

Swelling of compressed cellulose fiber webs in organic liquids

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Maximum liquid-holding capacities of various compressed fibers in water and in a series of various organic liquids have been investigated. The maximum liquid-holding capacity versus bulk density relationships gave polynomial curves, generally with a peak. Good relative correlations for cellulose, compressed fiber pellets and wood were found for the series of liquids tested. In general, liquids that swelled wood to a low to medium range (up to 6%) did not swell appreciably a -cellulose and sulfite pulp, while good to excellent wood-swelling agents swelled all the fibers very significantly. It was also found that the hydrogen-bonding parameter of the swelling liquid was the most important factor. The swelling rate of various compressed fiber systems in organic liquids was dramatically increased by raising the temperature. Activation energies and molar volume of the swelling liquid were linearly correlated.

KEYWORDS: Swelling of compressed fibers; swelling of wood; molar volume; cohesive energy density; hydrogen bonding parameter

INTRODUCTION

Approximately 40–45% of the dry substance in wood is cellulose; the cellulose is located predominantly in the secondary cell wall. Bundles of cellulose molecules are aggregated together in the form of microfibrils in which highly ordered (crystalline) regions exist with less ordered (amorphous) regions. The proportions of crystalline and amorphous regions in cellulose vary depending upon the type of the sample and the method of measurement. Cotton cellulose is usually more crystalline than wood cellulose. Young (1986).

Cellulose is insoluble in most solvents because of its crystalline nature; however, both intracrystalline and intercrystalline swelling is possible in certain solvents. Neale (1929), in his early work on cotton swelling in liquids, concluded that the action of a mild swelling agent is confined entirely to the amorphous portion of the fiber. As the fiber swells, intermolecular bonds are broken as a result of the internal stresses produced by swelling. The degree of order within the fiber is reduced and there is an increase in the surface area of the fiber. Also, with very strong cellulose-swelling agents, it is possible to reach a critical point where the entire crystalline structure of the fiber is disrupted and the fiber structure is lost. In this investigation an analysis is made of cellulose swelling in liquids which generally do not affect the crystalline structure of cellulose.

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Cellulose swelling in water and organic liquids

Only limited data are available for the cross-sectional swelling of cellulose fibers because of the time consumed in making a single accurate measurement and the need to measure a large number of fibers to obtain a reasonable average. Reported values for the percentage swelling, corrected for lumen area, ranged from 31–33% for cotton of different varieties and maturity, and 65% for viscose rayon fibers (Moore *et al.*, 1950; Welo *et al.*, 1952; Stamm, 1964). These results are much lower than those for swelling of cellophane, which swelled 137% in volume in water. Essentially all of the water that enters the voids in the cellophane results in swelling in this case (Stamm, 1956; Stamm, 1964).

Another method for determining the swelling of cellulose fibers is the measurement of centrifugal water retention value (Hopner *et al.*, 1955). This empirical method is frequently used because of simplicity, but it gives values which are very low for highly swollen pulps (Scallan and Carles, 1972). The solute exclusion technique, introduced by Aggebrandt and Samuelsson (1964), has been the most widely utilized method in recent years. Stone *et al.* (Stone and Scallan, 1967; Stone *et al.*, 1969; Scallan, 1977) applied the technique to determine the fiber saturation point of wood pulps using sugars and dextrans as the porous probe molecules. By measuring concentration changes for a series of solutions comprised of molecules of different sizes, they were able to determine the amount of accessible and inaccessible water. They found a wide range of swelling for both rayon and cellophane samples with textile rayon swelling to a greater extent than tire cord rayon, but both much less than cellophane (Stone *et al.*, 1969). Sulfite wood pulps were found to swell to a greater extent than kraft pulps. However, it is important to note that the large increases in the amount of water within the cell wall that accompanies pulping is not necessarily followed by a concomitant increase in swelling (Scallan, 1977).

Robertson (1964) carried out an investigation on cellulose-liquid interactions and based his swelling interpretations on accessibility measurements of the cellulose using a technique of solvent exchange with thallos ethylate in benzene. He evaluated the effects of molar volume, solubility parameter and liquid dipole interactions on swelling of cellulose fibers. He concluded that molar volume is important to swelling. None of the experimental liquids have a molar volume greater than 100 cc increased the swelling of cellulose to any appreciable extent, even though some of the liquids are capable of strong hydrogen bonding. Liquids which are strongly associated according to the Bottcher (1952) or Pauling (1950) criterion (dipole interactions) do not increase the swelling of cellulose fibers appreciably if they are not capable of participating in hydrogen bonding. Robertson found that hydrogen bonding liquids which are not associated (proton acceptors which do not have proton donor properties) form a second series of correlations in which the fiber swelling is correlated with cohesive energy density (solubility parameter). The remaining non-associated, non-hydrogen bonding liquids did not swell cellulose appreciably. Robertson noted with fibers, as did Nayer and Hossfeld (1949) with wood, that some binary mixtures of liquids can produce more swelling than either component alone. This synergistic effect is particularly notable when water is one of the liquids. In another publication, Robertson (1970) suggested that the factors that determine the effectiveness of the swelling liquid in cellulose include the hydrogen bonding properties and the existence of intermolecular forces that are summed up in the cohesive energy density. In addition, other factors such as

molecular volume and steric effects are also of importance. The interaction with cellulose fibers depends additionally on the structure and porosity of the fiber.

Chitumbo *et al.* (1974), in their experiments on the temperature dependence of swelling of homogeneous cellulosic gels, found that temperature had a significant influence on the swelling of cellulose gels. They used a thermostated cylindrical cell and followed progress by measuring the column height with a cathetometer. Particularly notable was the dramatic effect of temperature on the swelling of cellulose gels in dimethylsulfoxide (DMSO).

Thode and Guide (1959), by application of the Hildebrand volubility parameter, presented a hypothesis to explain the swelling behaviour of cellulose in organic liquids. They concluded that the apparent total surface (mostly internal) was a function of the swelling produced by the solvent. It was also noted that the greater the cohesive energy density of the liquid, the greater the ability of the retreating solvent layer to pull elements of the polymer structure together. They also found that a linear relationship existed between the volume increase swelling of cellulose fibers in various polar liquids and the solvent solubility parameter (δ). Amines characteristically did not follow this correlation. It is well known that these particular liquids can penetrate even the highly ordered crystalline regions of a cellulosic fiber (Stamm and Tarkow, 1950; Thode and Guide, 1959).

Philipp *et al.* (1973), in their work on the swelling of cellulose in organic liquids, found that no correlations whatsoever existed between maximum liquid retention value (LRV) and individual solvent properties such as dielectric constant, dipole moment, and cohesive energy density. However, three other parameters were found to be of importance to cellulose swelling in organic liquids: (a) the hydrogen bonding fraction δ_H and the polar fraction δ_P of the CED, (b) the solvent molar volume, and (c) the cellulose structure, especially the width and distribution of voids, and the lateral-order spectrum. It was also observed that a high δ_H and δ_P synergistically increased swelling. A high molar volume was not detrimental to swelling if connected with a high δ_H , and if a large enough void structure permitted the penetration of the liquid into the fibrous sample. The final LRV was found to be dependent mainly upon the interrelation between molar volume and the swelling agent and the void structure of the fiber sample.

Steiger and Kapur (1972), in their work on the liquid absorption by compressed cotton fibers, found that the weight capacity of various compressed fiber systems was a linear decreasing function of increasing bulk density. On the other hand, the volume capacity versus bulk density relationships were curves with a peak; each environmental pressure produced an optimum volume capacity in the region of a bulk density of about 0.8 g cm^{-3} . It was also observed that below a bulk density of about 0.2 g cm^{-3} , contact with liquid caused a reduction in the total volume of the absorbent (i.e. cotton, rayon).

Kress and Bialkowsky (1931) measured rates and maximum swelling values of cellulose fibers in various pure organic liquids at room temperature using a mercury dilatometer (expansion of mercury). The swelling was given as the volume percentage increase of the compressed pulp fibers (density $\sim 1.00 \text{ g cc}^{-1}$). The rate of swelling was generally very rapid and the maximum swelling was attained in a few hours. The swelling power of water was quite high (90%), while the swelling power of fuel oil was extremely low (2%). Formamide had an extremely high swelling power (125%). The swelling power of ethylene glycol (89%) was practically the same as that of water. The

swelling power of the alcohols (methyl, ethyl, propyl, butyl, amyl) decreased as the length of the hydrocarbon chain increased. The increase in pulp volume with methanol was 62%, with ethanol was 40%, and with the higher alcohols was extremely low (4-6%). The pulp swelling in furfural was also very low (8%). Using a similar but modified dilatometer, McKenzie (1956) also measured the swelling capacity of cellulose pulps in various liquids. He concluded that liquids which produce a significant amount of swelling are those which are capable of forming hydrogen-bonded complexes with the cellulose molecule.

Stamm and Tarkow (1950) found that fibers of cellulose and lignocellulosic materials such as wood can be directly penetrated only by polar liquids. The extent to which a liquid will penetrate fibers and swell them appears to be dependent upon the ability of the swelling liquid to form hydrogen bonds with the hydroxyl groups of cellulose or lignin, and also upon the size of the liquid molecules.

MATERIALS AND METHODS

Materials

Anhydrous organic liquids were used in this work. Drying over molecular sieves was performed for most of the solvents, however, since many of the solvents are hygroscopic the total absence of water is not absolutely certain. The various properties of the solvents are shown in Table 1 (molar volume, cohesive energy density (CED), and hydrogen bonding parameter). The chemical classification of the organic liquids is the same as that in Mantanis *et al.* (1994b), that is: (a) Class I: high CED, low molar volume (MV), and high hydrogen bonding parameter (HBP); (b) Class II: medium CED, low MV, and high to medium HBP; (c) Class III: high CED, low MV, and low HBP; (d) Class IV: low CED, low MV, and low HBP; and (e) Class V: very high MV (above 100 cc). Commercial α -cellulose was provided by the Sigma Chemical Corporation. Thermomechanical pulp (TMP, loblolly pine), avicell (high crystalline cellulose from wood pulp), and aspen fiber (ground wood) samples were provided by the USDA Forest Products Laboratory at Madison, Wisconsin. Cotton, rayon (spruce) staple, filter paper (cotton), sulfite pulp (sitka spruce), and kraft pulp (sitka spruce) samples were available or prepared in the Wood Chemistry Laboratory at the Department of Forestry, University of Wisconsin, Madison, Wisconsin, USA. The kraft pulping conditions were: active alkali 23%, sulfidity 25%, maximum temperature 171°C, time 114 min. The sulfite pulping conditions were: total S₀ 8.8%, combined S₀ 1.1% base Na₂CO₃, maximum temperature 135°C, time 312 min. The sulfite and kraft pulp fibers were unbleached and unrefined. The chemical composition of the pulp fibers is shown in Table 2.

Methods

In our experiment the following parameters were considered:

<i>Condition of reaction</i>	<i>Structure of fiber sample</i>	<i>Swelling liquid</i>
Room temperature (23°)	Pellet bulk density	Molar volume
Elevated temperatures	Type of fiber (pulp, cotton, α -cellulose, etc.)	Cohesive energy density Hydrogen bonding capability

TABLE 1. Organic liquids used in compressed fiber swelling experiment

	Liquids	Molar volume ^a (cc)	CED ^b (cal ml ⁻¹)	Hydrogen bonding ^c
Class I ^d	Water	18.02	448	high
	Methanol	40.70	166	high
	Ethanol	58.50	123	high
	Propanol	75.00	109	high
	Formamide	39.90	308	high
	Ethylene glycol	55.80	215	high
Class II	Pyridine	80.40	107	high
	Acetone	73.99	86	medium
	Dioxane	85.70	95	medium
	Methyl acetate	79.70	92	medium
	Ethyl acetate	98.50	83	medium
Class III	Nitromethane	54.00	150	low
	Butyrolactone	76.80	162	medium
Class IV	Ethylene dichloride	79.40	85	low
	Carbon tetrachloride	97.10	74	low
Class V	Toluene	106.40	80	low
	Benzyl alcohol	103.60	120	high
Others	DMSO	71.00	144	high
	Acetic acid	57.10	102	high
	Butylamine	98.83	76	high

^aData from Robertson (1964).^bData from Lieberman (1962).^dSame as classes in Mantanis et al. (1994b).**TABLE 2. Properties of sitka spruce kraft and sulfite pulp (Fernandez, 1993)**

Properties	Kraft	Sulfite
Klason Lignin (%)	7.4	8.0
Residual Lignin (g/g)	3.7	4.6
Residual Glucan (g/100 g)	38.1	46.2
Residual Xylan (g/100 g)	6.1	2.2
Residual Mannan (g/100 g)	1.5	2.1
Specific wettability (advancing) with water (dynes cm ⁻¹)	38.0	40.2

All samples were first disintegrated in a beater mill and then oven-dried at 65°C for 24 h. Mechanical disintegration can influence morphology and microstructure; however, since all samples were treated identically it was assumed that the mechanical treatment affected the samples similarly. Cotton was freed of waxes by scouring for 2 h in boiling 2% NaOH solution and then oven-drying for 48 h. After drying, the samples were placed in a die mold and compressed with a hydraulic press (Carver Laboratory Press) under various loads for 30 s to obtain a range of bulk densities. Each fiber pellet

sample weighed about 0.6 g. In some instances, it was necessary to reduce slightly the sample size in order to achieve the desired bulk density. All samples were then permitted to recover for 24 h in a desiccator (sodium aluminosilicate). To determine the bulk density of a fiber pellet at the start of the testing, the sample weight was determined with a scale to ± 0.001 g and the sample thickness was measured with an accurate digimatic caliper to ± 0.001 cm. The density was calculated by the formula of a cylinder. For the room temperature experiments, the swelling liquid was placed in a glass cylindrical column. A dry compressed fiber pellet was then placed carefully on the bottom of a graduated cylinder with small holes in the bottom. The diameter of the cylinder was slightly larger than that of the pellet (roughly 1.3 cm). The cylinder was then inserted slowly into the glass column. The swelling liquid immediately penetrated the cylinder from the bottom, came in contact with the fiber sample and swelled it upwards. The expansion of the fiber pellet was in most cases very quick. On first contact with the liquid, bulk densities are subject to drastic changes as the dimensions change. After 24 h of swelling, the external dimensional change of the fiber pellet was measured with the digimatic caliper. The percentage increase in the thickness direction was taken as the maximum liquid-holding capacity in the particular solvent (maximum fiber pellet swelling). All measurements were done at room temperature. Each experiment was replicated twice.

The liquid retention value (LRV) was determined analogous to water retention value (WRV) (Tappi Useful Methods, UM 256, 54/1991) (1.000 g of totally dry fiber and 30 min time of centrifugation (International Centrifuge, IEC)) after 2 h swelling at 23°C with an approximate fiber to liquid weight ratio of 1:70. All fiber samples were disintegrated before swelling in a beater mill in the dry state to form a fluff. The LRV experiment was run in duplicate and the average reproducibility of the LRV values was within 5%.

At elevated temperatures, compressed fiber swelling experiments were carried out in an apparatus described previously (Mantanis *et al.*, 1994a) using a computer linear variable displacement transformer (LVDT) which in this experiment was modified to increase sensitivity (very light aluminum gauge and highly sensitive low-pressure digimatic indicator). In a typical experiment, fiber pellets of a bulk density of about 1.0 g cc⁻¹ were inserted in the enclosed apparatus which was immersed in a constant temperature oil bath. Each pellet sample was placed in a stainless steel cylindrical holder (diameter about 1.4 cm) in the center of the vessel and contacted with the sensor of the LVDT. The preheated swelling liquids were then introduced into the preheated apparatus which was maintained at temperature throughout the experiment. The percentage increase in the thickness direction was taken as the maximum liquid-holding capacity. For each liquid, pellet swelling rate measurements were made at three temperatures (23, 40 and 60°C). A fresh aliquot of liquid was used at each investigated temperature.

Fiber pellet dimensional increases were continuously measured by computer until equilibrium was attained (Fig. 1). The slope of the initial linear portion of the fiber pellet swelling increase versus time plot was used for the determination of the swelling rate (Mantanis *et al.*, 1994a, b). Then, from the classical Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (1)$$

in which k = swelling rate constant (% min⁻¹), A = constant, R = gas constant, (J K⁻¹

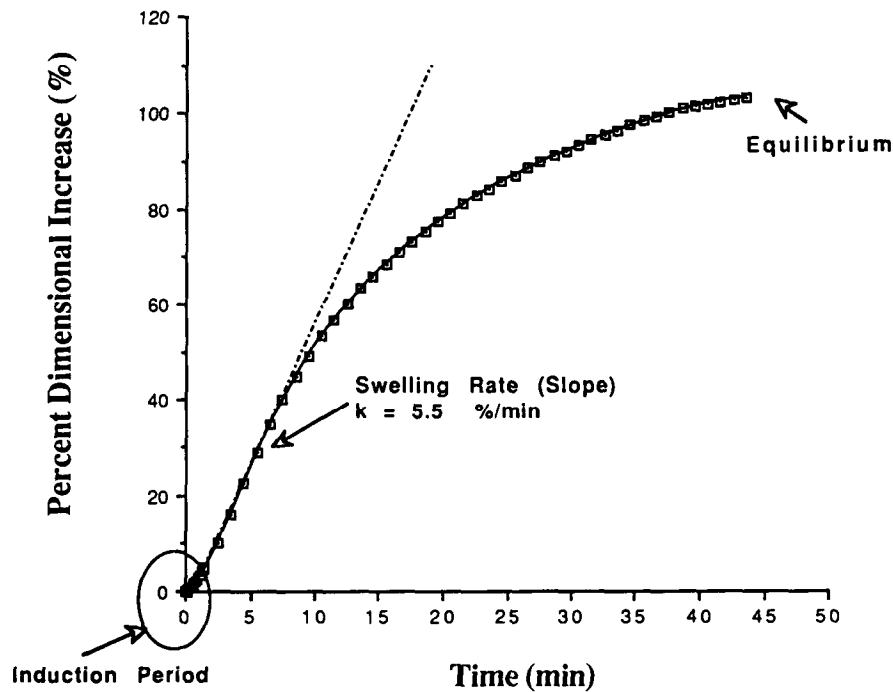


FIGURE 1. Swelling profile for compressed thermomechanical pulp fibers in ethanol at 23 °C (pellet swelling).

mol^{-1}), and T = temperature in degrees Kelvin, plots of $\ln k$ versus $1/T$ gave the activation energies for pellet fiber swelling, E_a . Small intervals of time (1-15 s), depending upon the temperature, swelling liquid, and type of fiber were utilized in order to determine the swelling rate constant k .

RESULTS AND DISCUSSION

Effect of bulk density on swelling of compressed fibers

Figure 2 shows a representative plot of the maximum liquid-holding capacity versus bulk density curves of α -cellulose, sulfite pulp, and thermomechanical pulp pellet swelling in methanol. All the curves appeared to exhibit a maximum capacity. Each curve, however, depending upon the type of the fiber and the swelling liquid, showed an optimum capacity in the region of a bulk density of 0.7 g cc^{-1} (α -cellulose in toluene) to 1.2 g cc^{-1} (thermomechanical pulp in water, except for TMP and β -cellulose in some solvents). Bulk densities below 0.4 g cc^{-1} were feasible to obtain but they did not result in a fiber pellet form with a workable shape. In addition, preliminary experiments showed that, below a specific bulk density of about 0.20 - 0.25 g cc^{-1} (non-compressed fiber systems), the contact of a fiber pellet with a liquid caused a reduction in the total volume. This observation is consistent with previous findings (Steiger and Kapur, 1972). The swelling action is due to the combined effect of both fiber cell wall swelling and loosening of the interfiber frictional bonds

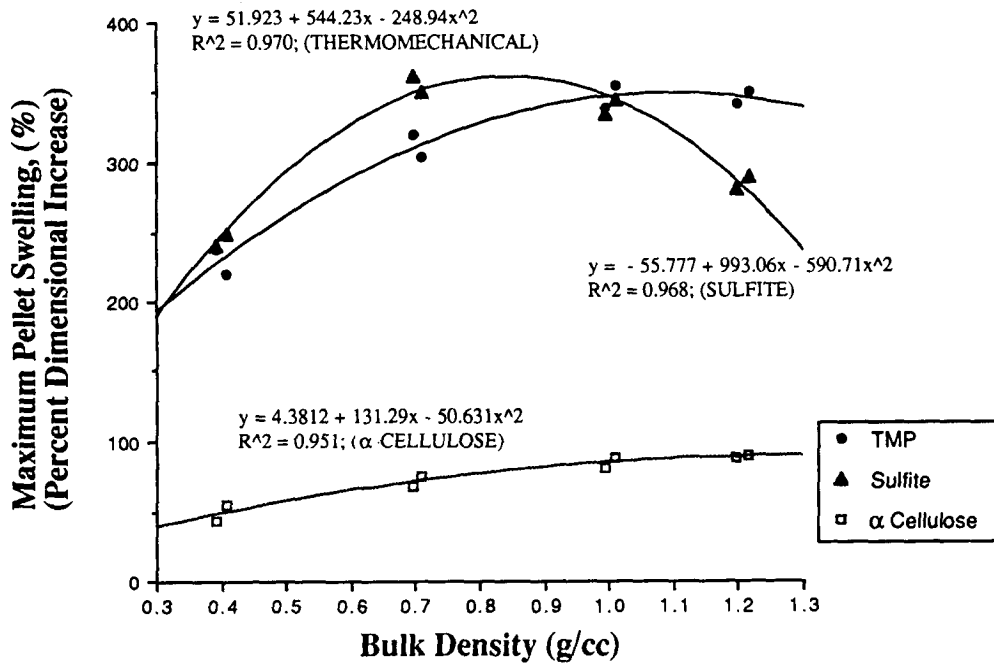


FIGURE 2. Maximum pellet swelling of fibers in methanol versus bulk density.

(curling or uncrimping) which involves fiber separation movements. The various crimps of the fibers in the pellet represent stored energy, with the higher the bulk density of a compressed fiber system, the higher the stored energy. Usually the fibers have the tendency to uncrimp rapidly on contact with water or another good swelling agent (formamide, methanol, etc.). The separating movement of the fibers thus results in expansion of the fiber volume and creates more room for the swelling solvent. In addition, the final maximum expansion of the fiber system depends, as mentioned, upon the absorbency of the fibers (fiber swellability) in the particular liquid, that is, the extent of swelling of the cell wall of the fibers. The shape and dimensions of the individual fibers will also affect the liquid interactions with the compressed fiber pellets. All these processes take place in the presence of the swelling liquid which, by means of its hydrogen bonding capability, molecular size and shape, cohesive energy density, surface tension, etc., directs this expansion so that the fibers tend to align into better defined capillaries (Steiger and Kapur, 1972). The greater maximum swelling of the TMP in the high CED and high hydrogen bonding power liquids compared with the lower swelling of the α -cellulose in these liquids (Fig. 2a-c) was unexpected and probably reflects a greater effect of physical rather than chemical factors in the swelling of these materials.

Compressed fiber swelling versus wood swelling

Figure 1 is a typical plot of the swelling of a thermomechanical pulp fiber pellet in ethanol at room temperature. The percent dimensional increase is plotted against time

(min). The final equilibrium swelling of the pellet is reached after about 50 min. A small induction time is noted in this case; however, in most cases, no induction time was observed. The expansion of most fiber systems investigated in this work was relatively fast and, in some instances, almost instantaneous (i.e. water, formamide). Generally a swelling rate constant k is derived from the slope of the initial linear portion of the swelling profile. Similar measurements were made for all the compressed fiber systems in the various organic liquids (Table 1).

The maximum liquid-holding capacities of α -cellulose and sulfite pulp in water and nineteen organic liquids at room temperature are shown in Table 3. The bulk density of the fiber systems was 0.5 g cc^{-1} . This density level was chosen to partially avoid the so-called 'springback' effect at the higher densities which would give spuriously high final swelling values. For comparison, the maximum swelling values of spruce wood measured with a similar apparatus (tangential direction) in the same solvents (Mantanis *et al.*, 1994b) are shown in Table 3. It is characteristic that liquids which swelled spruce wood to a low to medium degree (up to 6% tangential swelling) did not swell α -cellulose and sulfite pulp fibers appreciably, while the good to excellent wood swelling agents (butylamine, DMSO, formamide, ethylene glycol, water, methanol, acetic acid, ethanol, and butyrolactone) swelled the pulp fibers to an appreciable extent (Fig. 3). Results from Table 3 also indicate that butylamine, DMSO, formamide, and ethylene glycol swelled α -cellulose and sulfite pulp beyond the water-swollen dimensions. The largest increases were caused by butylamine and DMSO. On the other hand,

TABLE 3. Maximum liquid-holding capacities (percent dimensional increase) of α -cellulose and spruce sulfite pulp, and maximum tangential swelling of spruce wood in water and organic liquids

Liquid	α -Cellulose (%) ^a	Sulfite (%) ^a	Spruce wood (%) ^b
Water	85.0	403.0	8.4
Methanol	60.5	253.6	8.2
Ethanol	41.7	109.4	7.0
Formamide	179.6	470.7	11.2
Ethylene glycol	180.0	463.0	9.5
Pyridine	51.0	461.9	12.2
Dimethylsulfoxide	202.4	563.0	13.9
Acetic acid	76.4	280.4	8.7
Butylamine	209.6	601.8	14.5
Propanol	25.4	18.4	4.9
Dioxane	20.8	16.2	5.7
Acetone	13.4	47.6	5.7
Ethylacetate	18.9	5.9	2.6
Methylacetate	20.3	21.7	5.0
Nitromethane	29.4	45.3	4.5
Butyrolactone	33.4	96.0	7.2
Benzyl alcohol	39.6	10.0	2.9
Carbon tetrachloride	13.0	8.9	1.2
Toluene	8.0	11.6	1.6
Ethylene dichloride	15.3	17.3	2.1

^aAverage of two replicates (fiber pellet density $\sim 0.5 \text{ g cc}^{-1}$).

^bData from Mantanis *et al.* (1994b) (density $\sim 0.4 \text{ g cc}^{-1}$).

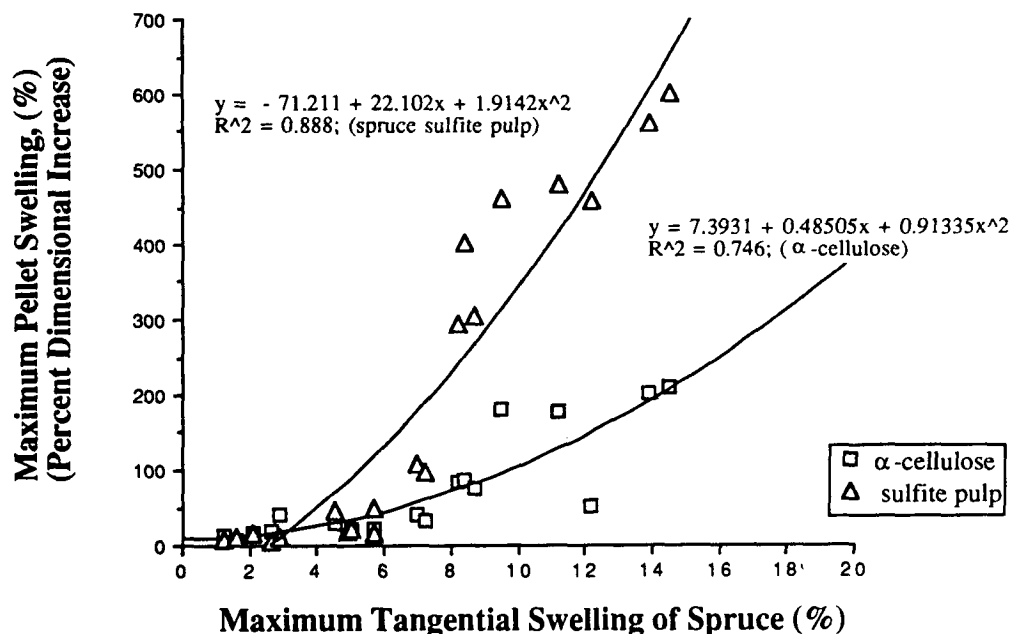


FIGURE 3. Maximum pellet swelling of fibers versus maximum tangential swelling of spruce in various organic liquids at room temperature.

toluene, carbon tetrachloride, ethylene dichloride, and ethyl acetate resulted in the lowest maximum liquid-holding capacities of the compressed fiber pellets. Notable was the swelling behaviour in pyridine which exhibited a very high swelling power on sulfite pulp fibers but it swelled α -cellulose only to a medium extent (lower than that of water). This result is possibly due to the strong swelling power of pyridine on the lignin in the cell wall of the sulfite pulps. The maximum liquid-holding capacities obtained within the homologous series of alcohols were in a descending order (Water > MeOH > EtOH > PrOH), an expected result based on previous investigations (Stamm, 1935; Stamm, 1964; Mantanis *et al.*, 1994b).

We divided the swelling liquids into five different chemical classes (Table 1) based upon three solvent properties (molar volume, CED, and hydrogen bonding capability). Results for α -cellulose pellet swelling within the five classes versus CED are plotted in Fig. 4a. The relationships shown in Fig. 4a are very similar with those reported in our previous work on the swelling of wood (Mantanis *et al.*, 1994b) and cellulose (Robertson, 1964) in organic liquids. It was also found that a rough linear correlation existed between the maximum liquid-holding capacity of α -cellulose in seventeen organic liquids and the cohesive energy density of the swelling liquid (Fig. 4b). This trend indicates that, in general, the higher the solvent CED, the higher the α -cellulose swellability (pellet swelling). A similar relationship was also reported by Thode and Guide (1959) for the cellulose maximum swelling behaviour in several organic solvents (against volatility parameter). However, in Fig. 4b there were three exceptions (butylamine, DMSO, and water). Generally, the liquids with a high molar volume (toluene, ethyl acetate) or a low hydrogen bonding parameter (ethylene dichloride,

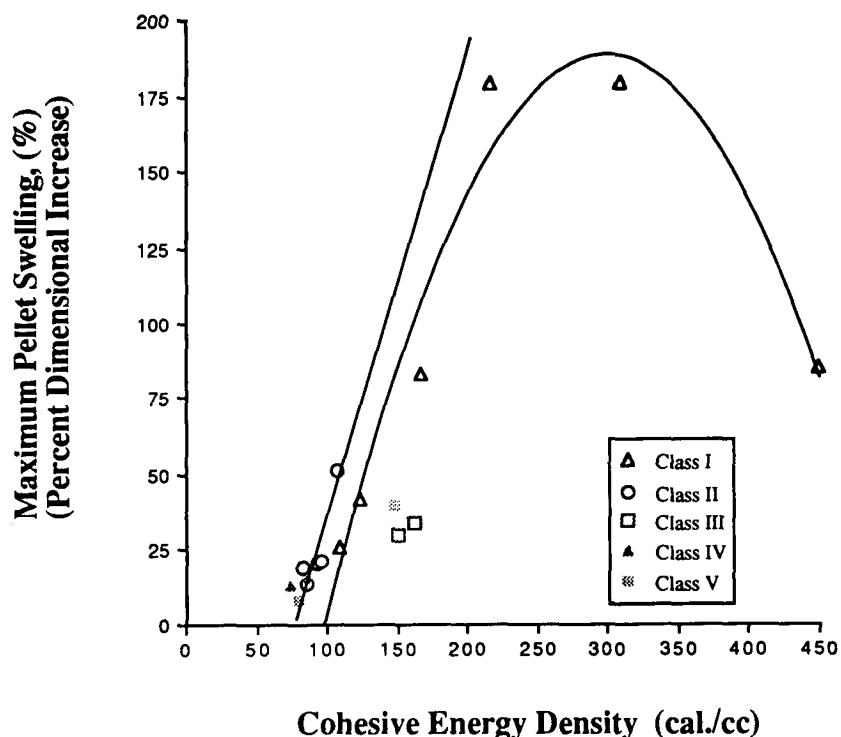


FIGURE 4a. Maximum pellet swelling of α -cellulose versus solvent cohesive energy density within various solvent chemical classes.

carbon tetrachloride, nitromethane) caused very low cellulose pellet swelling. The very high swelling power of butylamine, whose molar volume is quite high, is explainable based on its very high hydrogen bonding capability. It has been reported that amines can penetrate even the highly ordered (crystalline) regions of the cellulose fibers (Thode and Guide, 1959). It was also found that organic liquids with a high hydrogen bonding parameter (HBP) (Lieberman, 1962) swelled α -cellulose and sulfite pulp to the greatest extent (Fig. 5). Each bar in Fig. 5 represents the average maximum liquid-holding capacity (fiber swellability) in each solvent class (high, medium, and low HBP). Similar results have also been reported for the wood swelling in organic liquids (Mantanis *et al.*, 1994b). However, exceptions to this include the swelling in propanol (α -cellulose and sulfite) and in pyridine (α -cellulose).

Overall, it can be said that the hydrogen bonding capability of the swelling liquid seems to be the most important factor in the whole process which is in accord with the literature (Stamm and Tarkow, 1950; McKenzie, 1956; Robertson, 1964; Philipp *et al.*, 1973). However, the properties of liquids that determine their effectiveness in interaction with isolated cellulose or cellulosic fibers obviously cannot be assessed by just one or two individual parameters (Robertson, 1964). Besides hydrogen bonding, molar volume, and cohesive energy density, other properties such as steric hindrance and molecular shape or branching are also important and must be considered (Robertson, 1964; Mantanis *et al.*, 1994b).

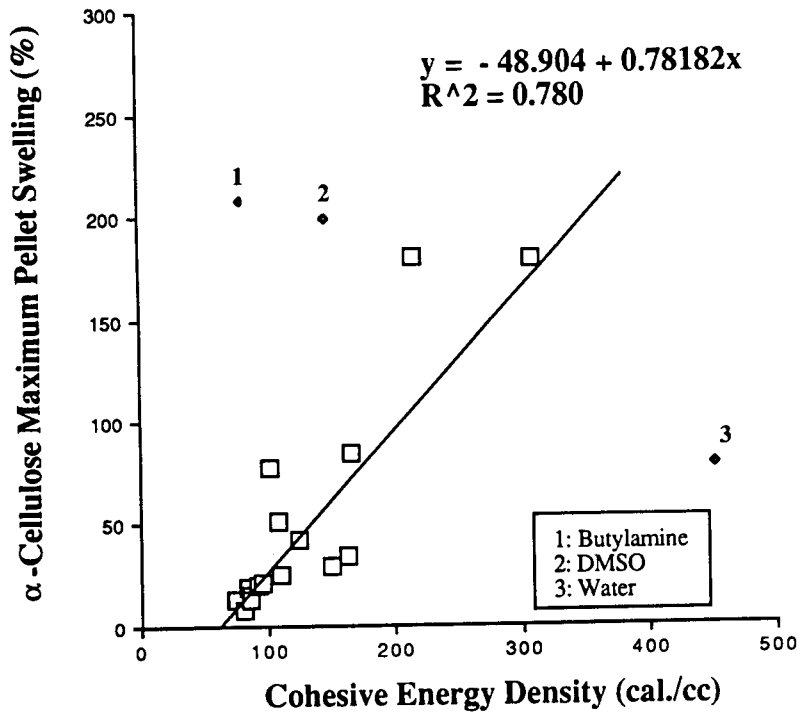


FIGURE 4b. Maximum liquid-holding capacity of α -cellulose pellets in various solvents versus solvent CED.

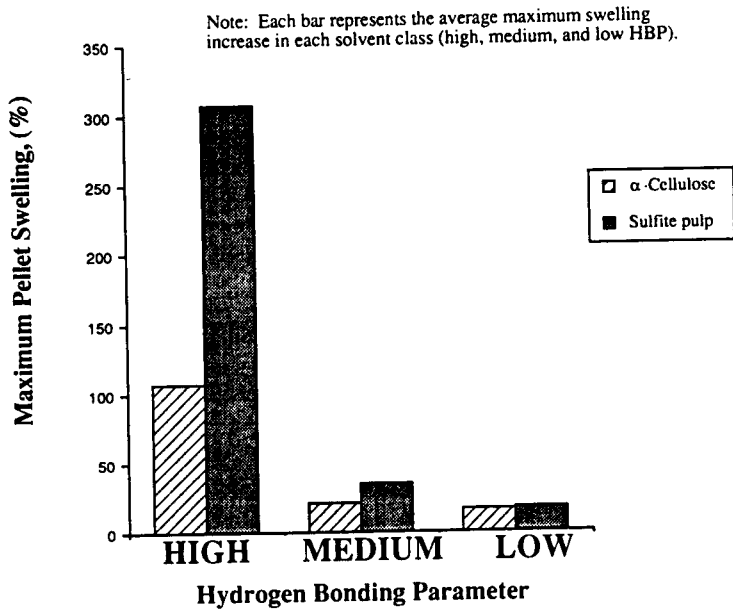


FIGURE 5. The effect of the hydrogen bonding parameter on the maximum pellet swelling of compressed fibers.

Swelling of various fibers in water and organic liquids

The data presented in Table 4 show the maximum liquid-holding capacities (maximum pellet swelling measured as increase in thickness) of nine different compressed fibers in ten various organic liquids at room temperature. The average pellet bulk density of all the fiber systems was 0.5 g cc^{-1} . In general, most fiber pellets exhibited the highest liquid-holding capacities with butylamine, DMSO, formamide, water, and acetic acid (in an approximate descending order). Pyridine was an excellent swelling agent for fiber pellets from thermomechanical pulp, sulfite pulp, kraft pulp, aspen fiber, and filter paper. It did not however swell appreciably pellets from cotton, rayon (regenerated cellulose), and α -cellulose (lower than water). Pyridine is known to be an excellent lignin solvent and may account, in part, for those differences. However, the reason for the high swelling of filter paper versus the low swelling of the other pure cellulose samples is unclear but is probably related to morphological factors. The low hydrogen bonding capability as well as high molecular volume liquids such as toluene and ethylene dichloride had, as expected, the lowest swelling powers on all of the fiber pellets, especially for avicell and cotton (almost negligible). Alpha-cellulose pellets swelled more than avicell pellets in all the solvents (except in pyridine) (Fig. 6a). This result can be explained by the very high degree of crystallinity of avicell. Pyridine and butylamine proved to be the most powerful swelling agents for avicell. Also, formamide, DMSO and butylamine swelled α -cellulose pellets more than twice as high as avicell pellets.

McKenzie (1956), using a mercury dilatometer, measured swellabilities of eucalypt α -pulp in various solvents and, a comparison with our results on α -cellulose is shown in Table 5 (A). The results are generally comparable. Sitka spruce sulfite and kraft pulp fiber pellets swelled to almost the same extent in liquids such as formamide, acetone, ethylene dichloride, and acetic acid (Table 4). Sulfite pulp pellets swelled slightly higher than kraft pellets in water; in accord with previous findings (McKenzie and Higgins, 1960; von Koeppen, 1964; Fernandez, 1993). In addition, pyridine swelled sulfite pulp pellets more than kraft, while butylamine swelled kraft pulp pellets higher than sulfite.

Philipp *et al.* (1973) measured the maximum liquid retention values (LRV) of spruce sulfite pulp samples; their results are compared with the maximum liquid-holding capacity of compressed fiber pellets from the present work in Table 5 (B). Except in pyridine, there is a good relative correlation of the swelling results in the various solvents using the two different approaches. Pyridine was an excellent swelling agent for thermomechanical pulp pellets (loblolly pine; 95% yield). Acetic acid did not swell rayon pellets to as great an extent as it did with the rest of the fiber pellets (Table 4).

Swelling measurements were also made on compressed disintegrated filter paper (density = 0.5 g/cc^3) in ten organic liquids in this work. Filter paper pellet swelling results are compared with Robertson's (1970) results in Table 5(C). Robertson made caliper measurements on immersed paper samples in several organic liquids. Robertson's swellability values for paper in Table 5(C) are relative to those in water since he made no reference to the apparent density of the paper in his work. Generally the results are in good agreement.

Figure 7 is a plot of the maximum swelling (percent increase in thickness direction) of aspen wood fiber pellets versus the maximum tangential swelling of aspen wood (Mantanis *et al.*, 1994b) in ten organic liquids. The almost linear correlation indicates

TABLE 4. Maximum liquid-holding capacities (percent increase in thickness) of various compressed fiber systems in organic liquids at 23 °C

Liquids	Fibers ^a									
	α -Cellulose	Avicell	TMP	Sulfite	Kraft	Aspen fiber	Filter paper	Cotton	Rayon	
Water	85.0	60.9	382.1	403.0	373.8	340.1	233.1	355.2	379.2	
Formamide	179.6	74.0	392.3	470.7	479.9	475.3	365.4	465.7	431.8	
Pyridine	51.0	89.7	432.1	461.9	332.9	474.2	296.1	35.3	22.1	
Acetone	13.4	5.9	78.4	47.6	43.1	110.0	21.1	19.7	18.7	
Nitromethane	29.4	5.7	66.9	45.3	50.4	123.2	24.9	22.1	27.2	
Ethylene dichloride	15.3	2.2	10.3	17.3	13.0	25.1	7.7	6.5	17.7	
Toluene	8.0	1.4	3.9	11.6	5.6	5.9	6.7	5.4	14.4	
DMSO	202.4	67.4	523.7	563.0	574.9	455.5	427.8	691.0	452.5	
Acetic acid	76.4	59.1	274.6	280.4	316.8	305.9	183.4	356.1	57.5	
Butylamine	209.6	103.7	503.1	601.8	691.6	497.4	517.2	640.1	595.4	

^aAverage of two replicates (pellet bulk density = 0.5 g cc⁻¹).

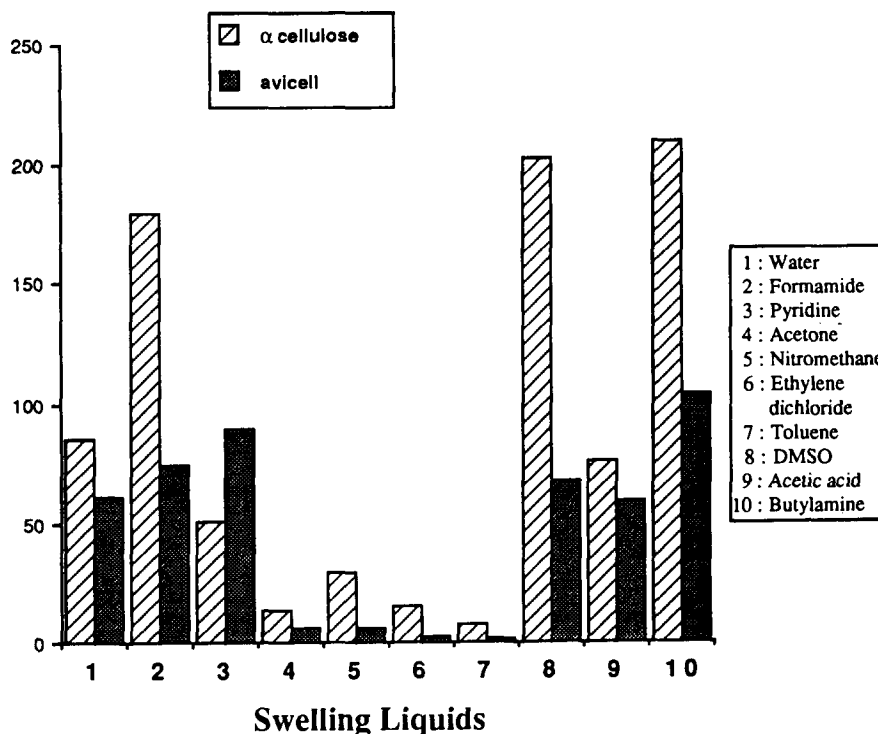


FIGURE 6. Comparison of α -cellulose versus avicell maximum pellet swelling in various organic liquids.

that these particular liquids produced almost analogous swelling effects on both wood and wood fibers (same wood species).

The liquid retention values (LRV) of various types of cellulosic fibers in ten organic liquids at room temperature are shown in Table 6. It must be emphasized that LRV is an empirical estimate of the swollen volume of fibers and cannot be considered as an unbiased measure of the degree of fiber swelling. However, the overall LRV methodology has gained considerable acceptance in recent years. It is obvious from the results in Table 6 that the structure and type of cellulose (pulp, cotton, wood species, etc.) influence the fiber swelling behaviour (measured as LRV) in different organic liquids whose swelling power varies greatly. Solvents such as DMSO, formamide, the ethylene glycol, as expected, resulted in higher fiber liquid retention values than those of water. The low hydrogen bonding and high molecular volume toluene and ethylene dichloride caused the lowest LRV, almost independent of the type of fiber, and had the lowest swelling powers. LRV data for spruce sulfite pulps in seven liquids are in relatively good agreement with LRV data reported by Philipp *et al.* (1973); our results are slightly higher (approximately 1.3 times, on the average). Sulfite pulp had a liquid retention value with water, (WRV), slightly higher than that of kraft pulp; in accord with the maximum liquid-holding capacity results (Table 4). A comparison between the LRV and pellet maximum liquid-holding capacity also reveals that both sulfite and kraft pulps had an almost analogous swelling behaviour in most of the swelling liquids.

TABLE 5. Swelling power of various reagents on cellulosic fibers

Reagent		Swelling index
(A)	McKenzie (1956) Oven-dry cellulose eucalypt α -pulp Volume swelling (%)	(Mercury dilatometer measurements) Present work: commercial α -cellulose, Thickness direction swelling (%)
Acetone	27.6	13.4
Ethanol	42.0	41.7
Water	117.6	85.0
Pyridine	120.0	51.0
Formamide	133.2	179.6
(B)	Philipp <i>et al.</i> (1973) Liquid retention values (max) (1 h/20 °C)	(Swellability relative to that of water) Present work: Max. liquid-holding capacity (%), (24 h/23 °C)
	Spruce sulfite pulp	Spruce sulfite pulp
DMSO	192.0	139.7
Formamide	134.9	116.7
Ethylene glycol	133.3	114.9
Water	100.0	100.0
Acetic acid	71.4	69.5
Pyridine	68.3	114.6
Methanol	52.4	72.8
Ethanol	50.8	27.2
(C)	Robertson (1970) Caliper measurements of immersed paper (%)	(Swellability relative to that of water) Present work: filter paper (%)
Acetone	2.6	9.0
Acetic acid	44.7	78.6
Water	100.0	100.0
Pyridine	100.0	127.3
Formamide	136.8	156.7
DMSO	189.5	183.5

It was found that the time necessary to reach an apparent maximum LRV in most of the liquids was usually less than one hour, except for cotton fibers whose LRV were very low even after two hours of swelling. Generally, cotton swelled in most liquids very slowly possibly due to its higher degree of crystallinity (LRV for cotton was thus measured after 24 h of swelling). Overall, no general relation between LRV and the solvent parameters such as density, viscosity or surface tension was found. This is consistent with previous literature (Stamm and Tarkow, 1950; Philipp *et al.*, 1973). In addition, no clear correlations existed between LRV and any of the individual parameters commonly used to characterize cellulose interactions with organic liquid molecules such as dipole moment, dielectric constant, and solubility parameter. However, it appears that a moderate trend exists between LRV and liquid molar volume (MV), that is, in general, as the MV increases, the LRV decreases gradually, especially when a high MV is associated with a low hydrogen bonding capability (i.e. toluene).

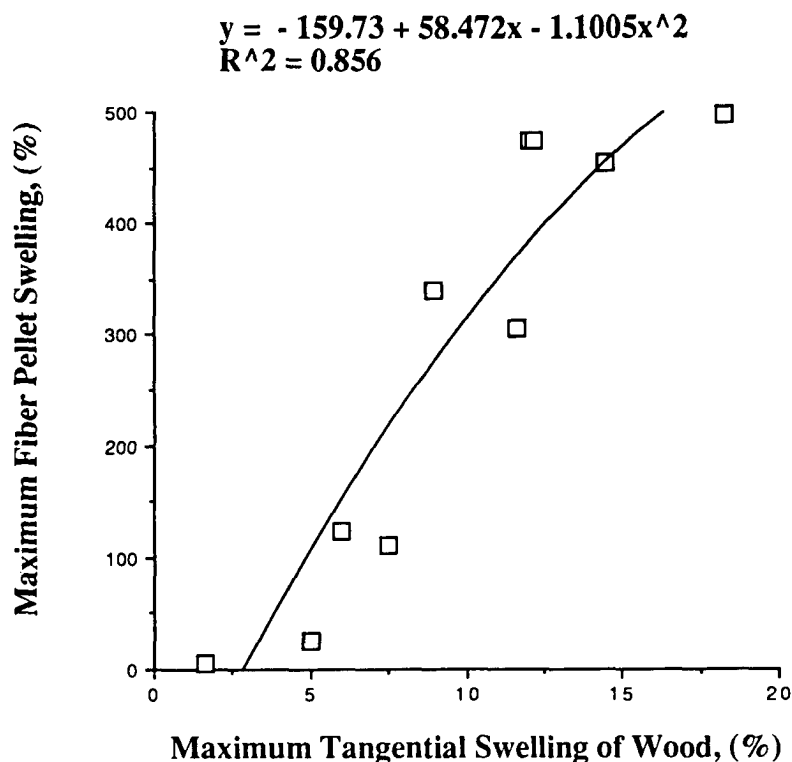


FIGURE 7. Maximum tangential swelling of wood versus maximum fiber pellet swelling in various organic liquids (quaking aspen).

TABLE 6. LRV of cellulose fiber samples in various liquids (%), (swelling time 2 h/23 °C)

Swelling liquid	Spruce sulfite	Spruce Kraft	TMP	Aspen fiber	Filter paper	Cotton
Water	97.4	92.4	58.6	64.9	75.2	42.3
Methanol	76.8	61.3	35.1	44.0	24.1	16.1
Ethanol	72.2	54.4	31.1	34.9	19.2	13.2
Nitromethane	45.2	32.2	6.3	21.4	7.5	9.1
Ethylene dichloride	15.2	22.1	1.1	1.3	1.5	3.1
Toluene	27.0	24.9	1.6	3.5	2.1	5.8
DMSO	168.4	162.6	112.5	127.7	127.0	64.4
Acetic acid	76.4	55.2	19.9	37.1	19.2	12.9
Ethylene glycol	132.6	126.5	93.2	95.1	80.1	52.5
Formamide	155.7	149.3	97.7	114.4	102.0	57.4

Also, a linear positive trend exists between LRV and solvent cohesive energy density (with the exception of water which has an extremely high CED). Indeed, all fibers used in this work had their highest LRV interactions with the high CED liquids such as DMSO, formamide, ethylene glycol, water, and methanol. Overall, no general relationship was found between LRV of various types of cellulose fibers and one single parameter of the swelling liquid; but rather the final LRV is determined mainly by the

interrelation between molar volume, hydrogen bonding capability, and cohesive energy density, and also is influenced by the molecular and morphological structure of the cellulose fiber.

Effect of temperature on swelling of compressed fibers (E_a)

Swelling rates, k , and activation energies, E_a , for fiber pellet swelling (TMP, sulfite pulp, aspen fiber, and filter paper) in several organic liquids are presented in Table 7. The calculation of activation energies was made for comparison purposes, but theoretically, fiber spring-back and uncurling in fiber pellet swelling do not involve chemical transition states; however the high R^2 values obtained indicate significant dependence of fiber pellet swelling on temperature, and fiber pellet swelling appears to obey the classical Arrhenius equation (equation 1).

Figure 8 shows the rate of pellet swelling of a thermomechanical pulp fiber (loblolly pine) in methanol at three different temperatures. It is apparent that the rate increased almost three times from room temperature (23°C) to 60°C. The activation energy of swelling, E_a , was then calculated using the Arrhenius equation. In general, the Arrhenius plots showed strong linear correlations with high R^2 (Table 7).

Generally the swelling of the compressed fibers in ethanol and ethylene glycol had the highest dependences upon the temperature (E_a) while the fiber swelling in the low molar volume liquids such as water and methanol showed the lowest E_a . It should be stressed that the swelling rates in water, formamide, and methanol were extremely high, that is, pellet fiber swelling increases were almost instantaneous. It was also noted that the swelling rates of compressed disintegrated filter paper were the lowest in all the liquids investigated except in water.

The rate of compressed fiber swelling was mainly affected by the molecular size of the swelling liquid similar to what was observed for the wood swelling in several liquids (Mantanis *et al.*, 1994a, b, c). Future work on the swelling of compressed fibers in a more extensive series of organic solvents should provide additional information and a better understanding of the whole process. However, it has been noted that liquids with a molar volume greater than 100–110 cc are relatively inactive in wood pulp and cotton studies (Robertson, 1964). It is anticipated therefore that the temperature effect on such interactions would be of significant importance.

A polynomial trend was additionally found to exist between E_a of pellet swelling and cohesive energy density of the swelling liquid in filter paper (pure cellulose) (Fig. 9). The R^2 of this correlation was 0.631. This indicates that, in general, the lower the CED of the swelling liquid, the higher the E_a of paper pellet swelling. This result is in good agreement with Robertson's (1964) conclusion that, assuming that the CED of cellulose is high, the greater interactions of cellulose should result with liquids having the higher cohesive energies.

SUMMARY AND CONCLUSIONS

Hydrogen bonding capability, molecular size, and cohesive energy density of the swelling liquid appeared to be the most important parameters in the swelling of various cellulosic fibers in organic liquids (compressed fiber systems). Correlations between cellulose, compressed fiber pellets, and wood swelling in the various liquids were

TABLE 7. Swelling rates (**k**) and activation energies (**Ea**) for the swelling of compressed fibers in several organic liquids

Solvents	T (Celsius)	Thermomechanical			Sulfite			Filter paper			Aspen fiber		
		k (% min ⁻¹)	Ea (KJ mol ⁻¹)	R ^{2a}	k (% min ⁻¹)	Ea (KJ mol ⁻¹)	R ²	k (% min ⁻¹)	Ea (KJ mol ⁻¹)	R ²	k (% min ⁻¹)	Ea (KJ mol ⁻¹)	R ²
Water	23	4631.7			638.0			2769.1			3877.8		
	40	6433.9	10.7	0.954	1264.5	31.8	1.000	4147.0	17.3	0.999	4707.5	11.1	0.987
	60	7518.9			2686.9			6055.4			6389.2		
Methanol	23	577.6			324.6			86.3			762.6		
	40	971.3	21.3	0.996	585.4	25.2	0.999	182.9	25.8	0.970	1534.4	29.4	0.998
	60	1509.3			1011.8			277.0			2880.0		
Ethanol	23	5.5			3.5			0.63			4.8		
	40	27.8	68.3	0.998	10.0	50.6	0.999	2.8	78.8	0.994	48.1	84.1	0.982
	60	120.4			34.4			22.0			215.6		
Ethylene glycol	23	11.1			31.8			24.9			11.2		
	40	89.9	66.1	0.944	136.2	49.9	0.968	68.9	37.0	0.981	61.6	71.9	0.998
	60	221.4			303.5			132.7			288.6		
Formamide	23	553.6			658.6			369.4			609.4		
	40	1745.8	33.7	0.915	1324.5	24.7	0.976	736.6	25.5	0.984	1273.9	29.5	0.994
	60	2553.4			2012.0			1169.5			2307.7		
DMSO	23	167.3			145.5			90.2			345.3		
	40	524.1	46.8	0.996	737.2	51.8	0.948	348.9	44.3	0.956	1268.2	46.0	0.976
	60	1384.7			1519.6			669.9			2765.3		

*R² = square of regression coefficient for Arrhenius plots.

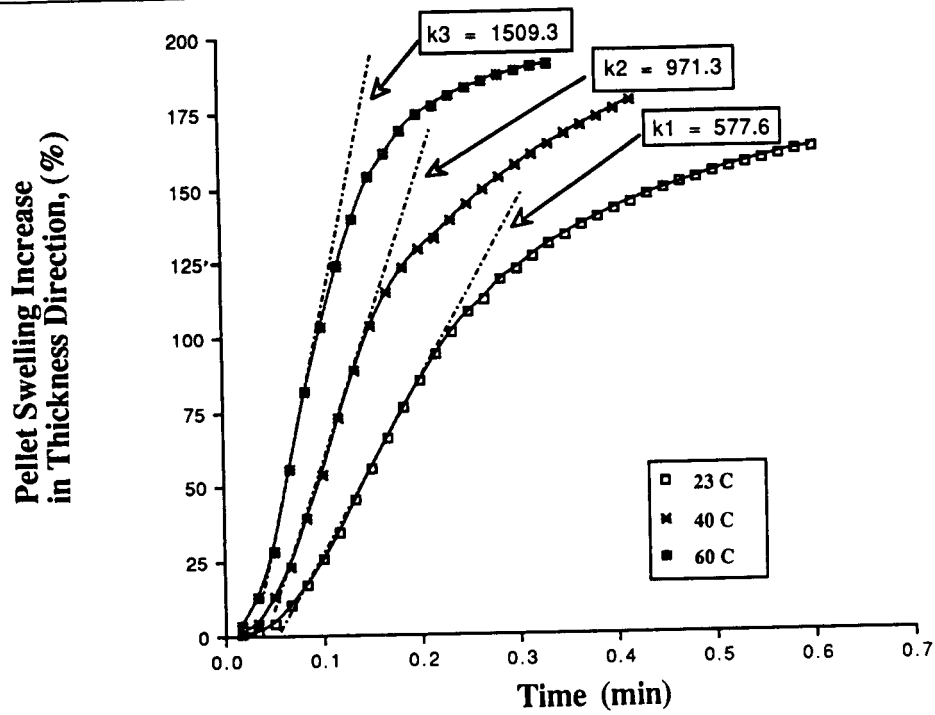


FIGURE 8. Thermomechanical pulp pellet swelling in methanol at various temperatures.

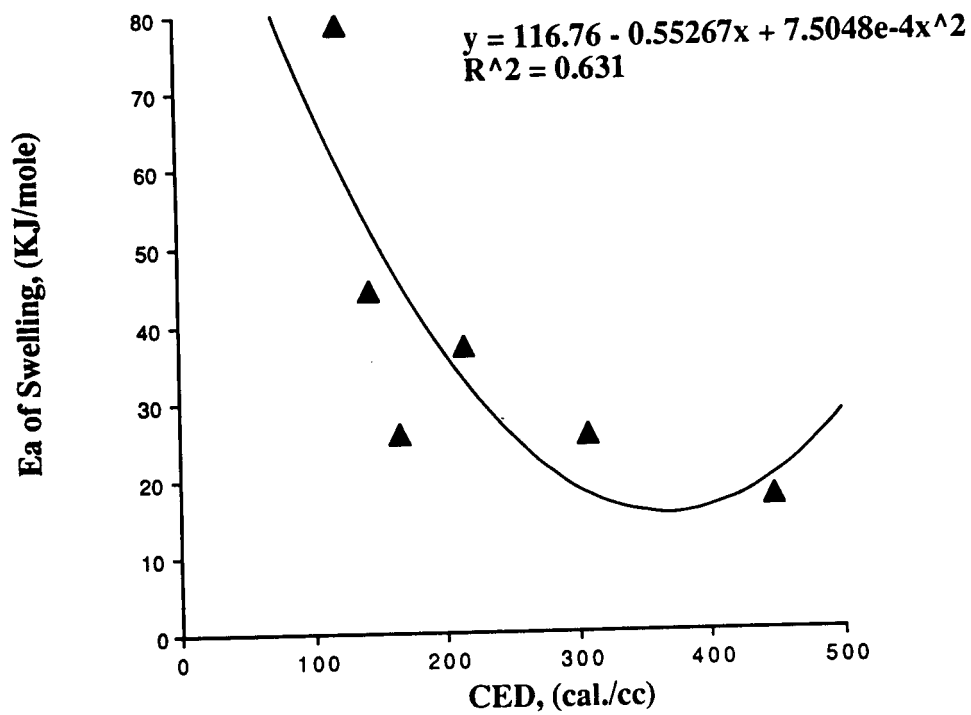


FIGURE 9. E_a of filter paper pellet swelling versus solvent cohesive energy density.

generally quite good. It was also found that the temperature had a large influence on the rate of swelling of four types of compressed fibers in several solvents. Activation energies (E_a) for the compressed fiber swelling in six liquids were evaluated with a computerized LVDT. E_a was linearly correlated with the solvent molar volume.

ACKNOWLEDGEMENTS

The authors thank Professor Ferencz Denes for his assistance. The special help of the Instrumentation Laboratory people such as Mr Dick Kinney, Mr David Simpson, and Mr Steve Hankel of the USDA Forest Products Laboratory at Madison, Wisconsin, is also gratefully acknowledged.

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