



Etude des mécanismes de gonflement et de dissolution des fibres de cellulose native

Céline Cuissinat

► To cite this version:

Céline Cuissinat. Etude des mécanismes de gonflement et de dissolution des fibres de cellulose native. Sciences de l'ingénieur [physics]. École Nationale Supérieure des Mines de Paris, 2006. Français. NNT : . pastel-00002729

HAL Id: pastel-00002729

<https://pastel.hal.science/pastel-00002729>

Submitted on 13 Jul 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



ECOLE DES MINES
DE PARIS

Ecole Doctorale 364 : Sciences Fondamentales et Appliquées

N° attribué par la bibliothèque

—| □□□□□□□□□□

T H E S E

pour obtenir le grade de
Docteur de l'Ecole des Mines de Paris
Spécialité «Sciences et Génie des Matériaux»

présentée et soutenue publiquement par

Céline CUISSINAT

24 Novembre 2006

**ETUDE DES MECANISMES DE GONFLEMENT ET DE
DISSOLUTION DES FIBRES DE CELLULOSE NATIVE**

SWELLING AND DISSOLUTION MECHANISMS OF NATIVE CELLULOSE FIBRES

Directeur de thèse : Patrick NAVARD

Jury :

M. Juergen Puls	Rapporteur
M. Herbert Sixta	Rapporteur
M. Thomas Heinze	Examineur
M. Herman Höfte	Examineur
M. Patrick Navard	Président

à Lui,

Remerciements

Je remercie la direction de l'Ecole Nationale Supérieure des Mines de Paris de m'avoir permis d'effectuer ce travail au sein du centre de Mise en Forme des Matériaux (CEMEF), à Sophia Antipolis.

J'adresse mes remerciements à Patrick Navard, mon directeur de thèse, qui a su enrichir notre collaboration par ses idées nombreuses et de qualité, et qui a toujours écouté mes suggestions.

Je remercie les membres du Jury, Messieurs Thomas Heinze, Herbert Sixta, Juergen Puls, Herman Höfte et Patrick Navard, d'avoir accepté d'évaluer mon travail et d'y avoir apporté leurs remarques.

J'adresse aussi mes remerciements à tous les représentants des entreprises et laboratoires qui ont contribué à l'avancée de mon travail. Je pense particulièrement à Thomas Röder de Lenzing (Autriche), Jonathan Marshall et Martin Cockroft d'Innnovia Films (Royaume – Uni), Thomas Heinze et Sarah Köhler du Centre d'Excellence de Recherche des Polysaccharide de l'Université de Jena (Allemagne), qui m'ont accueilli chaleureusement au sein de leur groupe de recherche pour partager avec moi leur connaissances scientifiques...et les plats typiques de leur pays.

Je voudrais témoigner toute ma gratitude aux personnes qui m'ont soutenue, écoutée et aidée au cours de ces trois années. Je pense tout d'abord aux personnes du groupe «Physico-Chimie des Polymères»: Olga, pour ses qualités humaines et son constant soutien, Tania, Edith, Roland, pour ses conseils et sa bonne humeur communicative, Patricia, les doctorants de 3^{ème} année (mes collègues de labeur dans le vaste univers des polysaccharides) et de 1^{ère} année (en particulier Monica et Nicolas). Je n'oublie pas non plus celles qui ont toujours été là pour résoudre les problèmes du quotidien (Marie – Françoise Guénégan et Sylvie Massol), et remercie aussi Emmanuel Levrat pour son immense patience. Je remercie très chaleureusement Monique Repoux pour son aide au quotidien. Et puis merci à tous ceux qui ont égayé mon travail par leur amitiés: Eric Tourette (mon binôme, qui a toujours subi mes humeurs et supporté mes lamentations avec le sourire), Magali Egal (pour son dynamisme, ses conseils et son immense disponibilité), Véronique Vaché et Nicolas Caillet.

Et enfin je tiens à remercier mes proches, qui m'ont permis d'arriver jusqu'ici: mes parents, (toujours là, même à des kilomètres), ma petite sœur qui m'apporte tant, Maryse, avenante et bienveillante, et surtout Aurélien, tout simplement parce c'est Lui.

Table of contents

Table of contents.....	1
Résumé francophone.....	3
Introduction	11
Chapter 1: Bibliography	15
Résumé francophone.....	15
Introduction	17
Table of contents.....	19
I. The fibre structure.....	20
I.1 Cellulose molecule.....	21
I.2. Supermolecular structure	24
I.3. Ultrastructure	28
I.4. Conclusion on the fibre structure	29
II. Structure of plant cell walls.....	30
II.1. Biosynthesis of cellulose	30
II.2. The cell wall constituents	32
II.3. The cell wall structure	38
II.4. Conclusion on the structure of plant cell walls.....	40
III. Swelling and dissolution of cellulose fibres	40
III.1. Dissolution mechanisms of dissolution.....	41
III.2. Important classes of cellulose solvents systems.....	43
III.3. Accessibility of cellulose fibres	46
III.4. Conclusion on cellulose dissolution	49
Chapter 2: Swelling and dissolution mechanisms of native cellulose fibres, part I: free floating cotton and wood fibres in N-methylmorpholine-N-oxide – water mixtures	55
Résumé francophone.....	55
Introduction	57
Article	59
Chapter 3: Swelling and dissolution mechanisms of native cellulose fibres, part II: free floating cotton and wood fibres in NaOH – water – additives systems	81
Résumé francophone.....	81
Introduction	83
Article	85
Chapter 4: Swelling and dissolution mechanisms of native cellulose fibres, part III: enzymatically – treated cotton and wood fibres in aqueous systems.....	99
Résumé francophone.....	99
Introduction	101
Article	103

Chapter 5: Swelling and dissolution mechanisms of native cellulose fibres, part IV: free floating cotton and wood fibres in ionic liquids.....	117
Résumé francophone.....	117
Introduction	119
Article	121
 Chapter 6: Swelling and dissolution mechanisms of native cellulose fibres, part V: free floating plant fibres in aqueous systems.....	 131
Résumé francophone.....	131
Introduction	133
Article	135
 Chapter 7: Swelling and dissolution mechanisms of native cellulose fibres, part VI: free floating cellulose derivatives in aqueous systems and ionic liquids	 145
Résumé francophone.....	145
Introduction	147
Article	149
 Conclusion.....	 157

Résumé francophone

Contexte et objectifs de l'étude

Les polysaccharides sont des polymères naturels, composés de molécules de sucres. Leurs fonctions principales dans la nature sont la structuration des plantes, du bois et du squelette animal (par exemple cellulose et chitine) et le stockage d'énergie (par exemple amidon et glycogène). Les polysaccharides sont des macromolécules composées d'un enchaînement d'un grand nombre de molécules unitaires, les monomères. On distingue les polymères naturels que l'on trouve dans la Nature comme la cellulose, l'amidon, le caoutchouc naturel, des polymères synthétiques fabriqués par l'homme comme le polyéthylène, le polyester ou le PVC. Chaque année, la Nature en produit environ mille milliards de tonnes. Renouvelables et complètement biodégradables, les polysaccharides sont les matériaux de demain par excellence, quand les ressources en pétrole commenceront à se tarir.

Les polysaccharides peuvent être considérés comme un matériau (fonction de structuration) dont les utilisations possibles sont proches de celles des matériaux plastiques issus de l'industrie pétrolière. Les polysaccharides ne se limitent pas à reproduire les caractéristiques de matériaux plastiques déjà connus, ils les améliorent notamment avec leurs caractéristiques biodégradables et biocompatibles. Des sacs en plastique «végétal» à base de polysaccharides existent déjà et ont les mêmes propriétés de résistance et de légèreté que les sacs plastiques synthétiques. Leur atout est la biodégradabilité : un sac de ce type se décomposera en quelques semaines contre quelques siècles pour un sac en polyéthylène. Parce qu'ils sont naturels, les polysaccharides bénéficient aussi d'une autre qualité : la biocompatibilité (compatibilité avec les tissus vivants). Les polysaccharides sont donc des biomatériaux qui peuvent notamment être utilisés dans la fabrication de médicaments, pansements ou prothèses médicales.

Les polymères naturels se distinguent des polymères synthétiques par leur complexité. Ainsi la cellulose extraite d'un chêne ayant poussé au nord de la France n'aura pas exactement les mêmes caractéristiques que celle extraite d'un eucalyptus ayant poussé au sud de l'Espagne. Il y a beaucoup plus de paramètres à prendre en compte qu'avec les polymères synthétiques. Jusqu'ici les efforts de la recherche sur les polymères étaient essentiellement concentrés sur les polymères synthétiques issus du pétrole et pour les polysaccharides, seule la cellulose a fait l'objet de recherches comme matériaux, principalement liées aux industries papetière et textile. La cellulose est déjà largement utilisée comme fil (coton) ou pour fabriquer du papier, des fibres (viscose), des films (cellophane) et des éponges (dites végétales). Or la plupart des procédés utilisés pour transformer la cellulose sont polluants. Afin de pouvoir généraliser et industrialiser l'utilisation des polysaccharides, il faut mieux comprendre ces matériaux et trouver des procédés d'extraction et de transformation plus propres et moins coûteux.

C'est sur ce problème que se penche notre travail : comment améliorer les procédés de transformation de la cellulose. Il faut savoir que la cellulose n'est pas un thermoplastique. Il est donc impossible de la mettre en forme par la fusion. Par conséquent, seules deux possibilités sont envisageables pour transformer la cellulose : il faut soit la dériver, soit la solubiliser. Nous nous intéressons particulièrement à la seconde possibilité : la solubilisation des fibres de cellulose. La dissolution de la cellulose est un problème complexe, la pénétration

d'un solvant n'étant possible uniquement par la rupture des liaisons hydrogène intermoléculaires. La voie de dissolution a donc été problématique jusqu'aux années 1950 et seul l'hydroxyde de cuprammonium était largement utilisé à cette époque. Le spectre des solvants de la cellulose a été largement élargi pendant la décennie qui a suivi. Par la suite, la recherche des procédés alternatifs de fabrication de fibres a conduit à la découverte d'un grand nombre de substances susceptibles de fournir de nouveaux solvants. Les procédés les plus répandus pour transformer la cellulose sont les suivants : procédé viscose (trempage de pâte de bois dans de la soude caustique puis ajout de sulfure de carbone), procédé carbamate (utilisation d'urée, d'ammonium liquide et de soude), procédé soude, procédé lithium-diméthylacetamide (Li/DMAc), procédé N-méthylmorpholine-N-oxyde (NMMO). Le seul procédé industrialisé est le procédé NMMO.

Au sein de tous ces procédés de transformation, l'étape de dissolution est une étape clé. Notre travail vise à mieux comprendre les mécanismes d'interaction entre les fibres de cellulose et les éventuels agents extérieurs afin de mieux maîtriser l'étape de dissolution et de définir de nouveaux solvants. Cela implique une observation détaillée des mécanismes de dissolution, ainsi que celle de l'étape de gonflement. L'objectif de notre travail est donc de revisiter les mécanismes qui conduisent à la dissolution de la cellulose native.

Cinq mécanismes ont été observés lors de notre étude, basée sur des fibres de cellulose native, d'origine diverse (coton, bois, ramie, jute, lin, chanvre, sisal et abaca). Les fibres sont étudiées dans une large gamme de solvant aqueux (NMMO – eau ou hydroxyde de sodium – eau) et des liquides ioniques. Les cinq modes observés de gonflement et de dissolution de fibres de cellulose natives sont les suivants :

- Mode 1 : dissolution rapide par désintégration de la fibre en fragments
- Mode 2 : gonflement par ballonnement, dissolution de toute la fibre
- Mode 3 : gonflement par ballonnement, dissolution partielle de la fibre
- Mode 4 : gonflement homogène, non dissolution de la fibre
- Mode 5 : pas de gonflement ni de dissolution (cas d'un système non solvant)

Ce résumé est organisé selon le même plan que le texte du mémoire. Pour commencer, nous ferons un point bibliographique sur la structure des fibres de cellulose et leur mode de dissolution et de gonflement, tout en présentant les différentes classes de solvants de la cellulose. Les cinq chapitres suivants décrivent les différents dispositifs expérimentaux testés et les résultats obtenus. Ces travaux seront proposés pour publication; c'est pourquoi les chapitres sont structurés sous forme d'article.

1. Etat de l'art.

Nous allons voir au cours de notre étude que la structure des fibres de cellulose influence les mécanismes de gonflement et de dissolution. C'est pour cela que nous décrivons au préalable leur structure, ainsi que la biosynthèse de la cellulose, à l'origine de la morphologie des fibres et des caractéristiques des parois externes de celles – ci. Ce chapitre comprend aussi une partie plus théorique sur la dissolution et le gonflement des polymères, suivie d'une classification des principaux solvants connus de la cellulose. La notion d'accessibilité est également expliquée.

La cellulose est un polymère naturel qui appartient à la famille des polysaccharides. Elle est renouvelable, biodégradable et peut être dérivée en de nombreux autres polysaccharides utiles. Nous nous intéressons à la structure de la cellulose aux niveaux moléculaire, supramoléculaire et morphologique. L'unité de base de la cellulose est le β -(1-4)-

anhydroglucose, et la configuration des unités anhydroglucosiques est une chaise de type 4C_1 . Chacun de ces motifs anhydroglucoses possède des groupes hydroxyles en position C-2, C-3 et C-6, susceptibles d'être impliqués dans des réactions mettant en jeu des alcools primaires ou secondaires. Les atomes d'oxygène réalisant un pont entre les cycles ou bien à l'intérieur même des cycles sont à l'origine des interactions intra- et intermoléculaires, principalement des liaisons hydrogène. Grâce à leur position équatoriale, les groupes hydroxyles sont disposés tout au long de la molécule étirée d'où leur faculté à engendrer des liaisons hydrogène. Les chaînes de cellulose ont une forte tendance à s'agréger entre elles pour former des entités structurales très ordonnées, en raison de la constitution chimique des chaînes et de leur conformation spatiale. Le regroupement des chaînes ainsi réalisé crée une structure semi-cristalline organisée au sein de laquelle on distingue: des zones très organisées (zones cristallines), des zones moins ordonnées (zones amorphes), un réseau poreux (cavités, capillaires, pores). L'arrangement de base de la cellulose sous forme cristalline est la microfibrille. Ces microfibrilles s'associent pour former des structures ordonnées plus grandes: les fibres. Celles-ci sont composées de plusieurs couches de microfibrilles dont l'orientation est précisément définie et qui dépend de l'origine de la cellulose.

Chaque fibre de cellulose provenant des végétaux présente, le plus souvent, trois couches ou parois (primaire, secondaire et tertiaire), chacune étant caractérisée par l'orientation des ses microfibrilles, ses constituants chimiques et leur répartition. Les propriétés varient en fonction de l'origine de la fibre de cellulose. Les hydrates de carbone (cellulose, hémicellulose, pectine) et la lignine sont les principaux composants chimiques des parois externes. Cette structure en parois trouve son origine dans la biosynthèse des fibres de cellulose. Chaque cellule végétale s'entoure d'une matrice lors de sa croissance, il s'agit de la paroi primaire. Une paroi secondaire se forme ensuite, par dépôt, lors de la maturation de la fibre de cellulose. Il est important de noter que la composition et l'agencement des composants de chaque paroi évolue dans le temps et varie en fonction de l'origine de la cellulose. L'orientation des microfibrilles est aussi déterminée lors de la biosynthèse.

Ce chapitre bibliographique comprend une dernière partie consacrée aux mécanismes de gonflement et de dissolution des polymères, et plus particulièrement de la cellulose puisque une classification des principaux solvants de la cellulose y est donnée. Nous distinguons les systèmes qui dissolvent la cellulose sans passer par un intermédiaire, et ceux passant par la formation d'un dérivé cellulosique. Cependant, avant l'étape de dissolution, il y a une étape de gonflement qui tient une place importante dans le mécanisme de dissolution et est fortement liée à la notion d'accessibilité. L'accessibilité traduit comment un agent externe va se comporter avec la fibre de cellulose, c'est-à-dire comment il va pénétrer au sein de la fibre, se diffuser et interagir avec elle. Dans le cas des fibres de cellulose, l'accessibilité est essentiellement déterminée par son système poreux. Le gonflement occasionné par l'interaction entre une fibre de cellulose et un agent chimique est défini par sa capacité à briser les liaisons secondaires entre les chaînes pour former ses propres liaisons avec le polymère. Il existe deux types de gonflement: inter cristallin (l'agent gonflant pénètre uniquement au sein des zones amorphes) et intra cristallin (l'agent gonflant pénètre aussi bien à l'intérieur des zones amorphes que de la maille cristalline, engendrant ainsi une distorsion du réseau cristallin).

2. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie I : fibres de bois et de coton dans le système NMMO – eau.

Les premières descriptions du gonflement et de la dissolution concernent les fibres de cellulose native (coton et bois) dans un des solvants le plus utilisé d'un point de vue

industriel: le système NMMO – eau. La teneur en eau de la solution NMMO – eau varie de 17 à 35%. L'immense avantage de ce mélange aqueux est que la variation de la teneur en eau permet de varier la qualité du solvant, de très bon à non solvant quand la teneur en eau tend vers 100%. Les mécanismes de gonflement et de dissolution des fibres de cellulose sont suivis par microscopie optique. Ce travail d'observation vise à détailler et décrire avec précision chaque étape du gonflement et de la dissolution.

Quatre des cinq modes de gonflement et de dissolution présentés précédemment sont observés en fonction de la teneur en eau du système NMMO – eau. Pour une concentration inférieure à 17%, la dissolution a lieu par désintégration de la fibre en fragments, il s'agit du mode 1. Pour une concentration en eau comprise entre 17 et 24 %, les fibres de coton et de bois commencent par gonfler de façon hétérogène (ballonnement) puis sont dissoutes (mode 2). En augmentant encore la concentration en eau (23-30%) du système NMMO – eau, seul le gonflement homogène des fibres par ballonnement est observé, avec une dissolution partielle à l'intérieur des ballons (mode 3). Entre 35 % et 45% en eau, le mécanisme du mode 4 est observé : les fibres de coton et bois subissent un gonflement homogène. L'étape de dissolution n'est jamais atteinte.

Les modes 2 et 3 sont particulièrement révélateurs de l'importance de la structure des fibres de cellulose puisque des ballons se forment le long des fibres lors de l'étape de gonflement. Nous définissons trois zones le long des fibres de cellulose: les ballons, la membrane des ballons, les sections non gonflées (zones situées entre les ballons).

Le mode 2 présente quatre phases dans le temps. Tout d'abord, des zones localisées le long de la fibre gonflent et forment des ballons (phase 1). Ces ballons sont entourés d'une membrane résistante. Le ballon continue de gonfler et son intérieur se dissout. Le moteur de l'expansion du ballon (phase 2) est la pression osmotique, qui, lorsqu'elle devient trop importante, fait éclater le ballon et disperser rapidement la solution de cellulose qui était à l'intérieur. Restent donc non dissoutes la membrane éclatée et les zones qui n'avaient pas gonflé entre les ballons. Ce sont ces zones qui se dissolvent ensuite, sans gonfler (phase 3). La membrane se dissout en dernier (phase 4).

Cette séquence d'événements n'est pas compatible avec l'explication classique d'une paroi primaire difficile à dissoudre qui se retrousserait comme un manchon ou un collet pour bloquer le gonflement de la cellulose. En outre, l'existence d'un réseau de lignes hélicoïdales autour des ballons doit être prise en compte. Nous proposons de considérer que la membrane est formée de la paroi primaire et d'une partie de la paroi secondaire (S1 à cause de l'angle de ses microfibrilles). Cette membrane difficile à dissoudre sert de support au ballon.

3. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie II : fibres de bois et de coton dans le système NaOH – eau – additifs.

Afin de déterminer si les premiers résultats obtenus sont intrinsèques aux solvants testés, nous avons observé les mêmes fibres de cellulose native (coton et bois) dans un autre système aqueux: NaOH – eau. La température (de -10°C à 5°C) et la teneur en soude (7.6% et 15%) varient lors de cette étude. Trois additifs (urée, oxyde de zinc et NMMO) sont également ajoutés au système NaOH – eau afin d'évaluer leur éventuelle influence sur le mode de gonflement et de dissolution des fibres.

Dans les meilleures conditions de dissolution selon le diagramme de phase cellulose – NaOH – eau (c'est à dire à une température de -5°C et une solution NaOH (7.6%) – eau), les fibres de coton et de bois gonflent de façon hétérogène, en formant des ballons. Il s'agit du mode 3. Augmenter la concentration en NaOH ou la température diminue la capacité à dissoudre du mélange NaOH–eau. En effet, les fibres de bois et de coton gonflent alors de façon homogène

(mode 4) dans ces conditions expérimentales. Quelques soient les condition expérimentales, le réseau de lignes hélicoïdales au niveau de la membrane est toujours observé. Les mécanismes de gonflement et de dissolution ne sont pas liés à la nature du système aqueux testé.

L'urée, l'oxyde de zinc ou encore la *N*-méthylmorpholine-*N*-oxide introduit comme additif au sein du système NaOH – eau ne modifient pas le mode de gonflement et de dissolution des fibres de coton et de bois. Le phénomène de ballonnement est toujours observé et la phase de dissolution n'est jamais atteinte (mode 3). Cependant, d'un point de vue cinétique ou de la capacité de la fibre à gonfler, quelques modifications peuvent être notées. L'addition d'urée permet aux ballons d'accroître leur diamètre. L'ajout d'oxyde de zinc accélère l'apparition des ballons. Quant à la NMMO, elle agit plutôt comme un inhibiteur sur le solvant NaOH – eau car les ballons se forment plus lentement et leurs diamètres restent inférieurs à ceux obtenus avec la solution de base NaOH – eau.

4. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie III : fibres de bois et de coton traitées par des enzymes en milieux aqueux.

Le phénomène de ballonnement ayant été largement observé et décrit, il est temps d'essayer de justifier sa présence lors du gonflement des fibres de cellulose native. Les explications concernant la structure et l'origine de la membrane entourant les ballons restent particulièrement vagues. Ce chapitre vise à éclaircir certains de ces points. Comme expliqué précédemment, nous avons émis l'hypothèse que la membrane des ballons seraient constituée de la paroi primaire et d'une partie de la paroi secondaire. Pour valider cela, nous avons travaillé avec des échantillons de fibres de coton et de bois, dépourvus d'une partie de leurs parois externes (paroi primaire et secondaire). Ceux - ci sont obtenus par traitement par des enzymes. Les mécanismes de gonflement et de dissolution des fibres de cellulose traitées sont observés dans les systèmes aqueux (NMMO – eau et NaOH – eau) et ainsi comparés à ceux obtenus avec les échantillons non traités.

Aucun des cinq modes de gonflement et de dissolution définis au préalable n'est observé, le mécanisme qui opère dans le cas des échantillons dépourvus d'une partie de leurs parois externes est tout à fait nouveau. Il se déroule en trois temps. La première phase consiste en un gonflement homogène des fibres traitées de coton et de bois. Ensuite, celles – ci se débloquent sur toute leur longueur et forment des sous - fibrilles (étape 2). La dernière étape concerne la dissolution de ces sous - fibrilles. En fonction des systèmes aqueux impliqués, toutes les étapes de ce mécanisme ne sont pas franchies. Par exemple, le système NaOH (7.6%) – eau, considéré comme un mauvais solvant, induit simplement le gonflement homogène des fibres.

Les fibres de bois et de coton, dépourvues de leur paroi primaire et secondaire ne gonflent plus par ballonnement. L'origine de ces ballons, et particulièrement de leur membrane, réside dans ce niveau morphologique de la fibre. La structure des fibres de cellulose native est ainsi le paramètre clé, influençant le mode de gonflement et de dissolution. L'origine de la naissance des ballons ainsi que la nature des lignes hélicoïdales au niveau de leur membrane sont liées à la paroi primaire et secondaire des fibres. Il est donc confirmé que la membrane des ballons est constituée de la paroi primaire et d'une partie de la paroi secondaire (S1).

L'autre donnée majeure retirée de ces expériences est l'influence des parois externes sur les fibres de cellulose et le gonflement. Nous pouvons à ce stade de notre étude faire l'hypothèse que l'étape de gonflement donnent aux fibres traitées la possibilité de se libérer des contraintes (mécaniques vraisemblablement) emmagasinées lors de leur biosynthèse. Cela se traduit par leur déroulement, aboutissant à leur explosion en sous fibrilles. La présence des parois externes empêcherait ce déblocage des fibres et induirait ainsi un mécanisme de dissolution autre.

5. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie IV : fibres de bois et de coton dans des liquides ioniques.

Les mécanismes de gonflement et de dissolution des fibres de cellulose native ayant été largement observés, détaillés et analysés en milieux aqueux, il est désormais nécessaire d'étendre notre domaine d'exploration des solvants. Les liquides ioniques font actuellement l'objet de nombreuses recherches car ils présentent des atouts intéressants en tant qu'agents gonflants ou de dissolution pour les fibres de cellulose. Ils sont en effet considérés comme des solvants «verts» : ils ne sont pas à l'origine de procédé industriel polluant et sont recyclables. Nous observons donc le comportement de fibres de coton et de bois (traitées enzymatiquement et non traitées) dans trois liquides ioniques: du chlorure de 1-N-butyl-3-méthylimidazolium (noté [C₄mim]Cl) auquel est ajouté environ un gramme de diméthyl sulfoxyde (DMSO); du bromure d'allylméthylimidazolium (noté CP040) et du bromure de butenylméthylimidazolium (noté CP041). Les liquides ioniques se composent d'un cation organique et d'un anion inorganique.

Le système [C₄mim]Cl – DMSO se révèle être un agent de dissolution pour les fibres de coton et de bois non traitées. En présence de ce liquide ionique, les fibres gonflent par ballonnement, puis sont dissoutes. Les quatre phases du mode 2 sont observées. Les ballons observés montrent clairement une structure enrobée par une membrane, présentant un caractère hélicoïdal. Les liquides ioniques CP040 et CP041 constituent uniquement des agents gonflants des fibres de cellulose native. En effet les fibres de coton et bois gonflent de façon homogène mais l'étape de dissolution n'est jamais atteinte (mode 4). Quant aux fibres de coton et de bois dépourvus de leur paroi primaire et secondaire, le ballonnement n'a jamais lieu, le gonflement est homogène. De même que pour les solvants aqueux, le mécanisme de gonflement et de dissolution se déroule en trois étapes (la phase de dissolution est atteinte ou pas en fonction de la qualité du solvant).

Les mécanismes de gonflement et de dissolution induits par les systèmes aqueux ou les liquides ioniques sont tout à fait similaires. Le mode de gonflement et de dissolution est ensuite contrôlé par la qualité du solvant, mais est indépendant de sa nature chimique. Les paramètres majeurs déterminants le mécanisme restent la structure de la fibre, et évidemment la qualité du solvant.

6. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie V : fibres de cellulose native, autres que coton et bois, en milieux aqueux.

Divers solvants (aqueux et liquides ioniques) ont été explorés pour cette étude sur le mécanisme de gonflement et de dissolution des fibres de cellulose native. Or toutes nos expériences portent uniquement sur les fibres de bois et de coton et nous avons vu que la structure de ces fibres occupe une place déterminante sur le mécanisme. C'est pourquoi une campagne d'expériences dédiée à l'étude de fibres de cellulose native d'autre origine a été conduite. Des fibres végétales extraites de feuille (sisal et abaca) ou de tige (lin, ramie, jute et chanvre) nous sont fournies sous deux formes: des fibres jamais traitées (que nous appellerons naturelles) et des fibres sous forme de plaque cartonnée où le végétal de cellulose a été traité pour en extraire la cellulose. Ces fibres de cellulose sont observées au contact de systèmes aqueux (NMMO – eau et NaOH – eau). La morphologie de ces fibres est voisine de celles des fibres de bois et de coton : elle diffère au niveau des composants chimiques présents au sein de chaque paroi, et surtout au niveau de l'angle d'orientation des microfibrilles par rapport à

l'axe de la fibre (plus faible pour ce type de fibres de cellulose native que pour le coton ou le bois).

Concernant les échantillons de fibres de cellulose issues de feuille ou de tige, n'ayant jamais subi de traitement, seuls les modes 1 et 4 sont observés. Le gonflement a toujours lieu tout le long de la fibre de façon homogène. La dissolution des fibres dépend ensuite de la qualité du solvant et de l'origine de la fibre. Le scénario du gonflement diffère dans le cas des fibres présentées sous forme de plaque cartonnée puisque le gonflement peut avoir lieu par ballonnement. Les modes 1, 2 et 4 sont en effet observés. Les ballons présentent toujours une hélice au niveau de leur membrane.

Ce qui est remarquable est que les mécanismes montrant un gonflement par ballonnement, dans le cas du coton ou des autres fibres de cellulose, sont exactement semblables: avec la même séquence d'événements aboutissant à la dissolution, et avec la même structure en hélice définie par un angle de spirale un peu près identique. La structure en hélice n'est donc pas liée aux microfibrilles déterminant une orientation par rapport à l'axe de la fibre, puisque cet angle change considérablement du coton au jute. La membrane entourant le ballon semble être moins résistante aux solvants que celle des fibres de coton et du bois, ce qui est compatible avec le fait que les fibres traitées soient plus faciles à dissoudre que celles de coton ou de bois (le système NMMO – eau avec une teneur en eau supérieure à 35% est un bon solvant pour le sisal ou l'abaca, alors qu'il ne l'est pas pour les fibres de bois et de coton). La présence des composants de fibre non cellulosique comme la cire et des pectines autour de la fibre empêche la formation des ballons, comme le montre les résultats obtenus à partir des fibres où le végétal a été traité pour en extraire la cellulose.

7. Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie VI : fibres de dérivés cellulosiques en milieux aqueux et dans des systèmes ioniques.

Toujours dans l'optique de généraliser nos conclusions et d'affiner notre raisonnement, une autre gamme de fibres de cellulose est étudiée. Il s'agit de dérivés cellulosiques. Pour cette étude, des fibres de cyanoéthylcellulose (-OH est remplacé par $-\text{CH}_2-\text{CH}_2-\text{CN}$), de nitrocellulose (-OH est substitué par $-\text{NO}_2$) et de xanthate de cellulose sont utilisées. Le nombre de groupements hydroxyles substitués par monomère est défini par le degré de substitution DS. Ces fibres sont observées par microscopie optique en présence de systèmes aqueux (NMMO – eau, NaOH – eau) ou de liquides ioniques (les même que ceux utilisés dans le chapitre 5).

Les fibres de nitrocellulose montrent des mécanismes de gonflement et de dissolution détaillés par les modes 1 et 4. Nos échantillons ont un DS identique mais varie en poids moléculaire. Les fibres de cyanoéthylcellulose, observées en milieux aqueux et avec les liquides ioniques, présentent des mécanismes de gonflement et de dissolution illustrés par les modes 2, 3 et 4. De nouveau, c'est la qualité du solvant qui détermine le mécanisme induit. Il est important de noter qu'avec ce type de dérivés cellulosiques, le gonflement par ballonnement est possible (contrairement aux fibres de nitrocellulose).

Que les fibres de cellulose soient natives ou dérivées, l'éventail de mécanismes de gonflement et de dissolution reste inchangé. La nature chimique du groupement accroché au monomère de la cellulose n'est donc pas un paramètre déterminant, pouvant être à l'origine du choix entre un gonflement homogène ou hétérogène. Cependant la nature du traitement effectué pour transformer les fibres de cellulose native joue tout de même un rôle puisqu'il peut empêcher la formation de ballons (cas des fibres de nitrocellulose).

Introduction

Polysaccharides (sometimes called glycans) are made of relatively complex sugar molecules (also called carbohydrates). The most common sugar found in polysaccharides is glucose. Polysaccharides are natural polymers. They have two main functions in Nature. The first consists in the structuring of plants, wood and animal skeleton (cellulose and chitin). The second function consists in energy storage (starch and glycogen). Nature produces thousand billion tons of polysaccharides every year. Natural polysaccharides, which are renewable, CO₂ neutral, completely biodegradable, have biocompatible characteristics (compatibility with living tissues) are one of the most promising materials of tomorrow. A complete new industry will emerge, based on glucose and its derivatives and polymers. The annual synthetic polymer production is a thousand time less important and mainly uses oil as raw material. But considering the pace of our consumption, oil will soon be completely exhausted (in 50 or 80 years according to predictions). Polysaccharides appear as a very appealing alternative of substitution, because they are a renewable raw material.

The best known polysaccharides are:

- Cellulose: it is the most widespread polysaccharide in Nature. It forms the primary structural component of plants and is made of repeated units based on the glucose monomer. It is not soluble in water and not digestible by humans but to eat the cellulose long fibres is good for health. Cellulose occurs naturally in almost pure form only in cotton fibres. Some animals, particularly ruminants and termites, can digest cellulose with the help of some micro-organisms.
- Starch: it is also a plant-based polysaccharide, which main function is the storage of energy. It is made of repeated units based on the glucose monomer but unlike cellulose, it is soluble in water and can be digested by humans. Starch stores the energy for plants, and it can usually be found in seeds or bulbs: potato, rice, wheat, and maize are major sources of starch in the human diet. Plants store glucose as amylose or amylopectin, which are glucose polymers collectively called starch.
- Glycogen: it is the storage form of glucose in animals. It is a branched polymer of glucose. In humans and other vertebrates, most glycogen is found in the skeletal muscles, but it is found in the highest concentration in the liver (10% of the liver mass). In the muscles glycogen is found in a much lower concentration (1% of the muscle mass). In addition, small amounts of glycogen are found in the kidneys.
- Chitin: it is a plant and animal-based polysaccharide, which main function is structuring. Chitin is one of the main components in the cell walls of mushrooms and in the epidermis (kind of shell) of arthropods (shellfish, insect).

Contrary to synthetic polymers, natural polymers are characterized by a structural complexity that is very variable. For example, cellulose extracted from oaks grown in the north of France will not have exactly the same characteristics as the one extracted from eucalyptus grown in the south of Spain. Compared with synthetic polymers produced by men, which properties are well-known and rather well - controlled, more parameters have to be taken into account regarding natural polymers.

Until now, research efforts on polymers have mainly concerned synthetic polymers coming from oil. Among polysaccharides, cellulose and starch has been subjected to an extensive research, mainly related to the paper and textile industries for cellulose and food for starch.

In this work, we will study cellulose. Apart from its utilisation in an unmodified form like wood and cotton, cellulose is mainly extracted to produce fibres for the paper industry. A small fraction is used for preparing cellulose derivatives that are mainly tailored to be structuring additives. Some derivatives are used as material like cellulose acetate making films or fibres. Pure cellulose is not widely used as a material. The main reasons are that it is not a thermoplastic, which hampers the manufacturing of complex pieces, and that finding suitable solvents is a difficult task. Pure cellulose is mainly processed through the viscose way (viscose fibres, cellophane, vegetable sponges) or through the *N*-methylmorpholine-*N*-oxide way, to produce fibres.

The full potential of cellulose has not yet been exploited for four main reasons: the historical shift to petroleum-based polymers from the 1940s onward, the lack of an environmental-friendly method to extract cellulose from its primitive resources, the difficulty in modifying cellulose properties, and the limited number of common solvents that readily dissolve cellulose. Traditional cellulose dissolution processes, including the cuprammonium and xanthate processes are often cumbersome or expensive and require the use of unusual solvents, typically with high ionic strength and use relatively harsh conditions. Moreover, these processes cause serious environmental problems. In recent years, the «green» comprehensive utilization of cellulose resources has drawn much attention from the governments and researchers. Traditional cellulose extraction and dissolution processes are facing challenges because of energy and environmental problems. Therefore, to make full use of cellulose resources, it is necessary to develop “green” cellulose extraction methods and suitable cellulose dissolution approaches.

Our work concerns the second point of this challenge: develop a suitable cellulose dissolution approach. Our aim is to detail with precisions the swelling and dissolution mechanisms of native cellulose fibre. To better understand how native cellulose fibres swell and may dissolve, it should help to design better solvents, and participate to the current efforts in understanding the cellulose fibres structure.

The manuscript is ordered in the following way. The first chapter is an bibliographical introduction on native cellulose fibre. The first part deals with the structure of cellulose fibre at molecular, supramolecular and morphological levels. As the ultrastructure takes play a major role in the interactions with chemical agents, the chemical constituents of cellulose fibres and their distribution among the cell walls are detailed. A last part concerns the theory on swelling and dissolution processes for polymer, especially for cellulose for which the notion of accessibility is explained.

The six others chapters are in the form of scientific articles. Chapter 2 is describing the behaviour of cotton and wood cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) and water mixtures. Five swelling and dissolution modes are observed and described. These five mechanisms will be the scale of comparison for all the work.

Chapter 3 describes the behaviour of the same type of cellulose fibres (cotton and wood fibres) in another aqueous solvent: sodium hydroxide (NaOH) and water solutions. The content of NaOH and the experimental temperature are modified to determine the influence of these parameters on the swelling and dissolution mechanisms. Addition of three different chemical components (urea, zinc oxide and NMMO) is investigated to estimate their influence on dissolution modes.

In the both previous chapters concerning aqueous solvents, the outer layers of cellulose fibres seems to play a key role in the swelling and dissolution process. In order to validate this assumption, enzymatically – treated cotton and wood cellulose fibres are dipped in similar aqueous systems and experimental conditions. Chapter 4 summarises these experiments.

Chapter 5 is expanding the range of solvent systems: cotton and wood fibres are dipping in ionic liquids (1-N – butyl – 3 – methylimidazolium chloride [C₄mim]Cl plus dimethyl sulfoxide (DMSO), allylmethylimidazolium bromide CP040 and butenylmethylimidazolium bromide CP041). Their swelling and dissolution mechanisms are described and compared with those observed in aqueous agents.

Chapter 6 is dealing with the behaviour of bast (ramie, flax, hemp and jute) and leaf (sisal and abaca) fibres, observed into aqueous systems: N-methylmorpholine-N-oxide (NMMO) – water with various contents of water and sodium hydroxide (NaOH) – water. Plant fibres are in two shapes: raw and pulps.

Chapter 7 deals with the swelling and dissolution mechanisms of derivatives cellulose fibres (nitrocellulose and cyanoethylcellulose) in aqueous solvents and ionic liquids.

The text ends with a conclusion part.

Chapter 1

Bibliography

Résumé francophone chapitre 1

Etat de l'art

Ce chapitre a pour but de rassembler les données sur la structure des fibres de cellulose afin de mettre en lumière l'importance et l'influence de celle – ci sur les mécanismes de gonflement et de dissolution des fibres.

Une description de la structure des fibres de cellulose (au niveau moléculaire, supramoléculaire et morphologique) est donnée dans une première partie. La cellulose est un homopolymère linéaire composé d'unités de D-anhydroglucopyranose (AGU) reliées entre elles par des liaisons glycosidiques β -(1 $\rightarrow$ 4). Parce que la cellulose est construite à partir d'un monomère qui est un sucre, elle appartient à la famille des polysaccharides. Les AGU se trouvent en conformation chaise et possèdent 3 fonctions hydroxyles, 2 alcools secondaires (en position 2 et 3) et un alcool primaire (en position 6). Des liaisons intramoléculaires et intermoléculaires peuvent se former entre fonctions alcools, ou entre fonctions alcools et les oxygènes d'autres AGU. Le degré de polymérisation diffère énormément selon l'origine de la cellulose, sa valeur pouvant varier de quelques centaines à quelques dizaines de milliers. Plusieurs dizaines de chaînes parallèles, liées par des liaisons hydrogènes et par des forces de Van der Waals, s'associent et forment ainsi une microfibrille semi – cristalline. Le terme de cellulose désigne ainsi non pas une seule molécule, mais un ensemble de polymères associés en une microfibrille.

La cellulose est un matériau semi – cristallin dans lequel on distingue des zones faiblement organisées (dites amorphes) et des zones très organisées (dites cristallines). L'arrangement cristallin de base est la microfibrille dont la taille peut varier de 2 nm à 20 nm selon l'espèce. Les microfibrilles s'associent pour donner des structures plus ordonnées de taille supérieure: les fibres. Ces dernières sont composées de plusieurs couches de microfibrilles orientées de manière unique, liée à l'origine de la cellulose.

A la vue des conclusions issues de nos travaux, il semble nécessaire de présenter dans ce chapitre les notions élémentaires sur la biosynthèse des fibres et de détailler la structure chimique et morphologique des parois externes. Les fibres de cellulose sont composées de trois parois externes (primaire, secondaire et tertiaire). Les principaux composants chimiques de ces parois sont les suivants: des hydrates de carbone (cellulose, hémicellulose, pectine) et de la lignine.

Au cours de sa croissance, chaque cellulose végétale s'entoure d'une matrice, la paroi primaire, constituée principalement de deux réseaux indépendants de polysaccharides (le réseau de cellulose et d'hémicellulose), et le réseau de pectines. La paroi secondaire provient quant à elle du dépôt de cellulose lors de l'élongation de la cellulose végétale. La structure de la paroi n'est pas statique : sa composition et son agencement sont modifiées au cours de la vie des cellules. La paroi primaire, fabriquée pendant la croissance des cellules, est résistante, mais aussi poreuse et expansible, autorisant l'augmentation du volume cellulaire. La paroi secondaire, élaborée par des cellules qui ont terminé leur expansion, est enrichie en composés rigidifiant, en premier lieu la cellulose, souvent combinée à de la lignine.

Si la composition de la paroi varie au cours de la vie des cellules et en fonction de l'origine des fibres, l'orientation des microfibrilles de cellulose joue aussi un rôle dans la structure des parois. Dans une cellule en élongation, la croissance se fait selon une direction privilégiée : les microfibrilles de cellulose nouvellement synthétisées sont quasiment toujours parallèles et transverses, c'est-à-dire perpendiculaires à l'axe de croissance. A l'inverse, dans les cellules

en fin de croissance, les microfibrilles les plus récemment fabriquées sont obliques. Ainsi chaque paroi est caractérisée par l'orientation de ses microfibrilles, qui varie en fonction de l'origine des fibres de cellulose.

La dernière partie englobe une approche plus théorique du gonflement et de la dissolution des polymères, ainsi que la présentation des différentes classes de solvants de la cellulose (notamment les solvants qui dissolvent la cellulose sans derivatisation et ceux qui conduisent à la formation de dérivés cellulosiques). Surtout, cette partie aborde la notion d'accessibilité des fibres de cellulose en décrivant sa structure poreuse et son aptitude à gonfler. Le gonflement est dicté par la capacité des agents à briser les liaisons secondaires entre les chaînes pour former ses propres liaisons avec le polymère. Il existe deux types de gonflement: inter cristallin (l'agent gonflant pénètre uniquement au sein des zones amorphes) et intra cristallin (l'agent gonflant pénètre aussi bien à l'intérieur des zones amorphes que de la maille cristalline, engendrant ainsi une distorsion du réseau cristallin).

The first chapter is a bibliographical introduction on native cellulose fibre. The first part deals with the structure of cellulose fibre at molecular, supramolecular and morphological levels. As the ultrastructure plays a major role in the interactions with chemical agents, the chemical constituents of cellulose fibres and their distribution among the cell walls are detailed. A last part concerns the theory on swelling and dissolution processes for polymer, especially for cellulose for which the notion of accessibility is explained.

I. The fibre structure	20
I.1. Cellulose molecule	21
I.1.1. Composition	21
I.1.2. Conformation	22
I.1.3. Intramolecular hydrogen bonding	23
I.1.4. Chain stiffness and length	23
I.2. Supramolecular structure	24
I.2.1. Fibrillar structure	24
I.2.2. Crystals modifications	25
I.2.3. Parallel and antiparallel arrangement	27
I.3. Ultrastructure	28
I.4. Conclusion on the fibre structure	29
 II. Structure of plant cell walls	 30
II.1. Biosynthesis of cellulose fibres	30
II.2. The cell wall constituents	32
II.2.1. Carbohydrate components	33
II.2.1.a. Cellulose	33
II.2.1.b. Hemicellulose	33
II.2.1.c. Pectic substances	33
II.2.2. Lignin	34
II.2.3. Other components	34
II.2.4. Repartition of chemical components in walls of woods	34
II.3. The cell wall structure	38
II.3.1. Primary wall	38
II.3.2. Secondary wall	39
II.4. Conclusion on the structure of plant cell walls	40
 III. Swelling and dissolution of cellulose fibres	 40
III.1. Dissolution mechanism of a polymer	41
III.1.1. Surface layer formation and mechanisms of dissolution	41
III.1.2. Effect of different factors on dissolution	42
III.1.3. Polymer dissolution models	42
III.2. Important classes of cellulose solvent systems	43
III.2.1. Nonderivatizing organic solvents for cellulose	43
III.2.2. Ionic compounds in aqueous solution as cellulose solvents	45
III.2.3. Aqueous solutions of transition metal complexes as solvents for cellulose	45
III.2.4. Derivatizing solvent systems for cellulose	46
III.3. Accessibility of cellulose fibres	46
III.3.1. Pore structure and inner surface	47
III.3.2. Types of swelling	48
III.3.2.a. Intercrystalline swelling	49
III.3.2.b. Intracrystalline swelling	49
III.4. Conclusion on the cellulose dissolution	49
 References	 51

As the most important skeletal component in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff – chain homopolymer is characterized by its hydrophilicity, chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semicrystalline fiber morphologies. In view of the considerable increase in interdisciplinary cellulose research and development over the past decade worldwide, this part assembles the current knowledge in the structure and chemistry of cellulose used in the development of innovative cellulose fibers for coatings, films, membrane, building materials and foodstuffs.

In 1838, the French chemist Anselme Payen described a resistant fibrous solid that remains behind after treatment of various plant tissues with acids and ammonia, and after subsequent extraction with water, alcohol and ether. He determines the molecular formula to be $C_6H_{10}O_5$ by elemental analysis, and observed the isomerism with starch. The term “cellulose” for this plant constituent was first used in 1839 in a report of the French Academy on the work of Payen [BROG39]. Thousands of years prior to the discovery of the “sugar of the plant cell wall”, cellulose was used in the form of wood, cotton and other plant fibers as an energy source, for building materials, and for clothing. Cellulose is the most common organic polymer, representing about $1.5 \cdot 10^{12}$ tons of the total annual biomass production. Wood pulp remains the most important raw material source for the processing of cellulose, most of which is used for the production of paper and cardboard. Approximately 2% (around 3.2 million tons in 2003) are used for the production of regenerate fibers and films, as well as for the synthesis of a large number of cellulose esters and ethers. Such cellulose derivatives produced on an industrial scale are used for coatings, optical films, as well as for additives in building materials, pharmaceuticals and cosmetics [KLEM05]. The fascinating aspects of the cellulose biopolymer are a result of its specific structure, which is described in more details in the following parts. The fusion of both carbohydrate and polymer chemistry in a macromolecule composed of repeating glucose units generates surprising specificity and impressively diverse architectures, reactivities and functions. In contrast to carbohydrates of low molar mass, the reactions and properties of cellulose are determined by intermolecular interactions, cross – linking reactions, chain lengths, and by the distribution of functional groups along the polymer chains. Cellulose differs from synthetic polymers by its distinct polyfunctionnability, its sensitivity toward hydrolysis and oxidation of the chain forming acetal groups, which determine its chemistry.

The present chapter aims to review the cellulose fibre structure and to describe its swelling and dissolution. A first part details the fibre structure by distinguishing three levels: molecular, supramolecular and ultrastructural. In the second part, the structure of plant cell walls is presented via the biosynthesis of cellulose fibre and by according a special attention to the cell wall constituents and the morphological structure in layers of fibres. The last section concerns the theory of swelling and dissolution for polymer and one paragraph is dedicated to the various classes of cellulose solvent systems. The accessibility of cellulose fibres is also presented in this last part.

I. The fibre structure

The chemical and physical properties of cellulose can only be properly understood by the combined knowledge (figure I.1) of the chemical nature of cellulose molecule and its structure and morphology in the solid, mostly fibrous, state. To be able to analyze the effects of structure on physical and chemical properties, a profound knowledge of the structural

features of cellulose substrates is a prerequisite. Before beginning the discussions on the interrelations between structure and reactivity with external agents as solvent systems, it is necessary to give an up-to-date review of what is known about the structure of cellulose fibers. In defining the structure of a polymeric substrate, such as cellulose fibers, one has to distinguish three structure levels:

- the molecule level (cf. I.1.), i.e. the chemical constitution, the steric conformation, the molecular mass, the molecular mass distribution, the presence of functional sites, the existence of intramolecular interactions, etc.
- the supramolecular level (cf. I.2.), i.e. the aggregation of the chain molecules to elementary crystals and fibrils, the degree of order within and around these fibrils, the degree of orientation with respect to the fiber axis, etc.
- the ultrastructure level (cf. I.3.), i.e. the spatial position of the fibrillar aggregation in the morphology of the fiber, the existence of distinct cell wall layers in native cellulose fibers.

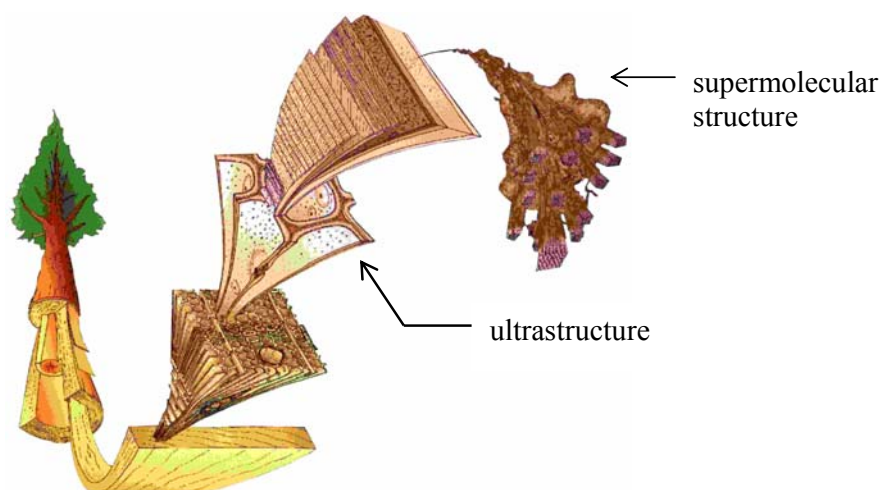


Figure I.1: structure levels of cellulose [<http://www.cermav.cnrs.fr>]

I.1. Cellulose molecule

Cellulose, a high molecular weight linear polymer, is composed of D – glucose building blocks, joined by β – 1,4 – glucosidic bonds. In native cellulose, up to 10 000 β – anhydroglucose residues are linked to form a long chain molecule. It means that molecular weight of native cellulose fiber is above 1.5 million. As the length of the anhydroglucose unit is 0.515 nm (≈ 5.15 Å), the total contour length of a native cellulose molecule is about 5 μm . Cellulose contained in pulp and filter paper has usually a degree of polymerization ranging from 500 to 2 100.

I.1.1. Composition

In 1838, Payen [PAYE42] was the first to determine the elemental composition of cellulose, the major component of plant tissue: with 44 - 45% carbon, 6.0 – 6.5% hydrogen, and the remainder being oxygen. From this it concluded that cellulose had the empirical formula $\text{C}_6\text{H}_{10}\text{O}_5$.

Cellulose is a linear syndiotactic homopolymer composed of D–anhydroglucose units (AGU), which are linked together by β – 1,4 – glucosidic bonds formed between the carbon atoms

C(1) and C(4) of adjacent glucose units (figure I.2). The β – link requires that the plane of the pyranose ring of each second glucose unit along the molecular chain is turned around C(1) – C(4) axis by 180° with respect to the glucose units lying in between.

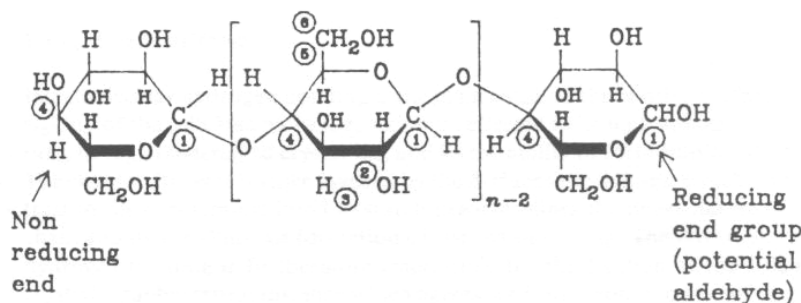


Figure I.2: molecular structure of cellulose
(n = DP, degree of polymerization)

The chain length of cellulose expressed in the number of AGU constituents (degree of polymerization, DP or n) varies with the origin and treatment of the raw material. In case of wood pulp, the values are typically between 300 and 1 700. Cotton and other plant fibers have DP values in the 800 – 10 000 range, depending on treatment. Regenerated fibers from cellulose contain 250 -500 repeating units per chain. By acid treatment and cellulase catalyzed hydrolysis, cellulose can be quantitatively decomposed down to D-glucose. Partial chain degradation yields powdery cellulose substrates of the microcrystalline cellulose type with DP values between 150 and 300. A $\beta(1 \rightarrow 4)$ linked glucan with 20 – 30 repeating units has all the properties of cellulose.

Terminal hydroxyl groups are present at each end of the cellulose chain molecule. However, these two groups are quite different in nature. The cellulose chain consists at one end of a D-glucose unit with an C4-OH group (the non – reducing end), the other end is terminated with an C1-OH group, which is in equilibrium with the aldehyde structure (the reducing end). Technical celluloses, such as bleached wood pulp, contain additional carbonyl and carboxy groups as a result of the isolation and purification processes that play a role in the processing of cellulose.

The molecular structure imparts cellulose with its characteristics properties: hydrophilicity, chirality, degradability and broad chemical variability initiated by the high donor reactivity of the OH groups. It is also the basis of the extensive hydrogen bond networks, which give cellulose a multitude of partially crystalline fiber structures and morphologies.

I.1.2. Conformation

From infrared spectroscopy and X – ray crystallography studies, it is known that the D, β – glucose exists in the pyranose ring form and that it adopts the 4C_1 – chair (figure I.3) conformation which constitutes the lowest energy conformation for D – glucopyranose. In this conformation, the free hydroxyl groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in vertical position (axial).

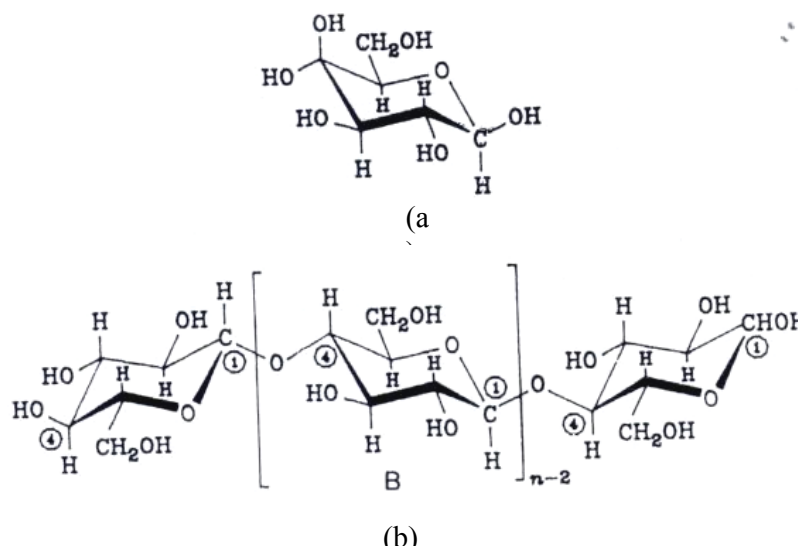


Figure I.3: Conformation of the D-glucose (a) and the cellulose (b) molecules [KRAS93]

I.1.3. Intramolecular hydrogen bonding

Besides being able to undergo chemical reactions, the three hydroxyls in each glucose based unit of the cellulose molecule are also able to interact with one another forming secondary valence bonds. The strength of these hydrogen bonds is of the order of 25 kJ.mol^{-1} [MORR69], which is very low in comparison with the value of the O-H covalent bond strength (460 kJ.mol^{-1}). There are two possibilities for hydroxyl groups in the cellulose molecule to form hydrogen bonds:

- by interaction between among – suitably positioned hydroxyls in the same molecule (intramolecular)
- by interactions between hydroxyl groups in neighboring cellulose molecules (intermolecular).

The intramolecular hydrogen bonds are formed between the hydroxyl groups on C(3) of one glucose unit and the pyranose ring oxygen O(5') of the adjacent glucose unit in the chain. The existence of another intramolecular bond between the hydroxyl groups on the carbon atoms C(6) and C(2') of neighboring glucose base units. Both possibilities of intramolecular hydrogen bondings are demonstrated on figure I.4.

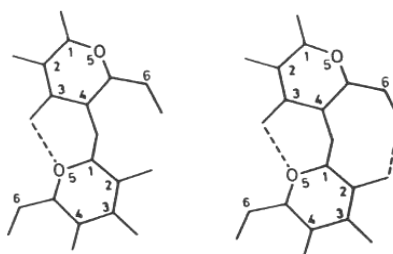


Figure I.4: Intramolecular hydrogen bonding [KRAS93]

I.1.4. Chain stiffness and length

Intramolecular hydrogen bonding is the main cause of the relative stiffness and rigidity of the cellulose molecule, which is reflected in its high tendency to crystallize and its ability to form

fibrillate strands. The chain stiffness is further favored by the β -glucosidic linkage, which, in contrast to the α -glucosidic bond in starch, predetermines the linear nature of the chain and by the chair conformation of the pyranose ring.

Concerning the length of chain, it can be evaluated by using the values of DP. The n in the formula of cellulose (see in figure I.3) designates the number of anhydroglucose units linked together by β -glucosidic linkages in the cellulose chain molecule (DP). Since each of AGUs unit ($C_6H_{10}O_5$) has a basic molecular mass of 162, the average molecular mass of a cellulose substrate having an average of polymerization n will be $(n \times 162)$. Depending of the applied treatments, the cellulose substrates used in practice have degrees of polymerization between 800 and 3 000, i.e. have average molecular mass of between 130 000 and 500 000. In the commonly used forms, cellulose substrates are always polydisperse, i.e. they are a mixture of molecules having the same basic composition but differing widely in their chain length. Thus, molecular mass or degree of polymerization values are considered as average values.

I.2. Supermolecular structure

As described before the cellulose chains have a strong tendency to aggregate to highly ordered structural entities due to their chemical constitution and their spatial conformation. The basic elements of the supermolecular structure of cellulose fibers are the crystallite strands.

It was during the XIX century that Nägeli developed a theory to deal with the birefringent materials in plant cells and starch grains. This theory led to the introduction of the concept of crystalline micelles having submicroscopic dimensions [HERM49]₁. According to Nägeli concept, the chain molecules are associated to form crystalline domains, called “micelles” or “crystallites”. Due to their length the chain molecules passes alternatively through several crystallites. An amorphous matrix is formed and localized between two crystallites. Although this concept has been very valuable for the understanding of the solid state of polymers, it did not, however, sufficiently take into account the distinct fibrillar nature of fibrous substrates.

I.2.1. Fibrillar structure

Fibrous substrates are built from fibrillar elements, which are known as “macrofibrils” and “microfibrils”. Dimensions of these fibrillar vary from several microns to few tenths of a micron. At the end of 1930s, with the development of electron microscopy, it was found that these macro- and microfibrils are aggregates of still thinner fibrillar units, having cross sections of only 2 to 4 nm and lengths of 100 nm. These basic elements are now called “elementary fibrils” (figure I.5).

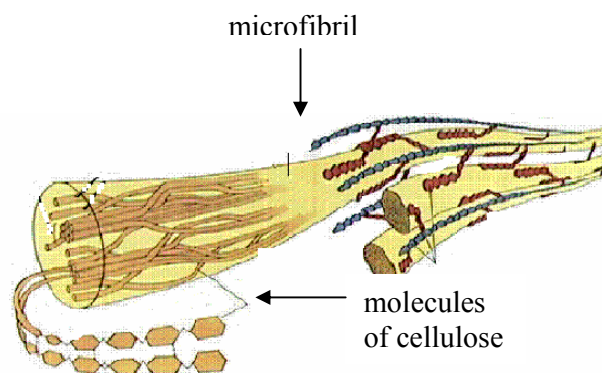


Figure I.5: fibrillar element of cellulose [BIGA02]

According to this structure model, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites held together by parts of the long molecules reaching from one crystallite to the next through less ordered interlinking regions (figure I.6).

An extensive description of the different aspects and modifications of the fiber structure model was given by Hearle [HEAR62]. He expressed the surely accurate opinion that all the possible structure states (wholly amorphous, fringed fibrillar, fibrillar and wholly crystalline) cannot be strictly separated. The structure model for the internal build up of cellulosic fibers, which best fits the experimental observations is given schematically in figure I.6. According to this model, the fiber is composed of elementary fibrils, i.e. strings of elementary crystallites, associated in a more or less random fashion into aggregations, and interlinked to a fibrillar network by isolated segments of fibrils fringing from one aggregation to another; The internal cohesion inside the elementary fibrils is being established by the transition of the long cellulose chain molecules from crystallite to crystallite (represented on figure I.6 by small rectangles). The coherence of the fibrils in their secondary aggregation is given either by hydrogen bonds at close contact points or by diverging molecules. Access into this structure is given by large voids formed by imperfect axial orientation of the fibrillar aggregates, interspaces of nanometer dimensions between the fibrils in the fibrillar aggregation, and by the less ordered interlinking regions between the crystallites inside the elementary fibrils.

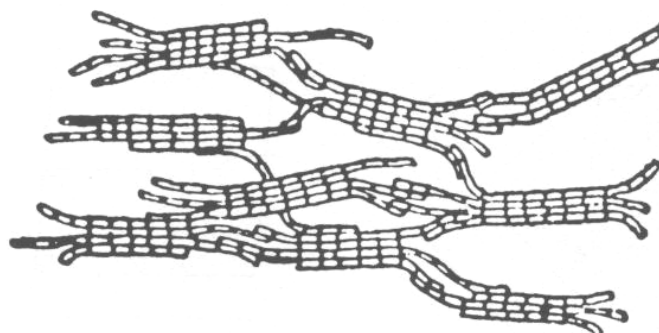


Figure I.6: Fringe – fibrillar model of fiber structure [HEAR62]

I.2.2. Crystals modifications

As a result of the supermolecular structure of cellulose, the solid state of cellulose is composed of both high order (crystalline) and low order (amorphous) regions. One subject to be discussed now is the crystalline arrangement of the cellulose molecules in crystallites.

The free hydroxyl groups present in the cellulose macromolecule are likely to be involved in a number of intra and inter molecular hydrogen bonds which may give rise to various ordered crystalline arrangements. In the case of cellulose these crystalline arrangements are usually imperfect to the extent that, in terms of crystal dimensions, even chain orientation and the purity of the crystalline form must be taken into consideration. The crystal density can be gauged from the crystallographic data. The density of the crystalline phase is 1.59 gcm^{-3} but, when determined for natural samples, is of the order of 1.55 gcm^{-3} which corresponds to value of about 70% for the crystalline component [HERM49]₂. The degree of crystallinity can also be estimated by infra-red spectroscopy as a function of the relative intensity of certain bands [FENG92].

Four principal allomorphs have been identified for cellulose: I, II, III and IV [HOWS63]. Each of these forms can be identified by its characteristic X-ray diffraction pattern. Progress achieved in the characterisation of cellulose ultrastructure has shown that within these four allomorphic families subgroups exist. The dimensions of cell are given in table I.1.

A – axis (Å)	b – axis (Å)	c – axis (Å)	$\gamma(\text{deg})^a$	Polymorph
7.85	8.17	10.34	96.4	Cellulose I
9.08	7.92	10.34	117.3	Cellulose II
9.9	7.74	10.3	122	Cellulose III
7.9	8.11	10.3	90	Cellulose IV

^a γ = lattice angle

Table I.1: unit cell dimensions of various cellulose allomorphs [KRAS93]

Cellulose I

The natural form of cellulose is called cellulose I or native cellulose. The crystal structure of native cellulose determined by X-Ray diffraction can be described by a monoclinic unit cell which contains two cellulose chains in a parallel orientation with a two fold screw axis [GARD74]. In the 1980s, ¹³C-CP/MASS NMR spectroscopy was used in the initial discovery that native cellulose is present in two different crystalline cellulose I modifications (I_α and I_β), which can be found alongside each other. The I_α/I_β ratio depends on the origin of the cellulose. For example, bacterial and valonia cellulose contain a large amount of I_α , whereas in ramie, cotton or wood cellulose the I_β phase is dominating. Sugija et al [SUGI91] describes, on the basis of electron diffraction experiments, the I_α phase as a triclinic P-1 structure, with one cellulose chain per unit cell, and assumed for the I_β modification a monoclinic unit cell of the Meyer – Misch type (space group P-2₁ with two chains per unit) (figure I.7). The I_α phase is metastable and can be transformed by annealing into the thermodynamically more stable I_β phase.

Cellulose II

Besides the cellulose I, the crystalline modification of cellulose II is the most important from a technical and commercial point of view. This allomorph is known by the term "regenerated" cellulose. In fact, it can be formed from cellulose I by treatment with aqueous sodium hydroxide (mercerisation) or by dissolution of the cellulose and subsequent precipitation / regeneration. The transition from cellulose I to cellulose II is not reversible and this implies that cellulose II is a stable form compared with the metastable cellulose I.

This monoclinic crystal structure of cellulose II, with two antiparallel chains in the unit cell (figure I.7) is characterized by the specific unit cell geometry with a modified H – bonding systems (cf. I.2.3.).

Cellulose III

The crystalline modification, cellulose III, is obtained by treating cellulose I or II with liquid ammonia below -30°C and subsequently recrystallizing sample by evaporation of the ammonia. Small differences in lattice dimensions obviously exist between the two sub modifications cellulose III_I and III_{II}.

Cellulose IV

As a fourth modification, cellulose IV may be mentioned briefly, which is formed on treating the others modifications in a suitable liquid at high temperature under tension.

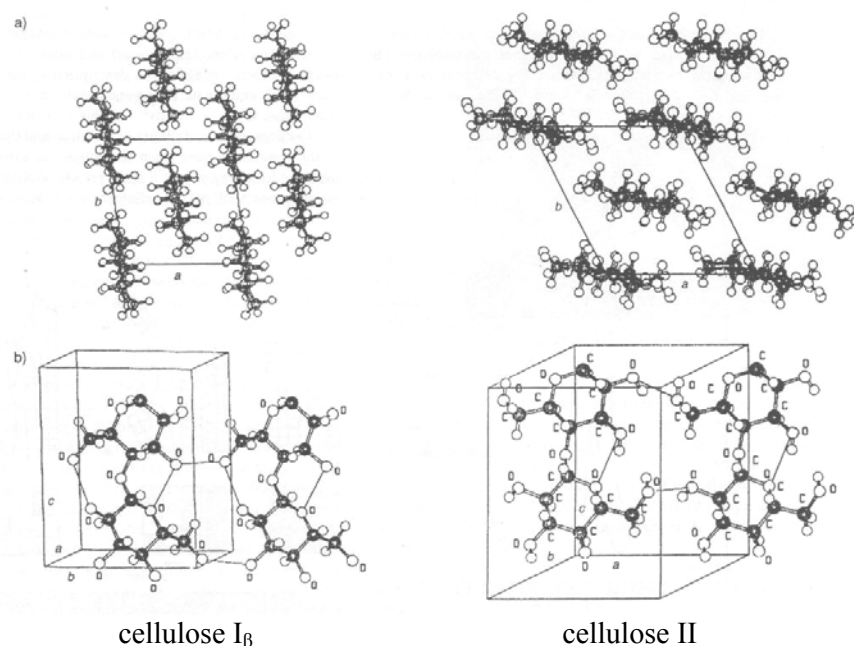


Figure I.7: Crystal structures of cellulose I_β and cellulose II.

a) projection of the unit cell along the a-b plane; b) projection of the unit cell parallel to the (110) lattice plane for cellulose I and the (010) lattice plane for cellulose II [ZUGE01].

I.2.3. Parallel and antiparallel arrangement

There are essentially two main structural families of celluloses: the parallel - chain and the antiparallel - chain structures. Native cellulose I is typical of the parallel - chain structures, and cellulose II is typical of the antiparallel - chain structures. In both cases, the chain conformations are very nearly identical, corresponding to the minimum energy. In the structures of both families, the chains pack into sheets in parallel orientation, with stabilization in two directions of the sheet provided by hydrogen bonds. The sheet structures in the two structural families are similar. The main difference between the parallel and antiparallel chain structures lies in the three dimensional packing of sheets: a parallel packing in the former, and a regularly alternating, up - down arrangement in the layer. The antiparallel packing affords a more extensive, three dimensional arrangement of hydrogen bonding. The increased hydrogen bonding results in cellulose II being more stable, of lower energy structure and partially explains why it cannot be made revert to higher energy, i.e. the parallel structure of cellulose I.

Figure I.8 explains in details the parallel and antiparallel - chain structures, based on the network of the H - bonds [KOLP76]. Intermolecular hydrogen bonds are formed in cellulose I by “linking” neighboring chains along the a-axis by an intermolecular hydrogen bond O-6 - - H-O(3), so that the chains form hydrogen bonded sheets of chain parallel to the a-axis, which means in the 020 plane. For the cellulose II, the -CH₂OH groups are in t-g position in the case of the center chain forming sheets very similar to those in native cellulose. Each chain has the O-3 - - HO-5' intramolecular bond but forms two intermolecular bonds, i.e. O-6 - - HO-2 to the next chain along the a-axis in the 020 plane and OH-2 - - O-2' to the chain along the diagonal in the 110 plane.

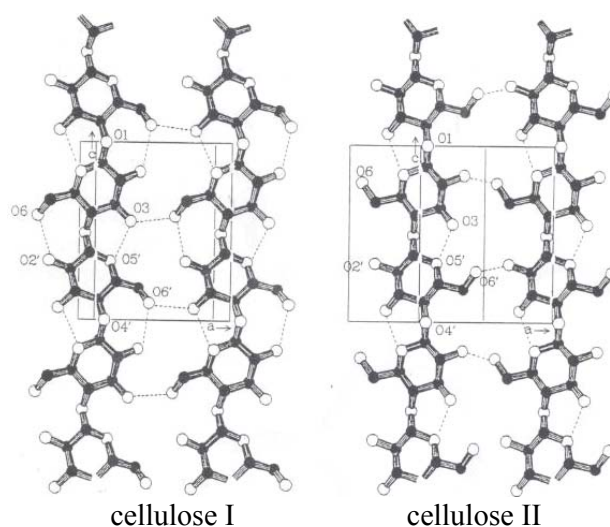


Figure I.8: parallel – chain and antiparallel – chain structures, respectively for cellulose I and cellulose II [KROO86]

I.3. Ultrastructure

As the skeletal component in all plants, cellulose is organized in a cellular hierarchical structure. In combination with the accompanying substances hemicelluloses, lignin, and pectin, this structure leads to the extraordinary properties of native composite materials, such as wood, cotton, flax, and hemp. Figure I.9 illustrates the cell walls of cotton and wood with differently structures layers, in which the secondary layer S2 contains the main quantity of cellulose.

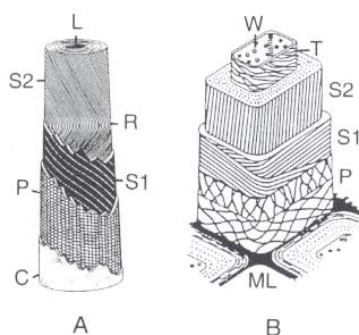


Figure I.9: Scheme of the “morphological architecture” of a cotton fibre (A) and a delignified spruce wood fibre (B) [KRAS93]

Legend: C = cuticle (rich in pectins and waxes), L = lumen, ML = middle lamella (mainly lignin), P = primary wall, R = reversal of the fibril spiral, S1 = secondary wall (winding layer), S2 = secondary wall (main body), T = tertiary wall, W = wart layer

The cellulose molecules organized in the cell walls in the form of microfibrils have characteristic orientations (helix angles), which differ as a function of the cell wall layer, and according to the plant type as well. In the outer layer, the so - called primary layer (P) wall of about 10 nm in diameter are positioned cross wise to a layer of about 50 nm thickness. The

secondary wall (S) consists of two layers S1 and S2. The thickness of the S1 layer is, in the case of cotton, about 100 nm, in the case of spruce pulp fibre, about 300 nm. The fibres are aligned parallel and densely packed in a flat helix, the direction of which may be opposite in subsequent S1 layers. The fibrils are well aligned in a helix. In the cotton fibre, a layered structure of S2 exists due to density fluctuations during growth, with an average distance of 100 – 200 nm, which becomes visible after suitable swelling treatment. The inner layer closest to the fibre lumen, i.e. the tertiary layer (T) in the case of wood fibres and the S3 layer in the case of cotton, is comparably thin and has the fibrils aligned in a flat helix.

I.4. Conclusion on the fibre structure

The principle characteristics of cellulose as a polymer material are to be seen in its complex structure (chain conformation, network of H - bonding, chain association, crystallinity, microfibril structure and organization). All these structural levels are presented schematically (figure I.10) including their relationship to the plant cell wall. A better knowledge of the different structural levels in which cellulose participates should allow a better use of this unique and metastable molecular assembly which is produced by biosynthesis.

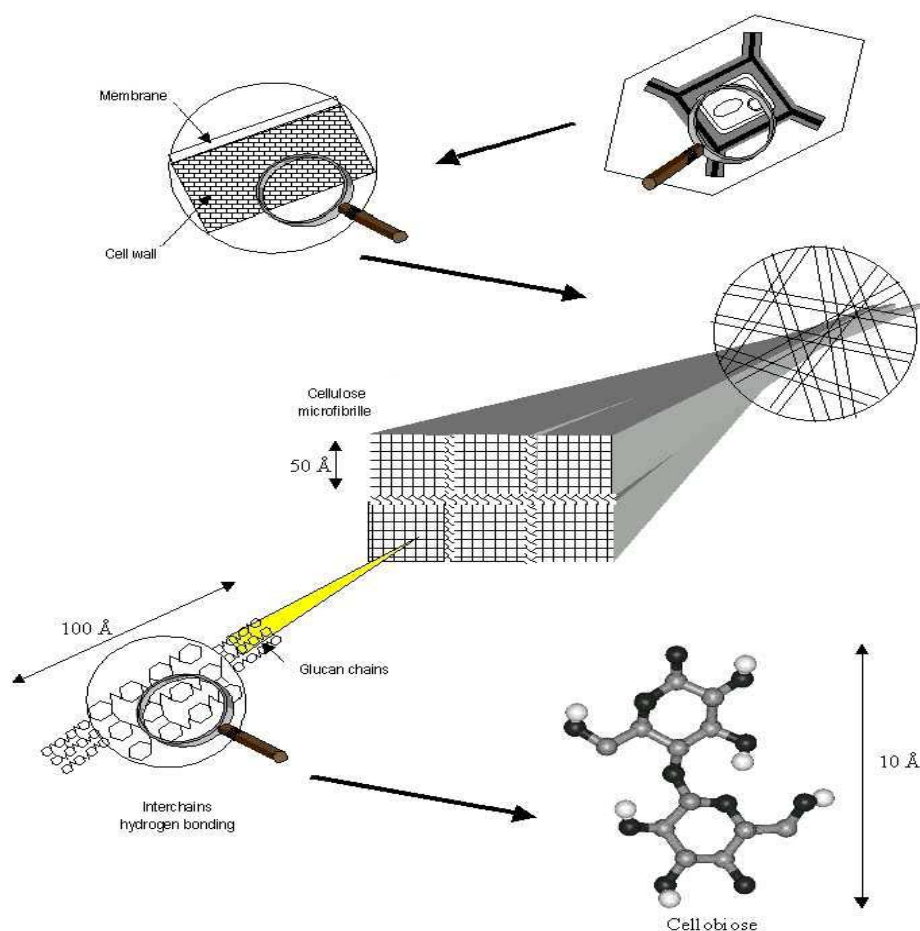


Figure I.10: relationship between the different levels of cellulose fibre (cellobiose = 2 units of glucose) [<http://www.cermav.cnrs.fr>]

The structure of plant cell walls comes from the biosynthesis (birth and growth of cellulose fibre), the chemical components, the orientation of microfibrils and others properties of each wall must be known to understand the interactions between cellulose structure and the external components. The next section details these points.

II. Structure of plant cell walls

As seen before (cf. I.3.), in a general construction scheme around a hollow lumen, fibrillar elements consisting of cellulose are wound in spirals to give the fiber its tenacity and flexibility. The cell wall determines the shape of the cell. Cell walls have supportive and protective functions, both as components of living cells and as remains of dead cells. They assist the aerial parts of plants in withstanding the stress of the force of gravity and protect them from desiccation. They play an important role in such activities as absorption for example.

The first part of this section reviews the biosynthesis of cellulose fibres and explains the birth of each outer layers (i.e. walls). The second part is devoted to the analysis of chemical components of walls, in function of the origin of fibre and of layers. The last part details the structure of primary and secondary walls.

II.1. Biosynthesis of cellulose fibres

Throughout their lifetime the cells of living plants continue to divide with the production of certain cells thus conferring the unusual property of being able to grow indefinitely while retaining the quality of young plants. These meristematic¹ cells and those deriving from them grow and then differentiate into specialised cells for various functions (support, protection, flow of sap etc). A collection of cells specialised for one function constitutes a tissue, a wall. The interpretation of the plant cell as consisting of the protoplast and cell wall agrees with the common observation that each cell within a tissue has its own wall. Plant cell walls are distinguished from animal cells by the presence, around the plasmalemma, of a wall within which complex physicochemical and enzymatic phenomena progress. In the course of cell growth the dimensions of the cell wall vary according to the type of macromolecule of which it is composed [ESAU65]. The cell walls of plants vary much in thickness in relation to age and type of cell. Generally, young cells have thinner walls than fully developed ones, but in some cells the wall does not thicken much after the cell ceases to grow. Whether thin and thick, the walls are of complex structure and often permit recognition of layers variable in chemistry and structure. On the basis on the development and structure, three parts are commonly recognized in plant cell walls (figure II.1):

- the intercellular substance or middle lamella
- the primary wall
- the secondary wall

The intercellular substances occur between the primary walls of two contiguous cells, and secondary wall is laid over the primary, that is, next to the lumen (the central cavity, from Latin, meaning light or opening) of the cell.

¹ Meristem is a type of embryonic tissue in plants consisting of unspecialized, youthful cells called meristematic cells and found in areas of the plant where growth is or will take place - the roots and shoots. Differentiated plant cells have shapes and structures that would make it problematic for them to produce cells of a different type. Thus, cellular divisions of the basic cells of the meristem provide new cells for expansion of tissues, providing the basic structure of the plant body. [<http://www.biologydaily.com>]

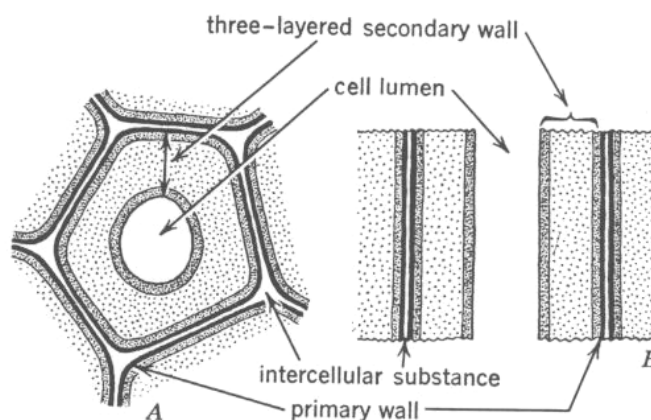


Figure II.1: Common type of wall structure in cells with secondary wall layers in transverse (A) and longitudinal (B) sections [BAIL54]

The first wall deposited after cell division is called the “middle lamella” and is essentially composed of pectic material. The middle lamella is amorphous and optically inactive. In woody tissues the middle lamella is commonly lignified. Since the intercellular substance is difficult to identify microscopically (amorphous zone), the term middle lamella has been used in the literature without much consistency. The distinction between the intercellular lamella and the primary wall is frequently obscured during the extension growth of the cell.

The primary wall is the first wall proper formed in a developing cell and is the only wall in many types of cells. It contains cellulose, hemicelluloses, and some pectin. It may become lignified. Because of the presence of cellulose, the primary wall is optically anisotropic. Since the primary wall is initiated before the cell enlarges, it passes through a period of growth in surface area, which may be succeeded or temporarily interrupted by a period or periods of growth in thickness. The two types of growth may be combined. Thus the primary wall may have a complex history as well as a complex structure. If the wall is thick, it often shows conspicuous lamination, showing that growth in thickness has occurred by a successive deposition of layers. Primary walls are usually associated with living protoplasts². The walls of dividing and growing meristematic cells are primary, and so are those of most of the cells which retain living protoplasts during their physiologic maturity. The changes that occur in primary walls are therefore reversible. The wall may lose a thickening previously acquired, and chemical substances may be removed or replaced by others. (Cambial walls, for example, show seasonal changes in thickness).

As its name implies, the secondary wall follows the primary in the order of appearance. It consists mainly of cellulose or of varying mixtures of cellulose and hemicelluloses. It may be modified through deposition of lignin and various other substances. Because of its high content of cellulose, the secondary wall is strongly anisotropic. The complexity and the lack of homogeneity in structure are pronounced in the secondary wall. The secondary walls are usually composed of three layers (S1, S2 and S3, cf. II.3.2.), and there are physical and chemical differences between the layers S1, S2 and S3. Generally, secondary walls are laid down after the primary wall ceases to increase in surface area.

In this section, more details are given on the biosynthesis of cellulose fibre at a biological level. Plant cell walls form by apposition of new material from the inside of the plasma

² Protoplast refers to that unit of biology which is composed of a cell's nucleus and the surrounding protoplasmic materials.

membrane. The wall matrix material of hemicellulose, pectins and glycoproteins is contained in Golgi³ vesicles that deliver their content into the existing cell wall after fusing of their membranes with the plasma membrane [MULD04]. In cell biology, the Golgi apparatus, Golgi body, Golgi complex, or dictyosome is an organelle found in most eukaryotic cells, including those of plants and animals (but not in most fungi). Cellulose synthases are thought to be assembled in the endoplasmic reticulum and brought to the plasma membrane via the pathway of Golgi stacks and Golgi vesicles [HAIG86]. The cellulose synthase is only active in producing cellulose microfibrils when located inside the plasma membrane. Thus the cellulose comes from plant cell, and constitutes the element for building the outer layers. They are transported through the plasma membrane of plant cell.

In considering the mechanism of wall growth, it is necessary to differentiate between growth in surface area and growth in thickness. Growth in thickness is particularly obvious in secondary walls but is common also in primary walls. It occurs by a successive deposition of wall material, layer upon layer, by a process known as apposition. Growth of walls by apposition is usually centripetal. In other words, it occurs from the outside and toward the lumen of the cell. Sometimes, however, wall growth has a centrifugal course, that is, in the direction away from the lumen. Centripetal growth is characteristic of cells forming tissues.

To summarize, we can say that the growth of primary wall occurs during the birth of cellulose fibre, while the secondary wall is developed during the growth of cellulose fibre. The stages of development are detailed on the figure II.2:

- a = the new cell has only a thin primary layer
- b and c = the cell enlarges and then wall the wall thickens as the secondary wall (S) forms inside of primary wall (P)
- d = wall continues to thicken with a build up of deposits

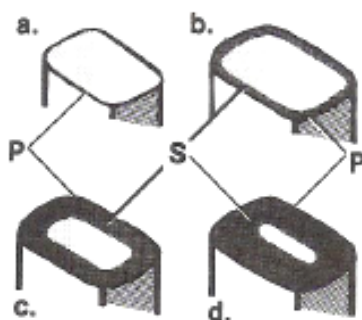


Figure II.2: stages of development for a cellulose fibre [<http://www.faculty.sfasu.edu>]

II.2. The cell wall constituents

The most common compound in plant cell walls is the carbohydrate cellulose. This substance receives its name because it is the basic constituent of almost all cell walls in vascular plants. It is associated with various substances, most often with other compound carbohydrates, and many walls, particularly those which are impregnated with lignin. The common carbohydrate constituents of the cell wall other than cellulose are hemicelluloses and pectic compounds. One of the most important wall substances is the lignin, a polymer of high carbon content distinct from the carbohydrates.

³ Its primary function is to process proteins targeted to the plasma membrane, and those that will be secreted from the cell, and sort them within vesicles. Thus, it functions as a central delivery system for the cell.

In a first part, the carbohydrates compounds (cellulose, hemicellulose and pectin) are detailed. Then the features and role of lignin is described. The last part concerns the repartition of the chemical agents in each wall in function of the origin of cellulose fibres (especially cotton or wood).

II.2.1. Carbohydrate components

II.2.1.a. Cellulose

Cellulose is a relatively hydrophilic crystalline compound having the general empirical formula $(C_6H_{10}O_5)_n$, as presented in the previous part (cf I.1).

II.2.1.b. Hemicellulose

Hemicellulose is a heterogeneous group of polysaccharides [ROEL59]. Hemicellulose is the collective name for all those polysaccharides occurring in the cell wall that dissolve either in cold or in hot alkali but are insoluble or only slightly soluble in cold and hot water. They are more easily hydrolysable in acid than cellulose is.

Hemicellulose is composed of shorter chain polysaccharides, and it is the principal non – cellulosic fraction of polysaccharides. The role of this component is to provide a linkage between lignin and cellulose. In its natural state, it exists in an amorphous form and can be divided into three groups, namely, xylans, mannans and galactans. These groups can exist separately as single components or collectively. The xylans are present as arabinoxylans, glucuronoxylans, or arabinoglucuronoxylans. The mannans are localised in wood as glucumannans and galactomannans. The galactans are relatively rare but are often found in the form of arabinogalactans. Xylans is a polymer of 4 – O – methyl – glucuronoarabinoxylan linked by a β - D (1-4) – bond, similar to the linkages of the glucose units in cellulose. In xylan, however, the hydroxyl groups are substituted with 4 – O – methylglucuronic acid, arabinose and acetyl groups. It is assumed that the glucomannans have a linear structure so that there is not branching at either of the two carbon positions, namely, (C-2) or (C-3).

The amount of hemicellulose varies considerably in different plants and also in different tissues of the same plant. Whereas the full growth cotton hair has at the most 1% of hemicellulose, the jute fibre contains 25%, wood 25 – 40%, the cell wall of the ivory nut more than 90%. The hemicellulose content varies greatly even in different layers of the same cell wall. In the middle lamella and the primary wall, it is usually much higher than in the secondary wall.

II.2.1.c. Pectic substances

Pectic substances are closely related to hemicelluloses but have different solubilities. They occur in three forms: protopectin, pectin and pectic acid, and belong to the polyuronides that are polymers composed mainly of uronic acid. All pectic substances contain as main constituent chain molecules composed of d-galacturonic acid with α – 1,4 bonds and with an average DP which in the most common original condition reaches a value of some hundreds. Pectic compounds are amorphous colloidal substances, plastic and highly hydrophilic. The latter property suggests a possible function of maintaining a state of high hydration in the young walls. Because of the outstanding ability of pectin to jell, it is an important industrial product. Pectic compounds not only constitute the intercellular substance but also occur associated with cellulose in the other wall layers, notably the primary.

Nota: Gums and mucilages (or slime) should also be mentioned among the compound carbohydrates of the cell walls. These substances are related to pectic compounds and share with them the property of swelling in water. Gums appear in plants mainly as a result of physiological or pathological disturbances that induce a breakdown of walls and cell contents (gummosis or gummous degeneration). The mucilages occur in some gelatinous types of cell

walls. Such walls are common in the outer cell layers of plant bodies of many aquatic species and in seed coats.

II.2.2. Lignin

Lignin, one of the most important wall substances, is a polymer of high carbon content, distinct from the carbohydrates. Lignin is probably the most complex and least well characterised molecular group among all these components. It is essentially a three dimensional phenylpropane polymer with phenylpropane units held together by ether and carbon – carbon bonds. The lignin constitutes 20 – 35% of the wood structure. Lignin gives the structural rigidity by stiffening and holding the fibres of polysaccharides together. A property that is of importance is its thermo – plasticity in the humid conditions.

It is an end - product of metabolism and seems to function primarily as a structural component of cell wall. Lignin possesses a high molecular weight and is amorphous in Nature. Physically, it is rigid. It is the most important representative of the incrusting substances, that is, substances impregnating the wall after its initial development. Lignin may be present in all three wall layers – the middle lamella, the primary wall, and the secondary wall. Lignification occurs in the primary wall and intercellular substance before it spreads to the secondary wall. In detail, lignification has been seen starting in the primary wall, adjacent to the corner thickenings of the middle lamella, then spreading to the intercellular layer and to the primary wall generally. In the secondary wall, lignification was found to lag considerably behind the synthesis of cellulose and other polysaccharides. In xylem⁴ elements, with secondary walls in the form of rings and helices, the primary wall does not become lignified. In woody tissues the middle lamella and the primary wall are more strongly lignified than the secondary wall. The insolubility of lignin have been explained by assuming that in cell wall the lignin is chemically bound to carbohydrates, especially to the hemicellulose which together with the lignin in the interstices between the cellulose microfibrils [HARR53]. The hemicelluloses become more readily soluble and more reactive after the lignin has been removed.

II.2.3. Other components

Because of their chemical nature and their peripheral position in the plant body, the fatty wall substances are considered to be effective in reducing perspiration and in protecting the foliage from leaching effects of rain. The relatively hard, varnish – like cuticle, specifically, may protect against penetration of living tissues by potential parasites and against mechanical injuries. Fatty materials are not restricted to the peripheral layers of the plant body. Inner cuticles develop in seeds during the transformation into seed coats. Fatty substances, identified as cutin and as suberin, occur as a coating on the mesophyll cell walls facing the internal air – space system of the leaf. The fatty compounds, cutin, suberin, and waxes, occur in varying amounts in the walls of many types of cells, especially abundantly in those that are located on the periphery of the plant body.

Various other organic compounds and mineral substances may be present, but they rarely play an essential part in wall structure.

II.2.4. Repartition of chemical components in walls of woods

The cellulose fibres show a structure composed of the primary wall (P), the thin outer layer (S1), the substantial middle layer (S2), and the very thin inner layer (S3) sometimes called the

⁴ In vascular plants, the xylem is the tissue that carries water up the root and stem [<http://www.biologydaily.com>]

tertiary wall. S1, S2 and S3 constitute the secondary layer. Figure II.3 shows the distribution of the chemical constituents in a typical cell wall. The middle lamellae is heavy in lignin and is about 1 – 2 μm thick. It is amorphous and generally porous. The primary wall (P) is usually very thin and remains so throughout the growth of the plant, whereas the secondary wall (S) thickens during cell growth and contains most of the cellulose. In a general construction scheme around a hollow lumen, fibrillar elements consisting of cellulose are wound in spirals. Furthermore, this cable is made waterproof by lignin and waxy compounds, which offer chemical resistance. Hemicellulose provides an intimate interlacing and even bonding between lignin and cellulose [FAN 87]. Especially in the case of woods, the effect of variety and maturity on chemical composition has been studied.

The repartition of chemical components in cellulose cellulose fibres extracted from wood is detailed in this section as a function of the variety and ages of woods. The woods can be classified in many categories:

- Softwoods: Softwood is the wood from conifers. In addition "softwood" is an adjective applied to the trees that produce such wood: softwood trees include pine, spruce, cedar, fir, larch, douglas-fir, hemlock, cypress, redwood and yew.

- Hardwoods: The term hardwood designates wood from angiosperm⁵ trees. Hardwood contrasts with softwood, which comes from conifer trees. On average, hardwood is of higher density and hardness than softwood, but there is considerable variation in actual wood hardness in both groups, with a large amount of overlap; some hardwoods (e.g. balsa) are softer than most softwoods. They have broad leaves and enclosed nuts or seeds such as acorns. They often grow in sub tropical regions like Africa and also in Europe and other countries.

- Earlywoods and latewoods: a layer of wood cells produced by a tree in one year, usually consisting of thin – walled cells formed early in the growing season (called earlywood) and thicker – walled cells produced later in the growing season (called latewood).

The global chemical composition of woods in function of cell wall is given in figure II.3. However, the composition of hardwoods and softwoods is significantly different:

- the lignin content of softwoods is generally higher than that of hardwoods,
- the hemicellulose content of hardwoods is similar to that of softwoods,
- the cellulose content of hardwoods is generally higher than that of softwoods.

It must be kept in mind, however, that wide variations in chemical compositions occur not only between different species but also within a single species.

Tables II.1 and II.2 show the chemical constituents of the extractive – free wood (e.g. woods without extractives, which are components at low molecular weight soluble in water or organic solvents) in five hardwoods and five softwoods, respectively. For these two groups of woods, the cellulose content is more or less the same ($43 \pm 2\%$). However, the hardwoods contain less lignin than the softwoods. The lignin content of hardwoods varies between 19% and 24%, whereas that of softwoods is in the range between 27% and 33%. However tropical hardwoods exceed often the lignin content of many softwoods [SAKA04].

⁵ Angiosperms are a major group of land plants. They comprise one of the two groups in the seed plants, distinct in covering their seeds by enclosing them in a true fruit. They bear the reproductive organs in a structure called a flower; the ovule is enclosed within a carpel, which will lead to a fruit. [<http://en.wikipedia.org>]

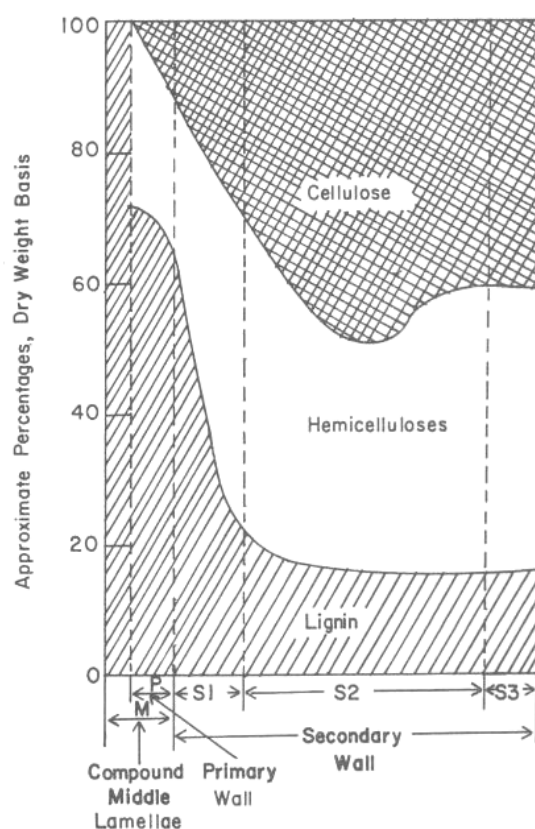


Figure II.3: Chemical constituents and their distribution in a wood cell wall [FAIT45]

Cell wall constituents	<i>Ulmus americana</i>	<i>Acerrubrum</i>	<i>Betula papyrifera</i>	<i>Fagu grandifolia</i>	<i>Populus tremuloides</i>
Cellulose	51	45	42	45	48
lignin	24	24	19	22	21
glucoronoxylan	19	25	35	26	24
glucomannan	4	4	3	3	3
Pectin, starch, ash,..	2	2	1	4	4

Table II.1: chemical constituents of the extractive – free wood in five hardwoods[TIME67]

Cell wall constituents	<i>Thuja occidentalis</i>	<i>Abies balsamea</i>	<i>Picea glauca</i>	<i>Pinus strobus</i>	<i>Tsuga canadensis</i>
Cellulose	41	42	41	41	41
lignin	31	29	27	29	33
glucoronoxylan	14	9	13	9	7
glucomannan	12	18	18	18	16
Pectin, starch, ash,..	2	2	1	3	3

Table II.2: chemical constituents of the extractive – free wood in five softwoods [TIME67]

In addition to these major cell wall components, various kinds of extractives, pectic substances and starch are present in much smaller quantities in both hardwoods and softwoods. Extractives of wood vary in quantity in the range of up to 10% that are always more abundant in heartwood than sapwood. Ash from inorganic matters usually makes up between 0.1% and 0.5% of wood, but tropical species often exceed this range.

The effect of the cell wall thickness on polysaccharide content of wood by comparing earlywood and latewood from the Scots pine (*Pinus sylvestris* L.) has been studied. As shown in table II.3, the latewood contains more glucomannan and less glucuronoarabinoxylan than the earlywood. Since the proportion of the latewood tracheid S2 layer to the whole wood is greater than that of the earlywood, the observed differences are due to mainly to the thicker S2 layer in latewood tracheids. It may therefore be concluded that the tracheid⁶ S2 layer has more glucomannan and less glucuronoarabinoxylan than other morphological regions.

polysaccharides	earlywood	latewood
Cellulose	56.7	56.2
Galactan	3.4	3.1
glucomannan	20.3	24.8
arabinan	1	1.8
glucuronoarabinoxylan	18.6	14.1

Table II.3: a comparison in polysaccharide composition between earlywood and latewood from Scots pine [TIME67]

⁶ Tracheids are elongated cells in the xylem of vascular plants, serving in the transport of water. The build of tracheids will vary according to where they occur.

II.3. The cell wall structure

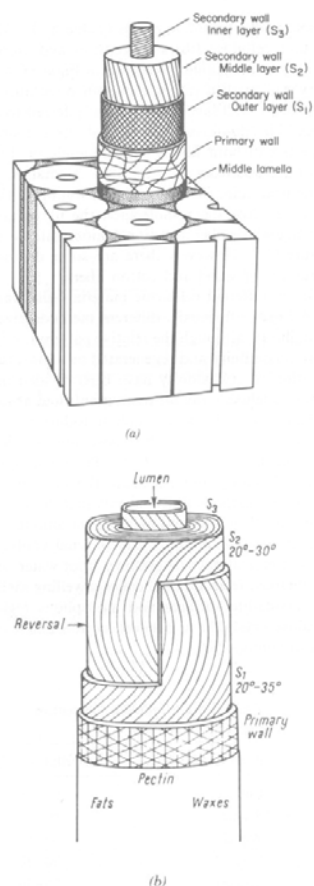


Figure 0.4: Structure of (a) wood and (b) cotton fibers showing microfibril orientations and relative size of different layer of cell wall [YOUN86]

Commercially, the two most important cellulose fibres are cotton and wood pulp, and their microfibrillar structures are similar as shown in figure II.4.

Both fibres contain a primary wall with a rather random orientation to the microfibrils and a thin S₁ secondary wall layer that is often referred to as the winding layer with cotton fibres. The dominant S₂ layer of the secondary wall essentially dictates the properties of both fibres, and the angle of the microfibrils in this layer depends on the origin of cellulose fibre (cotton or wood or bast fibres). A small layer S₃ layer is also present in both fibres. However, there are some distinct differences in the more detailed structure of wood and cotton fibres.

The features of every wall (primary and secondary) are given in the following section.

II.3.1. Primary wall

The primary wall is only few tenths of a micron thick and contains only 5% of the cellulose matter constituting the fibre. It consists, beside cellulose, mainly of pectin and waxes. When cotton fibres are purified by extraction with organic solvents and dilute alkali in order to remove wax and pectin impurities and stained (for examination in the polarizing microscope or electron microscope) an irregular network fibrillar element is revealed on the surface of the primary wall.

Especially for the cotton fibre, the fibre wall, when examined under the usual compound microscope, shows no evidence of structure, but it has been demonstrated that the cellulose in the primary wall forms an open mesh of very fine thread – like structures with anastomosis (it means they have a branching habit, like arteries) [MARS41]. The primary wall can be stained with Congo Red or zinc chloride – iodine and to be examined between crossed polarisers. The colouring matter is directionally adsorbed on the surface of cellulose and the double refraction of the orientated colouring matter, in addition to the double refraction of cellulose, makes the cellulose strands appear prominently. On young cotton, it was observed that there were

present two opposing systems of fine, spirally wound, threads of cellulose at an angle of about 70° to the long axis of the fibre. The cylindrical form of the young hair makes it possible to prove that the two systems of spiral threads exist in the same wall. Both right and left hand spiral were seen when the microscope was focused on the upper wall. They disappeared in the upper wall as the focal plane was lowered and appeared in the lower wall when the focus was established there. A third arrangement of the cellulose in the primary wall appeared when the stage of the polarising microscope was rotated so that the long axis of the fibre made an angle of 45° with the planes of polarisers. A system of transverse strands of cellulose became visible. These three systems of strands which make the cellulose framework of the primary wall seem to be uniform over the entire surface.

II.3.2. Secondary wall

The chemical composition of the secondary wall shows a much wider range of variability than that of the primary wall. The cellulose content of the secondary layer may vary from 0 to 97%, the lignin content between 0 and 30%, the hemicellulose content between 1 and 50%, the pectin content between 0.5 and 45%. The amount of polysaccharides varies between 0 and 50%, the mannan content between 0 and 60%, xylan between 0 and 40%, substances with lipid character between 1 and 60%, etc.

As the chemical composition of the secondary wall shows such a wide range of variability, it is certainly no wonder that the submicroscopical structure too differs considerably [ROEL59]. The three layers of the secondary wall, designed S1, S2 and S3, are organized. The S1 or S3, with a large microfibril angle to the cell is designed as a flat helix, and the S2, with a small angle, as a steep helix. It is composed of several lamellae with alternating S and Z helices of oriented microfibrils, and this structure in the S1 is termed “crossed fibrillar texture”. The middle layer of the secondary wall (S2) is the thickest within the layers of the secondary wall. Therefore, the S2 contributes most to the bulk of the cell wall material and is a compact region in which a high degree of parallelism of microfibrils exists. The S3 is a thin layer of flat helices of microfibril orientation as seen in S1. The S3 (or again called tertiary layer) is birefringent to a somewhat lesser degree than the S1: the S3 layer is poorly developed [HON 00].

The cellulose in the secondary wall is laid down in fibrils that form a spiral with frequent reversals about the axis of the fibre. At the base of the cellulose fibres, the spiral is generally left – handed, but undergoes reversals. At the reversals, the fibrils must be parallel to the fibre axis. The fibrillar nature of the cellulose and the orientation of the spiral to the fibre axis are very important for the understanding of the finer structure of the cotton. The first layer (S1) of secondary deposition appears to be different from the bulk (S2) of the cellulose that constitutes the secondary layer: the spiral angle of this layer was steeper than that of the rest of the secondary wall, and frequent reversals were found. The layer S1 is called “winding” layer. The microfibrils are oriented in a cross helical structure (S helix or Z helix). The relative position of the reversals in the different layers of the secondary wall changes and hence it is possible for the “winding” to have direction of spiral the same as subsequent layers [WARW66]. The S2 layer remains the most perfectly parallel oriented at the level of microfibrils. In the case of wood, helix angles varies between 50 and 70° for S1, 10 and 30° for S2, and 60 and 90° for S3. The angle of the spiral to the fibre axis varies between 35 and 45° according to the species of cotton, and alters on swelling.

Concerning the reversals, it is noted that the angle of orientation is different layers and change many times from an S and Z spiral, and vice versa, at irregular intervals along the fibre axis [OTT 54]. Frequently, although not invariably, the fibrils in the outer layer of secondary wall (S1) are oriented in a direction which is opposite from the spiral of the fibrils which lie immediately beneath it. It means, if the winding makes an S spiral, the fibrils beneath the

winding make a Z spiral. Furthermore, the places where the fibrils in different layers reverse their direction of spiral often coincide. This condition accounts for the extinction bands which are observed when unswollen fibres are placed approximately parallel to the plane of vibration of the light passing through one of two crossed nicol prisms. The relatively high birefringence of the fibres as a whole is then interrupted by dark extinction bands which coincide with the points where the fibrils reverse their direction of orientation. These reversals are sometimes preferred locations of break when the fibres are ruptured in tensions.

The structural features of the cotton or wood fibre have pronounced effects on the physical properties [ORR 61]. For example in the case of cotton, the high crystallinity of the fibrils possibly aids in recovery of elongation [ORR 57]. In such a structure, the reversals are vital to full utilisation of the spiral structure in extension. In fact, without reversals to allow untwisting of the spiral, high radial pressures and shear stresses would be developed within cellulose fibres. The untwisting was observed during the application of a freely hanging load to short lengths of fibre. Certain fibres turned clockwise, other counter-clockwise, and some not at all. The fibres untwist clockwise when load is applied were those with a net length of Z spiral, and vice versa.

II.4. Conclusion on the structure of plant cell walls

The structure of plant cell walls is the key feature that governs the properties of cellulose fibres (cotton or wood). The history of each cellulose fibre is described by the relationships between the chemical components and their contents because they come from the biosynthesis of fibre (birth and growth of every layer). The complexity and the large variety of combination at the level of the structure of walls, and each layer, reveals the wealth and the complexity of cellulose fibres in Nature. The cellulose fibres are essentially structured by two walls (primary and secondary) whose chemical components (carbohydrates components as cellulose, hemicellulose, pectic substances; and lignin, and other components as fatty or wax substances) have a content and bonding network determined by the origin, the age and the treatment of fibre. The primary wall is formed during the birth of cellulose fibre, by deposition of cellulose produced by golgi vesicles of plant cell and transported through plasmic membrane of plant cell. The secondary wall is created during the growth of fibre. This wall is composed of three layers: S1, S2 and S3. The orientation of microfibrils is a major parameter of the structure of plant cell walls, because the swelling or mechanical properties are notably influenced by this parameter.

Moreover, the role of cellulose fibre structure in determining the interactions and the behaviour with external agents like solvents is primordial, as explained in the following section.

III. Swelling and dissolution of cellulose fibres

A large part of the cellulose chemistry, physics and technology deals with its swelling and dissolution. It is thus natural that these topics have been attracted the attention of thousands of technologists, entrepreneurs and researchers. 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. One of these is the way cellulose structures are dissolved. It is generally admitted that cellulose is difficult to dissolve due to a tight array of inter and intra hydrogen bonds that hard to break to free individual cellulose chains. It is also admitted that cellulose needs to be “accessible” to be dissolved. One of the classical points of view is that cellulose crystals are difficult to dissolve and they are the limiting point for dissolution. Nevertheless, a lot of vague, empirical and often conflicting statements are given in the numerous papers dealing with these subjects. Thus the

objective of this section is to revisit the data on polymer dissolution, especially for cellulose fibres (accessibility notion, swelling and dissolution modes) and to give a classification of known solvent system for cellulose material.

III.1. Dissolution mechanism of a polymer

Polymer dissolution [MILL03] 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 generally controlled by the external mass transfer resistance through a liquid layer adjacent to the solid-liquid interface. However the situation is quite different for polymers. The dissolution of a polymer into a solvent involves two transport processes, namely solvent diffusion and chain disentanglement.

When an uncrosslinked, amorphous, glassy polymer is in contact with a thermodynamically compatible solvent, the solvent will diffuse into the polymer. Due to plastification of the polymer by a solvent, a gel like swollen layer is formed along with two separate interfaces, one between the glassy polymer and gel layer and the other between the gel layer and the solvent. The concentration of the gel layer decreases and the polymer dissolves. However, there also exist cases where a polymer cracks and no gel layer is formed.

III.1.1. Surface layer formation and mechanisms of dissolution

One of the earliest contributions to the study of polymer dissolution was due to Ueberreiter [UEBE68] who studied the surface layer formation process. First the solvent begins its move by pushing the swollen polymer substance into the solvent, and, as time progresses, a more dilute upper layer is pushed in the direction of the solvent stream. Further penetration of the solvent into the solid polymer increases the swollen surface layer until, at the end of the swelling time, a quasi stationary state is reached where the transport of the macromolecules from the surface into the solution prevents a further increase of the layer. Ueberreiter summarised the structure of the surface layers of glassy polymers during dissolution from the pure polymer to the pure solvent as follows: the infiltration layer, the solid swollen layer, the gel layer, and the liquid layer (figure III.1).

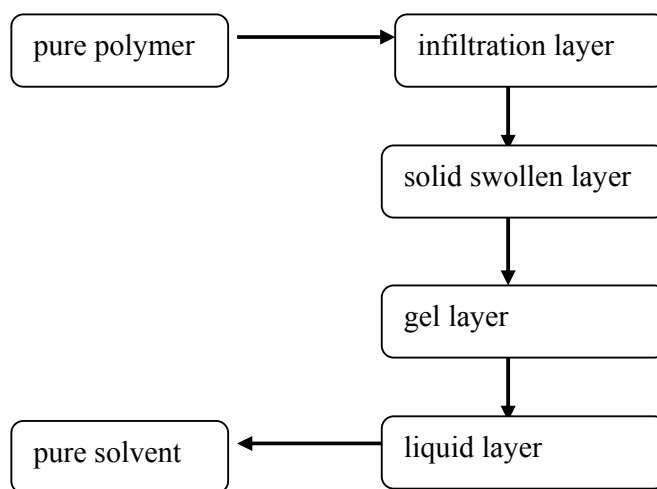


Figure 0.1: Schematic diagram of the composition of the surface layer [MILL03]

The infiltration layer is the first layer adjacent to the pure polymer. A polymer in the glassy state contains free volume in the form of a number of channels and holes of molecular dimensions, and the first penetrating solvent molecules fill these empty spaces and start the diffusion process without any necessity for creating new holes. The next layer is the solid swollen layer where the polymer – solvent system building up in this layer is still in the glassy state. Next, the solid swollen layer is followed by the gel layer, which contains swollen polymer material in a rubber – like state, and a liquid layer, which surrounds every solid in a streaming liquid, respectively.

Two types/mechanisms of dissolution were proposed. With the first type of dissolution, termed “normal dissolution”, all the layers described above are formed. The second type of dissolution occurs when no gel layer is observed.

III.1.2. Effect of different factors on dissolution

One of factors influencing on the polymer dissolution is the polymer molecular weight. It was found that the dissolution rate decreases with increased polymer molecular weight.

Besides the molecular weight of the polymer, the dissolution process can also be affected by the chain chemistry, composition and stereochemistry. The polymer dissolves either by exhibiting a thick swollen layer or by undergoing extensive cracking, depending on how fast the osmotic pressure stress that builds up in the polymer matrix is relieved. Therefore, the nature of the polymers and differences in free volume and segmental stiffness are responsible for behavior variations from polymer to polymer.

The type of penetrating solvent can also have a profound affect on polymer dissolution. External parameters such as agitation and temperature as well as radiation exposure (photo degradation in the wavelength region from the far UV to the infrared, or high – energy radiation as electron beam) can influence the dissolution process. The velocity of dissolution increases with the agitation and stirring frequency of the solvent due to a decrease of the thickness of the surface layer, and the dissolution rate approaches a limiting value if the pressure of the solvent against the surface of the polymer is increased (at all the temperatures). The effects of agitation are the following. With no agitation, the solvent molecules penetrate the polymer, and a gel layer forms. However, the gel layer decreases in magnitude with time due to desorption of the polymer chains. On the other hand, when agitation is present, no gel layer is formed because it is stripped off rapidly by the stirring process. In the latter case, the sorption of solvent molecules is immediately followed by desorption of the polymer chains from the solid swollen layer.

III.1.3. Polymer dissolution models

Several models have been formulated to explain the experimentally observed dissolution behaviour and have been reviewed. There are five main approaches to modelling polymer dissolution:

- Phenomenological models with Fickian equation: these models attempt to physically describe the dissolution process using Fickian conditions and the moving boundaries present in the system.
- Models with external mass transfer as the controlling resistance to dissolution: these models assume that the controlling factor in dissolution is resistance due to an external mass transfer.
- Stress relaxation models and molecular theories : these models predict the polymer relaxation response to solvent uptake.
- Analysis using transport models for swelling and scaling laws for chain disentanglement: these models are used to calculate polymer dissolution in the anomalous transport and scaling models.

- Continuum framework models: these take into account the viscoelastic effects and mobility changes of the polymer during dissolution while using anomalous transport models to predict the behaviour of solvent diffusion

III.2. Important classes of cellulose solvent systems

Several proposals have been made in recent years for a systematisation of the vast number of solvent systems known today [KLEM98]. From the viewpoint of the organic chemistry of cellulose, a classification according to the two categories of nonderivatizing and of derivatizing solvents is considered most appropriate. The term “nonderivatizing solvent” denotes systems dissolving the polymer by intermolecular interaction only. Aqueous metal transition – complex solvent systems are conveniently included in this category despite an often very strong interaction, as no covalent derivatization occurs. 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. A specification within the large group of systems derivatizing cellulose with a change from a heterogeneous to a homogeneous system, is given by the criterion that the derivative formed in a so – called derivatizing solvent system is easily decomposed to regenerated cellulose by changing the pH – value of the system. Both categories of solvent systems comprise aqueous as well as nonaqueous compositions.

This section will be structured according to nonderivatizing and derivatizing solvent systems, covering in each category aqueous as well as nonaqueous ones. The transition metal-complex solvent systems are added to the category of nonderivatizing solvents as a special group.

III.2.1. Nonderivatizing organic solvents for cellulose

Due to their relevance for the organic chemistry of cellulose under homogeneous conditions, the numerous solvents having an organic liquid shall be considered first and in some detail before turning to aqueous solutions of some bases and of transition metal complexes showing solvent action on cellulose.

From an historical point of view, combinations of some simple inorganic compounds, i.e. of SO_2 , NH_3 , and a suitable ammonium salt, can indeed be considered as the origin of two large groups of nonderivatizing solvent systems, and also inorganic compound N_2H_4 , i.e. water free hydrazine has been described as an efficient also somewhat exotic solvent for cellulose.

The first group to be mentioned comprises a large number of systems containing SO_2 in combination with aliphatic amines and a suitable polar organic liquid. The sulfur component may be modified by employing SOCl_2 . Suitable polar liquids employed as the third component are for example *N,N* - dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N,N* - dimethylacetamide (DMAc), or formamide. The interaction of these solvents can be understood as an electron donor - acceptor interaction. But also a transition to some kind of covalent interaction may occur. The SO_2 – containing systems obviously have no chance of technical realisation due to aggressiveness of SO_2 , but they have been used successfully for special derivatizations under homogeneous conditions (for example benzylation of cellulose).

The second group of solvents systems considered consists of an amino – group – containing an active component in a suitable polar organic liquid with a further component such as ethanolamine and/or a suitable inorganic salt like sodium bromide being added to facilitate cellulose dissolution. This group of solvents therefore exhibits a very broad spectrum with regard to chemical composition, without a clear cut systematization and interpretation of chemical binding forces being possible up to now.

Another group of nonderivatizing organic solvent systems for cellulose, which has to be considered today as the most relevant one with regard to practical use, takes advantage of the strong intermolecular interaction between the polymer and some dipolar aprotic organic

compounds with $N \rightarrow O$ or $C=O$ dipoles. From the experimental point of view, as well as with regard to the interaction mechanism, this class of solvents has to be subdivided into the two groups of salt-free and salt – containing systems, the latter generally using LiCl as an additional component with rather high solubility in the dipolar aprotic compound.

N-methylmorpholine-*N*-oxide (NMMO) and its monohydrate form the basis of an alternative process now used for cellulosic manmade fibre manufacture, already on a technical scale. NMMO – 1 H₂O dissolves even high DP cellulose rather quickly at a temperature of about 90°C to a clear melt solution. The aminoxide can be diluted with an aprotic compound like DMF or DMSO down to a ratio of about 1:1 without losing its solvent power. The interaction between NMMO and cellulose can be interpreted as a hydrogen – bond – complex formation with a superimposed ionic interaction (figure III.2):

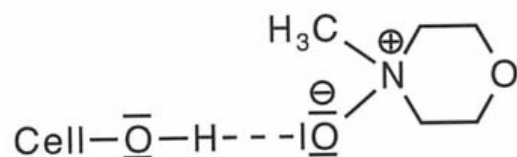


Figure 0.2: Hydrogen bond complex formation due to the interaction between NMMO and cellulose [KLEM98]

Moreover, water is included in the electron donor – acceptor interaction between cellulose and NMMO via hydrogen bonds involving the O- and the H- atoms of the cellulose hydroxy groups, as well as H₂O molecule of the NMMO monohydrate, as the solvent – active species.

Another important solvent is the sodium hydroxide system. It has been well known for many decades that upon an interaction between aqueous sodium hydroxide and cellulose, a limited part of the polymer is dissolved, the amount depending on lye concentration as well as on cellulose structure, and being composed mainly of easily accessible short cellulose chains. As has been shown [SOBU39], there is a dissolution window of 5 - 10 % of NaOH at low temperatures (from -7°C to -2°C). A rather complete solubility in 10% aqueous NaOH is observed with viscose rayon after acid hydrolysis to the level – off DP of 30 – 40 or with xylan obtained by alkaline extraction from beech wood or wheat straw [KLEM98]. The solubility of cellulose samples in aqueous NaOH can be significantly enhanced by adding zinc oxide [DAVI37] or urea or thiourea [RUAN04] to the system and/or by lowering the temperature of the treatment. Addition of zinc oxide leads to an in situ formation of a zincate complex facilitating dissolution of cellulose chains up to a DP of about 200, even at room temperature.

The addition of urea and thiourea is increasing the solvent power of NaOH - water. The effect of urea can be understood by a breaking of the clustered water structure enhancing the content of free monomolecular water, which promotes swelling and dissolution of the polymer. The increase in solubility by lowering the temperature of the system is in agreement with an exothermic heat of dissolution, and has been investigated thoroughly in recent years with regards to a possible fibre spinning from cellulose – NaOH solutions at low temperature [KLEM98].

Another important solvent is LiCl – DMAc, that can be used for cellulose etherification and esterification under homogeneous conditions. After preactivation, even high molecular cellulose samples can be dissolved without residue and detectable chain degradation. This can be considered as an important asset of this solvent for analytical purposes, as well as for homogeneous cellulose derivatisation.

Cellulose dissolution without covalent derivatisation in general can be understood as an acid – base interaction with the amphoteric cellulose taking the role either the acid or the base in independence on the solvent structure. This acid – base concept may be useful for aqueous solvents, but obviously is of minor relevance in connection with organic solvents of limited polarity or ionizability. An electron donor – acceptor interaction is considered to be the driving force of many dissolution processes of cellulose in organic system, assuming a participation of the O – atom as well as the H – atom of the cellulosic hydroxy group with the same or with different compounds of the solvent. Such scheme is presented in the figure III.3.

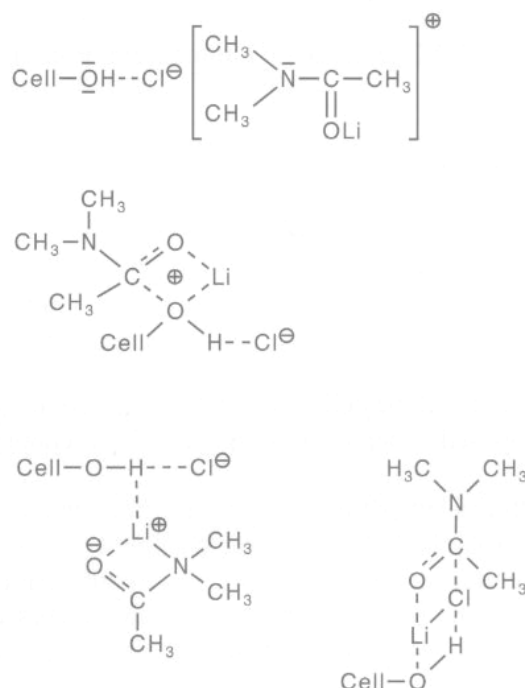


Figure 0.3: Schematic interaction of cellulose with LiCl – DMAc [KLEM98]

III.2.2. Ionic compounds in aqueous solution as cellulose solvents

Some inorganic acids, strong bases, and some inorganic salts in concentrated solution can act as cellulose solvents of limited solvent power. Especially in the case of acids and concentrated salt solutions at higher temperature, the dissolution is accompanied by severe chain degradation, limiting further the practical relevance of these classes of solvent.

Only a small number of all these compounds reported to dissolve cellulose are of a real practical interest in cellulose chemistry. Aqueous phosphoric acid with an acid content of about 85% has long been known as a solvent for cellulose.

Some tetraalkylammonium hydroxydes in concentrated aqueous solution, like dimethylbenzylphenylammonium hydroxyde or triethylbenzylammonium hydroxide could be included in this group. The tested ionic liquids used in this work could be included in this group (they are detailed in chapter 5).

III.2.3. Aqueous solutions of transition metal complexes as solvents for cellulose

Solvent of practical relevance for analytical are the copper complexes with ammonia (cuoxam) and ethylenediamine (cuen), the cadmium complex with ethylenediamine (Cadoxen) and the ferric tartaric acid complex in alkaline aqueous solution (FeTNa). All of these four complex systems are able to dissolve cellulose completely without residue, the

nitrogen – containing complexes being rather quickly, the ferric tartaric acid complex more slowly.

III.2.4. Derivatizing solvent systems for cellulose

In contrast with many of the nonderivatizing solvents considered above, the chemical interaction between cellulose and the solvent on the molecular level is rather well defined and well understood in the case of most derivatizing solvent systems. Open questions still arise in connection with the interference of the hydrogen – bond system along and between the polymer chains on the course of the simultaneous derivatization and dissolution, and also with regard to the course and state of solvation of the substituted and nonsubstituted sites within the anhydroglucose unit.

A selection of nonaqueous as well as aqueous derivatizing solvent systems is presented in table III.1:

System	Cellulose derivatives formed
H ₃ PO ₄ (> 85%) / H ₂ O	Cell – O – PO ₃ H ₂
HCOOH / ZnCl ₂	Cell – O – (O)CH
CF ₃ COOH / CF ₃ (CO) ₂ O	Cell – O – (O)CCF ₃
N ₂ O ₄ / DMF	Cell – O – N=O
Me ₃ SiCl / pyridine	Cell – O – SiMe ₃
(CH ₂ O) ₃ / DMSO	Cell – O – CH ₂ OH
CCl ₃ CHO / DMSO / TEA	Cell – O – CH(OH) – CCl ₃
CS ₂ / NaOH / H ₂ O	Cell – O – C – (S) – SNa

Table 0.1: Examples of aqueous and non – aqueous derivatizing and solubilizing systems for cellulose [KLEMM98]

The three acidic systems, i.e. concentrated formic acid in the presence of ZnCl₂ or H₂SO₄ as a catalyst, trifluoroacetic acid and N₂O₄ / DMF are able to dissolve even high DP cellulose, which is accompanied, however, by more or less severe hydrolytic chain degradation. Therefore, trifluoroacetic acid is used frequently for simultaneously dissolving and hydrolyzing cellulose samples.

III.3. Accessibility of cellulose fibres

Chemical processing of cellulose proceeds during in whole course or at least in the initial phase in a heterogeneous reaction medium. Rate and final degree of conversion in these heterogeneous reactions depend strongly the availability on the hydroxy groups in the anhydroglucose units, so – called accessibility. From the sight of cellulose structure, accessibility depends largely on the available inner surface, and also on supramolecular order and fibrillar architecture. But it is important to emphasize that the accessibility of a cellulose sample is by no means a constant structural parameter, as it depends decisively on the interaction considered. For example, only the AGUs situated at the inner surface of the pore and void system are accessible for sorption of inert gases, whereas even the cellulose chains in the highly ordered crystalline regions are accessible to aqueous NaOH of suitable concentration. Due to this key principle of accessibility and type of interaction in question, the results obtained with the different methods of accessibility determination published cannot be expected to coincide, and only data assessed by the same technique with different samples should be compared. For a routine characterisation of cellulose accessibility, often the interaction with water is employed, which is able to destroy weaker hydrogen bonds but cannot penetrate into the regions of high order.

The accessibility is determined by the ability of external agent to penetrate and/or react with the cellulose structure. Thus the pore structure and inner surface on cellulose fibre influence the accessibility and is describing in the following part. Then, different kind of swelling are described because it is a way to understand how an external agent could interact with cellulose structure.

III.3.1. Pore structure and inner surface

Complementary to the fibril architecture of the fibre cell wall is a system of pores, capillaries, voids, and interstices. These pores are by no means uniform in size and shape, and besides a total pore volume and an average pore size parameter, information on size distribution and even on the shape on the pores would be necessary for a complete description of the pore system, which plays a decisive role in all heterogeneous chemical reactions of cellulose [KLEM98].

Quantitative information on pore volume and pore size is available by small x-ray scattering SAXS in the range of 2-80 nm and by mercury porosimetry in the range of about 15-1000 nm of pore diameter. The latter technique, however, is limited to voids available from the fibre surface. SAXS and mercury porosimetry overlap somewhat with regard to pore size range covered and supplement each other with respect to the pore criterion assessed.

	Volume of pores (%)	Inner surface of pores (m ² /g)	Parameter of average pore size (nm)
Cotton linters	1.7 – 1.8	5.3 – 6.0	11.6 – 13.1
Sulfite dissolving pulp	0.7 – 1.5	1.7 – 3.2	10.1 – 25.4
Sulphate pulp ^a	1.2	3.7	13.1
Cellulose powder ^b	1.4	5.2	10.4
Cellulose powder mercerized	1.7	15.8	4.4
Cellulose powder enzyme-treated	2.5	6.2	15.9

^a prhydrolyzed

^b prepared from spruce sulfite pulp by partial hydrolysis and mechanical disintegration

Table 0.2: Data on pores of various cellulose samples as calculated by SAXS measurements [FINK92]

The data (table III.2) indicate a broad variability of pore criteria within the group of sulfate dissolving pulp. Mercerisation of a level-off degree of polymerisation cellulose powder results in a significant decrease in pore diameter in connection with a remarkable enhancement of micropore surface. Enzyme treatment, on the other hand, obviously enlarges the existing pores, as to be concluded from the increase in pore volume and pore diameter.

The total pore volume and the pore size distribution are very sensitive to swelling and drying treatments of the cellulose fibre samples: it has long been known that the first drying of cellulose results in a significant and irreversible reduction of the pore volume due to a so-called hornification by a tight cohesion of fibrillar elements. Intercrystalline swelling (as detailed in the next section III.3.2.a) by water or ethanol amine, however, leads to an increase in pore volume, which can be preserved by suitable drying techniques like freeze drying or solvent exchange.

Due to the pore and void system, the total surface area of cellulose exceeds by far the geometrical outer surface. The so – called inner surface area is a decisive factor with regard to

accessibility and reactivity in dissolution and derivatisation processes of the polymer; The data published on inner surface area cover a wide range, from below 1 to 1000m²/g, depending on origin and history of the sample, as well as on the procedure of determination. Some data on the inner surface of cellulose materials obtained by N₂ sorption and supplied by Jocabasch [JOCA84] are presented in table III.3. The data indicate a much higher inner surface in the presence of water than that calculated in the presence of inert gas sorption in the dry nonswollen state. As already emphasized in connection with pore volume and pore size, the data on inner surface are strictly comparable only if assessed by the same technique, as the various procedures can differ on the one hand with regard to the size of accessible interstices, and on the other hand with regard to changes of the inner surface properties by interaction, e.g. swelling, of the cellulose with the substance employed.

	pretreatment	Surface (m ² /g)
Spruce sulfite pulp		0.35
Spruce sulfite pulp	H ₂ O swollen, freeze - dried	5.3
Cotton		0.60 – 0.72
Viscose rayon staple		0.3 – 0.4

Table 0.3: Inner surface of some samples calculated from N₂ sorption [JOCA84]

Nevertheless, some conclusions of a more general nature can be drawn from the available data: the first drying of a cellulose fibre from the never – dried state usually leads to a significant decrease in available inner surface area, which can only partially be reversed by subsequent re - swelling. For cotton and cotton linters, a smaller inner surface area has been generally reported compared to wood pulp. Under comparable conditions, viscose rayon staple exhibited a considerably higher inner surface than cotton [BRED89].

Swelling is a characteristic which is closely associated with most cellulose reactions and with most stretching and forming operations necessary for the production of strong regenerated films and fibres. According to Katz, a solid is said to swell when it imbibes a liquid while at the same time it does not lose its apparent homogeneity, its dimension are enlarged, its cohesion diminished and it becomes soft and flexible.

Solid which can undergo swelling are, in a most cases, substances of high molecular weight. Furthermore, many of these solids consist of a large number of discontinuous crystalline regions which are separated by regions of lower cristallinity, and are usually composed of macromolecules containing polar groups capable of forming fairly strong interchain bonds. The swelling behaviour of these solids is frequently dictated to a great extent by this interchain bonding. Liquids or vapours which cause swelling must be capable of breaking these secondary bonds between molecules and of forming their own bonds with the polymer. As a corollary, it follows that in any solid containing both crystalline and amorphous regions, it will be more difficult for the swelling liquid to disrupt the dense hydrogen bond network of the crystalline regions than to disrupt the dense hydrogen bond network of less crystalline regions. Cellulose fibres, as high molecular weight solids in which the molecules are held together by at least three types of bonds (Van der Walls forces, polar hydrogen bonds, and primary valence bonds), fulfil all the conditions for complex swelling and associated phenomena.

III.3.2. Types of swelling

On –the basis of the X-ray diagrams of swollen cellulose, Katz has defined two principal types of swelling as “intermicellar” and “intramicellar” swelling. Now these phenomena are defined as “intercrystalline” and “intracrystalline” swelling, respectively.

In intercrystalline swelling, the swelling reagent penetrates only the intercrystalline amorphous regions. In intracrystalline swelling, the swelling agent penetrates the interior of the crystalline as well as the intercrystalline material.

III.3.2.a. Intercrystalline swelling

The best example of cellulose intercrystalline swelling is the swelling of the cellulose fibres in water. As soon as water sorption begins, the fibres start to swell. The swelling increases in regular fashion as the total sorbed water increases with increasing relative humidity and attains its maximum value on immersion of the fibre in excess water. The total volume of the system increases with increasing swelling in such a manner that as a first approximation each water molecule entering the fibre can be assumed to contribute its normal molecular volume to the system. The magnitude of the swelling varies from fibre to fibre as shown by the fact that the maximum increase in cross-sectional area on swelling in water is 20-35% in natural fibre and 55-70% in regenerated fibres.

Organic liquids in general swell cellulose less than water, the swelling being chiefly dependent on the polarity and molecular volume of the liquid. Thus methanol swells cellulose less than does water; with increasing molecular weight, the swelling by normal alcohols decreases until it becomes low in n-butanol. Swelling beyond the water – swollen condition is also caused by aqueous solutions of various organic compounds such as thiourea.

As a general rule, a cycle of intercrystalline swelling and subsequent deswelling by removal of the swelling reagent does not affect the network structure to any great extent unless the structure has been set in metastable state by some extreme condition during its formation or some other factors such as temperature has been varied.

III.3.2.b. Intracrystalline swelling

When a swelling reagent capable of intracrystalline swelling is added to cellulose, the changes occurring may be divided into three steps as indicated by x-ray diagrams. When very little swelling reagent is added, the crystalline pattern is that of the original fibre. At some intermediate concentration or range of concentration of swelling reagent, the x-ray diagram consists of the pattern of the original fibre and a pattern characteristic of a swollen modification. With increasing concentration, the pattern of unchanged cellulose diminishes in intensity until only the pattern of the swollen modifications remains. The last step may take one of three courses with increasing concentration: (i) the diagram may change continuously with swelling reagent concentration until solution results (unlimited intracrystalline swelling), (ii) the diagram of swollen cellulose may indicate a crystalline structure as well defined as that of original cellulose and remain unchanged with further addition of swelling reagent (limited intracrystalline swelling), or (iii) the sharp diagram of case (ii) may change to a new crystalline form or begin to change continuously as in case (i) on further addition of swelling reagent.

III.4. Conclusion on the cellulose dissolution

Both the phenomena of swelling and of dissolution of cellulose induce a more or less complete destruction of the molecular order of the native polymer by overcoming the intermolecular interactions of the macromolecules by stronger intermolecular forces or by covalent derivatisation.

Swelling in aqueous as well as in non - aqueous media can occur in the easily accessible regions of cellulose only, or can affect the crystalline regions too. In both cases intermolecular cohesion between the polymer chain of cellulose are broken to a variable extent but the β – glucosidic link between the polymer chain is still maintained even in the case of the

intracrystalline swelling, mainly due to the limited solvation of the interaction compound. If swelling takes place in the easily accessible regions only (intercrystalline swelling), the increase in weight and volume of the samples results from a filling of the pore system by the swelling, combined with a rupture of interfibrillar bonds and from the uptake of swelling agent. In the case of intracrystalline swelling, usually an additional increase in lattice dimensions of the crystalline regions takes place, often resulting in an increase of one of the lattice spacings due to a so-called layer lattice reaction of the swelling agent with the cellulose.

The explanations on the swelling and dissolution for polymer and especially for cellulose fibres are required for this work. It becomes clear that the morphological architecture of fibres is among the key – parameters for swelling and dissolution mechanisms. The specific structure in layers born of biosynthesis will be determining in this study.

The following chapters detail the obtained results as a function of cellulose fibre origin and type of tested chemical agents. A large range of cellulose samples (cotton, wood, leaf and bast fibres) in various solvent systems (aqueous as N-methylmorpholine-N-oxide (NMMO) and water mixtures or sodium hydroxide (NaOH – water – additives solutions, and ionic liquids) have been explored.

References

- [BAIL54] I.W. Bailey, Contributions to Plant Anatomy, Waltham, Mass., Chronica Botanica Company, **1954**.
- [BIGA02] O. Biganska, Doctorat Science et Génie des Matériaux de l'Ecole des Mines de Paris, Sophia Antipolis, **2002**.
- [BRED89] K. Brederick, Textilveredlung **1989**, 24, 146.
- [BROG39] A. Brogniart, A.B. Pelonze, R. Dumas, Rapport interne de l'Académie Française **1839**, 8, 51.
- [DAVI37] G.F. Davidson, J. Text. Ind. **1937**, 28, 27.
- [ESSA65] K. Esau, Plant anatomy, Willey & Sons, New York, 2nd Edition, **1965**.
- [FAIT45] W.L. Faith, Ind. Eng. Chem. **1945**, 37, 9.
- [FAN 87] L.T. Fan, M.M. Gharpuray, Y.H. Lee, Cellulose Hydrolysis, Biotechnologies Monographs, Springer - Verlag, New York, **1987**.
- [FENG92] D. Fengel, Holzforschung **1992**, 46, 283.
- [FINK92] H.P. Fink, B. Philipp, C. Zschunke, M. Hayn, Acta Polym. **1992**, 43, 270.
- [GARD74] K.H. Gardner, J. Blackwell, Biopolymers **1974**, 13, 1975.
- [HARR53] E.E. Harris, Tappi **1953**, 36, 402.
- [HAIG86] C.H. Haigler, R.M. Brown R, Protoplasma **1986**, 134, 111.
- [HEAR62] J.W.S. Hearle, J. Text. Inst. Proc. **1962**, 53, 143.
- [HERM49]₁ E.H. Herman, J. Polym. Sci. **1949**, 4, 135.
- [HERM49]₂ E.H. Herman, Physics and Chemistry of cellulose fibres, Elsevier Publishing Company, Inc, New York, **1949**.
- [HON 00] N.S.D. Hon, N. Shiraishi, Wood and Cellulosic Chemistry, 2nd Edition, Marcel Dekker Inc, New York, **2000**.
- [HOWS63] J.A. Howsmon, W.A. Sisson, Structure and properties of cellulose fibers, B-Submicroscopic Structure, in Cellulose and Cellulose Derivatives **1963**, Part I, 231.
- [JOCA84] B. Jocabasch, Oberflächen Faserbildender Polymere, Berlin: Akademie Verlag, **1984**.

- [KATZ33] J.R. Katz, Trans. Faraday Soc. **1933**, 29, 279.
- [KLEM05] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Angew. Chem, Int. Edit **2005**, 44, 3358.
- [KLEM98] D. Klemm, B. Philipp, T. Heinze, Fundamentals and Analytical Methods, Comprehensive Cellulose Chemistry, vol 1, Wiley-VCH, Weinheim, Germany, **1998**.
- [KOLP76] F.J. Kolpak, J. Blackwell, Macromolecules **1976**, 9, 273.
- [KRAS93] H.A. Krässig, Cellulose: Structure, Accessibility and Reactivity, Polymer Monographs, Gordon and Breach Science publisher, New York, vol 11, 1993.
- [KROO86] L.M.J. Kroon – Batenburg, J. Kroon, M.G. Nordholt, Polym. Commun. **1986**, 27, 290.
- [MARS41] J.Y. Marsh, Mercerising, Chapman & Hall Ltd, London, **1941**.
- [MILL03] B.A. Miller – Chou, J.L. Koenig, Prog. Polym. Sci. **2003**, 28, 1223.
- [MORR69] J.L. Morrison, M.A. Dzieciuch, Can. J. Chem. **1969**, 37, 1379.
- [MULD04] B. Mulder, J. Schel, A.M. Emons, Cellulose **2004**, 11, 395.
- [ORR 57] R.S. Orr, L.B. De Luca, A.W. Burgis, J.N. Grant, Text. Res. J. **1957**, 29, 114.
- [ORR 61] R.S. Orr, A.W. Burgis, L.B. De Luca, J.N. Grant, Text. Res. J. **1961**, 31, 302.
- [OTT 54] E. Ott, H.M. Spurlin, M.W. Grafflin, Cellulose and Cellulose Derivatives, Part 1, Intersciences Publisher, New York, **1954**.
- [PAYE42] A. Payen, Troisième mémoire sur le développement des végétaux - Extrait des Mémoires de l'Académie Royale des Sciences: Tome III des Savants étrangers, Imprimerie Royale, Paris, **1842**.
- [ROEL59] P.A. Roelofsen, The plant cell-wall, Encyclopedia of Plant Anatomy, Berlin – Nikolasse, **1959**.
- [RUAN04] D. Ruan, L. Zhang., Y. Mao, M. Zeng, X. Li, J. Membrane Sci. **2004**, 241, 265.
- [SAKA04] S. Saka, Wood as natural raw materials - Cellulose Acetates: properties and applications, Macromolecular Symposia, Rustemeyer Ed, Freiburg, **2004**.
- [SOBU39] H. Sobue, H. Kiesslig, K. Hess, Z. Physik. Chem. B **1939**, 43, 309.
- [STAU32] H. Staudinger, Die hochmolekularen organischen Verbindungen – Kautschuk und Cellulose, Springer Verlag, Berlin, **1932**.
- [SUGI91] J. Sugijama, R. Voong, H. Chanzy, Macromolecules **1991**, 24, 4168.

- [TIME67] T.E. Timell, Wood Sci. Technol. **1967**, 1, 45.
- [UEBE68] K. Ueberreiter, The solution process, in Diffusion in polymers, Academic Press publisher, New York, **1968**.
- [WARW66] J.O. Warwicker, R. Jeffries, R.L. Colbran, R.N. Robinson, A review of the literature on the effect of caustic soda and other swelling agents on the fine structure of cotton, Shirley Institute Pamphlet number 93, England, **1966**.
- [YOUN86] R.A. Young, R.M. Rowell, Cellulose: structure, modification and hydrolysis, John Wiley & Sons, **1986**.
- [ZUGE01] P. Zugenmaier, Prog. Polym. Sci. **2001**, 26, 1341.

<http://en.wikipedia.org>

(Advanced Research)

<http://www.biologydaily.com>

(The Science of life, Advanced Research)

<http://www.cermav.cnrs.fr>

(S. Pérez, W. Mackie, Structure and morphology of cellulose)

<http://www.faculty.sfasu.edu>

(http://www.faculty.sfasu.edu/mcbroommatth/Lectures/Wood_Science/Lecture_3_Wood_Cells.pdf)

Chapter 2

Swelling and dissolution mechanisms
of native cellulose fibres, part I:
free floating cotton and wood fibres in N-
methylmorpholine-N-oxide – water mixtures

Résumé francophone chapitre 2

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie I : fibres de bois et de coton dans le système NMMO – eau.

La première étape de notre étude sur les mécanismes de gonflement et de dissolution s'appuie sur l'observation de fibres de coton et de bois dans un mélange aqueux *N*-méthylmorpholine-*N*-oxide (NMMO) – eau. Le pourcentage d'eau dans le système NMMO – eau varie de 17 à 35% (rapport massique). Le but de cette première étude est de détailler au mieux le processus de gonflement et de dissolution de ces fibres natives par microscopie optique.

Nous répertorions cinq modes pouvant décrire le mécanisme d'interaction entre des fibres de cellulose native et un agent chimique externe :

- Mode 1 : dissolution rapide par désintégration de la fibre en fragments
- Mode 2 : gonflement par ballonnement, dissolution de toute la fibre
- Mode3 : gonflement par ballonnement, dissolution partielle de la fibre
- Mode4 : gonflement homogène, non dissolution de la fibre
- Mode5 : pas de gonflement ni de dissolution (cas d'un système non solvant)

Dans cette étude, quatre modes sont observés en fonction de la teneur en eau du système NMMO - eau. Pour une concentration en eau inférieure à 17%, les fibres de coton et de bois sont dissoutes rapidement par désintégration, il s'agit du mode 1. Une seconde gamme de solvants (NMMO – eau avec une concentration en eau comprise entre 17 et 24%) induit un gonflement hétérogène des fibres de bois et de coton, suivi par une dissolution totale de la fibre (mode 2). Des ballons, entourés par une membrane, naissent tout le long de la fibre, séparés par des zones non gonflées. La cellulose à l'intérieur des ballons est dissoute. Ce processus est découpé en quatre étapes temporelles : apparition des ballons, éclatement des ballons, dissolution des zones non gonflées et dissolution de la membrane des ballons. En augmentant encore la concentration en eau (23-30%) du système NMMO – eau, seul le gonflement homogène des fibres par ballonnement est observé, avec une dissolution partielle de la cellulose à l'intérieur des ballons (mode 3). Entre 35 et 45% en eau, le mode 4 est observé : les fibres de coton et bois subissent un gonflement homogène. L'étape de dissolution n'est jamais atteinte.

Les observations microscopiques réalisées dans le cas des modes 2 et 3 révèlent l'étonnante morphologie des ballons, entourés par une membrane. Une structure hélicoïdale est nettement visualisée au sein de cette membrane.

Dans la suite de ce travail, ces premiers travaux constitueront notre base de comparaison. Nous nous intéresserons particulièrement à l'étude de la membrane : son origine et surtout son influence sur le mécanisme de gonflement et de dissolution observé.

Chapter 2 is describing the behaviour of cotton and wood cellulose in *N*-methymorpholine-*N*-oxide (NMMO) and water mixtures. Five swelling and dissolution modes are observed and described. These five mechanisms will be the bench - marks for all our work.

Swelling and dissolution of cellulose Part I: free floating cotton and wood fibres in N-methylmorpholine-N-oxide – water mixtures

Celine Cuissinat,¹ Patrick Navard*^{1,2}

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Materiaux (CEMEF), Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207, 06904 Sophia Antipolis France

² Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu; Tel: 33 (0)4 93 95 74 66; Fax: 33 (0)4 92 38 97 52; E-mail: Patrick.Navard@ensmp.fr

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 unswollen sections. The whole fibre will completely dissolve (mode 2) in four successive steps (growth of the balloons, burst of the balloons, dissolution of the unswollen 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; swelling; *N*-methylmorpholine *N*-oxide

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] 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 for ex]. 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. The *middle lamella* is connecting the individual 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 an uncrosslinked, 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 fibers dipped in a chemical 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 exhibits a high hygroscopicity 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 seen 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 fibers 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.

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 *M_n*, *M_w* or *M_z* are determined by gel permeation chromatography (GPC).

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

- 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.

- 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 was attached by adhesive tape on plate in order to avoid the fibre to be too much affected by the solvent convection, which caused 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

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:

Lb = length of a balloon

Di = initial diameter of the fibre in the dry state

Df = diameter of a balloon

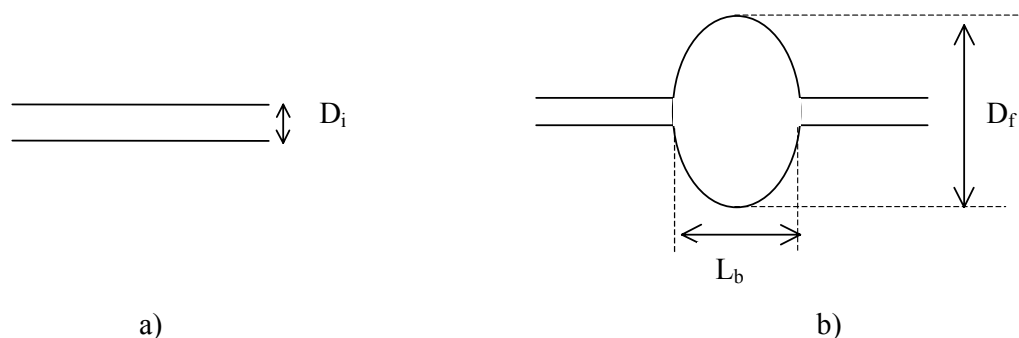


Figure1. a) schematic drawing of the geometry of native cellulose at dried state; b) schematic drawing of the geometry of native cellulose fibre at swollen state.

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).

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 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 was 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 exhibited 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 an unoriented 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 pretreatment 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 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).

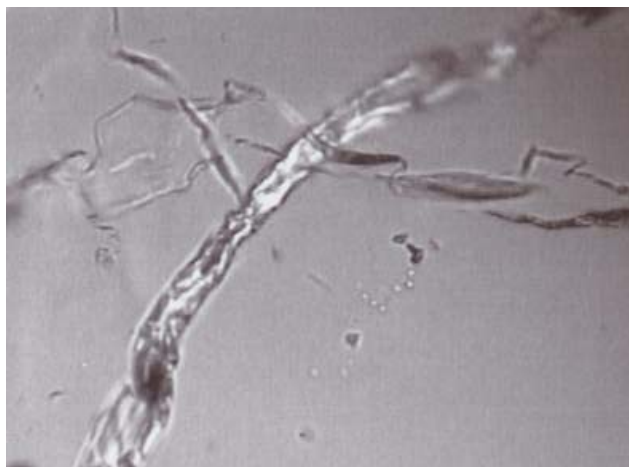


Figure 2. Borregaard fibre swollen in NMMO – water at 17% (optical microscopy in transmitted light).

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).

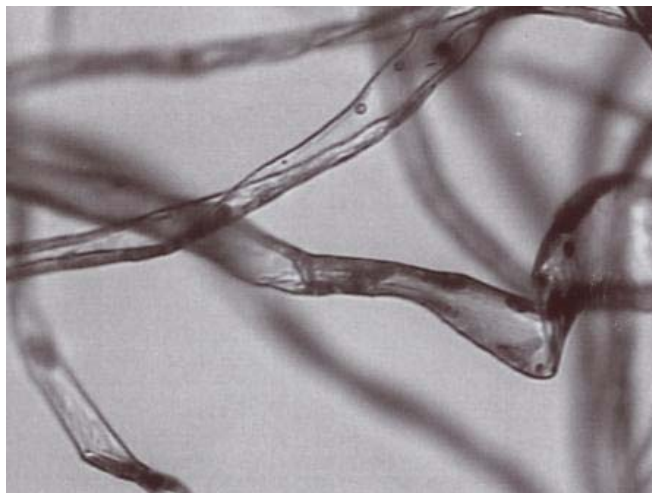


Figure 3. Cotton fibre swollen in NMMO – water at 35% (optical microscopy in transmitted light).

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 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 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.

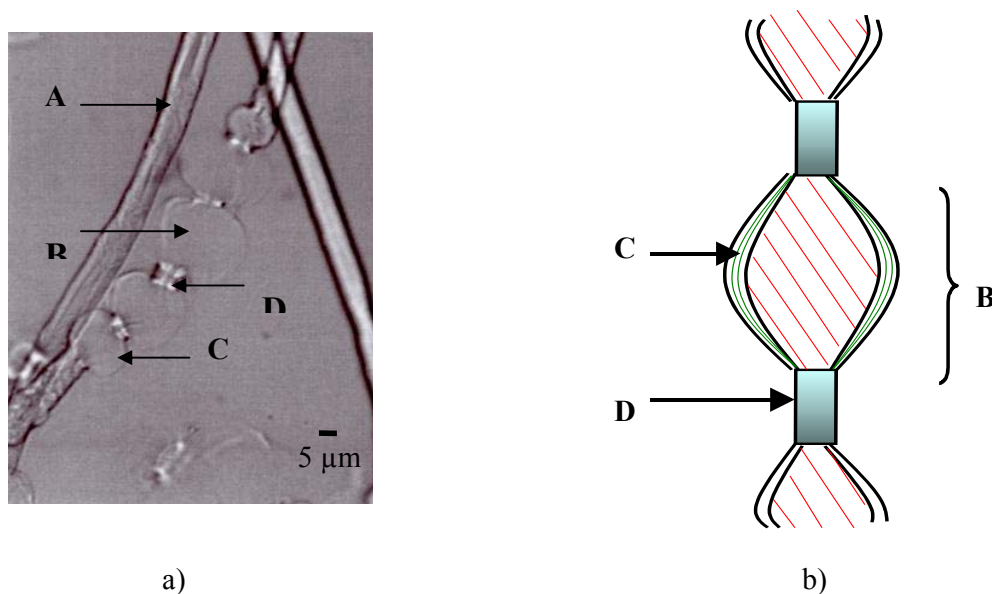


Figure 4. a) native cellulose swollen fibres (Borregaard fibre in NMMO – water at 23.5%, optical microscopy in transmitted light). A = unswollen fibre; B = balloon; C = membrane; D = unswollen section between two balloons. b) schematic drawing of a swollen fibre of native cellulose. B = balloon; C =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

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:

- *unswollen 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 *unswollen 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} = 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	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

Table 4. Values of D_{fm} / D_i for cotton and wood fibres in NMMO – water (at water content 23.5%). 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.

	<i>Borregaard</i>		<i>Buckeye</i>		<i>Cotton</i>	
	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

E. Dissolution: swelling by ballooning, followed by a complete dissolution of the fibre (mode 2)

We 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 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 *membrane* remain then attached to the *unswollen sections* of the fibres (seen in figure 5, photos E and F).

Phase 3: dissolution of the *unswollen sections*

During this phase the dissolution of the *unswollen sections* of the fibres occurs. This dissolution begins at the *unswollen 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.

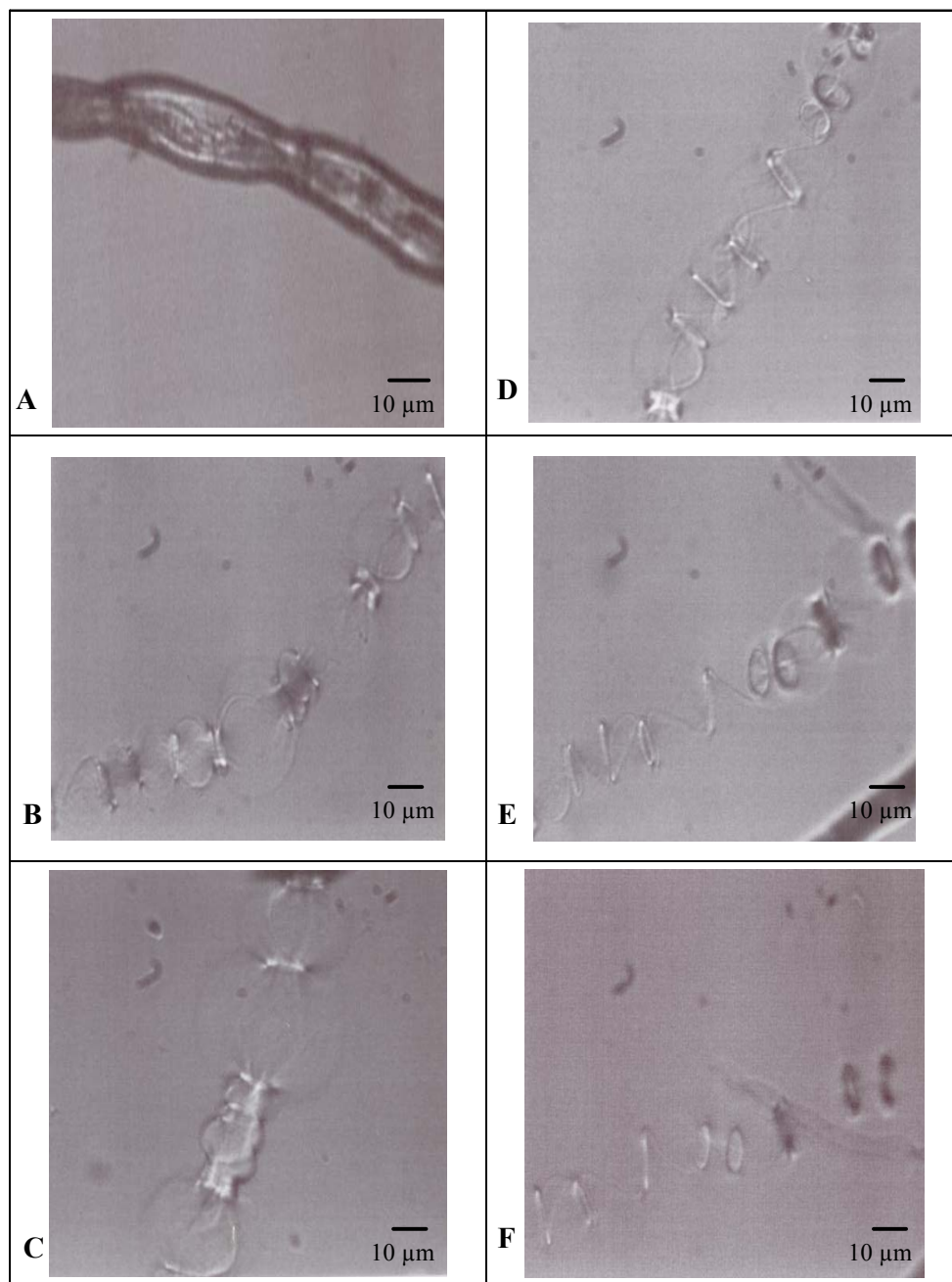


Figure 5. Evolution of swelling by ballooning. (Borregaard fibre swollen in NMMO – water at 19%, optical microscopy in transmitted light). $t = 0$ min is the time where the solvent is introduced. Photo A ($t = 1$ min) = the fibre begins to swell. Photo B ($t = 4$ min) = the first balloons appear. Photo 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 unswollen fibre sections are seen.



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

- Phase 1 : balloon formation

The formation of balloons is as follows. At some intervals along the fibres, certain zones of about the same length L_b starts to swell. With time, the zones swell more and more, keeping their original length L_b . 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 *unswollen sections* which are between balloons while the balloons are swelling.

Let's suppose 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 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 what 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 held by a membrane.

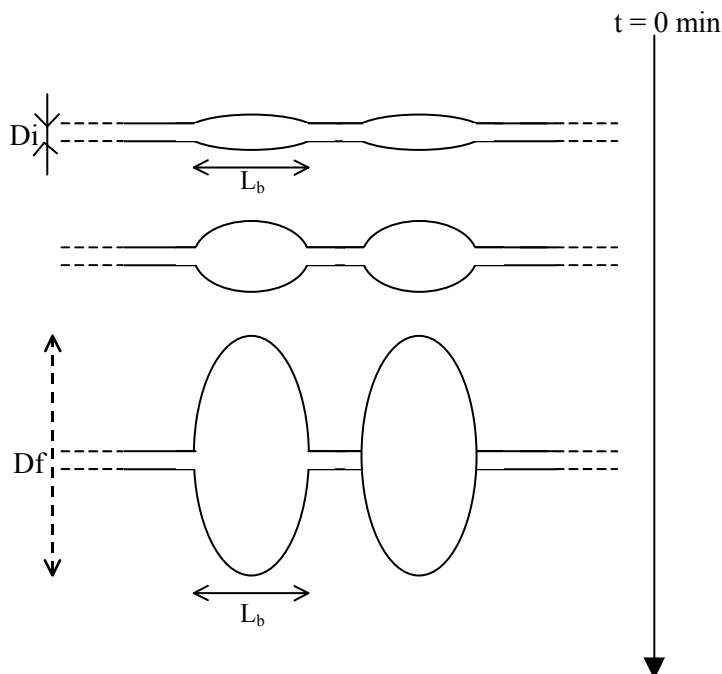


Figure 7. Schematic drawing of the growth of balloons along a native fibre.

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*.

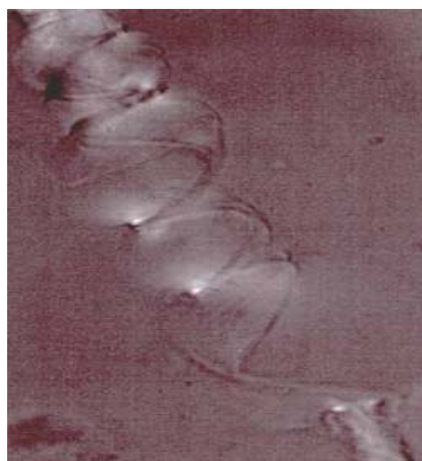


Figure 8. Helical ribbon surrounding the balloons membrane (cotton in NMMO – water at 20%, optical microscopy in transmitted light).

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 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.



Figure 9. Regular helical ribbon in the balloons membrane (cotton swollen in NMMO – water at 20%, optical microscopy in transmitted light, $T = 90^{\circ}\text{C}$).



Figure 10. Regular helical ribbon in the balloons membrane (Buckeye fibre swollen in NMMO – water at 23.5%, optical microscopy in transmitted light, $T = 90^{\circ}\text{C}$).

The swelling by ballooning occurs 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 *unswollen 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 these 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 *unswollen 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 losing most of their birefringence, keeping four bright zones localised close to the two *unswollen 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 (figures 12) turns in the opposite direction of the rotation of the polarisers, with an angle equal to the rotation angle of the polarisers.

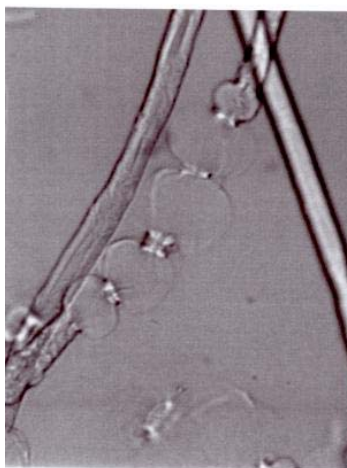


Figure 11. Borregaard fibre swollen in NMMO – water at 23.5% in phase 1 (optical microscopy in transmitted light).

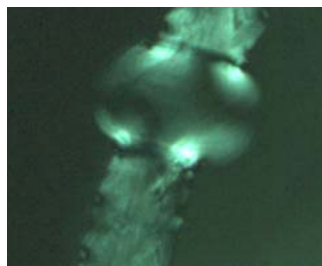


Figure 12. Borregaard fibre swollen in NMMO – water at 23.5% in phase 1 (optical microscopy in transmitted light with crossed polarisers).

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 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 *unswollen sections*. This chain orientation is due to the way the balloon expands.

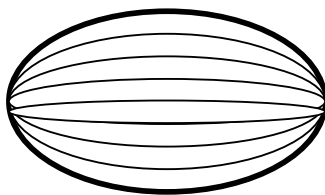


Figure 13. Schematic drawing of the chains orientation in a bipolar nematic droplet.

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.

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 *unswollen 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 *unswollen 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 *unswollen 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 $0.4 \text{ Pa.s}^{[17]}$ a low value in agreement with the rapid flow of the fluid during bursting.

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

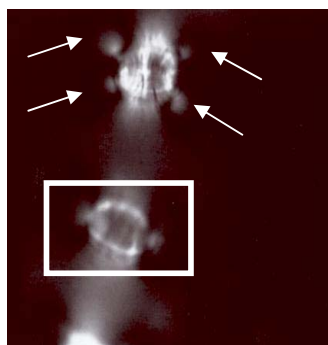


Figure 14. Borregaard fibre swollen in NMMO – water at 19% in phase 2 (optical microscopy in transmitted light with crossed polarisers). The white arrows show the brightest zones belongs to the membranes scraps; the white rectangle indicates the unswollen fibre section.

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 *unswollen sections*

After the burst of the balloons, two parts of the original fibre are still undissolved: the scraps of the *membrane* and the *unswollen sections*, which was the link between two balloons. First, the dissolution of the *unswollen sections* occurse. 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).

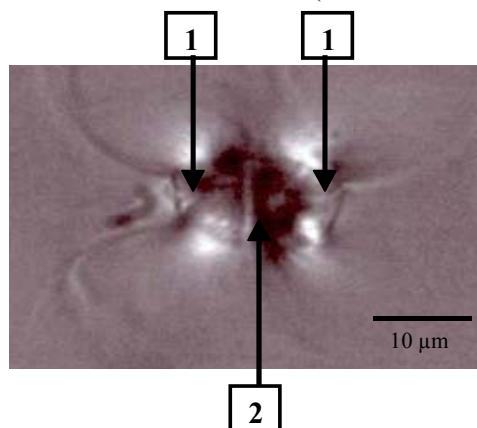


Figure 15. Bursting of balloons (Borregaard fibre swollen in NMMO – water at 19%, optical microscopy in transmitted light).

The fact that this is the *unswollen 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 *unswollen section*. This is strongly contradicting the hypothesis of Ott [10] that an outer *membrane* is slipping down to “*unswollen part*” and preventing it to swell. The *membrane* is everywhere, and curiously, the scraps of the *membrane* that was around the balloon is not dissolving at the same time that the *membrane* around the *unswollen parts*. It is the later ones that are dissolving first. The dissolution of the *unswollen 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 *unswollen 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 undissolved (*unswollen section* and *membrane*) cellulose parts.

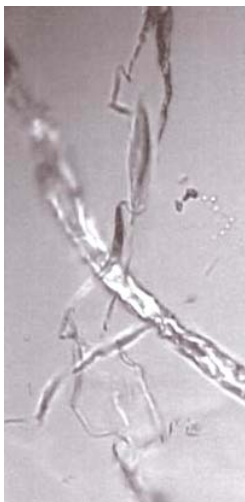
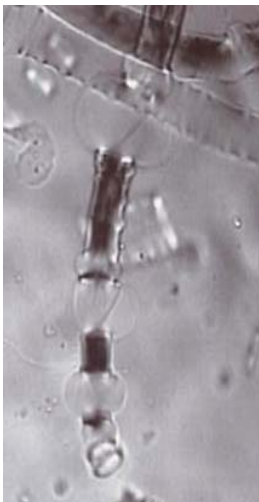
G. Homogeneous swelling (high water content) with no dissolution (mode 4)

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 $D_{\text{swollen}} / D_{\text{di}}$ 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.

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 

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, *unswollen sections* and *membrane*) that have different swelling and dissolution mechanisms:

Phase 1: balloon formation

Phase 2: balloon bursting

Phase 3: dissolution of the *unswollen 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 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 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 “unswollen 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 biosynthesis 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, *Appl. Polym. Symp.* **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, “*Supramolecular 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.

Chapter 3

Swelling and dissolution mechanisms
of native cellulose fibres, part II:
free floating cotton and wood fibres
in NaOH – water – additives systems

Résumé francophone chapitre 3

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie II : fibres de bois et de coton dans le système NaOH – eau – additifs.

Nous étendons notre étude des mécanismes de gonflement et de dissolution des fibres de cellulose native à un autre solvant aqueux, également très utilisé dans les procédés de transformation de la cellulose. Le comportement des fibres cellulosiques de coton et de bois dans une solution d'hydroxyde de sodium (NaOH) - eau est donc observé par microscopie optique et comparé aux résultats obtenus dans notre premier système aqueux, NMMO – eau. L'influence de deux paramètres expérimentaux est évaluée, il s'agit de la concentration en NaOH de la solution NaOH – eau (7.6% et 15%) et de la température (-10°C, -5°C, 0°C et 5°C). Trois additifs (urée, oxyde de zinc et *N*-méthylmorpholine-*N*-oxide) sont également ajoutés au système NaOH – eau, afin de déterminer leur action sur le mécanisme de gonflement et de dissolution des fibres cellulosiques de coton et de bois.

Dans les meilleures conditions de dissolution selon le diagramme de phase cellulose – NaOH – eau (c'est à dire à une température de -5°C et une solution NaOH (7.6%) – eau), les fibres de coton et de bois gonflent de façon hétérogène, en formant des ballons. La membrane des ballons présente toujours une structure hélicoïdale. Il s'agit du mode 3 où la dissolution de la fibre est partielle : uniquement la cellulose au sein des ballons est dissoute. Augmenter la concentration en NaOH ou la température diminue la capacité à dissoudre du mélange NaOH – eau. En effet, dans ces conditions expérimentales, seul un gonflement homogène des fibres de cellulose est constaté.

Quant à l'ajout d'additif, il ne modifie pas le mécanisme de gonflement et de dissolution des fibres. Le système NaOH – eau – urée provoque un ballonnement des fibres de coton et de bois, avec des ballons aux diamètres plus importants. La capacité à dissoudre la cellulose du mélange NaOH – eau est donc accrue grâce à l'addition d'urée. Concernant l'oxyde de zinc, il n'influence pas le diamètre des ballons mais influe sur la cinétique du mécanisme, qui se déroule plus vite. Le dernier additif testé, la *N*-méthylmorpholine-*N*-oxide, agit comme un inhibiteur sur le système NaOH – eau d'un point de vue de sa capacité à dissoudre les fibres de cellulose native, telles que le coton ou le bois.

Les mécanismes de gonflement et de dissolution des fibres de coton et de bois ne sont pas déterminés par la nature du système aqueux testé. Les modes observés sont similaires pour les solutions *N*-méthylmorpholine-*N*-oxide – eau ou d'hydroxyde de sodium eau.

Chapter 3 describes the behaviour of the same type of cellulose fibres (cotton and wood fibres) studied in the previous chapter, but in another aqueous solvent: sodium hydroxide (NaOH) and water solutions. The aim of this work is to establish if the nature of aqueous solvent may influence the swelling and dissolution mechanisms. The obtained results in NMMO – water mixtures and NaOH – water solutions are compared.

The content of NaOH and the experimental temperature are modified to determine the influence of these parameters on the swelling and dissolution mechanisms. Addition of three different chemical components (urea, zinc oxide and NMMO) is investigated to estimate their influence on dissolution modes.

Swelling and dissolution of cellulose Part II: free floating cotton and wood fibres in NaOH – water – additives systems

Celine Cuissinat,¹ Patrick Navard*^{1,2}

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Materiaux (CEMEF), Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207, 06904 Sophia Antipolis France

² Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu; Tel: 33 (0)4 93 95 74 66; Fax: 33 (0)4 92 38 97 52; E-mail: Patrick.Navard@ensmp.fr

Summary: The swelling and dissolution mechanisms of native cotton and wood cellulose fibres in NaOH – water are studied. The cellulose fibres exhibit a heterogeneous swelling by ballooning in the best dissolving conditions (-5°C, 7.6% of NaOH). This corresponds to the mode 3 of the swelling-dissolution (see companion paper). In this region of the mixture phase diagram, cellulose is only dissolved inside the balloons. A lot of insoluble parts are present. Increasing the temperature and/or the content of NaOH decreases the quality of the solvent. In this case, the cellulose fibres do not show ballooning, but only a homogeneous swelling (mode 4). Three components are tested as additives: urea, zinc oxide and *N*-methylmorpholine-*N*-oxide (NMMO). The swelling and dissolution mechanisms in NaOH- water and NaOH – water – additives stay the same. Adding urea to NaOH-water (-5°C, 7.6% of NaOH) gives the same ballooning mechanisms, but with a larger expansion of the balloons, indicating that the solvent is better. Zinc oxide does not increase the expansion of the balloons, but the kinetics of swelling is faster. NMMO acts as a dissolution inhibitor.

Keywords: Cellulose; cotton; dissolution; swelling; sodium hydroxide; urea; zinc oxide

Introduction

As the most important skeletal component in plants, cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff – chain homopolymer is characterised by its chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semi-crystalline fibre morphology. Cellulose does not melt before thermal degradation because of strong intra- and intermolecular hydrogen bonding. In order to fulfil the various demands for its industrial use, it is often modified by physical, chemical, enzymatic, or genetic means. Modification leads to changes in the solubility, properties and behaviour of the polymer ^[1].

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 covering different mechanisms. It is usually stated that cellulose crystals are difficult to

dissolve, being a limiting point for dissolution. For many decades, the manufacture of cotton and wood celluloses in the form of fibres and film has been based on dissolution. These last decades, there has been an intensive search for new solvents being environmentally friendly and able to produce new materials, opening new markets for cellulosic products. Among the many aqueous and non aqueous cellulose solvent systems reported in the past three decades, only *N*-methylmorpholine-*N*-oxide (NMMO) has been successful for the production of regenerated cellulose textile fibres.

In the first paper of this series ^[2], it was shown that the dissolution of cellulose fibres in mixtures of NMMO and water is complex, depending on the quality of the solvent. Five modes of dissolution were 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 order to assess the universality of this classification, another aqueous solvent has been studied. The mixture of NaOH and water was chosen due to its strong potential for commercial use, despite the reported difficulties to dissolve cellulose. The interactions between cellulose and NaOH has been the subject of numerous studies and publications after the discovery of Mercer in 1851 that, under specific conditions, the properties of cotton can be drastically improved after a dipping in an NaOH-water mixture^[3]. It was first recognised by Sobue^[4] that there exists specific interactions between cellulose and NaOH-water in a limited range of NaOH concentration (from 7 to 9%) and temperature (from -7 to -3°C). The result of dipping cellulose in this region of the NaOH-water phase diagram was called cellulose Q region^[4-7]. In the 1980's, Japanese scientists^[5, 8-11] found that cellulose can be dissolved in the Q region and even processed. In 1984, Kamide and his co-workers^[5] discovered that cellulose regenerated from cuprammonium cellulose solution in aqueous sulphuric acid, after partially and slowly evaporating ammonia from the cast solution in the air, could be dissolved completely in aqueous hydroxide within a limited range of alkaline concentration. Yamashiki and his co-workers^[8-9] succeeded in preparing alkali-soluble steam exploded cellulose with cellulose I crystal form of cellulose I. Although the range for reaching a complete solution of cellulose is limited (i.e. aqueous NaOH between 8 and 9 wt% at 4°), these cellulose samples are defined as “alkali-soluble” celluloses. Kamide^[10] established for alkali-soluble regenerated cellulose some empirical relations between the solubility towards aqueous NaOH with a concentration between 8 and 9% and the degree of breakdown of the intramolecular hydrogen bonds at C₃ originally existing in soluble natural cellulose. Further on, Kamide^[11] showed by using NMR that cellulose is dissolved without any chemical reaction with alkali in aqueous alkaline solution.

More recently, there was a strong increase of research to find ways to solve the dissolution difficulties and reach an acceptable solubility state, compatible with processing. An extensive study on the dissolution of cellulose using a novel solvent, namely NaOH/urea, or NaOH/thiourea aqueous solution has been carried out^[12-16]. These solvents are reported to have a strong power to dissolve cotton linters and other natural cellulose, showing significant advantages including non – pollution, simple and safe dissolution procedure. The authors showed that a moderate addition of urea to the NaOH solution significantly improved the solubility of cellulose. They suggest that NaOH (6%) – urea (4%) aqueous solution (w/w) or thiourea is a new and cheap solvent class of cellulose, having strong potential applications.

For example, novel microporous membranes from cellulose in NaOH/thiourea aqueous solution were obtained by coagulation with ammonium sulphate aqueous solution. The mean pore size and water permeability of the membranes are significantly larger than those from viscose and cuprammonium rayon process as well as NaOH/urea aqueous solution.

A thermodynamic study has been carried out these last years in our laboratory. The latest results^[17-18] show that microcrystalline cellulose can be fully dissolved in the Q region. NaOH-water has a eutectic behaviour in this region, with a eutectic mixture melting at -33°C. Addition of cellulose decreases the capability of forming the eutectic mixture without changing the amount of free water formed. From this finding, it was possible to deduce that the cellulose chains interact with NaOH hydrates: when $C_{\text{cell}}(\%)/C_{\text{NaOH}}(\%) > 0.5$, four NaOH are linked to each anhydroglucose corresponds to the limit of cellulose dissolution. Thus, for microcrystalline cellulose, the maximum concentration of cellulose by weight is equal to the amount of NaOH in the solvent mixture (i.e. for a 8%NaOH-water mixture, the maximum cellulose concentration will be 8%). It was also shown^[19] that cellulose of high DP is not easily dissolvable. A lot of insoluble parts are present in the solution. In order to increase the solvent power of NaOH-water, additives have been searched. Among the ones tried, ZnO^[20-21], urea and thiourea^[12-16] seem to have some efficiency.

Kunze and Fink^[16] have reported investigations on the activation of cellulose by mixed solutions of caustic soda and urea. The concentration of NaOH was varied in a range from 0 to 8% and the urea concentration in a range from 15% to 40% at ambient temperature and -25°C. The results obtained by ¹³C-CP/MAS-NMR show that the cellulose activation the NaOH concentration of the caustic soda could be remarkably improved by adding urea. The spectra of the samples treated with urea containing lye is similar, but not identical, to the spectra of the sodium celluloses I or II, suggesting a specific urea-NaOH –cellulose complex. This complex is also formed by treating sodium cellulose I with concentrated urea solutions.

The effect of urea has also been understood as a breaking of the clustered water structure enhancing the content of free monomolecular water with cellulose, promoting swelling and dissolution of the polymer. The increase in solubility by lowering the temperature of the system is in agreement with an exothermic heat of dissolution, and has been investigated thoroughly in recent years with regards to a possible fibre spinning from cellulose – NaOH solutions at low temperatures^[22]. Zinc oxide shows some efficiency for delaying gelation. Addition of zinc oxide was supposed to lead to an in-situ formation of a zincate complex facilitating dissolution of cellulose chains up to a DP of about 200, even at room temperature.

The purpose of this paper is to show that the dissolution of cellulose in NaOH-water can be understood with the help of the results obtained in NMMO-water. In particular, we will study the way cellulose dissolves, its importance for a possible use as a commercial solvent, and the influence of the addition of ZnO and urea, known to increase the solubility. Another additive (NMMO), decreasing the solvent power, has also been used for the sake of comparison.

Experimental part

- Cellulose samples

Three 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 measured by Fourier transform infrared spectrometry ^[23]. The values of Mn, Mw or Mz are determined by gel permeation chromatography (GPC).

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

- Solvent systems

The swelling and dissolution treatments were performed with mixtures of sodium hydroxide (NaOH) and water, with or without additives. NaOH – water is a mixture containing 7.6 or 15% (in weight) of NaOH. The NaOH powder comes from Fisher and is pure to about 97%. Three types of mixtures containing additives were prepared with 7.6%NaOH-water:

-urea: mixtures with urea (Fisher) were prepared with the following composition (w/w): NaOH (7.6%), urea (12%), water (80.4%).

- N-methylmorpholine *N*-oxide (NMMO): NMMO with 3% water (w/w) was obtained from Sigma Aldrich (powder). Two mixtures (in w/w) with NMMO as an additive were tested: NaOH (7.6%), NMMO (2%), water (90.4%) and NaOH (7.6%), NMMO (10%), water (82.4%).

- zinc oxide (ZnO): this product (powder pure at 98%) is supplied by Prolabo. The composition (w/w) is NaOH (7.6%), water (90.9%) and ZnO (1.5%).

- Preparation and observation of the solutions

The solutions were prepared by mixing cellulose and the given solvent mixture in a container made of two glass plates, suitable for optical microscopy observations. The procedure is as described in companion paper^[2].

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

The swelling and dissolution experiments were performed between -10°C and +5°C.

- Studied parameters

Cotton and wood cellulose fibres can swell and dissolve with different mechanisms. The studied parameters are the same than those describing in the companion paper ^[2].

Results and discussion

The swelling and dissolution of wood and cotton fibres in various mixtures based on 7.6 or 15% NaOH-water are described below. As it will be evident, these NaOH-water mixtures, with or without additives, are not very good solvents for cellulose. They are unable to dissolve completely the cellulose fibre. This is what is causing difficulties for using them in commercial applications.

A. Swelling and dissolution in 7.6%NaOH-water at -5°C

According to literature^[4], the best dissolution conditions are obtained at a temperature of -5°C for solvents having 5 -10 % of NaOH in water. A concentration of 7.6% of NaOH at -5°C was chosen as the standard condition for dissolution. The three studied native fibres (bleached cotton, Buckeye, Borregaard) are strongly swelling in this solvent through a ballooning mechanism. An example of such ballooning is seen in figure 1. The fibres, having a rather regular diameter in a dry state, 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 the balloons seen in figure 1. These balloons are growing until they reach a maximum diameter (called D_{sm}) from which a stable situation is attained. Without shaking the fibres, the fibres and the balloons are staying as they are. This is the case of the mode 3 of swelling-dissolution that was described for NMMO-water^[2]. As in the case of balloons seen in NMMO-water solvents, we can distinguish the same three different zones within one fibre during the ballooning (seen in figure 1). These various zones are unswollen fibre parts (A), balloons (B) surrounded by a membrane (C) and unswollen sections (D). An unswollen fibre (A) is the part of one fibre, or a full fibre, that did not start yet the swelling process, but that will swell later as balloons.

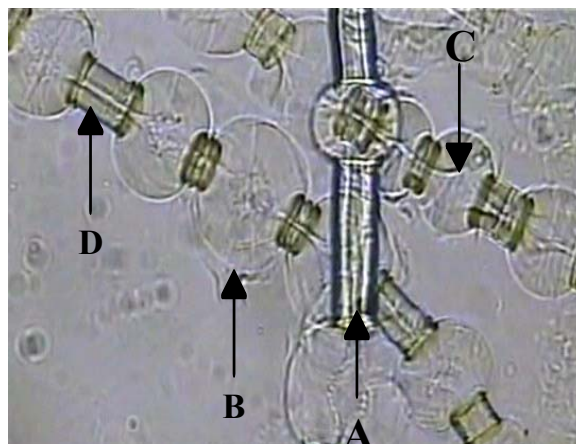


Figure 1. Swelling by ballooning in NaOH – water solutions (Borregaard fibre swollen in 7.6% NaOH – water, $T = -5^{\circ}\text{C}$, optical microscopy in transmitted light): an unswollen fibre (A), a balloon (B) surrounded by a membrane (C) and a section (D)

All these features are exactly similar to what was seen for NMMO-water in some concentration range of water. At some random intervals along the cellulose fibres, localised zones of about the same length L_b start to swell. The zones between the balloons seem to keep their original diameter. The unswollen sections between balloons do not swell. The balloons have the aspect of a beaded structure. The balloons do not appear at the same time along cotton or wood fibres and have various growing speeds. The balloons are not spherical,

their size is larger perpendicularly than along the fibre and they do not have symmetry of revolution, having a complicated shape around the fibre axis. The repartition of balloons seems to be made at random. In the case of bleached cotton, the balloons distribution is more or less regular. Each balloon is separated by unswollen sections which length is between 10 and 20 μm . In the case of wood fibres (Borregaard and Buckeye), the swollen zones are distributed per group (between 2 and 6 balloons per group).

Helical ribbons are clearly observed at the balloons surface (figure 2). This helical membrane can be seen as a line surrounded the balloons from one unswollen section to another. This helical membrane surrounding the balloons has always been observed with the NMMO – water mixtures^[2], when the swelling occurs by ballooning. It seems to be a general feature, also observed by many observers^[24]. The influence and role of this helical feature will be examined in a forthcoming paper.

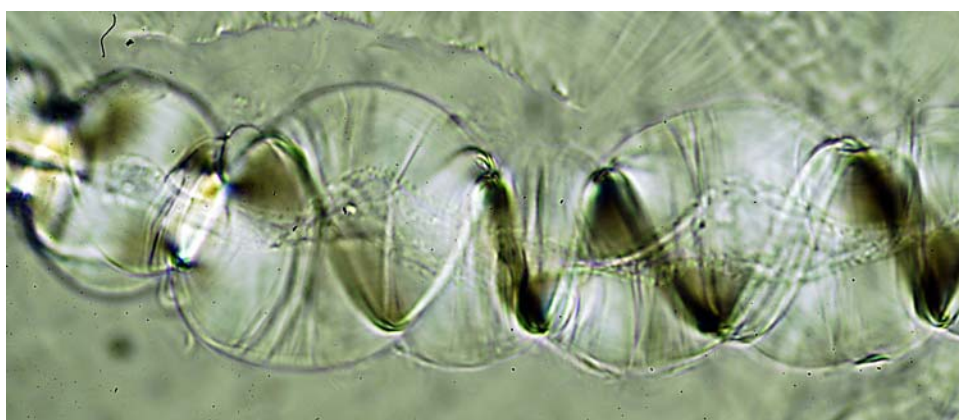


Figure 2. Helical ribbons at the balloons surface (Buckeye fibre swollen in 7.6% NaOH – water, $T = -5^{\circ}\text{C}$, optical microscopy with transmitted light)

The swelling mechanism of cellulose fibres in NaOH-water at 7.6% and -5°C shows that the solvent is not very good. This is what has been already found. Only cellulose of low DP like microcrystalline cellulose can be nearly fully dissolved, with very few insoluble particles present. As soon as cellulose fibres of larger DP and having kept their original structure are put in contact with this solvent, it behaves in the mode 3 of swelling-dissolution. Only cellulose present in the balloons is dissolved. The membrane and the unswollen sections cannot dissolve. The balloons never burst since the osmotic pressure inside the balloons is smaller than the breaking resistance of the membrane. When mechanically broken, the inside of the balloon can flow out and it was shown to be a cellulose solution^[25]. This is indeed what is occurring when cellulose is mixed in a mechanical mixer. Cellulose solutions prepared in this way have a lot of insoluble particles that are easy to recognise as remains of membranes and unswollen sections.

B. NaOH solution at 7.6% at various temperatures

The aim is to explore the swelling and dissolution mechanisms of native cellulose in NaOH solution at 7.6% at different temperatures, from -10°C to 5°C . Two main domains of temperature (figure 3) are found, looking at the observed mechanisms: one from -10 to -5°C , another one from 0 to 5°C .

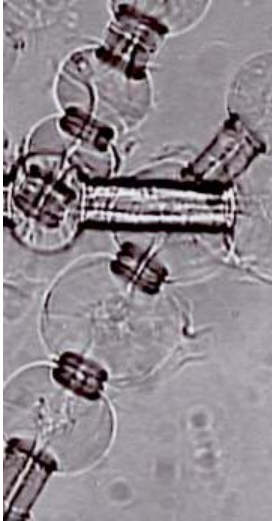
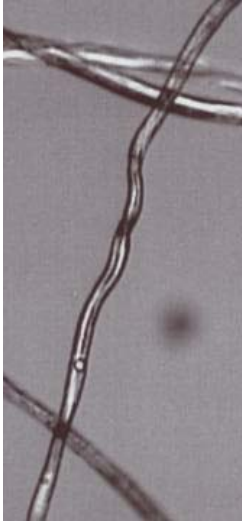
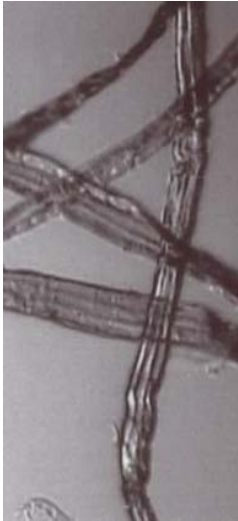
experimental temperature	T = -10°C	T = -5°C	T = 0°C	T = 5°C
swelling and dissolution mechanism	swelling by ballooning no dissolution		homogeneous swelling no dissolution	
	Wood fibre  10 µm	Wood fibre  10 µm	Cotton fibre  10 µm	Wood fibre  10 µm

Figure 3. Swelling and dissolution mechanisms in NaOH-water solutions at 7.6%, at various temperatures (-10°C, -5°C, 0°C and 5°C)

At -10°C and -5°C, cotton and wood fibres swell heterogeneously by ballooning and the total dissolution of the fibres is not reached. Decreasing the temperature does not influence the swelling and dissolution mechanism, still in mode 3. However, D_{sm}/D_i , expressing the extent of swelling of the balloon, is lower at -10°C than at -5°C. D_{sm}/D_i is a good indicator of the quality of the solvent, since the better the solvent is, the larger the osmotic pressure is and thus the larger the balloons are. Table 2 gives the values of D_{sm}/D_i for various solvent systems: NMMO-water at 20 % of water (solvent in mode 2, which can be considered as a reference because the balloons reach their maximum size at burst), NMMO-water at 30% of water which is in mode 3 (the maximum size of the balloons is smaller than the size at which they will explode), NaOH – water at 7.6% at -5°C, and NaOH – water at 7.6% at -10°C. The D_{sm}/D_i value of cotton and wood fibres in NaOH – water system at -5 and 10°C are lower than the values obtained in mode 2 (NMMO-water at 20% of water) and in the same range as the values for NMMO-water at 30% (mode 3).

Table 2. Final over initial diameter ratio in the case of native fibres swollen in NaOH – water solutions at 7.6 %, at various temperature (-10°C and -5°C), in NMMO – water (at 20% and 30% of water, T = 90°C).

	Bleached cotton	Borregaard	Buckeye
crystallinity	55	43	46
Dsm/Di in NaOH (7.6%) – water, T = -5°C	3.2	3.6	3.6
Dsm/Di in NaOH (7.6%) – water, T = -10°C	3.0	3.5	3.4
Dsm/Di in NMMO – water (20% of water), T = 90°C	4.8	5.9	5.2
Dsm/Di in NMMO – water (30% of water), T = 90°C	3.9	4.1	4.1

This is fully in agreement with the idea that the quality of the solvent decreases from mode 2 to mode 3 and that the maximum expansion of the balloons is a good indicator of the quality of a solvent. The value Dsm/Di of cotton and wood fibres in NaOH – water system at -10°C are slightly lower than the values obtained at -5°C. This seems to indicate that decreasing the temperature below -5°C is decreasing the quality of the solvent. This is in agreement with the authors that defined this small Q range of dissolution ^[4,10,11].

At 0°C and 5°C, cotton and wood fibres swell homogeneously as seen in figure 3. The value Dsm/Di varies between 1.3 and 1.5, which is about the value found in pure water. 7.6%NaOH –water solutions at 0°C and 5°C cannot dissolve cellulose.

These experiments at different temperatures confirm that the temperature dissolution window is very narrow. What will be explored in the following paragraph is the case where the NaOH concentration is increased.

C. NaOH solution at 15% at various temperatures

Outside the Q dissolution region, it is well known that NaOH has a dramatic effect on cellulose. When increasing the NaOH concentration, the area of the phase diagram where mercerisation occurs is reached (between 10 to 30% NaOH - water mixtures, at 18 – 20°C. We will explore the behaviour for a NaOH concentration of 15% at three temperatures, -5°C, 0°C and +5°C.

At 0°C and +5°C, the cotton and wood fibres swell homogeneously, in mode 4 (figure 4). The swelling is larger at 0°C than at 5°C, as shown by the values Dsm/Di (table 3). The swelling is significant at 0°C since Dsm/Di is rather large (2.2 – 2.6). At +5°C, the NaOH solution at 15% is a very poor solvent with Dsm/Di values are similar to the NaOH solution at 7.6% at +5°C.

Cellulose in 15% NaOH-water at -5°C shows in most of the cases a homogeneous swelling of mode 4, with rather large Dsm/Di values. A very interesting point shown on figure 4 is the presence of few balloons at this temperature. This is not always seen. It could mean that in some cases, cellulose may dissolve inside the balloons, as in mode 2.

Table 3. Final over initial diameter ratio in the case of native fibres swollen in NaOH – water solutions at 7.6 % and 15% ($T = -5^{\circ}\text{C}$, 0°C or 5°C), in NMMO – water (at content of water $> 35\%$, $T = 90^{\circ}\text{C}$).

	NaOH at 7.6% $T = -10^{\circ}\text{C}$	NaOH at 15% $T = +5^{\circ}\text{C}$	NaOH at 15% $T = 0^{\circ}\text{C}$	NaOH at 15% $T = -5^{\circ}\text{C}$	NaOH at 15% $T = -10^{\circ}\text{C}$	NMMO – water (water content $> 35\%$)
Dsm/Di for cotton and wood fibres	1.3 – 1.5	1.3 -1.6	2.2 – 2.6	2.2 – 2.6	1.8 – 2.8	2.3 – 2.6

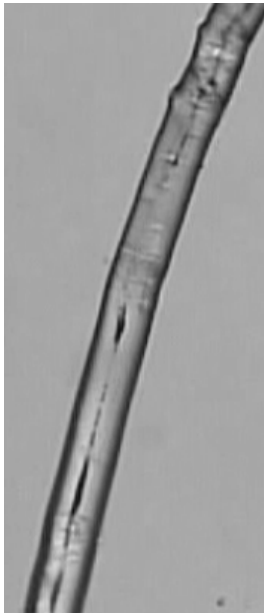
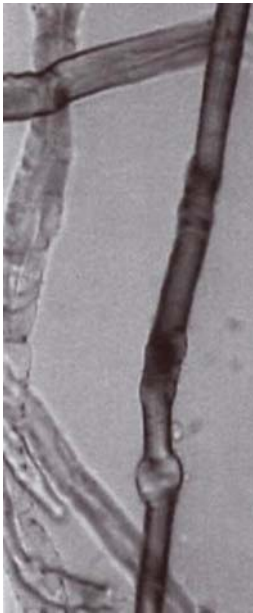
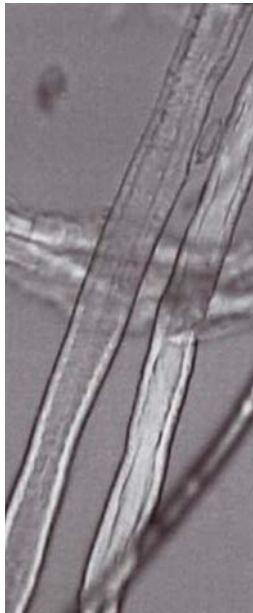
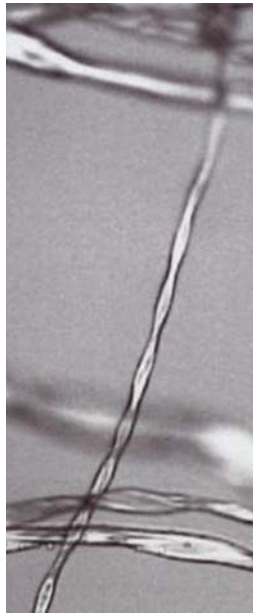
experimental temperature	$T = -10^{\circ}\text{C}$	$T = -5^{\circ}\text{C}$	$T = 0^{\circ}\text{C}$	$T = 5^{\circ}\text{C}$
swelling and dissolution mechanism	homogeneous swelling no dissolution	few balloons appear + homogeneous swelling no dissolution	homogeneous swelling no dissolution	homogeneous swelling (low) no dissolution
•• 15 μm	Wood fibre 	Wood fibre 	Wood fibre 	Cotton fibre 

Figure 4. Swelling and dissolution mechanisms in NaOH-water solutions at 15%, at various temperatures (-10°C , -5°C , 0°C and 5°C)

D. NaOH – water – urea system

The three native fibres have been tested at -5°C with NaOH (7.6%) – urea (12%). The swelling still occurs by ballooning as in the case without urea. Unswollen sections, balloons and its membrane are seen by optical microscopy (figure 5). The balloons appear more rapidly with the presence of urea and the final to initial diameter D_{sm}/D_i ratio values are greater to those obtained in the same conditions with pure NaOH – water solutions (table 4). These features are a clear indication that the addition of urea in NaOH – water increases the quality of the solvent.



Figure 5. Swelling by ballooning in NaOH – water - urea solutions (Buckeye fibre swollen in NaOH (7.6%) – water – urea (12%) solution, $T = -5^{\circ}\text{C}$, optical microscopy in transmitted light)

Table 4. Final over initial diameter ratio of native fibres swollen in NaOH (7.6%) – water mixtures with or without additives (urea, ZnO or NMMO).

	Bleached cotton	Borregaard	Buckeye
crystallinity	55	43	46
D_{sm}/D_i in NaOH (7.6%) – water, $T = -5^{\circ}\text{C}$	3.2	3.6	3.6
D_{sm}/D_i in NaOH (7.6%) – water – urea (12%), $T = -5^{\circ}\text{C}$	3.9	3.7	3.7
D_{sm}/D_i in NaOH (7.6%) – water – ZnO (1.5%), $T = -5^{\circ}\text{C}$	2.8	2.8	2.3
D_{sm}/D_i in NaOH (7.6%) – water – NMMO (2%), $T = -5^{\circ}\text{C}$	1.6	2.3	2.2

E. NaOH – water – ZnO system

The studied system is composed by NaOH at 7.6%, water at 90.9% and ZnO at 1.5% (w/w). As seen on the figure 6, the cotton and wood fibres swell by ballooning. The helical membrane surrounded the balloons is clearly observed on this picture. ZnO is increasing the swelling kinetic: the balloons appearing as soon as the solvent is in contact with the fibres. However the balloon expansion decreases with the addition of ZnO with values of D_{sm}/D_i being lower than without ZnO (table 4). Such behaviour should indicate that the solvent quality is decreased with the addition of ZnO, a feature which seems in contradiction with the faster swelling kinetics.



Figure 6. Swelling by ballooning in NaOH – water - ZnO solutions (Borregard fibre swollen in NaOH (7.6%) – water – ZnO (1.5%) solution, $T = -5^{\circ}\text{C}$, optical microscopy in transmitted light)

F. NaOH – water – NMMO system

Two amounts of NMMO were added to NaOH – water solution: 2 and 10% (w/w). In the case of NaOH (7.6%) – water – NMMO (2%); the fibres swell by ballooning (figure 7). The balloons are always surrounded by a helical membrane and separated by unswollen sections. However the balloon formation is very slow. The values D_{sm}/D_i is strongly decreased by adding only 2% of NMMO in NaOH – water solution (table 4). Adding 10% of NMMO has a very strong effect on NaOH – water mixtures: the fibres show a very weak swelling (figure 8), the mean diameter increasing by less than 10%. Most probably, the sodium hydroxyde hydrates that are acting in dissolving cellulose are not anymore formed in the presence of NMMO that is itself attracting strongly water.

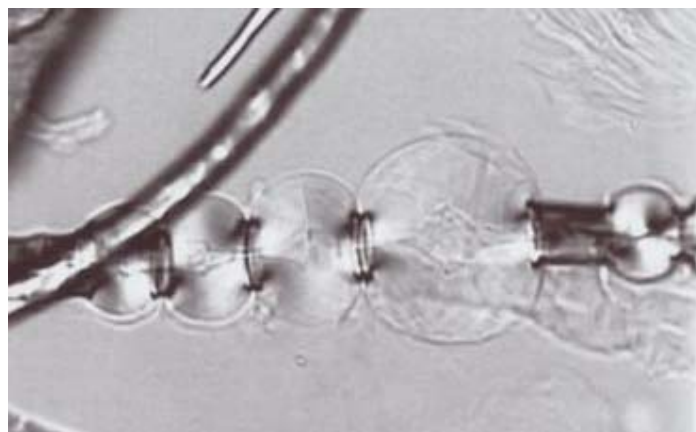


Figure 7. Swelling by ballooning in NaOH – water - NMMO solutions (Buckeye fibre swollen in NaOH (7.6%) – water – NMMO (2%) solution, $T = -5^{\circ}\text{C}$, optical microscopy in transmitted light)

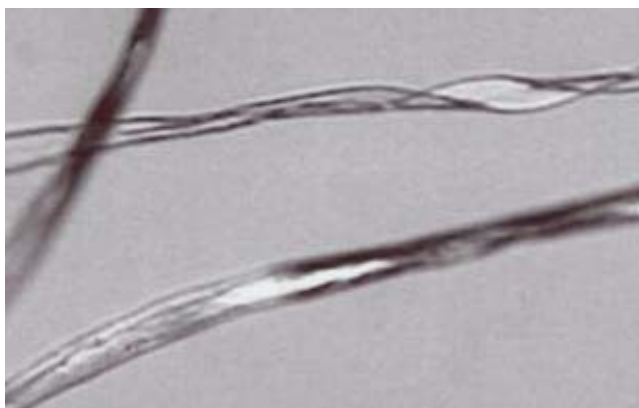


Figure 8. Swelling by ballooning in NaOH – water - NMMO solutions (Cotton fibre swollen in NaOH (7.6%) – water – NMMO (10%) solution, $T = -5^{\circ}\text{C}$, optical microscopy in transmitted light)

Conclusions

Observing the way a cellulose fibre is swelling and/or dissolving is a good way to assess the quality of a solvent. The observations performed with NMMO-water showed that five modes can be identified. Two of these modes (mode 3: ballooning without total dissolution, mode 4: homogeneous swelling) can be seen with the different NaOH-water systems.

The results confirm that the best dissolution conditions are obtained in a narrow range of temperatures and concentrations (around -5°C and with 7-9% of NaOH). In these conditions, a cellulose fibre swells by ballooning, with cellulose being dissolved inside the balloons. The morphology of the fibre swollen in NaOH-water and their evolution mechanisms are similar to the case of NMMO-water, showing the universality of the classification by these five modes (this will be also shown for non aqueous solvents, for other types of fibres and for some cellulose derivatives, in forthcoming papers).

When increasing temperature, the solvent quality of 7.6% NaOH-water decreases strongly. Adding urea is clearly increasing the quality of the solvent, with ballooning occurring faster and with a larger expansion. Adding ZnO gives a mixed result, with balloons being smaller, which should indicate a smaller osmotic pressure inside them, and thus a worse quality solvent, but with a swelling kinetic being faster, which should indicate a better solvent.

Adding NMMO strongly decreases the quality of the NaOH-water solvent. Adding more than 10% (w/w) of NMMO on NaOH-water systems seems to prevent cellulose fibres from interacting with the solvent.

Figure 9 summarizes the results concerning the balloon size and the kinetics of balloon formation. A comparison between the three additives on these two points is given in table 5.

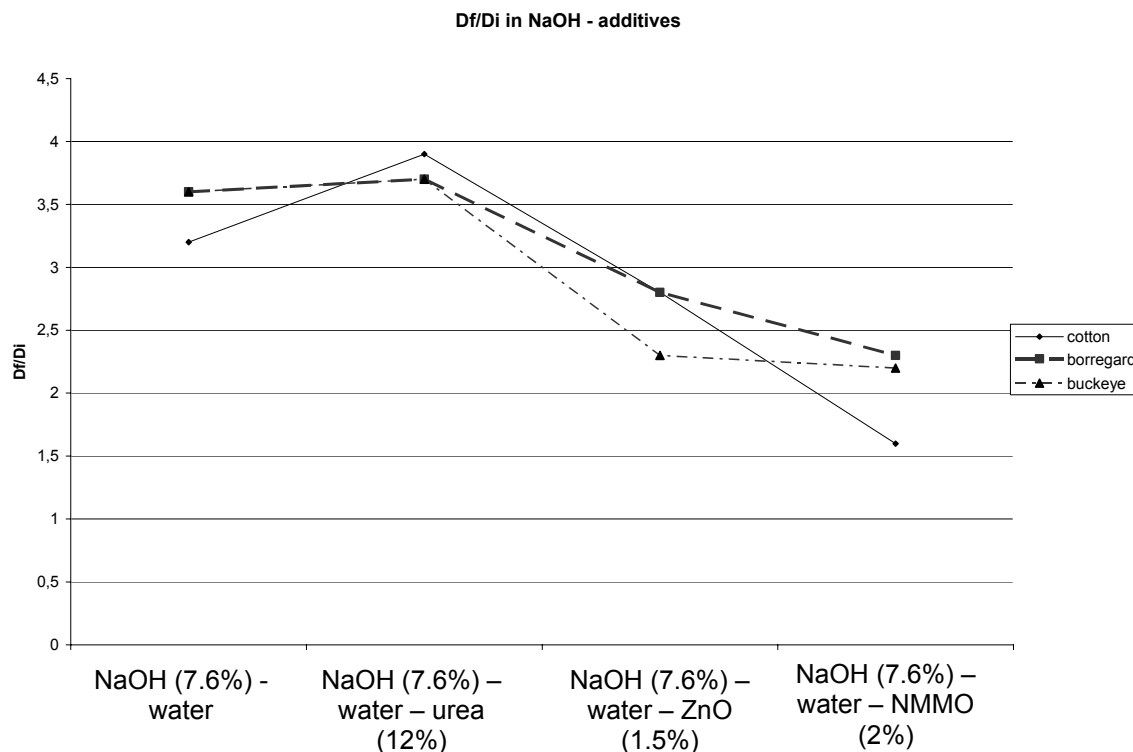


Figure 9. Values Df/Di for cotton, Borregaard or Buckeye fibres swollen in NaOH – water systems and NaOH – water – additives systems (additives = urea, ZnO or NMMO)

Table 5. Comparison of the additives influence (urea, ZnO and NMMO) on NaOH – water system

	Urea (12%)	ZnO (1.5%)	NMMO (2%)
Balloons size	+	-	-
Kinetic of balloons formation	+	+	-

Acknowledgements

The authors would like to thank M. Egal and N. Le Moigne (PhD students in the group of P. Navard) for their help in performing experiments with NaOH-water-additives systems.

- [1] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, *Angew. Chem. Int. Ed.* **2005**, 44, 3358.
- [2] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part I: free floating cotton and wood fibres in *N*-methylmorpholine *N*-oxide water mixtures. *Macromol. Symp.* **accepted**.
- [3] J. Mercer, *J. Franklin Instit.* **1851**, 52, 202.
- [4] H. Sobue, H. Kiessig, K. Hess, *Z. Physik Chem. B.* **1939**, 43, 309.
- [5] K. Kamide, K. Okajima, T. Matsui, K. Kowsaka, *Polym. J.* **1984**, 12, 857.
- [6] K. Kamide, K. Okajima, K. Kowsaka, *Polym. J.* **1992**, 24, 71.
- [7] C. Yamane, M. Saito, K. Okajima, *Sen'i gakkaiishi* **1996**, 52, 310.

- [8] T. Yamashiki, T. Matsui, M. Saitoh, K. Okajima, K. Kamide, T. Sawada, *International symposium on new fonctionnalisation developments in cellulotics and wood*, *Cellusion* 88, Kyoto, Japan, 1988.
- [9] K. Kowsaka, K. Kamide, K. Okajima, *International symposium on new fonctionnalisation developments in cellulotics and wood*, *Cellusion* 88, Kyoto, Japan, 1988.
- [10] T. Yamashiki, K. Kamide, K. Okajima, K. Kowsaka, T. Matsui, H. Fugase, *Polym. J.* **1988**, 20, 447.
- [11] K. Kamide, K. Yasuda, T. Matsui, K. Okajima, T. Yamashiki, *Cellulose Chem. Technol.* **1990**, 24, 23.
- [12] L. Zhang, J. Zhou, D. Ruan, Casting of cellulose film, *China Patent ZL 00 114485.5* **2003**.
- [13] L. Zhang, D. Ruan, J. Zhou, *Ind. Eng. Chem. Res.* **2001**, 40, 5923
- [14] L. Zhang, D. Ruan, S. Gao, *J. Polym. Sci. Part B: Polym. Phys.* **2002**, 40, 1521
- [15] D. Ruan, L. Zhang, Y. Mao, M. Zeng, X. Li, *J. Membr. Sci.* **2004**, 241, 265
- [16] J. Kunze, H.P. Fink, *Macromol. Symp.* **2005**, 223, 175
- [17] C. Roy, T. Budtova, P. Navard, O. Bedue, *Biomacromol.* **2001**, 2, 687.
- [18] M. Egal, T. Budtova, P. Navard, *Biomacromol.* **Submitted**
- [19] C. Roy, These Science et Genie des matériaux de l'Ecole des Mines de Paris, France, 2002.
- [20] G.F. Davidson, *J. Text. Ind.* **1937**, 28, 27.
- [21] T.P. Dirske, C. Postmus, J.R. and R. Vandenbosch, *J. Am. Chem. Soc.* **1954**, 76, 6022.
- [22] D. Klemm, B. Philipp, T. Heinze, Fundamentals and analytical methods, comprehensive cellulose chemistry, vol 1, Wiley – VCH, Weinheim, 1998.
- [23] T. Baldinger, J. Moosbauer, H. Sixta, “*Supramolecular 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.
- [24] V.A. Krakhmalev, A.A. Paiziev, *Cellulose* **2006**, 13, 45
- [25] N. LeMoigne, P. Navard, advanced report on the swelling and dissolution mechanisms of cotton fibres, Internal Report from CEMEF - Ecole des Mines de Paris, 2006.

Chapter 4

Swelling and dissolution mechanisms
of native cellulose fibres, part III:
enzymatically - treated cotton and wood
fibres in aqueous solvents

Résumé francophone chapitre 4

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie III : fibres de bois et de coton traitées par des enzymes en milieux aqueux.

Les étonnantes images obtenues par microscopie optiques à propos de l'hélice visible au niveau de la membrane des ballons nécessitent une recherche spécifique. Vu que cette structure semble liée à la morphologie (parois externes) des fibres de cellulose, la méthode utilisée pour éclaircir ce point est d'étudier des fibres dépourvues d'une partie de leurs parois externes. Les fibres de coton et bois préalablement testées dans les solvants aqueux (*N*-methylmorpholine-*N*-oxide (NMMO) – eau, hydroxyde de sodium (NaOH) – eau et NaOH – eau -urée) subissent donc un traitement enzymatique afin de supprimer leur paroi primaire et secondaire. Le mécanisme de gonflement et de dissolution des fibres traitées de coton et de bois est alors observé et comparé à celui des fibres non traitées.

Aucun des modes définis préalablement pour les fibres de cellulose native ne permet de décrire le mécanisme de gonflement et de dissolution des fibres traitées. Celui – ci se déroule en trois étapes: gonflement homogène, déroulement de la structure de la fibre donnant naissance à des sous fibrilles, dissolution de ces fibrilles. Les systèmes aqueux considérés comme des mauvais solvants (par exemple NaOH (7.6%) – eau) ne parviennent pas à dissoudre les fibres de cellulose traitées, elles restent simplement à l'état gonflées. Ces résultats sous entendent qu'une fois les fibres gonflées dans un système suffisamment actif pour atteindre l'étape de dissolution, les fibres de cellulose traitées peuvent se libérer des contraintes mécaniques emmagasinées lors de leur biosynthèse, ce qui provoque le déroulement de leur structure, aboutissant à leur dissolution.

De plus, comme les fibres ne gonflent pas par ballonnement, les parois externes détachées de la fibre sont bien à l'origine du gonflement hétérogène par ballonnement. La paroi primaire plus une partie de la paroi secondaire (certainement la paroi S1, connue pour l'angle d'orientation de ses fibrilles par rapport à l'axe de la fibre et ainsi peut être à l'origine du caractère hélicoïdal de la membrane) constituent la membrane des ballons.

In both previous chapters concerning aqueous solvents, the outer layers of cellulose fibres seems to play a key role in the swelling and dissolution processes. The formation of balloons is an intriguing effect. One obvious question is about the origin of the balloon membrane. In order to explore this point, enzymatically – treated cotton and wood cellulose fibres are dipped in similar aqueous systems and experimental conditions. In fact, a known thickness of the outer layer has been removed by a treatment based on an enzymatic solution. Thus, the behaviour of treated cotton and wood samples is modified and compared to the previous results of untreated cotton and wood cellulose fibres. Chapter 4 summarises these experiments.

Swelling and dissolution of cellulose Part III: enzymatically-treated cotton and wood fibres in aqueous solvents

Celine Cuissinat¹, Patrick Navard^{1,}*

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Matériaux (CEMEF),
Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207,
06904 Sophia Antipolis, France
Member of the European Polysaccharide Network of Excellence (EPNOE),
www.epnoe.eu

* To whom correspondence should be addressed. Tel: 33 (0)4 93 95 74 66; Fax:
33 (0)4 92 38 97 52; E-mail: Patrick.Navard@ensmp.fr

Summary: The swelling and dissolution mechanisms of enzymatically treated native cellulose fibres in aqueous systems (*N* – methylmorpholine *N*-oxide (NMMO) - water and NaOH – water (with or without urea) are studied varying the peeling rate, i.e. removing the primary wall layer and a certain part of the secondary wall. With good solvents, the swelling and dissolution of enzymatically treated cellulose samples occur in three steps: (i) a homogeneous swelling of the fibre, (ii) an unwinding of the fibres that separate into two sub fibres, (iii) dissolution of each of the two sub-fibres. Moderately good solvents that were able to dissolve cellulose inside the balloons in the case of untreated fibres are not able to dissolve the treated fibres, reaching only the first step of swelling without unwinding the fibre. Without primary wall, no ballooning is seen. The unwinding of the fibres suggests that upon swelling, mechanical stresses frozen during the biosynthesis or the drying are released.

Keywords: Cellulose, cotton, dissolution, swelling, enzymatic treatment, *N*-methylmorpholine *N*-oxide, sodium hydroxide

Introduction

Cellulose is a commonly used material in everyday life. Despite its qualities, it is not so easy to process, mainly because it cannot be melted and cannot be easily dissolved. The improvement of the dissolution capabilities of cellulose has been a central problem in biomaterial processing for more than 150 years. One way to improve dissolution is to understand the mechanisms that transform the complex cell structure into a polymer solution. A contribution to this understanding is the purpose of this series of paper dealing with the swelling and dissolution mechanisms of cellulose from various sources and of cellulose derivatives in aqueous and non-aqueous substances. When cotton or wood cellulose fibres are placed in a liquid, the resulting interaction is complex and is revealing some of the key structural aspects of the cell walls. In the first two papers of this series ^[1,2], it was shown that the dissolution of cotton and wood cellulose fibres in aqueous systems can be rationalized into five modes of dissolution:

Mode 1: fast dissolution by disintegration into fragments

Mode 2: large swelling by ballooning, and complete dissolution

Mode 3: large swelling by ballooning, and no complete dissolution

Mode 4: homogeneous swelling, and no dissolution

Mode 5: no swelling, and no dissolution

These modes reflect the quality of the solvents, decreasing from mode 1 to mode 5. Very good solvents disintegrate the cellulose fibre into long needles (mode 1) that are then dissolving. Moderate to bad solvent swells first the fibre into balloons that are then bursting (moderate solvent quality, mode 2) leading to complete dissolution of the fibre or not (bad solvents as NaOH at 7.6%, mode 3), only leading to a partial dissolution of the fibre. In both cases, at least part of the fibre (inside the balloons) has been dissolved. Non solvents can either swell homogeneously the fibres without dissolution (mode 4) or not interact at all with cellulose (mode 5).

The morphological features seen during swelling and dissolution in these various modes are due to the way the different components of the vegetal cell are assembling during the biosynthesis. The fine structure of cotton and wood fibres is well known. What is not well understood is how the cell forms. Knowledge of the biosynthesis mechanisms in the cell increased a lot this last decade with a rather good understanding of the cellulose production (assembling of the chain in the plasma membrane by plasma membrane rosettes that contain the cellulose synthase protein, with a direct deposition of 36 chains into the wall) but there is still a lack of knowledge on how the various components of the cell wall are arranging^[3]. Whatever the origin of the native fibre cells is, several common morphological structures can be found. A primary wall is first formed, composed of cellulose, hemicelluloses pectin and proteins^[4]. The cell is then elongating while a secondary deposition of mainly cellulose is taking place, forming the secondary wall. It is thought that elongation of the cell and growth of the cell wall may occur simultaneously^[5]. In the primary wall, fibrils of about 10 nm in diameter are positioned crosswise in a layer of about 50 nm thickness. The secondary wall (S) consists most of the time of two layers S1 and S2. The thickness of the S1 layer is about 100 nm for cotton and about 300 nm for spruce pulp fibres. The fibrils are parallel and are densely packed into a flat helix. The nature and organisation of the primary wall^[6] and the orientation of the fibrils in the secondary wall are two structural characteristics of cellulose which play a role in fibre swelling. The latter factor is for example responsible of the good wet properties of cotton fibres.

When placed into a moderately good solvent, cotton and wood cellulose fibres show a peculiar phenomenon called ballooning. The detailed structure of these balloons and the kinetics of their appearance and dissolution are described in the two preceding articles of this series^[1,2]. Ballooning has been observed quite frequently in cotton. In the 1950's, Ott et al.^[7] proposed an explanation about the origin of the balloons. He proposed that swelling agents act on the secondary cell wall, while the primary wall remains unswollen. Expansion of the secondary wall due to swelling results in a bursting and slippage of the primary wall, which forms collar at regular intervals, blocking the expansion in these zones. The resulting ballooning structure is therefore indicative of the primary wall and of a swollen secondary layer. They also noted that when the primary wall has been removed by alkaline digestion, irregular swelling forming sorts of balloons is seen. They ascribed this to the effect of the winding of the fibres. We showed^[1] that these explanations are not compatible with a detailed experimental study of the ballooning.

The purpose of this study is to re-examine the effect of the primary wall on the swelling and dissolution mechanisms of native cellulose fibres. To do so, the primary wall was selectively removed by an enzymatic treatment. The degradation of cellulose substrates in nature is an essential part of the carbon cycle. The classes of hydrolytically, oxidatively or otherwise active enzyme complexes which are involved in the biodegradation of cellulose in nature are known under the general term of "cellulases". This term always refers to a mixture of enzymes rather than to a single enzyme^[8]. The major constituents of cellulases are the β -1,4-

glyconases which catalyse the primary reaction of hydrolytically splitting the β -1,4-glycosidic linkages between the hydroglucose base units in the cellulose chain molecule. There are two types of hydrolytically acting enzymes, namely:

- the endo – enzymes (endo - β -1,4- gluconases), which cause cleavage of glycosidic linkages at random sites in the cellulose molecules, producing oligomeric mixtures of chain fragments,
- the exo – enzymes (exo - β -1,4- gluconases), which split glycosidic linkages in the cellulose molecules at specific locations adjacent to the non – reducing end, thus yielding specific low molecular mass fragments, mainly cellobiose (cellobiohydrolases) or glucose (glucohydrolases).

Native crystalline cellulose is water insoluble, and its structure and complexity render it highly resistant to the hydrolytic action of enzymes. In most cellulosic organisms, several cellulase components form a cellulose complex which hydrolyses cellulosic substrates. The susceptibility of cellulose to enzymatic hydrolysis is determined largely by its accessibility to cellulosic enzymes. Direct physical contact between the enzymes and the substrates molecules of cellulose is prerequisite to hydrolysis. Since cellulose is an insoluble and structurally complex substrate, this contact can be achieved only by diffusion of the enzymes into the complex structural matrix of cellulose. Any structural feature that limits the accessibility of cellulose to enzymes will diminish the susceptibility of cellulose to hydrolyse. In considering the action of cellulase enzyme complexes on cellulose substrates the internal structure of the substrates must thus be taken into account. Fibrous cellulose substrates are accessible through narrow channels having average diameters of 20 nm. This phenomenon allows the penetration of larger reactants, such as active enzyme proteins, only to the surface of fibrils or fibrillar aggregations. The interfibrillar interstices in fibrillar aggregates and the molecular distances in the less ordered interlinking regions between crystallites in the individual elementary fibrils, however, are much smaller (below 4 nm) and are therefore practically inaccessible for the enzyme proteins. Cellulose molecules or molecular segments inside the cellulose crystallites are completely inaccessible for the enzyme proteins. The rate of the enzymatic degradation is influenced by the crystallinity or the transverse dimensions of fibrils or fibrillar aggregates^[9]. De-crystallinity and to a lower extent swelling treatments of the cellulose substrate enhance the enzymatic action and allow degradation by both endo- and exo-gluconases^[10]. Such treatments reduce the degree of fibrillar aggregation and/or crystallite dimensions creating larger interstices and accessible surface, thus exposing more complete cellulose molecules to the action of the enzymes. Swelling treatments will enhance the accessibility of the fibrous cellulose substrate for the enzyme complex. This higher accessibility will cause a somewhat different course of the degradation. The molecular mass of the insoluble residue will be markedly lower than that of the starting substrate. With regard to the course and the mechanism of the enzymatic degradation of cellulose substrates, these facts lead to the conclusion that the enzyme complexes, in a synergistic action of endo- and exo- glucanases^[11], cause a statistic breakdown of accessible molecules to oligosaccharides. This are then suited for the further conversion to cellobiose and glucose. The inaccessible bulk of the substrate is structurally somewhat loosened, but remains molecularly almost unchanged. This is an important phenomenon that is causing a specific degradation of dry, mature cotton fibres.

In addition to crystallinity and swelling that may influence the action of enzyme solutions on cellulose fibres, another major parameter is the internal structure of the cellulose fibre. Kassenbeck^[12] showed that the secondary wall is drastically modified upon drying, in a way that is not homogeneous around the fibre, using various enzymatic treatments. This is the result of the asymmetry of the mechanical strains which appear in the cotton hair during its

very first drying from the form of a swollen cellular tube to a flat fibre. In the cross sections of mature fibres, three zones may be distinguished which differ not only in the organization of their fine structure but also in their accessibility to reagents and their behaviour during the swelling step. Four zones are seen:

- Zone A corresponds to the highly curved extremes of the bean – shaped cross section of cotton. It shows the highest density of packing of fibrils and it is the least accessible zone.

- Zone B, the convex part has a well defined structure of concentric layers. This zone is more accessible to reagents than the zones A, especially in its peripheral region.

- Zone C, which forms the collapsed or concave part of the cross section is the most accessible and the most reactive zone. It has a disorganized and more open structure contrary to zones A and B.

- Zone N is located at the boundaries between zones A and C. This is a very accessible part of the secondary wall.

In zones A and B, which are subjected to radial compressive forces, the packing density and the parallelism of the membranes is large. They are smaller in zone C which is subjected to tangential compressive forces. At the boundaries between C and A, the negative and positive strains balance each other and no deformation is produced in these restricted areas or in neutral zones N, which, therefore, remain particularly “open” and form the most accessible part of cotton fibre. This model explains the typical bean-like shape of cotton hair.

The morphological study of kinetics of enzymatic digestion of cotton cellulose indicates that the degradation by enzymes starts in the more accessible parts of the fibres, i.e. the N and C zones. These zones are completely removed before a beginning of any severe degradation can be observed in the zones having a higher density of fibrillar packing (zones A and B). This leaves the cotton fibre opened without the lumen inside.

In the present study, cotton and wood fibre samples were treated with an enzymatic solution, varying treatment time. The treated cotton and wood samples are characterised by a peeling rate. The higher the peeling rate, the more external surface of the fibre has been removed. The treated samples were placed in NMMO - water and NaOH - water mixtures and the swelling and dissolution mechanisms were observed in the same way as in previous articles^[1,2]. These results are compared to those obtained with untreated cotton and wood fibres, in order to investigate the influence of the peeling of the outside layer of the fibres on swelling and dissolution mechanisms.

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^[13]. The enzymatic treatments were performed in the research laboratory of Lenzing AG, Austria) to obtain cotton and wood cellulosic fibres without outer layers. The samples (bleached cotton, Borregaard and Buckeye) were treated with a mixture of cellulase and xylanase enzymes. The hypothesis is that the enzymes remove layer after layer of the fibre, peeling the primary wall first, attacking the secondary layer after. The results of Kassenbeck^[12] suggest that this peeling may not be uniform all around the fibre.

Table 1. Properties of the cellulose samples.

	Bleached cotton	Buckeye VFC	Borregaard VHF
Cristallinity (%)	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

Enzyme treatments were performed with a gentle shaking, leading to very low mechanical forces on the fibres. The enzymatic reaction was stopped by washing in cold water and heating 30 minutes at 40°C. The extent of the peeling was characterised by the «peeling rate», the percentage of solubilised sugars analysed in the supernatant by capillary electrophoresis per fibre weight. Nine different enzymatically treated cotton and wood fibres were prepared, with various peeling rate (table 2). We will particularly consider samples which peeling rate is around 10%. At this rate, only the primary and part of the secondary wall are put out. The characteristics of the samples having a peeling rate of around 10% are given in table 3.

Table 2. Peeling rate of treated cotton and wood (Borregaard, Buckeye) samples.

	Bleached cotton			Buckeye VFC			Borregaard VHF		
Peeling rate	2.5	4.9	10.0	24.9	15.3	9.4	31.0	16.6	11.2

Table 3. Properties of the enzymatically treated cotton and wood samples, with a peeling rate around 10%.

	Bleached cotton		Buckeye VFC		Borregaard VHF	
Peeling rate (%)	0	10.0	0	9.4	0	11.2
Cristallinity (%)	55	57	46	47	43	48
Mn (* 1000) (g/mol)	262.9	172.1	63.9	53.8	152.6	115.8
Mw (*1000) (g/mol)	606.3	512.3	121.1	114.1	766.7	449
Mz (* 1000) (g/mol)	998.4	907.8	215.2	216.1	1600.5	1411.5
w (DP < 50)	0.1	0.3	0.3	0.7	0.3	0.6
w (DP < 200)	1.1	2.9	9.3	14.2	4.7	6.0
w (DP > 2000)	68.1	57.9	4.7	4.9	63.1	51.9

- Solvent agents

The swelling and dissolution treatments were performed in two types of aqueous solvents, *N*-methylmorpholine *N*-oxide (NMMO) – water, and NaOH – water solutions (with or without urea). 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 (19, 20, 23.5 % per mass of water). All the swelling and dissolution experiments in NMMO – water systems were carried out at 90°C.

NaOH – water is a mixture contained 7.6% (in weight) of NaOH. The NaOH powder comes from Fisher and is pure to about 97%. Mixtures with urea (Fisher) were prepared with the

following composition: NaOH (7.6%), urea (12%), and water (80.4%). All the swelling and dissolution experiments in NaOH solutions were carried out at -5°C .

- Preparation and observation of the solutions

The preparation of samples and the technique used are similar as the process described in the previous articles^[1,2]. 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 an adhesive tape on the 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.

Results and discussion

A. General swelling and dissolution mechanisms of treated cotton and wood fibres

The treated cotton and wood fibres homogeneously swell without the appearance of balloons. When the solvent is good enough, these swollen fibres dissolve. The dissolution occurs by an unwinding of the fibre structure occurring before the dissolution phase. The swelling and complete dissolution mechanisms for the enzymatically treated fibres can be divided in three main steps:

Step 1: homogeneous swelling of the treated fibres.

The treated cotton and wood fibres swell along all its length (figure 1). The homogeneous swelling is low. Contrary to the swelling and dissolution mechanisms observed in the case of cotton and wood cellulose fibres^[1,2], swelling does not occur by ballooning.



Figure 1. Homogeneous swelling of the enzymatically treated Borregard fibres with a peeling rate of 11.2%, swollen in NMMO – water at 23.5%

Step 2: unwinding of the treated cotton and wood fibres.

Once the treated cotton and wood fibres are swollen, an unwinding of its structure occurs. The treated cellulose fibres turn about their axis (figure 2) and each fibre is separated in two sub - fibres (figure 3).

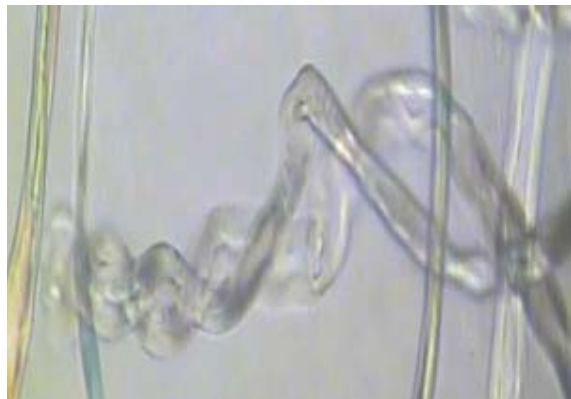


Figure 2. Unwinding of a treated cellulose fibre (enzymatically treated cotton whose peeling rate is 4.93%, swollen in NMMO – water at 20%)



Figure 3. Separation of treated wood fibres into two sub – fibres during the swelling and unwinding step (enzymatically treated Buckeye sample at a peeling rate of 9.41%, swollen in NMMO – 20%)

Step 3: dissolution of the cellulose fibres.

The sub – fibres are disintegrated into fragments as seen in figure 3 at one of the extremity of the fibres. Then, these fragments are dissolved (figure 4).



Figure 4. Dissolution by fragmentation of treated cellulose fibres (treated cotton fibre at a peeling rate of 10% in NMMO – water solution at 20%)

The three steps are not seen with all the solvents. Only NMMO – water mixtures at water content from 19 to 23.5% have these three steps up to the full dissolution, with a homogeneous swelling, unwinding and dissolution. NaOH solutions (at 7.6%, with or without urea) only swell the fibres but there is neither unwinding nor dissolution. It must be noted that NaOH-water is able to dissolve the cellulose contained in the balloons (i.e. coming from the secondary wall) in the case of untreated fibre while it seems to only swell the treated fibres, although they are composed of secondary wall cellulose. A possible explanation is that unwinding is absolutely necessary to occur for fibres to dissolve in poor solvents. This is possible for untreated fibres in localized areas (balloons) while it could be prevented for the treated fibres.

Table 3 shows that with a peeling rate of about 10%, crystallinity increases (enzymes degrade preferentially amorphous zones) and low molar mass chains are produced.

B. Description of step 1: homogeneous swelling

The observed swelling for enzymatically treated fibres is homogeneous, whatever the used solvent is. No balloon appear along the treated cotton and wood fibres, swollen in aqueous solvents (note that the same is also true for the same fibres placed in ionic liquids, Cuissinat, Navard, Heinze, paper in preparation, chapter 5). The quantitative description of the swelling for enzymatically treated fibres is based on the measurement of the ratio $D_{\text{swelling}} / D_{\text{dried}}$. This parameter indicates the ability of a treated cellulose fibre to interact with a solvent agent. This parameter measured for the treated fibres can be compared with the value of $D_{\text{fm}} / D_{\text{i}}$ (maximum expansion of the balloon / initial diameter in dry state) measured in the same solvent with the untreated cotton and wood fibres where ballooning occurs^[1]. Table 4 gives the variation of $D_{\text{swelling}} / D_{\text{dried}}$ as a function of the type of treated fibres. The evolution of $D_{\text{swelling}} / D_{\text{dried}}$ as a function of the peeling rate is given in table 5. The values of $D_{\text{swelling}} / D_{\text{dried}}$ in a large range of solvents systems are given in table 6.

Table 4. Values of $D_{\text{swelling}} / D_{\text{dried}}$ for treated cotton and wood fibres, of $D_{\text{fm}} / D_{\text{i}}$ for untreated cotton and wood fibres (in NMMO – water 20%).

	Cotton samples			Buckeye samples			Borregaard samples		
Peeling rate	4.9	2.5	10	24.8	15.3	9.4	31.0	16.6	11.2
$D_{\text{swelling}}/D_{\text{dried}}$	4.5	4.5	4.5	5	4.7	4.7	6.2	6.0	6.0
$D_{\text{fm}}/D_{\text{i}}$ (for untreated fibres)	4.8			5.1			5.7		

Table 5. Values of $D_{\text{swelling}} / D_{\text{dried}}$ (for treated fibres) for various peeling rate and $D_{\text{fm}} / D_{\text{i}}$ (untreated fibres).

	treated Buckeye samples		
Peeling rate (%)	24.8	15.3	9.4
$D_{\text{swelling}}/D_{\text{dried}}$ in NMMO – water 20%	5.0 dissolution	4.7 dissolution	4.7 dissolution
$D_{\text{swelling}}/D_{\text{dried}}$ in NMMO – water 23.5%	5.0 dissolution	4.5 dissolution	4.5 dissolution
$D_{\text{fm}} / D_{\text{i}}$ (reference value, untreated fibres)	5.1		

Table 6. Values of $D_{\text{swelling}} / D_{\text{dried}}$ (for treated Buckeye fibres) and $D_{\text{fm}} / D_{\text{i}}$ (for untreated Buckeye fibres) in various solvent agents.

	Buckeye sample
Peeling rate (%)	9.4
$D_{\text{swelling}}/D_{\text{dried}}$ in NMMO – water 20%	4.7
$D_{\text{swelling}}/D_{\text{dried}}$ in NMMO – water 23.5%	4.5
$D_{\text{fm}}/D_{\text{i}}$ in NMMO – water (reference value, untreated fibres)	5.1
$D_{\text{swelling}}/D_{\text{dried}}$ in NaOH 7.6%	3.6
$D_{\text{fm}}/D_{\text{i}}$ in NaOH 8% (reference value, untreated fibres)	3.6
$D_{\text{swelling}}/D_{\text{dried}}$ in NaOH (7.6%) – urea (12%)	3.7
$D_{\text{fm}}/D_{\text{i}}$ in NaOH (7.6%) – urea (12%) (reference value, untreated fibres)	3.5

Table 4 shows that the ratio $D_{\text{swelling}} / D_{\text{dried}}$ is independent of the removed amount of outer layers, for a given cellulose fibres when the peeling rate is higher than 2.5%. Once the chemicals systems has penetrated inside the cellulose and been propagated, the diameter of fibres increases whatever the percentage of removed layers is. This result is validated by the data presented in table 5, which indicates that it occurs whatever the quality of solvent system is. When the peeling rate is at least larger than 2.5%, a homogeneous swelling is seen in all the solvents and the ratio of swelling of the treated cellulose fibres is constant.

Tables 5 and 6 allow comparing the ability to swell of treated and untreated cellulose fibres in several solvent systems. When the solvent is very good, able to completely dissolve the fibres (case of NMMO – water mixtures), the ratio $D_{\text{swelling}} / D_{\text{dried}}$ of the treated fibres is smaller than the value $D_{\text{fm}}/D_{\text{i}}$ of the untreated fibres (maximum expansion of the balloons). However, when the solvent is not able to dissolve the fibre as with NaOH mixtures, the ratio $D_{\text{swelling}} / D_{\text{dried}}$ is equal to the maximum expansion of the balloons $D_{\text{fm}} / D_{\text{i}}$ in untreated fibres. The quality of the solvent is not changing if the fibre is treated. The presence or absence of the outer layers of cellulose fibres influence the swelling and dissolution

mechanism since when it is present, ballooning occurs, but this does not change the solvent quality.

C. Description of step 2: unwinding of the structure

This step follows the homogeneous swelling and is possible only after the swelling. The unwinding of the structure induces the fragmentation of fibres, and thus is the precursor of dissolution. The unwinding step depends on the quality of solvent agents since it is only observed with good solvent systems (as NMMO – water mixtures, with water content between 17 and 23%). In the case of moderately good solvents (NaOH – water solution), the unwinding of fibres never occurs. The fibres remain in the swollen state. Even if chemical agents are active enough to penetrate the treated samples, they are not able to induce unwinding. The unwinding of enzymatically treated cotton and wood fibres occurs in the following way. The treated fibre undergoes a left handed untwisting, which ends up at its separation in two sub fibres. Once the fibres are swollen, an internal helical structure is observed and progressively turns on itself (figure 5). With time, the pitch of the helical structure increases (figure 6). The unwinding of structure is fast. The pitch of the helical structure is at least multiplied by 2. The consequence of the structure fibres unwinding is the fragmentation of treated cellulose fibres. All fibres undergoing an untwisting are separated in sub - fibres.

A major question is the origin of the untwisting and why this seems to be a necessary condition for dissolution. Phenomena related to untwisting of fibres have been reported in the past. It relates to the macroscopic response of a fibre to change in moisture content. When placed into a given atmosphere where the relative humidity is varied, fibres rotate about their axis^[15,16]. The rotation increases with the percentage of relative humidity and is reversible. This phenomenon was ascribed to a specific hydrogen bonding scheme between the microfibrils^[16]. Such a twisting effect was thought by other authors to be linked to the amount of swelling a fibre can undergo in a given solvent. They measured the number of revolutions cotton fibres are doing when placed in a large variety of solvents (number between 0 for butyl acetate and 46 for ethylene diamine, water being at 24) and claimed that this is a direct method to evaluate the swelling behaviour of these solvents^[17]. If cellulose fibres twist and untwist when placed into a swelling agent, it means that a mechanical stress is build-in the fibre and is released or regained when the physical reason that is blocking it is removed or put again. This is a very common phenomenon in natural (hair, wool) and man-made materials. Any bilateral structure will lead to twisting and untwisting as soon as the external conditions that can reveal it (temperature, moisture, etc.) are changed^[18]. For example, an anisotropy of cooling conditions on two opposite sides of a spun fibre leads to the production of twisted fibres^[19,20]. This should be the case of cellulose fibres. They are twisting and untwisting because there is a morphological asymmetry that is revealed during swelling by stress relaxation. This asymmetry can be either already existing in the fibre during its biosynthesis or created during drying. It is known that the cellulose microfibril organisation has a spiral nature in most plant cells. It was supposed that these spiral structures results from the superposition of the rotary movement of cellulose microfibrils, which are being deposited on the internal cellular surface, and the forward movement of the cell fibre during its development^[21]. The correlation between the internal stresses born during the biosynthesis and the behaviour of cellulose fibre in presence of a extern agent has ever been underlined by Orr et al.^[22]. Untwisting of untreated cotton fibres was observed in clockwise direction for fibres with a Z spiral structure and counter clockwise direction for fibres with a S spiral structure. These structural features fibres have pronounced effects on the twisting behaviour

of fibres. This relation between the direction of the spiralling of the fibrils in the secondary layer with the macroscopic twisting and untwisting of the cotton fibre with moisture content changes is a strong indication of their relationship. Nevertheless, several of the experiments reported above were performed with jute fibres where there is nearly no spiralling, the microfibrils being at a very low angle about the fibre direction. There is no clear reason why the deposition process of cellulose fibrils on the secondary wall should occur with a difference between one side of the fibre and the other, considering that the deposition is performed by moving perpendicularly to the fibre. The elongation of the wall is the only event that could induce an asymmetry of structure if the cell is rotating. It must be remembered that for bringing a twisting, there must be a structural asymmetry that is blocked by either a fast cooling or a fast solvent evaporation. During the elongation of the cell, it does not seem that the moisture content is changing at a rate that could freeze stresses due to an impossibility to release chain conformation. Drying is clearly the primary phenomenon that must be looked for in the search of the origin of the untwisting phenomenon.

An interesting point is the relation between untwisting and ballooning. Warwicker et al.^[23] noticed that if raw cotton is placed in cuprammonium hydroxide, or other reagents as sulphuric acids, the fibre rapidly untwists. The outer skin splits in a spiral fashion to form collars. The inner cellulose layers swell rapidly and bulge out between the restrictive collars of the outer layers forming the beaded structure we called balloons. This is the only mention that ballooning is related to untwisting.



Figure 5. Unwinding step for the treated cotton and wood fibres (treated cotton fibre at a peeling rate of 10% in NMMO – water solution at 20%)

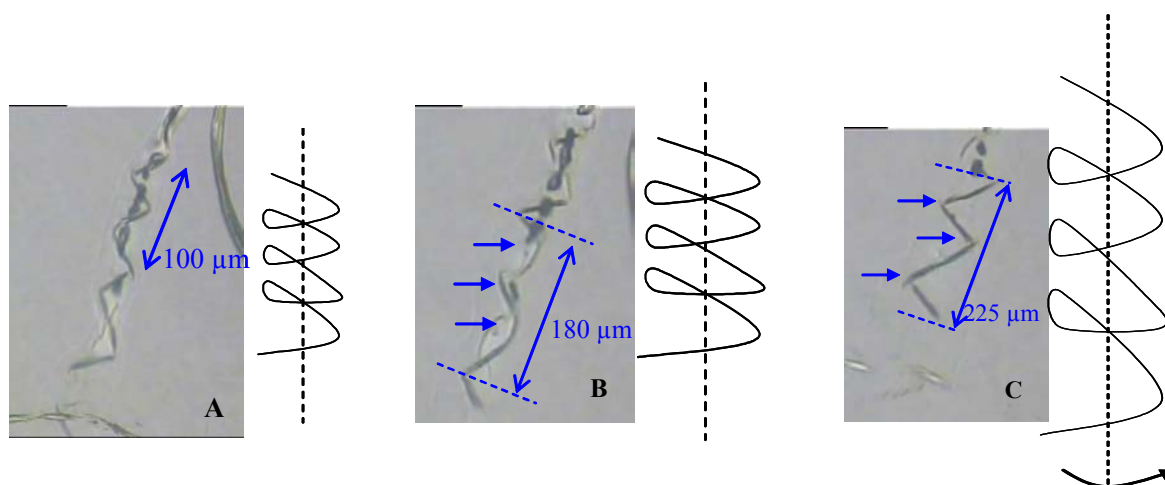


Figure 6. Evolution of the pitch of the structure of treated cellulose fibres during the unwinding step (treated cotton fibre at a peeling rate of 4.93% in NMMO – water solution at 20%, optical microscopy in transmitted light). Pictures A, B and C are respectively taken 5 min 25s, 5 min 41s and 6min after the introduction of the solvent

D. Description of step 3: dissolution

Only the best solvents as NMMO – water mixtures (at 19, 20 and 23.5 % of water) are able to dissolve all the cellulose fibres. The unwinding of treated cellulose fibres induces the division of fibres into sub - fibres and seems necessary for having dissolution. The dissolution never occurs without the unwinding phase. The sub fibres are dissolved by disintegration. They burst into fragments, which are dissolved (figure 4). This type of dissolution by fragmentation is similar to the mechanism observed for strong solvents (as NMMO – water at 17%) where the fibres are totally disintegrated into rod-like fragments and then dissolved.

Conclusion

Cotton and wood samples devoid of primary and / or secondary layer by enzymatic peeling have a swelling and dissolution mechanism which is different from untreated samples. The swelling is homogeneous and follows by an unwinding of cellulose fibre during the dissolution. This mechanism differs from what is observed with untreated cotton and wood fibres where the swelling occurs by forming balloons and dissolution takes place in many steps. However, the swelling ratio is in the same order of magnitude between enzymatically treated or untreated samples. When the solvent is good enough, the fibres show a homogeneous swelling, then an unwinding of the fibre with a separation into two sub-fibres, and finally the dissolution of the sub – fibres by fragmentation. The presence of the outer layers prevents the homogeneous swelling of the whole fibre. Since without the primary wall layer, the fibre strongly unwinds, it can be suggested that the presence of the primary wall layer hampers the possibility of untwisting and that untwisting is necessary to occur for cellulose fibres to dissolve in moderately good solvents (good and very good solvents are able to break the whole fibre in fragments, called mode 1, without the need to untwist the fibre). With the primary wall layer present, untwisting can only occur in localised zones that are then

swelling in the form of balloons. The precise origin of the asymmetry of structure leading to untwisting and the magnitude of the built stresses remain to be understood.

Acknowledgements

The authors are grateful to the Lenzing AG Company (H. Sixta, T. Röder) for having helped C. Cuissinat to perform the enzymatic peelings and the associated analysis.

- [1] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part I: free floating cotton and wood fibres in *N*-methylmorpholine *N*-oxide water mixtures. *Macromol. Symp.* **accepted**.
- [2] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part II: free floating cotton and wood fibres in NaOH – water – additives systems, *Macromol. Symp.* **accepted**.
- [3] O. Lerouxel, D. M. Cavalier, A. H. Liepman, K. Keegstra, *Plant Biol.* **2006**, 9, 1.
- [4] C. Bret, K. Waldron, “*Physiology and biochemistry of plant cell walls*, 2nd edition”, Chapman and Hall, London, 1996.
- [5] G. Refrégier, S. Pelletier, D. Jaillard, H. Höfte, *Plant Physiol.* **2004**, 135, 959.
- [6] J. F. Kennedy, G. O. Philipp, P.A. Williams, “*Cellulose and exploitation, industrial utilisation, biotechnology, and physical – chemical properties*”, Horwood limited publisher, London, 1990.
- [7] E. Ott, H. M. Spurlin, M. W. Grafflin, “*Cellulose and cellulose derivatives (Part 1)*”, Interscience Publisher, New York, 1954.
- [8] H. A. Krässig, “*Cellulose : structure, accessibility and reactivity. Polymer Monographs (vol 11)*”, Gordon and Breach, New York, 1993.
- [9] K. Selby, C. C. Maitland, K. V. A. Thomson, *Biochem. J.* **1963**, 88, 288.
- [10] B. Focher, A. Marzetti, C. Santoro, V. Sarto, L. D. Angiuro, *Macromol. Chem. Phys.* **1982**, 102; 187.
- [11] M. Streamer, K. Eriksson, B. Petterson, *Eur. J. Biochem.* **1975**, 59; 607.
- [12] P. Kassenbeck, *Text. Res. J.* **1970**, 40, 330.
- [13] T. Baldinger, J. Moosbauer, H. Sixta, “*Supramolecular 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.
- [15] C. R. Noder, *J. Textile Inst.* **1922**, 13, 161.
- [16] Kh. M. Mannan, Z. Robbany, *Polymer* **1996**, 37, 4639.
- [17] J. H. Carra, V. W. Tripp, R. S. Orr, *Text. Res. J.* **1962**, 32, 1041.
- [18] M. Horio, T. Kondo, *Text. Res. J.* **1953**, 23, 373
- [19] F. Hensen, *Intern. Polym. Processing* **1989**, 4, 67.
- [20] T. Matsuo, S. Kase, *J. Polym. Sci.* **1965**, A3, 2541.
- [21] V. A. Krakhmalev, A. A. Paiziev, *Cellulose* **2006**, 31, 45.
- [22] R.S. Orr, A. W. Burgis, L. B. De Luca, J. N. Grant, *Text. Res. J.* **1961**, 31, 302.
- [23] J. O. Warwicker, R. Jefries, R. L. Colbran, R. N. Robinson, “*A Review of the Literature on the Effect of Caustic Soda and Other Swelling Agents on the Fine Structure of Cotton*”, Shirley Institute, Manchester, 1996.

Chapter 5

Swelling and dissolution mechanisms
of native cellulose fibres, part IV:
free floating cotton and wood fibres
in ionic liquids

Résumé francophone chapitre 5

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie IV : fibres de bois et de coton dans des liquides ioniques.

Afin d'élargir nos conclusions à d'autres type de solvants, les fibres de coton et de bois (traitées par une solution d'enzyme et non traitées) sont immergées dans trois liquides ioniques: 1-N – butyl – 3 – methylimidazolium chloride $[C_4mim]Cl$ plus du diméthyle de sulfoxyde (DMSO), du bromide d'allylmethylimidazolium CP040 et du bromide de butenylmethylimidazolium CP041. Leur mécanisme de gonflement et de dissolution est observé par microscopie optique.

Le système $[C_4mim]Cl$ – DMSO provoque le gonflement par ballonnement des fibres de coton et de bois, qui seront ensuite complètement dissoutes (mode 3). Les liquides ioniques CP040 et CP041 sont simplement des agents gonflants : les fibres de cellulose non traitées gonflent de façon homogène (mode 4). Les fibres traitées par une solution enzymatique ont un comportement similaire, qu'elles soient mise en milieu aqueux ou dans des systèmes ioniques. Le mécanisme de gonflement et de dissolution étant identique dans les solvants aqueux et les liquides ioniques, cela indique que le processus de dissolution des fibres de cellulose native n'est pas contrôlé par la nature chimique du solvant. Le paramètre clé influençant les phénomènes de gonflement et de dissolution des fibres de cellulose native est lié à leur structure morphologique.

Chapter 5 is expanding the range of solvent systems: cotton and wood fibres are dipping in ionic liquids (1-N – butyl – 3 – methylimidazolium chloride [C₄mim]Cl plus dimethyl sulfoxide (DMSO), allylmethylimidazolium bromide CP040 and butenylmethylimidazolium bromide CP041). Their swelling and dissolution mechanisms are described and compared with those observed in aqueous agents.

Swelling and dissolution of cellulose Part IV: free floating cotton and wood fibres in ionic liquids

Celine Cuissinat,¹ Patrick Navard^{*1,2}, Thomas Heinze^{2,3}

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Materiaux (CEMEF), Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207, 06904 Sophia Antipolis France

² Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu; Tel: 33 (0)4 93 95 74 66; Fax: 33 (0)4 92 38 97 52; E-mail: Patrick.Navard@ensmp.fr

³ Centre of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Humboldtstrasse 10, D-07743 Jena, Germany

Summary: Native and enzymatically treated cellulose fibres (cotton and wood fibres) are dipped into three ionic liquids (1-N-butyl-3-methylimidazolium chloride [C₄mim]Cl plus dimethyl sulfoxide (DMSO), allylmethylimidazolium bromide [Amim]Br and butenylmethylimidazolium bromide [Bmim]Br) and their swelling and dissolution mechanisms are described. [C₄mim]Cl – DMSO is a bad solvent of cotton and wood samples with a swelling by ballooning and then dissolution. [Amim]Br and [Bmim]Br are only swelling agents with a homogeneous swelling but no dissolution. The swelling and dissolution mechanisms of cellulose in ionic liquids are similar to those observed in aqueous solvents like *N*-methylmorpholine-*N*-oxide/water and NaOH/water. It indicates that the swelling and dissolution mechanisms are controlled by the quality of the solvent, not by its chemical nature.

Keywords: Cellulose; cotton; dissolution; swelling; ionic liquids

Introduction

Cellulose is a polydisperse linear polyglucan which forms hydrogen – bonded supramolecular structures. Cellulose is insoluble in water and a lot of common organic liquids. The growing willingness to develop new cellulosic material results from the fact that cellulose is a renewable resource, although many of the technologies currently used in cellulose processing are non – green. For example, viscose rayon is prepared from cellulose xanthate (production over 3,000,000 tons per year) utilising carbon disulfite as both reagent and solvent. Most recently, processing using more environmentally acceptable non-derivatising solvents (*N*-methylmorpholine-*N*-oxide, NMMO) appeared. With increasing governmental regulations restricting the use of current cellulose solvents, the need to replace them is becoming more important. Among the potential new solvents, ionic liquids have gained considerable attention. Ionic liquids ^[1] are composed of an organic cation and an inorganic anion. Considered “green” (environmentally friendly) due to the fact they could be fully recycled, ionic liquids are very effective solvents for a wide variety of solutes, ranging from organic to inorganic and from small molecules to polymers. There are numerous ways in which ionic liquid can be defined, and perhaps the most widely accepted definition is: a *material that is*

composed of ions, and has a melting point below 100°C. The notable characteristics of ionic liquids are their thermal stability, wide liquid temperature range, and good solvating properties for various kinds of materials. Another important feature of ionic liquids is their miscibility with water or organic solvents, which can be tuned through side chain lengths on the cation and choice of anion. Furthermore, they can be functionalised to act as acids, bases or ligands. Because of their properties, ionic liquids attract great attention in many fields, including organic, chemistry, electrochemistry, and engineering. In addition, their non-volatility results in low impact on the environment and human health.

Graenacher^[2] first suggested in 1934 that molten *N*-ethylpyridinium chloride in the presence of nitrogen-containing bases could be used to dissolve cellulose. However this seems to have been treated as a novelty of little practical value since the molten salt system was, at this time, somewhat esoteric and has a relatively high melting point (118°C). The availability of a wide and varied range of ionic liquids, coupled with the current understanding of their solvent properties, should allow tailoring and controlling dissolution, processing and the final properties. The ability of ionic liquids to dissolve cellulose fibres could be explained by studying the behaviour of non derivatizing solvents for cellulose^[3]. These cellulose solvents affect dissolution by disrupting and breaking the intermolecular hydrogen-bonding network. For *N,N*-dimethylacetamide (DMAC)/LiCl solvents, complex of lithium ions with DMAC mobilises chloride ions which interact with cellulose hydroxyl groups. In a typical 10 wt % LiCl/DMAC solution, free chloride ion concentration is about 6.7 mol %. In contrast, [C₄mim]Cl, which is an ionic liquid, has a chloride concentration almost three times higher, (approximately 20 mol %). In all these cases, the chloride ions are non-hydrated. The assumption is that the high chloride concentration and activity in [C₄mim]Cl is very effective in breaking the extensive hydrogen-bonding network present, thus bringing a much quicker dissolution, and dissolving higher concentration of cellulose than the traditional solvent systems. The ionic liquids can also be applied as reaction media for the synthesis of cellulose derivatives like carboxymethyl cellulose and cellulose acetate^[4-6].

As we have seen in the preceding papers of this series^[7,8], five modes describing the behaviour cellulose fibres dipped into NMMO-water or NaOH-water agents 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

These modes reflect the quality of the solvents, decreasing from mode 1 to mode 5. Very good solvents disintegrate the cellulose fibre into long needles (mode 1) that are then dissolving. Moderate to bad solvent swells first the fibre into balloons that are then bursting (moderate solvent quality, mode 2) or not (bad solvents as NaOH at 7.6%, mode 3). In both cases, at least part of the fibre (inside the balloons) has been dissolved. Non solvents can either swell homogeneously the fibres without dissolution (mode 4) or not interact at all with cellulose (mode 5).

The objective of this paper is to investigate the swelling and dissolution behaviour of cellulose in ionic liquids which are non-aqueous solvents to see if the description of the cellulose-chemical interaction through five modes is valid.

Experimental part

- Cellulose samples

Three native fibres, one bleached cotton and two wood fibres, Buckeye VFC (pine wood pulp obtained after a treatment by vapour hydrolysis, cooking in a sodium sulfite and soda solution) and Borregaard VHF (fir tree pulp obtained by an acid process with calcium bisulfite) were used either as received or after an enzymatic peeling treatment. These samples were treated with an enzyme mixture of cellulose and xynalase to obtain cotton and wood cellulosic fibres without outer layers. The peeling rate (i.e. the percentage of solubilised sugars analysed in the supernatant by electrophoresis per fibre weight) characterizes the strength of the treatment. The characteristics of samples are given in table 1, the crystallinity is obtained by Fourier transform infrared spectrometry^[9].

Table 1. Properties of the used cellulose samples.

	Bleached cotton		Buckeye VFC		Borregaard VHF	
Peeling rate (%)	0	10.00	0	9.41	0	11.26
Crystallinity (%)	55	57	46	47	43	48
Mn (* 1000) (g/mol)	262.9	172.1	63.9	53.8	152.6	115.8
Mw (*1000) (g/mol)	606.3	512.3	121.1	114.1	766.7	449
Mz (* 1000) (g/mol)	998.4	907.8	215.2	216.1	1600.5	1411.5
w (DP < 50)	0.1	0.3	0.3	0.7	0.3	0.6
w (DP < 200)	1.1	2.9	9.3	14.2	4.7	6.0
w (DP > 2000)	68.1	57.9	4.7	4.9	63.1	51.9

- Ionic liquids

Three ionic liquids were investigated:

- 1-N-butyl-3-methylimidazolium chloride (noted [C₄mim]Cl),
- allylmethylimidazolium bromide (noted [Amim]Br)
- butenylmethylimidazolium bromide (noted [Bmim]Br).

The molecular structures of [C₄mim]Cl, [Amim]Br and [Bmim]Br are respectively given in figure 1, 2 and 3. The experiments are performed at 100°C with [Amim]Br and [Bmim]Br, at 80°C with [C₄mim]Cl.

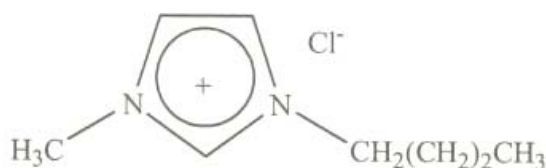


Figure 1. Molecular of ionic liquid [C₄mim]Cl.

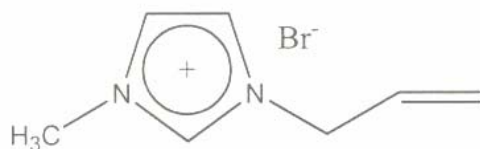


Figure 2. Molecular structure of ionic liquid [Amim]Br.

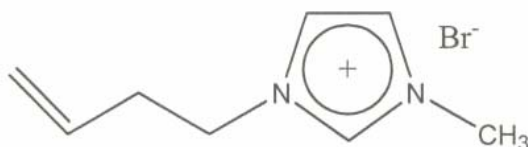


Figure 3. Molecular structure of ionic liquid [Bmim]Br.

[C₄mim]Cl is a very good solvent for cellulose. As a consequence, the swelling and dissolution of cellulose are occurring too fast for their mechanisms to be observed. The first idea was to decrease the speed of swelling and dissolution by adding a small amount of water. However, the presence of water in the ionic liquid was shown to significantly decrease the solubility of cellulose, presumably through competitive hydrogen – bonding to the cellulose microfibrils^[3]. When water was added to the ionic liquid at concentrations greater than 1 wt%, the solvent properties were significantly decreased, and cellulose was no longer soluble. Adding DMSO in [C₄mim]Cl allowed to slow down the kinetic of dissolution by decreasing the ionic strength of cation and anion. DMSO is not a solvent for cellulose, however, cellulose swells in DMSO. But DMSO molecules solvate the cation of the ionic liquid. As the dissolution of cellulose in ionic liquids depends on the interaction between the anion and the cation, with the hydrogen bonds at the level of cellulose structure, the solvating action of [C₄mim]Cl is decreased.

- Preparation of samples

The solutions were prepared by mixing cellulose and solvent in a container made of two glass plates. No agitation was applied. 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 one 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. Due to the method employed for studying the swelling and dissolution, the cellulose concentration between the two glass plates is not well controlled. This will not allow obtaining quantitative kinetics data.

The swelling and dissolution of cellulose fibres were observed by transmission optical microscopy with a Metallux3 (Leitz) equipped with a Linkam TMS 91 hot stage.

Results and discussion

The swelling and dissolution of cotton and wood fibres in three ionic liquids, $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO, $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$, is described. A comparison with aqueous solvents (NMMO – water mixtures, and NaOH solutions) is given. The behaviour of untreated and enzymatically treated fibres in $[\text{C}_4\text{mim}]\text{Cl}$ – DMSO is described first, followed by the results with $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$.

- Swelling and dissolution mechanism in $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO

Cotton and wood fibres:

Cotton and wood samples swell by ballooning in $[\text{C}_4\text{mim}]\text{Cl}$ – DMSO system at 100°C , before dissolved. Dipping native cellulose fibres in an ionic liquid as $[\text{C}_4\text{mim}]\text{Cl}$ – DMSO induces a swelling and dissolution mechanism defined as mode 2^[7].

The native cellulose fibres start to swell in isolated points along the fibre, forming balloons. They increase their size, which leads to the appearance of a beaded structure (figure 4). The fibre has thus a series of swollen transparent parts, of a rounded shape. The balloon diameter increase up to the point where the balloons burst.

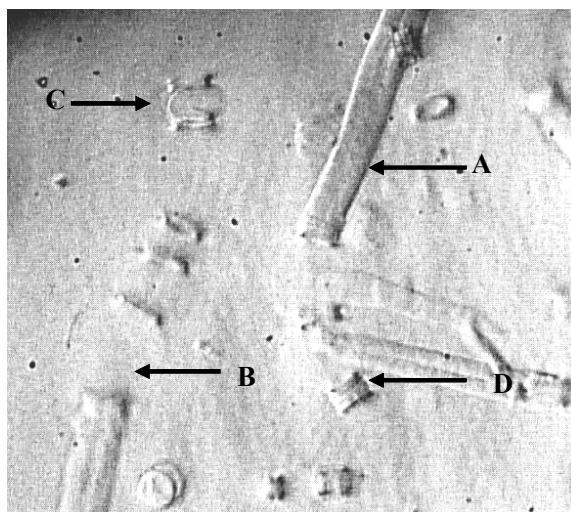


Figure 4. Swelling by ballooning in ionic liquid. Borregaard wood fibres in $[\text{C}_4\text{mim}]\text{Cl}$ – DMSO seen by optical microscopy in transmitted light ($T=100^\circ\text{C}$). A = unswollen fibre, B = balloon, C = membrane and D = unswollen section between two balloons.

As for the aqueous solvents^[7,8], the structure of a swelling fibre consists on several well defined zones: unswollen section fibre along a fibre (A), unswollen part between two balloons (D), balloon (B) surrounded by a helical membrane (C), as seen in figure 4. Each of these zones has a specific way of swelling and dissolving. Cotton and wood fibres, in ionic liquid $[\text{C}_4\text{mim}]\text{Cl}$ with few grams of DMSO, are following the same sequence of the four phases leading to the full dissolution as described previously for aqueous solvents:

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

The mechanism is the following. The outside of the fibre acts as a semi-permeable membrane, allowing the solvent to penetrate inside the fibre to dissolve cellulose. But the cellulose chains remain inside the fibre and cannot go out. This phenomenon occurs only at some zones along the fibre, called balloons. The solvent penetration increases the volume of the balloons, and expands the membrane that is holding it (phase 1). The balloons do not appear all at the same time along the fibre. The balloons are not exactly spherical, and they do not present a regular diameter. They are held by a membrane that is bursting when the expansion of the balloon reaches a certain diameter (phase 2) and the liquid cellulose solution inside flows out very rapidly. The burst is not simultaneous for all the balloons along a given fibre. After the balloon bursting, only two parts remain in the solvent agent: the unswollen sections that were between the balloons and the scraps of the membrane. The next parts to be dissolved are the unswollen sections (phase 3). No swelling occurs during the dissolution of this part, which begins at the outer surface of the unswollen section. The last parts to be dissolved are the scraps of the balloon membranes (phase 4).

These experiments show that $[C_4mim]Cl$ – DMSO is not a good solvent for studied cotton and wood samples. The described swelling and dissolution mechanisms are similar to what was found for aqueous solvents of bad dissolution quality^[7,8]. It clearly shows that the swelling and dissolution mechanisms through ballooning (called mode 2) is due to the structure of the cellulose fibres, not to a specific solvent.

Another comparison between behaviour of native cellulose fibres in aqueous solvents and ionic liquids $[C_4mim]Cl$ can be performed with regard to swelling ratio $D_{swelling} / D_{dried}$. $D_{swelling}$ is the diameter of the balloons, before bursting, D_{dried} is the diameter of cellulose fibre before being penetrated by a solvent systems. The values of $D_{swelling} / D_{dried}$ are indicated in Table 2.

Table 2. Swelling ratio $D_{swelling} / D_{dried}$ for cotton and wood fibres (Borregaard, Buckeye and bleached cotton) in aqueous solvents and ionic liquid $[C_4mim]Cl/DMSO$. $D_{swelling}$ is the maximum diameter during the swelling by ballooning. D_{dried} is the fibre diameter without solvent. The values in bold indicates that the balloon is swelling up to burst.

		Borregaard	Buckeye	Bleached Cotton
Aqueous Solvents	NMMO – water (19%)	5.3	5.3	4.8
	NMMO – water (20%)	5.2	5.2	4.7
	NMMO – water (23.5%)	4.8	4.8	4.9
	NaOH (at 7.6%)	3.6	3.6	3.2
	NaOH (at 7.6%) with 12% urea	3.7	3.7	3.9
Ionic Liquid	$[C_4mim]Cl$ - DMSO	4.1	4.7	4.2

The swelling ratio $D_{swelling} / D_{dried}$ of cotton or wood fibres in $[C_4mim]Cl$ - DMSO is slightly above 4. These values remain lower than those observed in the case of NMMO – water mixtures, but are higher than those observed with NaOH solutions. The swelling ratio indicates the ability of solvent to penetrate the cellulose fibres and to swell them. It can be seen as a first indicator of solvent quality since the swelling is directly linked to the osmotic pressure generated inside the cellulose fibre by the penetration of the solvent and the dissolution of the cellulose chains. All the NMMO – water mixtures at water content between 19 and 23.5% induces a swelling and dissolution mechanisms referred as mode 2 where the balloons are swelling so much that they burst. On the contrary, solvents based on NaOH are not swelling the balloons so much, and they do not burst. Only the cellulose inside the

balloons is dissolved. It can be collected when the balloons are mechanically broken during mixing, which is not occurring in the type of experiments that are performed here under the microscope. This is what was called mode 3 of dissolution. $[\text{C}_4\text{mim}]\text{Cl}$, with few grams of DMSO has a swelling and dissolution mechanism described as mode 2. An interesting factor is the swelling ratio at which the balloons burst. Clearly, the better is the solvent in this mode 2, the larger is the swelling ratio at burst. This may be due to the kinetics of the dissolution. The better is the solvent, the faster is the swelling of the balloon. The balloon will burst when the membrane is not able to sustain the pressure inside the balloon. This resistance of the membrane is directly linked to its thickness. We can imagine that the thickness of the membrane is smaller when the swelling is slow, which leads to a burst at a lower swelling ratio.

$[\text{C}_4\text{mim}]\text{Cl}$ – DMSO is a solvent of cotton and wood fibres, better than NaOH solution at 7.6 % but not as good as than NMMO – water mixtures with water content between 19 and 23.5%.

Treated cotton and wood fibres:

It was previously shown that treated cotton and wood fibres swell homogeneously and then dissolve in aqueous solvents^[10]. This is due to the fact that the enzymatic treatment is eroding the primary wall and part of the secondary wall in a specific way that is leading to the unwinding of the helical structure.

The same effect is found with $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO. No balloons appear during the swelling step. A balloon membrane composed of primary wall plus some part of secondary wall resists dissolution and is responsible for the formation of the balloons. As the enzymatic treatment destroys the outer layers of cellulose fibres, the treated cotton and wood samples swell homogeneously and dissolve.

The detailed description of swelling and dissolution mechanisms is as follows. The mechanism of dissolution for the treated cotton and wood fibres in aqueous solvent shows three steps. The first step is a homogeneous swelling. Then, an unwinding of the cellulose fibres occurs. The cotton and wood fibres without outer layer turn on themselves, from right to left. This untwisting induces the separation of each fibre into two sub fibres. Then in a third step these sub fibres dissolve by fragmentation (Figure 5).



Figure 5. Treated Buckeye sample in $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO seen by optical microscopy in transmitted light, $T = 100^\circ\text{C}$

In the case of $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO, the same mechanisms appear. The first step of swelling is very low (swelling ratio of about 1.5) Then the unwinding of the fibres occurs. Comparatively with the NMMO – water mixtures (at water content between 19 and 23.5%), the unwinding is slower. The division of fibres into sub fibres appears before the total unwinding of the fibres. The pitch of helical structure for treated cotton and wood fibres is multiplied by about 2 during the unwinding in NMMO – water (20%) mixtures. In the case of $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO, the treated samples have not enough time to become totally untwisted before the dissolution begins.

Thus the same three steps are present in aqueous solvent and $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO, even if the last two steps follow one another more rapidly in the case of ionic liquid.

- Swelling and dissolution mechanism in $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$

Cotton and wood fibres:

The cotton and wood fibres dipped in $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ swell homogeneously. No dissolution occurs after the swelling step. This swelling and dissolution mechanism is defined as mode 4. The two ionic liquids $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ are swelling agents for our cotton and wood samples. The fibres stays without change in a swollen state (figure 6).

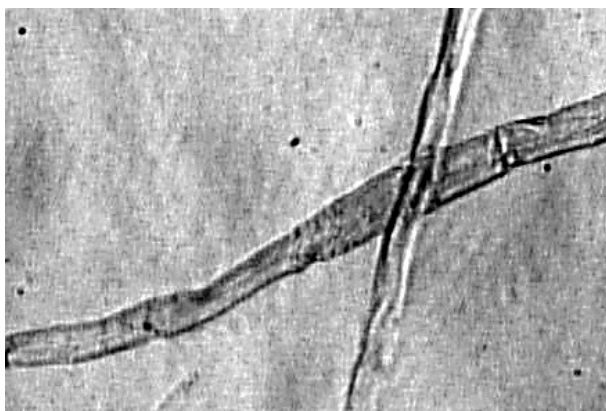


Figure 6. Homogeneous swelling in ionic liquid. Borregard sample in ionic liquid $[\text{Bmim}]\text{Br}$ seen by optical microscopy in transmitted light, $T = 80^\circ\text{C}$

The maximum diameter of fibre is reached very quickly after the contact with the ionic liquids. Thus, the penetration and the diffusion of these agents is fast. The absence of balloons, as in mode 2 with $[\text{C}_4\text{mim}]\text{Cl}$ - DMSO, is due the very low ability of the ionic liquids $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ to dissolve cellulose. The molecules can penetrate the fibre, but cannot break the intermolecular hydrogen bonding network of cellulose. The fact that these ionic liquids penetrates quickly into the fibre is suggesting that they are able to swell well the amorphous cellulose but unable to interact with the crystalline parts.

Treated cotton and wood fibres:

The treated cotton and wood fibres are tested in $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$. $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ are only swelling agents for untreated cotton and wood fibres. In the same way, enzymatically treated cotton and wood fibres in $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ ionic liquids swell homogeneously, but no dissolution occurs (figure 7).



Figure 7. Treated cotton sample in ionic liquid [Bmim]Br seen by optical microscopy in transmitted light, $T = 80^{\circ}\text{C}$

This swelling and dissolution mechanism is compared with those observed with the same fibres in [C₄mim]Cl - DMSO. As described before, [C₄mim]Cl induces a homogeneous swelling and dissolution by dewinding of cotton and wood fibres. This phenomenon is divided in three steps: homogeneous swelling, untwisting of fibres and dissolution. In the case of [Amim]Br and [Bmim]Br, only the first step of homogeneous swelling is observed. [Amim]Br and [Bmim]Br are less efficient than [C₄mim]Cl - DMSO for dissolving cellulose in the case of untreated cotton and wood fibres. The same is occurring for the treated samples, as [Amim]Br and [Bmim]Br are not able to dissolve cellulose. The values of swelling ratio are given in the table 3.

Table 3. Average of Dswelling / Ddried ratio for cotton and wood fibres (Borregaard, Buckeye and bleached cotton) in ionic liquids ([C₄mim]Cl, [Amim]Br and [Bmim]Br). Dswelling is the reached maximum diameter during the homogeneous swelling. Ddried is the fibre diameter without solvent.

		swelling ratio Dswelling / Ddried
Treated cotton and wood fibres	[Amim]Br, [Bmim]Br	1.2
	[C ₄ mim]Cl	1.5
Untreated cotton and wood fibres	[Amim]Br, [Bmim]Br	1.2

The ability to swell in [Amim]Br and [Bmim]Br ionic liquids is not linked to the presence of outer layers. The values of swelling ratio of treated or not cotton and wood fibres is the same ($\text{Dswelling} / \text{Ddried} = 1.2$) in [Amim]Br and [Bmim]Br. The comparison between the swelling ratio obtained for treated cotton fibres in the two type of ionic liquids indicates that all the three ionic liquids do not react with the same ability. The swelling ratio is higher for [C₄mim]Cl - DMSO (1.5) than for [Amim]Br or [Bmim]Br (1.2).

Conclusion

Three ionic liquids have been investigated to study the swelling and dissolution mechanisms of cotton and wood fibres. [C₄mim]Cl is a very good solvent, dissolving cellulose very quickly. Adding DMSO is strongly decreasing its solvent capability. [Amim]Br and [Bmim]Br are not solvents for cellulose. The main result is that untreated and enzymatically -

treated cotton and wood fibres behaves in the same way in these ionic liquids and in aqueous solvents. The complex swelling and dissolutions mechanisms that are observed do not seem to be linked to the nature of the solvent. They reflect the way the cellulose fibres are structured. An interesting feature is that the penetration of [Amim]Br and [Bmim]Br inside the fibre and the associated swelling is fast despite these two chemicals are unable to dissolve cellulose.

- [1] D. J. Adams, P. J. Dyson, S. J. Taverner, *Chemistry in Alternative Reaction Media, Chap 4: ionic liquids*. J.Wiley & Sons, New York 2004.
- [2] C. Graenacher, *Cellulose solution, U.S. patent 1 1934*, 943, 176
- [3] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R.D. Rogers, R., *J. Am Chem. Soc.* **2002**, 124, 4974.
- [4] T. Heinze, K. Schwikal, S. Barthel, *Macromol. Biosci.* **2005**, 5, 520.
- [5] S. Barthel, T. Heinze, *Green Chem.* **2006**, 8, 301.
- [6] K. Schlutter, H.P. Schmauder, S. Dorn, T. Heinze, *Macromol. Rapid Commun.* **2006**, 27, 1670.
- [7] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part I: free floating cotton and wood fibres in *N*-methylmorpholine *N*-oxide water mixtures. *Macromol. Symp.* **accepted**.
- [8] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part II: free floating cotton and wood fibres in NaOH-water-additives systems. *Macromol. Symp.* **accepted**.
- [9] T. Baldinger, J. Moosbauer, H. Sixta, *Supramolecular 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.
- [10] Cuissinat, C., Navard, P. Swelling and dissolution of cellulose, Part III: enzymatically – treated cotton and wood fibres in aqueous solvents. *Carbohydr. Polym.* **in preparation**.

Chapter 6

Swelling and dissolution mechanisms
of native cellulose fibres, part V:
free floating plant fibres
in aqueous systems

Résumé francophone chapitre 6

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie V : fibres de cellulose native, autres que coton et bois, en milieux aqueux.

Comme l'architecture morphologique des fibres natives de cellulose est un paramètre déterminant dans leur mode de gonflement et de dissolution, il est intéressant de tester d'autres fibres natives, que le coton et le bois, pour lesquelles la structure des parois externes diffère légèrement. Des fibres extraites des tiges de plante (lin, ramie, chanvre et jute), ainsi que des fibres extraites de feuille (sisal et abaca) sont trempées dans les systèmes aqueux *N*-methylmorpholine-*N*-oxide (NMMO) – eau, hydroxyde de sodium (NaOH) – eau. Ces échantillons de fibres cellulosiques extraits des tiges ou des feuilles se présentent sous deux formes: matériaux purs jamais transformés dits naturels et sous forme de plaque cartonnée.

Dans le cas des fibres naturelles, le gonflement par ballonnement dans les systèmes aqueux n'est jamais observé. Nous avons soit un gonflement homogène (mode 4), soit une dissolution totale (mode 1). En ce qui concerne les fibres reçues sous forme de plaque cartonnée, les modes de gonflement et de dissolution sont différents puisque le phénomène de ballonnement peut être observé. Les modes 1, 2, 3 ou 4 sont induits par les systèmes aqueux en fonction de la qualité du solvant. Les ballons observés sur les fibres gonflées, extraites de feuilles ou de tiges, sont également entourés d'une membrane et présentent une structure en hélice, tout comme ceux observés sur les fibres de bois et de coton. La structure en hélice n'est donc pas liée aux microfibrilles déterminant une orientation par rapport à l'axe de la fibre, puisque cet angle change considérablement du coton au jute.

Le phénomène de ballonnement est lié à la structure morphologique des fibres de cellulose native, particulièrement aux parois externes. Le traitement des fibres de lin, ramie, jute, sisal ou abaca en plaque cartonnée semble modifier la structure de celles – ci, si bien que leur mécanisme de gonflement et de dissolution en est bouleversé. La faible, mais néanmoins détectable, différence au sein de l'architecture morphologique entre les fibres cellulosiques de coton, de bois et celles extraites des tiges ou des feuilles influe sur leur modes de dissolution. Il reste à déterminer exactement la nature du paramètre clé au sein de l'ultra structure des fibres (nature, teneur ou répartition des composants chimiques en fonction de chaque paroi externe) de cellulose qui autorise ou non un gonflement hétérogène (ballonnement).

As the range of solvent systems has been extended in chapter 5 with the ionic liquids, the range of native cellulose samples is too expanded. Chapter 6 is dealing with the behaviour of bast (ramie, flax, hemp and jute) and leaf (sisal and abaca) fibres, observed into aqueous systems: N-methylmorpholine-N-oxide (NMMO) – water with various contents of water and sodium hydroxide (NaOH) – water. Plant fibres are in two shapes: raw and refined. The aim is to explore the behaviour in dissolution of other cellulose fibres than cotton or wood, to detail the influence of the origin and structure of cellulose fibres on swelling and dissolution mechanisms. In particular, two major features are of interest. The first one is the existence of balloons. Are balloons typical of wood and cotton or are they present in all plant fibres? The second feature is the presence of an helical structure during swelling that seems to play a major role for the dissolution. Is this helix related to the large angle the wood and cotton microfibrils are making with the main fibre or is it also present in fibres with very low microfibrillar angle?

Swelling and dissolution of cellulose Part V: free floating plant fibres in aqueous systems

Céline Cuissinat¹, Patrick Navard^{1,*}

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Matériaux (CEMEF),
Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207,
06904 Sophia Antipolis, France
Member of the European Polysaccharide Network of Excellence (EPNOE),
www.epnoe.eu

* To whom correspondence should be addressed. Tel: +33 (0)4 93 95 74 66; Fax:
+33 (0)4 92 38 97 52; E-mail: Patrick.Navard@enscm.fr

Summary: Raw and refined flax, hemp, abaca, sisal, jute and ramie fibres are dipped into *N*-methylmorpholine *N*-oxide (NMMO) – water with various contents of water and into hydroxide sodium (NaOH) – water. The swelling and dissolution mechanisms of these plant fibres are similar to those observed for cotton and wood fibres. Disintegration into rod-like fragments, ballooning followed or not by dissolution and homogeneous swelling are observed as for wood and cotton fibres depending on the quality of the solvent. The results show that the helical feature seen on the balloon membrane is not related to the microfibrillar angle. Plant fibres are easier to dissolve than wood and cotton. This is not related to the molar mass of the cellulose chain. When the plant fibre is raw, with its non-cellulosic components present, this prevents the formation of balloons.

Keywords: Cellulose, hemp, jute, flax, ramie, dissolution, swelling, *N*-methylmorpholine *N*-oxide, sodium hydroxide

Introduction

Plant fibres, such as flax, hemp, ramie, sisal, abaca and jute, are a cheap renewable source of fibres with a high potential for applications, either keeping the whole fibre as a reinforcement agent, or extracting its various components. Plant fibres are composed of cellulose, hemicellulose, lignin, pectin and wax. The average composition of the major plant fibres is given in Table 1. The major component of all the plant fibres is cellulose.

Table 1. Annual production and chemical composition of plant fibres^[1].

Fibre type	World annual production (10 ³ tonnes)	cellulose	hemicellulose	lignin	pectin
Cotton	18 450	92	6	-	<1
Jute	2 850	72	13	13	-
Flax	830	81	14	3	4
Sisal	378	73	13	11	2
Hemp	214	74	18	4	1
Ramie	170	76	15	1	2

All plant cells have a primary wall, which is soft and flexible in order to expand as the cell grows. During and after growth has stopped, cells develop a thick and rigid secondary cell wall mainly composed of cellulose, deposited by a succession of layers. In flax, for example, this secondary wall is particularly thick, making up 90% of the total cross section of the cell^[2]. In ramie, hemp, flax and jute, the primary wall is rather tenuous.

An important parameter of the structure of the secondary wall is the angle that the cellulose microfibrils are making with the main fibre direction. This angle varies depending on the origin of the fibre (cotton, wood fibres, bast fibres like jute, hemp, ramie, flax, leaf fibres like sisal, abaca) as shown in Table 2. Bast or leaf fibres have only one orientation per layer, contrary to cotton or wood cellulose fibres. The secondary wall of cellulose or wood fibres is divided in three sub-layers (S1, S2 and S3). Each of these sub-layers for cotton and wood fibres has a different microfibrillar orientation. The major orientation is the one of the S2 sub-layer, being about 45° in the case of cotton.

Table 2. Average content of cellulose and values of microfibrillar angle for various cellulose fibres^[3].

	Microfibrillar angle (°)
Flax	10
Ramie	7.5
Hemp	6.2
Jute	8
Sisal	20

In the other papers of this series^[4-7], it was shown that the dissolution of cotton and wood cellulose fibres in aqueous systems or ionic liquids can be rationalised by considering five modes of dissolution:

- Mode 1: fast dissolution by disintegration into fragments
- Mode 2: large swelling by ballooning, and complete dissolution
- Mode 3: large swelling by ballooning, and no complete dissolution
- Mode 4: homogeneous swelling, and no dissolution
- Mode 5: no swelling, and no dissolution

These modes reflect the quality of the solvents, decreasing from mode 1 to mode 5. Very good solvents disintegrate the cellulose fibre into long needles (mode 1) that are then dissolving. Moderate to bad solvents swell first the fibre into balloons that are then bursting (moderate solvent quality, mode 2) or not (bad solvents, mode 3). In both modes 2 and 3, the cellulose inside the balloons is dissolved. Non solvents can either swell homogeneously the fibres without dissolution (mode 4) or not interact at all with cellulose (mode 5). This classification is valid for wood and cotton fibres. It is important to check whether it is applicable to other types of fibres. In particular, two major features are of interest. The first one is the existence of balloons. Are balloons typical of wood and cotton or are they present in all plant fibres? The second feature is the presence of a helical structure during swelling that seems to play a major role for the dissolution. Is this helix related to the large angle the wood and cotton microfibrils are making with the main fibre or is it also present in fibres with very low microfibrillar angle (Table 2)?

The mechanisms leading to dissolution of other than cotton and wood have never been studied as a function of the solvent quality, with the exception of the work of Chanzy et al.^[8]. They observed by optical microscopy the swelling and dissolution of ramie fibres in (*N*-methylmorpholine-*N*-oxide (NMMO) – water with various contents of water at 80°C. They

observed that at low water content, the fibres are fully dissolving as rod-like segments. When increasing the water content, the mechanisms are a homogeneous irreversible swelling (cellulose II is produced after regeneration), then a reversible swelling (cellulose I is kept after regeneration).

The swelling and dissolution mechanisms of bast fibres (jute, hemp, flax, and ramie) and leaf fibres (sisal and abaca) are studied here in aqueous solvents (*N*-methylmorpholine-*N*-oxide (NMMO) – water with various contents of water and sodium hydroxide – water). The results will be compared with those obtained with cotton and wood cellulose fibres.

Experimental part

- Samples

Both refined and raw plant fibres have been used. Refined hemp, sisal, abaca and jute fibres were kindly given by Celulosa de Levante, S.A., Spain. The main properties of these pulps are listed in table 3.

Table 3. Properties of samples supplied by Celulosa de Levante

Fibre type	flax	sisal	abaca	jute
Degree of polymerisation	1045	1093	1838	1256
Viscosity (cc/g)	720	750	1200	850
Brightness (%)	83.5	88	87	72
Fibre length (mm)	2.0 – 6.0	1.8 – 3.9	3.5 – 6.8	1.6 – 3.7

Raw plant fibres were given by EPNOE laboratories:

- Ramie provided by INRA (Nantes – France)
- Flax and Ramie provided by University of Innsbruck (Austria)
- Flax provided by Fraunhofer IAP (Postdam - Germany)
- Flax, sisal, abaca and hemp provided by A&F Innovations (The Netherlands)

- Solvent systems

The swelling and dissolution treatments were performed in two different aqueous solvents:

- *N*-methylmorpholine *N*-oxide (NMMO) and water with various contents of water. The NMMO – water solvents were prepared as follows. The mixtures were prepared with 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 and 35% in weight of water). All the swelling and dissolution experiments were carried out at 90°C.

- sodium hydroxide (NaOH) and water. NaOH – water is a mixture containing 7.6% (in weight) of NaOH. The NaOH powder comes from Fisher and is pure to about 97%. All the swelling and dissolution experiments were carried out at -5°C

- 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 was attached by an adhesive tape on plate in order to avoid the fibre to be too much affected by the solvent convection, which was 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 in transmission mode by optical microscopy with a Metallux 3 (Leitz) equipped with a Linkam TMS 91 hot stage.

Results and Discussion

- Raw plant fibres

The fibres have never been mechanically or chemically treated. The raw plant fibres are dipped in NMMO – water mixtures (at 17, 19, 20 and 23.5% of water) and NaOH (7.6%) - water. The swelling and dissolution mechanisms are detailed in table 4 referring to the five modes defined in the case of cotton and wood fibres.

Table 4. Swelling and dissolution modes for the raw plant fibres in aqueous solvents

	NMMO – water (17%) T=90°C	NMMO– water (19%) T=90°C	NMMO – water (20%) T=90°C	NMMO – water (23.5%) T=90°C	NaOH (7.6%) - water T=-5°C
Ramie (INRA)	Mode 1	Mode 1	Mode 1	Mode 1	Mode 4
Ramie (University of Innsbruck)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Flax (University of Innsbruck)	Mode 1	Mode 4	Mode 4	Mode 4	Mode 4
Flax (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Flax (Fraunhofer IAP)	Mode 1	Mode 1	Mode 4	Mode 4	Mode 4
Sisal (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Abaca (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4
Hemp (A&F Innovations)	Mode 4	Mode 4	Mode 4	Mode 4	Mode 4

The swelling and sometimes dissolution of the raw plant fibres happen only in two of five modes described in the case of cotton and wood fibres ^[4]. Only mode 1 (fragmentation of fibres) and mode 4 (homogeneous swelling, without dissolution) occur. Mode 1 happens only in a few cases:

- Ramie provided by INRA in NMMO – water whatever the content of water between 17 and 23.5% is.
- Flax provided by the university of Innsbruck in NMMO – water at 17%.
- Flax provided by Fraunhofer IAP in NMMO- water at 17 and 19%.

Mode 1 requires good solvents like the NMMO – water mixtures with a lower content of water. As soon as a contact is made with the solvent, the fibres are broken over all their length, producing large rod-like pieces (figure 1). They will then dissolve quickly. No visible swelling occurs before the disintegration of the fibre structure in rod-like fragments.

The fibre fragmentation is due to an easier penetration of the solvent in weak zones (amorphous regions or pores). A breaking in longitudinal fragments, much more long than

wide, expresses the fact that there are long, connected paths that extend all along the fibre, deep inside the secondary wall and over quite long distances, where the solvent will quickly dissolves cellulose chains. The described swelling and dissolution mechanisms are similar to what was found for cotton and wood fibres in aqueous solvents ^[4,5]. Long weak paths seem to exist in all the types of plant fibres, most probably due to the extension of cells.

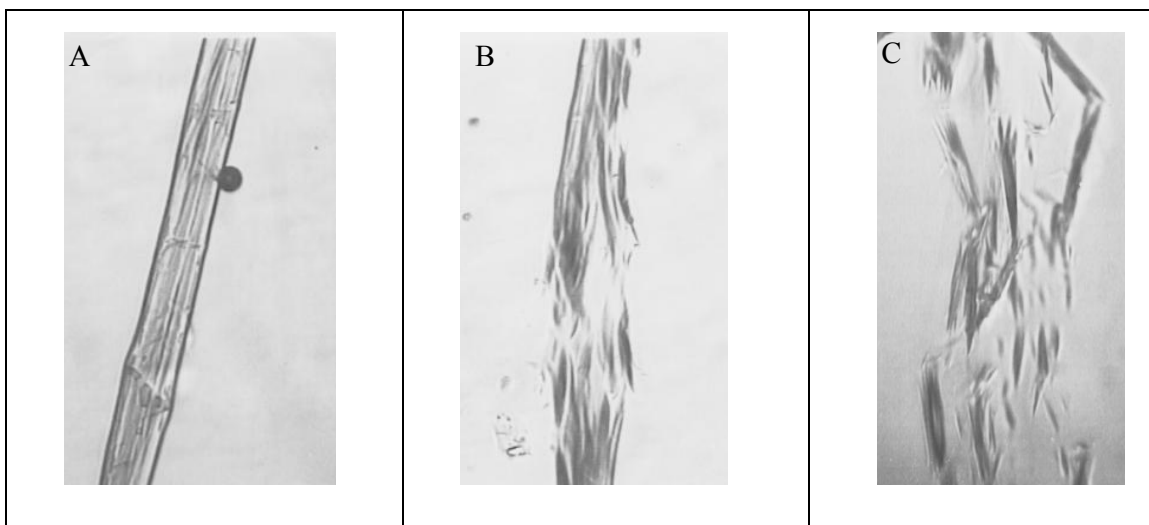


Figure 1. Dissolution by disintegration into fragments (called mode 1). Ramie (from INRA) in NMMO – water (17%), optical microscopy, T=90°C. A=ramie fibre at dried state, B=ramie fibre, 2 minutes after the introduction of solvent, C=ramie fibre, 3 minutes after the introduction of solvent.

The homogeneous swelling without dissolution (mode 4) is the most frequent mechanism seen for raw plant fibres in aqueous solvents (NMMO – water mixtures or NaOH solutions). The cellulose fibres swell immediately as soon as the solvent is introduced. The swelling is homogeneous along all the fibre. The outer layers and the core of the fibres show similar mechanisms. In the case of good solvents such as NMMO – water with a water content between 17 and 20%, the diameter swells by a factor of at least three (figure 2). The swelling ratio decreases with the quality of the solvent. The swelling ratio is between 1.5 and 2.2 for NMMO - water (23.5%) or NaOH (7.6%) - water system (figure 3). The higher is the water content in NMMO, the worse is the quality of the solvent. The results confirm that NaOH-water is not a good solvent ^[5].

It is interesting to note that no swelling by the ballooning mechanism was seen. We can make the assumption that an essential morphological feature is missing. One possibility is to note that ballooning is also absent when the outer layer is removed ^[6]. In the present case, the outer layer is present, but not composed of pure cellulose. Wax and pectin are present the fibre. We will see in the next paragraph that when these chemicals are removed, ballooning is seen.

A noticeable point is that fibres from the same origin may behave differently, like the two ramie samples we tested (ramie from INRA and from the university of Innsbruck behave differently, respectively mode 1 and mode 4).

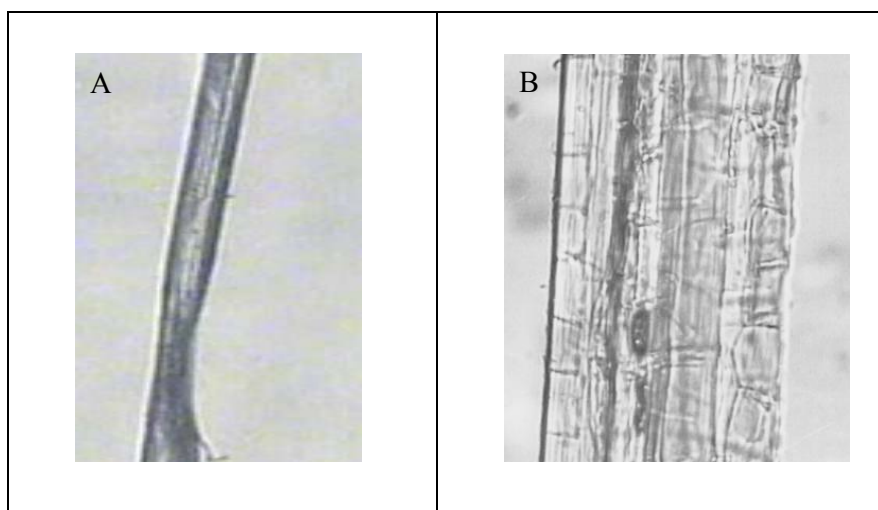


Figure 2. Homogeneous swelling. Ramie (from University of Innsbruck) at dried state (A) and swollen (B) in NMMO – water (20%).

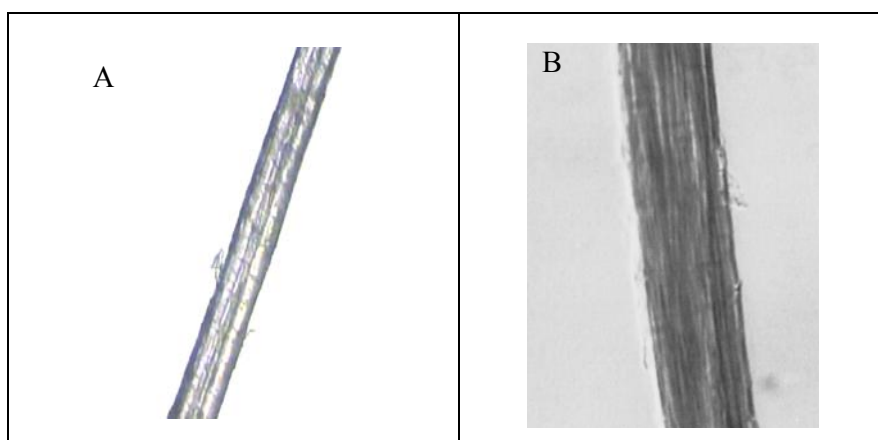


Figure 3. Homogeneous swelling. Sisal (from A&F Innovations) at dried state (A) and swollen (B) in NaOH (7.6%) – water system.

- Refined fibres

Refined pulp fibres provided by Cellulosa de Levante have been studied. The situation is very different from the case of raw fibres since four out of the five modes seen for cotton and wood are observed here (Table 5).

Mode 1 and mode 4 are seen in refined and raw fibres, in a similar way (good solvents are inducing rod – like fragmentation and bad solvents are giving homogeneous swelling). The important difference with raw fibres is that ballooning (modes 2 and 3) is seen with refined fibres (figure 4). The difference between mode 2 and 3 is the presence or not of a complete dissolution after the balloon appearance and growth.

Table 5. Swelling and dissolution modes for refined fibres

	NMMO – water (17%) T=90°C	NMMO – water (19%) T=90°C	NMMO – water (20%) T=90°C	NMMO – water (23.5%) T=90°C	NMMO – water (25%) T=90°C	NMMO – water (35%) T=90°C	NaOH (7.6%) – water T=-5°C
Flax	Mode 1	Mode 1	Mode 1	Mode 2	Mode 4	Mode 4	Mode 4
Jute	Mode 1	Mode 2	Mode 2	Mode 2	Mode 3	Mode 4	Mode 4
Abaca	Mode 1	Mode 2	Mode 2	Mode 2	Mode 2	Mode 2	Mode 4
Sisal	Mode 1	Mode 2	Mode 2	Mode 2	Mode 2	Mode 2	Mode 4



Figure 4. Swelling by ballooning, mode 2. Pulp jute in NMMO – water at 20%, T = 90°C.

As for the cotton and wood fibres in aqueous solvents ^[4,5], the structure of a swelling fibre consists on several well defined zones: unswollen fibre along a fibre (A), balloon (B) surrounded by a helical membrane (C), unswollen section between two balloons (D), as seen in figure 4. Each of these zones has a specific way of swelling and dissolving. In mode 2, refined plant fibres are following the same sequence of four phases leading to the full dissolution both in NMMO – water and in NaOH – water, exactly as for wood and cotton in aqueous solvents:

- Phase 1: balloon formation
- Phase 2: balloon bursting
- Phase 3: dissolution of the unswollen sections
- Phase 4: dissolution of the balloon membrane scraps

The mechanism is the following. The solvent penetrates inside the fibres through the primary wall of the fibres, which acts as a semi – permeable membrane. The cellulose chains of the secondary wall dissolve, staying inside the primary wall that is expanding. This mechanism does not occur all along the fibre at the same time, but at more or less regular intervals, which

gives the shape of “balloons” to the swelling zones (phase 1). The balloons are not exactly spherical, and they do not present a regular diameter. As in the case of wood and cotton, a helical feature is seen around the balloons, making one turn along one balloon length (or between two adjacent unswollen sections, which is the same). Figure 4 clearly shows that this helix is rather steep with an angle close to 45° . This rule out the possible connection between the angle of this helix and the angle of the microfibrils in the plant since jute, for example, has a very low microfibrillar angle (Table 2). The balloons burst when the expansion of the balloon reaches a certain diameter (phase 2) and the liquid cellulose solution contained inside flows out very rapidly. The scraps of membrane remain attached to the unswollen section after bursting. The next part to dissolve is the unswollen sections (phase 3, see figure 5). No swelling occurs during the dissolution of this part, which begins at the outer surface of the unswollen section. The last parts to dissolve are the scraps of the balloon membranes (phase 4).



Figure 5. Third phase of mode 2 (Abaca in NMMO – water at 25%, $T = 90^\circ\text{C}$): The balloons have already burst. What is left in the solution are the membrane scraps (very thin and not visible in the picture) and the unswollen sections that were between the balloons, seen as small cylinders regularly spaced.

The ratio between the diameter of the balloons at burst and the diameter of fibres at dried state is around two. This value is much smaller than those observed in the same conditions with cotton or wood fibres (around five). An interesting result is the fact that a solvent that was considered bad for cotton and wood, like NMMO – water with a content water higher of 35% where only a homogenous swelling without dissolution occurred (mode 4), is good for abaca and sisal (mode 2, swelling by ballooning with complete dissolution), despite their rather high degree of polymerisation.

The swelling ratio of raw fibres is higher than the one of refined fibres in mode 4. The homogeneous swelling for refined fibres is around 1.5 in NaOH (7.6%) – water solutions.

Conclusion

The swelling and dissolution mechanisms for plant fibres, cotton and wood fibres in aqueous solvents are the same, as soon as most of the non-cellulosic components are removed. What is remarkable is that the ballooning mechanisms are exactly similar, with the same sequence of events leading to the complete dissolution and the same helical feature around the balloon, at about the same helix angle, with a pitch equal to the length of a balloon. The helical feature is thus not linked to the microfibrils making an angle to the main direction of the fibre, since this

angle varies greatly from plant to plant. The membrane that is holding the balloon seem to be less resistant to the solvent than in the case of wood and cotton, that is compatible to the fact that the plant fibres are easier to be dissolved than cotton and wood (NMMO – water with a content water higher of 35% is a good solvent for sisal and abaca, while not being a solvent for wood and cotton). The reason of this difference in the solvent quality is not the length of the cellulose chain. This result is very remarkable and opens new perspective for solvent improvements.

The presence of the non-cellulosic components like wax and pectins around the fibre prevents the formation of balloons (raw fibres never showed ballooning), as if the outside wall of the fibre must be very flexible and permeable to the solvent.

Acknowledgements

The authors would like to thank Cellulosa de Levante, INRA (H. Bizot), university of Innsbruck (T. Bechtold), Fraunhofer IAP (H. P. Fink) and A&F Innovations (J van Dam) for kindly providing the fibres.

- [1] L. Y. Mwaikambo, P. A. Martin, *J. Appl. Polym. Sci.* **2002**, 84, 2222.
- [2] A. M. Donald, O. M. Astley, *J. Mater. Sci.* **2003**, 38, 165.
- [3] C. Baley, *Techniques de l'ingénieur* **2004**, ref AM5130.
- [4] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part I: free floating cotton and wood fibres in *N*-methylmorpholine *N*-oxide water mixtures. *Macromol. Symp.* **accepted**.
- [5] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part II: free floating cotton and wood fibres in NaOH – water – additives systems, *Macromol. Symp.* **accepted**.
- [6] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part III: enzymatically – treated cotton and wood fibres in aqueous systems, **in preparation**.
- [7] C. Cuissinat, P. Navard, T. Heinze, Swelling and dissolution of cellulose, Part IV: free floating cotton and wood fibres in ionic liquids, **in preparation**.
- [8] C. Chanzy, P. Noe, M. Paillet, P. Smith, *Appl. Polym. Symp.* **1983**, 37, 239.

Chapter 7

Swelling and dissolution mechanisms
of native cellulose fibres, part VI:
free floating cellulose derivatives
in aqueous systems and ionic liquids

Résumé francophone chapitre 7

Mécanisme de gonflement et de dissolution des fibres natives de cellulose, partie VI : fibres de dérivés cellulosiques en milieux aqueux et dans des systèmes ioniques.

Afin de mieux définir quels paramètres peuvent induire une modification du mécanisme de gonflement et de dissolution des fibres de cellulose native, des fibres de cellulose dérivée sont observées par microscopie optique en présence de systèmes aqueux (*N*-methylmorpholine-*N*-oxide (NMMO) – eau, hydroxyde de sodium (NaOH) – eau) ou de liquides ioniques (1-*N* – butyl – 3 – methylimidazolium chloride [C_4mim]Cl plus du diméthyle sulfoxyde (DMSO), du bromide d'allylmethylimidazolium CP040 et du bromide de butenylmethylimidazolium CP04). Les fibres de cellulose dérivée proviennent de fibres de cellulose dont les groupements hydroxyles (-OH) ont été remplacés lors d'une réaction hétérogène par d'autres groupements chimiques. Pour cette étude, des fibres de cyanoethylcellulose (- OH est remplacé par -CH₂-CH₂-CN) et de nitrocellulose (-OH est substitué par -NO₂) sont utilisées. Le nombre de groupement hydroxyle substitué par monomère est défini par le degré de substitution DS.

Les modes de gonflement et de dissolution observées sont similaires à ceux décrits dans le cas de fibres de cellulose native, comme le coton ou le bois. Cependant, les fibres de nitrocellulose semblent ne pas pouvoir gonfler par ballonnement (seul un gonflement homogène est visualisé), alors que les fibres de cyanoethylcellulose passent par une étape de ballonnement. Le traitement chimique pratiqué pour dériver les fibres de cellulose influe sur le mécanisme de dissolution, en permettant ou pas un gonflement hétérogène. Les modes de gonflement – dissolution ne dépendent pas du solvant, mais sont spécifiques de la structure des fibres. La dérivation n'atteint pas le paramètre morphologique déterminant pour le mode de gonflement et de dissolution, étant donné que les fibres de dérivés cellulosiques présentent les mêmes modes de gonflement et de dissolution que les fibres de cellulose native.

An other type of cellulose fibres (cellulose derivatives) is investigated because the modification of chemical hydroxyl group may be changed the accessibility of cellulose samples, and thus, interact with the induced swelling and dissolution mechanisms.

Chapter 7 deals with the swelling and dissolution mechanisms of derivatives cellulose fibres (nitrocellulose, cyanoethylcellulose and xanthate cellulose) in aqueous solvents and ionic liquids.

Swelling and dissolution of cellulose Part VI: free floating cellulose derivatives fibres in aqueous systems and ionic liquids

*Celine Cuissinat,¹ Patrick Navard^{*1,2}, Thomas Heinze^{2,3}*

¹ Ecole des Mines de Paris, Centre de Mise en Forme des Matériaux (CEMEF), Unité Mixte de Recherche Ecole des Mines de Paris/CNRS n° 7635, BP 207, 06904 Sophia Antipolis France

² Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu; Tel: 33 (0)4 93 95 74 66; Fax: 33 (0)4 92 38 97 52; E-mail: Patrick.Navard@ensmp.fr

³ Centre of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Humboldtstrasse 10, D-07743 Jena, Germany

Summary: The swelling and dissolution mechanisms of cellulose derivatives (nitrocellulose, cyanoethylcellulose and xanthate fibres) are observed in aqueous systems (N-methylmorpholine-N-oxide – water with various contents of water, or hydroxide sodium – water) and ionic liquids. The results are compared with the five modes describing the swelling and dissolution of cotton and wood cellulose fibres. The mechanisms observed for the cellulose derivatives are similar to the ones of cotton and wood fibres. Swelling by ballooning is also seen with cellulose derivatives, showing that this phenomenon is linked to the fibre morphology, which can be kept after undergoing a heterogeneous derivatisation.

Keywords: cellulose, cyanoethylcellulose, nitrocellulose, xanthate, swelling, dissolution, N-methylmorpholine N-oxide, ionic liquids

Introduction

Cellulose is the most abundant renewable material in the world. Cellulose-containing materials have been widely used in human societies. Apart been used in unmodified forms, such as wood or cotton, cellulose can be extracted from its natural sources and then be either used for the paper industry and in a smaller scale for some specific applications like regenerated fibres (lyocell or viscose) or for obtaining chemically-modified materials by chemical, enzymatic or microbiological methods. The [hydroxyl groups](#) of [cellulose](#) can be partially or fully reacted with various [chemicals](#) to provide derivatives with many different properties. [Cellulose esters](#) and [cellulose ethers](#) are the most important [commercial cellulose](#) derivatives.

Cellulose has three reactive hydroxyl groups per anhydroglucose unit that form inter- and intramolecular hydrogen bonds. These bonds strongly influence the chemical reactivity and solubility of cellulose. As a result, cellulose is insoluble in most common solvents, and the successful preparation of derivatives requires a special approach. There are two categories of cellulose reactions: homogeneous reactions where the cellulose is dissolved during synthesis and heterogeneous reactions where cellulose stays in a solid or more or less swollen state

during the chemical modifications. The polyfunctionality of cellulose resulting from the presence of three available hydroxyl groups within each repeating unit offers a lot of freedom for tailoring chemical transformations, but brings difficulties with regard to the uniformity of the reaction products. The susceptibility of the glycosidic bond between adjacent anhydroglucose units to hydrolytic cleavage is promoting molecular weight loss, especially in acid system^[1]. Complete or partial esterification or etherification of the hydroxyl groups are the principal reaction routes to all the cellulose derivatives available commercially today. Typical examples of cellulose esters are cellulose acetate, cellulose xanthogenate or cellulose carbamate and of cellulose ethers are methylcellulose, carboxymethylcellulose and hydroxypropylcellulose.

All the derivation reactions occur one way or another in a swollen or dissolved state, which stresses the importance of understanding the mechanisms underlining swelling and dissolution. A contribution towards this goal has been made in our previous work^[2-6] where the dissolution of various natural cellulose fibres was studied in aqueous solvents and/or ionic liquids. Five modes of dissolution can be described, 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). These modes reflect the quality of the solvents, decreasing from mode 1 to mode 5. Such a description of the swelling and dissolution mechanisms seem to be rather universal for cellulose fibres extracted from vegetal cells. This is related to the complexity of plant structures.

An interesting question is whether such structures are kept after derivatisation. If the cellulose derivative is prepared in a homogeneous way, i.e. is fully dissolved in a solvent during the chemical reaction, there is no reason why the regenerated product should keep the original structure of the native fibre. But when the reaction occurs in a heterogeneous way, this could happen. As we saw in the previous papers of this series and has been seen before by many authors, one of the swelling modes shows a typical feature called ballooning. Indeed, it is possible to find reports in literature where balloons are described during the swelling of viscose fibres^[7] or carbomethyl cellulose^[8] but without a description of the ballooning mechanisms.

The motivation of this study is to find if cellulose derivative fibres prepared in heterogeneous ways are showing the same modes of swelling and dissolution than native cellulose fibres, and if yes, to investigate the mechanisms and the influence of parameters like the degree of substitution. To this end, we studied three cellulose derivatives from the ether and ester families, nitrocellulose, cyanoethylcellulose and xanthate cellulose.

Experimental part

- Cellulose samples

Cyanoethylcellulose samples were prepared by the “Centre of Excellence for Polysaccharide Research” at the University of Jena, Germany, as follows. A suspension of 20 g (0.11 mol) cellulose pulp in 400 ml of NaOH (18%) – water mixtures is stirred for one hour at room temperature to make alkalicellulose. It is then removed and washed in water. The wet alkalicellulose is placed in NaOH (2%) – water and cooled to 5°C under stirring. Then 7.27 l of acrylnitrile (0.11 mol) are carefully added by drops and the mixture is warmed up to 40°C and stirred for 30 minutes. The product is then neutralised with acetic acid, washed with 1 l of distilled water and dried at 60°C under vacuum. Six cyanoethylcellulose samples were

prepared with degree of substitutions of 0.03, 0.06, 0.08, 0.11, 0.31 and 0.47. The degree of substitution (DS) is the average number of hydroxyl groups modified per anhydroglucose unit.

Nitrocellulose fibres: five nitrocellulose samples of different molecular weights were kindly provided by Wolff Cellulosics. Nitrocellulose samples were damped with 30% of isopropanol in order to stabilise the nitrocellulose (deactivating the hazardous properties of dry nitrocellulose, as high flammability or high burning rates). The received samples were dried in vented hood and after in oven at 50°C to remove isopropanol. All samples have the same degree of substitution of 2.2 – 2.35 nitrate groups per anhydroglucose unit, equal to 11.8 – 12.3% N – content, which makes the nitrocellulose samples soluble in esters, ketones or glycolethers. Fives samples have been investigated, noted E560, E620, E845, E950 and E1160. The molecular weight of nitrocellulose samples are given in table 1.

Table 1. Molecular weight of nitrocellulose samples. (the values are obtained by size exclusion chromatography – SEC).

Nitrocellulose samples	Molecular weight (g/mol)
E560	32 190
E620	14 800
E845	not determined
E950	25 700
E1160	30 000

Xanthate of cellulose: cellulose xanthate was prepared in Innovia Films Company, England. They are formed by the reaction of soda cellulose (prepared by treating cellulose with strong sodium hydroxyde solution) with carbon disulfite CS₂. Dissolved in sodium hydroxide, this alkaline cellulose xanthate forms a thick solution called viscose. One important parameter for xanthate fibres is the content of CS₂. The three samples have 35, 25 and 15% of CS₂.

- Solvents

Two types of aqueous solvents were used:

- 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 45 per mass of water). Increasing the water content in NMMO – water system decreases its ability to dissolve cellulose. The experiments were carried out at 90°C.

- Mixtures of sodium hydroxide (NaOH) and water containing 7.6% (in weight) of NaOH. The NaOH powder comes from Fisher and is pure to about 97%. The experiments were performed at -5°C.

Three ionic liquids were investigated:

- 1-*N* – butyl – 3 – methylimidazolium chloride (noted [C₄mim]Cl) with dimethyl sulfoxide (DMSO). The proportion in weight is [C₄mim]Cl (75%) – DMSO (25%).

- allylmethylimidazolium bromide (= [Amim]Br)

- butenylmethylimidazolium bromide ($=[\text{Bmim}]\text{Br}$).

The molecular structures of $[\text{C}_4\text{mim}]\text{Cl}$, $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ are given in a previous article^[5]. The experiments were performed at 100°C with $[\text{Amim}]\text{Br}$ and $[\text{Bmim}]\text{Br}$ and at 80°C with $[\text{C}_4\text{mim}]\text{Cl}$.

- 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 each cellulose fibre is attached by an adhesive tape on one 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 transmission optical microscopy with a Leitz Metallux 3 equipped with a Linkam TMS 91 hot stage.

Results and discussion

- Nitrocellulose

The five nitrocellulose samples provided by Wolff Cellulosics have been studied in NMMO – water mixtures with water content between 17 and 45% and in NaOH (7.6%) – water system. The five samples dissolve in mode 1 for NMMO-water solvents with the water content from 17% to 35%, at 90°C. Mode 1 corresponds to a fast dissolution of fibres by bursting of the structure. Right after the introduction of the solvent, the nitrocellulose fibres are immediately separated in small parts, which burst in fragments (figure 1). This mechanism is the one occurring for cotton or wood cellulose fibres in a good solvent^[2] like NMMO – water 17%. The reaction via mode 1 between nitrocellulose samples and chemical agents is very fast. The dissolution by fragmentation seems to be faster for E 560 than for E 1160 for a given solvent. The increase of viscosity in nitrocellulose sample slows slightly down the dissolution. The dissolution mechanism is not influenced by the molecular weight. Molecular weight changes only the kinetics of the process.

The length and the width of fragments are varying a lot, the length being between 4 and 25 μm , and the width being between 2 and 6 μm , whatever the nitrocellulose samples and the solvent are.

When the solvent agent becomes bad for this cellulose derivative (NMMO – water with a water content of 45% or NaOH (7.6%) – water, dissolution is never reached. Only a homogeneous swelling takes place, typical of mode 4. This swelling is comparable to the homogeneous swelling observed with cotton or wood fibres in the same solvent systems. The swelling is very low: the ratio between the diameter of swollen fibre and fibre at dried state being at best 1.5 for the nitrocellulose samples. This value is an average of all the nitrocellulose samples. The swelling ratio is not influenced by the molecular weight of each sample. The homogeneous swelling of nitrocellulose is not larger in NaOH (7.6%) – water than in NMMO – water at 45%. The nature of the aqueous systems does not seem to change the ability of nitrocellulose fibres to swell. The surface of the swollen fibre is smooth, without visible helical features.

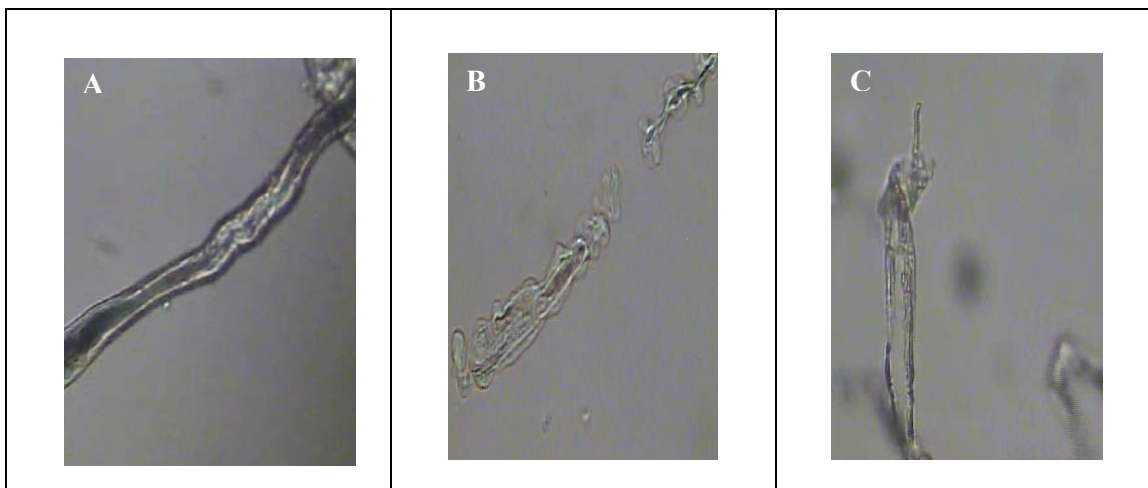


Figure 1. Swelling and dissolution mechanisms by fragmentation of fibres (mode 1) for nitrocellulose samples. E 1160 sample in NMMO – water at 35%, optical microscopy, $T=90^{\circ}\text{C}$. A=nitrocellulose sample at dried state, B=division of fibres in segments, C=fragmentation fibres

- Cyanoethylcellulose samples

Aqueous systems

All cyanoethylcellulose samples are first swelling by ballooning in aqueous systems. In the three NMMO solvents, the swelling is followed by a complete dissolution, as in mode 2. On the contrary, the balloons never burst in the NaOH (7.6%) – water, $T=-5^{\circ}\text{C}$, and a full dissolution is never reached, as in mode 3.

The swelling and complete dissolution mechanisms are similar to what has been described in the case of cotton and wood cellulose fibres dissolving in NMMO – water system^[2]. Only localised zones (called balloons) swell along the fibres (figure 2). The balloons do not appear in the same time along the fibres and they do not reach their final diameter at the same time. All the balloons are transparent and surrounded by a membrane. The balloon membrane shows a helical feature like a ribbon surrounding each balloon at its surface. The distance between balloons and the number of balloons vary in a random way. At a certain expansion ratio, the balloons burst allowing the cellulose solution contained inside the balloon to flow out. Then the unswollen sections (part of the fibres situated between two balloons) are dissolving. The last part of the fibres to be dissolved is the balloon membrane.

The behaviour of cyanoethylcellulose samples and native cotton or wood cellulose fibres are similar with the appearance of the four phase from balloons formation, balloons bursting, dissolution of unswollen sections till the dissolution of balloons membrane^[2]. The total dissolution of cyanoethylcellulose is taking more time (about two times) than the dissolution of cotton and wood fibres in the same experimental conditions. The degree of substitution does not influence the mechanism of dissolution since all fibres show the same sequence of balloons formation, balloon bursting, dissolution of unswollen sections and dissolution of balloon membrane whatever the value of the degree of substitution is. It is possible to note that the total dissolution kinetics and the number of balloons per unit length are decreasing with increasing the degree of substitution. The total dissolution of cyanoethylcellulose with a

DS at 0.47 is around 2.5 times lower than dissolution occurring with cyanoethylcellulose at very low DS (0.03 or 0.06). Concerning the number of balloons per unit length, it is twice lower for cyanoethylcellulose at high DS (0.47) than at low DS (0.03).

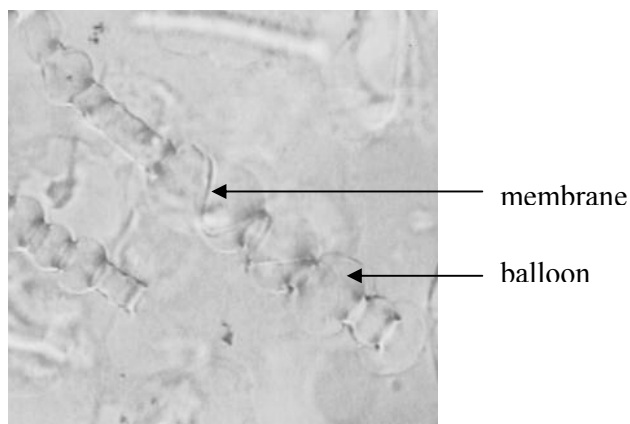


Figure 2. Swelling by ballooning. Cyanoethylcellulose sample (DS = 0.31) in NMMO – water 20%, optical microscopy, T=90°C.

Ionic liquids

Cyanoethylcellulose fibres placed in [C₄mim]Cl – DMSO swell by ballooning. The swelling and dissolution mechanism clearly corresponds to mode 2, and presents the same features than those described previously for aqueous solvents (figure 3). Cyanoethylcellulose fibres swell homogeneously in [Amim]Br and [Bmim]Br without reaching dissolution (mode 4). The swelling agents are diffusing along the fibres and cause a low and homogeneous swelling of the fibres. Cyanoethylcellulose samples present the same behaviour in ionic liquids as cotton and wood samples. These experiments with cyanoethylcellulose show that the substitution of a fraction of the hydroxyl groups does not prevent the cellulose derivatives to form balloons.

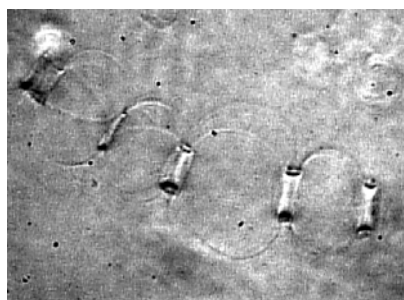


Figure 3. Swelling by ballooning. Cyanoethylcellulose sample (DS = 0.03) in [C₄mim]Cl – DMSO solvent, optical microscopy, T=100°C.

- Cellulose xanthate

The experiments with cellulose xanthate fibres with NaOH (6%) – water at -4°C. These parameters were chosen because they are close to the viscose process. The swelling and

dissolution mechanism is mode 2 for cellulose xanthate fibres, with ballooning and complete dissolution. However, the four steps typical of mode 2 are difficult to be seen clearly. During the dissolution phenomenon, the balloon formation, their bursting and the dissolution of each part of fibres follow one other too quickly. Nevertheless the typical helical feature can be seen (figure 4). The content of CS₂ does not influence the dissolution mode. But the kinetic is slightly modified with the CS₂ content, the dissolution being faster when the content of CS₂ is lower.



Figure 4. Swelling by ballooning. Xanthate cellulose sample (with a content of CS₂ of 35%) in NaOH (6%) – water solution, optical microscopy, T= 4°C.

Conclusion

The swelling and dissolution mechanisms of cellulose derivatives fibres like nitrocellulose, cyanoethylcellulose and xanthate fibres in aqueous systems and ionic liquids are similar to those described for cotton or wood cellulose fibres. The chemical change of the hydroxyl group into nitro, cyanoethyl or xanthate functions does not influence the dissolution mechanism to a great extent. Kinetics or change of mode can be seen compared to the cellulose fibre due to the fact that the solvent can decrease its quality when the chemical nature of the chain is modified. The interesting point of this study is that ballooning and the helical feature can be seen also with derivatives. This shows in an unambiguous way that these events are due to the fibre morphology, and that this morphology is not necessarily altered when conducting a heterogeneous derivatisation.

Acknowledgements

The authors would like to thank Wolff Cellulosics (J. Engelhardt) and Innovia Films (J. Marshall and M. Cockroft) for their help.

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

[2] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part I: free floating cotton and wood fibres in *N*-methylmorpholine *N*-oxide water mixtures. *Macromol. Symp.* **accepted**.

- [3] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part II: free floating cotton and wood fibres in NaOH – water – additives systems, *Macromol. Symp.* **accepted**.
- [4] C. Cuissinat, P. Navard, Swelling and dissolution of cellulose, Part III: enzymatically – treated cotton and wood fibres in aqueous systems, **in preparation**.
- [5] C. Cuissinat, P. Navard, T. Heinze, Swelling and dissolution of cellulose, Part IV: free floating cotton and wood fibres in ionic liquids, **in preparation**.
- [6] C. Cuissinat, P. Navard, Swelling and dissolution mechanisms of native cellulose fibres, part V: free floating plant fibres in aqueous systems, **in preparation**.
- [7] B. Bergen, W. Kraus, in “*Textile fibre atlas, a collection of photomicrographs of common textile fibres*”, American Wool Handbook Company, NewYork, 1942.
- [8] K. Jardeby, U. Germgard, B. Kreutz, T. Heinze, U. Heinze, H. Lennholm, *Cellulose* **2005**, 12, 167.

Conclusion

The focus of our work is the swelling and dissolution mechanisms of native cellulose fibres. A large range of cellulose samples have been investigated in various chemical agents (aqueous and non-aqueous as ionic liquids). We are able to propose a systematization of the different dissolution modes, largely influenced by the structure of cellulose fibres.

I. Previous knowledge

- A fast increasing knowledge of the biosynthesis mechanisms in the cell with a rather good understanding of the cellulose production (assembling of the chain in the plasma membrane by plasma membrane rosettes that contain the cellulose synthase protein, with a direct deposition of 36 chains into the wall) but still a lack of how the various components of the cell wall are arranged.
- A lot of results, some very old, concerning the possibility to dissolve cellulose, described either from a chemical point of view (which chemical is effective and how practically to dissolve?) or from a processing point of view (how to use the solution?).
- Many mentions of the ballooning phenomenon reported mainly in cotton, with a few additional reports about its existence in cellulose derivative fibres.
- One paper giving an explanation about the origin of ballooning in cotton (Ott, 1954).
- One paper showing that upon varying the quality of the solvent, the mechanisms are changed (Chanzy, 1983).
- Topic not seen as interesting (everything is known!) despite many things seem unclear.

II. Main results of our study

Whatever are the type of solvent, the source of plant cellulose (cotton, wood, sisal, hemp, flax abaca, ramie....) or its location in the plant (leaf, bast or seed), the mechanisms of swelling and dissolution are similar:

- The interaction between cellulose fibres coming from vegetal sources and a chemical can be rationalized into five different modes of interaction:
 - Mode 1: fast dissolution by disintegration into fragments. The penetration of solvent system causes rapidly an explosion of fibres into fragments, which are then dissolved.
 - Mode 2: swelling by ballooning, and dissolution. Three zones are distinguished along the cellulose fibres: the balloons, the unswollen sections and the membrane of balloons. All the studied fibres are following the same sequence of events from start of swelling to the complete dissolution. We divide the mechanism into four steps:
 - Phase 1: formation of balloons
 - Phase 2: bursting of balloons
 - Phase 3: dissolution of the unswollen sections
 - Phase 4: dissolution of balloon membrane
 - Mode 3: swelling by ballooning, and no complete dissolution. This mechanism is closed to the mode 2, but the solvents are not good enough to reach a complete dissolution. Only the swelling by ballooning occurs (phase 1), but the cellulose is dissolved inside the balloon.

➤ Mode 4: homogeneous swelling, and no dissolution. The chemical is not good enough to induce balloon formation, which implies a partial dissolution of cellulose. Only a homogeneous swelling takes place.

➤ Mode 5: no swelling, and no dissolution, case of a non – solvent.

- Good solvents are splitting the fibres into elongated fragments that reflect the fact that accessible zones are interconnected and lying in the direction of the fibres.
- Ballooning is a very common phenomenon, seen in all the vegetal fibres we studied. The main characteristics of the ballooning phenomenon with its four phases are the same whatever the source of cellulose is. The balloons and the unswollen regions are associated with a helical feature that has a large angle even in cellulose fibres with a very low fibril angle.
- Aqueous solvents and non aqueous induce the same swelling and dissolution mechanisms.
- Some cellulose derivatives that are prepared in the heterogeneous way have also the mechanisms seen in the native fibre, like ballooning. In this case, the degree of substitution is not having another role than changing the solubility parameter, thus changing the mode of dissolution.
- When peeling the outside layer of the fibre, there is no balloon anymore. Cotton and wood fibres split, unwind and dissolve.
- When the solvents are not very good, the ballooning state is the only one reached (mode 3). The cellulose is dissolved only inside the balloons. The cellulose solution is liberated by the mechanical effects of a mixer. The membranes and the unswollen sections are left in the solution.

III. Main conclusions and possible mechanisms

The fact that the mechanisms are specific neither to a type of plant nor to a type of solvent suggests a very general common organisation of the cellulose in the vegetal cell, whatever is the type of plant and a very common type of interaction with chemicals. A common feature of all cells is that they are composed of at least two layers or walls with different deposition mechanism, function and composition and that they are elongating.

Mode 1

The elongation during the development of vegetal fibres is most probably the cause of the specific mechanism seen in mode 1 (fast splitting of the fibre in elongated fragments), with very good solvents. The deposition of the microfibrils in primary and secondary walls is done in a rather disordered manner, probably inducing regions with different densities of cellulose. Upon elongation of the cell, the less dense regions will create long, less and less dense in cellulose areas that orient in the direction of the fibre. The decrease of cellulose density can probably be such that voids are created, especially when the non-cellulosic components are removed. These regions will be more accessible to the penetration of the solvent that will quickly dissolve these regions. This will leave the cellulose fibre with a lot of elongated dissolved regions and induce the detachment of the undissolved regions; that will have a rod-like shape (as a sort of negative print of the dissolved regions).

Modes 2 and 3

Balloons are very common to all types of fibres. It is not related to the composition of walls (that varies from plant to plant), nor to the structural arrangement of the secondary wall. It is directly related to the presence or not of the primary wall. The ability to dissolve all the

cellulose fibre or only the cellulose contained in the balloons depends only on the quality of the solvent. In the range of solvents not good enough to penetrate quickly into the fibre to destroy the weak part and split the fibre into rod-like fragments (mode 1), but being good enough to dissolve slowly cellulose, balloons are forming. The balloons are the location of dissolving regions where the cellulose solution is maintained into a membrane. It means that the membrane, i.e. the primary wall, is more difficult to dissolve than the secondary wall. The regions between balloons (unswollen sections) that are not dissolving when the solvent is not so good (mode 3) are not different in composition than the regions where balloons are forming (results coming from another study). What is always seen is the occurrence of a helical line that is playing a major role in the dissolution process. It is hampering dissolution when it cannot unwind. It is these helices that are blocking the dissolution of the membrane and of the unswollen sections. This helical morphological feature is not linked to the angle of the fibrils, and thus not linked to the organisation of the secondary wall. It is placed in the primary wall (recent work performed outside our work confirms this). It was impossible during the course of this work to isolate and study the composition of the regions where this helix was present. What we can say is that we have two possibilities concerning the origin of this helical feature. It can be either already present in the fibre when it is synthesized in the plant or formed when placed in contact with the solvent. Our results are not allowing us to tell which possibility is correct. Plant biologists never say such feature in plant and cannot trace from which origin it could be, thus advocating more towards a building of this helix during the swelling of the fibre.

Mode 4

The ability of solvent system to dissolve cellulose fibre decreases from mode 1 to mode 5. Mode 4 is the last mechanism before considering a chemical agent as unable to interact with cellulose fibres. In the previous mechanisms, the external agent is able to penetrate inside the fibres (through the external layers, lumen and void network) and to dissolve cellulose chains. In the case of mode 4, the chemical system can only penetrate and be propagated along the cellulose fibres, which swell homogeneously. The general organisation of cellulose fibre is not modified. The solvent mixture is present only in voids and among the less – ordered network.

Unwinding and stress release

The swelling and dissolution mechanism of cellulose fibres without one part of their outer layers is unique. They swell, unwind and dissolve. The unwinding of structures induces the dissolution step. If unwinding of cellulose fibres is fully possible, the dissolution becomes possible in moderately good solvents. The untwisting of cellulose fibres is most probably linked to internal stresses which were accumulated inside the fibres. The stress release causes the unwinding and is possible since the swollen fibres are not confined by the outer layers.

IV. Remaining questions

- One of the major unanswered questions is why there is a helical feature around balloons and unswollen sections, and why it seems to hamper dissolution. This seems to be a very limiting factor for dissolving cellulose in moderately good solvents like those based on NaOH – water.
- Another interesting question is why stress is built in a fibre. Is this due to the drying of the fibres or is this already present during either deposition (during coagulation of the

- fibres outside the rosette) or during elongation? From a mechanical analysis of the unwinding, it could be possible to get an idea of the amount of stress is released.
- Finally there is a need to correlate all these data to the large amount of knowledge on the biosynthesis of the vegetal cell, to see how the swelling and dissolution mechanisms can help to better understand the cell structure.

La cellulose, polymère naturel appartenant à la famille des polysaccharides, est non fusible. Pour la mettre en forme, il est donc nécessaire soit de la dériver, soit de la solubiliser. L'objectif de notre travail est de préciser les mécanismes qui conduisent à la dissolution de la cellulose native. Cinq mécanismes sont observés lors de cette étude, basée sur des fibres de cellulose native d'origine diverse (coton, bois, ramie, jute, lin, chanvre, sisal et abaca). Chaque échantillon est observé dans une large gamme de systèmes aqueux (NMMO – eau à différentes teneurs en eau ou hydroxyde de sodium – eau – additif) et des liquides ioniques. Des données recueillies sur des échantillons dépourvus de leurs parois externes suite à un traitement enzymatique, ainsi que des dérivés cellulosiques, viennent compléter cette étude. Nous avons identifié cinq mécanismes de gonflement et de dissolution de fibres de cellulose native :

Mode 1: dissolution rapide par désintégration de la fibre en fragments

Mode 2: gonflement par ballonnement, dissolution de toute la fibre

Mode 3: gonflement par ballonnement, dissolution partielle de la fibre

Mode 4: gonflement homogène, non dissolution de la fibre

Mode 5: pas de gonflement ni de dissolution (cas d'un système non solvant)

Malgré les différences morphologiques entre toutes les fibres de cellulose testées et les dérivés cellulosiques, les mécanismes de gonflement et de dissolution restent similaires.

Trois zones le long des fibres de cellulose sont définies lors d'un mécanisme impliquant un gonflement par ballonnement: les ballons, la membrane des ballons, les sections non gonflées (zones situées entre les ballons). Chacune de ces zones présentent un mécanisme de dissolution particulier. Le mode 2 est donc détaillé en 4 étapes. Les ballons sont des entités constituées d'une membrane (paroi primaire, plus une partie de la paroi secondaire), caractérisée par une structure hélicoïdale. La membrane est la partie de la fibre la plus difficile à dissoudre. Il est important de noter que la cellulose à l'intérieur des ballons est dissoute.

Les mécanismes de gonflement et de dissolution ne sont pas liés à la nature chimique des agents solvants. La qualité du solvant influe évidemment sur le mode de dissolution induit, mais le facteur clé des mécanismes est la structure morphologique de la fibre.

Mots-clé: cellulose, native, coton, bois, gonflement, dissolution, ballonnement, morphologie, *N*-méthylmorpholine-*N*-oxyde, hydroxyde de sodium, liquide ionique.

Cellulose is a natural polymer, which belongs to polysaccharide family. Cellulose offers numerous product development opportunities but cellulose is difficult to process: it can not be melted. Thus cellulose must be either solubilised or derivetised. This is the main reason that pushed us to study and understand the swelling and dissolution mechanisms of native cellulose fibres (cotton, wood, sisal, abaca, hemp, flax and ramie). Data obtained with cotton and wood samples without outer layers, and cellulose derivatives allow us further information. The chemical agents, investigated as solvent or swollen agents, are aqueous (*N*-methylmorpholine *N*-oxide – water with various water content, or sodium hydroxide – water – additives) or ionic liquids. We identified five modes describing the behaviour of cellulose native fibres dipped in chemical agents:

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

Despite the morphological differences between the different types of vegetal fibres or cellulose derivatives, they all follow the same modes of swelling and dissolving.

We can distinguish different zones with one fibre during the ballooning. The three main components are the followings: the balloons, the membrane (surrounded the balloons with helicoidal feature) and the unswollen section. Each of these parts undergoes a typical swelling and dissolution behaviour. The components of the balloon membrane are the primary wall, plus part of the secondary wall. The membrane is the most difficult part to dissolve. Cellulose inside the balloons is not only swollen, but dissolved.

The swelling and dissolution mechanisms of native cellulose fibres are not determined by the chemical nature of chemicals tested as solvent systems. Even if the quality of solvent plays a major role concerning the induced mechanisms, the key parameter is the morphological architecture of native cellulose fibres.

Key-words: cellulose, native, cotton, wood, swelling, dissolution, ballooning, morphology, *N*-methylmorpholine-*N*-oxide, sodium hydroxide, ionic liquid.