % delignification. Above 20 % delignification, the specific volume of the fibre, v_f, is a function of the weight fraction of lignin, w_ℓ given by the best fit to the data

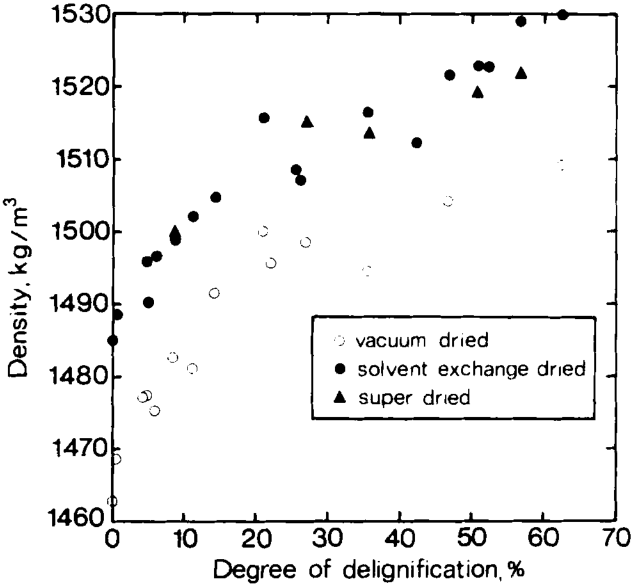

FIGURE 1 Density in carbon tetrachloride-toluene at 23°C of spruce pulp fibres of different final lignin contents. The samples have been dried using the three different drying strategies.

$$v_f = (0.067\ w_\ell + 0.649) \cdot 10^{-3}\ m^3/kg \qquad (2)$$

If it is assumed that the densities of lignin and hemicellulose are constant above 20 % delignification, the specific volumes of holocellulose and lignin in situ can be evaluated from Eqs. (1) and (2). The specific volume of holocellulose ($w_\ell = 0$) is $0.649 \cdot 10^{-3}$ m^3/kg and the specific volume of lignin ($w_\ell = 1$) is $0.716 \cdot 10^{-3}$ m^3/kg. The corresponding densities for holocellulose and lignin are 1541 and 1397 kg/m^3, respectively.

Influence of Acid Chlorite Delignification on the Physical State of the Wood Polymers

The density values for lignin and holocellulose calculated in

TABLE 2

Specific Volume of Wood Fibres in Carbon Tetrachloride-Toluene at 23°C (cf. Table 1).

Degree of Delignification %	Weight Fraction of Lignin	Specific Volume $(m^3/kg)\cdot 10^3$
0	0.263	0.673
0.4	0.262	0.671
4.6	0.251	0.668
4.9	0.250	0.671
6.1	0.247	0.668
8.4	0.241	0.667
11.4	0.233	0.666
14.4	0.225	0.665
20.9	0.208	0.660
25.5	0.196	0.663
25.9	0.195	0.663
27.0	0.192	0.660
35.7	0.169	0.660
35.7	0.169	0.661
42.2	0.152	0.661
46.8	0.140	0.657
51.0	0.129	0.658
52.1	0.126	0.657
56.7	0.114	0.656
62.4	0.099	0.654

the present study using Eq. (2) are compared with literature data in Table 3.

The good agreement between the lignin density in this study and literature data justifies the assumption that the densities of lignin and holocellulose are constant and additive between 20 and 60 % delignification. The changes in the fibre density as a function of delignification thus seem to be fully accounted for by the loss of lignin, and it is concluded that there is no change in the density of the holocellulose or the lignin due to the acid chlorite treatment between 20 and 62.4 % delignification.

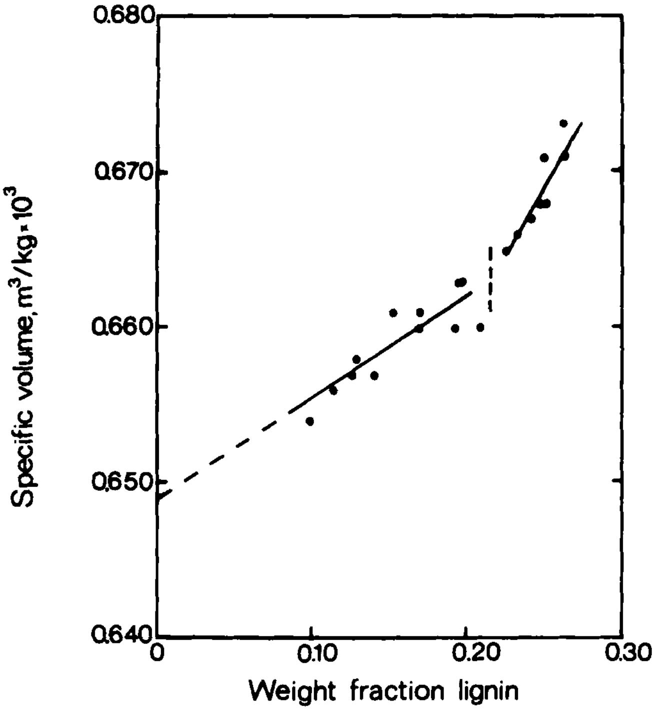

FIGURE 2 Specific volume in carbon tetrachloride-toluene at 23°C of spruce pulp fibres of different final weight fractions of lignin.

TABLE 3

Density of Lignin and Holocellulose.

Origin	Lignin Density kg/m^3	Holocellulose Density kg/m^3	Reference
Spruce, TMP-holocell.	1397	1541	present study
Douglas fir, Hemlock, Cedar-kraft pulp	1375	1549	Tichy, Procter[14]
Bulk lignin	$1.4 \cdot 10^3$	-	Goring[25], Mark[26]
Isolated spruce lignin	1335-1376		Stamm[9,10,27]

The slopes of the linear regression lines in Fig. 2 indicate that the increase in fibre density in the initial stage of delignification cannot be accounted for solely by the loss of lignin. This implies that in the beginning of the oxidative delignification some densification of the fibre substance takes place. α-cellulose is known to be resistant to oxidative attacks. The physical changes which cause the increase in fibre density during the initial delignification thus most likely involve the lignin or hemicellulose components. Rapid initial changes in both lignin and hemicellulose have been suggested in the literature. Wood and coworkers[28] studied changes in the UV-absorptivity of lignin in wood and found a distinct initial decrease in the absorbance, which they ascribed to some rapid initial oxidation reaction involving the lignin. Timell[29] found a rapid initial depolymerization of hemicelluloses and Ahlgren[30] discusses the possibility of removal of the arabinose substituent of xylan and the subsequent crystallization of the hemicellulose in the early stages of acid chlorite delignification. Neither xylans nor galactoglucomannans will crystallize without prior removal of a portion of their side chains or some reduction of their chain length and they are believed to be present in the amorphous state in the living tree[31].

Stamm[10] has reported that the density of oxidized and hydrolysed lignin increased by only 3 % after 55 % acid chlorite delignification of spruce pulp[32]. The almost identical density values obtained for lignin in acid chlorite delignified fibres and in kraft pulps (Table 3) also suggest that the density of lignin is not readily affected by oxidative attack. It therefore seems unlikely that the oxidation of lignin could be responsible for the increase in fibre density between 0 and 20 % delignification in the present study. The initial increase in fibre density is consequently most likely due to the densification of the hemicellulose in situ. It was earlier shown[24] that the weight ratios of α-cellulose and hemicellulose in the holocellulose of delignified fibres are 0.6 and 0.4 respectively. Assuming additivity of the specific volumes of α-cellulose and hemicellulose and choosing the value $0.643 \cdot 10^{-3}$ m^3/kg measured for the specific volume of α-cellulose in carbon tetrachloride-toluene[7], the specific volume of hemicellulose can be calculated. Between 20 and 62.4 % delignification the specific volume of hemicellulose is $0.658 \cdot 10^{-3}$ m^3/kg, which corresponds to a density of 1520 kg/m^3. This value is of the same magnitude as the value $1.49 \cdot 10^3$ kg/m^3 chosen by Frey-Wyssling[33] for the mean density of native hemicelluloses, but lower than the densities of $1.6\text{-}1.8 \cdot 10^3$ kg/m^3 determined by Beall[8] for isolated softwood hemicelluloses. This confirms that hemicellulose in situ is much less ordered than the isolated hemicelluloses.

EXPERIMENTAL

Materials

The wood pulp fibres were a thermomechanical spruce pulp which had been treated with acid chlorite solutions at 65°C to different degrees of delignification[24]. Lignin content values are the sum of gravimetrically determined Klason lignin and spectroscopically determined acid-soluble lignin in Klason hydrolysates.

The solvents used in the solvent exchange drying and in the density measurement columns were analytical grade isopropanol, toluene and carbon tetrachloride which were stored over sodium sulphate or calcium sulphate and filtered through filter paper prior to use. The 3Å and 4Å molecular sieves used in drying and purifying ethanol and carbon tetrachloride were manufactured by Union Carbide.

Drying of Fibre Samples

The wood fibre samples were prepared for density measurements in carbon tetrachloride using three different drying strategies. In the first case the fibres were air dried from water and the air dried fibres were evacuated in the presence of dry carbon tetrachloride. In the second case the air dried samples were soaked in absolutely dry ethanol and then in carbon tetrachloride, which were continuously circulated over 3Å and 4Å molecular sieves respectively. In the first sequence the 3Å molecular sieves were used to absorb the water from the ethanol, and in the second sequence the 4Å sieves were used to absorb the ethanol and water from the carbon tetrachloride. In the third case the neutral suspension of delignified fibres was solvent exchanged with isopropanol and carbon tetrachloride. The samples prepared according to the three different drying procedures are called "vacuum-dried", "super-dried" and "solvent-exchange-dried" fibres respectively. The latter two are jointly described as "solvent-dried" fibres. The methods are explained in detail below and are summarized in Fig. 3.

<u>The vacuum-dried fibres</u> were prepared in the following manner. 100 mg of air-dried fibres were immersed in a 100 ml two-necked groundjoint flask. Through one neck the flask was connected via a vacuum stopcock and two flasks containing phosphor pentoxide to a rotary vacuum pump. Through the other neck the flask was connected to a 100 ml ground-joint flask containing 50 ml dry carbon tetrachloride. The system was closed using the stopcock, and the flask containing the carbon tetrachloride was immersed in an ethanol-carbon dioxide slush bath at a temperature of -78°C. When the carbon tetrachloride was frozen the stopcock was opened and the system evacuated. After evacuation for 15 minutes at a pressure of $6 \cdot 10^{-2}$ torr the stopcock was closed and the carbon tetrachloride was allowed to melt. The degassed carbon tetrachloride was again frozen and the system evacuated for 1 to 2 hours. The system was again closed and the flask containing the fibres was immersed in a water-ice-salt slush bath. When the

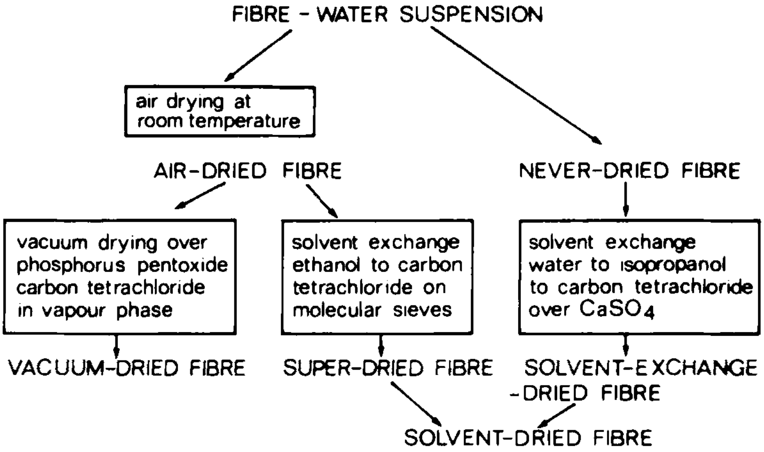

FIGURE 3 Drying methods for delignified fibres.

flask containing the carbon tetrachloride was warmed in water the carbon tetrachloride was distilled over to the fibre-containing flask. The system was finally flushed with nitrogen and the flask containing the fibre carbon tetrachloride suspension was detached and stoppered.

The super-dried fibres were prepared using the super dryer type apparatus described by Weatherwax[34]. 100 mg of an air-dried sample were placed in a small basket made of thin copper mesh which was introduced in a sample-holding bulb. 50 ml of 99.5 % ethanol were added and the sample-holding bulb was closed. Two coolers and a drying bulb were fitted to a three-necked flask and nitrogen was flushed through the system, entering at the top of a vertical cooler and escaping at the top of the dryer bulb. About 70 ml of 3Å molecular sieves were poured into the dryer bulb and 200 ml of 99.5 % ethanol were poured into the three-necked flask. The nitrogen stream was discontinued, 99.5 % ethanol was added to cover the molecular sieves and the system was closed using glass stoppers. The sample bulb and its cooler were attached to the system which was closed by two ball joints connecting the two vertical coolers. The three-necked flask was heated and the vertical cooler was circulated with water at a temperature of 85°C. The system reached an equilibrium with a solvent circulation rate of 4 ml per minute. The solvent was circulated for 16 hours. After the first drying sequence the system was allowed to cool. The dryer bulb was removed and interchanged with a bulb containing 4Å molecular sieves in carbon tetrachloride. The sample basket was removed using fibre tweezers and stored in a stoppered glass containing dry carbon tetrachloride while the apparatus was emptied and recharged with carbon tetrachloride. The same procedure was repeated with the new solvent. When the carbon tetrachloride had circulated for 16 hours the system was allowed to cool and the sample was immersed in super dry carbon tetrachloride and stored in a stoppered glass in a desiccator over phosphor pentoxide.

The solvent-exchange-dried fibres were prepared in the following manner. A sample of 20 ml of the neutral water suspension of delignified fibres containing about 80 mg of fibres was poured onto a sintered glass filter and the excess water was allowed to drain. The wet fibre mat was washed on the filter with three successive portions of dry isopropanol with spontaneous draining after each washing. The glass sinter with the soaked fibre was immersed in a 150 ml weighing glass containing 30 ml of dry isopropanol. Water suction was applied to the sinter whereupon the dry isopropanol rose through the filter and soaked the fibre mat. Finally, enough dry isopropanol was added to the drying glass to give the same liquid level inside and outside the glass sinter and some drying salt was added to the isopropanol outside the sinter. The weighing glass was closed with a lid and was stored in a desiccator over phosphor pentoxide for one week. The solvent exchange from isopropanol to carbon tetrachloride was performed in an identical manner yielding carbon tetrachloride suspensions of solvent-dried fibre, which were stored in stoppered glasses in a desiccator over phosphor pentoxide.

Density Measurements

The densities of the fibre samples were measured at 23°C in mixtures of carbon tetrachloride and toluene using a density measurement apparatus (Davenport Ltd., Welwyn Garden City, Herts., U.K.). The apparatus employs the density gradient column method of determinating densities as specified in the standard methods of BS 3715 and ASTM D. 1505.

The columns were charged with different ratios of toluene and carbon tetrachloride to give density ranges of 40 kg/m^3 each, between 1430 and 1560 kg/m^3. The density gradients of the columns were determined using calibrated reference floats (five significant digits; Davenport Ltd.). Calibration curves were made by plotting the observed positions of the floats against their known densities. The accuracy of the method is 0.1 kg/m^3.

The standard routine for measuring the density of a fibre sample was as follows. Two to 10 mg of water-free fibres in dry carbon tetrachloride were gently squeezed in the liquid using two tweezers to form a small tight fibre bundle. The fibre bundle was lifted from the carbon tetrachloride and immediately immersed in the column and released just under the liquid surface. The position of the fibre sample in the column was observed at frequent intervals. Equilibrium was normally reached after 20 hours. The density values reported in this study correspond to the position of the sample after 48 hours in the column. The densities of the samples were obtained to the nearest 0.1 kg/m^3 by graphical interpolation from calibration curves. When two or more samples of the same fibre were measured the mean value is reported.

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