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Swelling and Dissolution of Cellulose Part 1: Free Floating Cotton and Wood Fibres in N-Methylmorpholine-N-oxide–Water Mixtures

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Summary: Five modes describing the behaviour of cellulose fibres dipped in a chemical have been identified:

–Mode 1: Fast dissolution by disintegration into rod-like fragments
–Mode 2: Large swelling by ballooning, and then dissolution of the whole fibre
–Mode 3: Large swelling by ballooning, and partial dissolution of the fibre, still keeping its fibre shape
–Mode 4: Homogeneous swelling, and no dissolution of any part of the fibre
–Mode 5: No swelling and no dissolution (case of a non-solvent)

In the case of the behaviour of wood and cotton cellulose fibres in *N*-methylmorpholine-*N*-oxide (NMMO) and water mixtures, four domains of water content have been identified. Below 17% of water up to monohydrate (13%), the fibres are disintegrated into rod-like fragments and dissolve (mode 1). In NMMO – water mixtures containing 19–24% water, the cellulose fibres exhibit a heterogeneous swelling by forming balloons (composed of dissolved cellulose holds inside a membrane) separated with non-swollen sections. The whole fibre will completely dissolve (mode 2) in four successive steps (growth of the balloons, burst of the balloons, dissolution of the non-swollen sections and finally dissolution of the membrane). With still greater water contents (25–30%), only the ballooning phenomenon is observed, with a partial dissolution inside the balloon (mode 3). Above 35% of water, the fibres swell homogeneously and are not dissolving (mode 4).

Keywords: Cellulose; cotton; dissolution; *N*-methylmorpholine *N*-oxide; swelling

Introduction

A large part of the cellulose chemistry, physics and technology deals with the swelling and the dissolution of native cellulose. It is thus natural that this topic has been attracted the attention of thousands of technologists, entrepreneurs and researchers over the last centuries. Despite cellulose is the more abundant biopolymer produced on Earth and that it may be of greater and greater importance over the next years, a lot of important questions have yet to be understood. The first deals with the mode of biosynthesis of the vegetal cell where cellulose is buried among other polysaccharides and substances. Another is the exact organisation of the cellulose structures among natural substances and the origin of its variability. Another of less general scope, but of scientific and technological importance, is the way cellulose structures dissolve.

Cellulose is the major constituent of plant cells and is present in most of them.[1]

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Plant cells are usually composed of several well documented layers or walls that have their origin in the way plant cells grow [Albersheim 1974, Heller 1985, Esauk 1965, e.g.]. A first wall, called *primary wall*, is formed during the first stages of the development of the cell. It contains cellulose, hemicelluloses (xylan, mannan, galactan, etc) and pectins. It is a composite material with a complex, mainly isotropic, structure. It is an extensible structure, able to accommodate the subsequent growth of the cell. A second stage in the plant growth sees the formation of the *secondary wall*. It is formed by the successive deposition of successive cellulose layers along the primary wall. The secondary wall is usually much thicker than the primary wall. It is also much more oriented than the primary wall,[2] but the orientation is very variable, from fully aligned to lying at large angle along the fibre direction. Such orientation variation depends on the type of plant, of the type of growth, and is also present inside the secondary wall itself. The secondary wall structure is thus complex, and the descriptions found in the literature (for example the number of sub-layers that are present in the secondary wall) greatly vary from one paper to another, depending mainly on the sample used. At a later stage, the *middle lamella* is formed, as glue between the cells. In wood, the middle lamella is mainly composed of lignin. Water should not be forgotten as it is a major component of plant cells. This is this complex cell structure, very variable in structure and composition, which must be purified in order to extract cellulose.

Cellulose is present in several forms in the cell walls, as it is expected from a semi-crystalline polymer. Non–crystalline (called amorphous) regions of different levels of order are co-existing with crystalline regions of cellulose I crystal structure. Cellulose I is thought to be in a parallel arrangement, with two types of structures called α and β. A very interesting point is that the parallel arrangement is not the most stable structure for a cellulose crystal. When dissolved and recrystallised, cellulose adopts a new crystalline structure when the cellulose chains are in an anti-parallel arrangement called cellulose II. The transition from Cell I to Cell II has brought a lot of work. To avoid having to completely change the direction of one chain over two, a very unfavourable energetic situation, it has been postulated that Cell I crystals are randomly produced with up and down orientations. The transition to cell II crystals requests then only a translational movement.

The literature is full of papers describing the swelling and the dissolution of cellulose. Substances are thought to be either inactive or bringing decomposition, fine dispersions, strong swelling and dissolution.[3] Swelling is occurring by the transport of the swelling agent through a system of pores and channels, leading to some splitting of hydrogen bonds of the cellulose dense, but accessible (meaning most of the time amorphous) regions.

It is generally admitted that cellulose is difficult to dissolve due to a tight array of inter and intra hydrogen bonds that are hard to break to free individual cellulose chains. For this reason, cellulose needs to be "activated" or "accessible" to be dissolved, even if these notions are not clearly defined. It is usually stated that cellulose crystals are difficult to dissolve and that they are the limiting point for dissolution.

Of interest for our work are the notions of swelling agents and of dissolving substances. Many materials are reported to swell cellulose, among them water. When looking to the way swelling is described in literature, several cases called "irreversible swelling"[4] or "infinite swelling"[3] are associated with the fact that when regenerated from such a state, cellulose recrystallizes in the Cell II form.

Polymer dissolution[5] in solvents is an important area of interest in polymer science and engineering because of its many applications in industry such as membrane science, plastic recycling and drug delivery. The dissolution of non – polymeric materials is different from polymers because the dissolution process is in the former case generally controlled by the external mass transfer resistance through a liquid layer adjacent to the solid-liquid interface. The situation is quite different for polymers. The dissolution of a polymer into a solvent may involve two transport processes, one controlled by solvent diffusion and the other by the chain disentanglement. When a non-crosslinked, amorphous, glassy polymer is in contact with a thermodynamically compatible solvent, the solvent will diffuse into the polymer. Due to the plastification of the polymer by the solvent, a gel like swollen layer is formed along with two separate interfaces,[6] one between the glassy polymer and gel layer and the other one between the gel layer and the solvent.

As we will see in the following paragraph, the swelling and dissolution of cellulose fibres is not following this pattern, due to its complex chemical and physical structure. The aim of this series of papers entitled Swelling and Dissolution of Cellulose is to revisit the swelling and dissolution of cellulose structures by taking advantage of the availability of solvents which solvent power can be varied and controlled. One of the challenging issues that will be examined is the difference between swelling and solvating agents. The present report is the first of this series and it concerns the dissolution of cotton and wood fibres in the aqueous solvent *N*-methylmorpholine *N*-oxide-water. The cotton and wood fibres are floating freely in the solution: at least one extremity of the cellulose fibre is accessible by the solvent molecules and the fibre is free to move and rotate.

As we will see all along this series of paper, five modes describing the behaviour of cellulose fibres dipped in a liquid have been identified:

Mode 1: Fast dissolution by disintegration into fragments
Mode 2: Large swelling by ballooning, and dissolution
Mode 3: Large swelling by ballooning, and no dissolution
Mode 4: Homogeneous swelling, and no dissolution
Mode 5: No swelling and no dissolution

Four of them (mode1, 2, 3 and 4) are describing in this paper.

Swelling and Dissolution of Cellulose

Several proposals[7] have been made in recent years for a systematisation of the rather large number of cellulose solvent systems known today. From the viewpoint of the organic chemistry of cellulose, a classification according to the two categories of nonderivatizing and of derivatizing solvents has been proposed. The term ‘‘nonderivatizing solvent’’ denotes systems dissolving the polymer by breaking intermolecular interactions only. The group ‘‘derivatizing solvents’’, on the other hand, comprises all the systems where dissolution of cellulose occurs in combination with the covalent derivatization to an unstable ether, ester, or acetal. Both categories of solvent systems comprise aqueous as well as non aqueous compositions.

Many solvents have been reported to only swell cellulose, without being able to dissolve it completely. In addition, complete dissolution up to the molecular level has been challenged for nearly all solvents. Light scattering studies systematically show that cellulose aggregates of at least several hundred chains are present. The swelling of native cellulose has been the topics of thousands of papers due to its extreme technological importance, especially when the solvent is based on water. Cellulose is highly hygroscopic due to the favourable interaction of its hydroxyl groups with water molecules, but it usually considered that it is prevented from being dissolved in water because of its highly dense and ordered supramolecular structure.

The swelling and dissolution of cellulosic fibres seem to depend first on the origin of the fibre. Chanzy et al.[4] showed flax fibres dissolving in *N*-methylmorpholine *N*-oxide-water undergo dissolution through a sort of ‘‘disintegration’’ of the fibre into a series of spindle-like fragments, without swelling. On the contrary, cotton fibres swell first showing the often-described ‘‘ballooning’’ effect. If the ‘‘disintegration’’ of cellulose fibres has not been documented in literature, the "ballooning" effect of cotton fibres has attracted much attention due to its spectacular appearance. This quite intriguing effect is found when some native cellulose fibres like cotton or wood cellulose are placed into a swelling agent or a solvent. This swelling is not homogeneous along the fibres.[8] It takes place at some selected places along the fibres. This localised swelling gives the impression of having "balloons" growing. This ballooning seems to have been first reported by Marsh et al.[9] (they used cotton hair fibre swollen with alkali and carbon bisulfite), despite it was surely observed much before. Ott[10] proposed an explanation of this phenomenon that is widely accepted. Because the bulk of the fibrils in the secondary wall are oriented at an acute angle with respect to the long axis of the fibre, Ott deduced that the swelling is greater transversely than lengthwise (as it is generally for fibres where the orientation of the cellulose chains is mainly in the fibre direction).[11] Consequently, when raw cotton fibres are placed in certain swelling agent, the radial expansion of the cellulose in the secondary wall was thought to cause the primary wall to burst. As the expanding swollen cellulose pushes its way through these tears in the primary wall, the latter rolls back in such a way as to form collars, rings or spirals which restrict the uniform expansion of the fibre. This ballooning is occurring only when the primary wall is present on the fibre.

The explanation of Ott has been widely accepted. It supposes that each of the balloons seen for cotton fibres is a region where cellulose is in a swollen state, i.e. in a solid, gel form where the cellulose chains are not free, but trapped between network junctions. It supposes also that the primary wall rolled to same regular places along the fibre, preventing these regions to swell. We will re-examine all these facts in the present paper by studying cotton and wood fibres in aqueous solvent, N–methylmorpholine-N-oxide (NMMO) and water mixtures. This solvent offers the great advantage of having a variable solvent power by changing the amount of water. It can thus go from a very good solvent with low water content (below 17%) to a bad swelling agent when the water content is very large (larger than 35%).

Experimental Part

Samples

Three native fibres, one bleached cotton and two wood fibres, Buckeye VFC (pine wood pulp obtained after a treatment by vapour hydrolysis, the cooking having occurred in a sodium sulfite and soda solution) and Borregaard VHF (fir tree pulp obtained by an acid process with calcium bisulfite) have been used. The characteristics of the samples investigated are given in Table 1. The crystallinity is obtained by Fourier transform infrared spectrometry.[12] The values of Mn, Mw or Mz are determined by gel permeation chromatography (GPC).

Solvent Systems

The swelling and dissolution treatments were performed with mixtures of *N*-methylmorpholine-*N*-oxide (NMMO) and water with various contents of water.

The NMMO–water solvent was prepared as follows. The mixtures were based on the NMMO with 3% water (w/w) from Sigma Aldrich (powder). A quantity of distilled water is added to the NMMO powder in order to obtain one of the NMMO – water systems (17, 19, 20, 23.5, 25, 30, 35 and 40% per mass of water). All the swelling and dissolution experiments were carried out at 90 °C.

Table 1.
Properties of the cellulose samples.

	Bleached cotton	Buckeye VFC	Borregaard VHF
Crystallinity (%)	55	46	43
Mn (*1000) (g/mol)	262.9	63.9	152.6
Mw (*1000) (g/mol)	606.3	121.1	766.7
Mz (*1000) (g/mol)	998.4	215.2	1600.5
w (DP < 50)	0.1	0.3	0.3
w (DP < 200)	1.1	9.3	4.7
w (DP > 2000)	68.1	4.7	63.1

Preparation and Observation of the Solutions

The solutions were prepared by mixing cellulose and solvent in a container made of two glass plates. No agitation was applied to the system. About ten fibres were placed between the two glass plates. The fibres can move freely between the two plates. Only one extremity of cellulose fibres is attached by adhesive tape on plate in order to avoid the fibre to be too much affected by the solvent convection, which is causing difficulties for the optical observations. The solvent contained in a pipette was introduced by capillary forces between the two plates.

The swelling and dissolution of cellulose fibres were observed by optical microscopy with a METALLUX 3 (LEITZ) equipped with a LINKAM TMS 91 hot stage. The samples were investigated in transmission mode.

Information on the orientation of chain segments during swelling was obtained using a LEICA IM optical microscope in transmission with crossed polarizer and a LINKAM TMS 91 hot stage. Crossed polarizers were kept crossed at right angle while being rotated against the fixed fibres.

Studied Parameters

a) The following parameters have been studied in the case of heterogeneous swelling (balloons)

The geometry of the swelling fibre (see Figure 1) is defined by:

L_b = length of a balloon
D_i = initial diameter of the fibre in the dry state
D_f = diameter of a balloon

The maximum expansion of a balloon gives L_{bm} (maximum length of the balloon) and D_{fm} (maximum diameter of the balloon). The maximum expansion is reached either because the balloon bursts (solvents good enough to dissolve completely the fibre) or because its expansion is reaching a maximum and stops (bad solvents).

b) The following parameter has been studied in the case of homogeneous swelling: The ratio of fibre diameter after (noted $D_{swollen}$) and before (noted D_i) swelling is studied. The parameter $D_{swollen}/D_i$ indicates if the homogeneous swelling is significant.

Results and Discussion

The detailed description of the different swelling and dissolution mechanisms of cotton and wood fibres in NMMO-water mixtures is given below.

A. General Considerations about the Swelling and Dissolution in NMMO – Water

N-methylmorpholine-*N*-oxide (NMMO) is a crystalline compound that is melting at 182 °C.[13] It can form several stable and crystalline hydrates with water. The monohydrate (13% of water, melting temperature 74 °C[14]) has been shown to be a good solvent for cellulose.[15] It is now used

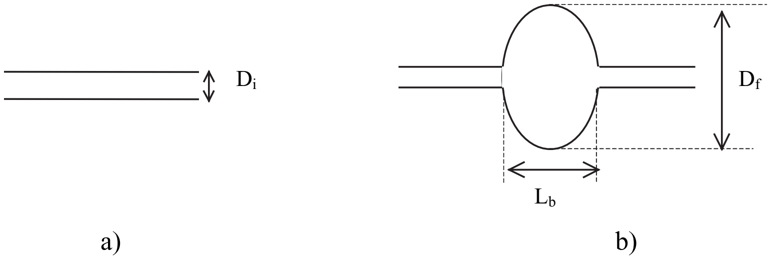


Figure 1.
a) Schematic drawing of the geometry of native cellulose at dried state; b) schematic drawing of the geometry of native cellulose fibre at swollen state.

commercially in the preparation of homogenous cellulose-NMMO-water solutions for manufacturing fibres, films and three-dimensional cellulose objects. Chanzy et al.[4] investigated the swelling behaviour and the dissolution process of various cellulosic fibres, both native and regenerated in *N*–methylmorpholine-*N*– oxide–water mixtures. Three domains of water concentration in the NMMO-water mixture were found to be important. When only a low percentage of water is present (below 16% of water), cellulose fibres, such as ramie, cotton, etc., dissolve readily without noticeable swelling in the NMMO-water system brought above its melting point, i.e. above 80 °C. At a higher water concentration (around. 19% for ramie), the cellulose fibres exhibit an extensive swelling but no dissolution. In this case, the removal of the swelling agent and the regeneration of the cellulose fibre in water showed that the initial cellulose I fibres were converted into a non-oriented cellulose II crystalline structure. Obtaining cellulose II and not cellulose I means that the crystal structure have been severally modified by the solvent, with a penetration of solvent in the crystalline areas and a freeing of the chains. The difference between dissolution and this irreversible swelling is an interesting question. With ever more water (above 20% for ramie), only a partial swelling (not everywhere along the fibre) is observed, and the native cellulose fibres kept their initial cellulose I structure after regeneration. When water concentrations exceeded 28% by weight, no visible changes occurred on the cellulose fibres immersed in the mixtures.

The designation «reversible swelling» corresponds to the case where no change of crystalline structure occurs within the diffracting crystals but does not exclude the occurrence of other irreversible structural and morphological modifications. There is a gradual change from one phenomenon to another with changing water content. The water concentration values of the three regions ranges may vary slightly with the origin, crystallinity, morphology, and pre-treatment of the cellulose samples used.

Nevertheless, it is remarkable that by changing the water concentration merely from 16 % to 20 % w/w, such a dramatic change from the dissolution of cellulose without swelling to reversible swelling was observed. We will use the capability of decreasing the quality of the solvent by adding water to NMMO to study in greater details the swelling and possible dissolution of cotton and wood fibre native cellulose. All the fibres have been investigated in a mixture of NMMO and water at 90 °C. The percentage of water in the swollen system NMMO–water was between 17 and 40%. Before swelling, the diameter of the studied initial dry fibres ranges between 5 and 10 μm.

B. Observations of the Swelling and Dissolution Mechanisms

The swelling and dissolution mechanisms of cotton and wood fibres vary in function of content of water in NMMO–water mixtures. Cotton and wood cellulose fibres in NMMO–water at 17% are disintegrated into a series of spindle – like fragments (Figure 2).

In the NMMO–water mixtures 19–23.5%, swelling by ballooning occurs and is followed by cellulose fibres dissolution. Upon increasing the water content to above 25%, balloons appear but they never reach the step of dissolution by bursting. In the range 35–40% of water in NMMO–water mixtures, the swelling process changes of nature: the fibres swell homogeneously and weakly (Figure 3).

C. Dissolution by Disintegration into Spindles

From the NMMO monohydrate (13%) to 17% of water in NMMO-water mixtures, the cotton and wood fibres are readily dissolved. Figure 2 shows the disintegration of wood fibres into a series of rod-like fragments. This mode of dissolution is called mode 1. Mode 1 requires good solvents. As soon as a contact is made with the solvent, the cellulose fibres are broken over all their length, producing

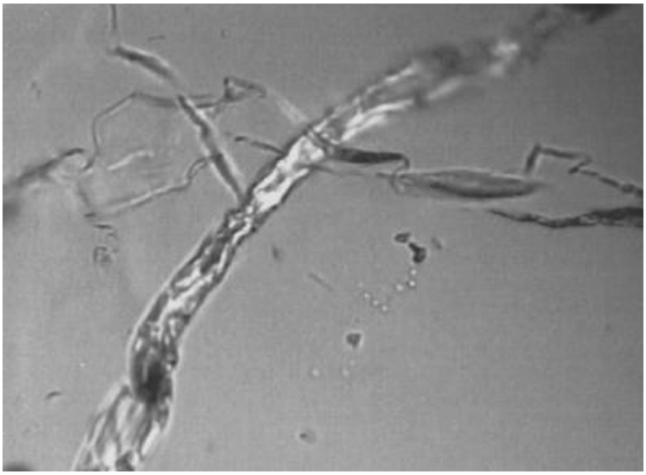


Figure 2.
Borregaard fibre swollen in NMMO–water at 17% (optical microscopy in transmitted light).

large rod-like pieces of cellulose fibers. They will then dissolve a short time after. No visible swelling occurs before the disintegration of the fibre structure in rod-like fragment.

The cotton or wood fibres are cut up at certain places along the fibre and the fibre ''opens'' by producing long fragments. Fragments are between 2 and 5 μm wide and between 30 and 50 μm long.

This fragmentation may be explained by considering that a good solvent will penetrate very quickly in weak zones, i.e. in amorphous regions or may be in some voids. A breaking in longitudinal fragments, much more long than wide, expresses the fact that there are long, connected, amorphous zones (where the solvent will quickly dissolves cellulose chains) and or voids that extend all along the fibre (where the solvent will penetrate by capillary forces), deep inside the secondary wall and over quite long distances. The fragments that are produced are then

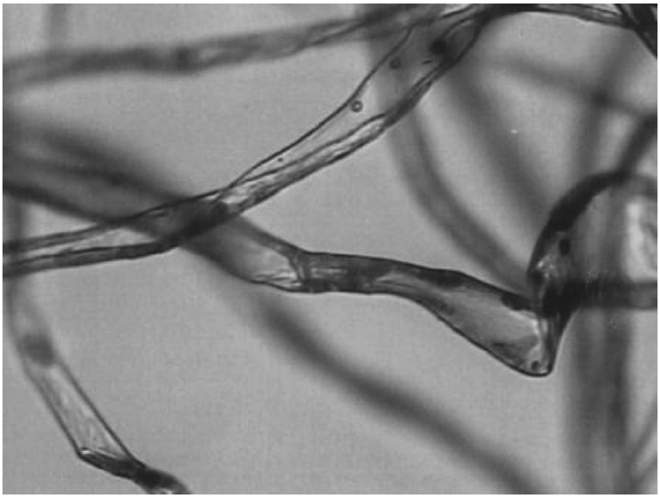


Figure 3.
Cotton fibre swollen in NMMO–water at 35% (optical microscopy in transmitted light).

dissolving as would do a normal polymer. It means that the dissolution occurs from the surface of the fragment, where cellulose chains are swelling locally up to there disentanglement point and then diffusing into the solvent. It is difficult to see if the dissolution is different at the surface coming from the inside of the fibre (which is made of secondary wall materials, i.e. nearly pure cellulose) or at the surface coming from the outside of the cellulose fibre (primary wall materials). A more detailed study of the produced fragments, if possible to isolate them is clearly needed.

D. Swelling and Dissolution Mechanism with Ballooning (Mode 2 and 3)

All the fibres studied show a first step of ballooning, whatever is the water concentration between 19 and 30%. An example of such ballooning is seen in Figures 4a and 4b. The fibres start to swell at given isolated points along the fibre.

The zones where the swelling starts increase their size, which leads to the appearance of Figure 4a. The fibre has a series of swollen transparent parts, of rounded shape, that we will call balloons. These balloons are growing until they reach a maximum size at which they will burst. In the following, we will call the "maximum diameter of balloon" (defined by the diameter D_{fm}) the size at which balloons burst, if they do. The bursting or not of the balloon is defining the two modes mode2 and mode 3:

Mode 2: the balloons reach a certain maximum expansion and burst. The whole fibre will then dissolve. This will be the case, for NMMO-water at 90 °C, of water contents between 19 and 24 %.

Mode 3: the balloons reach a certain maximum expansion, smaller than the one of mode 2, and the process stops. The fibre stays like this without dissolving completely. This will be the case, for NMMO-water at 90 °C, of water contents between 25 and 30%.

We can distinguish different zones within one fibre during the ballooning (seen in Figure 4). These various zones are called:

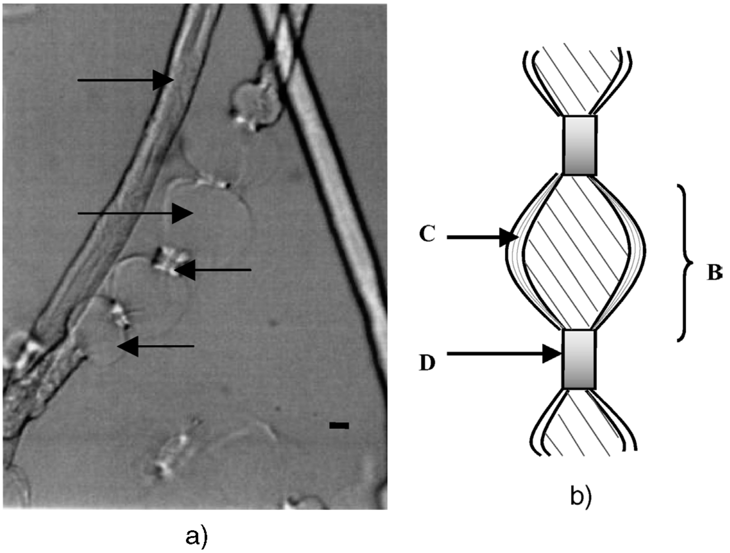


Figure 4.
a) Native cellulose swollen fibres (Borregaard fibre in NMMO – water at 23.5%, optical microscopy in transmitted light). A = non-swollen fibre; B = balloon; C = membrane; D = non-swollen section between two balloons. b) Schematic drawing of a swollen fibre of native cellulose. B = balloon; C = membrane; D = non-swollen section between two balloons.

- *non-swollen fibre* (A), part of one fibre, or a full fibre, that did not start yet the swelling process, but that will start later;
- in parts of the fibre that started to swell, one can distinguish three regions: the balloon (B) composed of cellulose swollen then dissolved inserted in a *membrane* (C) that is the wall of the balloon and *non-swollen sections* (D) which are situated between two balloons.

Maximum Expansion Degree

The swelling is always followed by the full dissolution in the case of all the studied fibres in NMMO-water having water concentration in the range 19 to 23.5% (mode 2). The dissolution will always occur if the experiment lasts long enough. In the largest water concentration (25%), the fibres will swell by ballooning, but the balloons will reach a size smaller than in mode 2, and the ballooning structure will stay as a stable situation. The balloons will not burst and the whole fibre will not dissolve.

The total dissolution kinetics and the maximum expansion degree depend on the type of fibre. After the completion of the swelling process, the native fibres showed balloons which diameter is 4 to 6 times higher than the initial larger diameter of the dry fibre. The diameter D_{fm} of balloon is the maximum diameter of the balloon, reached either because the balloons burst (concentration of 19–23.5%, mode 2), or because the expansion stops (concentration larger than 25%, mode 3). The D_{fm}/D_i values for each type of fibre are given in Tables 2, 3 and 4 for the various water concentrations.

Table 2.
Values of D_{fm}/D_i for cotton and wood fibres in NMMO – water (at water content 19%). D_{fm} = maximum diameter reached by the balloon before bursting, D_i = initial diameter of the fibres in the dry state, L_b = maximum length of the balloon.

	Borregaard		Buckeye		Cotton	
	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b
average	6.01	39.7	4.82	46.2	4.91	50.3
standard deviation	1.52	14.5	1.36	16.8	1.55	14.2

Table 3.
Values of D_{fm}/D_i for cotton and wood fibres in NMMO–water (at water content 20%). D_{fm} = maximaximum diameter reached by the balloon before bursting, D_i = initial diameter of the fibres in the dry state, L_b = maximum length of the balloon.

	Borregaard		Buckeye		Cotton	
	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b
Average	5.92	40.0	5.25	45.0	4.75	50.8
Standard deviation	2.02	16.5	1.14	14.5	1.42	13.8

E. Dissolution: Swelling by Ballooning, Followed by a Complete Dissolution of the Fibre (Mode 2)

We will examine the different stages from swelling to dissolution for the NMMO-water mixture at 19, 20 and 23.5%. All the studied fibres are following the same sequence of events from the start of swelling swell till the complete dissolution. Swelling and dissolution take place for all fibres in four subsequent phases. We will see in the forthcoming papers of this series that this sequencing of phases of swelling and dissolution called mode 2 takes place also in other solvents, for many cellulose fibres other than wood and cotton, and also for some cellulose derivative fibres.

Phase 1 = Appearance of Balloons Along the Fibres. After the introduction of the solvent, balloons appear along the fibres. The time needed for their formation depends on the type of native fibres, and of the quality of the solvent. The balloons do not appear at the same time along the fibre. The balloons give the aspect of a beaded structure, with the beads distributed in more or less regular

Table 4.
Values of D_{fm}/D_i for cotton and wood fibres in NMMO–water (at water content 23.5%). D_{fm} = maximaximum diameter reached by the balloon before bursting, D_i = initial diameter of the fibres in the dry state, L_b = maximum length of the balloon.

	Borregaard		Buckeye		Cotton	
	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b	D_{fm}/D_i	L_b
Average	5.27	38.6	5.29	45.3	4.84	47.6
Standard deviation	1.68	14.3	1.48	15.1	1.32	16.1

way depending on the type of native fibres (seen in Figure 5, photos A, B, C and D).

Phase 2 = Bursting of Balloons. The balloons continue to swell until they reach a maximal swelling ratio. They remain in this swollen state a certain time (that again depends on the type of native fibres) and then burst. The bursting occurs in the following way. It is very clear that the balloons are made of a *membrane*, which will break at its points of maximum extension. The *membrane* breakage is accompanied by a very rapid ejection of the liquid being inside the *membrane*, as if it were under pressure. This phenomenon is not simultaneous for all the balloons along a given fibre (seen in Figure 6). The scraps of the balloon

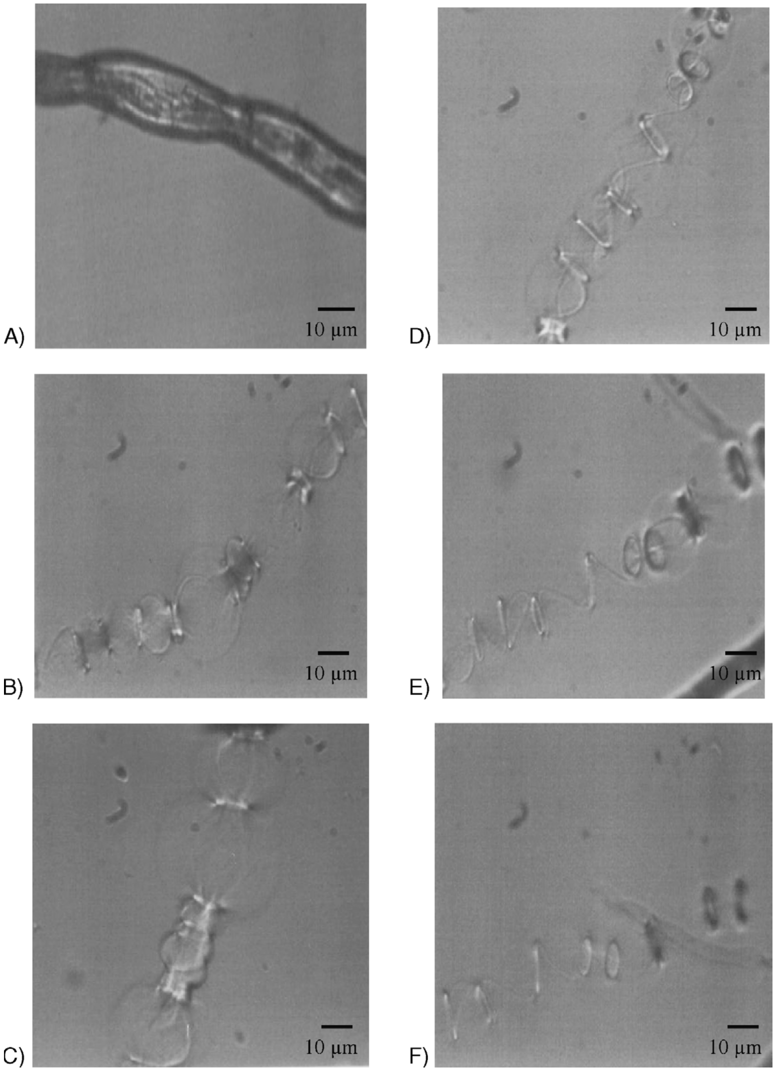


Figure 5.
Evolution of swelling by ballooning. (Borregaard fibre swollen in NMMO–water at 19%, optical microscopy in transmitted light). t = 0 min is the time where the solvent is introduced. Photo A (t = 1 min) = the fibre begins to swell. Photo B (t = 4 min) = the first balloons appear. Photo C (t = 8 min) = the balloons grow. Photo D (t = 12 min) = the maximum diameter is reached. Photo E (t = 19 min) = the first balloons burst. Photo F (t = 24 min) = all the balloons have burst; only the non-swollen fibre sections are seen.

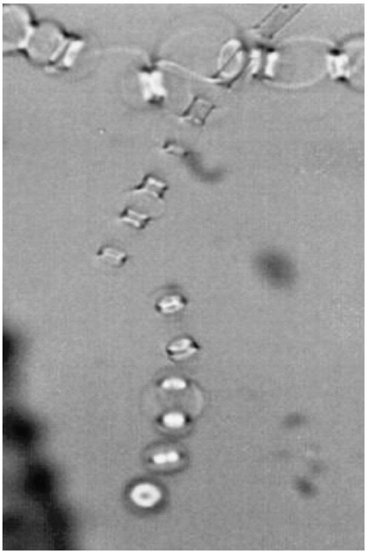


Figure 6.
Swelling and dissolution mechanisms – phase 2 (cotton swollen in NMMO–water at 20%, optical microscopy in transmitted light).

membrane remain then attached to the *non-swollen sections* of the fibres (seen in Figure 5, photos E and F).

Phase 3: Dissolution of the Non-Swollen Sections. During this phase the dissolution of the *non-swollen sections* of the fibres occurs. This dissolution begins at the *non-swollen sections* surface (and not at the two extremities) and goes on towards the fibre centre.

Phase 4: Dissolution of the Balloon Membrane Scraps. During this last stage, the scraps of the balloon *membrane* are dissolving. At the end of this stage, all the cellulose fibre is dissolved.

Phase 1: Balloon Formation

The formation of balloons is as follows. At some intervals along the fibres, certain zones of about the same length Lb starts to swell. With time, the zones swell more and more, keeping their original length Lb. The evolution of the shape of the balloons is detailed on Figure 7. The zones between the balloons keep their original size and the optical aspects of the initial fibre. No visible modifications occur in the *non-swollen sections* which are between balloons while the balloons are swelling.

Let's supposed that the outside of the fibre, primary wall plus a certain fraction of the secondary wall, that we called membrane), is not easy to dissolve. It acts as a semi-permeable membrane, allowing the solvent to penetrate inside the fibre to

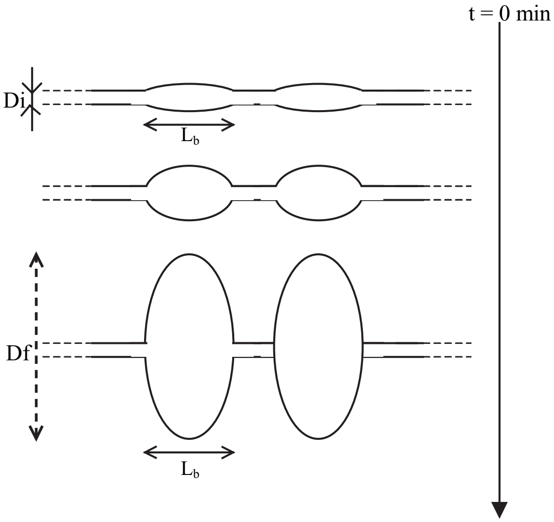


Figure 7.
Schematic drawing of the growth of balloons along a native fibre.

dissolve the cellulose of the secondary wall, but not allowing the cellulose chains to go out. The osmotic pressure thus created is increasing the volume of the balloon, and expanding the *membrane* that is holding it. At a certain moment, the balloon membrane will burst and the liquid inside will flow extremely rapidly out of the balloon region. The fact that when the balloon bursts, the material inside is flowing very rapidly shows that this material is fluid, of very low viscosity and that the inside of the balloon is at a higher pressure than the outside liquid medium. A major output of this finding is the cellulose must be dissolved and of low concentration. Otherwise, the behaviour of the inside of the balloon should be very different. In particular, if the balloon would be in a swollen, not dissolved, state, there would be no such type of rapid flow. It shows that was is usually described as a swollen state for these balloons is in fact a dissolved state. The balloon is a region where a cellulose solution is hold by a membrane.

After the introduction of the solvent, balloons appear along the fibres. The time needed for their formation depends on the type of native fibres. The balloons are not spherical: the size is larger perpendicularly than along the fibre. Furthermore, they do not present a regular circular perimeter. The border shape of the balloons is defined by a kind of helical ribbon (Figure 8) which surrounds the thin balloon wall we called *membrane*.

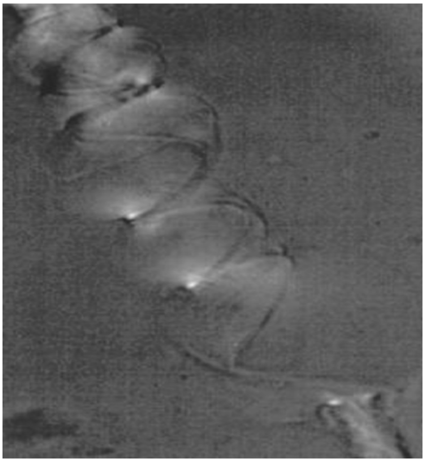


Figure 8.
Helical ribbon surrounding the balloons membrane (cotton in NMMO – water at 20%, optical microscopy in transmitted light).

In fact, these balloons are not smooth and do not have a symmetry of revolution around the fibre axis. They present a regular helical form. This can be seen in the series of pictures in Figure 9 and 10. Such helical ribbon has been noted long ago, mainly in cotton where they are the most visible. This helical ribbon can be seen as lines going from one *unswollen section* to the next with one turn. There are several lines per balloon, but their number varies

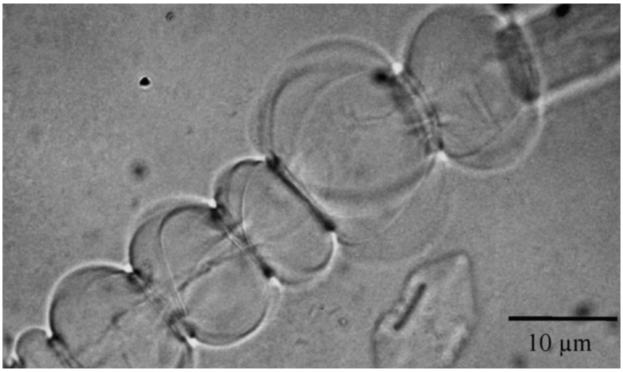


Figure 9.
Regular helical ribbon in the balloons membrane (cotton swollen in NMMO–water at 20%, optical microscopy in transmitted light, T = 90 °C).

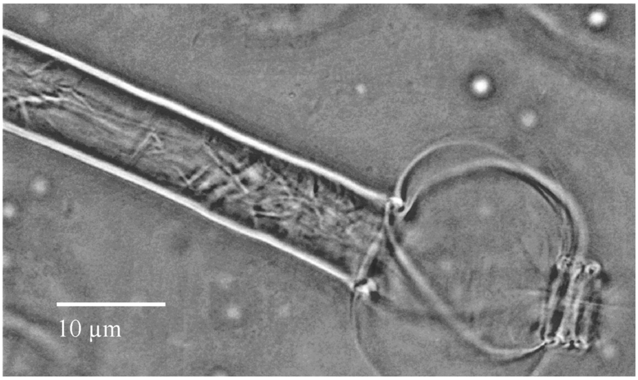


Figure 10.
Regular helical ribbon in the balloons membrane (Buckeye fibre swollen in NMMO–water at 23.5%, optical microscopy in transmitted light, T = 90 °C).

from one sample to another. Since the inside of the balloon is dissolved when the balloons are large, the regions with the ribbons are part of the *membrane*. When the swelling fibres were rotating around their axis due to solvents flow, it was clear that these helical ribbons were locations where the *membrane* was loosing its perfectly circular shape, making a sort of "fold down". The cellulose balloons are thus made of sorts of hills and valleys, the valleys being seen as lines turning in a helical manner around the fibre axis.

The swelling by ballooning occurred for the three studied cellulose fibres. The morphological aspects are identical for the three fibres in the three cases of NMMO–water solvents at 19, 20 and 23.5% but the positioning of balloons seems to depend on the origin of the fibres. The positioning of balloons along the fibre can vary. The balloons can be positioned in a periodic and regular way all along the fibre. It is the case for bleached cotton where the balloons are separated by *non-swollen sections* of 10 to 20 μm length. The balloons can also take place in groups of few balloons. These groups are randomly arranged. This occurs for wood fibres (Buckeye and Borregaard). The distance between two balloons groups fluctuates between 20 and 60 μm. The number of balloons per group is between 2 and 6. The distance between the balloons groups and the number of balloons varies in a random way. The effect of disordered balloon repartition along a fibre is accentuated in the case of Buckeye because the number of gathered balloons does not exceed three and theses groups are more distant than those of Borregaard fibre.

Before the introduction of a swelling agent, a fibre is birefringent because it is uniaxially oriented, the cellulose chains being oriented on average along the fibre direction. The birefringence changes differently in the various regions of the fibre after the start of swelling. The *non-swollen sections* of the fibre stay birefringent as the original fibre was and no modification is noticed during the growth of the balloons. The zones where the fibre starts to swell and where balloons are appearing (Figures 11 and 12) are loosing most of their birefringence, keeping four bright zones localised close to the two *non-swollen sections* (Figure 12). The location between these bright zones forms a sort of cross, as illustrated in Figure 13. When rotating the crossed polarisers, the dark cross (Figure 12) turns in the opposite direction of the rotation of the polarisers, with an angle equal to the rotation angle of the polarisers.

This property can be used to map the chain orientation inside the balloon by analogy with what is known for the orientation of the director of a nematic fluid confined into a sphere.[16] The way the dark

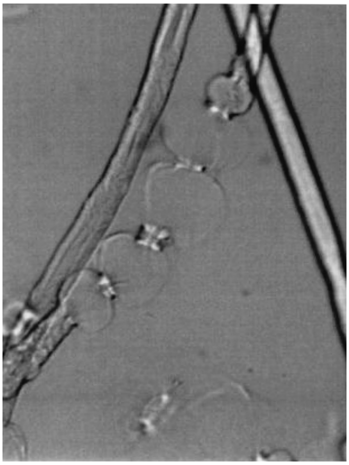


Figure 11.
Borregaard fibre swollen in NMMO–water at 23.5% in phase 1 (optical microscopy in transmitted light).

cross behaves when rotating the polarizers shows that the orientation of the cellulose chains that are leading to birefringence is similar to a bipolar nematic droplet (Figure 13). The two poles are at the extremities of the *non-swollen sections*. This chain orientation is due to the way the balloon expends.

Phase 2: Balloon Burst

The balloons are growing up to a certain diameter that is controlled by the quality of the solvent and the extension resistance of the *membrane*. When the solvent is good enough (NMMO-water at 19, 20 and 23.5%), its penetration through the *membrane* is not stopped by the mechanical resistance of the *membrane* and it continues to enter the balloon to dilute cellulose, thus increasing the expansion of the *membrane* up to its burst.

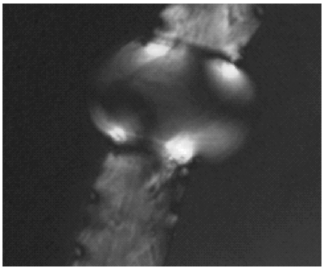


Figure 12.
Borregaard fibre swollen in NMMO–water at 23.5% in phase 1 (optical microscopy in transmitted light with crossed polarisers).

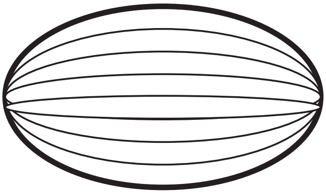


Figure 13.
Schematic drawing of the chains orientation in a bipolar nematic droplet.

The burst of the balloon occurs along the surface where the diameter of the balloon is the larger, i.e. about at the middle point of the balloon. This inside part is very fluid at the time of burst since it flows out very rapidly. After this liquid expulsion stage, only pieces of the broken *membrane* are left, floating in the solvent but still attached to the *non-swollen sections* of the fibres. These thin *membrane* scraps can be barely seen by light microscopy, being very transparent. All balloons are not bursting at the same time because they do not reach their maximal diameter at the same time. After this phase, only the scraps of the *membrane* balloons and the *non-swollen sections* remain.

Balloons are thus composed of a thin *membrane* containing the dissolved cellulose polymer. The fact that the balloon is growing means that solvent is penetrating inside the balloon to dissolve the cellulose chains, the *membrane* acting as a semi-permeable barrier: the solvent can penetrate, but the cellulose chains cannot go out. For the balloon to grow, the *membrane* must be able to deform. The length of the *membrane* from one *non-swollen section* to the next one is multiply by two during balloon growth, decreasing its thickness by a factor of four during the swelling.

The inside part of the balloon is very fluid at the time of bursting since it flows out very rapidly. The cellulose concentration inside a balloon C_i is equal to the inverse of the expansion degree if all the cellulose is dissolved, giving a concentration of 5–7% at burst. If we consider an average cellulose concentration C_i at 6%, the viscosity is around 0.4 Pa s[17] a low value in agreement with the rapid flow of the fluid during bursting.

After bursting, the *membrane* which is floating, attached to the *non-swollen* part, is still birefringent, showing four brightest points (Figure 14). They are localised very close to the *non-swollen* fibre sections. This shows that the *membrane* is made of oriented chains. No more helical structure can be seen.

A very important feature that was observed for the three types of fibres in mode 2 is that, for a given type of fibre, the swelling always leads to balloons that burst at the same expansion degree, independent on the solvent quality. This maximal diameter at burst does not seem to depend on water content of the NMMO–water solvent. For a given type of fibre, what differs from one selected fibre to another, or from one solvent to another, is the time needed to reach this maximum expansion degree before bursting. Increasing the water content of the NMMO–water solvent always increases the time for the balloons to reach their busting expansion ration and the time of total dissolution (dissolution of all the fibre parts), which is easily explained by the fact that the quality of the solvent is decreasing when increasing the water content. The kinetics of swelling may depends on it, but we were not able to check this.

Phase 3: Dissolution of the NON-Swollen Sections

After the burst of the balloons, two parts of the original fibre are still non-dissolved. The scraps of the *membrane* and the *non-swollen sections*, which was the link between two balloons. First, the dissolution of the *non-swollen sections* occurs. This phenomenon begins at the outer surface of the section (zone defined by 1 on the Figure 15). The border of dissolution goes progressively from the surface to the fibre centre (zone defined by 2 on the Figure 15).

The fact that this is the *non-swollen sections* (and not the *membrane* scraps), which is dissolving next, is intriguing. Even more intriguing is the fact that the dissolution occurs in the outer surface, not from the ends of the *non-swollen* section. This is strongly contradicting the hypothesis of Ott[10] that an outer *membrane* is slipping down to ''*non-swollen* part'' and preventing it to swell. The *membrane* is everywhere, and curiously, the scraps of the *membrane*

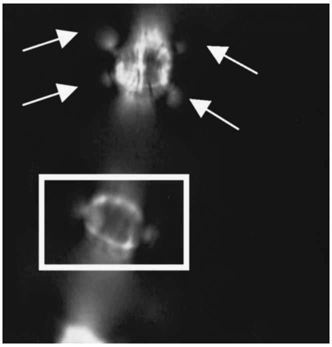


Figure 14.
Borregaard fibre swollen in NMMO–water at 19% in phase 2 (optical microscopy in transmitted light with crossed polarisers). The white arrows show the brightest zones belongs to the membranes scraps; the white rectangle indicates the non-swollen fibre section.

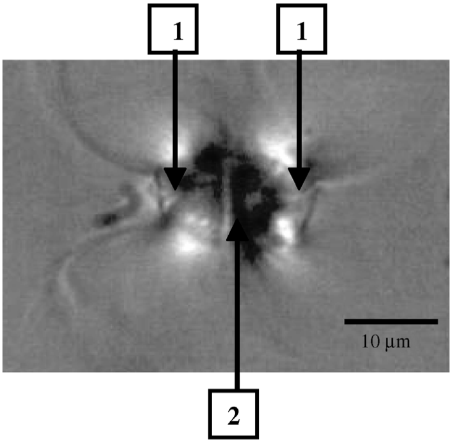


Figure 15.
Bursting of balloons (Borregaard fibre swollen in NMMO–water at 19%, optical microscopy in transmitted light).

that was around the balloon is not dissolving at the same time that the *membrane* around the *non-swollen* parts. It is the later ones that are dissolving first. The dissolution of the *non-swollen sections* goes smoothly, without swelling.

Phase 4: Dissolution of the Balloons Membrane Scraps

The scraps of balloons *membrane* are the last part of the fibres to be dissolved. Dissolution occurs just after that of the *non-swollen sections*. This phenomenon takes place rapidly. At this phase, the birefringence experiments show only the four brightest points. They correspond to the regions where the scraps of the balloons *membrane* are located. When rotating the crossed polarisers, there is an alternation of extinction and brightness for a given piece. The brightest zones become dark at an angle of 45° between the crossed polarisers.

The studied native fibres swell in the form of a ballooning process, and then completely dissolve even if the water content is as high as 23.5%. The balloon bursts at an expansion degree that does not depend on the quality of the solvent (the solvent must nevertheless be good enough to be in mode 2). The kinetics of the balloon growing and of the total fibre dissolution is slower with increasing the water content in the NMMO-water mixture, thus decreasing its quality.

F. Swelling with Balloons, but no Dissolution of the Whole Fibre (Mode 3)

As it was said, the balloons are growing up to a certain diameter that is controlled by the quality of the solvent and the extension resistance of the *membrane*. For not so good solvents like NMMO-water between 25 and 30%, the growth is stopped because the resistance of the membrane exceeds the osmotic pressure of the solvent that wishes to dilute the cellulose solution. Equilibrium is attained and the maximum swelling degree of the balloon is thus a measure of the quality of the solvent. As will be seen in the following paper that is dealing with the swelling and dissolution mechanisms of cellulose in NaOH-water, even when the balloons are not able to swell up to their bursting diameter, cellulose is still dissolved inside the balloon. In mode 3, the cellulose fibre is a mixture of dissolved (inside of the balloon) and non-dissolved (*non-swollen section* and *membrane*) cellulose parts.

G. Homogeneous Swelling (High Water Content) with no Dissolution (Mode 4)

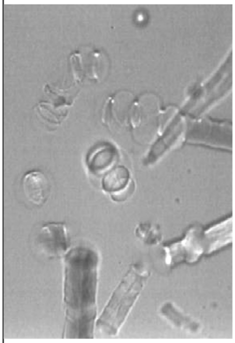
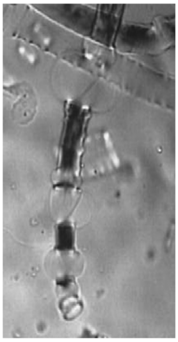
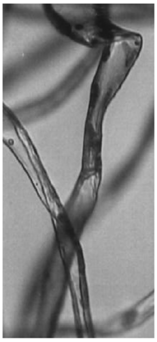
The cotton and wood fibres swell homogeneously (Figure 3) in NMMO-water mixtures with water contents higher than 35%. This behavior is called mode 4. It is characteristic of bad solvents. The swelling occurs very slowly, sometimes within hours. The fibres stay in this swollen state. Its main feature is that it does not dissolve cellulose, In this mode, the $D_{swollen}/D_i$ ratio is from 2.5 (for NMMO–water at 35%) down to a bit more than 1.5 when the water content is increased up to pure water, at 90 °C. This state is a real swollen state, where we can suppose that the chemicals are penetrating loose regions (pores, less dense disordered areas) without touching much the general organization of the fiber. In this mode, the cellulose crystals are not affected by the solvent.

Conclusions

The swelling and dissolution mechanisms change as a function of the water content in the NMMO-water mixtures (Table 5). Among the five swelling and dissolution modes we identified, four of them occur in NMMO–water mixtures at 90 °C.

Mode 1: the cotton and wood cellulose fibres are disintegrated in NMMO-water at 17%).
Mode 2: in the range of 19 and 25 % of water, the swelling and dissolution of native cellulose fibres are composed of four phases, concerning three zones (balloon, *non-swollen sections* and *membrane*) that

Table 5.
Different swelling and dissolution mechanisms for cotton and wood fibres in NMMO – water mixtures at various water content.

Content of water	< 17%	19 – 24%	25 – 35%	> 35%
Swelling and dissolution mechanism	Dissolution by disintegration in spindle (Mode 1)	Swelling by ballooning, dissolution (Mode 2)	Swelling by ballooning, no dissolution (Mode 3)	Homogeneous swelling, no dissolution (Mode 4)
10 μm	Wood fibre 	Wood fibre 	Wood fibre 	Cotton fibre 

have different swelling and dissolution mechanisms:

Phase 1: balloon formation
Phase 2: balloon bursting
Phase 3: dissolution of the *non-swollen sections*
Phase 4: dissolution of the balloons *membrane* scraps

Mode 3: above water concentrations of 25%, only the swelling by ballooning takes place (Phase 1 above), but the balloon does not burst. Only the part of the cellulose fibre that is inside the balloon is dissolved.
Mode 4: at water content higher than 35%, the cotton and wood fibres swell homogeneously and are not dissolved.

The ballooning phenomenon has been observed long ago. The observation of its kinetics in solvents where the quality can be varied offers the opportunity to draw several conclusions. The commonly adopted explanation about ballooning is:[10] "… *When raw mature cotton fibres are placed in certain swelling media, expansion of the cellulose in the secondary wall often causes the primary wall to burst. As the expanding cellulose pushes its way through theses tears in the primary wall, the latter rolls back in such a way as to form collars, rings or spirals which restrict the uniform expansion of the fibre*".

This description and explanation cannot resist to a careful examination of the different steps that lead to the dissolution of a cellulose fibre in modes 2 and 3. One of the most important findings of this study is that the so-called swollen balloons are in fact composed of a membrane holding a dissolved cellulose solution under pressure, able to flow out of the balloon if the membrane is broken. There is so a "membrane" around the balloon. If now the primary wall would slip down to the "non-swollen sections", making them difficult to "swell", it would mean that the most difficult part to dissolve would be this part. This is not the case since the last part to dissolve is the membrane holding the balloon.

The observed phenomena are clearly due to the way cotton and wood cellulose fibres are arranged, due to their biosy1nthesis and to their subsequent treatments, like drying or purification. An explanation of these phenomena requires studying more types of fibres and more solvents, first to see if they are general or only due to these fibres in this solvent. This is the topic of the next papers of this series.

[1] J. F. Kennedy, G.O. Philipp, P.A. Williams, "*Cellulose and exploitation, industrial utilisation, biotechnology, and physical – chemical properties*", Horwood limited publisher, London, **1990**.

[2] K. M. Mannan, Z. Robbany, *Polym. J.* **1996**, *37*, 4639.

[3] H. Leipner, S. Fischer, E. Brendler, W. Voigt, *Macromol. Chem. Physic.* **2000**, *201*, 2041.

[4] H. Chanzy, P. Noe, M. Paillet, P. Smith, *J. Appl. Polym. Sci.* **1983**, *37*, 239.

[5] B. A. Miller-Chou, J. L. Koenig, *Prog. Polym. Sci.* **2003**, *28*, 1223.

[6] K. Ueberreiter, in: "*The solution process, Diffusion in polymers*", Academic Press publisher, New York **1968**, p. 219.

[7] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, in: "*Fundamentals and analytical methods. Comprehensive Cellulose Chemistry (vol 1)*", Wiley-VCH, Weinheim, **1998**.

[8] H. A. Krässig, "*Cellulose: structure, accessibility and reactivity. Polymer Monographs (vol 11)*", Gordon and Breach, New York, **1993**.

[9] J. T. Marsh, "*The growth and structure of cotton, Mercerising*" Chapman & Hall Ltd, London **1941**.

[10] E. Ott, H. M. Spurlin, M. W. Grafflin, "*Cellulose and cellulose derivatives (Part 1)*", Interscience Publisher, New York **1954**.

[11] M. M. Roy, M. K. Sen, *J. Text. Inst.* **1952**, *43*, 396.

[12] T. Baldinger, J. Moosbauer, H. Sixta, "*Supermolecular structure of cellulosic materials by fourier transform infrared spectroscopy (FT-IR) calibrated by WAXS and 13C NMR*", Internal report from LENZING AG, A- 4860 Lenzing, Austria, **2005**.

[13] H. P. Fink, P. Weigel, H. J. Purz, J. Ganster, *Prog. Polym. Sci.* **2001**, *26*, 1473.

[14] P. Navard, J. M. Haudin, *J. Therm. Anal.* **1981**, *22*, 107.

[15] R. M. Armstrong, C. C. Corsley, J. K. Varga, *Proceedings of the fifth international Tappi dissolving pulp conference, Vienna*, **1980**, *100*.

[16] P. S. Drzaic, "*Liquid crystals dispersion, series on liquid crystals (vol 1)*", World Scientific publisher, London **1995**.

[17] J. F. Blachot, N. Brunet, P. Navard, J. H. Cavaille, *Rheol. Acta* **1998**, *37*, 107.