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NEW INSIGHTS INTO FIBRE SWELLING, INTERFIBRE BONDING AND WET STRENGTH

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Synopsis The various modes in which ordinary and modified cellulose fibres and surface modified cellulose microfibrils can interact with water are reviewed. The hydrogel state of fibres can be extruded and dried to form a continuous oriented strand: 'one dimensional paper'. A colloidal suspension of surface modified cellulose microfibrils can be converted into a paracrystalline gel which exhibits birefringent domains and responds to extrusion through a cylindrical orifice to yield a continuous fibre whose density and x-ray diagram are characteristic of cellulose: 'reconstituted native cellulose'. The mechanical properties of these two novel materials are reported.

The mechanism of wet strength development in 'one-dimensional paper' which had been encapsulated with nascent polyethylene was studied. The polyethylene was confined to the exterior of the substrate and while it does not prevent fibre wetting and swelling the rate of wetting is considerably slowed. As a result, disruption of interfibre bonds is incomplete.

Introduction

EVEN in the absence of lignin, native cellulose fibres are only weakly swollen by water. Because of this, the appellation 'hydrophilic' is more appropriate than 'swollen' and it is this quality which is the basis for most uses of cellulose in the 'sanitary-disposable' domain. The so-called 'hydrated state', familiar to the 'fine paper' specialist, wherein the pulp slurry exhibits a slimy feeling and slow drainage is related to colloid characteristics and not to a high degree of swelling in the macromolecular sense of the word.(1) To provide a proper mental scaffold for this discussion, let us use the Fig. 1 diagrams to define five different ways in which free water can be immobilised in materials systems which are frequently referred to as gels.(2, 3)

Under the chairmanship of Dr N. K. Bridge

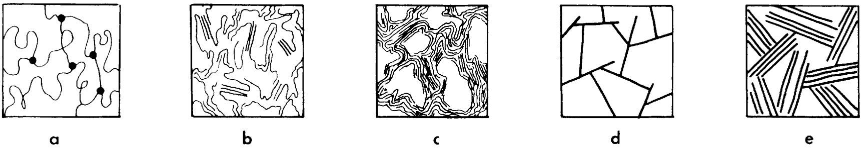

Fig. 1—Models of water immobilising systems at the molecular and colloid level; (a) crosslinked macromolecular network, 'hydrogel'; (b) partially crystalline two phase system with crystallite 'pseudocrosslinks' and swollen amorphous phase: (c) partially crystalline three phase system, the third phase being pure solvent; (d) colloidal particles forming random 'house of cards' structure; (e) paracrystalline structure with swelling agent between regularly spaced rods organised in domains

Diagram (a) is the classical crosslinked network where a swelling limit is imposed by a balance between the thermodynamic forces due to polymer-solvent interaction and the entropic force of coiled polymer chains.

Model (b) is a similar situation where an insoluble crystalline phase acts as a pseudocrosslink. In such a state the swollen phase is a supersaturated solution where kinetic factors prevent formation of additional crystals. This type of system may give rise to the three-phase situation illustrated in (c) where pockets of pure diluent are dispersed uniformly in the polymer-diluent matrix. At some characteristic temperature the 'supersaturated' phase becomes simply 'saturated' and in equilibrium with the crystalline phase.(4)

The last two systems, (d) and (e), are colloidal rather than macromolecular. The tendancy for rigid, anisotropically shaped particles to display differences in charge distribution at the ends or edges compared to the faces is well known and this can lead to the familiar 'house of cards' structure. It has long been appreciated(5, 6) that a random suspension of anisotropic and rigid particles can spontaneously order into a paracrystalline state such as shown in (e). The phase separation phenomenon and the concentration of the paracrystalline phase is concentration dependant. Likewise, the characteristic and uniform interparticle distance gives rise to Bragg diffraction(7) and iridescence when the system is sufficiently uniform. Addition of diluent or a change in the chemical potential of the latter brings about reversible changes in this characteristic interparticle spacing.

Under suitable conditions, cellulose systems can display all the states described above. Frequently, intermediate states are to be found. When native cellulose fibres are used to prepare one or the other of these gel states, the added feature of a microparticulate gel is introduced where the fibre shape and dimensions delimits each gel particle. Indeed this feature if of particular importance to pulp and paper manufacture as it can give new properties to papermaking materials.

The chemical modification of the cellulose molecule into commercially viable derivatives ran its course almost a decade ago.(8) These derivatives, from nitrocellulose to carboxymethyl cellulose, have found outlets as films, fibres, lacquers and gums like a host of other man-made macromolecules. A new generation of cellulose derivatives are the superswelling fibres which take advantage of the fibre domain itself to create a microgel substance.(9) The swelling mechanism can be based on model (a) or (e) or hybrids thereof as the following examples will attempt to show. Of particular interest, subsequently, is the response of these microgel materials to the classical manipulations and physical processes which are operative in papermaking. Included in this spectrum will be a study of how interfibre bonding in systems with such a high swelling potential are protected from water by encapsulation with nascent polyethylene.(10)

Fibrous hydrogels and paracrystalline gels of cellulose

WHEN structures such as model (a) above are swollen in water, the product is referred to as a 'hydrogel'. A wide range of commercial materials from 'soft' contact lenses to chromatographic substrates, such as crosslinked dextrans, conform more or less to this model.(11) Since native cellulose fibres are not soluble in water, it is necessary to both crosslink and to carboxymethylate them in order to arrive at a state equivalent to model (a). Furthermore, according to the patent literature, the product, albeit swollen by a factor of 30, maintains its fibre form. Commercially available products made by the Buckeye Cellulose Co. and by the Hercules Powder Co. were examined in this study and the samples correspond to the following analyses:

TABLE 1—PROPERTIES OF CARBOXYMETHYL CELLULOSE HYDROGEL FIBRES

Source	Buckeye Cellulose Co.	Hercules Powder Co.
Fibre origin	Softwood pulp	Cotton linters
Crosslinking agent	Epichlorohydrin	Heat
Max. Swelling in H_2O	30X	25X
Trade name*	CLD	AQUALON

* The superabsorbent fibres known as 'CLD' are produced from a dissolving grade softwood pulp which is first converted to alkali cellulose then crosslinked with epichlorohydrin. The crosslinked alkali cellulose fibre is treated with monochloroacetic acid to achieve a degree of carboxymethylation which is normally sufficient to assure water solubility, were it not for the crosslinks. The same product can be obtained by first carboxymethylating the alkali cellulose in butanol-2 and subsequently crosslinking. AQUALON is prepared by first carboxymethylating then by crosslinking the purified fibrous CMC via a heat treatment which produces ester crosslinks.

A second category of superswelling cellulose fibres which were examined were prepared by ceric ion grafting of acrylonitrile onto both purified wood pulp and absorbent cotton. The procedure which we have used has been previously described(12) and the various products prepared were labelled CG for 'cellulose grafted' (C_p, when the starting material was a wood pulp and C_c when it was cotton). The label CH_AG was used when the starting product had been given an acid hydrolysis treatment using 3N.HCl at reflux for 15 min followed by a wash in water, 3 per cent NaOH, water and drying at 70° C after washing in isopropanol. Table 2 summarises the various samples prepared.

TABLE 2—LEVELS OF POLYACRYLONITRILE GRAFTING FOR DIFFERENT CELLULOSE SUBSTRATES

Sample	*Label*	*Grafting* (%)	*Maximum Swelling in H_2O after base hydrolysis**
Wood pulp	C_pG	130	30X
	C_pH_AG	110	—
Cotton	C_cG	50	19X
	C_cH_AG	100	—

* As measured by the centrifugal 'water retention value'.

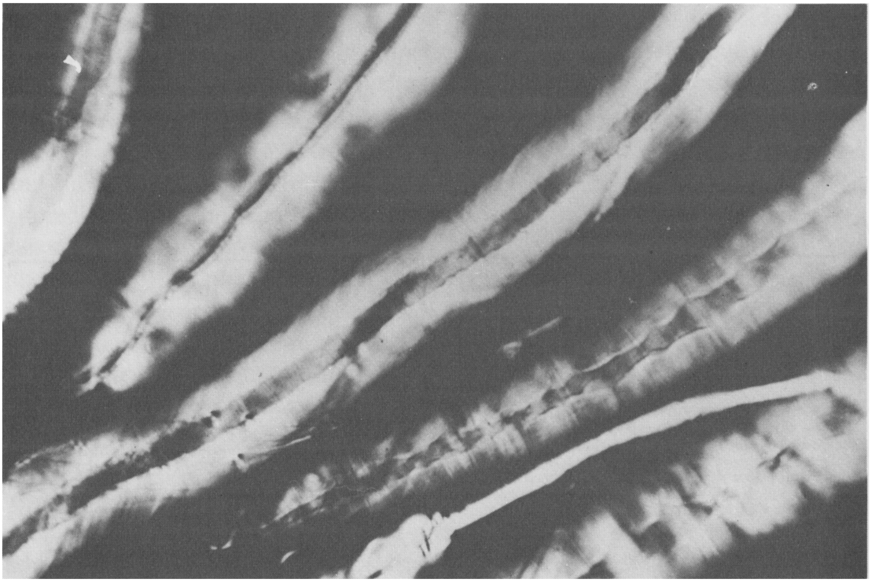

Fig. 2—Grafted and hydrolysed woodpulp, C_pGH_B, in the water swollen state as viewed between crossed Nicols. The swollen volume in water is ~ 30X except for the unswollen segment along one of the fibres

These samples were subsequently treated with a 3 per cent aqueous NaOH solution at the boil for 15 min followed by washing in a series of water/methanol solutions of increasing methanol content and finally they were dried at 70° C after washing in isopropanol. The alkali treatment converts the polyacrylonitrile (PAN) graft into a nearly equimolar copolymer of acrylamide and acrylic acid salt, leaving the fibre in a highly swollen state. Subsequent washing in an organic solvent causes deswelling which is then followed by a drying step at 70° C. After base hydrolysis the samples are labelled CGH_B or CH_AGH_B etc.

The appearance of CGH_B in the swollen state as viewed between crossed polars is shown in Fig. 2. Since the birefringence, the native cellullose X-ray pattern and the microfibrils themselves have been shown to be retained, it is concluded that model (e), above, best describes the behaviour of this system. The term 'constrained paracrystalline gel' is proposed for this case where the domain of correlated orientation is over the volume of the fibre. The swelling mechanism involves lateral separation of the microfibrils due to the swelling potential of the sodium polyacrylate/polyacrylamide copolymer between them. A model for such a system based on small angle X-ray diffraction is shown in Fig. 3. It would appear that weak mechanical forces only are responsible for maintaining the fibre's coherence in water as a short vigorous mechanical treatment is sufficient to disperse the product into its microfibrillar elements which form a thixotropic gel at a solid content of < 0·1 per cent.

In these studies sample CH_AGH_B, which was a hydrocellulose powder before grafting, was especially easy to disperse into its microfibrillar elements.

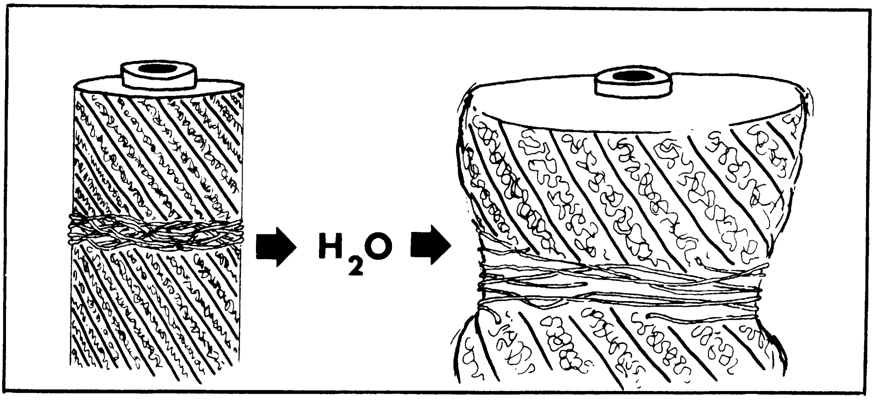

Fig. 3—Model for swollen C_PGH_B fibres corresponding to 'constrained paracrystalline microgel'

In this respect, its behaviour was similar to the cellulose crystallites produced by hydrolysis with strong sulphuric acid as first reported by Mukherjee and Woods.(13) It is believed that in the latter case formation of sulphate esters at the surface of the cellulose is responsible for the surface charge which spontaneously disperses the hydrocellulose powder into microfibrillar elements. In the case of the CH_AGH_B sample the grafted acrylic polyelectrolyte performs the same function. The average size of these crystallites is 50–100 Å in width and 500–3 000 Å in length, depending on the starting material.

In the case of the microfibrillar fragments prepared by strong sulphuric acid hydrolysis, a *paracrystalline gel* was observed when a dilute suspension was spun down in an ultracentrifuge.(14) The same behaviour was found for the mechanically dispersed CGH_B and CH_AGH_B samples and although the iridescence phenomenon was far less marked, the birefringence and development of axial orientation on shearing was the same. A characteristic feature of the paracrystalline gels is that the individual particles are held in the organised state by weak interactions between charged surfaces. They are therefore able to swell without limit and eventually pass into a concentration range where there is a two phase equilibrium between an ordered phase and a random colloidal phase.(6)

One-dimensional paper

In order to record the wide and small angle X-ray scattering envelopes for these samples some degree of orientation for a collection of fibres was sought. This was achieved with surprising ease by extruding an aqueous suspension of either CLD, AQUALON, or CGH_B through a capillary ($<0{\cdot}1$ cm diameter) onto a solid plate whose surface had been rendered hydrophobic by an appropriate treatment. The product was a wisker-like monofilament of indefinite length. On cursory examination it was clear that the process was equivalent to a spinning operation in the textile or synthetic fibre sense, i.e. fibres were oriented thanks to the shearing forces of the extrusion yet they were much too large and too crowded to relax their orientation by a Brownean process. On drying the usual interfacial forces were operative to produce a radial compression and densification which was coincident with the buildup of interfibre bonding and mechanical strength in the oriented fibrous wisker to be called 'superfibre' or 'one-dimensional paper'.

The appearance of the 'superfibre' is shown in Fig. 4 where three different states are shown each in a roman cross arrangement which was produced by extruding consecutive strands orthogonally and superposed. The centre sample is fresh, undried material (3 per cent solids) which is translucent. To the left is a material which has been freeze dried and to the right an air dried

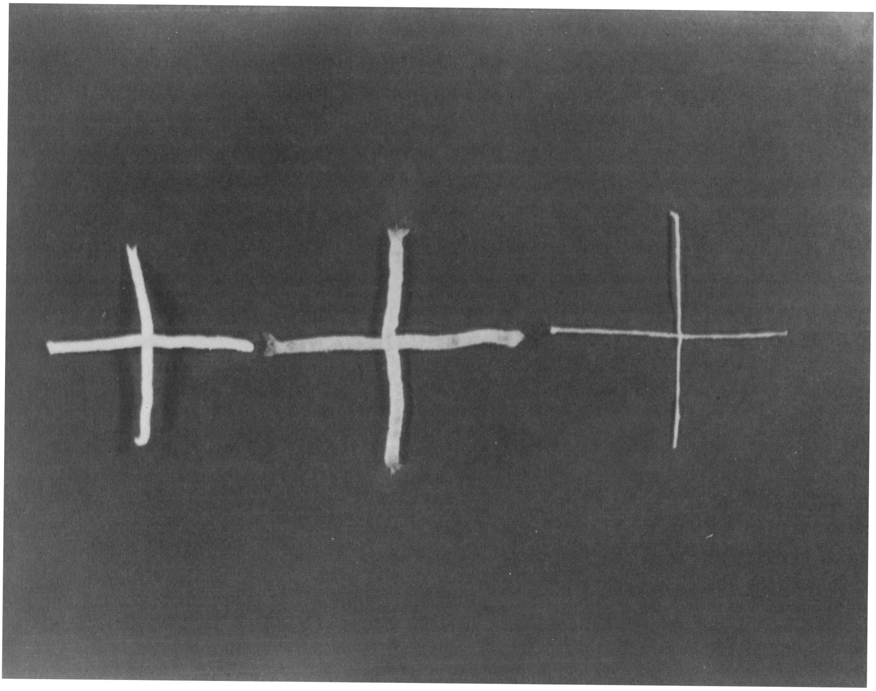

Fig. 4—Appearance of CLD superfibres; the centre sample is 'as extruded', on the left is the freeze dried material and on the right, the air dried 'one-dimensional paper'

sample. Because of the hydrophobic nature of the substrate on which extrusion and drying occurred, the loss of water and subsequent compaction took place with cylindrical symmetry. In the case of the air dried sample the radial collapse is evident from the narrower diameter. The position of the fibre crossing developed into an inter-superfibre bond which was stronger than the air dried 'superfibre'. The freeze dried sample maintained its wet dimensions and exhibited strong opacity.

Examination of one-dimensional paper in the polarising microscope showed that pronounced axial orientation of the fibres had developed, especially after drying. This was confirmed by X-ray diffraction as shown in Fig. 5 where the characteristic oriented pattern of native cellulose is readily recognised for both C_cGH_B and C_pGH_B. In the case of the CLD and AQUALON systems, fibre orientation was also detected by X-ray diffraction (Fig. 6). While the

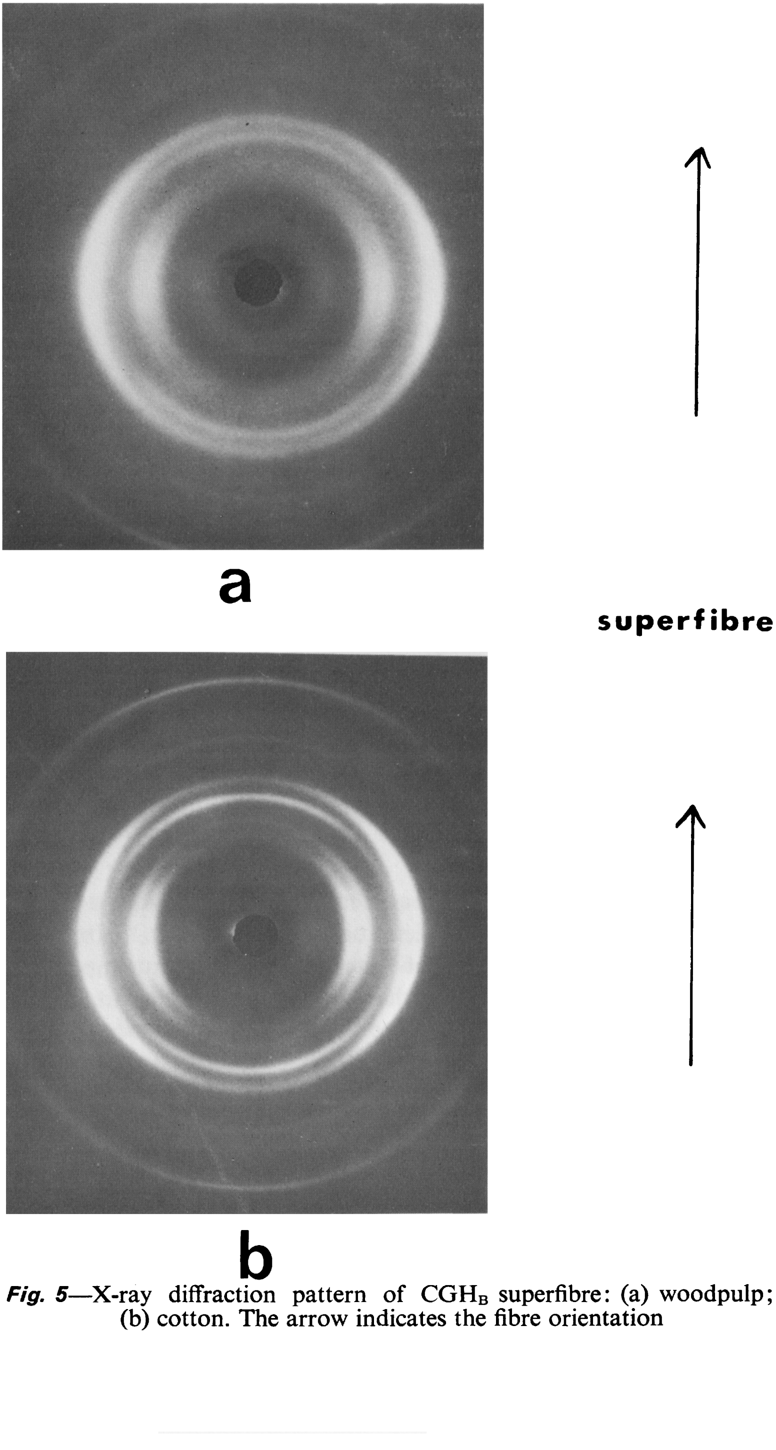

Fig. 5—X-ray diffraction pattern of CGH_B superfibre: (a) woodpulp; (b) cotton. The arrow indicates the fibre orientation

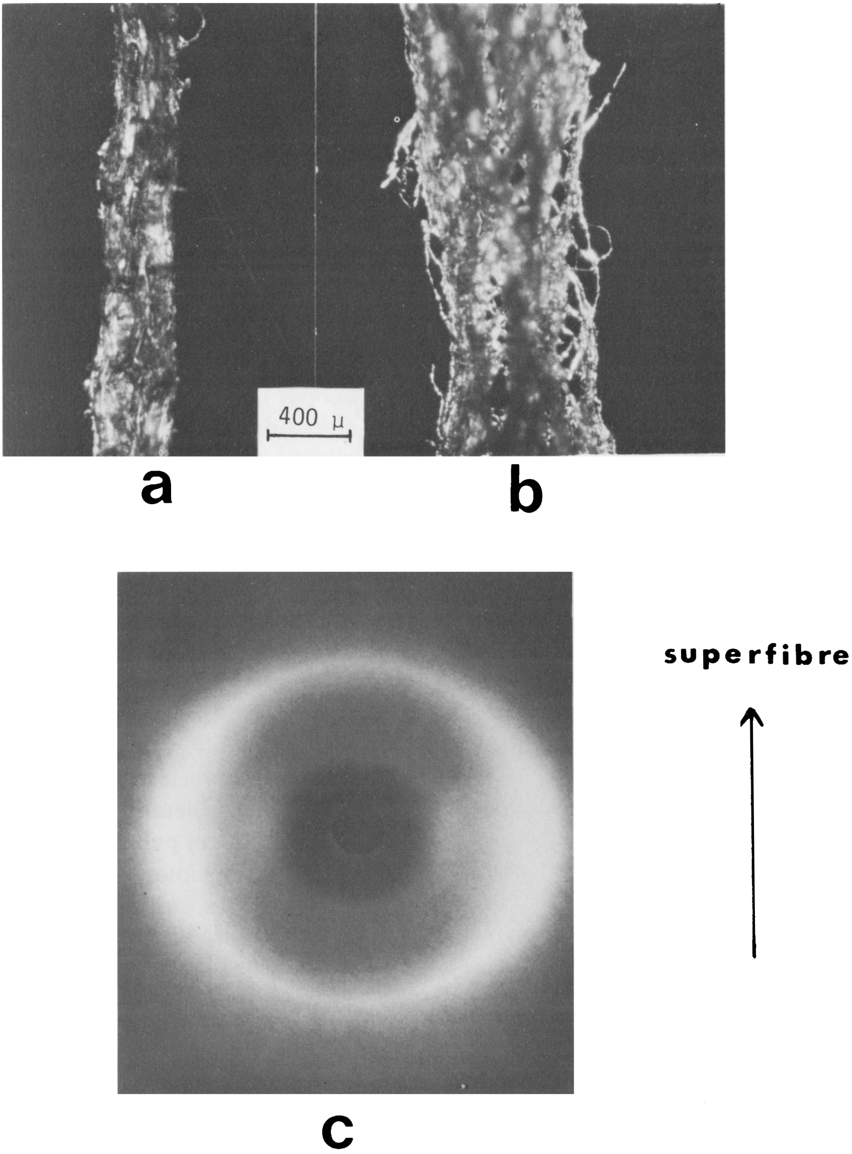

Fig. 6—Polarising microscopy of CLD and AQUALON superfibres (a) and (b) respectively. The fibre axis is at 45° with respect to the crossed Nicols. The characteristic X-ray diffraction pattern from both samples is shown in (c)

pattern showed traces of cellulose II it was characteristic of an oriented non-crystalline partial derivative of cellulose.(15) In Fig. 6 the difference in bulk density of the CLD and AQUALON one dimensional paper is clearly visible. The latter has a bulk density of $\sim 0{\cdot}5$ g/cm^3 while the former was $\sim 1{\cdot}3$ g/cm^3. In this respect both C_cGH_B and C_cGH_B resembled the AQUALON sample, i.e. response to surface tension forces during drying was far less than for CLD. It is believed that this reflects the internal homogeneity of substitution and crosslinking as well as certain intrinsic properties of the starting material such as the average fibre length.

Differences in bulk density of CLD and AQUALON are best visualised in the scanning electron micrographs shown in Fig. 7. Large micropores are visible in the AQUALON system and a substructure consisting of aggregates of several oriented linters fibres is visible. A similar kind of texture probably was present at some stage in the drying of CLD but the surface tension forces reduced this to a minimum on drying. By freeze drying the superfibre immediately after extrusion (Fig. 8) a microporous state similar to that of AQUALON is obtained. The air dried superfibres of CGH_B were similar in appearance to those of AQUALON.

To justify the use of the term one-dimensional paper, the development of mechanical properties during drying was observed. This was achieved by allowing freshly extruded superfibres to air dry for a period of time; then the remainder of the drying was achieved by sublimation. The mechanical properties of each sample were recorded after sublimation, in the conditioned state. The most important variables observed for superfibres prepared from CLD fibres are plotted against time in Fig. 9. It is readily seen that the behaviour as a function of time and ultimate values are characteristic of paper.

The sigmoidal shape of the curves in Fig. 9 is of considerable interest in papermaking. It is well known(1) that the compressive forces pulling hydrated papermaking fibres together are inversely related to the thickness of the liquid layer between the fibres. The uniform gel properties and the uniaxial geometry of the extruded strand of swollen CLD fibres has produced a high degree of co-operativity in the drying forces so that the inflections in the drying curves are unusually pronounced compared to similar data on paper.(16) The mid-point of the 'breaking length' curve is at 60 per cent water content: g.H_2O per g. wet material, the usual water content where interfibre bonding is thought to begin in paper made with normal fibres.(16)

Reconstituted cellulose fibres

WHEN paracrystalline gels of cellulose crystallites, prepared either by strong sulphuric acid hydrolysis or mechanical disintegration of $C_cH_AGH_B$, where

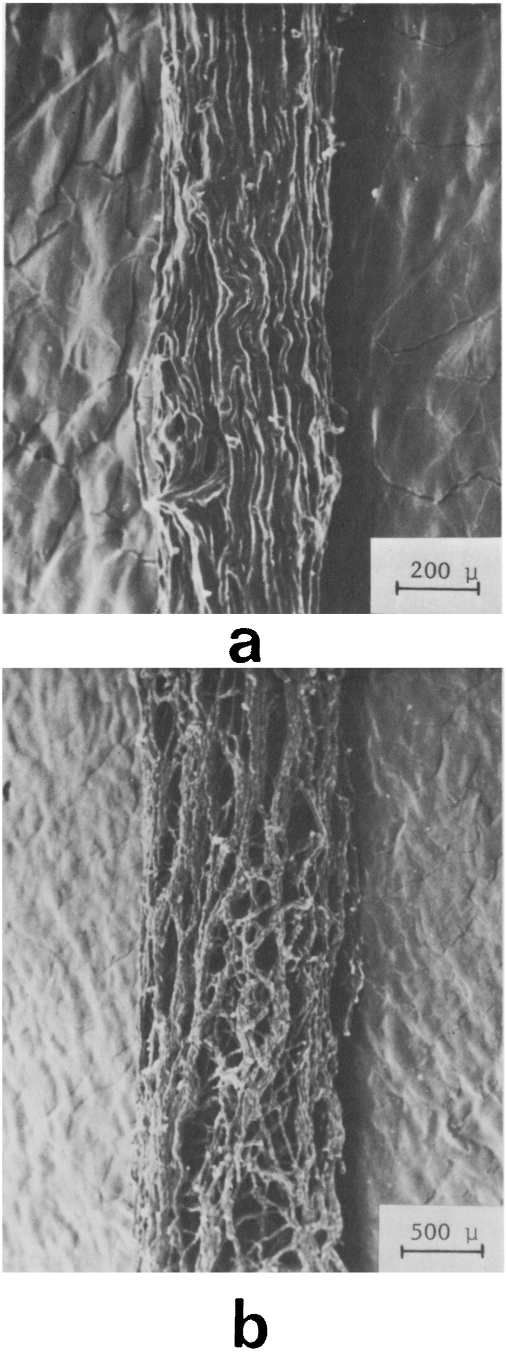

Fig. 7—Scanning electron micrograph of air dried superfibres: (a) CLD; (b) AQUALON

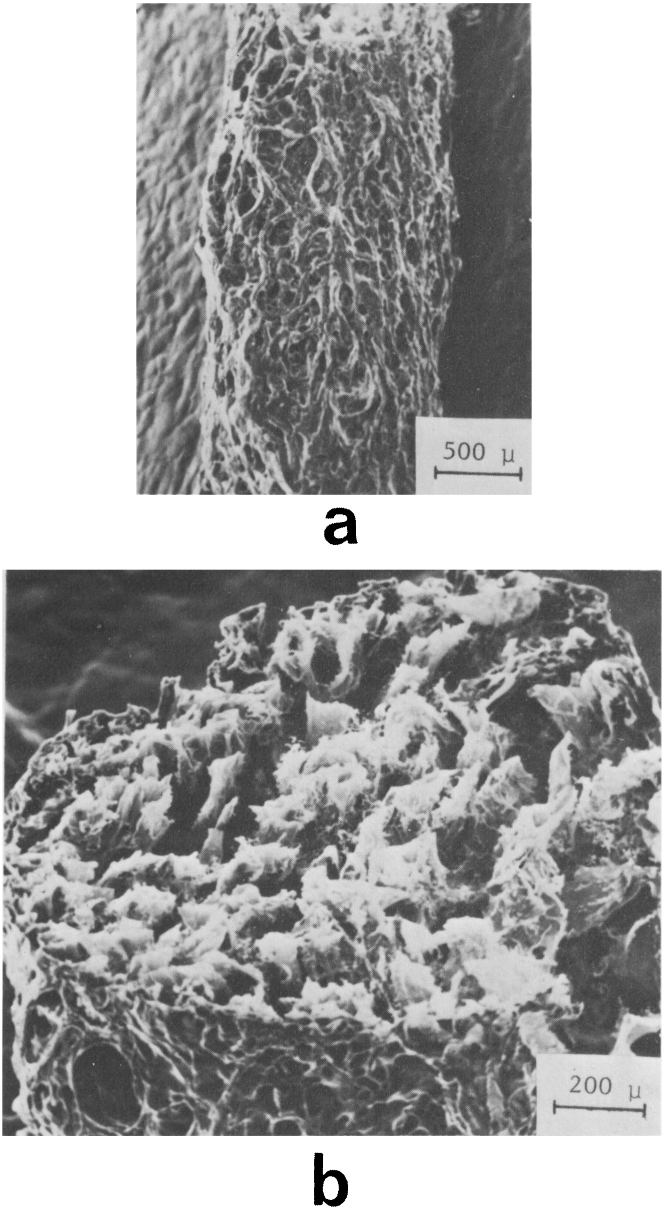

Fig. 8—Scanning electron micrographs of freeze dried CLD superfibre: (a) surface view; (b) cross-section

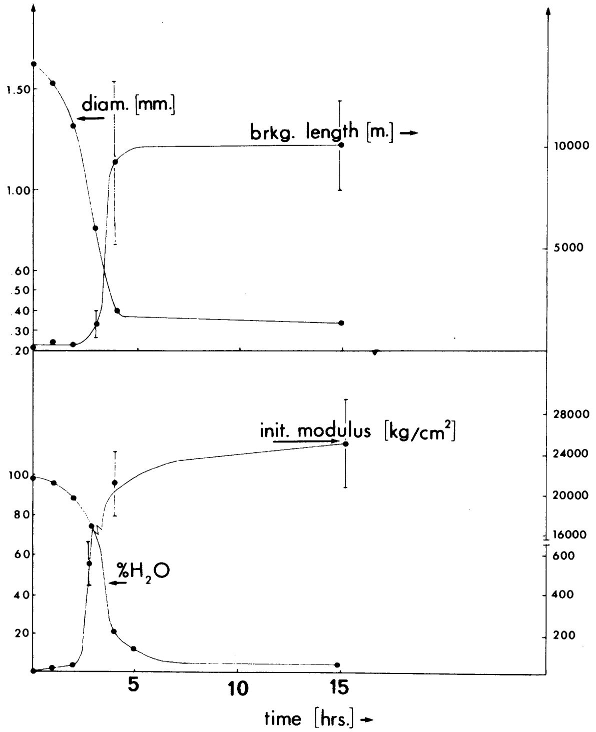

Fig. 9—**Study of changes in CLD superfibres as a function of drying time before freeze drying**

extruded in similar fashion to that used to prepare one-dimensional paper an oriented product was also obtained. The density of the continuous fibre from the sulphuric acid prepared crystallites was 1·57 g/cm³ (the CH_AGH_B fibre was not studied as to density because the polyacrylic graft was swollen in the organic liquids of the density gradient column) while its X-ray pattern showed about the same crystallite orientation as a cotton fibre (cf. Fig. 10). For this reason we refer to fibres and films of this material as 'reconstituted continuous filaments of native cellulose'. Because these fibres lack the continuity which would be provided by the 'fringe' in a 'fringe-micellar' structure (here, overlapping of the crystallites is the source of continuity) it was deemed worthwhile to measure their mechanical properties. Because of brittleness problems with reconstituted fibres it was easier to make measurements on unoriented crystallite films prepared by air drying a suspension. These measurements gave the results in Table 3.

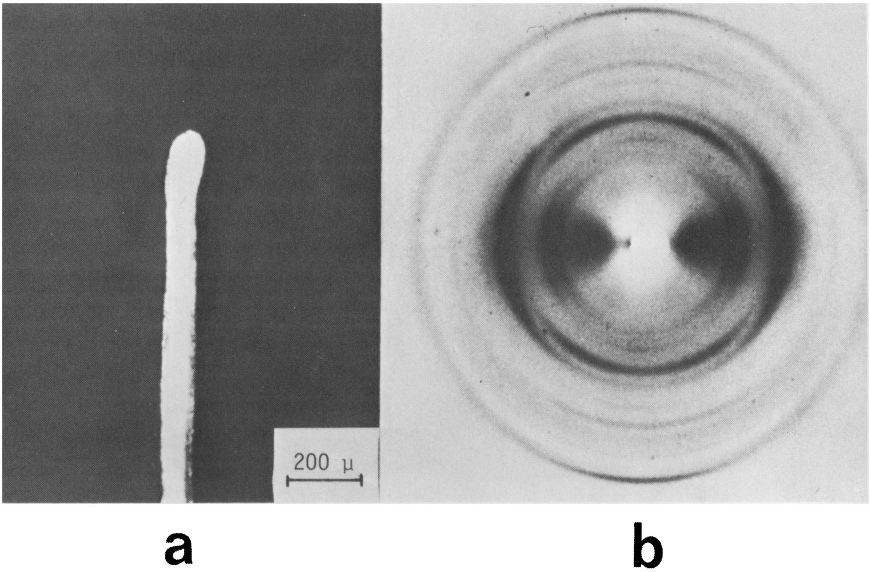

Fig. 10—Polarising micrograph of 'reconstituted cellulose fibre', (a), and its X-ray fibre diagram, (b)

TABLE 3—MECHANICAL PROPERTIES OF UNORIENTED CELLULOSE CRYSTALLITE FILMS* (RECONSTITUTED CELLULOSE)

Thickness (*μm*)	*Breaking force* (*g*)	*Elongation to break* (%)	*Initial mod.* (*kg/cm*^{2})
11·75	330	0·38	96 250

* Samples were 1·5 cm wide and 2·5 cm long, a strain rate of 0·05 cm/min. was used.

The rather modest breaking force and elongation at break attests to the brittle character of the samples. However it is to be noted that the initial modulus is typical of what was found for the superfibres (Fig. 9) of CLD. Since only hydrogen bonding forces are present between the crystallites, we conclude that these results support an often repeated thesis: with cellulosics the initial modulus is determined by the density of hydrogen bonds whether between crystallites, microfibrils, or cellulose molecules.(17)

'Wet strength' by polyethylene encapsulation

THE physical and mechanical properties of paper encapsulated with nascent polyethylene have been described previously(10, 18, 19) and a continuous process for modifying paper in this way has been developed.(20, 21) The study to be described in this section was undertaken in order to shed light on the mechanism of wet strength development as a result of nascent polyethylene 'add on' by this process.

One-dimensional paper prepared from CLD fibres as described above was used as a model substrate. Because of the exceptional density of the air-dried substrate, it did not absorb the polyethylene polymerisation catalyst; hence it was necessary to use a one-dimensional paper where part of the water was removed by freeze drying. The samples correspondng to '2 hours' in Fig. 9 was our starting material for the preparation of a series of samples with increasing polyethylene 'add on' up to 92 per cent 'by weight'. Fig. 8 corresponds closely to the physical appearance of the fibre that was used in this study. On placing the untreated superfibre in water it disperses spontaneously and within seconds into the individual fibres.

Despite considerable effort to adjust the polymerisation conditions, it was not possible to produce a uniformly encapsulated substrate. The nascent polyethylene was present as a skin uniformly mixed with the outer 10–20 per cent of the fibre diameter. Fig. 11 shows a scanning electron micrograph of a section of treated fibre. The core is similar to what is shown in Fig. 8 while the dense, polyp-like, nascent polyethylene skin is just visible at the surface.

The system was deemed an interesting model for testing how protection of interfibre bonding takes place. Because the untreated material undergoes immediate and complete dispersal when placed in water, it was rather astonishing to find that a polyethylene encapsulation of only 20 per cent was sufficient to indefinitely protect the substrate from dispersal.

The protection does not seem to be due to the strength of the polyethylene coating since tests have shown that the coating itself is too fragile to be tested when the cellulose is dissolved away. Furthermore, as was to be expected because of the heterogeneity of the coating, the fibres in the centre of the encapsulated one dimensional paper were wetted and swollen. The results of the stress-strain observations on the sample with 70 per cent polyethylene 'add on' are shown in Table 4.

TABLE 4—COMPARATIVE DATA TO SHOW WET STRENGTH DEVELOPMENT ON POLYETHYLENE ENCAPSULATION OF ONE-DIMENSIONAL CLD PAPER

Samples	*Diameter (mm)*	*Density* (g/cm^3)	*Breaking Strength (g)*	*Elongation to break (%)*	*Initial Modulus* (g/cm^2)	*Breaking Length (m)*
Control	1·20	0·11	42	10	45 000	350
Encap. (70% polyeth.)	1·20	0·18	90	9	120 000	465
Encap.+24 hrs. H_2O*	1·50	—	22	27	5 400	—

* Water soaked fibres were exposed to a vacuum to ensure good penetration.

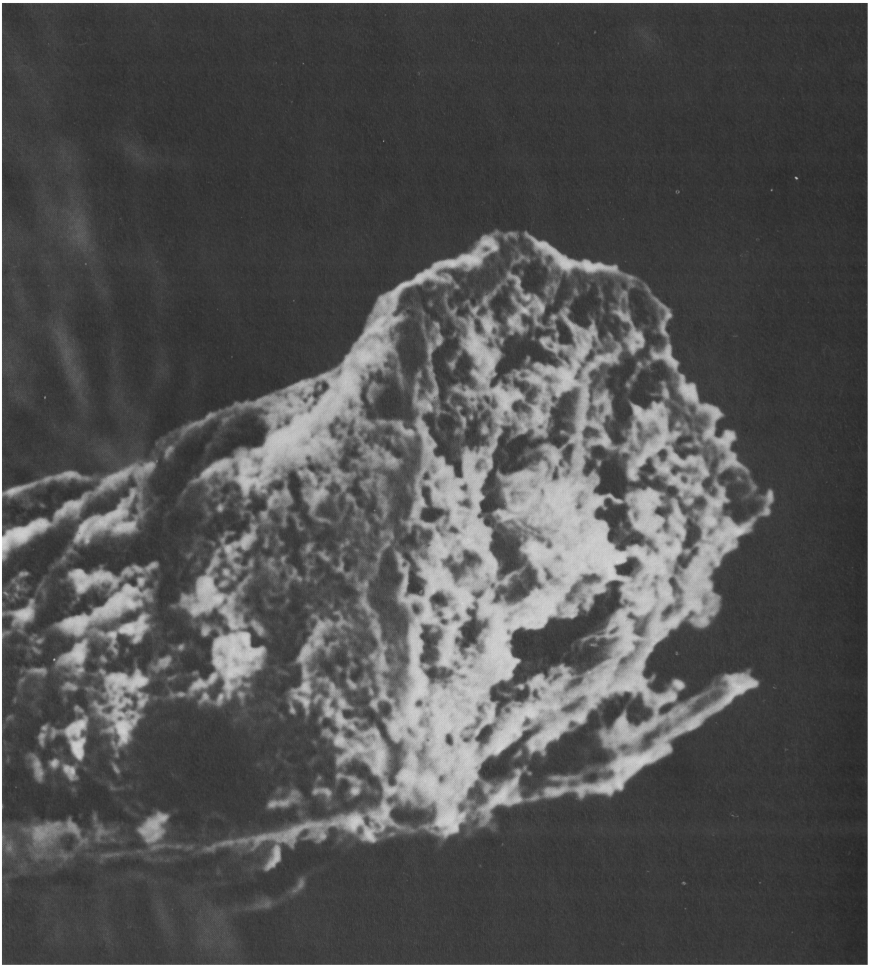

Fig. 11—**Scanning electron micrograph of sectioned encapsulated freeze dried CLD superfibre. The core is mostly cellulosic while the polyethylene is concentrated in the skin**

The increase in fibre diameter reflects the swelling of the central core. The marked increase in elongation to break and decrease in initial modulus leads one to conclude that considerable bond breaking has occurred. However the persistence of the fibrous strand suggests that breakage of interfibre bonds is a phenomenon more related to solvation of the individual fibres than attack of the interfibre bonds by water. Therefore, to the extent that the polyethylene

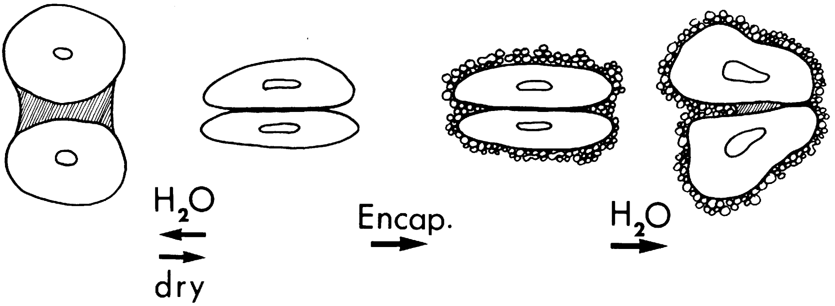

Fig. 12—**Schematic diagram to show influence of polyethylene encapsulation in restraining swelling of bonded cellulose fibres. With untreated fibres the swelling–deswelling process is reversible; for the encapsulated system, swelling is non-uniform and some interfibre bonds persist**

protected and restrained some part of the 'superfibre' from swelling and shape change, some interfibre bonds persisted and wet strength was imparted.

Since it is a property of the polyethylene encapsulate to intimately surround the surfaces to which it accedes, it would seem that it prevents a micro-reversibility of the deswelling process as shown in Fig. 12. In the case of filter paper where a far more intimate and uniform contract between nascent polyethylene and cellulose was achieved, a 50 per cent retention of strength was found for about 15 per cent 'add on'.(10)

Conclusions

A DISCUSSION of interfibre bonding has always been so intimately related to fibre preparation that it is impossible to discuss one without the other. It has always been difficult to separate the influence of fibre swelling from fibrillation since both were often produced simultaneously. CLD fibres are an example of a highly swollen system whose response to drying stresses demonstrate that fibrillation is not important if fibre plasticity is sufficient. By comparison, C_PGH_B does not comply, to the same degree, even through intrinsic swelling is about the same. This is attributed to a more heterogeneous structure, related to a preservation of the native microfibrils.

Both of these fibres are examples of the 'new look' in chemically modified cellulose, where the fibre morphology is used or enhanced by the treatment. The ease of extrudability of these systems brings the paper technologist to consider a papermaking process which does not depend on fibre settling. In view of the current interest in high consistency forming, an extrusion process with swollen fibres of the type discussed above has to be considered as a valid sheet forming process with a resultant high level of fibre orientation. This approach was used to convert pulp fibres into self bonded continuous filaments which are highly absorbent and have a fast wicking rate.(22)

Finally, it is interesting to note how easily CGH_B treated fibres are dispersible into microfibrils.(23) Although the chemical attachment of the polyacrylate to the cellulosic is often taken for granted, this is not easy to prove nor is it a matter of importance. The dispersion is reminiscent of the well known quince slime system(24) where an intimate mixture of cellulose microfibrils and an acidic polysaccharide gives the same uniform dispersion of microfibrils. Since rayon and papermaking technology respectively monopolise the cellulose molecule and the wood fibre it seems reasonable to expect that eventually some process will use the cellulose microfibril as a new supermolecular entity for materials exploitation.

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Discussion

Mr H. E. Lundström We have noticed with these 'super fibres' that after beating and drying they have a decreased absorption. Do you have an explanation for that?

Marchessault No I don't. What we did was to look for fibrils in the case of the carboxymethylated fibres versus the grafted fibres. Everything I said about the reconstituted cellulose based on the sulphuric acid system works equally well for the grafted fibres if you disperse them. In the case of the carboxymethylated fibres we looked for fibrillation without much success. We feel that the fibrillar structure has been badly damaged by the caustic which is used in making them.

Dr A. de Ruvo Have you tried to change the morphology by straining the fibres that you produced during drying? I am thinking of the super fibres?

Marchessault No, we let them dry freely.

de Ruvo As I understand it, in the carboxymethylated fibres you didn't obtain any crystallinity, and I thought maybe straining could produce this.

Marchessault We could have improved the orientation by drying under tension. However, at that degree of substitution it is difficult to get crystallinity.

Mr K. Bradway I would like to go back to the question of loss of absorption. This possibly comes back to Dr Goring's question which was why don't the fibres fly apart completely? I think the answer to that is that the swelling forces aren't great enough to overcome the forces holding them together. But the other question is, why don't they close up completely in water? I think such a reversion happens occasionally and could explain why you

Under the chairmanship of Dr N. K. Bridge sometimes see a reversion of the beating action. This may explain why the super fibres would seem to get less sorptive after they have been beaten.

Marchessault You noticed in my schematic diagram that I was implying a mechanical force was responsible for holding them. I am sure that it is more complicated than that. It is a fact that in the grafted case simple treatment in a Waring blender is enough to disperse the fibre into microfibrillar elements, as long as one is at the proper level of grafting. Your comment seems to tie in with Mr. Lundström's that the effect of beating is to decrease the hydratability.

Bradway All I meant was that the beating may bring these molecular chains together so that they can recrystallise. I think that would be a reasonable explanation for what Mr Lundström has observed.

Dr D. A. I. Goring If you dry these super fibres, particularly those that are made from crystallites—the reconstituted native cellulose—do they redisperse when rewetted?

Marchessault They re-swell, they do not completely redisperse.

Goring How much do they re-swell?

Marchessault I haven't got the exact figures here but I would guess they go back to about 25 per cent solids. One would imagine that there are some kind of residual domains that do not quite let go without a little mechanical treatment.

Goring This then is my question. Are you sure that the forces holding a super fibre together are only hydrogen bonds or is there also van der Waals bonding or, what in water would be, hydrophobic bonding between the non-OH containing surfaces of the cellulose crystallites?

Marchessault I would not be so bold as to claim only hydrogen bonds. When you have solids in such close contact there must be van der Waals forces of some kind. One has sulphate ester groups there so that there is obviously something other than just hydroxyls, however I believe that the main forces are the hydrogen bonds. According to the crystallography of native cellulose hydroxyl groups would be about equally present on all the surfaces of the microfibrils and on that basis that the forces would be similar on all faces.

Dr A. H. Nissan Thank you for drawing my attention to the figure you have. If the only bonds were hydrogen bonds for a material like that, the modulus should be of the order of 10^{-11} dynes/cm^2. You give here 9 600 kg/cm^2 which is approximately $9{\cdot}5 \times 10^{-10}$ dynes/cm^2 which is approximately 10^{-11} dynes/cm^2.